Reductions in ozone at high concentrations of stratospheric halogens

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An increase in the concentration of inorganic chlorine to levels comparable to that of oxidized reactive nitrogen could cause a significant change in the chemistry of the lower stratosphere leading to a reduction potentially larger than 15% in the column density of ozone. This could occur, for example by the middle of the next century, if emissions of man-made chlorocarbons were to grow at a rate of 3% per year. Ozone could be further depressed by release of industrial bromocarbon.

Our understanding of the stratosphere has grown steadily since Chapman's original discussion of photochemical processes in a pure oxygen system. Milestones include the introduction of reactions involving hydrogen compounds, recognition of the importance of oxides of nitrogen and, more recently, realization that a complete model must allow for reactions involving chlorine and bromine. Current models for stratospheric chemistry include as many as 200 reactions coupling various forms of oxygen, hydrogen, nitrogen, chlorine and bromine.

The emphasis here is on chemical processes in the lower stratosphere, between 20 and 30 km. Much of the work in recent years has been concerned with assessing the effects of various forms of anthropogenic activity on the stability of the ozone column. Emissions of chlorocarbons are thought to influence ozone (O₃) primarily in the region above 30 km. We shall argue that important reductions in [O₃] could take place also below 30 km if the concentration of chlorine were to rise above that of NO₂ (defined as the composite of all oxidized forms of nitrogen, excluding N₂O). Changes below 30 km might be expected to lead to an abrupt drop in the column density of O₃ with increasing levels of chlorine, in association with a marked change in the chemical characteristics of the lower stratosphere.

Chemistry of the stratosphere

The abundance of OH in the lower stratosphere is at present controlled mainly by:

\[ \text{O}^1\text{D} + \text{H}_2\text{O} \rightarrow \text{OH} + \text{OH} \]  \hspace{1cm} (1)

followed by

\[ \text{OH} + \text{HNO}_3 \rightarrow \text{H}_2\text{O} + \text{NO}_3 \]  \hspace{1cm} (2)

and

\[ \text{OH} + \text{HNO}_4 \rightarrow \text{H}_2\text{O} + \text{NO}_2 + \text{O}_2 \]  \hspace{1cm} (3)

Nitric acid is the most abundant form of NO₃, followed by NO₂, N₂O₅ and HNO₄. At higher levels of chlorine, ClNO₃, formed by

\[ \text{ClO} + \text{NO}_2 + \text{M} \rightarrow \text{ClNO}_3 + \text{M} \]  \hspace{1cm} (4)

is more important. Concentrations of NO₂, HNO₃ and HNO₄ decrease rapidly as ClNO₃ becomes the dominant form of NO₃. Removal of OH is then effected by the less efficient loss mechanisms:

\[ \text{OH} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2 \]  \hspace{1cm} (5)

\[ \text{OH} + \text{HCl} \rightarrow \text{H}_2\text{O} + \text{Cl} \]  \hspace{1cm} (6)

and

\[ \text{OH} + \text{HOCI} \rightarrow \text{H}_2\text{O} + \text{ClO} \]  \hspace{1cm} (7)

with additional production of odd-hydrogen due to oxidation of CH₄, formed by

\[ \text{Cl} + \text{CH}_4 \rightarrow \text{HCl} + \text{CH}_3 \]  \hspace{1cm} (8)

The concentration of OH increases rapidly at higher levels of chlorine, as illustrated in Fig. 1, owing in part to titration of NO₂ to ClNO₃, in part to enhanced production of O(1D) caused by deeper penetration of ultraviolet radiation resulting from reduction in the overlying column of O₃. Similar shifts in the chemistry of OH and NO₂ were noted earlier by Prather et al., who emphasized the dramatic alterations in radical chemistry which occur when NO and NO₂ are converted to ClNO₃. They raised the possibility of multiple steady states for OH in the high latitude winter stratosphere, under conditions where inorganic chlorine ([Cl] = [ClO] + [ClO₂] + [ClNO₃] + [HOCl] + [HCl]) exceeds [NO₂].

