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AN ASSESSMENT OF THE ROLE OF CF_4 AND C_2F_6 AS GREENHOUSE GASES

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Executive summary

The initiative to perform this evaluation of the current understanding of the importance of CF_4 and C_2F_6 as greenhouse gases was taken by the European Aluminium Association (EAA) and the Aluminum Association, Incorporated. The evaluation of lifetimes, distribution and sources of CF_4 and C_2F_6 is based on information obtained from published literature, while estimates of radiative forcing and Global Warming Potentials (GWP) are done as part of this evaluation.

A review of the existing knowledge of the removal of CF_4 and C_2F_6 from the atmosphere support earlier findings that the two gases are extremely stable and that they remain in the atmosphere once they are released. All the identified loss processes for CF_4 and C_2F_6 have been examined out and are found to yield lifetimes larger than 10 000 years.

The emission of CF_4 and C_2F_6 per tonnes aluminium is not well established but is known to vary widely. The current knowledge of present and past emissions of CF_4 and C_2F_6 from the aluminium industry has therefore large uncertainties. Efforts should be made to decrease these uncertainties.

The concentrations of CF_4 and C_2F_6 in the atmosphere are reasonably well known with greater uncertainties in the case of C_2F_6. These concentrations are consistent with crude estimates of the cumulative emission from the industry within the very large uncertainties in these emissions.

Improved atmospheric measurements coupled with emission data could at best reveal whether the lifetime is less than about 100 years, which is highly unlikely based on present knowledge of the removal processes.

A single literature value exists for the annual increase in atmospheric CF_4 mixing ratios, which is consistent with the estimated annual emission rates from the aluminium industry. However, the uncertainties in the atmospheric measurements coupled with those of the emission estimates prevent drawing significant conclusions from this comparison. Reanalysis of air samples from the past and continued measurements of C_2F_6 and CF_4 in the future will strongly increase our knowledge of the emissions of the two gases.

One measurement of the rate of emissions of C_2F_6 to CF_4 in the plume downwind of an aluminium plant show significant differences from the ratio of the two gases in ambient air. As this is a potentially powerful means of distinguishing the emissions from the aluminium industry from those of other industrial or natural sources, measurements should be made of the ratio from emissions from a representative member of aluminium plants, as well as in the ambient atmosphere.

The conclusions that has been drawn from height profiles that 65% of the CF_4 in the atmosphere is due to natural sources and only 35% in the atmosphere is due to the aluminium industry can be challenged. The measurements should be reevaluated and the model calculations redone.

Radiative forcing for CF_4 and C_2F_6 was calculated by one narrow band model and by two broad band models. The model results are in reasonably good agreement (the uncertainty is estimated to be about 20%). Recommended values for the two compounds are: 0.10 Wm^{-2}/ppbv and 0.30 Wm^{-2}/ppbv respectively. For comparisons, the recommended IPCC value for $CFCl_3$ was 0.22 Wm^{-2}/ppbv.

There is a strong spectral overlap with water vapour, methane and nitrous oxide in the region where CF_4 has its main absorption. This leads to a reduced value, and increases the uncertainty in the calculated radiative forcing for the latter compound. Although no direct estimate of the uncertainty has been done it will probably not exceed 20%. The uncertainties should be examined using accurate line by line calculations.

GWP are calculated for three time horizons: 20 years, 100 years, 500 years. The values are 3700, 5100, and 8800 for CF_4, and 7300, 10.000, and 17.300 for C_2F_6 for the three time horizons respectively. The values are within the range recommended by IPCC, with GWP for CF_4 close to the lower limit.

Calculations of the radiative forcing of the two gases for an atmospheric composition of the greenhouse gases corresponding to the atmosphere in 2030, gave values slightly less than those obtained for the current atmosphere, indicating that the calculations are relatively unsensitive to moderate changes in the atmospheric composition of the greenhouse gases.

1. INTRODUCTION

The 1985 Ozone Assessment (WMO, 1985) compiled the existing information on measured distributions and trends for selected halocarbons in the atmosphere, including CF_4 and C_2F_6. This assessment shows that there are atmospheric observations of the two compounds which go back to 1979.

