

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

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Abstract

A detailed understanding of the sources, transformations, and fates of organic species in the environment is crucial because of the central roles that organics play in human health, biogeochemical cycles, and Earth's climate. However, such an understanding is hindered by the immense chemical complexity of environmental mixtures of organics; for example, atmospheric organic aerosol consists of at least thousands of individual compounds, all of which likely evolve chemically over their atmospheric lifetimes. Here we demonstrate the utility of describing organic aerosol (and other complex organic mixtures) in terms of average carbon oxidation state ($\overline{\text{OS}}_{\text{C}}$), a quantity that always increases with oxidation, and is readily measured using state-of-the-art analytical techniques. Field and laboratory measurements of $\overline{\text{OS}}_{\text{C}}$, using several such techniques, constrain the chemical properties of the organics and demonstrate that the formation and evolution of organic aerosol involves simultaneous changes to both carbon oxidation state and carbon number (n_{C}).

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Introduction

The atmospheric oxidation of organic species is central to several key environmental chemical processes that directly influence human health and global climate. These include the degradation of pollutants, the production of ozone and other toxic species, and the formation and evolution of fine particulate matter (aerosols). This last topic is inextricably linked to the oxidation of atmospheric organics, since organic aerosol material makes up a substantial fraction (20%-90%) of submicron aerosol mass¹. A large fraction of organic particulate matter is secondary organic aerosol, formed from the oxidation of gas-phase organic species^{2,3}.

Current state-of-the art models have difficulty predicting the loadings, spatial and temporal variability, and degree of oxidation of ambient organic aerosol, indicating a gap in our understanding of atmospheric oxidation processes. The oxidation mechanisms of light volatile organic compounds are relatively straightforward, with the canonical example being conversion of methane into formaldehyde, CO, and ultimately CO₂⁴. However, the oxidation of larger organics associated with SOA involves a much larger number of reaction pathways, intermediates, and products, the detailed characterization of which is beyond the capabilities of most analytical techniques. This extreme chemical complexity has prevented the precise measurement and prediction of the oxidation dynamics associated with the formation and evolution of atmospheric organic aerosol.

Here we present a new metric for the degree of oxidation of atmospheric organic species, the average carbon oxidation state ($\overline{\text{OS}}_{\text{C}}$), a quantity that necessarily increases upon oxidation and that is measurable using several modern analytical techniques. The general concept of average carbon oxidation state has been used previously in other contexts, such as in soil chemistry for the measurement of ecosystem oxidative ratios⁵, in botany for the estimation of

growth yields⁶, in wastewater treatment for the determination of degradation mechanisms⁷, and in atmospheric chemistry to describe individual oxidation products of methane⁸ and α -pinene⁹. To our knowledge $\overline{\text{OS}}_{\text{C}}$ has never been used to describe the evolving composition of a complex mixture of organics undergoing dynamic oxidation processes.

Here we show that $\overline{\text{OS}}_{\text{C}}$, when coupled with carbon number (n_{C}), provides a framework for describing the chemistry of organic species in the atmosphere, and in particular atmospheric organic aerosol. These two fundamental quantities can be used to constrain the composition of organic aerosol, and moreover to uniquely define key classes of atmospheric reactions, providing insight into the oxidative evolution of atmospheric organics.

Results

Definition of $\overline{\text{OS}}_{\text{C}}$ and relationship with carbon number. The oxidation state of carbon is defined as the charge a carbon atom would take if it were to lose all electrons in bonds with more electronegative atoms but gain all electrons in bonds with less electronegative atoms. This quantity will necessarily increase in oxidizing environments such as Earth's atmosphere. The oxidation states of individual carbon atoms within a molecule, or within a mixture of molecules, may change differently upon oxidation, but the average oxidation state of the carbon ($\overline{\text{OS}}_{\text{C}}$) must increase. Thus the quantity $\overline{\text{OS}}_{\text{C}}$ is an ideal metric of the degree of oxidation of organic species in the atmosphere, and serves as a key quantity to describe organic mixtures as chemically complex as secondary organic aerosol.

In the atmosphere, the increase in carbon oxidation state arises from the formation of bonds between carbon and oxygen (and other electronegative elements), and/or the breaking of bonds between carbon and hydrogen (and other electropositive elements). This influence of both

electronegative and electropositive atoms has important implications for atmospheric oxidation. First, metrics of oxidation that involve only one of these, such as the oxygen-to-carbon molar ratio (O/C), may not accurately capture the degree of oxidation of the organics. For example, the oxidation of an alcohol to a carbonyl involves no change in O/C; conversely, O/C may be affected dramatically by non-oxidative processes such as hydration or dehydration. Second, since the oxidation state of a carbon atom is not affected by bonds to other carbon atoms, the number of carbons in a molecule (n_C) governs the range of possible values of $\overline{\text{OS}}_C$.

Figure 1 shows the possible combinations of $\overline{\text{OS}}_C$ and n_C for stable organic molecules with a contiguous carbon skeleton, as governed by chemical valence rules. Also shown are the locations in this two-dimensional space of organics that are either important in the atmosphere or commonly used as surrogates for atmospheric species. The vast majority of these species are reduced ($\overline{\text{OS}}_C \leq 0$); most known compounds with higher average oxidation states are small, with only 1-3 carbon atoms.

Reactions that govern the chemical transformation of atmospheric organics and the evolution of organic aerosol involve movement in $\overline{\text{OS}}_C$ - n_C space. The oxidative transformation of atmospheric organics can occur within a range of chemical environments, including in the gas phase, at the gas-particle interface, or within the bulk organic or aqueous phase; non-oxidative transformations (such as accretion reactions) may also occur. These chemistries can all be described in terms of three key classes of reactions (Fig. 1 inset): functionalization (the oxidative addition of polar functional groups to the carbon skeleton), fragmentation (the oxidative cleavage of C-C bonds), and oligomerization (the association of two organic molecules). These reactions are defined uniquely by the changes to $\overline{\text{OS}}_C$ and n_C of the organics; thus the $\overline{\text{OS}}_C$ - n_C space is an ideal conceptual framework to describe the chemical changes that atmospheric organics undergo

upon oxidation. This fundamental chemical nature of the $\overline{\text{OS}}_{\text{C}}-n_{\text{C}}$ space distinguishes it from other emerging two-dimensional treatments of organic aerosol¹⁰⁻¹². Such frameworks are extremely useful for describing or modeling aerosol based on experimental measurements, but they are based upon quantities that cannot be related to these general classes of chemical reactions in a straightforward manner, and so they provide limited insight into the nature of atmospheric chemical transformations (see Supporting Information for a more detailed discussion).