It is convenient to identify a family of species, including O₃ and other compounds, which convert rapidly to O₃ in the lower

![Graph showing changes in the chemistry of the stratosphere at 24 km as a function of total chlorine concentration. Model calculations allowed for the diurnal variations in sunlight and chemical species, as described in the text. Inorganic chlorine (HCl, Cl, ClO, ClNO₃, HOCl) accounts for approximately 70% of the total chlorine at 24 km, increasing to 100% by 40 km. The top panel shows a 20% decrease in [O₃] (10⁻² cm⁻³) as chlorine increases from 2 to 16 parts per 10⁶.](image-url)

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Table 1 Reaction sequences involving odd-oxygen

<table>
<thead>
<tr>
<th>Production of odd-oxygen</th>
<th></th>
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<tbody>
<tr>
<td>(0) ( O_2 + h\nu \rightarrow O + O )</td>
<td></td>
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<table>
<thead>
<tr>
<th>Loss of odd-oxygen</th>
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<tbody>
<tr>
<td>(I) ( O + O_3 \rightarrow O_2 + O_2 )</td>
<td></td>
</tr>
<tr>
<td>(II) ( HO_2 + O_3 \rightarrow OH + O_3 + O_2 )</td>
<td>( OH + O_3 \rightarrow HO_2 + O_2 )</td>
</tr>
<tr>
<td></td>
<td>( 2O_3 \rightarrow 3O_2 )</td>
</tr>
<tr>
<td>(III) ( NO_2 + O \rightarrow NO + O_2 )</td>
<td>( NO + O_2 \rightarrow NO_2 + O_2 )</td>
</tr>
<tr>
<td></td>
<td>( O + O_3 \rightarrow 2O_2 )</td>
</tr>
<tr>
<td>(IV) ( ClO + O \rightarrow Cl + O_2 )</td>
<td>( Cl + ClO \rightarrow ClO_2 + O )</td>
</tr>
<tr>
<td></td>
<td>( O + O_3 \rightarrow 2O_2 )</td>
</tr>
<tr>
<td>(V) ( BrO + O \rightarrow Br + O_2 )</td>
<td>( Br + O_3 \rightarrow BrO + O_2 )</td>
</tr>
<tr>
<td></td>
<td>( O + O_3 \rightarrow 2O_2 )</td>
</tr>
<tr>
<td>(VI) ( ClO + BrO \rightarrow Cl + Br + O_2 )</td>
<td>( Cl + ClO \rightarrow ClO_2 + O )</td>
</tr>
<tr>
<td></td>
<td>( Br + O_3 \rightarrow BrO + O_2 )</td>
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<tr>
<td></td>
<td>( 2O_3 \rightarrow 3O_2 )</td>
</tr>
<tr>
<td>(VII) ( ClO + HO_2 \rightarrow HOCl + O_2 )</td>
<td>( HOCl \rightarrow h\nu \rightarrow OH + Cl )</td>
</tr>
<tr>
<td></td>
<td>( OH + O_3 \rightarrow HO_2 + O_2 )</td>
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<tr>
<td></td>
<td>( Cl + ClO \rightarrow ClO_2 + O )</td>
</tr>
<tr>
<td></td>
<td>( 2O_3 \rightarrow 3O_2 )</td>
</tr>
<tr>
<td>(VIII) ( ClO + NO_2 + M \rightarrow ClNO_3 + M )</td>
<td>( ClNO_2 \rightarrow h\nu \rightarrow Cl + NO_3 )</td>
</tr>
<tr>
<td></td>
<td>( Cl + O_3 \rightarrow ClO + O_2 )</td>
</tr>
<tr>
<td></td>
<td>( NO_2 + h\nu \rightarrow NO + O_2 )</td>
</tr>
<tr>
<td></td>
<td>( NO + O_3 \rightarrow NO_2 + O_2 )</td>
</tr>
<tr>
<td></td>
<td>( 2O_3 \rightarrow 3O_2 )</td>
</tr>
</tbody>
</table>

No change in odd-oxygen

| (IX) \( HO_2 + NO_2 \rightarrow OH + NO_2 \) | \( OH + O_3 \rightarrow HO_2 + O_2 \) |
|                          | \( NO_3 + h\nu \rightarrow NO + O \) |
|                          | \( O_3 + O \rightarrow O_2 \) |

| (X) \( ClO + NO_2 + M \rightarrow ClNO_3 + M \) | \( ClNO_2 \rightarrow h\nu \rightarrow Cl + NO_3 \) |
|                          | \( Cl + ClO \rightarrow ClO_2 + O \) |
|                          | \( NO_2 + h\nu \rightarrow NO + O_2 \) |
|                          | \( NO + O_3 \rightarrow NO_2 + O_2 \) |
|                          | \( O_3 + O \rightarrow O_2 \) |

