

High-latitude ozone loss outside the Antarctic ozone hole

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Data taken during the 1987 Antarctic Airborne Ozone Experiment based in Punta Arenas, Chile, are used to show that from mid-August until the end of the mission in late September there was a high-latitude ozone loss outside the Antarctic ozone hole. Therefore, not only is the geographic extent of the ozone loss larger than that generally identified as chemically perturbed, but ozone is lost earlier in the year than previously reported. These results, when compared with long-term temporal trends of column ozone, indicate a possible anthropogenic component for this loss.

MEASUREMENTS from the past few years have shown that stratospheric ozone decreases substantially over Antarctica during September and October and that these decreases have intensified dramatically during the past decade. The intensification has been attributed to man's release of certain chlorine-containing compounds, primarily chlorofluorocarbons. The region of very high ozone decrease, usually referred to as the ozone hole, approximately covers the Antarctic continent, and is coincident with what is commonly called the polar vortex. Horizontally, the polar vortex is roughly defined by its perimeter, the polar night jet, a circumpolar wind belt in the stratosphere that seems to restrict exchange of air through the perimeter. The seasonal period of low ozone values is observed to terminate with the annual dissipation of the Antarctic vortex during the spring warming, at which time the air within the vortex is no longer restricted but allowed to mix freely with ozone-rich air from other latitudes. Transport towards the Equator and mixing of ozone-poor air with air at lower latitudes result in localized decreases of ozone¹. The extent and intensity of these decreases are of global concern.

The seasonal decrease in ozone is large enough to provide an unequivocal signature of loss that is easily distinguished from natural short-term dynamical variability, and has been verified from the ground, aircraft, balloons and satellites. In this paper 'ozone loss' is used to identify a change in ozone due to chemical mechanisms (rather than dynamical processes) that is not predicted within standard gas-phase photochemistry models. We do not intend to imply the loss is necessarily due solely to chlorine. Measurements of total column ozone (total number of ozone molecules vertically above some area of the Earth) made from the ground and from a single station first identified ozone loss over Antarctica². Satellite column measurements then verified that it was not just a local phenomenon³. Measurements obtained from balloons provided snapshots of the vertical distribution of ozone at a few Antarctic locations and presented striking accounts of large ozone decreases when comparing profiles from August with those from October^{4,5}. But the changes observed were not simply a gradual deterioration of the ozone layer, but included a substantial day-to-day variability and frequent horizontal layering. This means that the region of decreased ozone is neither vertically nor horizontally homogeneous, and that quantification of the altitude-dependent

decrease of ozone requires good temporal and geographic coverage. Although satellite measurements of total column ozone are frequently available, they cannot identify the altitude dependence of the ozone loss. *In situ* aircraft measurements can provide vertical profiles and extended horizontal coverage, but they are still insufficient to sample the entire geographic extent of the vortex frequently.

Here we present a different approach to estimating the ozone (O_3) loss inside and, more interestingly, outside the ozone hole—one that completely avoids the problems of sampling an inhomogeneous air mass. As standard gas-phase photochemistry is very slow in the region of this analysis (that is, during high-latitude winter in the lower stratosphere where O_3 has a photochemical replacement time of more than a year^{6,7}), O_3 can be used effectively as a conservative tracer. The sum of the reactive nitrogen species (abbreviated as NO_y , and including in that sum NO , NO_2 , NO_3 , HNO_3 , N_2O_5 and $ClONO_2$) and nitrous oxide (N_2O) are also conserved in this environment. By combining *in situ* measurements of these tracers with empirically derived formulations that are supported by two-dimensional atmospheric models, minimum reference values for unperturbed O_3 can be estimated for any air parcel sampled. This reference value for O_3 can then be compared with the measured value, and the difference is a deviation from conservative behaviour that can be interpreted as a chemically induced change not within the standard gas-phase photochemistry. The formulations presented are first applied outside the region usually referred to as chemically perturbed. Then the analysis is used in a different manner, but this time both outside and inside. It is assumed for the analysis that there has been sufficient simultaneous sampling of the trace constituents NO_y , N_2O and O_3 ,

