

Changes in tropospheric composition and air quality

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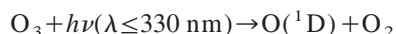
Abstract

Reductions in stratospheric ozone (O_3) cause increased penetration of ultraviolet-B (UV-B) radiation to the troposphere, and therefore increases in the chemical activity in the lower atmosphere (the troposphere). Tropospheric ozone levels are sensitive to local concentrations of nitrogen oxides (NO_x) and hydrocarbons. Model studies suggest that additional UV-B radiation reduces tropospheric ozone in clean environments (low NO_x), and increases tropospheric ozone in polluted areas (high NO_x). Assuming other factors remain constant, additional UV-B will increase the rate at which primary pollutants are removed from the troposphere. Increased UV-B is expected to increase the concentration of hydroxyl radicals (OH) and result in faster removal of pollutants such as carbon monoxide (CO), methane (CH_4), non-methane hydrocarbons (NMHCs), sulfur and nitrogen oxides, hydrochlorofluorocarbons (HCFCs), and hydrofluorocarbons (HFCs). Concentrations of peroxy radicals (both inorganic and organic) are expected to increase, leading to higher atmospheric levels of hydrogen peroxide (H_2O_2) and organic peroxides. The effects of UV-B increases on tropospheric O_3 , OH, methane, CO, and possibly other tropospheric constituents, while not negligible, will be difficult to detect because the concentrations of these species are also influenced by many other variable factors (e.g., emissions). Trifluoroacetic acid (TFA, CF_3COOH) is produced in the atmosphere by the degradation of HCFC-123 (CF_3CHCl_2), HCFC-124 (CF_3CH_2Cl), and HFC-134a (CF_3CH_2F), which are used as substitutes for ozone-depleting substances. The atmospheric oxidation mechanisms of these replacement compounds are well established. Reported measurements of TFA in rain, rivers, lakes, and oceans show it to be a ubiquitous component of the hydrosphere, present at levels much higher than can be explained by reported sources. The levels of TFA produced by the atmospheric degradation of HFCs and HCFCs emitted up to the year 2020 are estimated to be orders of magnitude below those of concern, and to make only a minor contribution to the current environmental burden of TFA. No significant effects on humans or the environment have been identified from TFA produced by atmospheric degradation of HCFCs and HFCs. Numerous standard short-term studies have shown that TFA has, at most, moderate toxicity. © 1998 UNEP. Published by Elsevier Science S.A. All rights reserved.

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1. Introduction

Ultraviolet-B radiation (UV-B, 280–315 nm) is sufficiently energetic to cause photolysis of atmospheric trace gases such as ozone (O_3), nitrogen dioxide (NO_2), hydrogen peroxide (H_2O_2), formaldehyde (HCHO), and nitric acid (HNO_3) (e.g., Refs. [1,2]). The products of photolysis: O, NO, OH, H, HCO, and eventually HO_2 and organic peroxy radicals, are highly reactive. The oxidizing capacity of the troposphere is controlled by these photolytic products, especially hydroxyl radicals (OH), which originate from the photolysis of ozone in the presence of water vapor:



Ozone photolysis in the troposphere is strongly dependent on the available UV-B radiation, and therefore is sensitive to absorption by stratospheric ozone. Fig. 1 shows the rate coefficients for this process, measured at Mauna Loa (HI, USA), as a function of the amount of ozone in the path of the solar beam.

Important atmospheric trace gases, such as CH_4 and other hydrocarbons, several halocarbons, NO_2 , as well as sulfur-containing species, are primarily removed by OH. In addition, OH plays an important role in the production of tropospheric ozone. UV-B radiation is a key environmental factor con-

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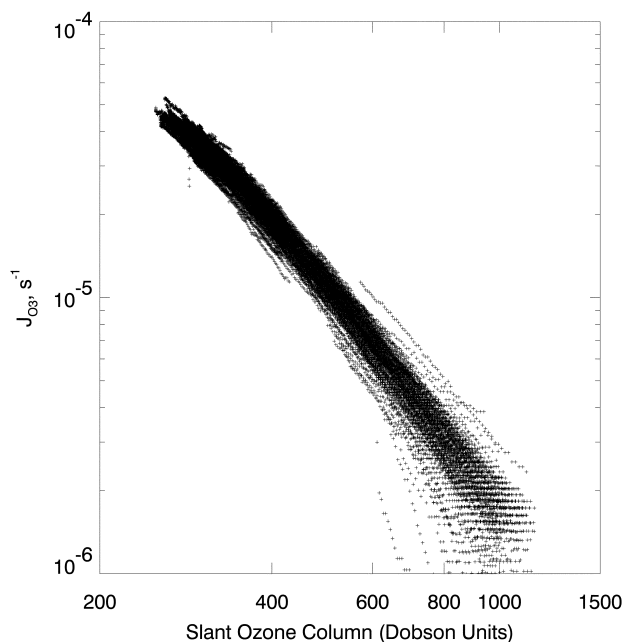


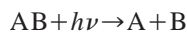
Fig. 1. Dependence of the rate coefficient J_{O_3} for the reaction $O_3 + h\nu$ ($\lambda \leq 330$ nm) $\rightarrow O(^1D) + O_2$ on the amount of ozone in the path of the solar beam (the slant ozone column). The points give over 33 000 direct measurements of J_{O_3} obtained with a chemical actinometer at Mauna Loa, HI, during 1991–1992 by Shetter et al. [3].

trolling tropospheric chemistry. Stratospheric O_3 reduction and its consequence of increased surface UV-B radiation on a global scale have been confirmed [4,5]. A general increase in tropospheric photochemistry and perturbations to concentrations of O_3 and OH radicals are expected. These changes may affect tropospheric composition and air quality. The magnitude of these effects is uncertain because of the complexity and non-linear nature of tropospheric chemistry and is the subject of active research. An assessment of the state of knowledge is presented below.

Hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs) are substitutes for ozone-depleting substances. HCFCs and HFCs are degraded in the atmosphere, and some of these compounds produce trifluoroacetic acid (TFA), which has no known significant atmospheric degradation mechanism. TFA formed in the atmosphere is expected to enter the hydrosphere (mostly via precipitation), and may have detrimental effects on biota if accumulated in sufficient quantities. Production of TFA during the atmospheric degradation of HFCs and HCFCs is assessed below.

