Probing Stratospheric Ozone

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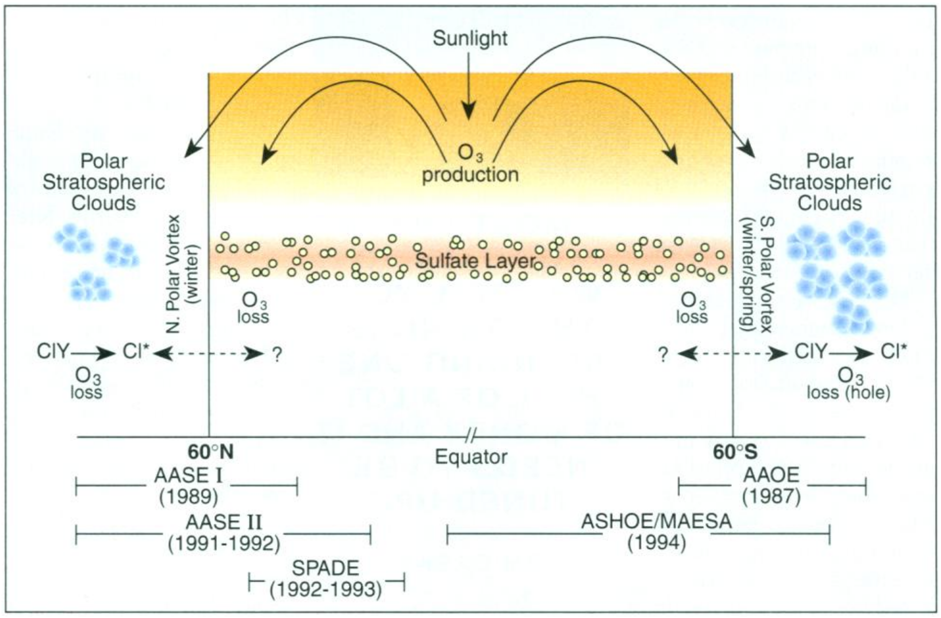
The discovery of the so-called "Antarctic ozone hole" in 1985 sharpened concerns throughout the world about the stability of the stratospheric ozone layer, which shields the biosphere from harmful ultraviolet radiation. Aircraft campaigns to Antarctica in 1987 [Airborne Antarctic Ozone Experiment (AAOE)] and to the Arctic in 1989 [Airborne Arctic Stratospheric Expedition (AASE I)], together with numerous ground-based measurements [for example, the National Ozone Experiment (NOZE) campaigns] (*1*), have provided first-order answers regarding the chemistry and meteorology controlling ozone in these regions. Results from the second AASE campaign, reported on pages 1130 to 1158 of this issue (*2*–*9*), have substantially expanded the information obtained in the previous Arctic campaign by both providing measurements of additional atmospheric constituents and extending the period of time covered by the measurements. These results present a consistent picture of chemical perturbations, established in the Arctic stratosphere at the beginning of the winter, which set conditions for ozone removal as sunlight returns at the end of winter. These measurements also indicate that stratospheric chemistry at mid-latitudes may be somewhat different from our previous understanding.

Ozone abundances are maintained by a delicate balance between production, transport, and removal (see figure). In particular, a decrease in ozone could be observed at mid-high latitudes if ozone transport from the tropics is reduced or chemical ozone removal is increased. For example, ozone transport to the polar regions could be curtailed by vortices in atmospheric circulation which appear during the respective winter and spring. Observations by the polar aircraft campaigns confirm this, although scientists still have not resolved the issue of exactly how much exchange takes place.

More important, previous aircraft campaigns established that, contrary to expectations, chemical removal of ozone by chlorine-catalyzed cycles is enhanced in the polar region during winter and spring. The main culprits for this aberrant behavior are seemingly innocuous solid nitric acid and ice clouds that are formed in the polar stratosphere during winter as a result of the extremely cold temperatures during this season. Although the existence of these polar stratospheric clouds (PSCs) has been known for over a century, their crucial role in stratospheric chemistry was not ascertained until the past few years. So-called "heterogeneous" chemical reactions take place on the surface of these particles, dramatically shifting the balance between inactive and active forms of chlorine and increasing the efficiency of chlorine in catalytic ozone removal.