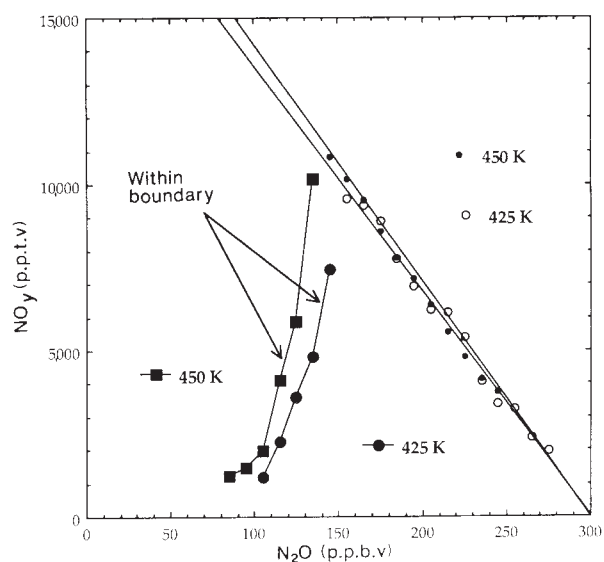


FIG. 1 NO_y against N_2O from 1987 AAOE for the 425-K and 450-K flight levels and averaged for the seven flights where data are available over intervals of 1° latitude. Data taken within clouds were excluded to obtain only gas-phase NO_y . Linear least-squares fits to the data outside the boundary are shown for each flight level.

spatially and temporally, to determine reliable reference formulations.

To discuss accurately the morphology of the ozone hole, the concept of the boundary of the chemically perturbed region is used as introduced and developed by Proffitt *et al.*⁸ from data taken during the 1987 Antarctic Airborne Ozone Experiment (AAOE). The boundary, defined by a level of chlorine monoxide ($\text{ClO} = 130$ p.p.t.v. (parts per 10^{12} by volume)), effectively locates where this critical component in the catalytic destruction of O_3 by chlorine has a sharp poleward increase. It was found that there were also dramatic poleward decreases in NO_y and H_2O at this boundary, hence the basis for describing the interior region as chemically perturbed. We shall refine this description slightly by referring to this region as 'high chemically perturbed', and thereby not exclude a possible lesser degree of chemical perturbation outside the boundary. Proffitt *et al.* have shown that this boundary is slightly poleward of the peak wind speeds of the polar night jet and that it coincides with the latitude of the strong poleward decrease in total column O_3 as measured by satellite. In addition, the boundary locates the perimeter of the large isentropic temporal O_3 decrease (ozone hole) to within at least 1° of latitude (~ 111 km).

Danielsen and Houben⁹ give heuristic arguments for wintertime diabatic cooling over Antarctica persisting into early spring, carrying ozone-rich mid-latitude air downward and poleward into the polar vortex. Proffitt *et al.*¹⁰ have presented supporting evidence from AAOE indicating a slow progression of diabatically cooling and descending lower stratospheric air advectively spiralling poleward as it crosses the polar jet into the ozone hole. This view can be compared with that of Tuck¹¹, who also concludes that there is a significant mass flow through the vortex, but argues that it is the downward diabatic motion within and outside the vortex that is important. With either view, the region near and within the ozone hole is being slowly replenished with mid-latitude ozone-rich stratospheric air during the period of O_3 decrease through diabatic descent. If this is the case, temporal trends in measured O_3 will not indicate the total loss of O_3 in a particular parcel of air unless the time series begins before there is any loss and the measurements follow the descending parcel throughout the time interval of the trend¹⁰. This is a difficult, if not impossible, sampling requirement, even with precise knowledge of a parcel's descent path. Possible mixing of air parcels of dissimilar origin during or following the O_3 destruction process further complicates the sampling problem.

