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Stratospheric ozone depletion and future levels of atmospheric chlorine and bromine

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The rise in atmospheric chlorine levels caused by the emission of chlorofluorocarbons and other halocarbons is thought to be the main cause of the appearance of the Antarctic ozone 'hole' in the late 1970s, and the more modest ozone depletion observed over parts of the Northern Hemisphere. Atmospheric bromine, also associated with halocarbon emissions, is believed to contribute to ozone depletion. Over the next decade, further increases in these compounds are inevitable. Model calculations show that by the end of the next century, atmospheric chlorine and bromine levels may return to those prevalent before the onset of the ozone hole, but only if more stringent regulations are applied to halocarbon production than those currently proposed.

HERE we look at projected future levels of stratospheric chlorine for those compounds currently regulated under the 1987 Montreal Protocol¹ (CFC-11, CFC1₃; CFC-12, CF₂Cl₂; CFC-113, CF₂ClCFCl₂; CFC-114, CF₂ClCF₂Cl; CFC-115, CF₃CF₂Cl), for other gases not specified in the current Montreal Protocol (carbon tetrachloride, CCl₄; methyl chloroform, CH₃CCl₃; HCFC-22, CHF₂Cl), and for possible new hydrochlorofluorocarbons (HCFCs) suggested as substitutes for the CFCs. A subset of these scenarios is also examined to study the effects of possible future increases in atmospheric bromine, resulting from emissions of halons as listed under the 1987 Montreal Protocol (CF₃Br, CF₂ClBr, CF₂BrCF₂Br) assuming constant levels of CH₃Br. All these halocarbons accumulate in the troposphere, are then readily transported into the stratosphere, and along with CH₃Cl, constitute the source of reactive chlorine and bromine species that destroy O₃. We focus on the bulk atmospheric abundances of these halocarbons as a direct measure of the concentration of chemically active chlorine and bromine species in the stratosphere, and hence, of the potential damage to stratospheric ozone.

The total stratospheric abundance of chlorine compounds today is about 3 p.p.b. (parts per 10⁹ molecules of air) and consists predominantly of the industrial halocarbons and their photochemical byproducts (for example, HCl and ClO). Reactions involving chlorine monoxide (ClO) and atomic chlorine (Cl) are able to catalyse the destruction of stratospheric ozone on a global scale, and the ClO dimer plays a key part in the formation of the Antarctic ozone hole². Bromine in the stratosphere, present at concentrations of ~0.02 p.p.b. also contributes globally to ozone loss^{3,4}. Concentrations of BrO and ClO are greatly enhanced in the winter stratosphere over the Antarctic and Arctic. During the austral spring of 1987, bromine was estimated to be responsible for between 10 and 30% of the ozone depletion with chlorine being responsible for the remainder⁵⁻⁷.

Atmospheric chlorine concentrations have increased from 0.6 p.p.b. a century ago to 2 p.p.b. in the late 1970s when the ozone hole was recognized to have first occurred^{8,9} and are now at

more than 3 p.p.b. In the Southern Hemisphere the ozone loss over Antarctica, amounting to about 50% of the ozone column in the spring, coincides with significant declines (as much as 10%) over the mid-latitudes during spring and summer¹⁰. In northern mid-latitudes, we have observed more modest ozone decreases in late winter and early spring, ranging from 3 to 6% in the ozone column over the past two decades¹¹. Recovery of the Antarctic ozone hole as we understand it, would not occur until chlorine levels fall below 2 p.p.b. (henceforth, the 2-p.p.b. date), although recovery might also depend on changes in the Antarctic climate and concentrations of other trace gases such as methane.

The largest ozone depletions in the future are expected to coincide with the peak chlorine loading of the atmosphere. Losses in the middle and upper stratosphere are driven by chemical reactions of chlorine monoxide with atomic oxygen and occur on a global scale. Using only these gas-phase reactions, the ozone depletion predicted as chlorine increases from 3 to 5 p.p.b. is modest, about 1-2% in the tropics and 4-6% at high latitudes¹². In the lower stratosphere, ozone depletion through chlorine- and bromine-catalysed reactions is greatly enhanced by heterogeneous reactions occurring on the surfaces of polar stratospheric cloud particles, and occurs at high latitudes during late winter and early spring. At present, global chemical models are unable to predict how the depth or extent of the ozone hole will change when chlorine increases to 5 p.p.b.. The rapid deepening of the Antarctic ozone hole over the last decade demonstrates the extremely nonlinear response of polar ozone to increasing chlorine levels. We must be prepared for the possibility of new thresholds of accelerated ozone loss in the Arctic as chlorine concentrations reach new record levels.

