

Reductions of Antarctic ozone due to synergistic interactions of chlorine and bromine

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The vertical column density of ozone observed in October over Antarctica has fallen precipitously over the past 10 yr. The concentration at Halley Bay (76° S 27° W), expressed conventionally in Dobson units (DU) (1 DU = 10⁻³ atmos. cm = 2.7 × 10¹⁶ molecules cm⁻²), has dropped from about 300 DU in 1975 to <200 DU in 1984 (ref. 1). Values in 1985 were even lower, comparable with the lowest values recorded anywhere on Earth². We suggest here that the loss of O₃ in Antarctica may be attributed to catalysis of O₃ recombination by a scheme in which the rate-limiting step is defined by the reaction ClO + BrO → Cl + Br + O₂. Concentrations of NO₂ must be low and heterogenous reactions involving particles in the polar stratospheric clouds must be an important element of the relevant chemistry. Industrial sources make important contributions to the contemporary budgets of both BrO and ClO and are likely to grow significantly in the future.

The decline in O₃ at Halley Bay does not simply reflect a local anomaly. It extends over at least 15° in latitude, according to measurements by the Total Ozone Mapping Spectrometer (TOMS) on Nimbus 7 (ref. 3). It is associated generally with air within the polar vortex, in a region offset some distance to the east with respect to the pole. The drop in O₃ begins in early September. The rate of decline in September 1983 averaged ~0.6% per day (ref. 3). The largest reductions in O₃ occur between 14 and 24 km, as evidenced by soundings from Syowa (69° S, 40° E)^{2,4}. The challenge for models is to account for the rate of change in September, and to rationalize the surprisingly short time constant implied by the observational data. It is particularly difficult to explain the large reductions observed at low altitude. A complete theory should account for the trend since 1975.

Several profiles adopted from ozonesonde data taken at Syowa^{2,4} are shown in Fig. 1. Curve *a* reflects the mean data for October before 1975. Curve *b* shows the average observed for the winter of 1982, while curves *c-e* illustrate conditions with much lower O₃ observed in October of 1982 and 1983. Temperatures were low for cases *c-e*, suggesting a significant contribution to the overhead column at these times due to air drawn from within the vortex. As noted above, reductions in O₃ are most striking near the peak at 70 mbar.

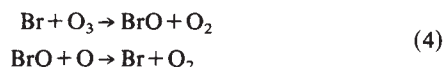
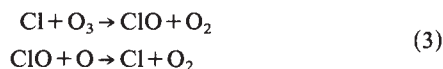
Ozone may be removed either by reaction with O,



or by reaction with itself,



These reactions proceed, for the most part, by indirect paths, catalysed by trace quantities of HO_x, Cl_x, Br_x and NO_x. Reaction (1) can occur through⁵⁻⁸



and

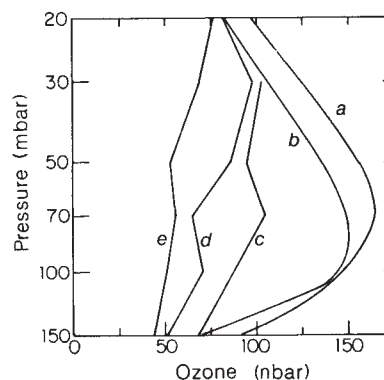
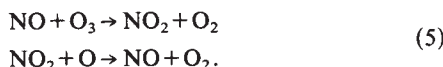
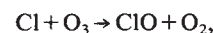
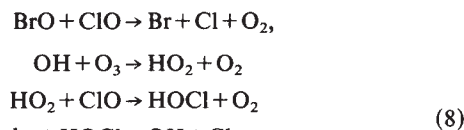
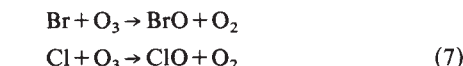
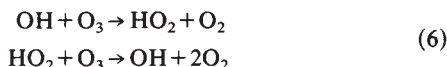
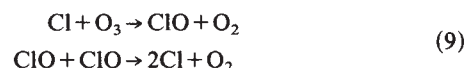


Fig. 1 Vertical distributions of ozone at Syowa (69° S, 40° E). *a*, An average of 26 soundings made between 1968 and 1974, in October. The average column density recorded during this period was 337 DU. *b*, An average of soundings made in June, July and August, 1982; the average ozone column was 320 DU. *c*, *d* and *e* were measured on 23 September 1982, 14 October, 1982, and 17 October, 1983; the ozone columns were 256, 241 and 217 DU, respectively. The mean ozone column for October 1982 was 236 DU; 260 DU for October 1983.