stratosphere. We term this family 'odd-oxygen': \( O, O_3, HO_2, NO_2, ClO \) and \( BrO \). Odd-oxygen is produced by photolysis of \( O_3 \) in the Herzberg continuum. It is removed by a variety of reaction sequences summarized in Table 1. The primary sinks are:

\[
\begin{align*}
O + O_3 \rightarrow O_2 + O_2 & \quad (9) \\
HO_2 + O_3 \rightarrow OH + O_2 + O_2 & \quad (10) \\
NO_2 + O \rightarrow NO + O_2 & \quad (11) \\
ClO + O \rightarrow Cl + O_2 & \quad (12) \\
ClO + HO_2 \rightarrow HOCl + O_2 & \quad (13) \\
ClO + BrO \rightarrow Cl + Br + O_2 & \quad (14) \\
\end{align*}
\]

and

\[
\begin{align*}
BrO + O \rightarrow Br + O_2 & \quad (15) 
\end{align*}
\]

Each of these reactions accounts for removal of two odd-oxygen equivalents. Formation of \( ClNO_3 \) provides a temporary sink for odd-oxygen. This is balanced mostly by release of odd-oxygen in the photolysis of \( ClNO_2 \) and \( NO_3 \) (Table 1: sequence X). Reactions (9)-(11) account for most of the odd-oxygen removal below 30 km in the present atmosphere; reactions (12)-(14) dominate at high levels of chlorine.

Effects of chlorine

Vertical profiles for \( O_3 \) were calculated using a one-dimensional model\(^6\) with diffusion coefficients calibrated to match observational data for \( CFCl_3, CF_2Cl_2, N_2O \) and \( CH_4 \) (ref. 10). Rates
for chemical reactions were taken from the National Aeronautics and Space Administration (NASA)\(^\text{11}\), except that for (12) for which we used more recent measurements by Leu\(^\text{12}\). Cross-sections for photolysis of O\(_2\) are consistent with observations by Herman and Mentall\(^\text{13}\) and Anderson and Hall\(^\text{14}\) (7.5 × 10\(^{-24}\) cm\(^2\) at 205 nm). Solar declination was set equal to 0° (equinox), and the temperature structure of the atmosphere follows the 30°N summer model of the US Standard Atmosphere\(^\text{15}\). Some calculations were carried out using rates for photolysis averaged over a 24-hour cycle, whereas others allowed for diurnal variations in sunlight. Both approaches have been used in previous investigations of the stratosphere\(^\text{6}\). Concentrations of CH\(_4\), N\(_2\)O, NO\(_x\), Cl\(_x\), Br\(_x\) and halocarbons were calculated self-consistently, for the present environment, using the one-dimensional formulation. The model for higher concentrations of chlorine was based on an assumption that growth in Cl\(_x\) is caused primarily by enhanced emission of CF\(_2\)Cl\(_2\) and CFC\(_3\). A variety of exploratory calculations were also carried out, in which stratospheric profiles of CH\(_4\), NO\(_x\) and Br\(_x\) were scaled by constant factors, to explore the sensitivity of model results to possible changes in the concentrations of these species.

Rates for removal of odd-oxygen averaged over a 24-hour cycle, and with the more complete model allowing for the diurnal variation in sunlight, are illustrated in Fig. 2. Figure 2a shows results for the present stratosphere where the chlorine abundance is taken as 2.6 parts per 10\(^{17}\)—significantly higher than the natural background, which is expected to be less than 1 part per 10\(^{18}\); note that reaction (12) (Table 1: sequence IV) is the principal loss process for odd-oxygen between 40 and 45 km in the present atmosphere; reaction (11) (sequence III) is dominant below this. Results with the chlorine abundance equal to 16.4 parts per 10\(^{18}\) are given in Fig. 2b: reaction (12) dominates over an extensive height range from 20 to 55 km; sequences II, III, VI, VII and VIII are comparably important, each contributing ~10% to the total loss of odd-oxygen below 25 km.

The enhanced role of reaction (12) in Fig. 2b reflects the much larger abundance of ClO throughout the stratosphere. The abundance of total chlorine in Fig. 2b exceeds that in Fig. 2a by a factor of 6; however, the abundance of ClO at 24 km is larger by a factor of 18. The non-linearity in ClO results in part from the large increase in [OH] which arises at high concentrations of chlorine. As [NO] decreases, further enhancement of [ClO] occurs owing to significant reduction in the rate at which ClO is cycled to CI and HCl by

\[
\text{ClO} + \text{NO} \rightarrow \text{Cl} + \text{NO}_2
\]

and reaction (8).