Chlorine loading and ODPs

The relative contribution of individual source gases to total atmospheric chlorine for the year 1985 is shown below. The known natural sources of chlorine make up only 20% of the total, and the CFCs listed under the Montreal Protocol account for about 50%. The chlorine loading calculated here is the instantaneous, bulk tropospheric mixing ratio (p.p.b.) of chlorine atoms in the form of all the halocarbons listed below.

Industrial sources	
CFC-11	22%
CFC-12	25%
CFC-113	3%
CFC-114	<1%
CFC-115	<1%
HCFC-22	3%
carbon tetrachloride	13%
methyl chloroform	13%
Natural sources	
methyl chloride	20%

This definition is a conservative measure of the amount of stratospheric chlorine that may be active in catalytic ozone destruction.

Ozone depletion potentials (ODPs) have been used to measure the relative contribution of different halocarbons toward destroying ozone^{13,14}. The ODP of a halocarbon is calculated using a chemical model for stratospheric ozone and assuming that the gas is in steady state between its emission and removal

TABLE 1 Halocarbon model

Halocarbon		Lifetime (yr)	Flux (kt yr ⁻¹)	Growth (kt yr ⁻¹ yr ⁻¹)	Concentration (p.p.t.)	Factor (kt p.p.t. ⁻¹)
CFC-11	CFCl ₃	60	360	14.4	220	23.2
CFC-12	CF ₂ Cl ₂	120	450	18.0	375	20.4
CFC-113	C ₂ F ₃ Cl ₃	90	165	6.6	30	31.6
CFC-114	C ₂ F ₄ Cl ₂	200	15	0.6	5	28.9
CFC-115	C ₂ F ₅ Cl	400	10	0.4	4	26.1
carbon tetrachloride	CCl ₄	50	80	3.2	100	25.9
HCFC-22	CHF ₂ Cl	15	140	5.6	80	14.6
methylchloroform	CH ₃ CCl ₃	6	600	24.0	130	22.4
methylchloride	CH ₃ Cl	1.5			600	
(sub. X)	C _x Cl	15			0	19.3
(sub. Y)	C _x Br	6			0	19.3
halon-1211	CF ₂ BrCl	15	10	0.40	1.5	27.9
halon-1301	CF ₃ Br	110	9	0.36	1.7	25.1
methylbromide	CH ₃ Br	1.5			15	

Lifetime (yr) is the global abundance divided by the annual average loss rate; values are taken from recent reports^{12,14} using the AFEAS review¹⁴ for species destroyed predominantly in the troposphere (CH₃CCl₃ and HCFC-22). Fluxes (kt yr⁻¹ = 1,000 tonnes per year) are based on estimates of production in the year 1985 and total 1,000,000 metric tons for CFCs alone. Growth (kt yr⁻¹ yr⁻¹), the increment to the flux each year from 1986 through 1990, is assumed to be 4% yr⁻¹ for all industrial halocarbons; such increases are conservative estimates of growth in the production of CFC-11 and CFC-12 during this period¹⁷. Concentration is the average tropospheric mixing ratio used to initialize the model and is based on available observations¹¹. Factor (kt p.p.t.⁻¹) relates concentration (p.p.t.) to global content (kt), assuming the compound is well mixed throughout 95% of the atmosphere. Methyl chloride and methyl bromide concentrations are fixed. The concentration (CONC) in YR + 1 is calculated recursively from the equation CONC[YR + 1] = CONC[YR] × DECAFY + FLUX[YR + 1] × (1 - DECAFY) × LIFETIME / FACTOR where DECAFY = exp(-1/LIFETIME).

from the atmosphere. For most CFCs the time taken for atmospheric concentrations to approach within 10% of steady-state conditions is more than 100 years. ODPs are usually defined relative to CFC-11 (dimensionless) rather than in absolute units. ODPs therefore reflect the relative contribution of CFCs towards ozone destruction after nearly constant emissions for a century. Transient ozone depletion potentials have also been used^{12,13}, but they do not clearly reflect the absolute contribution of different halocarbons to atmospheric chlorine concentrations.

Most of the chlorine atoms in CFC-11 are photolysed in the lower stratosphere and thus are available to participate in the catalytic destruction of ozone at all altitudes in the stratosphere. Other CFCs, such as CFC-12 and HCFC-22, are photolysed more slowly, and most of their chlorine atoms are available only in the upper stratosphere or near the winter poles. (Air in the winter polar stratosphere seems to be photochemically aged^{15,16}, having descended from the upper stratosphere.) For such compounds, the model-derived ODPs (relative to CFC-11) will be less than the relative chlorine loading in these scenarios. A warning about the accuracy of ODP calculations must be made: the current assessment models are limited to gas-phase chemistry and predict future ozone depletion predominantly in the middle stratosphere; they do not predict the Antarctic ozone hole or the possibility of similar heterogeneously driven loss in the Arctic lower stratosphere.