There have been few estimates of the potential role of CF_4 and C_2F_6 as greenhouse gases. Ramanathan et al. (1985) and Hansen et al. (1989) presented values for these two gases; however, they did so as part of an assessment of a large number of gases and gave little detailed attention to the two fluorocarbons. Ramanathan et al. (1985) estimated the impact on surface temperature from atmospheric increases of 1 ppbv of CF_4 and C_2F_6. According to their estimates CF_4 will lead to a surface heating which is approximately half of that of $CFCl_3$, while C_2F_6 gives a heating which is similar to the heating from an equal increase in $CFCl_3$. The contribution to increases in global warming from CF_4 and C_2F_6, based on the predicted increase in greenhouse gases between 1980 and 2030, was estimated to be small, considerably less than 1% of the increases in global warming from all greenhouse gases.

Apart from the 1985 Ozone Assessment (WMO, 1985) which gives the compilation of observations, there is no discussion of the distribution or the trend of CF_4 and C_2F_6 or their role as greenhouse gases in any of the international assessments of ozone or greenhouse gases that have been conducted during the last years.

The evaluation of GWPs of the greenhouse gases in the first IPCC Scientific Assessment on Climate Change (IPCC, 1990) did not include CF_4 and C_2F_6 at all. Although the two halogenated compounds were considered by the members of the working which prepared the Chapter on Radiative Forcing of Climate (Isaksen et al., 1992), it was felt that at time of the writing of the 1992 Scientific Assessment of Climate Change (IPCC, 1992), substantial uncertainties still existed about their lifetimes and their GWPs. Therefore, only lower limits for the lifetimes ($\tau > 500$ yrs) and for the GWPs (GWP of $CF_4 > 4500$ and GWP of $C_2F_6 > 6200$ for a time horizon of 100 yrs) could be given. Obviously a more thorough evaluation of the role of CF_4 and C_2F_6 as climate gases was needed.

In this evaluation, firstly a review of current knowledge of the loss processes of CF_4 and C_2F_6, the emission, distribution and trend in atmospheric concentrations will be performed. Thereafter, new calculations by three groups of the radiative forcing, and the GWPs for the two gases, will be presented for three different time horizons. Based on the calculated GWPs and the assumed increase in atmospheric abundancies, the man made contribution to the increase in global warming will be estimated.

2. LOSS PROCESSES OF CF_4 AND C_2F_6.

The role of various loss processes or sinks in the Earth's environment for the compounds CF_4 and C_2F_6 has been reexamined in this evaluation. Cicerone (1979) first considered a variety of potential sinks for CF_4, concluding that the dominant destruction processes would occur in and above the mesosphere, yielding an atmospheric residence time of over 10.000 years for this species. We arrive at a similar conclusion in terms of lifetime, after considering some recent measurements, listed in *Table 2.1*, which gives upper limits to the rate constants for the reactions of electronically excited oxygen atoms (O^1D) with CF_4 and C_2F_6, and which gives an upper limits to the absorption cross section of CF_4 at the Lyman-alfa wavelength, i.e. at 122 nm.

The measured upper limit of the rate constant for the reaction of O^1D with C_2F_6 is somewhat smaller than for the reaction with CF_4, and an actual value for the absorption cross section at 122 nm was obtained experimentally (see *Table 2.1*). However, for C_2F_6 the conclusion in terms of atmospheric residence time is similar to that of CF_4, namely it is likely to be over 10.000 years.

We have also investigated the efficiency of the destruction process consisting of the reaction of CF_4 with free electrons throughout the atmosphere, including the ionosphere, by taking into account the dependency of the reaction rate on electron energy. The lifetime against this sink is also over 10.000 years; the process is very inefficient because the very low atmospheric pressures prevailing in regions where the electron density becomes significant. In fact, even for a species such as SF_6 which reacts with thermal electrons, the lifetime against the sink in question is over 10.000 years. Similarly, we investigated the potential destruction of CF_4 by lightning: only a very small fraction of the atmosphere is being processed by lightning at any given time, so that this sink is also very inefficient, yielding a lifetime of well over 10.000 years. A similar situation arises with species being destroyed by thermal decomposition in combustion processes; it is essentially a negligible sink on a global scale.