2. Increases in UV-B photodissociation rate coefficients

Photodissociation reactions are of the general form



The photodissociation rate coefficient J of species x in the troposphere is calculated by evaluating the integral equation

$$J_x = \int F(\lambda) \sigma_x(\lambda, T) \phi_x(\lambda, T) d\lambda$$

In the above equation, $F(\lambda)$ represents the actinic flux and is independent of species, σ_x and ϕ_x denote the molecular absorption cross section and quantum yield (both dependent on the species x), T is the temperature of the air parcel, and λ is the wavelength of the radiation. The sensitivity of the response of J to increases of UV-B radiation varies significantly for different species [6,7]. To quantify the response to ozone change, Madronich and Granier [6] defined the sensitivity factor S_i :

$$S_i = \ln(J_i^*/J_i) / \ln(O_3^*/O_3)$$

where J_i^* and J_i are the photodissociation rate coefficients of a specific photolysis reaction corresponding to ozone column amounts O_3^* and O_3 , respectively. In essence, the value of S_i gives the percentage increase in J_i resulting from a 1% reduction of stratospheric ozone. Calculated values of S_i are given in Table 1 for selected species of tropospheric importance. As shown in the Table, the S_i for O_3 is the largest, while the S_i for NO_2 is very small. The response of J_{O_3} to stratospheric ozone depletion is significant, while that of J_{NO_2} is negligible. Values given in Table 1 are similar to those computed by Madronich and Granier [6], Madronich et al. [9,10], and Granier et al. [11]. Small differences stem from differences in conditions (e.g., latitudes, solar zenith angles) as well as some model differences.

Fuglestedt et al. [12] calculated monthly J values (for the 15th of each month) of 16 photolytic reactions from 1979 to 1993. Fig. 2 shows the changes in global total ozone observed by satellite-based instruments, and the corresponding calculated changes in globally averaged tropospheric J_{O_3} , the dissociation rate coefficient for O_3 yielding $O(^1D)$. Both are given as annual averages and normalized to 1979 levels. As shown in Fig. 2, the global total ozone column densities decreased by 8% while the J_{O_3} increased by 12% from 1979 to 1993.

3. Changes in tropospheric chemical composition

3.1. Changes in O_3

Tropospheric ozone plays an important role in the atmosphere because its photolysis in the presence of water vapor is

Table 1

Sensitivity (S_i) of photodissociation coefficients of several molecules, to changes in total column ozone. Calculations for upper troposphere, total ozone column of 328 Dobson Units. From [8]

Chemical formula	Name	S_i
O_3	ozone	1.45
HNO_3	nitric acid	0.89
CH_3CHO	acetaldehyde	0.73
CH_3COCH_3	acetone	0.60
HCHO	formaldehyde	0.38
H_2O_2	hydrogen peroxide	0.31
CH_3OOH	methyl hydroperoxide	0.31
N_2O_5	dinitrogen pentoxide	0.30
NO_2	nitrogen dioxide	0.02
HNO_2	nitrous acid	0.01

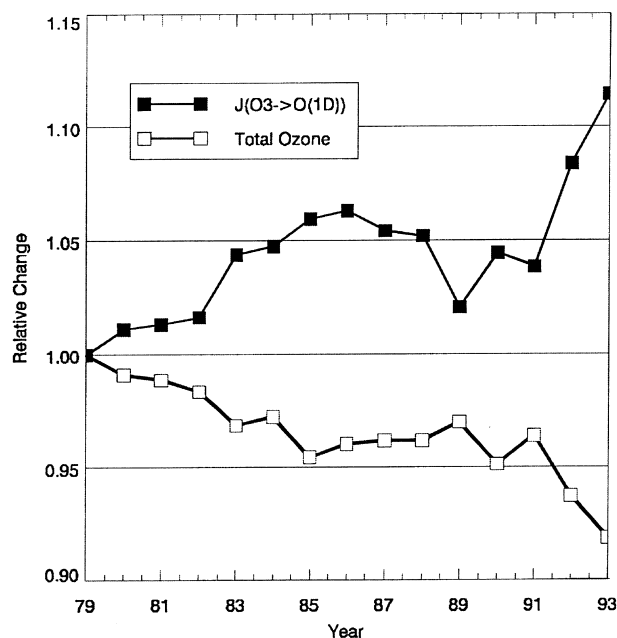
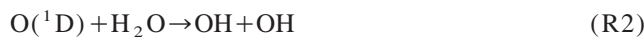
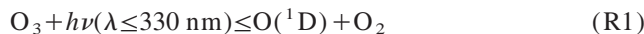


Fig. 2. Development of observed global total ozone densities and calculated averages of J_{O_3} given as annual averages normalized to 1979 levels (from Ref. [12]).

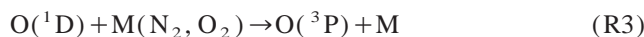
the primary source for hydroxyl radical (OH), which is responsible for the removal of many important trace gases. Moreover, it is an effective greenhouse gas (especially in the upper troposphere), is toxic to organisms, and contributes to global biogeochemistry because of its UV absorption (see Ref. [13]). Ozone also causes damage to many organic materials, particularly if carbon-carbon unsaturation is present, such as in rubber products.

Tropospheric ozone stems from two processes, downward transport from the stratosphere, and in situ photochemical production from the oxidation of hydrocarbons or carbon monoxide (CO) in the presence of NOx. Ozone is removed from the troposphere by in situ chemistry and by deposition at the Earth's surface. The effect of decreased stratospheric ozone on the influx of stratospheric ozone into the troposphere is unknown and is not discussed here. The general effect of increased UV-B radiation on the chemical budget of ozone is discussed below.

The photolysis of ozone followed by reaction of O(¹D) atoms with water vapor is a major photochemical sink for O₃, and the main source of OH radicals:



Only a small fraction of O(¹D) atoms react with water vapor; most O(¹D) atoms undergo relaxation to ground-state O(³P) via collisions with molecular oxygen or nitrogen:



Ground-state O(³P) atoms react mainly with molecular oxygen forming ozone again. The reaction of O(¹D) atoms with water vapor (R2) is the rate-determining step in the photo-

chemical loss of tropospheric ozone through the photolysis of O₃ itself. Additional losses of O₃ occur through reaction with HO₂ radicals via R4 and (to a lesser extent) through reaction of OH radicals with O₃ via R5:

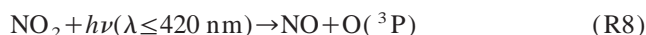


The photochemical loss rate of ozone is therefore approximately:

$$L_{O_3} = [O_3] \{ FJ_{O_3} + k_4[HO_2] + k_5[OH] \}$$

where F is the fraction of O(¹D) that reacts with water vapor (typically a few percent).

