Supplementary Information for

Carbon oxidation state as a metric for describing the chemistry of atmospheric organic aerosol

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I) Relationship of $\overline{OS}_C$-$n_C$ space to other proposed two-dimensional spaces for describing organic aerosol.

Several two-dimensional spaces have recently been proposed in an effort to consolidate the immense complexity of atmospheric organic species in ways that are conceptually or computationally tractable. These spaces are designed to assist calculations of important quantities such as concentrations of organic aerosol, to facilitate comparisons of measurements and model predictions, and/or to guide and enhance our fundamental understanding of the complex processes of organic degradation in the atmosphere. These approaches are complementary; each provides useful insight while sacrificing other details for the sake of simplicity. Here we summarize these spaces, and discuss the unique role of $\overline{OS}_C$ and the $\overline{OS}_C$-$n_C$ space presented in this work.

The first such space proposed was the “carbon number-polarity grid” of Pankow and Barsanti\(^1\). The purpose of this space is to provide simple yet accurate predictions of organic thermodynamic properties (vapor pressure and activity coefficients in mixtures). If one wants to predict thermodynamic properties with the minimum number of independent pieces of information, carbon number and dipole moment are a natural combination. Chemical evolution is fundamentally external to this space; it is designed to complement chemical mechanisms that predict concentrations of either all relevant compounds via an explicit chemical mechanism\(^2\), or a subset of surrogate compounds designed to represent the full set of organics\(^3\).
A second two-dimensional space, based on volatility ($C^*$) and the oxygen-to-carbon molar ratio (O/C), is described by Jimenez et al.\textsuperscript{4}. This 2D volatility basis set (2DVBS) space is an extension of the volatility basis set developed by Donahue et al.\textsuperscript{5}. In this framework, volatility is not predicted because it is the principal axis of the space; however, chemical reactions are considered based on whether they increase or decrease the volatility of reaction products relative to reactants. The second axis (O/C) allows for the degree of oxygenation of the organics to also be considered. The strength is that the consequences to phase partitioning are straightforward to see - the farther left in the space, the less volatile the material. This framework is fundamentally empirical, however. Chemical species are not directly identified (though they can be placed in the space), and trajectories associated with reaction mechanisms follow complex pathways through the space even for chemically straightforward sequences. The framework thus emphasizes the consequences of a chemical mechanism at the expense of illuminating the mechanism itself.

A third two-dimensional framework for describing OA is the Van Krevelen (H/C vs. O/C) plot. Heald et al.\textsuperscript{6} recently showed that bulk OA occupies a narrow region in Van Krevelen space, with the H/C and O/C ratios being tightly coupled for a wide range of OA types. This is a primarily descriptive framework, affording insight into the average chemical makeup of OA, as well as which individual compounds may (or may not) be broadly representative of OA as a whole. Atmospheric aging appears to involve well-defined movement in Van Krevelen space (along a line with a slope of -1). However such movement is difficult to interpret in terms of the underlying chemical reactions, since carbon number of the organic molecules (which changes for many classes of reactions) is not represented in this space.

The above three frameworks are aimed at the description and/or modeling of key properties of organic aerosol. The $\overline{OS}_C-n_C$ space differs from these in that it is a fundamentally
chemical space, providing insight into the chemical changes that atmospheric organics undergo in the atmosphere. Such changes include reactions in which oxygenated functional groups are added to a carbon backbone (functionalization), association reactions between organic molecules to increase the number of carbon atoms in a molecule (oligomerization), and degradation processes in which the carbon number decreases (fragmentation). $\bar{O}S_C - n_C$ space is the only proposed two-dimensional OA framework for which these classes of reactions are uniquely defined by their trajectories: oligomerization moves material to the left, functionalization straight up, and fragmentation to the right. Such reactions cannot be generally defined in the other 2D spaces; for example, individual classes of reactions can involve either increases or decreases in polarity and volatility (such as the addition of new functional groups vs. oxidation of a functional group to a less polar one), so are not defined by an overall directionality in carbon number-polarity or 2DVBS spaces. Similarly, as described above, oligomerization and fragmentation reactions cannot be easily represented in Van Krevelen space. By contrast, these reaction types may be simply and unambiguously described in terms of their changes in $\bar{O}S_C$ and $n_C$ (Figure 1 inset). Thus, by describing organics in terms of their fundamental chemical properties (the number and degree of oxidation of carbon atoms), $\bar{O}S_C - n_C$ space provides a powerful framework for interpreting proposed reaction pathways and OA composition data in terms of the key underlying chemical aging reactions.
II) Determination of Average Carbon Oxidation State of Atmospheric Organics (Table 1 and Figure 2)

a) HR-AMS: For laboratory and ambient measurements of OA using the high-resolution aerosol mass spectrometer\textsuperscript{7-12}, $\overline{OS}_C$ was determined from Eq. 2 ($\overline{OS}_C = 2 \text{ O/C-H/C}$), with O/C and H/C of the OA determined using the approach of Aiken, et al.\textsuperscript{7}. The range of values given is the highest and lowest reported for each aerosol type. The influence of heteroatoms (namely nitrogen) on $\overline{OS}_C$ is negligible, due to low measured abundances ($\text{N/C} < 0.02$)\textsuperscript{7}. Errors in $\overline{OS}_C$ associated with heteroatom-containing groups are also likely to be minimal because atoms in weakly-bound species (such as organonitrates or organosulfates) tend not to be measured or tabulated as “organic” using thermal methods\textsuperscript{13}.