The model for halocarbons

The data for halocarbons used in this model for chlorine- and bromine-loading are based directly on scenarios developed for the recent international ozone assessment¹². The UNEP/WMO study focused primarily on scenarios leading to increases in atmospheric chlorine; our study examines approaches to reduce chlorine abundance. Two other differences are (1) the lifetime of HCFC-22 is taken here as 15 yr (ref. 14) rather than 20 yr and (2) we assume that the cutback in CFC emissions will occur in a specified year rather than being phased in over the period from 1996 to 2000.

A simple numerical model is used to calculate the atmospheric abundances of the individual halocarbons, as described in Table 1. Fluxes of the chlorine- and bromine-containing species, except CH₃Cl and CH₃Br, are defined in each scenario, and reductions occur instantly at the end of the year. More detailed atmospheric models for the calculation of halocarbon concentrations are available; however, increasing the complexity of the

model is not justified for this work because first-order uncertainties, such as in the atmospheric lifetimes, overwhelm the differences between such models.

The reference scenario is chosen as an optimistic lower baseline for chlorine loading and assumes control over the atmospheric emissions of all industrial halocarbons as a group (CFCs, CCl₄, HCFC-22, CH₃CCl₃ and the halons). It is initialized in 1985, adopts conservative growth rates through 1990¹⁷, freezes emissions into the atmosphere at the 1990 rate, and cuts all emissions to zero at the end of the year 2000. From then on the atmospheric abundances of chlorine and bromine change solely by the slow decay of gases already in the atmosphere. In scenarios where only a partial cutback is assumed, the fraction of the flux allowed to continue refers to 1985 emissions.

Uncertainties

In these calculations the absolute timing of the atmospheric response may be imprecise because of basic uncertainties in modelling atmospheric composition (for example, CFC lifetimes) as well as simplifying assumptions particular to this model. For example, the stratospheric destruction of halocarbons is the predominant sink for CFCs and will lag emissions by about two years, the time it takes for air to travel from the upper troposphere to the middle stratosphere. In turn, the ozone depletion in response to halocarbons will be similarly delayed. Air over the winter pole may represent a mix of tropospheric halocarbons emitted over the past few years. These effects will be important only when tropospheric concentrations are changing rapidly and have not been accounted for here.

A more important and obviously systematic omission in these calculations is the failure to simulate the delay between halocarbon production and emissions. Depending on use, the halocarbons produced in a given year may not be emitted into the atmosphere until several years later. For example, CFC-11 used in blowing closed-cell insulating foams may take more than ten years to escape into the atmosphere, and CFC-12 used in hermetically sealed refrigeration systems will not be released until the refrigerant coils break, on average 20 years later. This accumulation of CFCs makes it difficult to stop emissions (as in the reference scenario) immediately on cessation of production. On the other hand, some applications will have little delay between production and emission: CFC-113 and CH₃CCl₃ are used primarily as cleaning agents, and their production reflects the amount lost during the cleaning process, presumably to the

TABLE 2 Peak chlorine loading and date to reach 2 p.p.b.

Option	Scenario	Peak chlorine (p.p.b.)	2-p.p.b. date
1	1995 (100% cut)	4.24	2055
	2000 (100% cut, ref.)	4.78	2073
	2005 (100% cut)	5.28	2091
2	2000 (90% cut)	4.78	2175
	2000 (80% cut)	4.78	never
4	2000/2015 (90/10% cut)	4.78	2079
	2000/2015 (80/20% cut)	4.78	2084
5	1995/2000 (50/50% cut)	4.24	2063
7	lifetimes -25%	4.47	2053
	lifetimes +25%	5.01	2095

atmosphere. As of 1987 the total amount or 'bank' of CFCs in products with an average retention time of >2 yr is estimated to be <2 yr of the annual production of all CFCs¹⁷. The net effect of such CFC accumulation may have similar results to a delay in compliance with CFC cuts (see option 4 below).

In spite of these uncertainties in the timing of atmospheric effects, the relative changes in peak chlorine loading or in the 2-p.p.b. date for each of the options considered below should be accurate.