The production of ozone in the troposphere occurs through the conversion of NO to NO₂ by peroxy radicals (HO₂ and RO₂), followed by photolysis of NO₂:



Hydrocarbons and carbon monoxide (CO) provide the peroxy radicals through their oxidation and are consumed in the process, while NOx is conserved and thus acts as catalyst in ozone formation. The conversion of NO to NO₂ by peroxy radicals is the rate-limiting step, since the photolysis of NO₂ (R8) and the subsequent reaction (R9) are rapid. The ozone formation rate is given approximately by

$$P_{O_3} = [NO] \{ k_6[RO_2] + k_7[HO_2] \}$$

The chemical budget of ozone in a given region is governed by the rate of net ozone production, $P_{O_3} - L_{O_3}$. The effect of increased UV-B radiation on the chemical budget of ozone, i.e., the change of $P_{O_3} - L_{O_3}$, is complex. An increase in UV-B radiation will increase J_{O_3} and hence increase the rate of ozone destruction L_{O_3} . Considering the production of ozone, J_{NO_2} is quite insensitive to increasing UV-B radiation (see Table 1), but the increase of UV-B radiation will lead to increased concentrations of hydroxyl radicals and thus to increased concentrations of HO₂ and RO₂ radicals, which will enhance the production of ozone if NOx is available. An increase in UV-B radiation will enhance both destruction and production process for tropospheric ozone. Since P_{O_3} is dependent on the NOx abundance and L_{O_3} is, to first approximation, insensitive to NOx, the sign and magnitude of trends in tropospheric O₃ (from UV-B radiation increases) are dependent on the NOx concentration.

Several model studies have addressed the question of how tropospheric ozone may respond to UV-B increases. Liu and Tranter [14] used a zero-dimensional model (chemistry only, no transport) to show that the sign (increase or decrease) of tropospheric ozone changes depends sensitively on the local NOx concentrations. At the high NOx levels typical of urban conditions, increases in UV-B are expected

to result in higher levels of surface ozone, so that more frequently air quality standards may be exceeded [15], or alternatively more stringent regulations may be required to meet current standards [16]. Qualitatively similar results were found using one-dimensional models (chemistry plus vertical transport) by Thompson et al. [17] and by Ma [8], but with quantitative results shown to depend also on other chemical constituents (e.g., hydrocarbons, CO). The study by Ma [8] further suggests that in the upper troposphere the changes in ozone are probably rather small, due to the usually very low concentrations of water vapor, which therefore reduce the importance of reactions R1–R3 (and thus of J_{O_3}). Increases in J_{O_3} become more important in the middle and lower troposphere, where higher levels of water vapor are found, and especially in the continental boundary layer if significant NOx concentrations are present. The results of these studies are sensitive to whether the calculations are carried out over polluted areas (e.g., the troposphere above industrialized regions) or more pristine regions (e.g., over remote ocean regions). Fuglestedt et al. [12,18] used a two-dimensional model of the global troposphere (i.e., allowing for variations with both altitude and latitude). Calculations suggest that at high latitudes of the Southern Hemisphere there is a large reduction in tropospheric O₃ in response to stratospheric ozone depletion in the spring, but the maximum effect, a 16% reduction in tropospheric O₃ at 2.5 km altitude over 60–80°S, is delayed relative to the October minimum in stratospheric ozone by about two months to early summer (December), when solar UV-B actinic fluxes are highest. At middle and high latitudes of the Northern Hemisphere, increased UV-B radiation is predicted to increase tropospheric O₃ in mid-spring (April) because of high levels of NOx and other ozone precursors (CO and hydrocarbons), but some reductions were also noted for high northern latitudes in late spring (May and June).

Very little observational evidence exists in support of these model calculations, due mostly to the sparsity of tropospheric ozone measurements (especially vertical profiles) and to the difficulty of attributing any observed trends to UV-B increases rather than any other of the numerous factors that also contribute to the tropospheric ozone budget, e.g., trends in emissions of the precursors NOx and hydrocarbons. The most relevant observations are those obtained in polar regions, because the changes in stratospheric ozone (and therefore tropospheric UV-B levels) are larger than those found for mid-latitudes and the tropics. Long-term observations at the South Pole indicate that some enhanced net destruction of surface O₃ may already have occurred in association with the large stratospheric ozone losses in that region [19]. More recently, Taalas et al. [20] have studied vertical profiles obtained from balloon-borne ozone sondes over 1988–1994 at Marambio, Antarctica (64°S), and at Sodankyla, Finland (67°N). During months with substantial stratospheric ozone loss, ozone levels were found to be reduced also in the upper troposphere (6–8 km), averaging 12.8% reductions in the Antarctic and 10.0% in the Arctic. It

was proposed that both reductions in the ozone flux from the stratosphere to the troposphere and the changes in the photochemistry of the upper troposphere are possible reasons for this correlation between upper tropospheric and lower stratospheric ozone concentrations. In the middle (3–5 km) and lower (0–2 km) troposphere, tropospheric ozone deviations were found to be negative over Antarctica but positive in the Arctic, in qualitative agreement with the model-derived expectations given the more polluted conditions present in the high latitudes of the Northern Hemisphere (relative to Antarctica).

Tropospheric ozone concentrations are sensitive not only to UV radiation, but also to many other factors including concentrations of nitrogen oxides, water vapor, carbon monoxide, methane, and non-methane hydrocarbons. Long-term changes in the emission sources of these compounds are known to be occurring, and their effects on tropospheric ozone, relative to the effects of increased UV radiation levels, are at present highly uncertain.

3.2. Changes in HOx

The odd-hydrogen radicals (HOx = OH + HO₂) play a key role in tropospheric chemistry, as already illustrated in reactions R1–R9. Important sources of these radicals include the photolysis of ozone, hydrogen peroxide (H₂O₂), formaldehyde (HCHO), and several other inorganic and organic species. Table 1 shows that many of the corresponding photolysis rate coefficients are sensitive to the amount of stratospheric ozone.