The analysis presented is based entirely on the *in situ* data taken during AAOE from the high-altitude ER-2 aircraft. During the mission the average latitude of the boundary was 66° S, but varied from 59° S to 71° S, its position responding to synoptic-scale meteorological forcing of the polar vortex. The data are generally restricted vertically to the two levels of 425 ± 10 K and 450 ± 10 K in potential temperature (corresponding to geometric altitudes ~ 17.5 km and 19 km respectively over Antarctica) and horizontally from 53° S to 72° S latitude at $\sim 65^\circ$ W longitude. The longitudinal coverage is quite restricted, extending only from the southern tip of South America to the region over or near the Antarctic Peninsula. Also, data were collected during the transit flights between Moffett Field, California (37° N) and Punta Arenas, Chile (53° S), where the twelve ER-2 Antarctic flights originated.

Lower limit for unperturbed ozone

The stratospheric source for NO_y is the very unreactive species N_2O . The primary destruction mechanism for N_2O is ultraviolet radiation at wavelengths ≤ 225 nm, has N_2 and $\text{O}(^1\text{D})$ as principal products, and occurs primarily in the middle of the stratosphere above 30 km. A secondary loss occurs also in the middle stratosphere where NO is created in the reaction of $\text{O}(^1\text{D})$ with N_2O , providing the primary source of NO_y . Plots of N_2O against NO_y outside the boundary show them to be linearly related (Fig. 1). These data are from the two flight levels of 425 K and

450 K of potential temperature and were analysed separately by averaging within 1° -latitude bins with respect to the boundary and over a one-month period. The data in Fig. 1 labelled as within the boundary (corresponding to $\text{N}_2\text{O} \leq 140$ p.p.b.v. (parts per 10^9 by volume)) are known to be from within the highly chemically perturbed region. Linear least-squares fits are shown for the data outside this region and it is apparent that the straight line that fits the data at the lower altitude (or potential temperature) also fits the data at the upper altitude rather well. The linear fit to all of the points in Fig. 1 outside the boundary is given by

$$[\text{NO}_y] = 20,800 - (69.8 \times [\text{N}_2\text{O}]) \quad (1)$$

where the mixing ratio for NO_y is in p.p.t.v and for N_2O is in p.p.b.v.^{10,12,13}. It is noteworthy that data taken during the flights from Punta Arenas to Moffett Field, where minimum values for N_2O of 210 p.p.b.v. were observed, also fall on the same straight line¹⁰. There are few further data available to verify the persistence of the linear relationship at other seasons, latitudes and altitudes, although the mid-latitude Southern Hemisphere balloon data taken by Galbally *et al.*¹⁴ up to 30 km have the same characteristic. This persistent linear relationship and lack of curvature results from a balance of photochemistry, transport