Changes in the vertical distribution of ozone as a function of increasing chlorine concentration are shown in Fig. 3: Fig. 3a shows model calculations for 13 parts per 10\(^{18}\) NO\(_x\) at 35 km—our best estimate of the present situation; Fig. 3b considers [NO\(_x\)] equal to 16.2 parts per 10\(^{18}\), near the upper range of present observational data. The maximum relative depletion in O\(_3\) occurs near 40 km, and [O\(_3\)] is a monotonic and nearly linear function of added chlorine at this altitude. The behaviour in the lower stratosphere is quite different: at the higher [NO\(_x\)] considered in Fig. 3b, addition of chlorine leads initially to a small increase in [O\(_3\)] centred near 24 km; for chlorine concentrations above ~12 parts per 10\(^{18}\), the increase disappears and, at higher levels of chlorine, reduction in [O\(_3\)] is observed at all altitudes. Conversion of NO\(_x\) to CINO\(_3\) requires less chlorine for the lower [NO\(_x\)] case modelled in Fig. 3a. Large reductions in [O\(_3\)] accordingly occur at smaller concentrations of chlorine, accounting for differences in the behaviour exhibited by the two cases in Fig. 3. These reductions arise despite significant enhancements (×2) in the production of odd-oxygen as illustrated in Fig. 1.

Figure 4a shows column densities of ozone for the cases summarized in Figs 2 and 3. Major reductions, >10%, occur for both the high and low [NO\(_x\)] cases when chlorine exceeds 18 parts per 10\(^{18}\). Further additions of chlorine, as little as 2 parts per 10\(^{18}\), can lead to a doubling of the resulting perturbation in ozone concentration.

The results in Figs 2, 3 and 4a account for the diurnal variations in sunlight and chemical species. Results in Fig. 4b–e explore the sensitivity of predicted ozone depletions to [NO\(_x\)], [CH\(_4\)] and other parameters of the model, using the computationally easier approach in which sunlight is averaged over a diurnal cycle. Use of an average flux to simulate the proper diurnal variation in sunlight leads to an overestimate for [NO\(_x\)] and consequently [CINO\(_3\)]. This accounts for the quantitative differences between the results in Fig. 4a and b: column [O\(_3\)] is higher in Fig. 4a and the onset of non-linearity is apparent at smaller values of [ClI].

Figure 4b illustrates the response of O\(_3\) to chlorine, for [NO\(_x\)] equal to 13.0, 16.2 and 19.5 parts per 10\(^{18}\) at 35 km. The concentration of NO\(_x\) the source of stratospheric NO\(_x\) is increasing now by between 0.2 and 0.4% per year\(^\text{16}\). The higher levels of NO\(_x\) envisaged here, 16.2 and 19.5 parts per 10\(^{18}\), would correspond to increases in [N\(_2\)O] of 25% and 50% respectively, relative to the present value of about 300 parts per 10\(^{18}\). The column density of O\(_3\) changes little with addition of chlorine, so long as the concentration of chlorine is significantly less than that of NO\(_x\).

Cicerone et al\(^\text{17}\) have reported evidence for nonlinear behaviour in total [O\(_3\)] as a function of chlorine concentration for values of [ClI] below 10 parts per 10\(^{18}\). This behaviour was also observed in the present study. Nonlinearities may arise at low chlorine concentrations owing to compensatory effects in the photochemistry of the lower stratosphere, enhancing production but also removal of odd-oxygen. However, the net impact on [O\(_3\)] is small, and results are quantitatively sensitive to details of the underlying model. The nonlinearity at high chlorine...
Fig. 4 The column abundance of ozone as a function of stratospheric chlorine. Results in panel a allow for diurnal variations in sunlight. The sunlight was averaged over 24 hours for b–c. Panel a shows results for our standard contemporary atmosphere (13 parts per 10^9 NO_2 at 35 km) and for an atmosphere with 25% more NO_3 (16.2 parts per 10^9). Panel b includes a case with 50% higher [NO_3] (19.5 parts per 10^9). Asterisks denote the point at which the ozone column has been depleted by 10% relative to the contemporary atmosphere (2.6 parts per 10^9 chlorine). Panel c considers effects of an increase in [CH_4] from 1.6 p.p.m. to 2.4 p.p.m. to 3.2 p.p.m. c also includes a case R in which the rate coefficient for reaction (6) was changed to 2.7 x 10^{-12} exp(-360/T); this reflects recent kinetic data (L. F. Kaiser, unpublished; ref. 36; see also ref. 17), indicating that this reaction may be 30% faster than previously suggested. Panel d compares ozone perturbations calculated for the standard model S with those for a model K with slow vertical diffusion (see text). Panel e presents results from calculations with bromine concentrations of 0, 20, 100 and 200 parts per 10^{12}.