Model calculations consistently show that increased UV-B actinic fluxes (associated with stratospheric ozone reductions) yield higher tropospheric concentrations of the HOx radicals [12,14,17,8,18,21]. For example, Fuglestedt et al. [12] calculated that the increases in UV-B radiation over 1979–1993 have led to an increase in OH on the global scale of about 8%, with the largest fractional increases (about 40%) found for high southern latitudes in October. The modeling study by Ma [8] investigated the potential changes in the concentrations of OH, HO₂, and CH₃O₂ in the troposphere for a 10% reduction of stratospheric ozone. The concentration of OH is predicted to increase by 8–9% in the lower troposphere over global scales, due mainly to the increase in J_{O_3} . The concentrations of HO₂ and CH₃O₂ are predicted to increase by about 4 to 6%, respectively, due to the increased oxidation rate of CO and hydrocarbons by OH.

There is little direct observational evidence in support of the model-predicted increases in HOx. Several studies have attempted to estimate recent global trends in OH concentrations based on measurements of methyl chloroform concentrations and the requirement that its sources (which are fairly well known) be balanced by its atmospheric sink, which is believed to be primarily reaction with OH. The study by Prinn et al. [22], which updates their earlier study [23], found no statistically significant trend on OH over 1978–1990. More recently, a re-analysis of the methyl chloroform data [24]

suggests a slight positive OH trend, about $0.4\text{--}0.5\%$ yr^{-1} , over 1978–1993 at the five monitoring stations considered. However, such OH trends can result from many different atmospheric changes, including increases in O_3 and H_2O_2 (precursors to OH) especially in the northern hemisphere as a result of changing emissions of NO_x , CO, and hydrocarbons; from increases in water vapor concentrations above tropical oceans (possibly associated with climate warming); and from changes in temporal and geographical patterns of other human activities (e.g., biomass burning). It is at present difficult to assess how much of any observed trends in global OH concentrations can be attributed to UV-B increases stemming from stratospheric ozone depletion.

3.3. Changes in CH_4 and CO

The atmospheric concentrations of methane (CH_4) and carbon monoxide (CO) are determined by the balance between emission sources (many of which are related to human activities) and atmospheric removal, mostly by OH radicals. For CO an important additional source is the atmospheric oxidation of CH_4 and other hydrocarbons. Short-term and long-term variations in atmospheric CH_4 and CO concentrations stem from the superposition of these sources and sinks, and, when local concentration measurements are considered, from transport processes that redistribute the gases to regions far from the original emission sources. The effect of possible tropospheric OH increases (from stratospheric ozone depletion) on the average concentrations of CO and CH_4 is estimated in many cases to be smaller than, or comparable to, the effects of changes in emission sources, and is therefore difficult to detect by inspection of the available long-term CO and CH_4 monitoring data records. The estimated effects of the tropospheric UV-B increases are not negligible (at least based on model estimates), and must therefore be given some consideration as contributing to the overall trends [6,12,14,17,18,21,25].

Analyses of polar ice cores [26] indicate that pre-industrial atmospheric CH_4 concentrations were about 650 ± 40 ppb. Atmospheric methane concentrations started to increase about 100 years ago, probably because of human activities linked to rising population. The rate of increase has not been constant. In the late 1970s the rate of increase was approximately 16 ppb yr^{-1} , while in the later part of the 1980s the increase was about 9 ppb yr^{-1} . To the extent that increased UV-B radiation is expected to lead to higher levels of OH, a correspondingly faster loss of CH_4 is expected. Fig. 3 shows the change of CH_4 concentrations, calculated with a two-dimensional model [12], that are expected to result from increased UV-B radiation alone. The changes in the global annual growth rate are also shown. The Figure shows that the increased UV-B radiation may have reduced the global methane concentration by as much as 30 ppb from 1980 to 1993, and thus may have contributed partly to the overall declining trend observed since 1980.

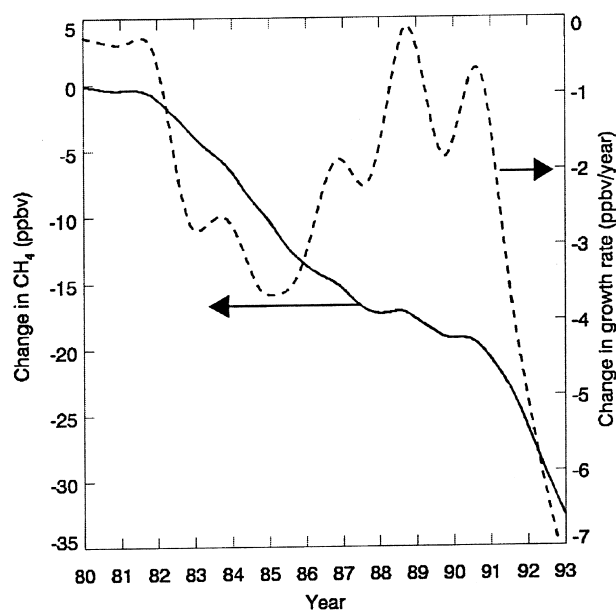


Fig. 3. Predicted change in the global level and growth rate of CH_4 due to UV increases (from Ref. [12]).

CO concentration measurements suggest an increase in the CO abundance of 1% yr^{-1} over the past 40 years in the Northern Hemisphere [27], while no significant trend was found in the Southern Hemisphere [28]. A large decrease in the CO concentrations was observed between 71°N and 41°S during June 1990–June 1993, with a decrease of 15–18 ppbv at most stations located north of 25°N , and of 8–12 ppbv between 41°S and 20°N [29]. To the extent that OH increases are expected in association with stratospheric ozone depletion, global decreases in CO concentrations are expected. Granier et al. [30] used a global three-dimensional chemical transport model to investigate possible causes for the observed CO decrease, and concluded that changes in total ozone abundance may be responsible for global decreases in CO of about 3.5 and 1.7 ppbv in the Northern and Southern Hemispheres, respectively, accounting for about 20% of the observed CO decreases. The large remaining decreases were attributed to decreased industrial and transportation CO sources, to decreased biomass burning, and to a global decrease in surface air temperatures for several years following the eruption of Mount Pinatubo (Philippines).