We have also reconsidered various other processes such as reaction with OH radicals and with H-atoms; dissolution in the oceans followed by hydrolysis; etc. We were unable to identify any destruction process which would yield a residence time in the environment of less than 10.000 years.

An alternative way to examine the importance of sinks in the environment for a given species is to compare its measured abundance in the atmosphere with emission rates. In the case of CF_4 these emission rates are at present not known sufficiently accurately for this approach to be useful. However, this has been done successfully for the CFCs: e.g., it is now clear that for CFC-12 (CF_2Cl_2) the predominant sink is photolysis in the stratosphere, and that there are no other sinks that would yield atmospheric lifetimes of less than about 100 years. Hence, it is highly unlikely that any such sinks exist for CF_4, since it is chemically more stable than CF_2Cl_2. In fact, the CF_3-F bond dissociation energy is 130 kcal/mole, in contrast to the much weaker CF_3-Cl bond strength, which is only 83 kcal/mole, so that most sinks that come to mind involve the weaker C-Cl chemical bond. From this consideration it follows that even processes that are difficult to quantify such as adsorption in soils followed by bacterial degradation cannot be important for the very stable perfluorinated species; some such processes have been shown to occur for CFC-11 and CFC-12, but their overall efficiency is too small to matter. For these reasons we conclude that the environmental lifetimes of CF_4 and of C_2F_6 are indeed extremely long.

Given the uncertainties in the emission figures for CF_4 and C_2F_6 we conclude that measurements of the average concentrations of these species in the atmosphere are very unlikely to yield information on loss processes in the environment. Furthermore, even for species of industrial origin for which the emissions are well characterized (e.g., the CFCs) such measurements cannot indicate the existence of slow sinks with characteristic times longer than about 100 years, a reason being that the bulk of the emissions of such species have occurred merely in the past few decades, and slow loss processes have not yet had time to remove a significant fraction of the amount emitted.

Table 2.1 Rate constants k for reactions with electronically excited oxygen atoms, O^1D, and absorption cross sections σ at the Lyman-α wavelength (122 nm).*

Reactant	$k(O^1D)$ $cm^3 molecule^{-1} s^{-1}$	σ (122 nm) $cm^2 molecule^{-1}$
CF_4	$< 3 \times 10^{-15}$	$< 8 \times 10^{-22}$
C_2F_6	$< 5 \times 10^{-14}$	- 10^{-20}

* Data from A. R. Ravishankara, private communication, 1992.

3. SOURCES OF CF_4 AND C_2F_6.

The concentration of CF_4 in the Earth's atmosphere in 1979 was determined by Penkett et al. (1981) to be 69.9 ± 7.2 pptv. The concentration of C_2F_6 is less well known, but is probably between 2 and 4 pptv. The aluminium industry is believed to be the major contributor to the emission of these gases into the atmosphere, although it still remains an open question what fraction of the atmospheric burden can be attributed to the Aluminium industry and how much to natural and other industial sources. Cicerone (1979) has suggested that the electrolytic generation of F_2, especially in carbon and graphitic electrode systems, the reduction of UF_4 and UF_6, the use of fluorspar in steelmaking, the burning of polyfluoroethylenes, rocket fuel combustion and inadvertent production in fluorocarbon manufacture as possible anthropogenic sources. No natural sources have been identified.

The question of interest then is to assess the total emissions of these two gases from natural and anthropogenic sources and the fraction of that total that is attributable to the aluminium industry. There are two approaches to this problem: (1) direct evaluation of emission inventories and (2) atmospheric measurements.

3.1 Emissions of CF_4 and C_2F_6

In view of the very long lifetimes of these compounds, even a very small natural source, operating over millennia, could make an appreciable contribution to the atmospheric burden. Since the present atmospheric concentrations are small, and the percentage change in atmospheric concentrations from such sources would be slow, such natural sources, if they exist, will be undetectable. Other industrial sources are likely to be small relative to the emissions from the aluminium industry but could, cumulatively, make a significant contribution. We have not tried to assess the contributions from each of the other possible sources.

