Organic Aerosol Growth Mechanisms and Their Climate-Forcing Implications

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Aerosol particles enter Earth’s atmosphere by direct emission of particles and by condensation of vapor-phase species. Heterogeneous and multiphase reactions in the atmosphere change chemical and physical properties of aerosol particles, but these processes are not understood well enough to predict accurately the evolution of the gas and particle-phase composition of the troposphere (1). Carbonaceous aerosol particles compose ∼37% of global submicrometer particle emissions (2), yet climate models have used an oxidation reaction rate equivalent to 60% of organic particle mass per day for these particles because atmospheric observations have not been available (3, 4). This assumption controls the associated lifetime, burden, and climate forcing predicted for atmospheric carbonaceous particles.

Because gas-to-particle conversion and heterogeneous chemistry control the composition of carbonaceous particles in ways that are poorly understood, the organic composition of atmospheric particles is also not well known (5). The oxidation of vapor-phase organic compounds, in which the number of alkyl bonds is reduced and the number of alcohol and carbonyl bonds is increased, produces compounds that may have sufficiently low vapor pressures to condense onto preexisting particle surfaces to form secondary organic aerosol (SOA). This condensation pathway accounts for an estimated 10% of global organic aerosol (4) and increases the fractional concentrations of the condensing species more rapidly for smaller than for larger particles because of larger surface area–to–volume ratios in smaller particles.

Condensed organic compounds originating from the vapor phase or from direct particulate emissions can become oxidized through heterogeneous reactions that are surface-limited or volume-limited (6). Typically these mechanisms are represented by a single lumped rate in climate models (4). Mixtures of large molecular-weight organic compounds with elemental carbon are also oxidized by atmospheric reactions. Volume-limited oxidation occurs when particle-phase diffusion of reactants is fast compared with the kinetics of chemical reaction. A uniform reaction extent results in an equally increased carbonyl carbon concentration for all particles regardless of size. Surface-limited oxidation may indicate efficient surface reactivity or highly viscous or solid aerosols, and the localization of the reaction at the surface results in an equally increased carbonyl concentration for all particles regardless of size. The oxidation of those organic compounds on particles surfaces, and oxidation of compounds that have diffused into particle volumes, as well as combina-

Fig. 1. Theoretical diagrams showing the effects of five oxidation and condensation mechanisms on organic mass composition ratios as functions of particle diameter. In each diagram, the vertical axis represents a unitless ratio and the horizontal axis represents particle size with diameters increasing toward the right for the size range from 0.4 to 5 μm in diameter. The exact size scale for each diagram varies with atmospheric parameters including processing time, temperature, and vapor-phase concentrations of the reacting or condensing species. Condensation, volume-limited oxidation, and surface-limited oxidation mechanisms can be distinguished with use of the three STXM variables shown here: the total carbon–to–total mass ratio, the carbonyl carbon–to–total mass ratio, and the carbonyl carbon–to–total carbon ratio. In all diagrams, R and R show aliphatic chains, hydrogen atoms, or alcohol groups. Subscripts refer to the reactant phase, and arrow labels indicate the reaction phase where oxidation occurs. Condensation followed by surface-limited vapor-phase reaction has the same organic composition dependence on size as the condensation of oxygenated organic compounds oxidized in the vapor phase. The particle-phase reaction of vapor-phase reactants absorb or condense onto aerosol particles before reacting.
Soft x-ray spectromicroscopy studies in the transmission mode (scanning transmission x-ray microscopy, or STXM) can detect organic functional groups within individual particles with a resolution below 0.1 μm (7). By using this technique, data from four atmospheric aerosol samples (Asian mixed combustion over the Sea of Japan, African mineral dust over the Caribbean Sea, and U.S. combustion in New Jersey) were analyzed (Fig. 2). Details for each sample are also summarized (Fig. 3). For each aerosol sample, two-dimensional maps of particle composition and morphology were compiled from STXM measurements (8). In Fig. 2, STXM absorbance ratios were converted to absolute mass ratios by using the Fourier transform infrared–measured compositions of simultaneously collected bulk submicrometer aerosol samples for calibration (9). Spatial distributions of measured composition ratios (Fig. 4) illustrate four different particle morphologies and mixing states. The four samples provide examples of the aerosol organic reaction mechanisms described in Fig. 1.

