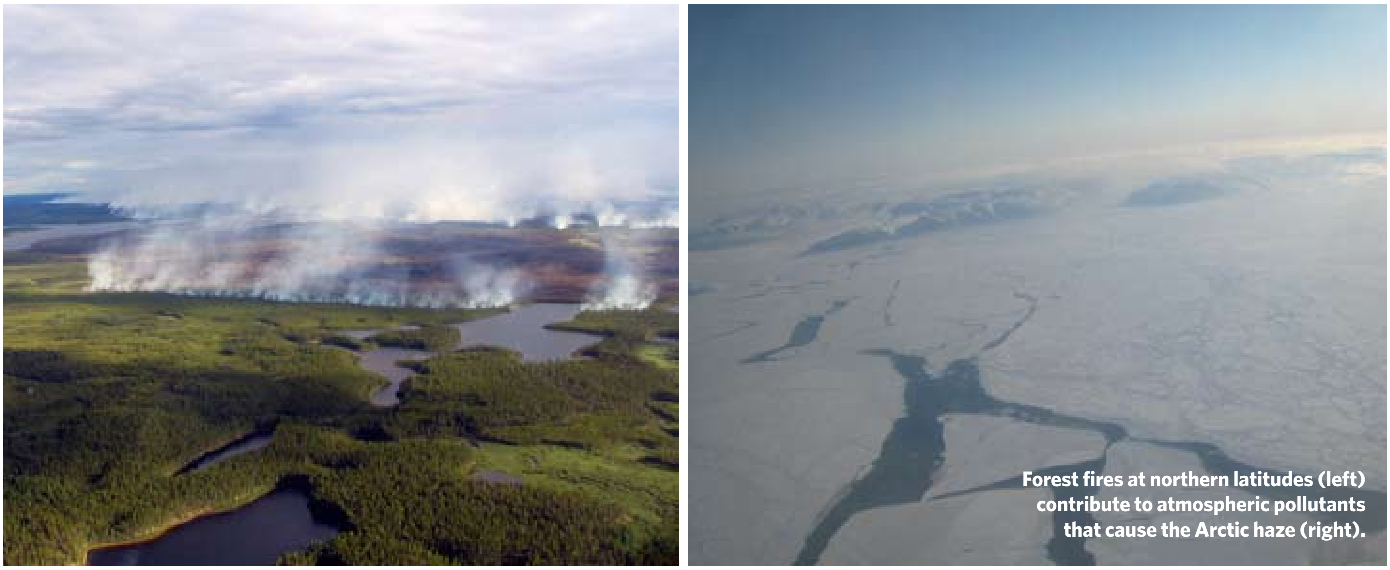
NEWS & VIEWS



Forest fires at northern latitudes (left) contribute to atmospheric pollutants that cause the Arctic haze (right).

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ATMOSPHERIC CHEMISTRY

A missing sink for radicals

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Air pollution can cause a widespread haze in the Arctic. A study of the lower atmosphere there suggests that haze particles might take up free radicals, and so extend the lifetime of air pollutants in the region.

The lowest part of the atmosphere, the troposphere, has a self-cleaning mechanism for dealing with pollution. This mechanism is largely regulated by hydrogen oxides (the radicals OH and HO_2, collectively abbreviated to HO_x), because the reaction of OH with pollutant gases is the first step in the pollutants' removal. The OH can then be recycled in chains of radical reactions in which HO_2 is an intermediate. What's more, hydrogen peroxide (H_2O_2, the reaction product of HO_2) is a sink for HO_x because it is deposited on Earth's surface, but it is also the main source of HO_x in the upper troposphere, both in the Arctic[1] and at lower latitudes[2]. Reporting in *Atmospheric Chemistry and Physics*, Mao *et al.*[1] describe their study of the Arctic troposphere, from which they conclude that haze particles can interrupt the tropospheric cleaning mechanism by taking up HO_2. Surprisingly, this process can reduce the concentrations of OH, HO_2 and H_2O_2 by about one-third compared with concentrations generated in conditions without aerosol particles.

Arctic haze has been reported since the 1950s, and is prevalent in winter and spring. It is mainly attributed to the long-distance transport of air pollution from Eurasian industrial sources, in particular coal burning in northern Russia[3]. The high pollutant concentrations in this haze are promoted by low removal rates in the otherwise pristine Arctic environment. The aerosol particles in the haze are composed of sulphates, nitrates, black carbon, heavy metals, dust and organic matter, the last of which originates largely from forest fires[3–5]. There is growing concern that pollutant emissions in the region will rise sharply if the Arctic Sea ice continues to recede, allowing shipping activity to increase.

Mao *et al.*[1] took measurements of a suite of atmospheric compounds as part of the Arctic Research of the Composition of the Troposphere by Aircraft and Satellites (ARCTAS) campaign[6]. The measurements were taken in April 2008 by aircraft over Alaska, northern Canada, Greenland and the North Pole, and targeted compounds that are appropriate for constraining models of atmospheric chemistry, including HO_x radicals and peroxides. The conditions during the study were typical for the Arctic, with low sun angles at polar sunrise, intense cold (of about −17 to −47 °C) and sunlight reflecting off the ice surface. Because the aircraft sampled the atmosphere almost exclusively in clear skies, chemistry within clouds did not play a part in determining the concentrations of the measured compounds.