Reaction (2) can proceed by^{9,10}



and



If we assume that the change in Antarctic O₃ should be attributed to effects of chlorine, we can estimate the maximum possible impact from reactions (3)-(9), as follows.

Assume that Cl_x is present mainly as ClO and consider a profile for ClO corresponding to a total stratospheric chlorine abundance of 3.0 p.p.b. (parts per 10⁹), as would be appropriate for 1983. The associated (maximum) rate for removal of O₃ by reactions (3)-(5) is too small by an order of magnitude to account for the reductions implied at lower altitudes by the perturbed profiles of Fig. 1. The abundance of O at low Sun angles characteristic of high southern latitudes in September is insufficient to permit an important role for reaction (1) below 26 km.

No such restriction applies for reaction (2). In contrast to reaction (1), reaction (2) allows for significant loss of O₃ near 70 mbar. If we assume that chlorine and bromine are present primarily in the form of the reactive oxides, ClO and BrO, and consider concentrations of ClO and BrO of 3 p.p.b. and 25 p.p.t. (parts per 10¹²) at high altitude, we find that the column abundance of O₃ could fall by >2% per day, a rate significantly larger than observed by TOMS³.

High concentrations of ClO and BrO in the lower stratosphere require that the abundance of NO₂ be small. At mid latitudes the concentrations of NO₂ are high enough for ClO and BrO

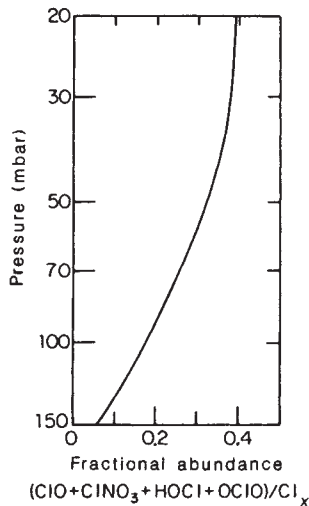
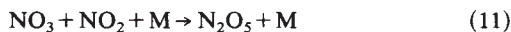
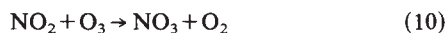


Fig. 2 Vertical distribution of the fraction of Cl_x present as ClO_x ($\text{ClO}_x = \text{ClO} + \text{ClNO}_3 + \text{HOCl} + \text{OCIO}$). The vertical profile of Cl_x was calculated at 30°S using a one-dimensional model, and Cl_x was estimated at 45° , 60° and 80° using slant mixing surfaces²⁵⁻²⁷. The fractional abundances of ClO_x were then calculated for the four latitudes using observed concentrations of ozone and a solar declination of 0° . The results of the four calculations are shown averaged along slant mixing surfaces approximately parallel to the tropopause. All calculations employed the rate constants recommended in ref. 22.

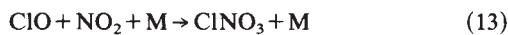
to be efficiently converted to ClNO_3 and BrNO_3 respectively. The abundance of NO_2 is very low at high latitudes in winter¹¹⁻¹⁴ and this is usually attributed to an influence of heterogeneous chemistry^{15,16} involving particles in clouds which form during the polar night^{17,18}. A plausible scheme is



and



Removal of ClNO_3 is possible also by¹⁹



or by



Reactions (12), (14) and (15) have been observed on the walls of reaction vessels in the laboratory²⁰⁻²². Reaction (15) is unlikely to occur in the atmosphere in that it requires an interaction of two minor species present simultaneously on particles composed primarily of H_2O and H_2SO_4 .