In determining the emissions from the aluminium industry two components have to be considered: (1) The world-wide tonnage of aluminium production. (2) The emission of CF_4 and C_2F_6 per tonne of aluminium. The current annual world production is known to be 18.5 MT with an uncertainty of less than 10%. On the other hand, the uncertainties in the emissions of the CF gases per tonne of aluminium are very large. According to Huglen (1992) these emissions depend on a number of variables such as the type of cell, the frequency, duration and strengths of the anode events and, possibly, on other parameters such as temperature. The analytical methods currently being used to characterize these factors suffer either from interferences between gases or from limited sensitivities, or time response. At present, the emissions remain uncertain to several hundred percent.

3.2 Comparison of the total atmospheric burden with cumulative production from the aluminium industry

It is relatively simple matter to calculate the total amount of CF_4 in the atmosphere from its measured atmospheric concentration. This can be compared with the cumulative emission calculated from the published annual world-wide production figures and the value of the CF_4 emission per tonne of aluminium production. If one assumes a value of 1 Kg CF_4 emitted per tonne of aluminium (Berge, 1992), reasonable agreement is reached between these two calculations. However, the large uncertainties of the emission figures do not put any constraints on the existence of other sources. All that can be said at present is that such calculations are not inconsistent with aluminium production being the sole source of CF_4 in the atmosphere.

3.3 Comparison of the current rate of increase in atmospheric concentration with annual production rate of aluminium

Khalil and Rasmussen (1985) measured CF_4 in air samples collected at the south pole in 1978-79 and in 1984. They report an increase in CF_4 of 1.8×10^7 Kg/yr with the 90% confidence lying in the range of 1.2 to 2.7×10^7 Kg/yr. This confidence limit may, however, be somewhat over-optimistic since different instruments, which were never intercompared, were used in the 2 sets of the measurements.

The assumption of an annual global production of 1.6 MT of aluminium over that time period with an emission rate of 1 Kg CF_4 per tonne of Al translates to an annual emission of 1.8×10^7 Kg/yr. This figure is consistent with the measurements of Khalil and Rasmussen (1985). However, the uncertainties both in the measurements and in the estimates of CF_4 emissions are so large that no definitive conclusions can be reached regarding source attribution to the aluminium industry.

3.4 CF_4/C_2F_6 Ratios

If CF_4 and C_2F_6 have significant natural, or anthropogenic sources other than the aluminium industry, it is very unlikely that the emissions of these 2 gases would be in the same ratio from all sources. Measurements of the ratio of C_2F_6/CF_4 could therefore provide a very powerful method for source determination. Penkett et al. (1981) found the ratio in background air to be 0.057. They also measured both gases in 4 samples collected in the plumes of an aluminium smelter in the state of Washington. The concentrations of both these compounds were found to be enhanced in the plumes by a factor of about two. The C_2F_6/CF_4 ration in the plume samples averaged 0.078. The authors did not consider the difference in the ratio between background and plume air to be significant within their experimental accuracy. In fact they conclude that "CF_4 and C_2F_6 escape from the aluminium plants in the same ratio of concentrations as observed in the atmosphere".

Based on the same data set, Fabian et al. (1987) reach the opposite conclusion, viz. that "the relative contribution of the aluminium production towards the global budget is larger for C_2F_6 than for CF_4", Fabian et al. (1987) actually found the ambient ground-level concentrations of C_2F_6 to be about 2 pptv - a factor of 2 less than the numbers reported by Penkett et al. (1981). They attribute this difference to calibration errors in the earlier work. Nevertheless, they argue that this does not affect their conclusions since the same calibration error was present both in the plume and in the ambient air measurements made by Penkett et al. (1981).

Khalil (1992, private communications) however, believes that not too much should be made of the plume measurements since they were done rather casually and did not constitute a systematic study.