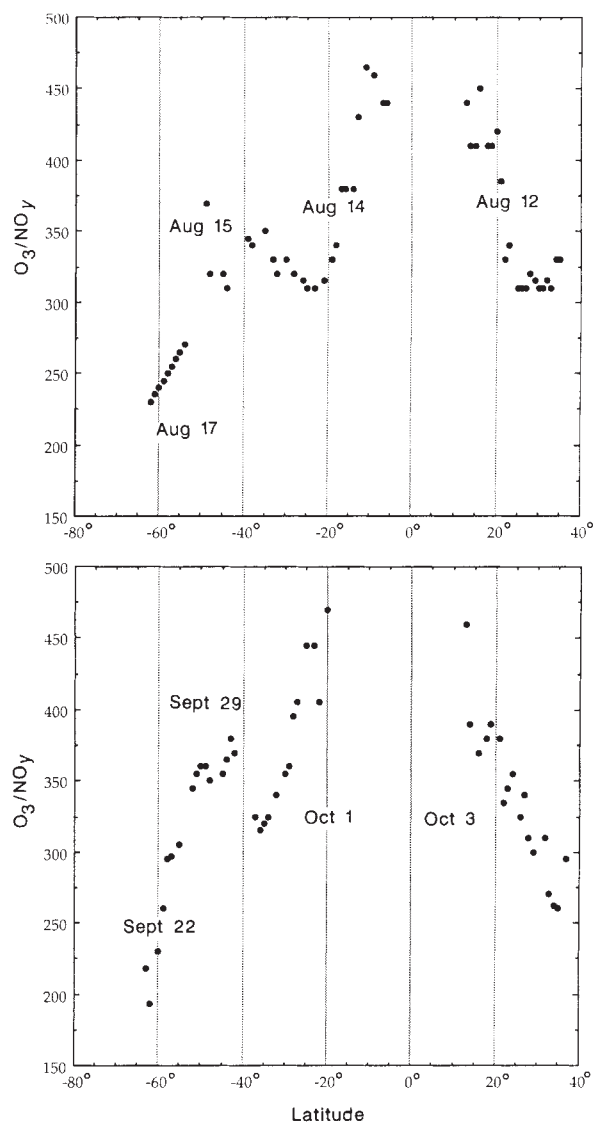


FIG. 2 O_3/NO_y latitude survey from a, 12 August to 17 August, 1987 and b, 22 September to 3 October, 1987.

and mixing. The N_2O intercept and slope are probably determined in the tropics where upper tropospheric and lower stratospheric air with N_2O of ~ 300 p.p.b.v. and $NO_y < 0.5$ p.p.b.v. (intercept) rises into the tropical middle stratosphere where NO_y is produced from N_2O apparently with an average efficiency of $\sim 7\%$ (slope). Mixing, as the middle stratospheric air proceeds poleward, probably contributes to the observed small variability from linearity observed at high latitudes.

The ratio of O_3 to NO_y (O_3/NO_y) can now be used to bring O_3 into the analysis. Figure 2a is a plot of O_3/NO_y against latitude taken at the start of the mission and includes data taken in transit from Moffett Field to Punta Arenas. The ratio is > 300 over a wide range in latitudes, but decreases at the most southerly latitudes. Figure 2b is a similar latitude survey including the last Antarctic flight and the transit flight data during the return to Moffett Field at the end of the mission. Still lower values at the southernmost latitudes and a few data points below 300 at about $35^\circ N$ are the primary differences between the two surveys. Both figures are restricted to pressure altitudes from between 18 km and 21 km, and all data within the boundary are excluded. In both plots $O_3/NO_y > 300$ at all latitudes north of $\sim 55^\circ S$, except on the flight of 3 October over California, where a few values as low as 260 are found. Both surveys also show an enhanced ratio in the tropics where, at 20 km, stratospheric air is apparently encountered that had recent O_3 production without the equivalent NO_y production required for the usual ratio found at mid-latitudes. Other latitude surveys of ER-2 data taken during the Stratosphere Troposphere Exchange Project in January and February 1987 from $40^\circ N$ to $30^\circ S$ have been analysed (D. M. Murphy *et al.*, manuscript in preparation) and show a minimum for the ratio of 280 when restricting the data to potential temperatures > 430 K. Also presented by Murphy *et al.* are two-dimensional model calculations^{15,16} and satellite data¹⁷ in the tropics and mid-latitudes covering pressures down to 7.5 mbar. Both the models and the data show that the O_3/NO_y ratio is > 300 in the lower stratosphere and indicate either no vertical change or a slight decrease with altitude. Qualitatively these observations are consistent with the well-known mid-latitude mixing ratio maximum for O_3 and NO_y at 30–35 km with the maximum for NO_y a few kilometres higher than the O_3 maximum. These maxima correspond to N_2O values of 30–100 p.p.b.v., values much less than those measured outside the boundary and, as seen in Fig. 1, generally less than any data from AAOE.

From the observations made during ER-2 latitude surveys it is reasonable to assert that if NO_y and O_3 are given in identical units (such as p.p.b.v.) the inequality

$$[O_3]/[NO_y] \geq 270 \quad (2)$$

is representative of late winter in the Southern Hemisphere north of the boundary. The data and model calculations indicate that a larger value of 300 for the minimum ratio could be justified. But there is no established record of simultaneous measurements of NO_y and O_3 covering all latitudes, seasons and altitudes of interest from which unequivocal formulations relating O_3 to NO_y could be derived. So the conservative approach taken here is appropriate, although it may underestimate the O_3 losses that have occurred.