Evidence of surface-limited oxidation is reflected in the chemical composition of Asian mixed combustion aerosol collected at 1500 m over the Sea of Japan. This sample contains two aerosol modes evident from the particle maps in Fig. 4, A and B, and the total carbon–to–total mass ratio in Fig. 2A: a carbonaceous mode and a mode containing very low carbon concentrations. The carbonaceous mode composition has a size dependence in Fig. 2B and C, and does not in Fig. 2A, consistent with a surface-limited oxidation mechanism (Fig. 1). The lack of size dependence of the total carbon–to–total mass ratio suggests that organic compounds were incorporated in the particle phase before the particles were emitted from their sources.

In the Asian mixed combustion particles, the strong absorption by carbon-carbon double bonds is consistent with products of incomplete combustion including polycyclic aromatic hydrocarbons and graphic elemental carbon, components whose light-absorbing properties have earned the popular appellation of black carbon (abbreviated in this work as BC). The particles were sampled in dry conditions more than 30 hours after emission (8) and may have been crystalline or amorphous solids. Particle composition is consistent with an oxidation rate of 24% of carbon mass per day, increasing the carbonyl–to–total carbon ratio by 5.5% per day. In Fig. 4H, the organic mode particles have larger carbonyl–to–total carbon ratios at particle edges, with ratios near 0.2 occurring exclusively in edge regions. Bulk filter analysis shows that the Asian mixed combustion submicrometer particles consist of organic compounds and sulfate with substantial BC and almost no dust (10). The mode with low carbon concentrations is probably largely sulfate. Particles from both modes are
Volume-limited oxidation signatures are observable in the boundary layer U.S. combustion sample collected in New Jersey on 12 August 2003 in the absence of precipitation or fog. The chemical composition of this aerosol is constant across all measured sizes (Fig. 2) with an average carbonyl carbon–to–total carbon ratio of 0.1. The lack of sensitivity to particle size indicates that the carbon distribution was not controlled by surface-limited processes (compare Fig. 2 to Fig. 1). Relative humidity (RH) was high (>75%) on 12 August 2003 with particles containing some condensed water, and this aqueous phase may have facilitated the diffusion of reactants within particles for volume-limited reactions. The carbonyl–to–total carbon ratio is spatially uniform with similar values within particles and at particle edges (Fig. 4F), consistent with volume-limited oxidation. Isentropic back trajectories suggest that the boundary layer particles were collected at least 10 to 15 hours after emission (8). The estimated times since emission of these particles are consistent with an oxidation rate of 21% of organic compound mass per day, increasing the carbonyl carbon–to–total carbon ratio by 4.8% per day.

Volume-limited oxidation also occurred in the U.S. aerosol collected during a fog event on 7 August 2003 with similar emission sources as on 12 August 2003 (8). The size dependence of the total carbon–to–total mass ratio in Fig. 2A, near 0.5 for 0.8-μm-diameter particles and 1 for 0.3-μm-diameter particles, indicates organic condensation. The similar size dependence of the carbonyl carbon–to–total mass ratio in Fig. 2B, ranging up to 0.1 for a diameter of 0.3 μm, suggests that the condensed organic compounds were oxidized. The uniformity of the carbonyl carbon–to–total carbon ratio in Fig. 2C, 0.1 for all particle sizes, demonstrates that the organic compounds were oxidized uniformly regardless of the original phase or proximity to the particle surface. The spatial distribution of the carbonyl carbon–to–total carbon ratio (Fig. 4H) during the fog event shows fairly uniform values near 0.1, consist
ent with Fig. 2C. These three trends of composition with size are consistent with condensation and volume-limited oxidation (Fig. 1).

