

The atmospheric fate and impact of hydrochlorofluorocarbons and chlorinated solvents

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Abstract: A very considerable body of data pertaining to the atmospheric behaviour of hydrochlorofluorocarbons (HCFCs) and chlorinated solvents is now available and leads to the following conclusions: (a) these compounds, with the exception of 1,1,1-trichloroethane, make a small or insignificant contribution to stratospheric ozone depletion, global warming, ‘photo-chemical smog’, ‘acid rain’, or chloride and fluoride levels in precipitation; (b) it seems highly unlikely that the chlorinated solvents degrade in the atmosphere to give chloroacetic acids as major products, as has often been claimed in the literature.

INTRODUCTION

In this chapter we will review briefly the atmospheric fate and impact of two classes of volatile chlorinated aliphatic compounds which are used on a large scale and provide considerable benefits to modern society:

1 The *hydrochlorofluorocarbons*, or HCFCs, which were introduced by industry as interim ‘first-generation’ substitutes for chlorofluorocarbons (CFCs), when it became clear that the latter were major contributors to the depletion of the stratospheric ozone layer. The main applications in which HCFCs are needed to replace CFCs are: refrigeration, air conditioning and the blowing of thermally insulating foams. The ‘second-generation’ replacements for CFCs, the hydrofluorocarbons or HFCs, will not be discussed here, since they contain no chlorine, although chlorine is used in their manufacture. The main HCFCs, considered here, are: CHClF_2 (HCFC-22), CF_3CHCl_2 (HCFC-123), CF_3CHClF (HCFC-124), CCl_2FCH_3 (HCFC-141b) and CClF_2CH_3 (HCFC-142b).

2 The *chlorinated solvents*: dichloromethane or methylene chloride (CH_2Cl_2 , MC), trichloroethylene ($\text{CCl}_2=\text{CHCl}$, TRI), tetrachloroethylene or perchloroethylene ($\text{CCl}_2=\text{CCl}_2$, PER) and 1,1,1-trichloroethane or methyl chloroform (CCl_3CH_3 , 111-T). The main applications for these solvents are: metal degreasing, dry cleaning, paint stripping, extraction of pharmaceuticals and foodstuffs, precision cleaning and electronic circuit-board production.

Like the CFCs, 111-T is regulated by international agreement. Under the original ‘Montreal Protocol on Substances that Deplete the Ozone Layer’ and its subsequent revisions, the production and consumption of 111-T have already been phased out in the developed countries. The use of HCFCs is restricted by the same Protocol. A ceiling or ‘cap’ has already been placed on their consumption. It will be phased down starting in the year 2004, with virtual elimination being achieved by 2020. Regulations in the European Union and the United States are even stricter than the Montreal Protocol.

In this brief overview, our objective is to describe how HCFCs and chlorinated solvents degrade in the atmosphere and what impact they have on the atmospheric environment. We will however, make no attempt at covering the subject comprehensively. Only broad conclusions will be given, together with references to key papers and recent review articles.

ENVIRONMENTAL PARTITIONING

As shown in Table 1, all the compounds considered are gases or moderately to very volatile liquids, and have low solubilities in water. The logarithms of their octanol/water partition coefficients are lower than 3, which indicates that they will have little potential for passive bioaccumulation in the fatty tissues of living

Table 1 Some physical properties

Compound		Boiling point (°C)	Solubility in water at 25 °C (and 1 bar, for gases), % by weight	log P _{octanol/water}
CHClF ₂	HCFC-22	-41	0.3	1.1
CF ₃ CHCl ₂	HCFC-123	28	0.4	2.4
CF ₃ CHClF	HCFC-124	-12	0.15	2.0
CCl ₂ FCH ₃	HCFC-141b	32	0.4	2.0
CClF ₂ CH ₃	HCFC-142b	-9	0.2	1.8
CH ₂ Cl ₂	MC	40	1.4	1.3
CCl ₂ =CHCl	TRI	87	0.1	2.3
CCl ₂ =CCl ₂	PER	121	0.02	2.8
CCl ₃ CH ₃	111-T	74	0.15	2.5

Table 2 Global atmospheric emission fluxes of HCFCs, kt/year [1]

Compound		1990	1991	1992	1993	1994
CHClF ₂	HCFC-22	195	204	215	213	219
CCl ₂ FCH ₃	HCFC-141b	0	0.3	3.1	11.3	23.1
CClF ₂ CH ₃	HCFC-142b	5.2	8.1	10.1	11.6	11.9

organisms, so they do not belong to the family of compounds known as 'PTBs' (persistent, toxic and bioaccumulative substances), also known as 'POPs' (persistent organic pollutants).

In view of their physical properties, these compounds will partition predominantly to the atmosphere on release to the environment, providing they do not enter a confined ecosystem, such as groundwater.

ATMOSPHERIC EMISSION FLUXES

The atmospheric input of the compounds considered here may be deduced from their worldwide sales into so-called 'dispersive' uses, that is applications in which the substance is ultimately emitted into the environment, albeit in some cases many years after first being consumed. Use as a feedstock for conversion into other chemical compounds is therefore excluded in this calculation. This exercise has been performed for three HCFCs. Global atmospheric releases, calculated from aggregate sales data provided by the developed-country producers, are given in Table 2 (in kt/year, or Gg/year).