In $\overline{\text{OS}}_{\text{C}}-n_{\text{C}}$ space, atmospheric oxidation has an inherent directionality: because carbon oxidation state must increase upon oxidation, the ultimate end-product of the oxidation of organic species (given enough time) is necessarily CO_2 ($\text{OS}_{\text{C}} = +4$). Reaching this oxidative end-product requires both the addition of oxygen-containing moieties (increasing $\overline{\text{OS}}_{\text{C}}$), and the breaking of C-C bonds (decreasing n_{C}). The oxidation of atmospheric organic species therefore involves an overall movement towards the upper right of Fig. 1 (blue arrows). Leftward movement towards larger carbon numbers (oligomer formation) certainly occurs in many cases³, but even the high-molecular weight products of accretion reactions are susceptible to oxidative degradation¹³ and ultimately will form CO_2 .

Measurements of $\overline{\text{OS}}_{\text{C}}$. A critical strength of $\overline{\text{OS}}_{\text{C}}$ as a metric of atmospheric processing of organics, in addition to the fact that it must increase upon oxidation, is that it can be measured rapidly and routinely using state-of-the-art analytical techniques. Carbon oxidation state is determined by the identity and abundance of non-carbon atoms in the organic compound(s):

$$\overline{\text{OS}}_{\text{C}} = -\sum_i \text{OS}_i \frac{n_i}{n_{\text{C}}} \quad (1)$$

in which the summation is over all non-carbon elements, OS_i is the oxidation state associated with element i , and n_i/n_C is the molar ratio of element i to carbon. Thus the measurement of $\overline{OS}_C$ requires that all non-carbon elements in the sample be characterized, in terms of their relative abundances and oxidation state.

Since atmospheric organics are primarily composed of carbon, hydrogen ($OS=+1$), and reduced oxygen ($OS=-2$), Equation 1 can often be simplified to:

$$\overline{OS}_C \approx 2 \text{ O/C} - \text{H/C} \quad (2)$$

This relation is exact for organics made up of only carbon, hydrogen, and most oxygen-containing functional groups (alcohols, carbonyls, carboxylic acids, ethers, and esters). The presence of peroxide groups (in which the O atoms have an oxidation state of -1) and heteroatoms (which can have a range of oxidation states) introduces deviations from this relation. These can be corrected for by measuring individual functional groups; however such moieties generally represent a minor component of organic aerosol (on a per-carbon basis), so such errors tend to be small. For example, the independent determination of O/C and peroxide content¹⁴ allows for an accurate determination of $\overline{OS}_C$ in secondary organic aerosol; however, even for such a peroxide-rich system, Eq. 2 yields an $\overline{OS}_C$ that is within 0.1 of the exact value (from Eq. 1). Similarly, the measurement of nitrogen-containing functional groups allows for N atoms to be explicitly included in the determination of $\overline{OS}_C$, though organic nitrogen is a sufficiently small fraction of organic particulate matter that this has a relatively minor effect on calculated $\overline{OS}_C$ (see Supporting Information). Nonetheless, in some cases these moieties might be present in relatively high abundances, and their effect on measured $\overline{OS}_C$ is an important topic for future research.

Here we focus on the simplified determination of $\overline{\text{OS}}_{\text{C}}$ from Equation 2, based on measurements of O/C and H/C only. A number of analytical techniques can be used to determine elemental ratios, and therefore $\overline{\text{OS}}_{\text{C}}$, of atmospheric particulate matter. These include combustion analysis (CHNS)¹⁵⁻¹⁷, ultrahigh resolution mass spectrometry with electrospray ionization (ESI)^{14,18-22}, nuclear magnetic resonance (NMR) spectroscopy²³, Fourier transform infrared spectroscopy (FTIR)²⁴, X-ray photoelectron spectroscopy (XPS)²⁵, and high-resolution electron impact aerosol mass spectrometry (HR-AMS)²⁶⁻³¹. Each technique has its own strengths and weaknesses for characterizing organic aerosol. For example, CHNS analysis is accurate and universal, but requires large amounts of collected organics, and oxygen content is usually determined only by subtraction. ESI can provide exact elemental ratios of individual compounds within a complex mixture, and requires very little sample volume; however it is a selective ionization technique, with response factors that may vary widely among different species. HR-AMS is a sensitive, online technique for measuring elemental ratios in real time, but is not as accurate as other techniques, since it requires uncertain empirical corrections to account for biases during ion fragmentation.²⁶ Because of the uncertainties associated with each technique, it is useful to examine results from a range of elemental analysis approaches in order to obtain an accurate, complete picture of the carbon oxidation state of organic aerosol.

Ambient organic aerosol and $\overline{\text{OS}}_{\text{C}}$. Table 1 presents compiled measurements of the mean carbon oxidation state of organic aerosol, taken from measurements of O/C and H/C using the three most widely-used elemental analysis techniques (CHNS, ESI, and HR-AMS). These include measurements of ambient organic aerosol, ambient aerosol fractions (by physical extraction or factor analysis), and laboratory-generated primary or secondary organic aerosol.

A consistent picture emerges from these results: the $\overline{\text{OS}}_{\text{C}}$ of organic aerosol ranges from -2 to +1, depending on the level of atmospheric aging. Individual species in organic aerosol, such as oxalate and other highly oxidized species, may have oxidation states greater than +1, but all available data suggest that the average carbon oxidation state of organic aerosol rarely exceeds this value. Even classes of organics that are generally considered to be highly oxidized, such as humic-like substances (HULIS) and oxygenated organic aerosol (OOA), have an $\overline{\text{OS}}_{\text{C}}$ below +1. It appears that more highly oxidized carbon is found predominantly in the gas phase, presumably because species with several (>3) adjacent carbonyl groups are thermodynamically or photochemically unstable.