3.5 CF_4 and C_2F_6 Height Profiles

Fabian et al. (1987) measured both CF_4 and CF_6 from balloons to altitudes of 35 km. They found that the concentration of CF_4 decreases from about 67 pptv in the lower troposphere to 60 pptv at 30 km. C_2F_6, however, decreases much more rapidly with altitude. They argue that a very long-lived species with no natural source should show a drop-off of mixing ratio with altitude in the stratosphere because its emission has been occurring over a much shorter period than its lifetime. They conclude that the observed C_2F_6 profile is consistent with this interpretation, whereas the relatively constant profile for CF_4 requires a long-term natural source. They used a 1-D model to conclude that 35% of the present atmospheric burden is attributed to the aluminium industry and 65% to natural sources.

This conclusion, if correct, implies a background CF_4 concentration in the atmosphere of about 50 pptv. However, the conclusion can be challenged both from the modelling and the measurement points of view. The C_2F_6 measurements are close to the detection limits and the model results appear to show a larger drop-off with height than expected for a gas like C_2F_6. It is worth noticing that calculated profiles in the upper regions are very sensitive to the way the upper boundary is treated in the model.

4. RADIATIVE FORCING DUE TO CF_4 AND C_2F_6.

A recent study of GWPs for these gases known has been performed by Stordal and Myhre (1991). The present work is partly intended to allow a direct comparison with their method, including a more detailed radiative transfer scheme. The work is done by three different models: Two broad band models, and one narrow band model. A major part of this assesment has been to perform a thorough comparison of the results obtained in the model studies. A detailed description of the calculations and of the comparisons is given in this section.

4.1 Models and spectral data

Three different models have been used in this study of radiative effects of CF_4 and C_2F_6. The main characteristics of the models are described in the following.

4.1.1 University of Reading (UoR)

A standard narrow-band radiative transfer model, which resolves the thermal infrared spectrum between 0 and 2500 cm^{-1} at 10 cm^{-1} intervals is used here (Shine, 1991). All absorption bands due to water vapour, carbon dioxide, methane, nitrous oxide, CFC-11 and CFC-12 are incorporated from spectral line data on the Hitran 1986 data base (Rothman et al. 1987) as well as a representation of the water vapour continuum following Clough et al. (1989). The atmosphere is divided into about 20 layers in the calculations presented here.

For the spectral regions of most importance for CF_4 and C_2F_6, this spectral resolution is higher than used by either Ramanathan et al. (1985) and Stordal and Myhre (1991), who embed these fluorocarbons in a wide band model (with CF_4 occupying 20 cm^{-1}, and C_2F_6 occupying 60 cm^{-1}), or Hansen et al. (1989) who use a 50 cm^{-1} spectral resolution. Nevertheless, evidence will be presented in Section 4.1.2 that even a 10 cm^{-1} spectral interval may be inadequate.

The spectroscopic data for the calculations come from a number of sources. For CF_4 high (0.015 cm^{-1}) resolution cross-sectional data from McDaniel et al. (1991) are averaged onto the resolution of the radiation scheme, for the interval 1250-1290 cm^{-1}. Figure 4.1 shows the relative cross-sections as a function of wavenumber. Within the experimental error of the measurements ($\pm$10%), McDaniel et al. (1991) consider the overall band strength to be independent of temperature; their 296 K value is used here. The integrated band strength of the 1255-1289 cm^{-1} absorption band is 1.61×10^{-16} cm^{-1}/ (molec cm^{-2}). Note that this value was calculated from

McDaniel et al's data files, but it is 7% lower than that given in *Table 1* of their paper. The data used in this report is the original observational data derived at NCAR; McDaniel et al. (1991) processed this data to force a smooth variation of cross-sections with temperature, and this altered their intergrated values (C. Cantrell, NCAR, personal communications). Previous estimates for this band range from 1.397×10^{-16} to 1.695×10^{-16} $cm^{-1}/(molec\ cm^{-2})$. The integrated band strength (1250-1301 cm^{-1}) from the MPI Mainz is 1.66×10^{-16} $cm^{-1}/(molec\ cm^{-2})$, in good agreement with the McDaniel et al. (1991) value. CF_4 contains a number of much weaker bands at other wavelengths. These values were taken from the MPI data.

