Atmospheric Organic Particulate Matter: Revisiting its Sources, Properties and Impacts

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An overview of the development of our understanding of the sources, formation mechanisms, physical and chemical transformations of atmospheric organic aerosol (OA) is presented. Until recently, organic particulate material was simply classified as either primary or secondary with the primary component being treated in models as nonvolatile and inert. However, this oversimplified view fails to explain the highly oxygenated nature of ambient OA, the relatively small OA concentration gradients between urban areas and their surroundings, and the concentrations of OA during periods of high photochemical activity. A unifying framework for the description of all components based on their volatility distribution (the volatility basis set) can be used for the treatment of a wide range of processes affecting organic aerosol loadings and composition in the atmosphere. These processes include direct organic particle and vapor emissions, chemical production of organic PM from volatile precursors, chemical reactions (aging) in all phases, as well as deposition of both particles and vapors and chemical losses to volatile products. The combination of this new framework with the recent results of laboratory studies can resolve some of the discrepancies between OA observations and laboratory results.

1. Revisiting the main assumptions about Primary Organic Aerosol

Primary Organic Aerosol (POA) has been traditionally assumed to be non-volatile and non-reactive in atmospheric aerosol models. Even if these assumptions are used today by the great majority of Chemical Transport Models (CTMs) and are integral parts of most mental models of the system, it has been clear for decades that neither is correct in many cases. Most measurements of ambient organic PM concentrations were accompanied by serious negative (particle evaporation after collection on the filter) and/or positive artifacts (vapor adsorption on the filter), providing strong hints about the semi-volatile nature of organic aerosol.

It has long been recognized that certain primary compounds were semivolatile. Polycyclic Aromatic Hydrocarbons (PAHs) have received special scrutiny because of their known toxicity; they range from completely volatile Napthalene to completely condensed Coronene, with intermediate molecular weight compounds occurring significantly in both phases. The semi-volatile character of many other ambient organics (Fraser et al, 1997; 1998) and sources (Schauer et al., 1999) has also been addressed extensively. However, the overall contribution of semivolatile material to ambient POA has not been comprehensively addressed until recently. For more than twenty years, dilution samplers have been used to measure POA emission factors. Development of these samplers was motivated by the semivolatile character of primary emissions; specifically upon heating. Initial studies focused on the effect of temperature on partitioning. Only modest amounts of dilution (about 100x) are required to reduce the temperature of the exhaust to ambient levels, which dramatically increases the amount of POA because of the strong dependence of vapor pressure on temperature. More recent experiments have demonstrated that POA emission factors decrease when the aerosol is isothermally diluted (Lipsky et al., 2006). Both of these changes are expected based on partitioning theory.

Although some primary emissions are clearly semivolatile, most CTMs have treated them as non-volatile. The implicit assumption is that the partitioning measured using a dilution sampler is representative over the full range of atmospheric conditions simulated by the model, and that the semi-volatile primary mass is a small fraction of the total POA.

It is also reasonable to expect that the organic aerosol compounds will react with atmospheric oxidants like the OH radical, O₃, NO₃, etc. leading to chemical changes. Limited studies of the heterogeneous chemistry of POA components and realistic POA have confirmed that these reactions are quite efficient in transforming POA to other compounds. At the same time, the POA components that evaporate after dilution as they move away from their sources will react in the gas-phase, forming products with lower volatility that can condense back in the particulate phase (Robinson et al., 2007). Both of these pathways oxidize primary emissions, forming oxygenated organic aerosol (OOA).

At this point the traditional simple framework and corresponding definitions of POA and SOA have broken down. Is the OA formed from a compound that starts its atmospheric life in the particulate phase, evaporates, reacts in the gas phase and then condenses primary or secondary? Further confusion arises because traditionally 'primary' and 'secondary' refer to the aerosol mass, and not the specific chemical compounds making up that mass.

2. The Volatility Basis Set as a Unifying Framework

The need to treat the volatility of primary OA, the formation of secondary organic aerosol (SOA), the reactions of both primary and secondary OA components, and the need to model the aging of semi-volatile compounds all motivated the development a new framework for the description of all OA components and their reactions. This framework blurs the distinction between the traditional primary and secondary organic aerosol, providing a more realistic picture of the behavior of atmospheric organic aerosol. Given the increased complexity of the system, the tens of major OA sources, and the hundreds of SOA precursors the framework should also result in computationally efficient modules for CTMs, so that the simulation of OA could still be tractable.