Probing stratospheric ozone. Ozone is produced by sunlight in the tropics and transported to mid-high latitudes, where chemical removal occurs. Removal processes are catalyzed by different chemicals; chlorine has been of concern because of its anthropogenic origin. Heterogeneous reactions on the global sulfate layer, or on the larger PSCs, can facilitate conversion of total inorganic chlorine (ClY) to active forms (Cl*), which destroy ozone. This process also needs sunlight and is particularly efficient within the Antarctic polar vortex. The impact of polar processes on mid-latitudes depends on the mass exchange across the vortex boundary, which is at present not well understood.

Processing of air by a PSC should leave a tell-tale footprint: enhanced concentrations of chlorine monoxide (ClO), which should persist in Arctic conditions for at least 1 to 2 weeks, even if the culprit PSC has since evaporated. The meteorological analysis presented by Newman *et al.* (*2*) enables the determination of the temperature history of an air parcel prior to being measured. In particular, this analysis tells us whether the air was cold enough for the likelihood of PSCs forming sometime in the previous 10 days. The results presented by Newman *et al.* and Toohey *et al.* (*3*) are convincing: There is a high correlation between high measured concentrations of ClO and conditions for PSC formation, as determined from the temperature history. The seasonal behavior of ClO (*3*) is also consistent with the meteorological analysis (*2*). Enhanced levels of ClO first appear in December, when the stratosphere gets cold enough for PSCs to form. The highest levels of ClO are observed in January; at this time, the PSC coverage is sufficient for most of the vortex air to have been processed (*2*). The amount of ClO starts declining in February when warming of the polar vortex leads to the disappearance of PSCs. This timing explains why we have not seen an Arctic ozone hole: Warming of the Arctic vortex usually occurs around February, before the arrival of sufficient sunlight for catalytic ozone removal to occur. In contrast, temperatures in Antarctica stay cold until at least early to mid-October, which is equivalent to April in the Northern Hemisphere.

Footprints of heterogeneous processing by PSCs are also found in other species. The ALIAS instrument (*4*) joined the family of ER-2 instruments for AASE II. This instrument yielded, among others, first-time in situ measurements of hydrochloric acid. This very stable and inactive form of chlorine had been calculated to be the major component of inorganic chlorine in the stratosphere. Reactions of HCl with $ClNO_3$ on PSC-like laboratory surfaces, however, have been shown to rapidly convert these species to active chlorine. The ALIAS measurements confirm this picture: Not only are enhancements in ClO associated

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with reductions in HCl, but the relative magnitudes of enhancements and reductions are as expected from the proposed laboratory reactions. However, the HCl data did provide surprises. The measured concentrations of HCl outside of the polar vortices, where no PSCs should occur, are also substantially lower than predicted by calculations, implying that HCl may not be the principal chlorine component in the mid-latitude atmosphere, and raising questions as to the extent of our understanding of this region.

The results from AASE II have also provided strong indication that heterogeneous reactions can occur outside the polar vortices. A ubiquitous layer of supercooled sulfuric acid aerosols, partly of volcanic origin, provides the necessary surfaces for heterogeneous reactions to occur. Although these reactions do not seem to occur at sufficient rates to explain the HCl observations, other AASE II measurements have provided crucial information on the importance of this global heterogeneous chemistry. Fortuitously, the atmosphere itself provided a natural laboratory in which the impact of heterogeneous reactions could be measured at different aerosol levels.

The eruption of Mount Pinatubo in June 1991 substantially increased the global aerosol loading; the spreading volcanic cloud reached a maximum enhancement of a factor of 30 in surface area by the beginning of 1992, relative to conditions sampled during AASE I (1989). Instruments aboard the ER-2 aircraft (*5*) were thus able to sample the changes in aerosol size and surface area after a volcanic eruption and the concomitant changes in the chemistry. The analysis of Wilson *et al.* (*5*) indicates again a footprint of heterogeneous reactions on ClO; this time, however, enhancements in ClO are not attributed to PSC appearance, but simply to higher concentrations of sulfate aerosols resulting from the spreading volcanic plume. Similar signatures of heterogeneous reactions were found in the reductions in nitrogen oxides measured during AASE II (*10*).

Some of the results even suggest that, at cold enough temperatures, heterogeneous reactions on sulfate aerosols could be as efficient as those on PSCs. Toon *et al.* (*6*) have presented measurements of HCl and $ClNO_3$ integrated column abundances above the DC-8. Reductions in both species were observed, in spite of the fact that meteorological analysis did not indicate formation of PSCs. Such results raise a flag for potential chlorine activation outside the polar vortices.