Figure 2 shows the approximate area in $\overline{\text{OS}}_{\text{C}}-n_{\text{C}}$ space corresponding to atmospheric organic aerosol, based upon the $\overline{\text{OS}}_{\text{C}}$ measurements shown in Table 1, and determinations of n_{C} from ultrahigh resolution ESI and/or known relationships between volatility and carbon number³². Results from AMS/volatility measurements and from ESI data are remarkably consistent, placing aerosol components in the areas of $\overline{\text{OS}}_{\text{C}}-n_{\text{C}}$ space corresponding to large and/or polar organics. Particle-phase organics, specifically the most oxidized fraction (HULIS, OOA, etc.), lie in between the large, reduced species ($n_{\text{C}} \geq 5$, $\overline{\text{OS}}_{\text{C}} < -1$) and the oxidative endpoint CO_2 . Thus secondary organic aerosol is not the product of only a few select hydrocarbons but rather is formed in the oxidation of most organic species. The only reduced organic species unlikely to contribute to aerosol formation upon oxidation are small (four carbons or fewer), though even those might form organic aerosol via oligomerization reactions. The potential formation of aerosol from such a wide variety of organic species is a likely contributor to underestimates of secondary organic aerosol concentrations, since models (and

the experiments on which they are based) typically focus on only a few select aerosol precursors³.

Chemical Complexity. Most points in $\overline{\text{OS}}_{\text{C}}-n_{\text{C}}$ space represent a multitude of compounds; for example, the point corresponding to $n_{\text{C}} = 2$ and $\overline{\text{OS}}_{\text{C}} = -1$ includes acetylene (C_2H_2), acetaldehyde (CH_3CHO), and ethylene glycol ($\text{HOCH}_2\text{CH}_2\text{OH}$) (these compounds are related to each other by the nominal gain/loss of H_2O , which involves no change in $\overline{\text{OS}}_{\text{C}}$ or n_{C}). The number of possible chemical structures (chemical complexity) is a strong function of not only n_{C} ³³ but also oxidation state. Figure 3 shows the number of possible structures for just a single carbon skeleton (an unbranched, acyclic carbon chain), with carbonyl, alcohol, and/or carboxylic acid groups. For a given carbon number, only one structure (the n -alkane) is possible at the lowest $\overline{\text{OS}}_{\text{C}}$ value. The number of possible structures then increases rapidly with $\overline{\text{OS}}_{\text{C}}$, due to the combinatorial addition of different functional groups to different carbon atoms. The maximum in chemical complexity is located at $\overline{\text{OS}}_{\text{C}} = 0$; for molecules in which the average carbon atom is oxidized ($\overline{\text{OS}}_{\text{C}} > 0$), the number of possible chemical structures then decreases with increasing oxidation state.

Many of the compounds that make up organic aerosol (Figure 2) lie in the region of maximum chemical complexity (Figure 3). This underscores the enormous experimental and theoretical challenges associated with describing aerosol in terms of its individual molecular components. The number of oxidized organics ($-1 \leq \overline{\text{OS}}_{\text{C}} \leq +1$) is far greater than can reasonably be constrained by measurements of ambient species, laboratory studies of reaction rates and products, or explicit models of the fate of individual atmospheric compounds. The sheer number of possible species in OA indicates that a completely speciated approach is

probably not feasible for a generalized description of OA. This is especially true for regional or global air-quality and climate models, which instead require concise descriptions of atmospheric organic mixtures in terms of measurable ensemble quantities such as $\overline{\text{OS}}_{\text{C}}$.

Oxidative transformations of atmospheric organics. In order to be accurate, such concise descriptions must properly capture the oxidation mechanisms of atmospheric organic species. This underscores the critical importance of the measurement of selected individual species within organic aerosol to characterize reaction pathways, as well as to identify aerosol sources and toxic species. Insight into oxidation mechanisms can be obtained from experimental studies of the multigenerational oxidation products of individual organics; results from several such studies, mapped onto $\overline{\text{OS}}_{\text{C}}-n_{\text{C}}$ space, are shown in Figure 4. These results were obtained using a range of analytical techniques, including ensemble measurements of condensed-phase organics (HR-AMS and XPS) and speciated measurements of gas- and particle-phase organics (various mass spectrometric techniques).

For all systems studied (Fig. 4), oxidation leads to increased functionality on the carbon skeleton (higher $\overline{\text{OS}}_{\text{C}}$), and, after only a few (1-4) generations of oxidation, a decrease in carbon number of the original carbon skeleton (lower n_{C}). Fragmentation reactions are therefore key processes in the oxidative aging of atmospheric organics, particularly for oxidized species, whose oxygen-containing (electron-withdrawing) groups weaken adjacent carbon-carbon bonds³⁴. This increase in $\overline{\text{OS}}_{\text{C}}$ towards CO_2 can occur via multiple reaction pathways, as illustrated by the numerous individual products of isoprene and α -pinene oxidation (circles in

Fig. 4). The ensemble measurements (lines in Fig. 4) constrain the mean values of $\overline{\text{OS}}_{\text{C}}$, with individual compounds spanning a range in oxidation state, carbon number, and volatility.

Discussion

Oxidation of organics has long been viewed as a source of atmospheric organic aerosol, via secondary organic aerosol forming reactions. However the ultimate dominance of fragmentation reactions (movement to the top right of $\overline{\text{OS}}_{\text{C}}-n_{\text{C}}$ space) means that oxidation may also serve as a organic aerosol sink, since oxidized organics may fragment and volatilize upon further oxidation. The effects of such oxidative degradation reactions on atmospheric aerosol are governed by reaction rates, given the relatively short lifetime of atmospheric PM via physical deposition (~ 1 week). This implies that better constraints on the kinetics of key organic “aging” reactions are needed for the accurate prediction of the loadings, properties, and effects of atmospheric organic aerosol.

Nonetheless, it is known that the heterogeneous degradation of organic PM by gas-phase oxidants is generally substantially slower than of gas-phase organics³⁵, since most particulate organics are shielded from gas-phase radicals interacting with the particle surface. Thus organic aerosol represents a “metastable state” in which partially oxidized organics can survive for a substantial period of time, even under highly oxidizing conditions. This view of organic aerosol as a chemically recalcitrant intermediate in the oxidation of organic species resembles the emerging view of the nature of humic materials in soils and aquatic systems^{36,37}. In this sense the similarities between atmospheric particulate organics and humic materials may extend well beyond their chemical complexity and physicochemical properties^{23,38}, to include their role as a “transition state” of organic matter³⁷. While detailed chemical structures and transformations are

likely to be quite different (for example, biological processes do not affect atmospheric organics to the extent that they do for humic substances), the similarities suggest strong commonalities in the description and experimental studies of such highly complex environmental organic mixtures.