Donahue et al. (2006) proposed using fixed logarithmically-spaced saturation concentrations bins: the volatility basis set (VBS). The volatility bins are separated by powers of 10, typically ranging from 0.01 μ g m⁻³ to 10⁶ μ g m⁻³ at 298 K, and they shift

with temperature according to the Clausius-Clapeyron equation. The purpose of this article is not to review the state of organic aerosol science but rather to view that science through the unifying lens of the VBS. Specifically, we seek to show how the VBS provides a concise platform to address semi-volatile emissions, SOA formation, and organic aerosol aging in a single, self-consistent framework.

2.1 OA Component Partitioning

Following the work of Pankow (1994), the partitioning of a constituent i between the vapor phase and a condensed phase with mass concentration C_{OA} can be described by a partitioning coefficient, ξ_i . If one assumes that the organic solution is ideal (or that the activity coefficients are approximately constant in the range of conditions of interest, pseudo-ideal solution) and the compounds involved have similar molecular weights then the fraction of this compound in the condensed phase is given by the following simple saturation curve:

$$\xi_{i} = \frac{1}{1 + \left(C_{i}^{*} / C_{OA}\right)} \tag{1}$$

where C_i^* is the effective saturation concentration of the compound (the inverse of a Pankow type partitioning coefficient). C* is simply a semi-empirical property that describes partitioning of a complex mixture. Because the C* values are semi-empirical, they are assumed to effectively include activity coefficients of the mixture; however, a limitation is that those activity coefficients are assumed to be roughly constant under atmospheric conditions.

The salient features of Eq. (1) are as follows:

- a. 50% of the material is in each phase when $C^* = C_{OA}$.
- b. Within about one order of magnitude on either side of this equipartition point the response curve is roughly linear and,
- c. Beyond this linear region almost all of the material is in one phase or the other, mostly in the condensed phase for $C^* < 0.1 C_{OA}$ and mostly in the vapor phase for $C^* > 10 C_{OA}$.
- d. Changing the total organic mass concentration C_{OA} will cause the partitioning to change. Consequently, partitioning close to a point source is very different from partitioning in the remote marine atmosphere.

The phase partitioning of a complex mixture can be accurately described by lumping material into volatility bins separated by an order of magnitude (at 298 K). This is not only convenient; it is a nearly optimal distribution. We refer to these bins as the volatility basis set (VBS). Details are in Donahue et al., (2006).

For the majority of this discussion we shall consider a VBS consisting of nine bins, starting at $C^* = 0.01 \ \mu g \ m^{-3}$ and ranging up to $10^6 \ \mu g \ m^{-3}$. Typical atmospheric C_{OA} levels are between 1 and 100 $\ \mu g \ m^{-3}$. To facilitate and standardize discussion, we propose three sub classes within this range:

Low Volatility Organic Compounds (LVOCs): $C^*= \{0.01, 0.1\} \ \mu g \ m^{-3}$. These compounds are mostly in the condensed phase in all but the most remote (and warm) parts of the atmosphere.

Semi-Volatile Organic Compounds (SVOCs): C*= $\{1, 10, 100\} \mu g m^{-3}$. Significant fractions of these compounds will be found in both phases under typical conditions.

Intermediate Volatility Organic Compounds (IVOCs): $C^* = \{10^3, 10^4, 10^5, 10^6\} \mu g m^{-3}$. These compounds are almost entirely in the gas phase, but they comprise an enormous number of difficult to measure compounds and (probably) a small but important fraction of the total atmospheric burden, as we shall see later.

There are two more classes outside the VBS range:

Volatile Organic Compounds (VOCs): $C^* > 10^6 \ \mu g \ m^{-3}$. The vast majority of emissions and routinely measured organics fall in this traditional category. These are typically represented explicitly or with lumped compounds in gas-phase chemistry mechanisms. *Nonvolatile Organic Compounds* (NVOCs): $C^* < 0.01 \ \mu g \ m^{-3}$. These compounds reside always in the particulate phase. They can be placed in the first bin (0.01 $\mu g \ m^{-3}$) of the VBS.

2.2 Emissions

The view of emissions we present here differs markedly from the conventional view: POA emissions have traditionally been viewed as non-volatile material in both emission inventories and models, and we now understand that the majority of these emissions fall in the SVOC and IVOC range of the VBS. POA emissions have always been modeled as purely non-volatile. This is in part because emissions measurements have traditionally been limited by the signal-to-noise of filter weight measurements or chromatographic characterization of individual compounds. Only very recently have primary emissions measurements been extended down to ambient mass loadings, and in every case examined to date the majority of material in the condensed phase under typical sampling conditions has evaporated by the time the emissions have been diluted to ambient conditions.