Ozone losses

On 17 August between $54^\circ S$ and $63^\circ S$ (Fig. 2a), there was a significant difference between the expected O_3/NO_y ratio (inequality (2)) and its measured value. As NO_y was not perturbed and O_3/NO_y is less than our reference level of 270, an O_3 loss is indicated in that region. The value for O_3/NO_y of 230 at $63^\circ S$ yields a 15% loss of O_3 outside the highly chemically perturbed region on 17 August. Data from the flight of 23 August also indicates a 15% loss outside the boundary, and the flights of 28 August and 22 September show a larger loss of 30%. But rather than giving flight-by-flight analysis, Fig. 3 shows averages

for the period 23 August to 22 September to summarize the results and demonstrate that the O_3 losses are not isolated events found on certain flights, but were prevalent throughout the period and clearly seen in the averages. This is achieved by referencing the flight-leg data for NO_y and O_3 relative to the boundary, and then averaging the O_3/NO_y ratio over bins of 1° latitude. Only data for which NO_y is believed not to be enhanced by particles (as indicated by simultaneous particle measurements) have been plotted. This averaging procedure is done independently for both of the flight levels. The vertical bars represent the sample standard deviation and indicate how flight-by-flight variability affects the results.

The abrupt increase south of the boundary is due to the high degree of denitrification within the highly chemically perturbed region¹³ and provides little information on the O_3 loss. We deal below with this region in a different way. However, outside the boundary where the NO_y is known to be unperturbed relative to N_2O , there are depressed ratios even below 200 near the boundary. These low ratios correspond to an average minimum O_3 loss of 15–30% in the first 5° of latitude outside the highly chemically perturbed region at these levels. It should be noted that the averaging over the one-month period is in a region where diabatic descent is believed to be taking place. An important feature in Fig. 3 is that outside the boundary the ratios at the 450-K level are $\sim 20\%$ higher than those at the 425-K level. This is not what would be expected from the model calculations and satellite data mentioned above, which show either no change in O_3/NO_y with altitude or a decrease. The implication is that the lowest values seen near but outside the boundary could not have come simply from vertical descent in this region. Proffitt *et al.*¹⁰ show that within the averaging procedure used for Fig. 1, $< 10\%$ of the air outside the boundary had come recently from the highly chemically perturbed region. Thus, if these results are accepted (that is, ongoing diabatic descent and little outward mixing at these potential temperatures) along with inequality (2), the decrease in the O_3/NO_y ratio, seen as the boundary is approached from the north, cannot be due to transport or mixing of air vertically nor horizontally, and therefore must be caused by some chemical mechanism operating at these levels outside the highly chemically perturbed region.

The isentropic temporal changes in O_3 outside the boundary

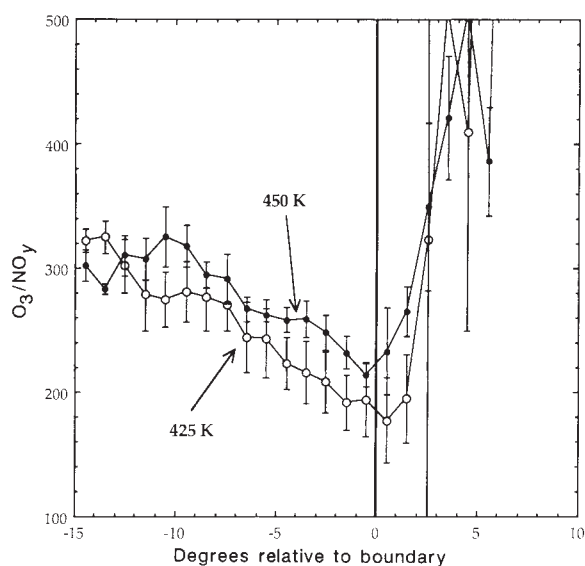


FIG. 3 O_3/NO_y against latitude relative to the boundary (heavy vertical line) for the 425-K and 450-K flight levels and averaged for the seven flights where data are available over intervals of 1° latitude. Data taken within clouds were excluded to obtain only gas-phase NO_y . Sample standard deviations are given as vertical bars.

during this one-month period are small in comparison with those inside, and in general are not significantly different from zero¹⁸. As discussed in the introduction, losses of O₃ in a parcel of air undergoing diabatic descent will not be represented accurately by a temporal trend calculated at a constant potential temperature, because the losses will be masked by the usual vertical gradient in O₃. Therefore the lack of a significant isentropic temporal trend outside the boundary in no way indicates that no loss of O₃ is occurring there.