The high-latitude stratosphere is coupled in autumn to lower latitudes by mixing along slant surfaces oriented roughly parallel to the tropopause^{23,24}. The average abundance of ClO_x (defined as $\text{ClO} + \text{ClNO}_3 + \text{HOCl} + \text{OCIO}$) relative to HCl along these surfaces may be estimated using one-dimensional model studies as a guide²⁵⁻²⁷. A mean profile, obtained from an average along the slant mixing surfaces, is given in Fig. 2. This should provide an appropriate representation of air entering the polar vortex. We expect the abundances of ClO_x and BrO_x (mostly $\text{BrO} + \text{BrNO}_3$) to remain essentially constant throughout the polar night. A combination of ClNO_3 formed by reaction (13), HOCl produced by reaction (14) and OCIO derived from



and



should represent the dominant forms of reactive chlorine. The potential importance of reaction (17) in this context was recognized first by Tung *et al.*²⁸.

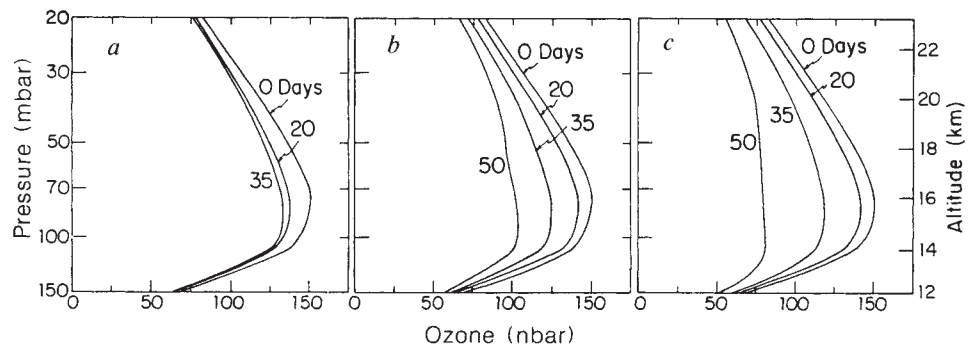
Consider two possibilities as the Sun returns to the high-latitude stratosphere in early spring: (I) Suppose that reactive chlorine is present mainly as OCIO . (The dominant source is reaction (17).) (II) Suppose that HOCl is more abundant. (This implies significant production by the heterogeneous reaction (14).) In either case BrO is likely to be the dominant form of reactive bromine. Assume that the initial abundance of NO_y (defined as all forms of reactive nitrogen other than HNO_3) is less than that of ClO_x .

In case I, OCIO provides an immediate source of ClO . The concentration of O_3 begins to fall, as illustrated in Fig. 3a. Removal is predominantly by reaction (7). Reduction in O_3 , and high concentrations of ClO and BrO , persist until the level of NO_y is comparable to that of ClO_x . Recovery of NO_y is regulated by decomposition of HNO_3 . The associated time constant for NO_y is about 10 days in mid-September.

In case II, photolysis of HOCl provides an immediate source of OH , in addition to Cl . If the subsequent chemistry were dominated by gas-phase processes, OH would react with HNO_3 leading to rapid growth in NO_y with conversion of ClO to ClONO_2 , short-circuiting the potential effect of reaction (7) as a sink for odd oxygen. A continuing role for reaction (7) requires that heterogeneous chemistry maintain a high ratio of ClO to ClONO_2 . We assume that reaction (14) proceeds with an

Fig. 3 Vertical distribution of ozone calculated for 20, 35 and 50 days after the end of polar night. The initial distribution of ozone was taken from Fig. 1b (320 DU). Chlorine and bromine abundances were 3.3 p.p.b. and 25 p.p.t. respectively, appropriate for 1985 (ref. 30). The initial fraction of Cl_x present as ClO_x was taken from Fig. 2; initial concentrations of NO_y were low, less than ClO_x . Calculations allowed for the diurnal variation of insolation, and ozone values were updated daily. Results are given for latitude 80°S .

a, Results for case I: ClO_x was assumed to be present as OCIO at the end of polar night, and the model allowed for gas-phase processes only. Results for 50 days are very similar to those for 35 days. b, Results for case IIa in which ClO_x was assumed to be present initially as HOCl , and the heterogeneous reactions (12) and (14) were allowed to proceed at a rate of $1.0 \times 10^{-5} \text{ s}^{-1}$. c, Results for case IIb, with a faster rate for reactions (12) and (14), $5.0 \times 10^{-5} \text{ s}^{-1}$. At 80°S , days 20, 35 and 50 correspond to 15 September, 1 October and 15 October. Model results indicate similar reductions in ozone one calendar week earlier at 75°S , two weeks earlier at 70°S .