Suggested halocarbon substitutes

The fundamental property of the substitute compounds that makes them more environmentally acceptable is a shorter atmospheric lifetime (<50 yr) so that they do not accumulate to large steady-state concentrations. Substitution levels assume a kg-per-kg replacement (in %) of the sum of halocarbon cuts referenced to their 1985 emission levels (1,000 kt yr⁻¹ of CFCs, 80 kt yr⁻¹ of CCl₄, 140 kt yr⁻¹ of HCFC-22, 600 kt yr⁻¹ of CH₃CCl₃). The focus here is on stratospheric ozone rather than greenhouse warming and thus on substitutes containing chlorine. (Halon substitution by bromine compounds is not considered.) The International Technical Panel (part of the UNEP assessment¹²)

predicts 30% of the CFC market (350 kt yr⁻¹ in 1985) could be replaced by short-lived substitutes containing chlorine, and that this market will grow at 3% yr⁻¹ until terminated. Estimates from the chemical industry are similar¹⁸. Substitution for CCl₄, HCFC-22 and CH₃CCl₃—if these compounds were phased out—are likely not to involve chlorinated replacements. Hence, in the reference scenario with a complete cut in all halocarbons (1,820 kt yr⁻¹ in 1985), the industry predictions would correspond to an initial substitution rate of about 20% in these scenarios.

Two surrogate compounds are chosen as arbitrary examples of possible replacements for the CFCs and are described in Table 1. Compound X has a lifetime of 15 yr (like HCFC-22), a single chlorine atom, a mean molecular weight of 115, and hence a steady-state chlorine loading factor of 0.10 relative to CFC-11. Compound Y has a lifetime of 6 yr (like CH₃CCl₃), a single chlorine atom, a mean molecular weight of 115, and hence a steady-state chlorine loading factor of 0.04 relative to CFC-11 (about one-third that of CH₃CCl₃). These substitutes are simply examples and do not correspond to any specific fluorocarbon¹⁴.

Environmental objectives

Several objectives must be considered when regulating the emissions of CFCs and halocarbons: (1) return chlorine loading to pre-industrial levels; (2) reduce chlorine abundances as soon as possible to those prevalent before the Antarctic ozone hole; and (3) minimize the peak chlorine loading of the atmosphere.

The pre-industrial atmosphere, insofar as chlorine is concerned, is not an achievable goal on a timescale of centuries, namely, the time to remove the present burden of CFCs from the atmosphere. Even in the reference scenario (complete phaseout of CFCs by the year 2000), chlorine levels remain above 1 p.p.b. until the year 2190. The more realistic goal (2) may be environmentally justified because the increase in atmospheric chlorine from pre-industrial levels up to the identification of the ozone hole was neither observed nor predicted to result

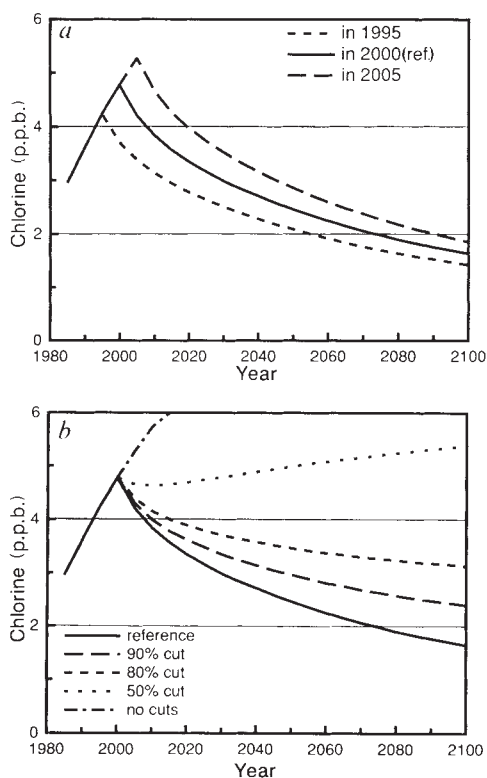


FIG. 1 a, Effect on chlorine concentrations of a 100% cut in all halocarbons; b, Partial cut in all halocarbons by year 2000.

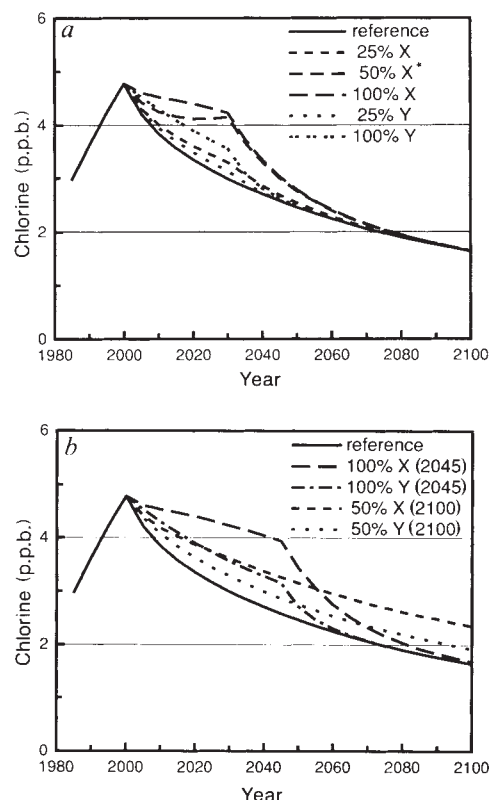


FIG. 2 Effect on chlorine concentrations from use of substitute compounds for (a) 30 years and (b) 45 years and beyond after the complete phaseout of halocarbons in the year 2000.

in decreases of column ozone greater than a few per cent³. Goal (3) may be viewed as reducing both global ozone depletion and the potential for an ozone hole in the Arctic. A number of scenarios are chosen to examine the possible options or controlling emissions that will affect the attainment of goals (2) and (3).