To extend our analysis into the ozone hole and provide a check for consistency between two methods, equation (1) and inequality (2) are now combined into an inequality relating unperturbed O₃ directly to N₂O. If O₃ and N₂O are both in p.p.b.v.

$$[\text{O}_3] \geq 5616 - (18.85 \times [\text{N}_2\text{O}]) \quad (3)$$

provides a minimum value for unperturbed O₃. First note that this formula is based on measured data and may reflect systematic errors in the measurements. In this regard, the O₃ measurement used here was generally within 2% of an independent measurement of O₃ made simultaneously on the ER-2^{19,20}. There was no independent check of the NO_y measurements except as they related to the O₃ data over a long history of more than 50 ER-2 flights, but they are reported to be accurate to within ±20% and repeatable (precise) to within at least 0.1 p.p.b.v.¹³. The values used for N₂O are from the ATLAS instrument^{21,22} and include a recent recalibration of the data that was not included in earlier papers^{8,10-13,21,22}. The reported accuracy of the N₂O measurements is ±10%.

There is more uncertainty in applying inequality (3) inside the boundary where N₂O < 140 p.p.b.v. (see Fig. 1), stemming from our lack of information to support equation (1) and inequality (2) at these more southerly latitudes. Outside the boundary, equation (1) was used to test where NO_y was perturbed, then inequality (2) was used to predict O₃. By extending the application of inequality (3) to 72° S with its lower values for N₂O it is assumed that equation (1) remains linear and inequality (2) is still representative of O₃/NO_y. The use of equation (1) at lower values of N₂O is supported by noting that the linear relationship between NO_y and N₂O is predicted to persist at mid-latitudes to at least 14 p.p.b.v. of NO_y in both a one-dimensional radiative convective photochemical model²³ and a two-dimensional model¹⁶. Furthermore, the model calculations discussed earlier indicate that inequality (2) is satisfied at flight altitudes throughout our latitude range. Therefore all information available supports inequality (3) for these low values of N₂O. Implicit in the above discussion is that the formulations do have limits of applicability, the most obvious one being that they do not apply at altitudes above the maximum stratospheric mixing ratios for O₃. For at such altitudes, N₂O and O₃ are both decreasing with altitude but inequality (3) implies that as N₂O decreases, O₃ increases. With this reservation a lower-limit estimate for unperturbed O₃ both outside and with increased reservation inside the boundary can now be calculated. Figure 4a, b shows measured O₃ against latitude with respect to the boundary where O₃ is averaged over all ten flights from 23 August to 22 September at both flight levels. Otherwise data are treated as in Fig. 3 for O₃/NO_y. Also plotted is the corresponding minimum value of unperturbed O₃ calculated from inequality (3). Figure 4c shows the O₃ loss with respect to the boundary, calculated as the percentage decrease in O₃ and based on Fig. 4a, b. The loss outside the boundary is typically 20–25% at 425 K for the first 5° with a maximum value indicated of ~30%. From Fig. 3 we obtained a maximum value of 30% O₃ loss outside the boundary, which is virtually identical to the loss shown in Fig. 4c, although the analysis of Fig. 3 includes only seven of the ten flights included in Fig. 4. This difference in number of flights is because particle-free NO_y data are available only from seven flights. Both analyses indicate that the loss is greater at the lower level, which is consistent with diabatic