The description of the chemistry of organic species in terms of changes to their average carbon oxidation state (a universal, unambiguous metric for the degree of oxidation of carbon-containing species) and carbon number may thus be useful for describing not only atmospheric oxidation but also other complex reactive systems as well. This includes the formation and evolution of humic substances in soil or aquatic systems, the combustion of complex organic species, the formation or weathering of fossil fuels, and the chemical transformation of organics in oxygen-limited environments. Such systems can involve reactions other than the oxidative processes that govern atmospheric reactions, and therefore may exhibit trajectories in $\overline{\text{OS}}_{\text{C}}-n_{\text{C}}$ space different than those shown in Figure 4. For example, reduction moves organics downward and to the right (towards methane, $\text{OS}_{\text{C}} = -4$ and $n_{\text{C}} = 1$), whereas radical association reactions in low-oxygen environments (such as fuel-rich flames and some planetary atmospheres³⁹), involve leftward movement, towards polycyclic aromatic hydrocarbons and eventually elemental carbon ($\overline{\text{OS}}_{\text{C}} = 0$ and $n_{\text{C}} \rightarrow \infty$). The measurement of $\overline{\text{OS}}_{\text{C}}$ allows for the determination of these trajectories for entire mixtures, offering the potential for simple, predictive models of these exceedingly complex chemical systems.

Methods

Determination of average carbon oxidation state.

All $\overline{\text{OS}}_{\text{C}}$ values reported in Table 1 and illustrated in Figures 2 and 4 were determined using Equation 2. The one exception is the $\overline{\text{OS}}_{\text{C}}$ of secondary organic aerosol formed from the photooxidation of alkenes¹⁵; the high contribution of organic nitrates ($\text{N/C}=0.1$) requires the explicit inclusion of nitrogen ($\text{OS}_{\text{N}}=+5$). A discussion of the potential errors associated with neglecting heteroatoms in Eq. 2 is given in the Supplementary Information.

Ensemble (average) elemental ratios were taken mostly from previously reported measurements. For AMS^{26-31,40,41} and CHNS data¹⁵⁻¹⁷, O/C and H/C ratios are taken directly from reported measurements. For ultrahigh resolution ESI data^{14,18-22}, O/C and H/C are determined by averaging the elemental ratios of all measured CHO species, weighted by ion intensity²⁰. For XPS data²⁵ (C1s spectra at 430 eV), all carbon was categorized as C=C, CH_x, C-OH, C=O and C(O)OH based on its measured binding energy, allowing for the estimation of O/C and H/C ratios. Additional details of these measurements are provided in the Supporting Information.

Estimation of carbon number.

The number of carbon atoms per molecule (n_{C}) in ambient organic aerosol (Figure 2) was either determined from speciated measurements (ESI data) or estimated based on measurements of particle volatility and OSc (AMS data). This latter approach utilizes the SIMPOL.1 structure-activity relationship⁴² to relate saturation vapor pressure, degree of oxidation, and n_{C} .³² Vapor pressures of organic aerosol classes are based on recent *in situ* thermodenuder measurements.⁴³

The effects of functional groups on vapor pressure is estimated by assuming that each oxygen atom decreases the volatility of an organic molecule by a factor of 0.06 (consistent with the addition of carboxylic acids to the carbon skeleton), with oxygen content calculated from $\overline{\text{OS}}_{\text{C}}$ using an empirical relationship that relates elemental ratios ($\text{O}/\text{C}+\text{H}/\text{C}=2$).¹² In the multigenerational oxidation experiments (AMS and XPS traces in Figure 4), ensemble values of n_{C} were determined by assuming fractional changes in carbon number are equal to the fraction of carbon remaining in the particle phase after oxidation.

Multigenerational oxidation experiments.

The oxidation trajectories in $\overline{\text{OS}}_{\text{C}}-n_{\text{C}}$ space (Figure 4) were determined from laboratory studies of the oxidation of individual organic species. Gas-phase and particle-phase (monomeric) products of the OH-initiated oxidation of isoprene and α -pinene were measured by various speciated techniques.⁴⁴⁻⁵⁰ The heterogeneous oxidation reactions of squalane, triacontane, and levoglucosan were carried out by sending nucleated particles into a flow reactor, where they were exposed to high concentrations of OH generated by ozone photolysis.^{40,41} Changes to particle mass and elemental ratios upon oxidation were characterized using a scanning mobility particle sizer and an HR-AMS. For the oxidation of coronene,²⁵ vapor-deposited thin films of coronene (4-6 Å thickness) were exposed to varying levels of OH or O₃, and the chemical changes measured using XPS at the Ambient Pressure Photoemission Spectrometer at beamline 11.0.2 of the Advanced Light Source, (Berkeley, CA). The evolving abundance and type of carbon in the film was determined using C1s spectra at 430 eV. Experimental details are provided in the Supporting Information.

Author Contributions: The work described here was originally conceived by J.H.K. with C.E.K. and D.R.W., with substantial input by N.M.D., J.L.J., M.R.C, S.H.K, and K.R.W. K.E.A., L.R.M., and A.S.W. provided the ESI data (Table 1 and Figure 2). S.H.K. carried out the combinatorial calculations to produce Fig. 3. Data on the aging of organics (Figure 4) were collected by J.D.S, S.H.K., J.H.K., and K.R.W. (squalane, triacontane, and levoglucosan) and E.R.M., J.D.S, K.R.W., and H.B. (coronene). J.H.K. wrote the paper with input from all co-authors, especially N.M.D., J.L.J, M.R.C., and C.E.K.; J.H.K., N.M.D., H.B. and E.R.M. wrote the Supporting Information.

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Table 1. Measurements of $\overline{\text{OS}}_{\text{C}}$ of organic aerosol, using a range of analytical techniques: aerosol mass spectrometry (AMS), ultrahigh resolution mass spectrometry with electrospray ionization (ESI), and combustion techniques (CHNS). Values listed are the $\overline{\text{OS}}_{\text{C}}$ ensemble averages for a given sample, with “...” denoting a range of reported values; $\overline{\text{OS}}_{\text{C}}$ values of individual molecules within a sample may be distributed around these averages, as illustrated in Figure 2.

