OZONE CHEMISTRY

Depletion on volcanic aerosols

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Volcano eruptions can so disturb the stratosphere that they may lead to significant destruction of ozone, according to new work by Hofmann and Solomon[1]. The effect was apparent after the massive eruption at El Chichon in 1982 which injected large quantities of sulphur dioxide into the stratosphere. Here, the gas condensed with water to form aerosol particles, which are the crucial catalytic sites for ozone destruction.

That chemical reactions on the surfaces of stratospheric particles can influence stratospheric composition is now widely recognized. Laboratory studies[2–4] suggest, and composition measurements[5–7] demonstrate that large perturbations to the partitioning of both the chlorine and nitrogen families of compounds can occur during the polar winter, when temperatures fall sufficiently for the formation of nitric-acid-trihydrate and/or water-ice clouds[8]. In air which has been exposed to these clouds, the mixing ratios of many reactive chlorine gases, particularly chlorine monoxide and the symmetric chlorine dioxide, can be 10–100 times larger than would be expected without such exposure.

A secondary, but important additional effect of these surface reactions and particle formation is the sequestration of reactive nitrogen oxides into the reservoir nitric acid, which may then be partially removed from the low stratosphere through condensation and subsequent sedimentation. The conversion or removal of reactive nitrogen compounds slows the photochemical recovery of the reactive chlorine back to reservoir forms[9]. In the presence of sunlight, significant depletion of ozone may then occur[9,10].

Over Antarctica, these events have led to the development of the ozone 'hole'. In the Arctic, large perturbations to the chlorine chemistry have been noted by Solomon *et al.*[11] and the recent Airborne Arctic Stratospheric Expedition, the beginnings of an ozone depletion being tentatively detected[12]. The extent of ozone depletion depends on the degree to which sunlight is present while the photochemistry is perturbed. In the Antarctic, the vortex remains largely intact, and cold temperatures persist, until well into spring, allowing a substantial depletion of ozone. In the less stable, warmer Arctic winter vortex, conditions for ozone depletion are less favourable.

Because of the dual requirement for cold temperatures (less than about 195 K) and sunlight, ozone depletion arising from these processes is broadly restricted to high latitudes in winter and early spring. Although cold temperatures do exist in equatorial latitudes, no equivalent ozone depletion is thought likely to occur, because insufficient chlorine has been released from reservoir forms (mainly chlorofluorocarbons) in this air of more recent tropospheric origin to allow reactive chlorine concentrations to build up to damaging levels. Thus, at first sight it seems that severe ozone depletion involving heterogeneous reactions on stratospheric clouds is restricted to high latitudes and to spring months.

In their new paper[1], however, David Hofmann and Susan Solomon argue persuasively that following the El Chichon eruption in 1982, the ozone concentration between 10° and 50° N was significantly depleted — by approximately 15 per cent locally (their Fig. 10). This was, they argued the result of heterogeneous reactions on sulphuric acid particles injected into the stratosphere by the Central American volcano.

The main, worrying difference between their hypothesized situation and the mechanism oulined above is that the requirement for temperatures to be sufficiently low for stratospheric clouds to form no longer exists. In mid-latitudes, significant quantities of chlorine have been made available from long-lived reservoirs. The region of high concentrations of reactive chlorine,

Dynamical effects spread the ozone hole

Mid-latitude ozone levels could be threatened not only by the heterogeneous chemical effects described by R. L. Jones, but also by dynamical redistribution towards the tropics of depleted air from the polar ozone hole. It has not been clear whether the ozone hole, generated each spring in the antarctic stratosphere since 1979, does spread at the onset of summer, but Atkinson *et al.* report on page 290 of this issue[1] that the ozone concentration over Australia and New Zealand was unusually low at the end of 1987. Whether this is linked to polar depletion is of special interest to those modelling the global threat to ozone.

Ozone concentrations in the Antarctic reached a record low in the spring of 1987. Furthermore, the polar vortex — the intense westward circulation extending out to 60° S that confines the ozone hole — did not break up until early December, about a month later than usual. The record-low ozone values over populated regions in New Zealand and Australia were also observed in December. The data examined by Atkinson *et al.*[1] come from Perth, Melbourne, Brisbane and Hobart in Australia and Lauder in New Zealand, covering an area from 43° to 30° S.

From an analysis of the meteorological conditions prevalent at the time, the researchers conclude that parcels of air from the edge of the decaying vortex carried cold, ozone-poor polar air over Australia. Such a dilution effect has already been suggested by modellers (refs 2 and 3) and clearly there are potentially serious implications, although the sensitivity of this effect to changes in atmospheric dynamics has yet to be assessed.

Although the chemistry of Antarctic ozone depletion is now probably understood, dynamical activity is also important. This is illustrated by the striking differences in the characteristics and scale of the 1987 and 1988 ozone holes (see the News and Views article by Mark Schoeberl[4]). It seems that the interannual fluctuations in total ozone concentrations in the Antarctic are linked to the tropical quasi-biennial oscillation[5] with relatively low (high) values occurring during the westerly (easterly) phase of this large-scale circulation. The marked drop in ozone concentrations over Australia is therefore likely to recur when ozone levels are low in the Antarctic.

The springtime polar vortex is isolated from ozone-rich air from mid-latitudes and forms a chemical containment vessel in which the cold temperatures allow the formation of polar stratospheric clouds. These provide surfaces for heterogeneous chemical reactions, releasing active chlorine and removing odd nitrogen, thus preconditioning the vortex for ozone depletion to take place when sunlight returns in the early spring.

There is some uncertainty, however, over how isolated the vortex must be for ozone depletion to take place. Some believe that the ozone-poor air within the vortex is tightly contained; others believe that air from lower latitudes descends through this region and is transported northwards at lower altitudes, so that the lower levels of the vortex effectively leak.

With more precise calculations, it might be possible to use early-spring observations from Australasia to distinguish the two models of the Antarctic ozone hole. According to both models, ozone-rich air from the tropics is deflected down onto Australasia by the vortex. But if the vortex is a leaky vessel, a small trickle of ozone-poor air will mix with this flow throughout the southern spring, whereas a sealed vortex would retain its contents until break up.

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