For C_2F_6 there is a dearth of available observations of spectral strengths. The only published quantitative measurements known to the authors are in Mills et al. (1958) and Varanasi and Chudamani (1988). For this study MPI Mainz has provided some data. Values from the three data sets are shown in *Table 4.1*.

Table 4.1.: Band strength for C_2F_6 ($\times10^{-18}$ $cm^{-1}/molec\ cm^{-2}$)

Band (cm^{-1})	Mills et al.	Varanasi and Chudamani	MPI Mainz
219	0.7		
522	1.3		0.6
714	5.4		8.4
1116	39.3	47.2	47.2
1250	136.0	168.0	161.5
1326			3.4

The Mills et al. (1958) data is that used by Ramanathan et al. (1985), Hansen et al. (1989) and Stordal and Myhre (1991), although they do not reference it as such. The MPI Mainz data became available too late for detailed calculations with the Reading model, but they are clearly in good agreement with the Varanasi and Chudamani data. Calculations for Mills et al. (1958) and Varanasi and Chudamani (1988) data are presented; the former are included to allow comparison with earlier model calculations. C_2F_6 also has three much weaker bands at 219, 522 and 714 cm^{-1}; these have been included for completeness, using the data from Mills et al. (1958).

CF_4 and C_2F_6 are included in the model assuming them to be absorbers at their weak limit, which is appropriate for present concentrations. The flux transmittance is given by an expression of the form exp(-2sx) where 2 is the diffusivity factor for optically-thin gases, s is the absorption cross-section and x is the path length of the absorber.

4.1.2 Norwegian Institute for Air Research (NILU)

A broad band approach is used to calculate infrared flux changes caused by CF_4 and C_2F_6. Each absorbing band in treated as an integral, with CF_4 occupying 20 cm^{-1}, and C_2F_6 occupying 60 cm^{-1}. The model, which was developed based broadly on the formulation of Ramanathan (1976), is described in Stordal (1988), and has earlier been used to calculate GWP values for CF_4 and C_2F_6 (Stordal and Myhre, 1991). The integrated band strengths for CF_4 are taken from the MPI Mainz dataset and for C_2F_6 from the Varanasi and Chudamani dataset (see Section 2.1). Overlap by H_2O vibrational rotational bands and continuum is included using values from Rodgers and Walshaw (1966). CO_2 and CH_4 overlap is treated using a fit based on Kiehl and Ramanathan (1983).

4.1.3 Max Planck Institute, Mainz (MPI)

A chemistry radiative-convective model has been used for calculations of infrared effects of CF_4 and C_2F_6. The radiative calculations are made with a broad band IR model, also based on Ramanathan (1976). In this model the stratosphere is assumed to be in radiative equilibrium, while the tropospheric and surface temperatures are calculated by iteration from the assumption that the net flux at the top of the atmosphere and at the tropopause has to vanish. A detailed description is given in Brühl and Crutzen (1988). In the normal operational mode this model accounts for chemical feedbacks in the troposphere and the stratosphere, here especially the change in vertical ozone distribution due to ozone destroying substances like CFCs or temperature changes.

In the infrared a broad band approach is used to calculate flux changes caused by halocarbons and other radiatively active species. Usually one transition is treated as a whole, so that typical spectral resolution is about 50 cm^{-1}. The integrated band strengths for CF_4 and C_2F_6 are taken from the high resolution MPI Mainz data set. Overlap by H_2O vibrational rotational bands and continuum is included using adjusted values from Rodgers and Walshaw (1966) and Roberts et al. (1976). CO_2 and CH_4 overlap is treated using a fit based on Kiehl and Ramanathan (1983).

4.2 Impact of fluorocarbons on clear sky irradiances

A convenient method of assessing the potential impact of gases, which allows ready comparison with other models, is to perform calculations of the effect of gases on the irradiance in a clear sky standard atmosphere, following the method of the international Intercomparison of Radiation Codes for Climate Models (ICRCCM) (see, e.g., Fels et al., 1991). In this section results and sensitivities are presented for the change in net thermal infrared irradiance at the tropopause, on adding CF_4 and C_2F_6. Note that these do not correspond to the radiative forcing due to these gases. This concept will be explained and results derived in Section 4.4.