<i>Ambient Organic Aerosol</i>	OS_{C}	Technique	Ref.
Urban/anthropogenic (Mexico City)	-1.6...+0.1	AMS	26
Remote/biogenic (Amazonian rainforest)	-0.9...-0.2	AMS	31
Aged (Whistler Mountain)	-0.6...+0.6	AMS	30
<i>Ambient Aerosol Fractions</i>			
Hydrocarbon-like organic aerosol (HOA)	-1.7...-1.6	AMS	26
Semivolatile oxygenated organic aerosol (SV-OOA)	-0.5...0.0	AMS	26
Low-volatility oxygenated organic aerosol (LV-OOA)	+0.5...+0.9	AMS	26
Humic-Like Substances (HULIS)	-0.4...-0.3	CHNS	16,17
Water-soluble organic carbon (WSOC) in rainwater	-0.9...-0.7	ESI	18
WSOC in aerosol	-1.0	ESI	21
WSOC in fogwater	-0.7	ESI	22
<i>Primary Organic Aerosol</i>			
Vehicle exhaust (gasoline, diesel)	-2.0...-1.9	AMS	26
Biomass burning aerosol	-1.0...-0.7	AMS	26
<i>Secondary Organic Aerosol</i>			
Monoterpene + O_3	-1.1...-0.5	AMS, ESI	20,26,27,29
Isoprene + OH or O_3	-0.8...-0.2	AMS, ESI	14,26,29
Monoaromatics + OH	-0.9...+0.1	AMS	26,29
Alkane/alkene photooxidation	-0.7...-0.4	AMS, CHNS	15,28
Methylglyoxal aqueous oxidation	-0.3	ESI	18

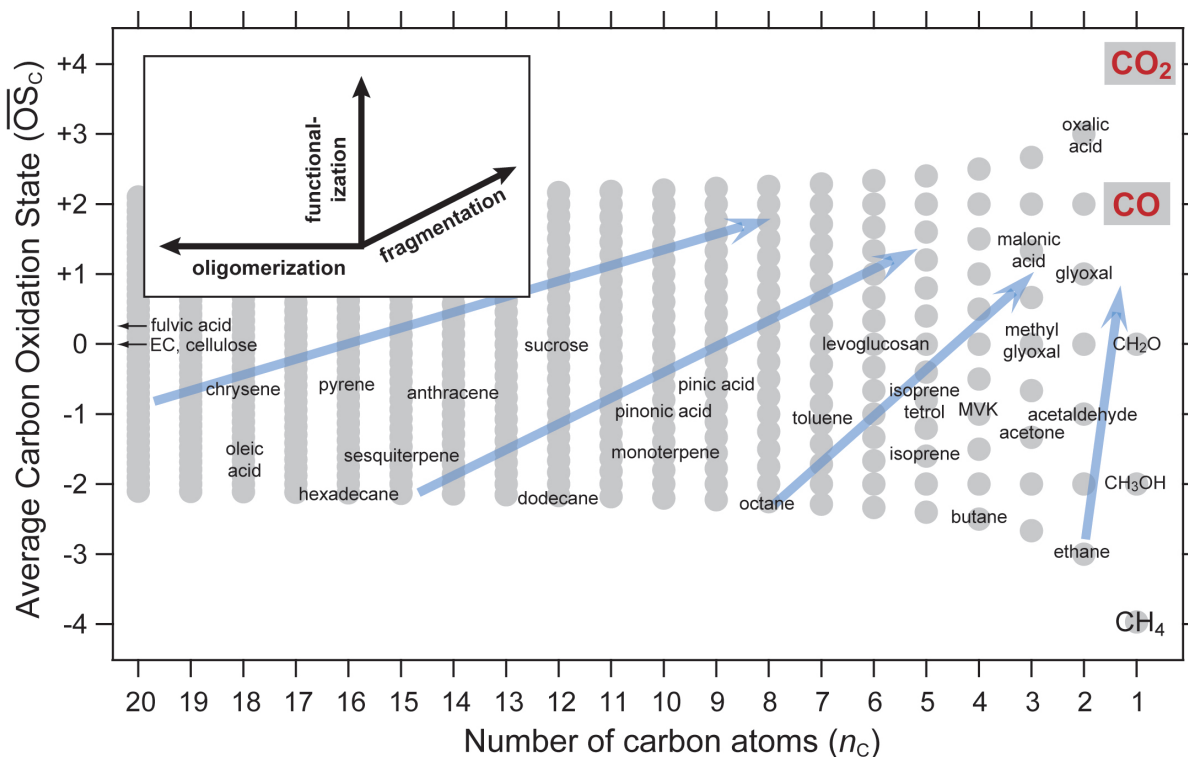


Figure 1. Possible combinations of average carbon oxidation state ($\overline{OS}_C$) and number of carbon atoms (n_C) for stable organic molecules. Any organic species can be placed in this two-dimensional space; the locations of key atmospheric organics (and common surrogate species) are shown. The vast majority of known atmospheric species are reduced ($\overline{OS}_C \leq 0$), with only the smallest compounds having higher oxidation states. Inset: vectors corresponding to key classes of reactions of atmospheric organics, functionalization (addition of polar functional groups), fragmentation (cleavage of C-C bonds), and oligomerization (covalent association of two organic species). The combination of these reaction types leads to complex movement through $\overline{OS}_C$ - n_C space; however, the inevitable increase in $\overline{OS}_C$ with atmospheric oxidation implies that, given enough time, organics will generally move up and to the right (blue arrows), towards CO_2 .