Considerable effort has been devoted to the question of how much ozone is being lost in the sampled regions. A simple-minded approach to deducing ozone losses would be to look at measurements *x* days apart and see how much the ozone has changed at a given altitude. This approach is doomed to fail because the transport of ozone by atmospheric motions can easily introduce changes at a given altitude. It is thus necessary to find a "coordinate," either meteorological or chemical, that is conserved in atmospheric transport and to relate ozone measurements to this coordinate.

Three different papers tackle the question of net ozone loss during Arctic winter: Browell *et al.* (*7*), Salawitch *et al.* (*8*), and Proffitt *et al.* (*9*). These authors used different sets of observations and methodologies to derive ozone losses but come up with consistent results: Chemical processes removed about 15 to 25% of the ozone at altitudes near 18 km during January and February, the months with the strongest perturbation in the chlorine chemistry.

One approach can be seen in the analysis of Browell *et al.* (*7*). The differential absorption lidar (DIAL) instrument yields lidar backscatter profiles that can be translated into both aerosol and ozone profiles above the DC-8 altitude (~10 to 12 km), up to altitudes above those sampled by the ER-2 (~19 to 20 km). By relating the measured ozone to potential temperature, a meteorological parameter that is approximately conserved over periods of a few weeks, the authors found ozone losses of about 15 to 25% between January and February.

The AASE II results allow the calculation of expected chemical ozone loss directly from the measured species, particularly ClO and BrO. This approach is exemplified by Salawitch *et al.* (*8*). Their calculated ozone loss (15 to 25% in January and February) are again consistent with those deduced directly from ozone observations. This consistency strengthens our confidence in our understanding of the ozone loss processes. The authors also use their model to explore hypothetical scenarios in which colder temperatures or higher chlorine levels could accelerate Arctic ozone removal.

Proffitt *et al.* (*9*) have used in situ ozone measurements aboard the ER-2 and related them to measurements of nitrous oxide, a conserved chemical "coordinate." Again, reductions in ozone of 20 to 30% are deduced. This paper, however, illustrates the uncertainties still inherent in the approach adopted by all three studies of the ozone loss: The mapping between ozone and the conserved coordinates is somewhat ambiguous and can slowly evolve over the months covered by AASE II. Ozone losses as high as 40% were obtained by Proffitt *et al.* (*9*) when a different ozone–nitrous oxide relation was adopted.

The importance of Arctic processes to ozone decreases at northern mid-latitudes is difficult to ascertain. Calculations with heterogeneous chemistry in the sulfate layer can account for about 3% (*11*) of the 6 to 8% per decade loss deduced from satellite measurements (*12*). The estimates of Proffitt *et al.* (*9*) indicate that Arctic chemistry could contribute as much as an additional 2.5%. This number is extremely sensitive to details of mass transport across the polar vortex, a subject of intense and lively discussion amongst atmospheric dynamicists (*13*).

The measurements by the AASE II campaign have confirmed some aspects of our understanding of stratospheric ozone. However, the ozone bill of health is precarious enough that future checkups are warranted. The workings of heterogeneous chemistry were again probed by the ER-2 instruments during the Stratospheric Photochemistry Aerosol and Dynamics Experiment (SPADE) in October 1992 and May 1993. Further probing of the atmosphere will occur in 1994 during the Airborne Southern Hemisphere Experiment (ASHOE) and Measurements for Assessing the Effects of Atmospheric Aircraft (MAESA). These campaigns, with extended deployments similar to AASE II, will fly mostly in the Southern Hemisphere.

Finally, we must stress that extrapolation of results from an aircraft campaign to the global scale relies heavily on the relation established amongst chemical constituents and dynamical parameters. These mappings and their implications will continue to be tested, not only by aircraft measurements, but by comparison with satellite data. Preliminary comparison with results from the Upper Atmospheric Research Satellite (UARS) is encouraging: The picture emerging from AASE II is qualitatively consistent with the UARS measurements (*14*) at a global scale. This type of multifaceted monitoring of ozone will be crucial in the next few decades as we nurse stratospheric ozone to recovery by reducing future emissions of chlorine species.

References and Notes

1. Results from polar measurements have been summarized in the following special issues: *Geophys. Res. Lett.*, **13** (no. 12) (1986); *ibid.* **17** (no. 4) (1990); *J. Geophys. Res.* **94** (nos. D9 and D14) (1989); *ibid.* **97** (no. D8) (1992).
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