b) CHNS: For the combustion analysis of HULIS samples\textsuperscript{14,15}, $\overline{OS}_C$ was determined from Eq. 2 ($\overline{OS}_C = 2 \text{ O/C-H/C}$). Inclusion of nitrogen introduces only a small uncertainty to the calculation of $\overline{OS}_C$, due to its low abundance ($\text{N/C} \approx 0.04$)\textsuperscript{14,15}: assuming N is fully oxidized ($\text{OS}_N = +5$) leads to a 0.2 decrease in calculated $\overline{OS}_C$, whereas assuming N is fully reduced ($\text{OS}_N = -3$) leads to a 0.15 increase. Such errors are likely within the uncertainty of the $\overline{OS}_C$ determination. In the case of SOA from alkene oxidation\textsuperscript{16}, generated under high-NO\textsubscript{x} conditions, the particulate nitrogen is almost certainly in the form or organic nitrates ($\text{OS}_N=+5$), so $\overline{OS}_C$ was determined by Eq. 1: $\overline{OS}_C = 2 \text{ O/C-H/C-5 N/C}$. Use of Eq. 2 (ignoring N and tabulating all nitrate oxygen as “organic”) leads to a calculated $\overline{OS}_C$ that is higher by 0.5. We believe this represents an upper limit to the error introduced by neglecting organic nitrogen, due to the very high nitrogen abundance of the sample ($\text{N/C}=0.1$), and the fact that other techniques (AMS and possibly ESI as well) do not normally tabulate nitrate oxygen as “organic”.
c) **Ultrahigh resolution ESI-MS**: Values of $\overline{O/C}$ from electrospray ionization mass spectrometry were determined from speciated molecular data described in refs. 17-22. Negative ion mode ESI data are used in all cases; for isoprene ozonolysis$^{21}$ and rainwater WSOC$^{18}$, data from positive ion mode ESI are also included. Details of sampling, extraction, and mass spectrometric analysis are provided in the individual publications. Average elemental ratios (O/C and H/C) of the samples were estimated using the approach described by Bateman, et al.$^{20}$, and were converted to $\overline{O/C}$ using Eq. 2 ($\overline{O/C} = 2 \overline{O/C-H/C}$). This averaging of elemental ratios is subject to errors arising from variations in ESI-MS response factors for different compounds; for the large number (hundreds to thousands) of compounds in these samples, such differences may approximately average out, though further characterization of ESI response factors is necessary to better constrain this. For ambient measurements, compounds with heteroatoms (N, S, and P) were excluded for simplicity, since the ranges in possible oxidation states of these atoms introduce some uncertainty to the $\overline{O/C}$ of a given molecule. However the effects of these heteroatoms on calculated $\overline{O/C}$ of the OA are generally small, due to their relatively low abundances, and the fact that most heteroatom-containing functional groups (-ONO$_2$, -NH$_2$, -OSO$_3$H, etc.) have only a minimal effect (+1 or -1) on the oxidation state of the adjacent carbon atom. Such effects will be investigated in detail in future work. In addition to the average values of $\overline{O/C}$ given in Table 1, individual organic compounds in ambient aerosol$^{19}$ and fogwater$^{22}$ are shown in Figure 2.
III) Determination of Average Carbon Oxidation State and Carbon Number for the multigenerational oxidation of organics (Figure 4)

a) OH + isoprene and OH + α-pinene. Speciated oxidation products shown in Figure 4 include known carbonyl products of isoprene oxidation (methacrolein/methyl vinyl ketone, methylglyoxal, and glyoxal) as well as multifunctional species measured in laboratory studies of isoprene + OH\textsuperscript{21,24} and α-pinene + OH\textsuperscript{25-29}. Both gas-phase and particulate products are shown; for simplicity, only species with contiguous carbon skeletons (in which all carbon atoms are connected to each other) with $n_C \geq 2$ (isoprene) or $n_C \geq 5$ (α-pinene) are shown. Multifunctional products measured in other studies\textsuperscript{30-34} have the same values of $\overline{\text{COS}}_C$ and $n_C$ as the products shown.

b) OH + organic particles (squalane, triacontane, levoglucosan). Particles composed of single organics (squalane and triacontane, C\textsubscript{30}H\textsubscript{62}, and levoglucosan, C\textsubscript{6}H\textsubscript{10}O\textsubscript{5}) were heterogeneously oxidized in a flow reactor, described in detail by Smith, et al.\textsuperscript{35} (squalane) and Kessler, et al.\textsuperscript{36} (levoglucosan). Oxidation of triacontane was carried out using the same approach as that of squalane\textsuperscript{35} except that triacontane particles were generated upstream of the reactor using a nucleation oven at 140°C, with the aerosol stream passed through a second annealing oven (T=75°C) in order to make the particles more spherical in shape.