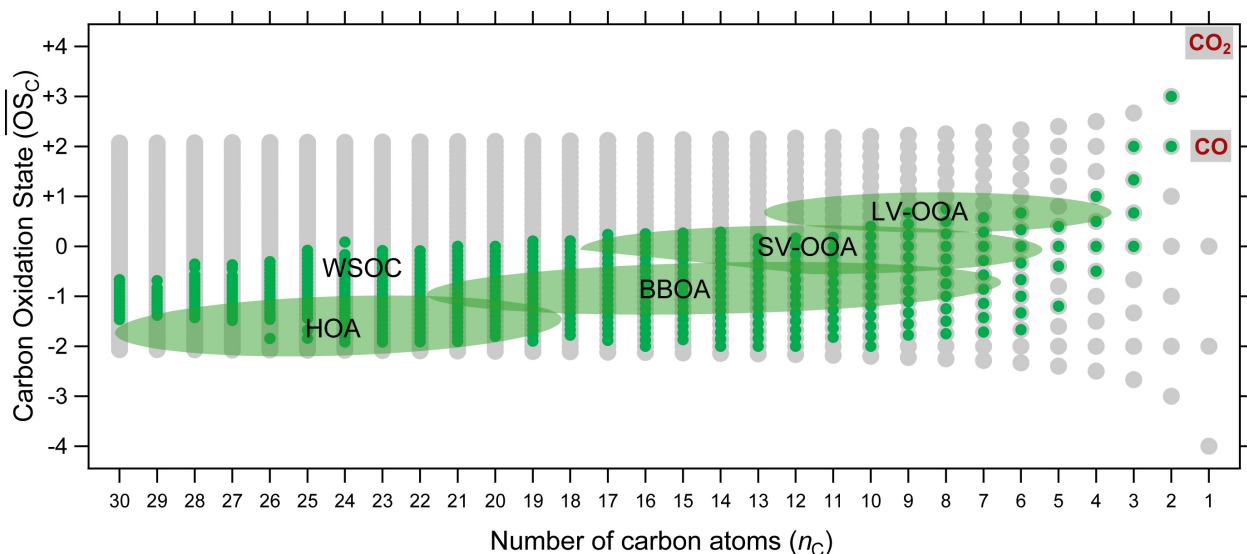


Figure 2. Location in $\overline{\text{OS}}_C$ - n_C space of organic aerosol, based upon $\overline{\text{OS}}_C$ measurements of organic aerosol (Table 1). Green circles: locations of individual components of water-soluble organic compounds (WSOC), as measured by ultrahigh resolution mass spectrometry with electrospray ionization.^{21,22} Green ovals: locations of different organic aerosol classes, as determined from factor analysis of AMS data²⁶ and volatility measurements to determine n_C ³². Hydrocarbon-like organic aerosol (HOA) and biomass burning organic aerosol (BBOA) correspond to primary particulate matter directly emitted into the atmosphere. Semivolatile and low-volatility oxidized organic aerosol (SV-OOA and LV-OOA) correspond to “fresh” and “aged” secondary aerosol produced by multi-step oxidation of gas phase precursors¹¹. These aerosol species and types fall along the rough oxidation trajectories shown in Fig. 1, according to their degree of oxidation. The apparent absence of large ($n_C \geq 5$), highly oxidized ($\overline{\text{OS}}_C > 1$) organics in organic aerosol is likely due to the thermodynamic and photochemical instability of such species.

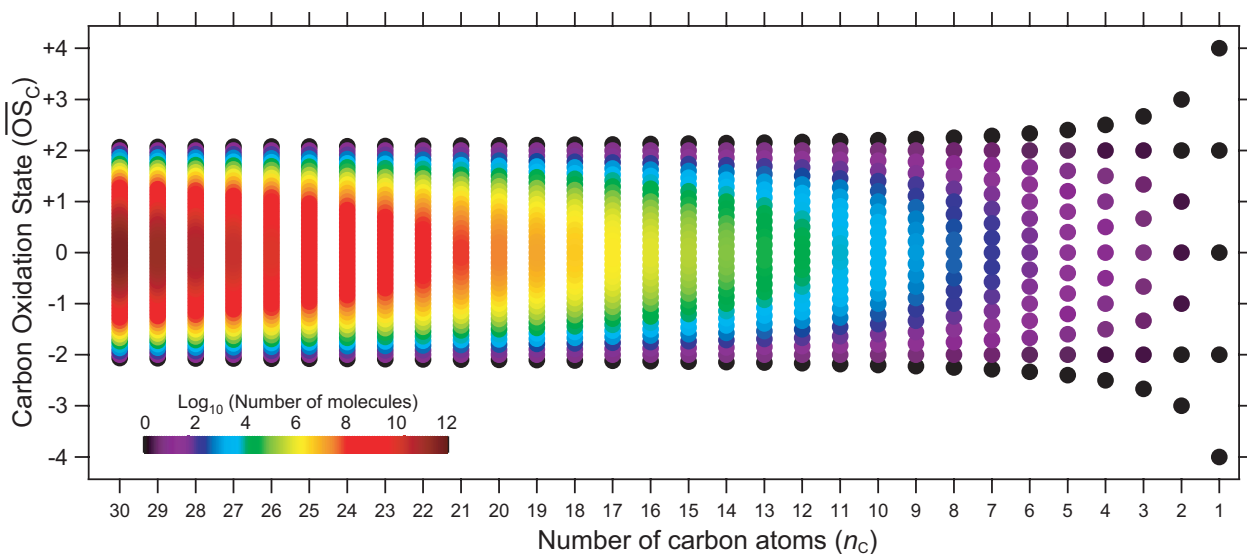


Figure 3. Chemical complexity of organics as a function of oxidation state and carbon number. Points are colored by the logarithm (base 10) of the number of possible compounds at a given $\overline{\text{OS}}_{\text{C}}$ and n_{C} , assuming an unbranched, acyclic carbon skeleton, and the addition of carbonyl, alcohol, and acid groups only. Including a wider range of carbon skeletons or functional groups will lead to a dramatically steeper increase in chemical complexity with $\overline{\text{OS}}_{\text{C}}$ and n_{C} ³³.