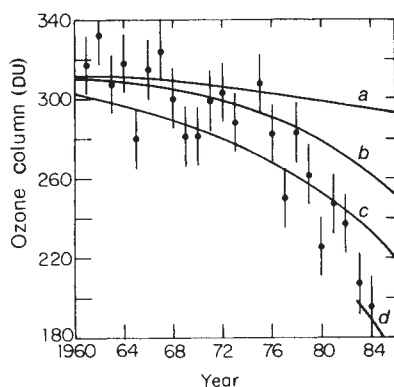


Fig. 4 Trend in the ozone column over Antarctica from 1960 to 1985. The circles correspond to October mean values from Halley Bay (76°S)¹. Results are given for 80°S , and assume an initial ozone column of 320 DU for each model year (see Fig. 3). The abundance of Cl_x was taken to be 1.0 p.p.b. in 1960, 2.1 p.p.b. in 1975 and 3.3 p.p.b. in 1985 (ref. 30); the abundance of Br_x was held constant at 25 p.p.t. *a-c*, Results for case I, Iia and Iib respectively, for day 50. *d*, Results for case Iib after 60 days. This curve illustrates the dramatic acceleration in O_3 loss which occurs if the aerosol burden persists.

accommodation coefficient of 2.5×10^{-2} and select an aerosol surface area appropriate for an extinction coefficient of $2 \times 10^{-3} \text{ km}^{-1}$. The associated reaction rate constant is $1 \times 10^{-5} \text{ s}^{-1}$. Extinction coefficients of $2 \times 10^{-3} \text{ km}^{-1}$ were typical for September in the Antarctic stratosphere before 1982 (ref. 17). Optical depths were much larger in 1983 (ref. 29) and 1984 following the arrival of the aerosol cloud associated with eruption of El Chichón (M. P. McCormick, personal communication). To account for additional aerosol loading, calculations were carried out also with a larger rate for reaction (14), $5 \times 10^{-5} \text{ s}^{-1}$. We shall refer to the low- and high-aerosol models as Iia and Iib. The polar clouds dissipate typically in late September when the aerosol burden is low¹⁷. They persisted longer in 1983 and 1984 when the aerosol burden was higher. The results in Fig. 3*b, c* should be interpreted accordingly.

The calculations summarized in Fig. 3 are appropriate for a latitude of 80°S . Sunrise at 80°S occurs at the end of August. Results for Syowa would be similar but the calendar date would be about 2 weeks earlier. With case I (Fig. 3*a*) there is a significant drop in O_3 over the first 2 weeks. The decline is slow thereafter, however, limited by the growth of NO_y and associated immobilization of ClO_x as ClNO_3 . The drop in O_3 persists longer if we allow for heterogeneous removal of ClNO_3 and N_2O_5 (Fig. 3*b, c*). The reduction at the peak, primarily due to reaction (7), is as much as 0.5% per day over the initial 30-day period if the rate constant for reaction (14) is as large as $5 \times 10^{-5} \text{ s}^{-1}$. The reduction exceeds 2% per day in the subsequent 15-day period, more than enough to account for the rate of decline observed by TOMS in 1983 (ref. 2). The faster decline at the later time is attributed to an increase in the abundance of ClO_x due to production of Cl by reaction of OH with HCl. If we allowed for heterogeneous removal of N_2O_5 and ClNO_3 , results for case I would agree with those for case II for times later than about 30 days.