Emissions of HCFCs-22 and 142b appeared to be reaching a plateau already in 1994, while those of HCFC-141b were increasing rather rapidly. No data are yet available on HCFCs-123 and 124, but the production of these compounds is believed to occur on a much smaller scale than for the other three HCFCs listed above. Note, by comparison, that the estimated total emissions of CFCs were 764 kt in 1990, falling to 405 kt in 1994 [1].

Atmospheric emissions of the chlorinated solvents have been estimated from sales data provided by the European, American and Japanese trade associations. The aggregate figures are shown in Table 3.

It can be seen that the emissions of MC, TRI and PER are all declining steadily, largely as a result of constant improvement in the efficiency with which they are being used and recycled. 111-T emissions

Table 3 Global atmospheric emission fluxes of chlorinated solvents, kt/year

Compound		1988	1989	1990	1991	1992	1993	Ref.
CH ₂ Cl ₂	MC	592	586	583	534	513	—	[2]
CCl ₂ =CHCl	TRI	260	235	241	212	197	—	[2]
CCl ₂ =CCl ₂	PER	454	423	366	342	295	—	[2]
CCl ₃ CH ₃	111-T	666	691	718	635	593	380	[3]

peaked in 1990 and fell sharply by 1993, a trend which has certainly continued since then, with the phase-out of this solvent under the Montreal Protocol.

For 1992, i.e. the most recent year for which data are available for all the compounds, the atmospheric emissions of HCFCs and chlorinated solvents contained a total of 1.4 Mt (Tg) and 0.1 Mt of organically bound chlorine and fluorine, respectively.

ATMOSPHERIC PERSISTENCE AND LIFETIMES

The CFCs are inert in the lower atmosphere (or troposphere) and within a period of 3–5 years after their release they are transported to the lower stratosphere where they are degraded to inorganic chlorine species capable of participating in reactions leading to the catalytic depletion of stratospheric ozone, as discussed elsewhere in this volume.

The HCFCs were chosen as alternatives to CFCs since they have similarly desirable properties (low toxicity, low or zero flammability, low gas-phase thermal conductivity, good chemical stability and low corrosiveness during use, reasonable cost, etc.), but since they have at least one C–H bond, they are degraded in the lower atmosphere by reaction with the naturally occurring hydroxyl radical (HO \cdot):



An analogous reaction occurs with MC and 111-T. In the case of TRI and PER, reaction with the hydroxyl radical results in addition to the double bond:



Reactions (1a) and (1b) initiate the atmospheric oxidation of the organic substrates and the rates of these reactions determine the persistence or lifetimes of the compounds. The subsequent fate of the radicals formed in these reactions will be discussed later.

As detailed in several recent reviews [ref. 4, chapter 12; refs. 5–7], reaction (1a) is the only significant degradation process for HCFCs in the troposphere. This is also the case for MC, while reaction (1b) is the dominant process for TRI. Perchloroethylene will also be degraded predominantly by reaction (1b), but it may also react to a slight extent with chlorine atoms; this will be discussed later. For 111-T, in addition to reaction (1a), ocean uptake and hydrolysis make a small but non-negligible contribution to removal from the troposphere [8].

A relatively small fraction of the parent compounds released at ground level will survive degradation in the troposphere and be transported to the stratosphere. This fraction decreases as the rate constants for reactions (1a) and (1b) increase, i.e. as the tropospheric lifetimes decrease.

The overall lifetimes for removal of the various compounds from the lower atmosphere are given in Table 4. The lifetime is the time required for the concentration to fall to $1/e$ of its initial value, once input

Table 4 Atmospheric lifetimes, ozone depleting potentials (ODPs) and halocarbon global warming potentials (HGWPs)

Compound		Lifetime (year)	ODP*	HGWP*
CHClF ₂	HCFC-22	13.3	0.04–0.05	0.36
CF ₃ CHCl ₂	HCFC-123	1.4	0.014–0.02	0.02
CF ₃ CHClF	HCFC-124	5.9	0.03	0.10
CCl ₂ FCH ₃	HCFC-141b	9.4	0.10	0.14
CClF ₂ CH ₃	HCFC-142b	19.5	0.05–0.066	0.44
CH ₂ Cl ₂	MC	0.41 §	see text	0.002
CCl ₂ =CHCl	TRI	0.018 §	see text	(< 0.001) ¶
CCl ₂ =CCl ₂	PER	0.36 §	see text	(0.002) ¶
CCl ₃ CH ₃	111-T	5.4	0.12	0.025

Lifetimes and ODPs taken from chapter 13 of ref. 4, HGWPs calculated from data given in chapters 4 and 5 of ref. 9, unless otherwise stated. * Relative to the value for CFC-11 taken as 1.0. § Estimated using the same procedure as in ref. 4. ¶ Rough estimate

into the troposphere is stopped.

For the chlorinated solvents MC, TRI and PER, the lifetimes are rather short, ranging from 1 week to 5 months. For 111-T and the HCFCs they are longer, from 1.4–20 years. In view of their relatively short lifetimes, once the release of these compounds to the atmosphere is stopped, their concentrations will fall off much more rapidly than in the case of the CFCs, whose lifetimes range from 50 to 1700 years.