This new understanding is based on multiple, independent lines of evidence, including: measured changes in partitioning of primary particulate emissions from diesel and woodsmoke upon isothermal dilution (Lipsky and Robinson, 2006, Shrivastava et al., 2006); volatility-based chromatography of primary emissions samples (Hildemann et al., 1991); similar volatility-based measurements of urban samples (Fraser et al., 1997; 1998). The bottom line is that all emissions with C* > 1 μ g m⁻³, corresponding roughly to a saturation mixing ratio greater than 0.1 ppbv, will be found, at least partially, in the gas phase under typical ambient conditions. These constitute 50-90% of the emissions that have traditionally been modeled as non-volatile POA.

2.3 Chemical Production of Organic Aerosol

Chemical production involves both reactions of VOCs that generate lower-volatility products in the ('traditional' SOA formation), and reactions within the VBS. Traditional SOA precursors such as α -pinene and toluene have very high C* (10⁷ or 10⁸ μ g m⁻³). The oxidation of these precursors result in a set of products, which can be schematically represented as

VOC + oxidant $\rightarrow a_1 P_1 + a_2 P_2 + \dots a_9 P_9$

where a_i are the set mass yields for products distributed over the VBS. This reaction is almost never an elementary reaction, but rather the left-hand-side represents the (initial) rate-limiting step of a reaction sequence, where subsequent reactions leading to the VBS products will be some combination of rapid gas-phase radical reactions and rapid condensed-phase reactions. As a consequence, the yields a_i may be functions of NO_x levels, temperature, relative humidity, etc. The current state of SOA research is summarized in an excellent recent review by Kroll and Seinfeld (2008). The VBS can help modelers simply address several facets of SOA chemistry, including mass balance, dependence on ambient conditions (NO_x, RH, UV, T), and ongoing aging.

It is clear that the VBS includes thousands of organic compounds in both the vapor and condensed phases, and that these compounds will continue to react while they reside in the atmosphere (Robinson et al., 2006). These reactions constitute "chemical aging", or reactions within the VBS. These reactions will almost certainly make products with altered volatility. Mechanisms based on explicit product representation or even multiple surrogates, develop a profusion of products when multiple generation reactions are treated. However, then volatility alone is considered, reactions within the VBS simply redistribute material from one bin to another. This greatly simplifies aging parameterizations, provided that the appropriate aging parameters can be constrained.

Most of the material in the VBS, both in the atmosphere and in most experiments, exists in the vapor phase. Partitioning theory demands this, and experiments on both growth and evaporation confirm it. The vast majority of SOA experiments show increasing mass fractions with increasing aerosol mass concentrations, and as predicted by partitioning theory (Pankow, 1994) in Equation 1. Likewise, both isothermal dilution (Grieshop et al., 2007; Lipsky and Robinson 2006) and thermal denuder measurements (An et al., 2007) show that SOA particles shrink when the driving force of mass transfer favors evaporation, again strongly implying the subsequent presence of vapors.

These VBS vapors are likely important precursors for additional chemical production of OA. The vapors produced by SOA experiments will be partially oxidized compounds. On the other hand, vapors from primary emissions will be highly reduced. In either case, we can be absolutely certain that these vapors will react in the atmosphere. They will react in the gas phase with the OH radical in the very least, and quite rapidly. Most of these compounds have a large number of CH₂ groups, and such compounds typically have rate constants k_{OH} near 3×10^{-11} cm³ molec⁻¹ s⁻¹ (Seinfeld and Pandis, 2006), giving an atmospheric lifetime of approximately 8 hours for 10^6 OH cm⁻³. It is also likely that the OH uptake coefficient to particles is close to unity, which would also result in a condensed-phase lifetime for organics of a day or so. Shrivastava et al. (2008) have described the chemical aging of the vapors in the VBS assuming a reaction of the form:

$POA_n(g) + OH \rightarrow OPOA_{n-1}(g)$

where $POA_n(g)$ is the gas-phase concentration of the components in the *nth* volatility bin of the VBS and $OPOA_n(g)$ is the gas-phase concentrations of an oxidized component in the (n-1)th volatility bin. This reaction (with rate constant k_{OH}) assumes that each oxidation step reduces the volatility of the compounds by one order of magnitude. This formulation with the definition of POA and OPOA surrogate components allows the simulation of the concentration of both the fresh POA and its oxidized products and the direct comparison of the results to those of the AMS: the POA should correspond to the HOA, while the sum of the OPOA and the traditional SOA should correspond to the OOA. More complicated reaction schemes are possible including reactions that increase the volatility of the VBS components (Donahue et al., 2006).