An additional study, though not directly related to stratospheric ozone depletion, illustrates the sensitivity of tropospheric CH_4 and CO to stratospheric transmission of solar UV-B wavelengths. Observations showed sharp increases in the growth rates of CH_4 and CO in the tropics and middle southern latitudes for several months following the eruption of Mount Pinatubo on 15 June, 1991. This volcanic eruption emitted approximately 20 Mt of SO_2 and $3\text{--}5$ km³ of ash into the upper troposphere and lower stratosphere. Calculations using a radiative transfer model showed that the tropospheric UV-B actinic flux in the tropics was attenuated by about 12% immediately after the eruption due to direct absorption by SO_2 , and was perturbed for up to one year after the eruption

due to scattering by sulfate aerosols [31]. This study suggested that the decreased UV-B flux caused a decrease of OH concentrations and therefore led to the observed anomalously large growth rates for CH₄ and CO during late 1991 and early 1992. Methyl chloroform, the atmospheric removal of which is also initiated by OH, showed a small positive anomaly in Cape Grim, Australia, consistent with observations for CH₄ at comparable latitudes. The increased growth rates were short lived, as CH₄ and CO growth rates showed strong decreases during late 1992 and 1993 [29,32]. Bekki et al. [25] suggested that for several years after the Mount Pinatubo eruption, faster rates of removal of CO and CH₄ may have resulted in lower stratospheric ozone (and therefore higher tropospheric UV and OH); however, measurements of the isotopic composition of CH₄ are more consistent with decreased emissions, possibly from biomass burning [33].

In summary, the potential perturbations to CO and CH₄ concentrations from increased tropospheric UV-B levels are only one of many factors contributing to the observed trends and variations. Changes in emission sources are well recognized, although not fully quantified. Changes in OH concentrations have also likely occurred due to many factors, in addition to UV-B changes, including trends in precursor species such as hydrocarbons and NO_x (and therefore tropospheric ozone), changes in emissions of biogenic (natural) hydrocarbons from changes in land use, climatic changes in temperature and water vapor, and possibly even other changes in actinic fluxes due to trends and variabilities of clouds and aerosols. The net response of atmospheric CO and CH₄ concentration is, to first order, a result of the superposition of multiple driving factors, but it remains exceedingly difficult to separate and quantify the importance of each of these contributions.

3.4. Changes in H₂O₂

Hydrogen peroxide (H₂O₂) is one the principal oxidants in the troposphere, and plays an important role in the aqueous-phase oxidation of SO₂ to SO₄²⁻. Model calculations (e.g., Refs. [12,18]) suggest that tropospheric H₂O₂ concentrations should increase in response to enhanced tropospheric UV-B actinic fluxes, in parallel to the expected increases in HO_x (especially HO₂). The calculated H₂O₂ increases are greatest in low NO_x regions, where the formation of peroxides is the predominant fate of HO_x radicals. Measurements at Eurocore (central Greenland, 72°N) showed a 50% increase of the H₂O₂ concentration in the firn/ice during the last 200 years, with most of the increase having occurred between 1960 and 1988 [34]. Recent studies at Summit, Greenland (72°N) in 1995 confirmed the H₂O₂ increases found in ice cores, and showed a further increase of the H₂O₂ concentration since 1988, leading to an overall increase of 60 ± 12% during the last 150 years [35]. Photochemical model calculations for Summit [36] indicate that ozone depletion over 1980–1990 (from 395 to 360 Dobson Units) gives an atmospheric H₂O₂ increase of about 7% for summer,

which could account for about one third of the increase observed over that time period. Anklin and Bales [35] proposed that the recent increase could be partly due to increasing UV-B radiation caused by the stratospheric ozone depletion and a combination of changes in tropospheric chemistry from other causes, such as increased emissions of hydrocarbons and CO.

4. Atmospheric production and fate of trifluoroacetic acid

Hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs) have been identified as alternatives to chlorofluorocarbons (CFCs). Among this class of products, HCFC-123 (CF₃CHCl₂), HCFC-124 (CF₃CHFCl), and HFC-134a (CF₃CH₂F) are expected to degrade to give trifluoroacetic acid (TFA). Environmental TFA can also be produced during the oxidation of other organofluorine compounds released to the atmosphere by human activities, e.g., halothane and isoflurane anesthetics. TFA is widely used in the chemical industry in processes where it is either consumed or becomes part of a chemical waste stream.

HCFCs and HFCs are used as CFC substitutes in a variety of applications. A substantial body of experimental and theoretical work has been undertaken to determine the atmospheric chemistry and environmental impact of these compounds. While some minor uncertainties exist, our current understanding of the atmospheric chemistry of the commercially important HFCs and HCFCs is now well established [37,38]. A generalized scheme for the atmospheric oxidation of a haloalkane that could degrade to give TFA is given in Fig. 4.

Oxidation is initiated by reaction with OH radicals giving a halogenated alkyl radical, which adds O₂ to give the corresponding peroxy radical (RO₂). Peroxy radicals react with three important trace species in the atmosphere: NO, NO₂, and HO₂ radicals. Reactions with HO₂ and NO₂ delay, but do not prevent, the conversion of peroxy (CF₃CXYO₂) into alkoxy (CF₃CXYO) radicals. Reactions of haloperoxy radicals with NO are rapid and give the alkoxy radical with essentially 100% yield. The atmospheric fate of the alkoxy radical, CF₃CXYO, is either decomposition or reaction with O₂. Decomposition occurs by C–C bond fission, or by the elimination of a Br, Cl, or CF₃ group. The atmospheric fate of CF₃C(O)X (X = F or Cl) is dominated by incorporation into rain–cloud–sea water followed by rapid hydrolysis to TFA. Photolysis is a competing loss mechanism for CF₃C(O)Cl and limits its conversion into CF₃C(O)OH to 60% [39]. There are no competing loss processes for CF₃C(O)F; it is converted entirely into CF₃C(O)OH. Although CF₃C(O)OH is produced in aqueous-phase chemistry, is highly soluble, and partitions into the water phase [40], the evaporation of cloud droplets can transfer CF₃C(O)OH to the gas phase, where it can react with OH radicals. However, this reaction is slow [41,42] and is only