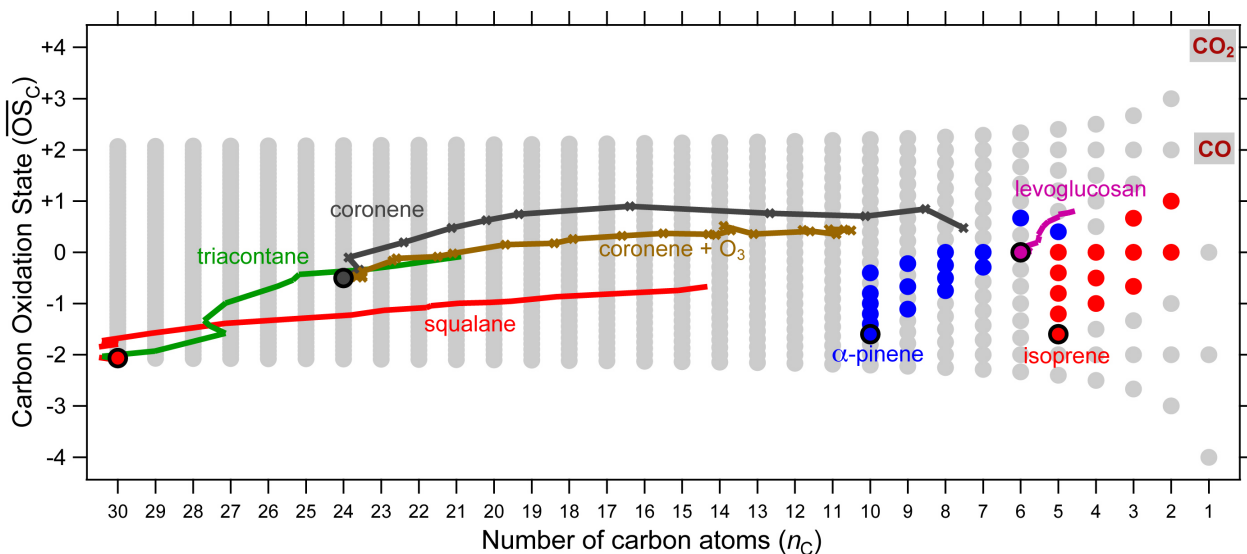


Figure 4. Oxidation trajectories in $\overline{OS}_C$ - n_C space, as determined from laboratory studies of oxidation reactions. OH is used as the oxidant except as noted. Results from three independent experimental and analytical approaches are shown: the heterogeneous oxidation of pure organic particles, measured with HR-AMS (solid lines)^{40,41}; the heterogeneous oxidation of thin films, measured by XPS (crossed lines)²⁵; and the gas-phase oxidation of hydrocarbons, measured by various techniques to speciate gas- and particle-phase organics (solid circles)⁴⁴⁻⁵⁰. In most cases, oxidation initially adds functional groups to the carbon skeleton (upwards movement), but later oxidation steps involve a decrease in n_C via the breaking of carbon-carbon bonds (movement upwards and to the right), indicating the crucial role of fragmentation reactions in photochemical aging and aerosol evolution. For clarity, only monomeric products are shown; the formation of oligomers also entails initial movement to the left, but since these oligomeric species are composed of monomeric subunits, they will display the same general trajectories upon oxidation.

References cited

1. Kanakidou, M. et al. Organic aerosol and global climate modelling: a review. *Atmos. Chem. Phys.* **5**, 1053-1123 (2005).
2. Zhang, Q. et al. Ubiquity and dominance of oxygenated species in organic aerosols in anthropogenically-influenced Northern Hemisphere midlatitudes. *Geophys. Res. Lett.* **34**, L13801, doi:10.1029/2007GL029979 (2007).
3. Kroll, J.H. & Seinfeld, J.H. Chemistry of secondary organic aerosol: Formation and evolution of low-volatility organics in the atmosphere. *Atmos. Environ.* **42**, 3593-3624 (2008).
4. Logan, J.A., Prather, M.J., Wofsy, S.C. & McElroy, M.B. Tropospheric Chemistry - a Global Perspective. *J. Geophys. Res. Oceans and Atmospheres* **86**, 7210-7254 (1981).
5. Masiello, C.A., Gallagher, M.E., Randerson, J.T., Deco, R.M. & Chadwick, O.A. Evaluating two experimental approaches for measuring ecosystem carbon oxidation state and oxidative ratio. *J. Geophys. Res. Biogeosci.* **113**, (2008).
6. McDermitt, D.K. & Loomis, R... Elemental Composition of Biomass and Its Relation to Energy Content, Growth Efficiency, and Growth-Yield. *Ann. Bot.* **48**, 275-290 (1981).
7. Vogel, F., Harf, J., Hug, A. & von Rohr, P.R. The mean oxidation number of carbon (MOC) - A useful concept for describing oxidation processes. *Water Res.* **34**, 2689-2702 (2000).
8. Jacob, D.J. *Introduction to Atmospheric Chemistry*. (Princeton University Press: Princeton, NJ, 1999).
9. Seinfeld, J.H., Erdakos, G.B., Asher, W.E. & Pankow, J.F. Modeling the formation of secondary organic aerosol (SOA). 2. The predicted effects of relative humidity on aerosol formation in the α -pinene-, β -pinene-, sabinene-, D3-carene-, and cyclohexene-ozone systems. *Environ. Sci. Technol.* **35**, 3272-3272 (2001).
10. Pankow, J.F. & Barsanti, K.C. The Carbon Number-Polarity Grid: A Means to Manage the Complexity of the Mix of Organic Compounds When Modeling Atmospheric Organic Particulate Matter. *Atmos. Environ.* **43**, 2829-2835 (2009).
11. Jimenez, J.L. et al. Evolution of Organic Aerosols in the Atmosphere. *Science* **326**, 1525-1529 (2009).
12. Heald, C.L. et al. A simplified description of the evolution of organic aerosol composition in the atmosphere. *Geophys. Res. Lett.* **37**, L08803, doi:10.1029/2010GL04273 (2010).
13. Carlton, A.G. et al. Atmospheric oxalic acid and SOA production from glyoxal: Results of aqueous photooxidation experiments. *Atmos. Environ.* **41**, 2588-7602 (2007).
14. Nguyen, T.B. et al. High-resolution mass spectrometry analysis of secondary organic aerosol generated by ozonolysis of isoprene. *Atmos. Environ.* **44**, 1032-1042 (2010).
15. O'Brien, R.J., Holmes, J.R. & Bockian, A.H. Formation of Photochemical Aerosol from Hydrocarbons - Chemical Reactivity and Products. *Environ. Sci. Technol.* **9**, 568-576 (1975).
16. Krivacsy, Z. et al. Study on the chemical character of water soluble organic compounds in fine atmospheric aerosol at the Jungfraujoch. *J. Atmos. Chem.* **39**, 235-259 (2001).
17. Kiss, G., Varga, B., Galambos, I. & Ganszky, I. Characterization of water-soluble organic matter isolated from atmospheric fine aerosol. *J. Geophys Res. Atmos.* **107**, (2002).
18. Altieri, K.E. et al. Oligomers formed through in-cloud methylglyoxal reactions: Chemical composition, properties, and mechanisms investigated by ultra-high resolution FT-ICR mass spectrometry. *Atmos. Environ.* **42**, 1476-1490 (2008).
19. Altieri, K.E., Turpin, B.J. & Seitzinger, S.P. Oligomers, organosulfates, and nitrooxy organosulfates in rainwater identified by ultra-high resolution electrospray ionization FT-ICR mass spectrometry. *Atmos. Chem. Phys.* **9**, 2533-2542 (2009).
20. Bateman, A.P., Nizkorodov, S.A., Laskin, J. & Laskin, A. Time-Resolved Molecular Characterization of Limonene/Ozone Aerosol using High-Resolution Electrospray Ionization Mass Spectrometry. *Phys. Chem. Chem. Phys.* **11**, (2009).
21. Wozniak, A.S., Bauer, J.E., Sleighter, R.L., Dickhut, R.M. & Hatcher, P.G. Technical Note:

- Molecular characterization of aerosol-derived water soluble organic carbon using ultrahigh resolution electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry. *Atmos. Chem. Phys.* **8**, 5099-5111 (2008).
22. Mazzoleni, L.R., Ehrmann, B.M., Shen, X.H., Marshall, A.G. & Collett, J.L. Water-Soluble Atmospheric Organic Matter in Fog: Exact Masses and Chemical Formula Identification by Ultrahigh-Resolution Fourier Transform Ion Cyclotron Resonance Mass Spectrometry. *Environ. Sci. Technol.* **44**, 3690-3697 (2010).
 23. Fuzzi, S. et al. A simplified model of the water soluble organic component of atmospheric aerosols. *Geophys. Res. Lett.* **28**, 4079-4082 (2001).
 24. Gilardoni, S. et al. Characterization of organic ambient aerosol during MIRAGE 2006 on three platforms. *Atmos. Chem. Phys.* **9**, 5417-5432 (2009).
 25. Mysak, E.R. et al. Competitive Reaction Pathways for Functionalization and Volatilization in the Heterogeneous Oxidation of Coronene Thin Films by Hydroxyl Radicals and Ozone. *Phys. Chem. Chem. Phys.* **submitted**, (2010).
 26. Aiken, A.C. et al. O/C and OM/OC ratios of primary, secondary, and ambient organic aerosols with high-resolution time-of-flight aerosol mass spectrometry. *Environ. Sci. Technol.* **42**, 4478-4485 (2008).
 27. Shilling, J.E. et al. Loading-dependent elemental composition of alpha-pinene SOA particles. *Atmos. Chem. Phys.* **9**, 771-782 (2009).
 28. Presto, A.A. et al. Intermediate-Volatility Organic Compounds: A Potential Source of Ambient Oxidized Organic Aerosol. *Environ. Sci. Technol.* **43**, 4744-4749 (2009).
 29. Chhabra, P., Flagan, R.C. & Seinfeld, J.H. Elemental analysis of chamber organic aerosol using the Aerodyne High Resolution Mass Spectrometer. *Atmos. Chem. Phys.* **10**, (2010).
 30. Sun, Y. et al. Size-resolved aerosol chemistry on Whistler Mountain, Canada with a high-resolution aerosol mass spectrometer during INTEX-B. *Atmos. Chem. Phys.* **9**, 3095-3111 (2009).
 31. Chen, Q. et al. Mass spectral characterization of submicron biogenic organic particles in the Amazon Basin. *Geophys. Res. Lett.* **36**, (2009).
 32. Donahue, N.M., Epstein, S.A., Pandis, S.N. & Robinson, A.L. A Two-Dimensional Volatility Basis Set: 1. Organic-Aerosol Mixing Thermodynamics. *Atmos. Chem. Phys. Discuss.* **10**, 24091-24133 (2010).
 33. Goldstein, A.H. & Galbally, I.E. Known and unexplored organic constituents in the earth's atmosphere. *Environ. Sci. Technol.* **41**, 1514-1521 (2007).
 34. Atkinson, R. Rate constants for the atmospheric reactions of alkoxy radicals: An updated estimation method. *Atmos. Environ.* **41**, 8468-8485 (2007).
 35. Lambe, A.T., Miracolo, M.A., Hennigan, C.J., Robinson, A.L. & Donahue, N.M. Effective Rate Constants and Uptake Coefficients for the Reactions of Organic Molecular Markers (n-Alkanes, Hopanes, and Steranes) in Motor Oil and Diesel Primary Organic Aerosols with Hydroxyl Radicals. *Environ. Sci. Technol.* **43**, 8794-8800 (2009).
 36. MacCarthy, P. The principles of humic substances. *Soil Sci.* **166**, 738-751 (2001).
 37. Reemtsma, T., These, A., Springer, A. & Linscheid, M. Fulvic acids as transition state of organic matter: Indications from high resolution mass spectrometry. *Environ. Sci. Technol.* **40**, 5839-5845 (2006).
 38. Graber, E.R. & Rudich, Y. Atmospheric HULIS: How humic-like are they? A comprehensive and critical review. *Atmos. Chem. Phys.* **6**, 729-753 (2006).
 39. Trainer, M.G. et al. Organic haze on Titan and the early Earth. *Proc. Natl. Acad. Sci. USA* **103**, 18035-18042 (2006).
 40. Kroll, J.H. et al. Measurement of fragmentation and functionalization pathways in the heterogeneous oxidation of oxidized organic aerosol. *Phys. Chem. Chem. Phys.* **11**, 8005-8014 (2009).
 41. Kessler, S.H. et al. Kinetics and Products of Heterogeneous Oxidation of Erythritol and Levoglucosan in Atmospheric Aerosol Particles. *Environ. Sci. Technol.* **44**, 7005-7010 (2010).
 42. Pankow, J. & Asher, W. SIMPOL.1: A simple group contribution method for predicting vapor

- pressures and enthalpies of vaporization of multifunctional organic compounds. *Atmos. Chem. Phys.* **8**, 2773-2796 (2008).
43. Cappa, C.D. & Jimenez, J.L. Quantitative estimates of the volatility of ambient organic aerosol. *Atmos. Chem. Phys.* **10**, 5409-5424 (2010).
44. Aschmann, S.M., Atkinson, R. & Arey, J. Products of reaction of OH radicals with α -pinene. *J. Geophys. Res. Atmos.* **107**, (2002).
45. Edney, E.O. et al. Polar organic oxygenates in PM_{2.5} at a southeastern site in the United States. *Atmos. Environ.* **37**, 3947-3965 (2003).
46. Surratt, J.D. et al. Chemical composition of secondary organic aerosol formed from the photooxidation of isoprene. *J. Phys. Chem. A* **110**, 9665-9690 (2006).
47. Kleindienst, T.E. et al. Estimates of the Contributions of Biogenic and Anthropogenic Hydrocarbons to Secondary Organic Aerosol at a Southeastern U.S. Location. *Atmos. Environ.* **41**, 8288-8300 (2007).
48. Szmigielski, R. et al. 3-methyl-1,2,3-butanetricarboxylic acid: An atmospheric tracer for terpene secondary organic aerosol. *Geophys. Res. Lett.* **34**, L24811, doi:10.1029/2007GL031338 (2007).
49. Paulot, F. et al. Isoprene photooxidation: new insights into the production of acids and organic nitrates. *Atmos. Chem. Phys.* **9**, 1479-1501 (2009).
50. Claeys, M. et al. Terpenylic Acid and Related Compounds from the Oxidation of α -Pinene: Implications for New Particle Formation and Growth above Forests. *Environ. Sci. Technol.* **43**, 6976-6982 (2009).