On 7 and 12 August 2003, similar U.S. combustion sources produced particles with very different organic compositions: one with a strong size dependence and the other with none. The similarity of sources means that the observed differences in composition result from condensation and reaction processes that occurred after emission. The high RH and the presence of fog on 7 August 2003 suggest that most of the aerosol particles on that day contained substantial water. Condensation and volume-limited oxidation during fog events are consistent with the mechanism proposed for oxalic acid formation in cloud droplets (13). The close correspondence between the observed particle-composition size dependence during the fog event and the expected theoretical relationships for condensation (Fig. 2, A and B) and volume-limited oxidation (Fig. 2C) provides evidence supporting this pathway for forming the organic fraction of this aerosol. The particle ages are consistent with an SOA formation rate equivalent to 17% of the primary organic compound mass per day, increasing the carbonyl carbon–to–total carbon ratio by 4% per day.

The four aerosol chemical signatures illustrate differences in atmospheric processing, with evidence for four mechanisms of condensation and reaction in the atmosphere. Volume-limited oxidation reactions were observed in boundary layer aerosol in which particles were largely aqueous. Surface-limited oxidation reactions were observed in particles at higher altitudes where lower RH and insoluble components were present. All four distinct aerosol compositions from different regions and with competing reaction mechanisms consistently demonstrate an oxidation rate that is a factor of 3 or more lower than the values currently used in climate model calculations. Because oxidation is the removal mechanism for hydrophobic organic and BC particles in climate models (4), larger predicted carbonaceous aerosol lifetimes and burdens result from the slower oxidation rates.

The direct effects of carbonaceous aerosol cause cooling by light scattering and warming by absorption, both of which increase nearly proportionally with the aerosol burden (4). The carbonyl groups associated with organic molecules exert influence on cloud properties (14), affecting cloud formation in what is termed an indirect forcing. Figure 5 shows simple estimates of changes in global burdens and associated top-of-atmosphere (TOA) forcings for the measured oxidation rates of 24% per day for BC and 13 to 21% for organic aerosol. The estimated direct effects assume constant hygroscopicity and scavenging with organic composition. More detailed calculations including the changes in these properties are not possible because an accurate global characterization of the variability of these properties with location and oxidation state does not exist.

The much slower oxidation rates mean that organic aerosol will be less hygroscopic, reflecting more radiation because of increased atmospheric lifetimes and an estimated 70% increase of the organic aerosol burden. This change in average SOA, primary organic aerosol, and BC burdens is calculated from the atmospheric oxidation rates of the samples measured here with use of a global model of parameterized burden derived from detailed climate model calculations (4). By incorporating similar parameterizations of the direct and indirect effects, the result is a direct organic aerosol forcing increase of up to −0.7 W m$^{-2}$ (15), and a BC forcing increase of up to + 0.3 W m$^{-2}$ (Fig. 5). The combined increases of cooling by 47% and warming by 61% represent an absolute difference of 1.1 W m$^{-2}$ associated with uncertainties in the oxidation rate of carbonaceous aerosols, comparable to the total uncertainty in aerosol forcing and half of the magnitude of the forcing change from doubling CO$_2$ (+2.2 W m$^{-2}$).

Supporting Online Material

www.sciencemag.org/cgi/content/full/306/5703/1921/DC1

Materials and Methods

Figs. S1 and S2

Table S1

References

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8. Materials and methods are available as supporting material on Science Online.

9. The average total carbon–to–total mass absorption ratio for each STXM sample was calibrated to the bulk aerosol organic carbon mass fraction. This calibration is rigorous for 0.2- to 2.0-μm-diameter STXM particle populations with mass average compositions that are equivalent to the submicrometer aerosol mass average measured for each sample.


15. Organic compounds may account for up to 63% of cloud condensation nuclei (16), corresponding to an indirect forcing estimated to be −1.5 W m$^{-2}$. The longer lifetime of hydrophobic organic compounds predicted here would magnify this effect, increasing the organic fraction of cloud droplets from 63% to 75% and increasing the global organic indirect effect to −2.2 W m$^{-2}$ (2). This estimated indirect effect gives an order-of-magnitude calculation by extending a limited set of observations and provides an upper bound on the forcing magnitude (gray region in Fig. 5).


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