OZONE DEPLETION

Relative contributions

As stated above, a small fraction of the compounds considered here will survive degradation in the troposphere and be transported into the stratosphere. Breakdown in the stratosphere can be initiated by photolysis by short-wavelength ultraviolet radiation ($\gamma < 240$ nm) or reaction with the hydroxyl radical or the excited-state oxygen atom (O^1D). These degradation channels ultimately lead to the formation of inorganic chlorine species capable of catalyzing stratospheric ozone depletion.

The relative efficiency, on a unit-mass basis, of the various compounds to cause ozone loss is expressed by their Ozone Depleting Potentials (ODPs), defined as the calculated ozone depletion due to release of 1 kg of the compound, divided by the calculated ozone depletion due to release of 1 kg of CFC-11 (CCl_2F).

In calculating model-derived ODPs, it is assumed that only inorganic chlorine and bromine species derived from the parent organic compounds are active in depleting ozone. A possible role of catalytic cycles involving fluorine species, such as CF_3O_x , $FC(O)O_x$, or FO_x was postulated in 1993, but sufficient evidence is now available to demonstrate that such mechanisms are highly inefficient, mainly because the chain-propagating reactions are slow compared to the chain-terminating ones [ref. 4, chapters 12 and 13; refs. 5–7].

The ODP values for the compounds considered here are given in Table 4. For the HCFCs, they are 10–50 times lower than that of CFC-11 (or of CFC-12, CCl_2F_2), mainly as a consequence of their shorter atmospheric lifetimes due to destruction in the troposphere. For the chlorinated solvents MC, TRI and PER, the lifetimes are much shorter still than those of the HCFCs or 111-T. The relative impact of these three solvents on stratospheric ozone will therefore be even smaller. However, the model-calculated ODPs of these solvents have not yet been determined satisfactorily. Indeed, compounds with lifetimes shorter than one year, as is the case here, do not become uniformly distributed in the atmosphere and to calculate ODPs would require resource-intensive '3-dimensional' (latitude, longitude, altitude) modelling. Furthermore, the ODP values finally obtained would depend on the point of release of the compounds to the atmosphere.

Absolute contributions

The calculated total chlorine and bromine loading of the stratosphere—past, present and projected for the future—is shown in Fig. 1 [10]. This chart includes the contributions of all the main anthropogenic sources of chlorine and bromine (CFCs, CCl_4 , 111-T, HCFCs, Halons and CH_3Br), as well as natural ones (CH_3Cl and CH_3Br). The contribution of bromine (which is some 50 times more effective than chlorine for depleting ozone) is expressed as 'equivalent chlorine'. For the sake of concision, we will use the term 'reactive halogens' to designate the appropriately weighted sum of chlorine plus bromine.

Figure 1 shows a peak in the stratospheric reactive halogen loading occurring approximately in 1996–97. A more detailed analysis [11] concludes that while the overall concentration of reactive halogens present in the various organic parent compounds went through a maximum in the troposphere in late 1993 to early 1994, the corresponding peak of reactive halogens will occur in the critical regions of the stratosphere between 1997 and 1999, on account of the time taken for transport to those regions.

Thus stratospheric reactive halogen loading will begin to decline before the end of the century, thanks to the reduced production and consumption of ozone-depleting substances required by the Montreal Protocol. As depicted in Fig. 1, however, it will take until the middle of the next century to fall to 2 ppbv, the level which existed before significant depletion of ozone began to occur above Antarctica, in around 1980. Hence, restoration of ozone levels will be a relatively slow process, on account of the long atmospheric lifetimes of the CFCs, which are the main contributors to reactive halogens in the stratosphere.

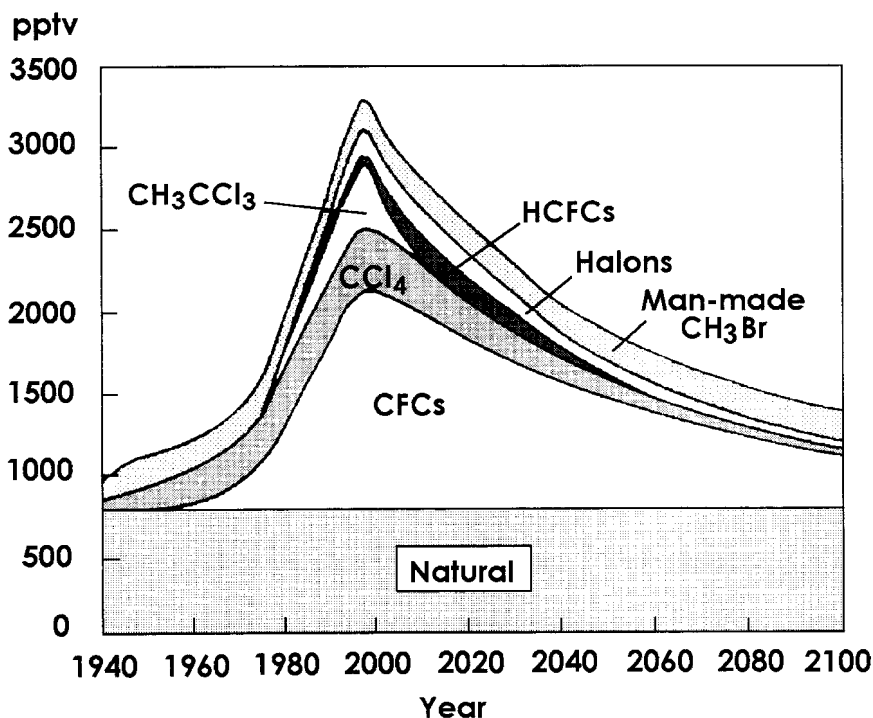


Fig. 1 Stratospheric reactive halogen loading [10].