Trends as a function of time are shown for total column O_3 in Fig. 4. The data, reflecting mean values for October at Halley Bay, are from ref. 1. As with Fig. 3, the model results are for a latitude of 80°S and are intended to illustrate the reduction expected 50 days after the end of polar night. The decline in O_3 would commence at the beginning of August in more northerly regions of the vortex. Effects would spread into the interior as the Sun advanced. The actual situation could be complicated by effects of transport, and precise comparison of model and

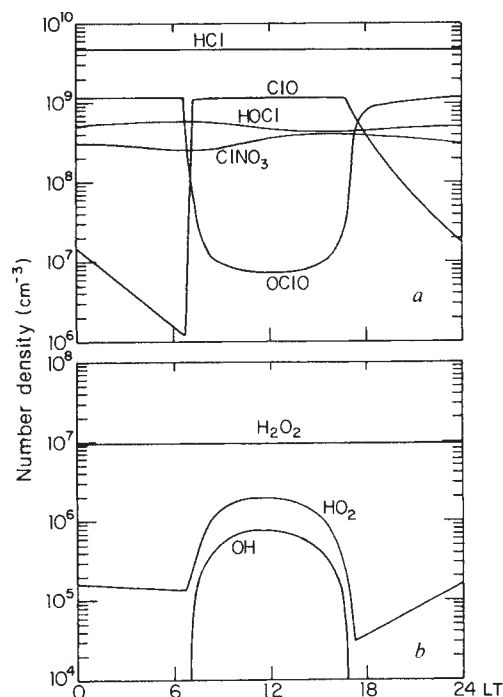


Fig. 5 Diurnal variations of Cl_x (*a*) and HO_x (*b*). Results are shown for case Iia, for day 20, 80°S latitude at 75 mbar ($\sim 16 \text{ km}$). The atmospheric density was $2.92 \times 10^{18} \text{ molecules cm}^{-3}$.

observational data is consequently difficult. The model results in Fig. 4 should be approximately applicable for mean conditions within the vortex at the beginning of October.

The model assumed an initial value of 320 DU for O_3 . The predicted year to year decline in O_3 at 50 days reflects the assumed growth of total chlorine, $4.7\% \text{ yr}^{-1}$ since 1973 (ref. 30). Case I, with only homogeneous processes considered, depicts a relatively small reduction in O_3 , about 25 DU in 1984. Reductions with case Iib should be as large as 100 DU for the same year. An intermediate effect is suggested for case Iia, 60 DU.

It is tempting to attribute the large reductions in O_3 observed in 1983 and 1984 to effects, both direct and indirect, of the aerosols from El Chichón. A reduction of 15% in O_3 was observed at northern mid-latitudes in winter and spring of 1983 (ref. 31), coincident with the time of maximum aerosol loading³². The reduction then could be associated with heterogeneous processes involving aerosols, enhanced perhaps by chlorine added to the stratosphere by the eruption³³. These effects could have an impact on Antarctic O_3 in addition to the $\text{ClO} + \text{BrO}$ contribution emphasized here and could contribute, at least in part, to the low values of O_3 observed since 1982.

The recombination scheme proposed here for O_3 is nonlinear, in the sense that the mechanism depends on the abundance, persistence and height distribution of aerosols. The rate-limiting step, reaction of ClO with BrO, involves a product of concentrations of two trace species each of which may be changing in time. The abundance of ClO is set mainly by decomposition of industrial sources of organic chlorine, notably CFCl_3 , CF_2Cl_2 and CH_2Cl_2 (ref. 5). The concentration of inorganic chlorine has increased steadily since 1960 (ref. 30). We assumed that the growth rate for inorganic bromine was comparatively small, and used a fixed concentration of 25 p.p.t. at high latitude in all calculations (ref. 27 and refs therein). There are reasons, however, to believe that the concentration of bromine may be increasing. Increases in production and use of CH_3Br , a fumigant, and CF_3Br and CF_2ClBr , employed extensively as fire extinguishers, are likely to have an important role in the future

course of stratospheric Br. Prospective levels could rise to as high as 100 p.p.t. (ref. 27).

The surprising results from Antarctica emphasize the potential importance and complexity of processes in the high-latitude stratosphere. Figure 5, for example, illustrates the diurnal variation expected for some of the dominant forms of Cl_x and HO_x . Observations are few and there is a need for additional data. Measurements of the abundance of aerosols, ClO, OClO, HOCl, BrO, NO_2 and HNO_3 in winter and early spring would be valuable and would serve as a check on the model developed here.