Average $\overline{\text{COS}}_C$ of the particulate organics was determined using Equation 2 and AMS measurements of O/C and H/C ratios. The average number of carbons per molecule ($n_C$) was determined by assuming fractional changes in carbon number are equal to the fraction of carbon remaining in the particle phase after oxidation. This assumption is broadly consistent with measured changes to particle volatility upon heterogeneous oxidation, which indicate that carbon
loss from heterogeneous oxidation occurs via the release of small volatile fragments from the particulate organics\textsuperscript{37}.

c) \textit{OH, O}_3 + coronene films. The XPS investigations of the oxidation of coronene by ozone and OH are discussed in detail by Mysak, \textit{et al.}\textsuperscript{38}. The XPS measurements were performed using the Ambient Pressure Photoemission Spectrometer at beamline 11.0.2 at the Advanced Light Source in Berkeley, CA\textsuperscript{39}. Thin films of coronene (97\% purity, Sigma Aldrich) were vapor-deposited on clean polycrystalline Au foil or Ag(111) single crystal substrates at a deposition rate of $\sim$0.2 Å min\textsuperscript{-1}, as measured by a quartz crystal microbalance. This growth rate yielded consistently homogenous films, as evidenced by both XPS and AFM measurements. The thickness of the unreacted coronene film was determined from the attenuation of the substrate signal using the inelastic mean free path (IMFP) of electrons in coronene at the given electron kinetic energy of 140 eV \textsuperscript{40}. Using a IMFP value of 8.5 Å the thickness of the unreacted coronene film was found to be 4-6 Å \textsuperscript{38}.

Ozone is produced by passing O\textsubscript{2} through a commercial corona discharge source (Yanco). The ozone flow is then diluted with N\textsubscript{2} and introduced via a precision leak valve into the sample chamber at a concentration of $\sim$1$\times$10\textsuperscript{8} molecules cm\textsuperscript{-3}. The ozone is directed at the surface through a Teflon doser located $\sim$2 cm from the sample surface. OH is produced by passing N\textsubscript{2} through a water bubbler, selecting a portion of this flow with a leak valve, and passing it through a microwave discharge cavity and into the chamber via a 1.27 cm O.D. quartz tube ending 3 cm from the sample surface. The OH concentration is estimated to be 9.8 $\times$ 10\textsuperscript{8} molecules cm\textsuperscript{-3}. The total operating pressure in the sample chamber for both the OH and O\textsubscript{3} experiments is fixed at 10\textsuperscript{-5} Torr. To measure heterogeneous kinetics, XPS spectra are collected as a function of reaction time at a fixed concentration of O\textsubscript{3} or OH. It was found that the OH reactions are sufficiently fast that it is necessary to turn off the OH source during the data collection period.
In contrast, the O₃ reaction proceeded slowly enough that the reaction is allowed to proceed continuously during data collection. Care was taken to avoid radiation-induced changes to the coronene films. The data shown in Fig. 4 were free of detectable radiation damage.

The values for \( n_C \) and \( \overline{O/S}_C \) were determined from C1s XPS data; examples of these spectra are shown in Fig. S1. The binding energy scale was calibrated by the Fermi energy of the Ag substrate. Fig. S1 shows C1s XPS spectra for the OH + coronene reaction at two reaction times, (a) 15 s and (b) 105 s. The C1s spectra are fit using five components, which were assigned to different carbon species (C=C, CHₓ, C-OH, C=O and C(O)OH) according to their binding energy by comparing to literature values 41. The validity of the assignment to those species was cross-checked by comparison to O 1s spectra (not shown), which also revealed the C-OH, C=O and C(O)OH species. \( \overline{O/S}_C \) was determined from measurements of elemental ratios (Eq. 2). The O/C ratio was determined directly from the C1s spectra by dividing the area of the O-related C1s peaks (with C(O)OH weighted by a factor of 2) by the peak area of the five C peaks; hydrogen atoms are not measured directly by XPS, so H/C was estimated by assuming each CHₓ, C-OH, and C(O)OH carbon has one H atom, and C=C carbon has on average 0.5 H atoms (the same as coronene). The number of carbons (\( n_C \)) was determined from the ratio of the total C1s peak area of the reacted film to the peak area of the unreacted film, normalized to 24 (the number of C atoms in coronene). This method may slightly underestimate the value for \( n_C \) since it does not take into account possible attenuation of the C1s signal due to the presence of O in the reacted films. Since it is not possible in these experiments to determine the relative positions of O and C atoms with respect to the surface, this effect cannot be quantified. However, we can estimate the upper limit for the error in the \( n_C \) measurements from the maximum value for the O/C ratio (~0.7) by assuming that all C are located at the substrate interface in one layer, while all O are
located on top of the carbons, also in one layer. We estimate that for that extreme case the value for $n_C$ is underestimated by less than 15%.

Fig. S1: C1s XPS spectra for the OH + coronene reaction at two reaction times, (a) 15 s and (b) 105 s. The C1s spectrum is fit using five components (C=C, CHx, C-OH, C=O and C(O)OH). The data were taken with an incident photon energy of 430 eV.

References Cited