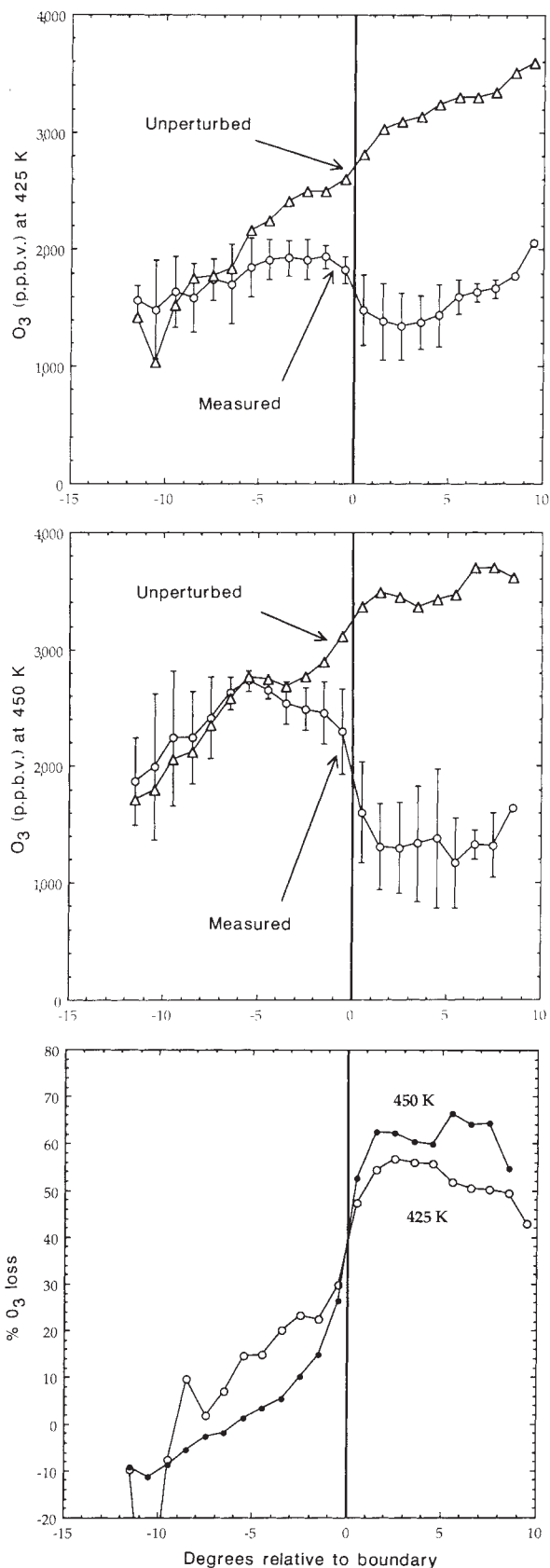


FIG. 4 a, O₃ against latitude referenced to the boundary (heavy vertical line) for the 425-K flight level. Data are averaged over intervals of 1° latitude and over all ten flights from 23 August to 22 September 1987. b, As in a except at 450-K flight level. c, Average percent O₃ loss over 30 days derived from a and b.

descent and a simultaneous chemical loss of O₃.

This analysis can also be applied to individual flights rather than averages of flights. For example, from data taken on 23 August, the first day that a flight clearly penetrated the boundary, we calculate a 40% loss in O₃ inside the boundary. On the last mission flight date, 22 September, still two weeks before the minimum column O₃ was measured in 1987 (ref. 24), there was a 70–80% loss within the boundary in the layer between 17.5 km and 19 km. This is substantially more than the 53% isentropic temporal decrease observed in the same region from 23 August to 22 September¹⁸.