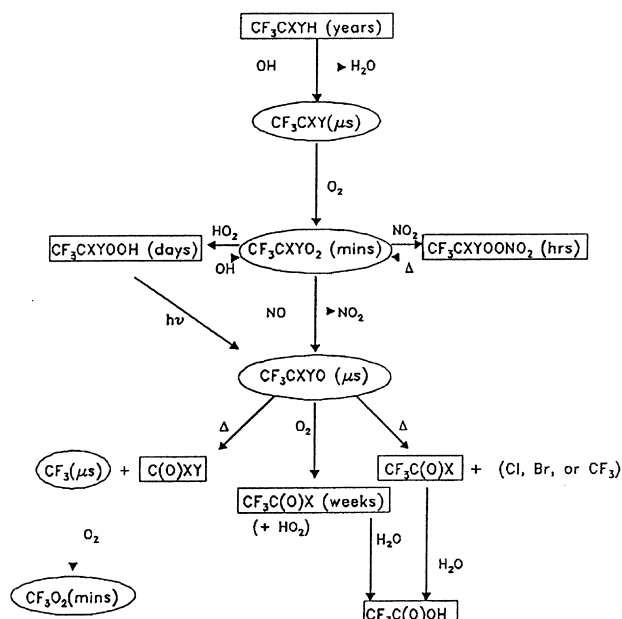


Fig. 4. Generalized scheme for the atmospheric oxidation of a halogenated organic compound, CF_3CXHYH ($X = \text{Cl}$ or F , and $Y = \text{Cl}$, H , Br , or CF_3). Radical intermediates are enclosed in ellipses. Typical lifetime estimates are given in parentheses.

a minor ($< 5\%$ [43]) loss of $\text{CF}_3\text{C}(\text{O})\text{OH}$. The main atmospheric fate of $\text{CF}_3\text{C}(\text{O})\text{OH}$ is rain-out to the surface.

To assess the potential for a halocarbon to produce TFA, it is necessary to quantify the yield of trifluoroacetyl halide in its gas-phase oxidation mechanism. This has been established for all the commercially significant halocarbons. Six compounds, listed in Table 2, have been identified that degrade to give trifluoroacetyl halide. With the exception of HFC-134a, the atmospheric oxidation mechanisms of the compounds given in Table 2 are relatively simple. Atmospheric oxidation of halothane [48], isoflurane, and HCFC-123 [49–51] gives $\text{CF}_3\text{C}(\text{O})\text{Cl}$, of which approximately 60% undergoes hydrolysis to give $\text{CF}_3\text{C}(\text{O})\text{OH}$. Oxidation of HCFC-124 [50,52] and HFC-227ea [53,54] gives $\text{CF}_3\text{C}(\text{O})\text{F}$, which is then converted into $\text{CF}_3\text{C}(\text{O})\text{OH}$. Current and projected use of HFC-227ea is minor. The oxidation mechanism of HFC-134a is complicated by two factors. First, vibrationally excited CF_3CFHO^* radicals are formed in the $\text{CF}_3\text{CFHO}_2 + \text{NO}$ reaction and two thirds of these vibrationally excited radicals undergo decomposition via C–C bond

scission on a time scale short compared to that needed for chemical reactions [55]. Secondly, reaction with O_2 competes with decomposition via C–C bond scission for the available thermalized CF_3CFHO radicals [56–58]. The net effect is that the molar yield of $\text{CF}_3\text{C}(\text{O})\text{F}$, and hence $\text{CF}_3\text{C}(\text{O})\text{OH}$, is approximately 0.13 [55].

An estimate for the concentration of $\text{CF}_3\text{C}(\text{O})\text{OH}$ in rain water can be obtained as follows. Halothane and isoflurane have been used as anesthetics for many years. It is estimated that the current emissions of halothane and isoflurane are 1500 and 750 t yr^{-1} , respectively [59]. The atmospheric lifetimes of halothane and isoflurane are short (see Table 2) compared to the time scale over which they have been emitted into the atmosphere. Assuming that these compounds are in steady state, then their degradation gives a combined yield of 1540 t yr^{-1} of $\text{CF}_3\text{C}(\text{O})\text{Cl}$. Accounting for photolysis, this results in a global deposition rate of 800 t yr^{-1} of $\text{CF}_3\text{C}(\text{O})\text{OH}$. Current atmospheric concentrations of HCFC-123 and HCFC-124 are at, or below, the detection limit of 0.1 ppt [59]. Thus, upper limits for atmospheric burdens of these gases are 2500 t for HCFC-123 and 2300 t for HCFC-124. Combining these burdens with the lifetime values given in Table 2 and accounting for photolysis of $\text{CF}_3\text{C}(\text{O})\text{Cl}$, it can be concluded that upper limits for the flux of $\text{CF}_3\text{C}(\text{O})\text{OH}$ from HCFC-123 and HCFC-124 are 760 and 320 t yr^{-1} , respectively. HFC-134a is present at a concentration of 2.5 pptv in the Northern Hemisphere and 1.2 pptv in the Southern Hemisphere [60,61], from which it can be estimated that the present atmospheric burden of HFC-134a is 31 000 t. Combining this burden with the lifetime and yield values in Table 2 gives a $\text{CF}_3\text{C}(\text{O})\text{OH}$ flux of 300 t yr^{-1} from the atmospheric oxidation of HFC-134a. Combining the contributions from these known sources gives an upper limit for the estimated contemporary TFA formation rate of $800 + 760 + 320 + 300 = 2180 \text{ t yr}^{-1}$. The known TFA precursors are relatively long lived and therefore distributed on a global scale. The annual global rainfall is $4.9 \times 10^{17} \text{ l}$ [62] and the global average TFA concentration in rainwater is expected to be less than 5 ng l^{-1} . Detailed computer modeling studies using appropriate global OH fields, halocarbon emissions, and rainfall patterns have confirmed that the simple approach adopted above provides a reasonable estimate of expected TFA concentrations in rainwater [43,63,64].

Table 2

Compounds known to produce TFA ($\text{CF}_3\text{C}(\text{O})\text{OH}$) in the atmosphere

Compound	Molecular weight	Common name	Molar $\text{CF}_3\text{C}(\text{O})\text{OH}$ yield	Atmospheric lifetime (years)
CF_3CHClBr	197.5	halothane	0.6	1.2 [44]
$\text{CF}_3\text{CHClOCHF}_2$	184.5	isoflurane	0.6	5 [45]
CF_3CHCl_2	153	HCFC-123	0.6	1.5 [46]
CF_3CHFCl	136.5	HCFC-124	1.0	6.0 [46]
$\text{CF}_3\text{CH}_2\text{F}$	102	HFC-134a	0.13	14.6 [47]
$\text{CF}_3\text{CHFCF}_3$	170	HFC-227ea	1.0	36.5 [47]

To assess the future contribution of HFCs and HCFCs to levels of TFA in rainwater, we need to consider future emission scenarios for these compounds, which are reviewed in detail elsewhere [59]. Use of halothane and isoflurane anesthetics is anticipated to remain constant, or perhaps decline. Production of HCFC-123 and HCFC-124 is regulated under the Montreal Protocol and will be phased out. Production of HFC-134a is not regulated and is anticipated to increase significantly. Using an emission scenario from the US Environmental Protection Agency (EPA) combined with a three-dimensional atmospheric model, Rodriguez et al [65] calculated that in the year 2020 the atmospheric decomposition fluxes of HFC-134a, HCFC-123, and HCFC-124 will be 115, 20, and 20 kt yr⁻¹, respectively. Multiplying by the appropriate CF₃C(O)OH molar yields in Table 2 and making the necessary adjustments for the molecular weights involved, a flux of 16.7 + 8.9 + 16.7 = 42.3 kt yr⁻¹ is estimated and translates to a global average concentration in rainwater of 86 ng l⁻¹. Kotamarthi et al. [66] estimated the global average TFA concentration in rain water for 2010 to be in the range 100–160 ng l⁻¹.