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- Farman, J. C., Gardiner, B. G. & Shanklin, J. D. *Nature* **315**, 207-210 (1985).
- Ozone data for the World*, Indexes 6, 14 and 19 (Atmospheric Environment Service, Toronto, Canada, 1985).
- Stolarski, R. S. *et al.* *Nimbus 7, SBUV/TOMS Measurement of Antarctica Ozone* (submitted).
- Chubachi, S. *Mem. natn. Inst. Pol. Res. (Tokyo), Spec. Iss. No. 34*, 13-19 (1984).
- Molina, M. J. & Rowland, F. S. *Nature* **249**, 810-812 (1974).
- Wofsy, S. C., McElroy, M. B. & Yung, Y. L. *Geophys. Res. Lett.* **2**, 215-218 (1975).
- Crutzen, P. J. *J. R. met. Soc.* **96**, 320-325 (1970).
- Johnston H. S. *Science* **173**, 517-522 (1971).

- Bates, D. R. & Nicolet, M. J. *geophys. Res.* **55**, 301-327 (1950).
- Yung, Y. L., Pinto, J., Watson, R. T. & Sander, S. P. *J. Atmos. Sci.* **37**, 339-353 (1980).
- Noxon, J. F. *Science* **189**, 547-549 (1975).
- Noxon, J. F. *Geophys. Res. Lett.* **5**, 1021-1022 (1978).
- Noxon, J. F., Henderson, W. R. & Norton, R. B. *J. geophys. Res.* **88**, 5240-5248 (1983).
- McKenzie, R. L. & Johnston, P. V. *Geophys. Res. Lett.* **11**, 73-75 (1984).
- Wofsy, S. C. *J. geophys. Res.* **83**, 364-378 (1978).
- Evans, W. J. F., McElroy, C. T. & Galbally, I. E. *Geophys. Res. Lett.* **12**, 825-828 (1985).
- McCormick, M. P., Steele, H. M., Hamill, P., Chu, W. P. & Swisler, T. J. *J. Atmos. Sci.* **39**, 1387-1397 (1982).
- Steele, H. M., Hamill, P., McCormick, M. P. & Swisler, T. J. *J. Atmos. Sci.* **40**, 2055-2067 (1983).
- Rowland, F. S. *Pap. at NASA Meet. Current Issues in our Understanding of the Stratosphere and the Future of the Ozone Layer* (Feldafing, FRG, 1984).
- Atkinson, R., Tuazon, E. C., MacLeod, H., Aschmann, S. M. & Winer, A. M. *Geophys. Res. Lett.* **13**, 117-120 (1985).
- Molina, L. T., Molina, M. J., Stachnik, R. A. & Tom, R. D. *J. phys. Chem.* **89**, 3779-3781 (1985).
- DeMore, W. B. *et al.* *Chemical Kinetics and in Stratospheric Modelling Evaluation No. 7* (Jet Propulsion Laboratory, Pasadena, JPL 85-37, 1985).
- List, R. J. & Telegadas, K. *J. Atmos. Sci.* **26**, 1128-1136 (1969).
- Telegadas, K. & List, R. J. *Science* **190**, 882-883 (1975).
- Logan, J. A., Prather, M. J., Wofsy, S. C. & McElroy, M. B. *Phil. Trans. R. Soc.* **290**, 187-234 (1978).
- Wofsy, S. C. & Logan, J. A. in *Causes and Effects of Stratospheric Ozone Reduction: An Update*, 167-205 (National Academy of Sciences, Washington DC, 1982).
- Prather, M. J., McElroy, M. B. & Wofsy, S. C. *Nature* **312**, 227-231 (1984).
- Tung, K. K., Ko, M. K. W., Rodriguez, J. M. & Sze, N. D. *Nature* (submitted).
- Hofmann, D. J. & Rosen, J. M. *Geophys. Res. Lett.* **12**, 13-16 (1985).
- WMO/NASA *Atmospheric Ozone: Assessment of our Understanding of the Processes Controlling its Present Distribution and Changes* (in the press).
- Angell, J. K., Korshover, J. & Planet. W. G. *Mon. Weath. Rev.* **113**, 641-646 (1985).
- Hofmann, D. J. & Rosen, J. M. *J. geophys. Res.* **89**, 4883-4890 (1984).
- Mankin, W. G. & Coffey, M. T. *Science* **226**, 170-172 (1984).

