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Atmospheric chemistry

The decay of organic aerosols

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The chemistry of organic aerosols has been somewhat neglected on the assumption that they are eliminated from the atmosphere mainly by rainfall. Laboratory studies indicate that a rethink is called for.

Fine particles and droplets suspended in the atmosphere have a key role in environmental issues such as climate and human health. Over the oceans, such aerosols consist mainly of sulphates, but above continents they are mostly organic matter¹. Organic aerosols come from many sources, including smoke particles from burning fuels and biomass, and the light-induced oxidation of volatile hydrocarbons, both natural and man-made¹. The main process that removes organic aerosols from the atmosphere has been assumed to be precipitation, but writing in *Geophysical Research Letters* Molina and colleagues² suggest that another elimination route could be just as important.

Gaseous organic compounds in the atmosphere interact with oxidants such as ozone and hydroxyl and nitrate radicals, reactions that provide an important sink for their eradication from the atmosphere³. For organic aerosols, however, the most common means of removal is by deposition, either sedimentation — simply falling out of the atmosphere — or precipitation⁴. Organic aerosols are usually less than a micrometre in size⁵, so it is generally assumed⁴ that precipitation is the major process by which they leave the atmosphere; larger particles would be more likely to settle out. Molina and colleagues² now identify another removal pathway whereby the organic surface on atmospheric particles is degraded by oxidation initiated by hydroxyl radicals (OH[•]). The efficiency of this process appears to be comparable to precipitation in removing organic aerosols from the atmosphere.

To model the reactions that organic aerosols might undergo in the atmosphere, Molina *et al.*² used two organic films deposited on glass slides: a paraffin film to represent aliphatic aerosols (molecules with carbon chains); and a pyrene film to represent aromatic aerosols (having carbon-ring structures). Aliphatic and aromatic hydrocarbons such as paraffin and pyrene have

been isolated from organic aerosols from various locations⁶.

To examine the oxidation reactions of solid organic compounds, the authors exposed the model aerosol surfaces to an 'atmosphere' of various ratios of NO_x:O₂:H₂O, and then varied the concentration of OH[•] from 0.1 × 10⁸ to 100 × 10⁸ molecules per cm³ (the average global atmospheric OH[•] concentration⁷ is about 10⁶ molecules per cm³). Using state-of-the-art analytical instruments, they then measured the rate of degradation of the organic surface, how quickly the OH[•] is used up, and the type and speed of formation of the gaseous products.

Molina and colleagues clearly observed the loss of organic carbon from both model substrates. They also observed that, over time, the depletion rate of the organic layer is linearly dependent on the OH[•] concentration. The aromatic carbon surface degraded more slowly than the aliphatic one, suggesting that the route of decay varies according to the compound. The gaseous products of the degradation reaction are small, volatile, one- and two-carbon species; which particular species are produced depends on the substrate.

From their observations, the authors propose a mechanism for the OH[•]-induced oxidative degradation of organic aerosols. According to this, the reaction leads predominantly to a scission of the carbon–carbon bond in paraffin, and to cleavage of the aromatic ring in pyrene. The authors assume that the rate of carbon loss from the organic film is directly proportional to the OH[•] concentration, and, given an average OH[•] concentration of 10⁶ molecules per cm³, they estimate that an aliphatic aerosol of 0.02–0.2 μm will be converted entirely into gaseous products in about six days². The lifetime of an organic aerosol has been estimated from atmospheric measurements and lab experiments to be four to five days⁸. Consequently, this study concludes that oxidative degradation and removal by precipitation occur at comparable rates, and that OH[•]-induced oxidation is

a significant mechanism that eliminates organic aerosols from the atmosphere.

Chemical reactions with the OH[•] radical have been established as the dominant processes by which most gaseous organic compounds are removed from the atmosphere³. In fact, OH[•] reactions occur at environmentally significant rates even for the chemically recalcitrant PCBs (polychlorinated biphenyls), so they are an important atmospheric sink for these pollutants^{9,10}. However, there is only very limited information on the reactions of gaseous OH[•] with organic liquids and solids^{2,11}, or indeed on any of the chemistry of organic aerosols.

Traditional analytical techniques used to characterize organic aerosols failed to analyse the water-soluble organic compounds (which account for 70–90% of the aerosol mass¹²) and were limited to identifying only the components that could be dissolved in organic solvents (6–20% of aerosol mass¹²). We know now that the water-soluble fraction of total fine particulate aerosol mass contains oxygenated and macromolecular polar organic substances with surface-active properties¹². But the atmospheric chemistry of these polar species is otherwise relatively unknown and difficult to study. In addition, the association of some species, such as the environmental pollutants polyaromatic hydrocarbons, with black carbon particles seems to show a potential inhibiting effect for their reaction with gaseous OH[•] (ref. 11).

Molina and colleagues² make a strong case that the heterogeneous reactions of organic aerosols with atmospheric oxidants are important for their fate. The results highlight the need for further studies to improve our understanding of the reactions and effects of organic aerosols in the environment. We need a thorough chemical characterization and quantification of the main components, details of their reactions in the presence of atmospheric oxidants, and improved knowledge of their surface properties and water uptake before and after heterogeneous reactions in the atmosphere. Finally, lab experiments are rarely definitive, of course: systematic field studies will also be required. ■

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