The contribution of HCFCs to stratospheric reactive halogens is relatively small, as can be seen in Fig. 1. They add only about 1% to the peak value, when the risk of ozone depletion is highest, and their whole contribution over the next 50 years is only 5% of the total [10]. Virtually all of that amount is added when reactive halogens, and hence the risk of ozone depletion, are declining.

As far as the chlorinated solvents MC, TRI and PER are concerned, it has been concluded [ref. 4, chapter 13] that these compounds probably contribute little to contemporary stratospheric chlorine loading and would pose a problem only in the event of major growth in emissions. However, as has been shown above, their release rates are actually declining and this trend is expected to continue in the future. The fact that PER is a very small contributor to stratospheric chlorine has also been demonstrated in ref. 12. Furthermore, TRI and PER are presumed to break down in the stratosphere to give phosgene as a major product and since the latter is sufficiently stable in the lower stratosphere to be partially removed by transport to the troposphere where it is destroyed by hydrolysis, not all of the chlorine contained in the already small fractions of TRI and PER reaching the stratosphere is actually converted into ozone-depleting species [13].

GLOBAL WARMING

Another atmospheric effect which depends to a large extent on the lifetimes of the contributing compounds is the so-called 'greenhouse effect' [see, for example, ref. 9]. Radiation from the Sun is mainly in the visible and ultraviolet regions of the spectrum. It is partly absorbed by atmospheric gases and partly reflected by clouds and at the Earth's surface. However, most of the radiation is absorbed by the Earth. The latter re-emits energy at a much longer wavelength. This infrared radiation is absorbed to some extent by gases present in the atmosphere, both natural components and pollutants (water, carbon dioxide, methane, nitrous oxide, CFCs, etc.) causing the lower atmosphere and the Earth's surface to warm slightly in order to maintain a balance between the incoming and outgoing energy fluxes.

The increase in infrared radiation flux directed towards the Earth, due to the presence of greenhouse gases, is called the radiative forcing. The contributions of various greenhouse gases to radiative forcing depends on:

- the amounts emitted and the lifetimes of the compounds, which determine the levels to which their

- concentrations build up (the greater the amounts and the longer the lifetimes, the higher the levels);
- the infrared absorption spectra. Fluorocarbons are rather efficient greenhouse gases because they absorb in the infrared 'window' of the atmospheric absorption spectrum at 7–14 μm .

Relative contributions

The relative contributions of various chlorine compounds to the additional (i.e. anthropogenic) greenhouse effect are expressed by their Halocarbon Global Warming Potentials (HGWPs). The HGWP is the time-integrated radiative forcing caused by the release of 1 kg of the compound, divided by the same quantity for 1 kg of CFC-11. Values are given in Table 4. HGWPs are lower for HCFCs than for the CFCs (for which the values range from 1 to 35). For the chlorinated solvents they are more or less insignificant.

Absolute contributions

Table 5 shows the current contributions to radiative forcing of various greenhouse gases, arising from the additional concentrations which have been added to the atmosphere since the beginning of the industrial era and still present.

It can be seen that the main contributors to the greenhouse effect are carbon dioxide, methane, tropospheric ozone, the CFCs and nitrous oxide. HCFCs currently represent less than 1% of total radiative forcing (mainly due to HCFC-22), and this proportion is unlikely to increase very significantly before the HCFCs are phased out early next century. The contribution of the chlorinated solvents is roughly estimated at only 0.04% of the total.

Total equivalent warming impact (TEWI)

When a chemical compound is used in refrigeration, air conditioning or foam blowing, as a solvent, or in other applications, any emissions of this compound to the atmosphere (by leakage during normal use or when the equipment or material is eventually discarded) will contribute to radiative forcing and hence to global warming. The overall impact on global warming of whole *systems* should however, *not be judged* on the basis of this 'direct effect' alone. In addition, the application consumes energy and in doing so leads to a corresponding release of the greenhouse gas CO_2 , resulting from the production of the energy from fossil fuels. This is called the 'indirect effect'. The two contributions can be added, using the appropriate global warming potentials of the halocarbons relative to CO_2 , to convert the direct part into 'equivalent CO_2 '. This sum is known as the Total Equivalent Warming Impact (TEWI) of the system. The TEWI concept was pioneered by the Alternative Fluorocarbons Environmental Acceptability Study (AFEAS) in collaboration with the US Department of Energy.

An analysis of TEWI values for systems using HCFCs or HFCs, as well as for non-fluorocarbon ('not-in-kind', NIK) technologies, shows that the relative importance of the direct and indirect effects varies widely depending on the type of application. For energy-intensive applications (refrigeration, air conditioning, foam blowing), the fluorocarbon systems may contribute less overall to global warming than the competitive NIK technologies, on account of the superior energy efficiencies of the former [14,15].