Temporal evolution of nitrogen compounds in Swedish precipitation since 1955

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Nitrate (NO_3^-) and ammonium (NH_4^+) ions are important determinants of the ionic strength and pH of precipitation¹. The deposition of these ions on vegetation and on the ground also constitutes a significant source of nutrients for plants. This is particularly the case in polluted regions, for example, Europe, where the deposition of nitrogen compounds is enhanced². There are indications (for example, increased run-off of nitrogen³) that forests in some parts of Europe have reached saturation levels with respect to nitrogen deposition; and excessive wet and dry deposition of nitrogen compounds has been suggested as a possible cause of the extensive damage to forests in Europe⁴. Data from Rothamsted, UK, indicate that the mean concentration of NO_3^- in precipitation doubled between the 1850s and 1960 (ref. 5); similarly, the NH_4^+ concentration probably increased between the 1880s and 1960. A review of precipitation chemistry data from Europe indicates an approximately threefold increase in NO_3^- deposition between the 1890s and the late 1970s⁶. The present analysis of data from the European Air Chemistry Network reveals that the NO_3^- concentration at most stations approximately doubled between the late 1950s and early 1970s, with a less pronounced increase in NH_4^+ . Detailed analysis of data from 12 Swedish stations showed no further increase of NO_3^- or NH_4^+ between 1972 and 1984. In contrast, the sulphate concentration decreased by ~30% for the same locations and time period.

The data that we have analysed are from the European Air Chemistry Network (EACN)^{7,8}. These data are obtained from monthly precipitation samples collected in bulk samplers at more than 50 stations in northern and central Europe since 1955. Details about the sampling and chemical analysis of ammonium

Table 1 Changes in concentration of NO_3^- and NH_4^+ in northern European precipitation between the late 1950s (median of all months 1955-59) and the early 1970s (1970-74)

Relative change %	No. of stations* (NO_3^-)	No. of stations* (NH_4^+)
> +250	3 (0)	1 (0)
+200-249	3 (0)	0 (0)
+150-199	6 (0)	3 (1)
+100-149	21 (5)	6 (0)
+50-99	20 (4)	12 (2)
0-+49	2 (0)	15 (3)
0-49	0 (0)	10 (2)
< -50	0 (0)	8 (1)
Total	55 (9)	55 (9)

* Numbers in parentheses refer to Swedish stations.

and nitrate ions as well as a listing of all the data between 1955 and 1979 are presented in refs 9 and 10, respectively.

Almost all (54 out of 55) EACN stations with sufficiently long records exhibit an increase in NO_3^- concentration between the late 1950s and the early 1970s. Table 1 shows the magnitude of the observed changes. At 75% of the stations the NO_3^- concentration increased between 50 and 150% during the 15-yr period, corresponding to an annual increase of 2-6%. Similar analyses have been published by Kallend *et al.*¹¹ and Horvath¹², who found an average annual increase of NO_3^- concentration at various sites to be ~6% and 7%, respectively. An increase in the NH_4^+ concentration was observed at 37 out of 55 EACN stations (Table 1). At half of the stations, the NH_4^+ concentration increased by 0-100%. Other previously published data¹² present no clear temporal trend of the NH_4^+ concentration between 1968 and 1981. Also, the variability in the NH_4^+ concentration was greater than that for NO_3^- . Note that the quality of some of the NH_4^+ data is dubious⁹, because microbiological activity may have an effect on the concentration of ammonium in the sample after collection.

For a more detailed analysis of temporal changes in nitrogen concentrations, we limited ourselves to the period between 1972 and 1984 and to Swedish stations only. We imposed this limitation mainly because this part of the network has been modified to meet more stringent sampling and analysis criteria¹³. For this period, data are available from 12 stations located in rural areas

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