The authors observed that the OH mixing ratio — the ratio of the OH volume to that of air — within the sampled air parcels was about 0.02 parts per trillion (p.p.t.) up to altitudes of 7 kilometres, increasing to about 0.08 p.p.t. at altitudes of 10 km. When they compared these data with the predictions of a widely used atmospheric-chemistry model, they found that the model tends to underestimate OH concentrations in the boundary layer (the lowermost region of the atmosphere that is in contact with Earth's surface), but overestimates OH concentrations in the upper troposphere. The underestimate in the boundary layer might be related to the model's neglect of bromine chemistry — near the surface, HO_x radicals can interact with reactive bromine (Br and BrO), which catalyses radical cycles, and can even lead to ozone destruction at polar sunrise[7,8].

Mao *et al.* found that the observed mixing ratios of nitrogen oxides[1], which are expected to increase OH concentrations, are well reproduced by the model. Their further analysis of these data indicated that a large fraction (more than 40%) of the nitrogen oxides detected is anthropogenic. But the mixing ratios that they observed for OH, HO_2 (about 3 p.p.t.) and H_2O_2 (about 300 p.p.t.) were much lower than the values predicted by the model. This is consistent with the results of an earlier study[9], which also showed that high-latitude measurements of H_2O_2 were substantially lower than predicted concentrations.

The discrepancies between the predictions and Mao and colleagues' results cannot be attributed to errors in the model with regard to the chemical sources of HO_x, because a similar disagreement is found in other simulations that factor in these sources, at concentrations recorded in the same data set as that used by the authors. Rather, the discrepancies point to chemistry that is completely absent from the model — a missing sink of HO_x radicals. The authors propose that multiphase reactions (those that involve more than one phase of matter) on aerosol particles could be the missing sink.

The aerosol scheme of the model used by Mao *et al.* explicitly accounts for the uptake and subsequent oxidation of sulphur dioxide by H_2O_2 in solution, but represents multiphase processes involving nitrogen oxides and HO_2 by using parameters known as reactive uptake coefficients (γ). Mao *et al.*[1] compiled values of $\gamma(HO_2)$ — the fraction of HO_2 collisions with a given type of aerosol particle that results in loss of the radicals in reactions — for different aerosol types, as quantified from previously published laboratory investigations. They found that aqueous aerosols (droplets of aqueous solutions) become more efficient at reactively removing HO_2 from the gas phase with decreasing temperature. This is because the sticking coefficient (the rate of absorption of a gas by aerosol particles) and the Henry's law coefficient (the gas solubility in water) for HO_2 are relatively high at low temperatures. Furthermore, $\gamma(HO_2)$ is higher in the presence of certain transition metals, especially copper.

From their analysis, Mao *et al.* conclude that, to significantly affect the tropospheric concentration of HO_x, the value of $\gamma(HO_2)$ must be at least 0.1 — that is, the probability that HO_2 will react with a given type of aerosol particle must be greater than 10%. What's more, the effect of HO_2 uptake is largest in the cold upper troposphere, even though aerosol concentrations are relatively low in this region. If the authors' hypothesis is correct, it implies that HO_2 uptake on aerosols may also be an important factor for the cold upper troposphere at lower latitudes, and not just in Arctic regions.

When Mao *et al.* incorporated the aerosol uptake of HO_2 into their model, they found that the revised model successfully predicted the experimentally observed HO_x concentrations at various altitudes. This bodes well for their theory, but several major unknown factors remain to be investigated. For example, in water, HO_2 can dissociate into O_2^- and H^+ ions, and take part in ion chemistry and chains of radical reactions. Unfortunately, only a few of these reactions have been studied, and so their influence on atmospheric chemistry is poorly known. What's more, the self-reaction of HO_2 in solution forms H_2O_2, as does the reaction of HO_2 with O_2^-. It has been assumed that such H_2O_2 is released to the gas phase, but this is clearly inconsistent with the authors' data[1] — so if Mao and colleagues' theory is correct, where is the putative H_2O_2 generated by aerosol uptake going?

Measurements[10] taken using mass spectrometric techniques show that atmospheric aerosols are largely organic, consisting of compounds that are in an intermediate oxidation state. The compounds originate from the chemically reduced hydrocarbons emitted by vegetation, from biomass burning, and can be processed in the atmosphere to highly oxidized, volatile reaction products. It is not known which of the reaction products volatilize and to what extent these compounds take part in solution photochemistry with HO_x radicals. To answer these questions, and to confirm Mao and colleagues' hypothesis[1] concerning the role of aerosols in HO_2 uptake, there is clearly a need for comprehensive investigations of multiphase aerosol photochemistry, both in the field and in the laboratory. ■

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