'PHOTOCHEMICAL SMOG'

In addition to ozone depletion and global warming, another potential concern arising from the presence of volatile organic compounds in the atmosphere is their possible contribution to the formation of ozone close to ground level, which is undesirable because of the irritating and toxic nature of ozone.

Basically, tropospheric ozone is formed as shown in the scheme below:



Table 5 Contributions to radiative forcing

Compounds	W/m ²	% of total	Ref.
CO ₂	1.56	54.9	(a)
CH ₄	0.47	16.5	(a)
N ₂ O	0.14	4.9	(a)
O ₃ (tropospheric)	≈ 0.4	14.1	(a)
CFCs-11 and 12	0.20	7.0	(a)
Other CFCs, CCl ₄ , CCl ₃ CH ₃	0.048	1.7	(b)
HCFCs	0.024	0.8	(b)
CH ₂ Cl ₂ , CCl ₂ =CHCl, CCl ₂ =CCl ₂	≈ 0.001	0.04	(c)
Total	2.84	100	

(a) From ref. 9, p. 194; (b) Calculated from known radiative forcing constants [ref. 9, p. 176] and mean atmospheric concentrations [11]; (c) Rough estimates from known [ref. 9, p. 176] or assumed radiative forcing constants and approximate atmospheric concentrations

Organic free radicals (R[•]), resulting from the degradation of pollutants (e.g. by reactions 1a and 1b), add to molecular oxygen, forming alkyl peroxy radicals (RO₂[•]); these species react in turn with nitric oxide to give alkoxy radicals (RO[•]) and nitrogen dioxide. The NO₂ is photolyzed in sunlight ($\lambda < 430$ nm) back to NO and an oxygen atom, and the latter reacts with an oxygen molecule to give ozone.

Tropospheric ozone formation, and the associated 'photochemical smog', is particularly severe in summer in areas close to urban centers, on account of the presence of high concentrations of both organic compounds and nitrogen oxides, resulting from vehicles and other combustion sources, in conjunction with sunlight.

Unlike many non-chlorinated organic compounds, however, the chlorinated aliphatic hydrocarbons considered here do not contribute appreciably to urban ozone formation. This is because they have relatively long lifetimes—generally several months or even several years—compared to the non-chlorinated aliphatic compounds, whose lifetimes are generally only hours or days. If the chlorinated hydrocarbons are emitted in urban areas, they therefore have time to be dispersed away from the emission source before reacting, so that they do not induce high local ozone formation.

The particularly low photochemical reactivity of the HCFCs has been discussed in ref. 16 [chapter X], in which it was shown that all the HCFCs together would contribute less than 0.1% to urban ozone formation. For the chlorinated solvents, Photochemical Ozone Creating Potentials (POCPs) have been calculated and compared to those of other volatile organic compounds [17]. Thus, on a unit-mass basis, the POCP of TRI is only 6.6% of that of ethylene, chosen as a reference 'VOC'. For MC, PER and 111-T, the POCPs are all less than 1% of that of ethylene.

DEGRADATION MECHANISMS AND PRODUCTS

Only a brief overview of the atmospheric degradation mechanisms of HCFCs and chlorinated solvents will be given here. The emphasis will be on degradation in the troposphere, since that is the region where most of the breakdown will occur. For further details of the tropospheric and stratospheric chemistry of the HCFCs, several excellent recent review articles are available [ref. 4, chapter 12; refs. 5–7]. Data on the atmospheric chemistry of 111-T have been reviewed recently in refs. 18 and 19, while ref. 20 presents an overview for PER.

Saturated parent compounds

Formation of primary gas-phase molecular products

The degradation of the saturated compounds is initiated mainly by H-atom abstraction by the hydroxyl radical:



and proceeds further by a free-radical mechanism. Thus, the alkyl radical formed ($R\cdot$) adds oxygen to give an alkyl peroxy radical ($RO_2\cdot$):



The latter can undergo reactions with NO, the $HO_2\cdot$ radical, or NO_2 :

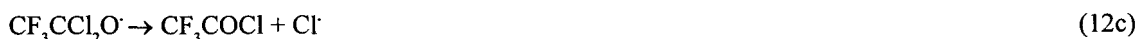


Reaction (3) leading to the alkoxy radical ($RO\cdot$) is generally the dominant pathway. The alkyl hydroperoxide (RO_2H) and alkyl peroxyxynitrate (RO_2NO_2) are believed to be rather short-lived intermediates, which will not have a significant impact on the overall degradation chemistry, since the main reactions they undergo will lead either to regeneration of $RO_2\cdot$ or formation of $RO\cdot$:



The chemistry of the haloalkoxy radical ($RO\cdot$), which is formed in the case of all the compounds under review, depends on its degree of substitution by halogens and the nature of the latter. For the compounds considered here, the possible processes are:

(a) *carbon-chlorine bond cleavage* (for CH_2Cl_2 and for HCFCs-22, 123 and 124):



The chlorine atom formed reacts with various atmospheric trace gases and is ultimately converted to HCl.

(b) *hydrogen-atom abstraction by molecular oxygen* (for CCl_3CH_3 and HCFCs-141b and 142b):



Certain haloalkoxy radicals may undergo *carbon-carbon cleavage*, but this possibility has been shown not to be important for the radicals arising from the breakdown of 111-T or of those HCFCs considered here [ref. 4, chapter 12; refs 5-7].