Water bodies characterized by little or no outflow and high evaporation rates may have the potential to accumulate TFA. Tromp et al. [67] developed a concentration-dependent model and estimated that TFA concentrations of 100 µg l⁻¹ could be achieved in this type of water body in as few as 30 years, with rainfall concentration only 1 µg l⁻¹. In contrast, a recent analysis by Boutonnet et al. [59] questioned the validity of the assumptions inherent in the Tromp et al. study, concluding that accumulation of TFA in seasonal wetlands ‘‘appears to be highly improbable’’. The potential for accumulation of TFA remains unclear.

High concentrations of TFA have been observed in contemporary water and air samples, suggesting the existence of one or more large unknown sources. Samples of rain and surface waters (oceans, rivers, lakes, and springs) have been obtained from many geographical areas (USA, Canada, Australia, South Africa, Germany, Israel, Ireland, France, Switzerland, Finland) and show that TFA is a ubiquitous contaminant of the hydrosphere [68–71], with values up to 40 900 ng l⁻¹ [69]. The average TFA concentration in rain water observed in Bayreuth during 1995 was 100 ng l⁻¹ [68]. The source of the currently observed levels is unknown and puzzling. The observed TFA concentrations are orders of magnitude larger than those predicted to result from the atmospheric degradation of the replacement HCFCs and HFCs.

5. TFA in the biosphere

5.1. Environmental distribution

Trifluoroacetic acid, CF₃C(O)OH or TFA, is a strong organic acid with a pK_a of 0.23 and it is miscible with water (solubility over 10 000 g l⁻¹). The vapor pressure is rela-

tively high, 105.7 hPa at 20°C, and the partition coefficient n-octanol/water (log) is -0.2. Laboratory studies have been performed to assess the strength of binding of TFA to a variety of soil types [72,73]. Some studies showed that TFA did not adsorb to soil; others showed that TFA generally interacted weakly with most soils but was strongly adsorbed by some soils containing high levels of organic matter. The data are not necessarily contradictory but may reflect the heterogeneity of soils tested.

5.2. Degradation

TFA is a stable ion in the aqueous phase and no significant loss process such as hydrolysis, photolysis, or formation of insoluble salts has been identified. There have been two reports of TFA degradation under anaerobic conditions. In the first study, natural sediments reduced TFA [74]. However, even though this work was done in replicate, the experimenters and others were unable to reproduce it in subsequent studies [75,76]. In the second study [77], labelled TFA was removed from a mixed anaerobic in vitro microcosm. Limited evidence of decarboxylation has also been reported for two strains of bacteria grown under highly specific conditions [77]. A field study indicated that TFA was retained in vegetation and soil of a temperate North American forest, especially in the case of wetlands with organic soils [73,78].

5.3. Bioaccumulation in animals and plants

Potential for bioaccumulation in animals is highly unlikely due to the extremely low logK_{ow} (-0.2). Due to its high solubility, TFA can accumulate in plants via root uptake of water. This phenomenon is supported by experimental data which demonstrate that TFA is a xylem mobile herbicide, transported through the stem and accumulated in leaves [79]. The bioaccumulation in vegetation calculated according to the equation logCF = 5.943 - 2.385logMW gives a value of 10.89 for the concentration factor (CF), of the same order of magnitude as those experimentally observed.

TFA is not concentrated in lower aquatic-life forms such as bacteria, small invertebrates, oligochaete worms, and some aquatic plants including *Lemna gibba* (duckweed). In terrestrial higher plants such as sunflower and wheat some bioaccumulation was seen [80]. This appeared to be related to uptake with water and then concentration due to transpiration water loss. When transferred to clean hydroponic media, some elimination of TFA was seen. Also, over 80% of the TFA in leaves was found to be water extractable, suggesting that no significant metabolism of TFA had occurred.

5.4. Ecotoxicology

5.4.1. Effect of TFA on activated sludge

The semi-continuous activated sludge test indicated that TFA had no discernible effect on the performance of the sludge for the biodegradation of organic carbon [81].

5.4.2. Effect of TFA on metabolism of microbial communities

The mineralization of acetate to carbon dioxide is a key link in the biogeochemical carbon cycle. Therefore it is essential to know whether TFA, which is structurally close to acetate, could interfere with acetate metabolism. Experimental results [82] suggest that TFA at concentrations several orders of magnitude higher than those anticipated in the environment did not impact on acetate mineralization to carbon dioxide nor did it affect incorporation of acetate into cellular material. The effect of TFA has been investigated in free-living nitrogen-fixing bacteria [83]. The experiments were designed to determine whether TFA was specifically toxic to nitrogen fixation. No effect of TFA on growth or N₂ fixation with ammonium ion as the nitrogen source was noted at concentrations as high as 100 ppm TFA. It has been shown that TFA has no effect on methanogenic environments where acetate is an important intermediate [74].