Option 1. Timing of the phaseout in CFCs, CCl₄, CH₃CCl₃ and HCFC-22. We examine the environmental impact of eliminating the emissions of all halocarbons as a group (CFCs, CCl₄, CH₃CCl₃ and HCFC-22) by the end of years 1995, 2000 (reference case), and 2005, without substitution of any new chlorine-containing compounds. Figure 1a and Table 2 show that each five-year delay in the phaseout of these chemicals results in the peak chlorine loading increasing by about 0.5 p.p.b. (87% of it due to the CFCs) and in the date by which atmospheric chlorine will drop below 2 p.p.b. increasing by about 18 years. The critical factor determining the 2-p.p.b. date is the timing of the phaseout of the long-lived halocarbons (CFCs and CCl₄), not the short-lived halocarbons (CH₃CCl₃ and HCFC-22). Accumulation of the long-lived CFCs, as well as laxity in compliance with the phaseout (see options 2 and 4), make the date for effective cessation of CFC emissions slip further into the future.

Option 2 Incomplete phaseout of halocarbons. Here we examine the impact of a partial phaseout in the emissions of all current industrial halocarbons without any substitution of new chlorine-containing halocarbons. All reductions (90%, 80%, 50%) refer to 1985 emissions and occur at the end of year 2000; the scenario without reductions (0%) continues 1990 emissions until the year 2100.

Figure 1b shows that substantial although incomplete cutbacks in halocarbons (80–90%) can rapidly reduce chlorine loading. In these cases, atmospheric chlorine concentrations peak in the year in which the cuts are made, but the decrease in chlorine loading is slowed, and its asymptotic steady-state value is significantly raised by continued emissions at the 10–20% level. In the reference case (100% reduction), the 2-p.p.b. date is 2073 (see Table 2). With a 90% reduction, the chlorine loading reaches 2.4 p.p.b. in the year 2100 and falls below 2 p.p.b. after the year 2175. With an 80% reduction, the chlorine loading is 3.1 p.p.b. in the year 2100 and approaches a steady-state limit of ~2.8 p.p.b. With 50% reductions the chlorine loading drops briefly after the year 2000 and then rises above 5.3 p.p.b. by the year 2100. Without a cutback (0%) the chlorine abundance in the atmosphere rises rapidly, exceeding 8.5 p.p.b. by the year 2050 and 10.5 p.p.b. by the end of the twenty-first century.

Option 3 Substitution of alternative compounds X and Y. Here, the complete phaseout in the year 2000 (100% = 1,820 kt yr⁻¹) is followed by the use of substitute compounds X or Y at constant rates (25%, 100%) or at an initial rate (50%) that grows by a factor of 1.03 each year thereafter. The scenario with 3% yr⁻¹ growth (denoted by 50% X* in Fig. 2a) becomes equivalent to the constant 100% scenario by the year 2030 and would greatly exceed that level if continued. In general, we have limited the period of substitution to 30 years (2001–30), but in some cases it is extended to 45 years, or continued indefinitely. Results are shown in Figure 2. (The effect of a 45-yr substitution with Y is discussed below.)

The maximum chlorine loading occurs at the time of phaseout of CFCs for these cases. Modest substitution for the years 2001 to 2030 (25% with X or 50% with Y) still results in rapid decreases in chlorine loading after the year 2000; the added burden on top of the reference scenario is never more than 0.3 p.p.b.. In the case of 100% substitution with compound X, however, chlorine loading remains high, above 4 p.p.b., to the year 2032. Equivalent substitution with compound Y has a much smaller impact on atmospheric chlorine because of the shorter lifetime.

The added chlorine loading associated with substitution drops rapidly when emissions of these short-lived compounds cease; ~86% of the compound will be destroyed within two lifetimes (30 yr for X and 12 yr for Y). The 2-p.p.b. date is delayed by four years at most if compound X is phased out before the year

2030 or compound Y, before the year 2045. With indefinite substitution even at the 50% level, however, it is difficult, if not impossible, to achieve chlorine concentrations below 2 p.p.b. by the end of the twenty-first century.