The primary gas-phase molecular products formed from the compounds reviewed are shown in the third column of Table 6.

Atmospheric fate of the primary products

All of the primary molecular products listed in Table 6 undergo significant chemical or physical transformation in the atmospheric compartment, including uptake into clouds and rainwater, and subsequent hydrolysis.

The fate of formyl chloride remains unclear [21]. Heterogeneous hydrolysis to formic acid is probably more rapid than photolysis or reaction with the hydroxyl radical, which would ultimately lead to the formation of HCl and CO_2 .

The principal fate of the other acid halides listed in Table 6 ($COCl_2$, $COClF$, COF_2 , CF_3COCl and CF_3COF) and of the HCl formed in the gas phase, is believed to be uptake into cloud water, followed by

rapid hydrolysis to the corresponding acids [ref. 4, chapter 12; refs. 5–7]. While there is considerable disagreement regarding the experimental values of the Henry's Law coefficients of the acid halides and of the rate constants for their hydrolysis, required for modelling their heterogeneous removal and destruction, it appears that their lifetimes with respect to these processes are in the range of a few days to a few months. Thus, the acid halides will be sufficiently short-lived to be destroyed almost completely in the troposphere and the chlorine-containing ones will not make any appreciable contribution to the ODPs of their parent halocarbons.

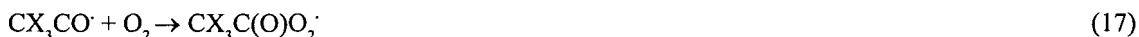
In the case of CF_3COCl , photolysis competes significantly with hydrolysis [22] and leads to the conversion of about 40% of this compound ultimately to HCl and carbon oxides, via a sequence of reactions involving the $\text{CF}_3\cdot$ radical, probably CF_3OH as an unstable intermediate, and COF_2 , the latter hydrolyzing to HF and CO_2 .

The haloaldehydes CCl_3CHO , CCl_2FCHO and CClF_2CHO are relatively unstable in the atmosphere. Their main degradation process is probably photolysis:



The $\text{CX}_3\cdot$ radical will undergo reactions analogous to the sequence of reactions (2), (3) and (12b), leading to the formation of COCl_2 , COCIF or COF_2 . Thus the ultimate degradation products, after hydrolysis of the carbonyl halides, are HCl , HF and carbon oxides. The lifetimes of the haloaldehydes, with respect to photolysis, are calculated to be only a matter of hours, assuming a photodissociation quantum yield of unity. Even if the latter is significantly lower, say comparable to that of acetaldehyde, photolysis is still expected to be the dominant tropospheric process [ref. 4, chapter 12].

The haloaldehydes may also undergo reaction with the hydroxyl radical, albeit to a minor extent, leading to the following reactions:



Reaction (16) will be much faster than the competitive reaction (17) in the case of the $\text{CCl}_3\text{CO}\cdot$ radical, which (taken together with the predominance of photolysis of CCl_3CHO over reaction with the hydroxyl radical) means that the atmospheric breakdown of 111-T leads essentially only to C_1 products. Recent model calculations on the atmospheric degradation of 111-T indeed conclude that the yield of trichloroacetic acid is only (0.06% [19]. For $\text{CCl}_2\text{FCO}\cdot$ and $\text{CClF}_2\text{CO}\cdot$, degradation will essentially follow the sequence of reactions (17), (18) and (21). The $\text{CX}_3\cdot$ radical formed in reactions (16) and (21) will degrade as detailed above, leading to COCl_2 , COCIF or COF_2 , which will then hydrolyze to CO_2 , HCl and HF .

In a similar manner to the alkyl peroxy radicals discussed earlier, the acyl peroxy radicals $\text{CX}_3\text{C}(\text{O})\text{O}_2\cdot$ can also form hydroperoxides or peroxy nitrates (reactions 19 and 20). Nevertheless the latter will be degraded by processes analogous to those for the corresponding alkyl compounds (reactions 8–11'). While the lifetimes for thermal decomposition of the acyl peroxy nitrates $\text{CX}_3\text{C}(\text{O})\text{O}_2\text{NO}_2$ attain thousands of years in the cold upper troposphere, these compounds will not contribute significantly to stratospheric chlorine loading, since: (a) their yield of formation is low, on account of processes which efficiently destroy one of their precursors (reactions 14, 16, 18 or 19); and (b) whatever peroxy nitrate is formed is likely to be photolyzed fairly rapidly or transported to the lower troposphere where thermal decomposition is rapid [ref. 4, chapter 12].