5.4.3. Aquatic toxicity

In acute toxicity tests no effects of NaTFA on water fleas (*Daphnia magna*) and zebra fish (*Brachydanio rerio*) were found at a concentration of 1200 mg l⁻¹ [84]. A seven-day study with duckweed (*Lemna gibba*) revealed a predicted No Effect Concentration (NOEC) of 300 mg l⁻¹ [85]. Based on the results of five toxicity tests with *Selenastrum capricornutum*, a NOEC of 0.12 mg l⁻¹ was found. However, algal toxicity tests with NaTFA and *Chlorella vulgaris*, *Scenedesmus subspicatus*, *Chlamydomonas reinhardtii*, *Dunaliella tertiolecta*, *Euglena gracilis*, *Phaeodactylum tricorutum*, *Navicula pelliculosa*, *Skeletonema costatum*, *Anabaena flos-aquae* and *Microcystis aeruginosa* resulted in NOEC values which were all higher than 100 mg l⁻¹ [86–88]. Recovery of the growth of *S. capricornutum* was found when TFA was removed from the test solutions; therefore TFA should be considered algistatic and not algicidal for *S. capricornutum*. The reason for the unique sensitivity of this strain is unknown, but a recovery of the growth rate was seen when citric acid was added, suggesting a competitive inhibition of the citric acid cycle.

One semi-field study [89] with mesocosm streams has been conducted with NaTFA to study the potential effects of TFA on freshwater algal communities and primary productivity. Long-term exposure to a mean NaTFA concentration of 31–32 µg l⁻¹ had no effect on the primary productivity of the diatom-dominated algal flora. Effects on organic carbon excretion, which were related to high levels of TFA, were noted in some experiments. TFA did not alter the algal species composition in the stream mesocosm.

5.4.4. Terrestrial plants

Application of NaTFA at 1000 mg l⁻¹ to seeds of sunflower, cabbage, lettuce, tomato, mungbean, soybean, wheat, corn oats, and rice did not affect germination [90,91]. Foliar application of a solution of 100 mg l⁻¹ of NaTFA to field-grown plants did not affect growth of sunflower, soya, wheat,

maize, oilseed rape, rice, and plantain [92]. When plantain, wheat, and soya were grown in hydroponic systems containing NaTFA, no effects were seen on plantain at 32 mg l⁻¹, on *Triticum* and soya at 1 mg l⁻¹, and on wheat at 10 mg l⁻¹ [92–94].

5.5. Mammalian toxicity

TFA is not metabolized in mammalian systems. The half-life of TFA in humans is 16 h. As expected, the free acid is more acutely toxic than the sodium salt. In one study, two out of five mice died from a dose of 150 mg kg⁻¹ of HTFA, an effect comparable to that seen with an equimolar dose of HCl [95]. In contrast, no deaths were seen when mice were given an oral dose of 5.000 g kg⁻¹ of NaTFA. In studies involving single intraperitoneal injections of doses up to 2 g kg⁻¹, only mild liver toxicity was seen [96,97]. There was only one report of an acute inhalation toxicity study [98]. This study involved single 2 h exposures of both rats and mice. The LC₅₀ for mice was 13.5 mg l⁻¹ (2900 ppm) and for rats it was 10 mg l⁻¹ (2140 ppm). This would classify TFA as having low inhalation toxicity. These same authors reported that the irritation threshold for humans was 54 ppm.

As one would expect of a strong acid, HTFA is a severe irritant to the skin [98,99]. Concentrations as low as 2% were moderate skin irritants. It would be expected to be a severe eye irritant. When conjugated with protein, it has been shown to elicit an immunological reaction [100–104]; however, it is unlikely that TFA itself would elicit a sensitization response [101,102,105]. Repeated administrations of aqueous solutions have shown that TFA can cause increased liver weight and induction of peroxisomes [106,107]. Relative to the doses (0.5% in diet or 150 mg kg⁻¹ day⁻¹) the effects are mild.

In a series of Ames assays, TFA was reported to be non-mutagenetic [108]. Its carcinogenic potential has not been evaluated. Although TFA was shown to accumulate in amniotic fluid following exposure of pregnant animals to high levels of halothane (1200 ppm), no foetal effects were seen. Given the high levels of halothane exposure, it is unlikely that environmental TFA is a reproductive or developmental hazard.

5.6. TFA risk assessment

The environmental risk from TFA as a degradation product of CFC substitutes can be deduced from the value of the ratio of exposure to effect, or of Predicted Environmental Concentrations to Predicted No Effect Concentrations (PEC/PNEC). To derive a PEC, production and releases of parent compounds, along with rates of transformation into TFA, have been modeled. A range of concentrations in rain water has been calculated, taking into account geographical variations (OH radical concentrations, amount of rain, regional releases of parent compound). A rough average concentration of 0.1 µg l⁻¹ in rainwater, by the year 2020, is taken as

a global PEC. But an important question remains concerning the origin of the large current levels of TFA that have been measured in the environment (fresh and marine surface waters, rain, and air) and which cannot be explained by the known industrial sources.

The physico-chemical properties of TFA allow a prediction of no bioaccumulation in animals. In terrestrial plants, accumulation can take place but is transient and effects on vegetation can be observed only in experiments using non-environmentally relevant concentrations ($102\text{--}106\text{ mg l}^{-1}$).

TFA is not retained in soils, with the exception of those having high organic content; in this case, it is uncertain if it can still be bioavailable. Generally speaking, TFA remains associated with water and has been shown to be ineffective on several types of metabolism related to basic biogeochemical cycles.

Given the fact that deposited TFA would remain in water, a number of studies have been done aiming to derive a PNEC in the aquatic compartment. Standard acute tests on fish and daphnia carried out with NaTFA show no effects on animals at large concentrations (up to 1 g l^{-1} TFA). This is reinforced by toxicological data on mammals. On the other hand, the NOEC for the standard algal species *Selenastrum capricornutum* is around 0.10 mg l^{-1} (as TFA). To see if this sensitivity was general among algae, 10 other species belonging to four different classes have been tested: no one was sensitive to NaTFA (NOEC $> 100\text{ mg l}^{-1}$). It is proposed to use as a PNEC_{aquatic} (the NOEC of this species of algae) as a worst case, without any further safety factor. So, PNEC_{aquatic} = 0.1 mg l^{-1} .

A large amount of research has been devoted to effects on higher plants, as they could be exposed to TFA in rain water through leaves and stems and to TFA in pore water through roots. A few tested species (selected among those having an important role in feeding people and cattle) show a significant sensitivity to TFA (as NaTFA). The threshold for effects on wheat and soya is around 5 mg l^{-1} with a NOEC = 1 mg l^{-1} . Other studies show that nitrogen fixation is not affected up to 1 mg kg^{-1} soil. Therefore, a conservative figure could be PNEC_{soil} = 0.1 mg l^{-1} .

No significant risk is anticipated from TFA produced by atmospheric degradation of the present and future production of HCFCs and HFCs, as there is a 1000-fold difference between the PNEC and the PECs.

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