3. Revisiting the Sources of Organic Aerosol

The volatility basis set described above has recently been implemented into the regional CTM PMCAMx to investigate the effects of partitioning and aging of primary emissions and multigenerational processing of traditional SOA precursors on urban and regional OA levels in the Eastern US (Shrivastava et al., 2008; Lane et al., 2008). Figure 1 shows average predicted ground-level organic aerosol and vapor concentrations during July 14-28 2001 and January 2002. Details of the modeling are described in Shrivastava et al. (2008).

This more physically realistic representation implemented reveals that ambient organic aerosols are a highly-dynamic system dominated by both variable gaspartitioning and chemical evolution. The majority of the traditionally defined POA emissions evaporate, substantially reducing the predicted POA concentrations. Figure 1a shows that in the summertime POA concentrations are only significant near heavily urbanized areas. In the summer, photochemical aging of these evaporated emissions creates large amounts of regional OPOA (Figure 1b). Wintertime simulations show a somewhat larger fraction of the primary organics partitioning into the particle phase (Figure 1d) and less production of OPOA (Figure 1e) due to the combination of lower temperatures and oxidant levels.

The substantial evaporation of existing POA is due to multiple factors. Although dilution samplers are used to measure POA emission factors, a large fraction of the low-volatility organics has been misclassified as POA because these samplers are often operated at unrealistically high concentrations that are orders of magnitude higher than typical ambient levels. This biases gas-particle partitioning towards the particle phase relative to atmospheric conditions (Lipsky and Robinson, 2006; Shrivastava et al., 2006). Interestingly, the same problem exists in many of the chamber SOA data sets, which were collected at unrealistically high OA concentrations. This underscores the need for future source tests (and chamber experiments) to be conducted at atmospherically relevant temperatures and concentrations. In addition, quartz filters used to measure POA concentrations collect a substantial amount of organic vapors (positive artifact) during source tests (Lipsky and Robinson, 2006). The net effect of these two problems is that POA emission factors greatly overestimate the amount of POA that exists at typical atmospheric conditions. The aging of evaporated POA reduces its volatility, and shifts its partitioning into the condensed phase. The net result is the production of significant amount of oxidized OA.

Explicit accounting of partitioning and aging of primary emissions only has a modest effect on the total amount of OA (much less than a factor of 2 throughout the domain) relative to a traditional model that assumes POA is non-volatile (Robinson et al., 2007). The change is modest because CTMs based on traditional emission inventories already contain substantial amounts of low-volatility organics, albeit misclassified as POA. For misclassified emissions, the effects of partitioning and aging partly offset each other, resulting in modest changes to the total OA concentrations but substantial increases in the fractional contribution of oxidized OA. If one only accounts for partitioning and aging of the existing primary emissions, the predicted OA levels are lower than the traditional model. In order to create additional OA, one must add emissions to the inventory above and beyond the existing POA emissions. The limited

available data suggests that the traditional inventories underestimate the emissions of low volatility organic vapors by a factor of 2 to 3. Accounting for these emissions has the potential to increase predicted OA concentrations by 10-50%. Therefore this mechanism has the potential to help close the gap between model predictions and ambient observations.



Figure 1. Predictions of average ground-level organic aerosol and vapor concentrations during July 2001 and January 2002: (a) primary organic aerosol during July, (b) oxidized primary organic aerosol during July, (c) secondary organic aerosol formed from traditional precursors during July, (d) primary organic aerosol during January, (e) oxidized primary organic aerosol during January, and (f) secondary organic aerosol formed from traditional precursors during January.

A more significant change associated with the revised framework for primary emission is the primary-oxidized OA split. Accounting for partitioning aging shifts the split towards oxidized OA throughout the domain; this brings model predictions into much better agreement with the ambient AMS data. Sensitivity analysis reveals that the PMCAMx cannot predict the high levels of observed oxidized OA unless a substantial fraction of the existing non-volatile primary emissions evaporate and react. Therefore, it helps resolve the inconsistencies between the ambient observations and model predictions that motivated the latest round of the debate regarding the oxidized-primary OA split.

4. References

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