Option 4 Delayed compliance of the phaseout by some producers. Here halocarbon emissions are cut substantially (80–90%), and the remaining fraction (20–10%) of their 1985 emissions are allowed to continue for 15 years until the end of year 2015. Substitution of compounds X and Y is considered as above, but with a 15-yr lag in fraction of emissions by the non-compliant producers (extending to the year 2045). Results are summarized in Figure 3 and Table 2.

An 80–90% cut (as in option 2) immediately reduces the peak chlorine loading in the year 2000. Furthermore, limiting the non-compliance to 15 yr results in only a 6 yr (90% cut) or 11 yr (80% cut) delay in the 2-p.p.b. date. When substitutes (X or Y) are added on top of the delayed phaseout, the largest increase in chlorine loading (relative to the corresponding substitution scenario in option 3) occurs just before the final halocarbon cuts (2015) and ranges from 0.2 p.p.b. (90% cut) to 0.4 p.p.b. (80% cut). In the case where 20% of the phaseout is delayed until the year 2015 and there is 100% replacement by compound X, the peak chlorine loading in the year 2000 (4.78 p.p.b.) is maintained out to the year 2015 (4.72 p.p.b.) and drops only slowly by the year 2030 (4.45 p.p.b.). Overall the greatest impact of this 15-yr delay in phaseout is to extend the duration of higher chlorine levels over the first quarter of the 21st century.

Option 5 A graduated phase-in of halocarbon cuts. Here we consider a two-step reduction in halocarbons (CFCs, CCl₄, CH₃CCl₃ and HCFC-22), first, to 50% of their 1985 levels at the end of year 1995 and, second, to a complete phaseout in the year 2000. This scenario is a hybrid of the 1995 and 2000 phaseouts in Option 1. Substitution is considered, also being

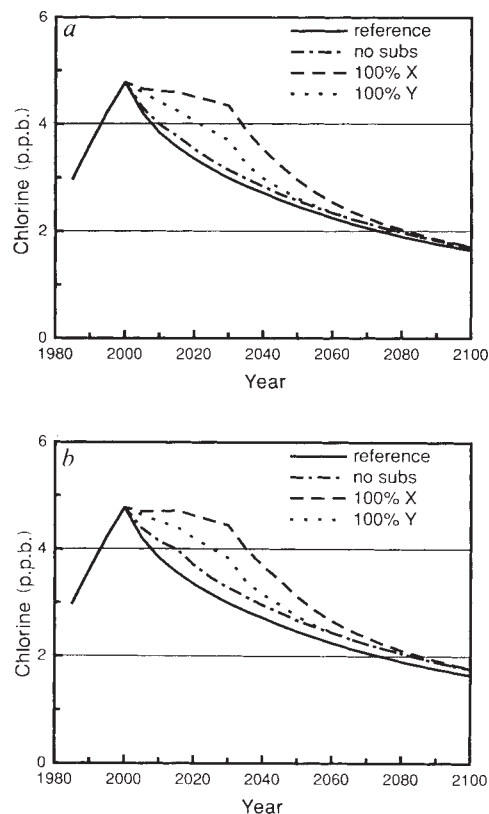


FIG. 3 Effect on chlorine concentrations of delaying the phaseout of final 10% of halocarbon emissions (a) and the final 20% of halocarbon emissions (b) by 15 yr.

phased in over 5 yr as with halocarbons. Results are given in Figure 4a and Table 2.

This complex scenario may be a more realistic outcome of current approaches to implement the Montreal Protocol and eliminate halocarbon emissions, recognizing that parts of the CFC market can phase out earlier, and including the effect of CFC accumulation in delaying release to the atmosphere. The history of chlorine abundance from this 50%/50% scenario lies between that of the year-1995 phaseout and that of the year-2000 phaseout. Peak chlorine loading occurs in 1995, and the 2-p.p.b. date is 2063, about 10 years earlier than in the reference case. Moderate substitutions (50% with X or Y) until the year 2030 give chlorine loadings in the latter half of the twenty-first century that are indistinguishable from the reference case.

Option 6 Continued use of CH_3CCl_3 . Methyl chloroform is a short-lived halocarbon (lifetime ~ 6 yr) with properties similar to some CFC alternatives; continued use would be equivalent to substitution with $1,800 \text{ kt yr}^{-1}$ of compound Y. Here we examine the impact of CH_3CCl_3 on chlorine loading by eliminating the emissions of CFCs, CCl_4 and HCFC-22 in the year 2000, but continuing CH_3CCl_3 emissions at 1990 levels until the year 2030. Results are summarized in Fig. 4b.