Concentration is large and robust: it can be interpreted essentially as a local photochemical effect and should be apparent in all models where [Cl_2] exceeds [NO_2]. The concentration of atmospheric CH_4 appears to have risen by between 1 and 2% per year over the past several years, and perhaps by as much as a factor of 2, since the sixteenth century. An increase in [CH_4] favours production of HCl through reaction (6), with consequent reduction in the ratio of [ClO] to total chlorine concentration; it may be expected also to result in an enhanced concentration of stratospheric H_2O. The implications for ozone are summarized in Fig. 4c. Abundance of H_2O were calculated as functions of altitude, allowing for the CH_4 source, with the mixing ratio of H_2O fixed at 3 p.p.m. at the tropopause. The major effect in Fig. 4c reflects the influence of CH_4 as a sink for reactive chlorine. At high [CH_4], the sharp decline in [O_3] occurs at higher concentrations of chlorine. For example, a 15% reduction in [O_3] is predicted to occur, in Fig. 4c, at a chlorine concentration of 16 parts per 10^9 for present levels of CH_4. A comparable reduction in [O_3] would be postponed to a chlorine concentration of 18 parts per 10^9, if the abundance of CH_4 was equal to twice its present value.

The results in Fig. 4a–e suggest that the average column density of O_3 should be ~1.1 x 10^{19} molecules cm^{-2}, or 410 Dobson units, for the present environment. This is higher than observed values, which are centred around 330 Dobson units (ref. 21). The discrepancy may reflect deficiencies in the one-dimensional model, in particular, its inability to account for the large spatial (\times 2) and temporal (50%) variability in ozone concentration. It could also reflect deficiencies in our understanding of the relevant chemistry, or the approach used to simulate vertical transport. Holton suggested that effective diffusion coefficients for chemically active gases are smaller than those for inert species. He offered a method whereby diffusion coefficients could be corrected to allow for effects of a finite chemical lifetime. Results in Fig. 4d incorporate this modification, setting the diffusion coefficient for O_3 equal to 3 x 10^{10} cm^2 s^{-1} throughout the lower stratosphere. The role of vertical transport is diminished accordingly. Photochemical processes are relatively more important for O_3, and our estimate for the present-day column is reduced to approximately 370 Dobson units, in better agreement with observation. The response of O_3 to elevated chlorine concentration is similar, however, to the behaviour exhibited in the results given above.

The concentration of chlorine in the present stratosphere is set mainly by anthropogenic sources of CFC-11 (20%), CFC-12 (20%), CCl_4 (20%) and CH_2Cl_2 (15%). Release rates for these gases are now about 260 x 10^9, 420 x 10^9, 120 x 10^9 and 500 x 10^9g yr^{-1}, respectively (ref. 24–28). Associated lifetimes are 70, 130, 55 and 10 yr (refs 24–28). The concentration of stratospheric chlorine is expected to rise eventually to ~10 parts per 10^9, if the release rate remains constant. This is less than the level required to induce the sharp reductions in [O_3] below 30 km, and calculated perturbations to the ozone column are consequently small (refs 10, 29). Figure 5 indicates, as a function of the assumed growth rate, the year in which chlorine would be expected to rise to about 16 parts per 10^9—our estimate for the threshold needed to induce a 15% reduction in [O_3]. If we focus, for example, on effects over the next 50 years, the results in Fig. 5 indicate that large reductions in [O_3] are possible if the compounded growth of chlorofluorocarbon emissions exceeds 5% per year.
Effects of bromine

Emissions of bromine could also lead to a significant reduction in stratospheric ozone, according to reaction sequences V and VI (Table 1). A major fraction of bromine is present in the stratosphere in the reactive form BrO, and bromine is consequently more efficient than chlorine as a catalyst for removal of odd-oxygen. The concentration of organic bromine is now accounted for 25% and 35% with methyl bromide (CH₃Br) and dimethyl bromide (CH₂Br₂) accounting for 30 to 70% of the present atmospheric burden. The lifetime of CH₂Br₂ is about 3 yr and known industrial sources account for approximately half of the current release. The gases ethylene dibromide (C₂H₄Br₂), 2.4 parts per 10¹² as Br₂, and fluorocarbons FC-1301 (CF₃BrF, 1 part per 10¹⁶) and FC-1211 (CF₃CBF₃, 1 part per 10¹⁶) are mainly anthropogenic in origin and account for about 15% of the current bromine content of the atmosphere.