The significant final atmospheric degradation products are listed in the last column of Table 6. The environmental fate and impact of trifluoroacetic acid (TFA), which is the only 'xenobiotic' on the list, is being investigated by the Alternative Fluorocarbons Environmental Acceptability Study [23,24]. Conclu-

Table 6 Atmospheric degradation products from CH₂Cl₂, CCl₃CH₃ and the HCFCs

Parent compounds		Primary gas-phase products	Final atmospheric products
CH ₂ Cl ₂	MC	HCOCl, HCl	HCO ₂ H (?) CO ₂ (?) HCl
CHClF ₂	HCFC-22	COF ₂ , HCl	CO ₂ , HCl, HF
CF ₃ CHCl ₂	HCFC-123	CF ₃ COCl, HCl	CF ₃ CO ₂ H, CO ₂ , HCl, HF
CF ₃ CHClF	HCFC-124	CF ₃ COF, HCl	CF ₃ CO ₂ H, HCl, HF
CCl ₃ CH ₃	111-T	CCl ₃ CHO (→COCl ₂)	CO ₂ , HCl
CCl ₂ FCH ₃	HCFC-141b	CCl ₂ FCHO (→COClF)	CO ₂ , HCl, HF
CClF ₂ CH ₃	HCFC-142b	CClF ₂ CHO (→COF ₂)	CO ₂ , HCl, HF

sions to date may be resumed briefly as follows: (a) TFA is chemically very stable; there are no known significant abiotic sinks in the environment; (b) laboratory studies have shown that certain bacteria can degrade TFA, but on the whole it appears rather refractory to microbial degradation; (c) the concentration of TFA in rainwater, arising from alternative fluorocarbons, is predicted to reach a global mean of 0.16 µg/L by the year 2010 (mainly from HFC-134a, rather than from HCFCs-123 and 124); (d) at this concentration, TFA is unlikely to have any impact on micro-organisms, plants or animals; (e) TFA will not bioaccumulate; (f) TFA has already been detected in rain and surface water in various areas of Europe; the levels are nevertheless too high (0.1 µg/L) to be explained by the current degradation of HCFCs and HFCs; the origin is therefore uncertain; (g) the question has been raised as to whether TFA could accumulate, from one season to the next, in 'seasonal wetlands', i.e. water bodies with little or no outflow; (h) TFA will be the subject of an environmental risk assessment to be carried out this year.

Unsaturated parent compounds

The atmospheric fate of the unsaturated compounds (TRI and PER) has been less unequivocally established than for the saturated ones and indeed there is considerable confusion in the literature which requires clarification. A recent review has focussed specifically on the case of PER [20].

It is well known that under conditions in which the free-radical oxidation of TRI and PER is initiated by addition of a chlorine atom to the double bond of these olefins, the main reaction products are dichloroacetyl chloride (DCAC) and trichloroacetyl chloride (TCAC), respectively. The mechanisms leading to these products were clearly established some 30 years ago [25,26].

The difficulty which arises in conducting and interpreting studies on the 'simulated atmospheric degradation' of these compounds is that even if the oxidation is not initiated by deliberately adding a source of chlorine atoms, the latter are liable to be formed at some stage of the breakdown and their addition to the double bond, which is extremely facile, tends to become the predominant reaction of the parent olefin. DCAC and TCAC have therefore been interpreted as being the likely atmospheric degradation products of TRI and PER [see, for example, ref. 27]. Whether or not this is the case will depend however, on the relative atmospheric importance of chlorine-atom addition to the unsaturates, vs. hydroxyl-radical addition, and on the nature of the products arising from the latter pathway.

Considerable progress has been made in recent years towards answering these questions. In an important study [28] on the oxidation of TRI and PER, initiated by a source of hydroxyl radicals, it was demonstrated that while DCAC and TCAC were major products, their formation was greatly reduced (DCAC) or completely suppressed (TCAC) when ethane was added to the system to scavenge chlorine atoms. Under these conditions, phosgene became the dominant product, although the mass balance in these experiments was well below 100%. It has recently been confirmed that in systems free from chlorine atoms, the yields of C₂ products formed in the oxidation of TRI and PER are negligible [29].

Since the rate constant for addition of a chlorine atom to PER:



is about 300 times greater than that for the addition of the hydroxyl radical:



the possibility of a significant role for reaction (22) in the atmosphere has been raised. If this process

occurred to an appreciable extent, it would indeed lead to the formation of CCl_3COCl , and hence to trichloroacetic acid (TCA) by hydrolysis [20]:



Phosgene would also be formed as a minor product (yield 15%).

The relative atmospheric importance of reactions (22), leading ultimately to TCA, and (1b), leading to C_1 products, will depend however, not only on the ratio of their rate constants, but also on the relative atmospheric concentrations of chlorine atoms and hydroxyl radicals. While the levels of the latter have been fairly well established by modelling and measurement, no direct tropospheric measurements of chlorine atom concentrations have been performed and only indirect evidence is available.

A number of recent studies have indicated that chlorine atoms are much more abundant in the marine boundary layer (up to roughly 1.5 km altitude over the oceans) than in the rest of the troposphere [see, for example, refs. 30–32 and literature cited therein] and from the available evidence it would appear likely that levels of chlorine atoms are high enough relative to hydroxyl radicals for reaction (22) to be faster than reaction (1b) in this boundary layer. For example, ref. 31 reports a $[\text{Cl}]/[\text{HO}\cdot]$ molar ratio of 0.1, so that, taking into account the rate constant ratio of reaction (22) to reaction (1b) of 300, the addition of the chlorine atom would be 30 times faster than that of the hydroxyl radical.