The phaseout of CH_3CCl_3 contributes to the rapid fall in chlorine loading after the year 2000 in the reference scenario, because the gas contributes about 0.5 p.p.b. to the total chlorine loading and is eliminated quickly from the atmosphere. However, continued use of CH_3CCl_3 for 30 yr gives no increase in the peak chlorine loading and little change in the 2-p.p.b. date. Owing to the accumulation of CFCs, a simultaneous cut in production of both CH_3CCl_3 and CFCs results in an almost immediate cessation of CH_3CCl_3 emissions and an extended period of CFC release. Under such circumstances, continued use of CH_3CCl_3 might lead to increases in the peak chlorine loading relative to the reference scenario, but this situation does not apply because the current CFC bank is not large enough.

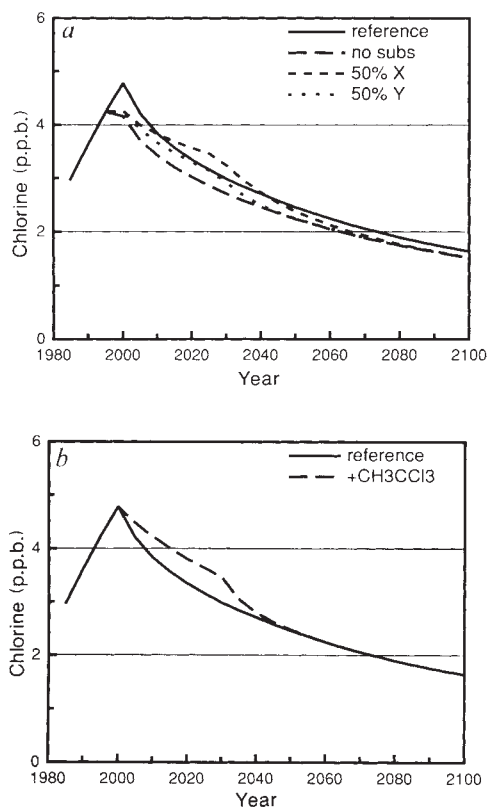


FIG. 4 a, Effect on chlorine concentrations of a two-step reduction in halocarbons: 50% cut in 1995 and complete phaseout at 2000; and b, effect of continuing methylchloroform emissions until 2030.

Option 7 Uncertainty in the atmospheric lifetimes of halocarbons.

Here we examine how predicted chlorine loading is affected by a $\pm 25\%$ uncertainty in the halocarbon lifetimes. Such ranges are extreme (for example, CFC-11 lifetimes vary from 45 to 75 yr) and cover the most probable range in CFC lifetimes from current atmospheric models and from budget analyses using observations and historical emissions¹⁹⁻²¹. Results are given in Fig. 5 and Table 2. When halocarbon lifetimes are reduced by 25%, the more rapid destruction of these compounds lowers the peak chlorine concentration by 0.3 p.p.b. (to 4.5 p.p.b.) and reduces the 2-p.p.b. date by 20 years (to the year 2053). When lifetimes increase by 25%, the peak chlorine concentration rises by 0.2 p.p.b. (to 5.0 p.p.b.) and extends the 2-p.p.b. date to the year 2095.

The uncertainty in predicting atmospheric chlorine concentrations following a halocarbon phaseout is not large, only a few tenths of a p.p.b. If these uncertainties in the atmospheric models are resolved in the near future, then the scenarios considered above (options 1-6) may need to be shifted as a group, but the calculated relative differences should be robust.

Option 8 The impact of halon emissions on bromine loading. The change in bromine loading is calculated from the emissions of the halons 1301 (CF_3Br) and 1211 (CF_2ClBr); halon 2402 ($\text{CF}_2\text{BrCF}_2\text{Br}$) is assumed to be negligible at present and in the future. (Short-lived compounds such as bromoform, CHBr_3 , are expected to contribute little to stratospheric bromine.) This scenario is similar to that for chlorine loading and examines the effects of cutting halon emissions by 100%, 80% and 50% of their 1985 levels, as well as freezing emissions (0% cut) at their 1990 levels. Results are shown in Fig. 6.

In 1985 the halons 1301 and 1211 together contributed about one-sixth of the total bromine loading. If their emissions

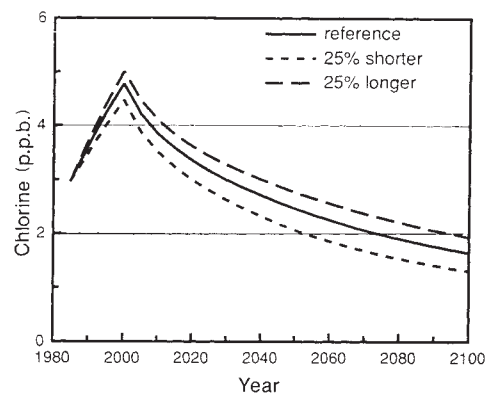


FIG. 5 Sensitivity of chlorine concentrations to uncertainties in the atmospheric lifetimes of CFCs and other halocarbons.