The concentration of industrial bromocarbons is likely to rise in future, with the possible exception of ethylene dibromide which is derived mainly from use of leaded gasoline. Production of CH₃Br has increased four to fivefold since 1972 (ref. 34) and may be anticipated to rise further if it replaces ethylene dibromide. Since the concentration of brominated fire extinguishers is growing, and concentrations of these gases in the atmospheric appearance have increased at a rate of >10% per year from 1978 to 1983 (R. A. Rasmussen and M. A. K. Khalil, personal communication, 1984). Residence times for FC-1301 and FC-1211 are long, about 110 yr and 25 yr respectively. Associated concentrations may therefore be expected to increase to levels of ~2 and 5 parts per 10¹⁵ in steady state, if release rates remain constant. The abundance of stratospheric bromine would rise eventually to about 100 parts per 10¹⁵ if emissions of brominated fire extinguishers were to grow to 20 x 10⁶ gyr⁻¹, approximately six times the present release. Allowing for possible growth in concentration of other brominated species, it seems appropriate to investigate the impact of a range of bromine concentrations, including values as much as an order of magnitude higher than those observed now.

Results for O₃ with bromine concentrations of 20 and 200 parts per 10¹⁵ are illustrated in Fig. 3c: maximum effects arise near 20 km; perturbations above 30 km are minimal. The absence of a significant bromine-related perturbation to O₃ in the upper stratosphere ensures that radiative feedbacks are relatively unimportant for bromine, in contrast to the situation for chlorine. Also, the concentration of bromine is much less than that of NO₃ and formation of BrNO₃ provides an insignificant sink for NO₃. The response of the stratosphere is thus fairly linear with respect to addition of bromine.

Effects of bromine and chlorine are illustrated in Fig. 4e. Under present conditions for chlorine and NO₃, an increase in bromine from 20 to 100 parts per 10¹⁵ is calculated to cause a 4% reduction in the column density of O₃. Effects of chlorine and bromine are nearly additive. For a chlorine concentration of 16.4 parts per 10⁹, the reduction in O₃ is predicted to grow from 18% to 23%, as bromine is increased from 20 to 100 parts per 10¹⁵. The results in Fig. 4e suggest that the column density of O₃ in the present atmosphere, is <1% less than it might otherwise be, in the absence of bromine.

Conclusions

In summary, models suggest modest, less than 3%, depletion in column O₃ if emission rates of chlorinated and brominated halocarbons remain constant. There are reasons, however, to believe that an increase in release rates could cause future problems for stratospheric O₃. In particular, the chemistry of the lower stratosphere could undergo a significant change if the concentration of chlorine were to rise above that of NO₃. The concentration of OH could increase markedly and that of ozone could drop, with reductions potentially larger than 15% in the column density of O₃. The O₃ column is expected to remain relatively constant before the onset of the NO₃ to chlorine transition below 30 km. It is important not only to monitor the total NO₃ column density of O₃, but to search also for evidence of change in the chemical composition of the lower stratosphere.

The large effects predicted here occur primarily below 30 km and involve major changes in the chemistry of radicals such as OH and ClO. Observational data for these species at lower altitudes are inadequate and yet are urgently required to test the validity of current models in a region containing the bulk of atmospheric ozone.

The present results are based on a one-dimensional model. They should be extended to consider variations of stratospheric chemistry with latitude and season. Extension of the model to more than one dimension may be particularly important in studying the impact of high concentrations of chlorine, as results should depend sensitively on details of the calculated latitudinal distributions of chlorine and NO₃.

Investigations of the radical chemistry of the stratosphere have in the past focused on the region above 30 km. It is clear that the emphasis should shift now to lower altitudes.

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Note added in proof: Preliminary independent studies (F. S. Rowland and H. Sato, personal communication; M. J. Molina, personal communication) suggest that HCl may react with CINO₂ with subsequent release of Cl₂. This could exacerbate the effects of the nonlinearities discussed here. An exploratory calculation indicates that reductions in column O₃ in excess of 15% could arise for chlorine concentrations as small as 10 parts per 10⁹ if the associated rate for this reaction were as large as 10⁻¹⁶ cm³⁻¹ s⁻¹.


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