On the scale of the whole atmosphere, however, the picture is very different. In ref. 33, the rate of removal of PER by reaction with the hydroxyl radical is calculated, using as input observed mean tropospheric distributions and seasonal cycles of PER together with model-derived hydroxyl fields. The 'budget' of PER (removal by chemical destruction compared to anthropogenic input) is then balanced by assuming an additional sink due to reaction with chlorine atoms. It is concluded that the latter sink is small or nil. Thus, for the troposphere of the northern hemisphere (NH), where most of the PER is emitted and degraded, and where the budget calculation can therefore be performed with greater certainty than in the southern hemisphere, it is concluded that the mean chlorine atom concentration may be close to zero and is at most 500 molecule/cm³. A similar budget analysis is presented in ref. 34, which also takes into account the possibility of natural production of PER in the oceans, and concludes that the source-strength of the latter is about 100 kt/year and that the global-mean tropospheric chlorine-atom concentration is 500 molecule/cm³.

From the conclusions presented in refs. 33 and 34, and taking the average hydroxyl radical concentration as 10⁶ molecule/cm³ [8], one can conclude that reaction of PER with the chlorine atom may be as high as $(500/10^6) \times 300 = 0.15$ times as fast as reaction with the hydroxyl radical, leading to a yield of 13%. Assuming atmospheric emissions of PER of 400 kt/year (300 kt/year anthropogenic + 100 kt/year natural), the total amount of TCA formed would be 51 kt/year. Further assuming the amounts of TCA formed in each hemisphere to be proportional to the observed hemispheric PER concentrations, namely about 15 pptv (NH) and 2.5 pptv (SH) [refs. 12, 33–34], and taking the annual rainfall in each hemisphere to be 2.5×10^{14} t/year, the calculated mean TCA concentration in precipitation—arising from PER—should be 175 ng/L in the NH and 30 ng/L in the SH. While these levels are of the same order of magnitude as the observed concentrations of TCA in precipitation in remote areas, which are generally in the range 10–100 ng/L [35,36], their distribution is very different, since the concentrations observed in Antarctica are comparable to those found in Arctic and sub-Arctic regions. This evidence strongly suggests that the main source of TCA in precipitation is not PER.

Atmospheric formation of dichloroacetic acid (DCA) from TRI is even less likely than that of TCA from PER, since the rate constant for reaction of TRI with the chlorine atom is only 30 times greater than that for reaction with the hydroxyl radical, compared to a factor of 300 in the case of PER. Furthermore, DCA also appears to be fairly evenly distributed in precipitation in remote areas of both hemispheres [35,36].

The often hypothesized formation of chloroacetic acids (CAAs) in the atmospheric degradation of chlorinated solvents [see, for example, refs. 37–42 and literature cited therein] does not therefore seem very plausible on the basis of either the mechanistic and kinetic evidence, or of the observed global distribution

of CAAs in precipitation. One cannot however, exclude a minor contribution of PER to atmospheric TCA.

Another hypothesized atmospheric product of the degradation of PER, which would have a significant environmental impact if actually formed, is the ozone-depleting substance CCl_4 . This was observed as a product, with a yield of about 8%, in 'smog chamber' studies in the 1970s [43]. More recent work undertaken to check the mechanism of CCl_4 formation in laboratory studies suggests that heterogeneous processes involving TCAC and TCA play an important role and that in the real atmosphere the overall yield of CCl_4 from PER is likely to be lower than 0.1% [20,44].

'ACID RAIN'

Although the chlorinated aliphatic hydrocarbons discussed here break down to give acidic products, which are taken up in rainwater, their contribution to 'acid rain' is in fact very small. The main contributors to the acidity of precipitation, on a global scale, are nitric and sulphuric acids, arising from both natural and anthropogenic sources. Together they represent an acidity of roughly 10^{13} mol H^+ /year [45]. If one assumes that the 1992 emissions of all the compounds considered here (the fluxes of which are given earlier in this chapter) completely degrade to HCl and HF, then the resulting acidity represents less than 5×10^{10} mol/year, i.e. less than 0.5% of the overall acidity from all sources.

CHLORIDE AND FLUORIDE IN RAINWATER

Atmospheric chloride ion production from the compounds reviewed here, totalling about 1.4×10^{12} g/year, is quite insignificant compared with the natural atmospheric chloride flux of roughly $0.6\text{--}1.0 \times 10^{16}$ g/year, arising mainly from sea-salt aerosols [ref 16, chapter XI; ref. 30].

Fluoride production from the HCFCs, amounting to roughly 10^{11} g/year, is low compared with the estimated total atmospheric fluoride flux of $1.0\text{--}8.0 \times 10^{12}$ g/year [ref. 16, chapter XI]. It would contribute about 0.2 $\mu\text{g/L}$ to the fluoride level of rainwater. This should be compared with typical fluoride concentrations in background rainwater of around 10 $\mu\text{g/L}$, i.e. 50 times greater, and with levels of about 1 mg/L used for the fluoridation of drinking water, i.e. 5000 times greater.

CONCLUSIONS

The hydrochlorofluorocarbons (HCFCs) and chlorinated solvents make a small or insignificant contribution to stratospheric ozone depletion (with the exception of 1,1,1-trichloroethane), global warming, 'photochemical smog', 'acid rain' or chloride and fluoride levels in precipitation.

It seems highly unlikely that the chlorinated solvents degrade in the atmosphere to give chloroacetic acids as major products, as has often been claimed in the literature.

In view of their superior environmental acceptability, HCFCs have played an essential role, as interim replacement compounds, in ensuring the speedy elimination of CFCs.

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