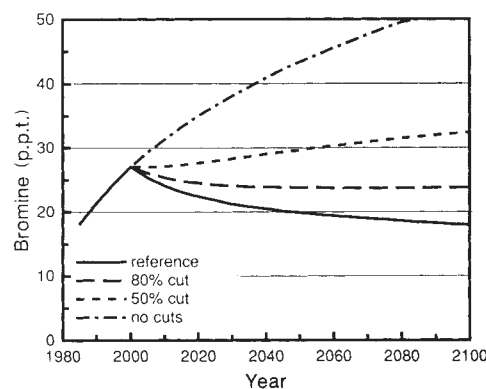


FIG. 6 Effect on bromine concentrations of cuts in halon emissions.

continued at the estimated 1990 production levels then the atmospheric abundance of bromine in the future would approximately triple from about 18 p.p.t. (parts per 10^{12}) (3 p.p.t. halons) in the year 1985 to 53 p.p.t. (38 p.p.t. halons) by the year 2100. In these calculations CH_3Br remains constant; but observations²² suggest that large sources are associated with northern continents and human activity (for example grain fumigation).

To evaluate the impact of bromine increases, it would be useful to define a factor relating bromine-catalysed destruction of ozone to that of chlorine. Such a simple factor is difficult to derive because ozone depletion is occurring over a wide range of photochemical environments, ranging from global scales in the upper stratosphere (near 40 km altitude where bromine contributes little to the restricted environment of the Antarctic ozone hole (near 20 km altitude where BrO is part of a key catalytic cycle). Further, much of the bromine-catalysed loss depends on the ClO abundance. One can estimate this factor to be about 30 (refs 7–10) with a large uncertainty ranging from 10 to 50. With a freeze on halon emissions (0% cut) the increase in bromine loading by the year 2100 is ~ 35 p.p.t., or the equivalent of adding ~ 1 p.p.b. of chlorine to the atmosphere.

Conclusions

We must constrain our emissions of chlorine- and bromine-containing compounds to reverse the ozone depletion that has occurred to date and to reduce the potential for even greater ozone losses in the future. These objectives require a truly global effort and cannot be achieved by the action of a single industry or group of nations. A phaseout of almost all emissions of halocarbons is needed in the next century in order to decrease

the atmospheric abundance of chlorine below 2 p.p.b. before the year 2100 (the minimum necessary for recovery of the Antarctic ozone hole). Each year's delay means an extra 0.1 p.p.b. in the peak chlorine loading and pushes the 2-p.p.b. date 3.6 years further into the future.

Ideally, we should cease emissions of CFCs and other halocarbons immediately. All other options result in enhanced levels of stratospheric chlorine and bromine sometime in the future. In reality, we may need to accept compromises to achieve global cooperation with a halocarbon phaseout early in the next century. We have therefore examined possible options of delayed and partial compliance as well as substitution of long-lived CFCs with short-lived HCFCs. The purpose of these scenarios is to identify options that do not substantially enhance the risk of greater ozone depletion.

The environmental goals outlined above might best be achieved if we phase out production/emission of long-lived halocarbons (CFCs and CCl_4) as soon as possible; achieve as great as possible compliance with an immediate phaseout of CFCs and CCl_4 at the expense of substituting short-lived HCFCs; allow a 15-year lag in implementing the CFC phaseout by a small fraction (10–20%) of the community if it prevents long-term non-compliance; make significant cutbacks in the emissions of abundant, short-lived halocarbons, particularly CH_3CCl_3 , if it becomes necessary to reduce rapidly the peak chlorine loading; phase out the chlorine-containing halocarbon substitutes sometime by the middle of the next century; and stabilize stratospheric bromine levels by greatly reducing (by 80% or more) the production of halons, especially the long-lived CF_3Br . □

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Nonlinear forecasting as a way of distinguishing chaos from measurement error in time series

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An approach is presented for making short-term predictions about the trajectories of chaotic dynamical systems. The method is applied to data on measles, chickenpox, and marine phytoplankton populations, to show how apparent noise associated with deterministic chaos can be distinguished from sampling error and other sources of externally induced environmental noise.

TWO sources of uncertainty in forecasting the motion of natural dynamical systems, such as the annual densities of plant or animal populations, are the errors and fluctuations associated with making measurements (for example, sampling errors in estimating sizes, or fluctuations associated with unpredictable environmental changes from year to year), and the complexity of the dynamics themselves (where deterministic dynamics can easily lead to chaotic trajectories).

Here we combine some new ideas with previously developed techniques^{1–7,16,24–26}, to make short-term predictions that are