Discussion and conclusions

Since the ozone hole was first identified in 1985 it has been considered to be a recurring springtime event with a nearly monotonic increase of intensity over its history of ~10–15 years²⁵. Here we have presented strong evidence of significant O₃ loss occurring as early as mid-August both inside and outside the highly chemically perturbed region, and that this loss is chemical in origin rather than a result of atmospheric dynamics. Although the mechanism for the chemical loss outside the boundary cannot be inferred from this approach, there is evidence of a temporal column O₃ decrease over the past decade in this region, therefore indicating that the chemical loss that we report has an anthropogenic component. In particular, ref. 26 shows, by comparing satellite data from 1979–80 with 1986–87, a nine-year temporal decrease from 6% to 18% in column O₃ between 60° S and 66° S during August and September, a region near, but on the average outside, the boundary during AAOE. In ref. 27 the data were analysed with a linear fit of the yearly data, starting with 1978 and ending with 1988. This analysis produced virtually identical trends from 60° S to 66° S from mid-August through September. Both studies also show a long-term temporal decrease of more than 10%, poleward of 66° S during August. These analyses present a consistent picture of mid-August O₃ decreases, both inside and outside the vortex, that have intensified during the past ten years. The results we have presented co-locate a region of chemical O₃ loss with these long-term temporal decreases in O₃, suggesting that at least part of the loss has an anthropogenic origin.

The cause of the O₃ loss outside the boundary, where the measured ClO is only 5–10% of the level measured inside the boundary, is not known, and more experimental investigation is warranted. But it has been suggested by Tuck¹¹ that O₃ losses may occur near the boundary and outside the highly chemically perturbed region during June, July and August as long as there is sunlight. Such losses would be due to reactive chlorine, as is the case within the ozone hole itself. Support for this conclusion comes from photochemical model studies made along isentropic trajectories outside the boundary²⁸. These studies point out that

the discrepancy between observed and measured values of ClO and NO indicates significantly perturbed photochemistry in this region without substantial denitrification. In sunlight the formation of polar stratospheric clouds (PSCs) outside the boundary can perturb chlorine and nitrogen chemistry, initiating catalytic destruction cycles. Observed temperatures are above the frost point on average, but low enough for PSCs to form that contain nitric acid, a component of NO_y^{13,29}. The NO_y measurements indicate that PSC formation does not generally lead to denitrification. The maximum frequency of PSC formation over the continent and inside the vortex occur to the east of the ER-2 flight tracks over the Weddell Sea³⁰, downwind from the ER-2 flight track. The perturbed levels of reactive chlorine initiated by the PSCs cannot be long-lived because of the lack of denitrification. In sunlight, nitric acid will gradually photolyse to produce NO₂, and this will reduce ClO levels to near unperturbed values. With such intermittent chemical perturbations, this region may contain sufficient recurrent enhancements in ClO to destroy O₃ to the extent indicated in our analysis.

Obtaining values for unperturbed O₃ in the Antarctic from other species must carry with it some uncertainty, but the analysis presented here has been conservative. In particular, if the value of 300 had been chosen for O₃/NO_y as is indicated by the Southern Hemisphere data, the analysis would have produced somewhat larger O₃ losses. The negative O₃ loss 10–15° outside the boundary (Figs 3 and 4c) shows that the choice of 270 for the ratio is conservative. Nevertheless, the method is more reliable than the simple 'before and after' comparisons of O₃ profiles which we strongly caution against when analysing losses of O₃ at high latitudes unless the losses are very large, as within the Antarctic ozone hole.

We have analysed winter-time high-latitude O₃ changes in a region where O₃ is considered under dynamical control and standard gas-phase photochemistry is extremely slow. We have estimated a reference state for O₃ in this region from other conserved trace species and compared this with measured values to determine a minimum loss in ozone. In this context we can summarize the important conclusions as follows: (1) There is a substantial O₃ loss by mid-August both inside and outside the highly chemically perturbed region; (2) For the first 5° outside the boundary, the average O₃ loss from 23 August to 22 September was at least 15–30% at 17.5 km and 4–25% at 19 km; (3) The O₃ loss found outside the boundary is chemical in origin and did not occur within the highly chemically perturbed region. An anthropogenic component cannot be ruled out; (4) For the first 5° inside the boundary and in the layer between 17.5 and 19 km the air observed on 23 August had an O₃ loss of about 40%. By 22 September there was an O₃ loss of at least 75%, much larger than the average isentropic temporal decrease of 53% from 23 August to 22 September.

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