The results here use the McClatchey et al. (1972) mid-latitude summer atmosphere for temperature, ozone and water vapour. The concentrations of the well-mixed radiatively-active gases are taken from *Table 1.3* of IPCC (1990) and reference therein. These are: CO_2 353.93 ppmv; CH_4 1717 ppbv; N_2O 309.68 ppbv; CFC-11 0.28 ppbv; CFC-12 0.484 ppbv. Following ICRCCM the tropopause is defined to be at 179 mbar.

The issues involved in calculating the tropopause irradiance change concern the effects of other molecules whose spectral features overlap those of the gases of interest, the effects of the different spectral bands, and the sensitivity to changes in strength.

Table 4.2: Decrease in net tropopause irradiance in a clear sky mid-latitude summer atmosphere on adding 1 ppbv of CF_4.

Case	Gases included	Spectral Region (cm^{-1})	Irradiance Change (Wm^{-2})		
			UoR	NILU	MPI*
1	H_2O	1250-1290	0.176	0.149	0.191
2	H_2O, CH_4	1250-1290	0.139		0.148
3	H_2O, N_2O	1250-1290	0.131		0.156
4	H_2O, N_2O, CH_4	1250-1290	0.105	0.101	0.107
5	N_2O, CH_4	1250-1290	0.183	0.177	
6	As 4, but strength H_2O	1250-1290	0.131		
6a	As 4, reduced CH_4, and H_2O overlap				0.132
7	H_2O, N_2O, CH_4, CO_2, O_3, CFC-11, CFC-12	0-2500	0.111	0.111	

* includes all bands in the region 500-1400 cm^{-1}

Table 4.2 shows the impact of adding 1 ppbv of CF_4 (at all levels in the atmosphere) on the net tropopause irradiance for different combinations of absorbing gases. The main band at 1250-1290 cm^{-1} is only overlapped by CH_4, N_2O and H_2O, so only the effects of these gases are given. The effect of an addition of any greenhouse gas in the troposphere is to decrease the net irradiance at the tropopause. For convenience this decrease will henceforth be referred to as a positive quantity.

It can be seen from this table that the effect of overlap is extremely important. The inclusion of both CH_4 and N_2O in an atmosphere containing H_2O decreases the irradiance change from 0.176 to 0.105 Wm^{-2} in the UoR model (cases 1 and 4), with N_2O and CH_4 contributing almost equally to this reduction (cases 2 and 3). Retaining CH_4 and N_2O but removing H_2O (case 5) increases the change to 0.183 Wm^{-2}. In the coarser MPI and NILU models the effect of overlap with N_2O and CH_4 is similar to the effect in the UoR model.

There is some question mark over the precise strength of the H_2O overlap, since the strongest lines in the 1280-1290 cm^{-1} region lie at above 1285 cm^{-1}, whilst the CF_4 absorption dominates below 1285 cm^{-1}. A simplified illustrative line-by-line calculation (using Killinger and Wilcox, 1992) of the absorption due to water vapour between 1250 and 1290 cm^{-1} for a 1 km path at the surface with typical mid-latitude H_2O calculations is shown in *Figure 4.1*. Note that the CF_4 cross-section peak happens to fall in a region of relatively high transmittance. Because of this, a further case (case 6) was run with the UoR model in which the H_2O band parameters in the 1280-1290 cm^{-1} region were reduced to these in the 1280-1285 cm^{-1} region. The irradiance change increases from 0.105 to 0.131 in this case. This indicates that there is an uncertainty of about 20% using the current UoR radiation scheme because of the uncertainty in handling the overlap.

In the sensitivety study performed with the MPI model (case 6a) to look at the problem with overlap, the spectral intervals 1278.3 to 1281.5 cm^{-1} 1281.9 to 1283.3 cm^{-1} were treated separately (CH_4 in the first interval, H_2O in the second, see also *Figure 4.1)*. The results are similar to what was obtained in case 6 with the UoR model. The uncertainty in the NILU model is probably somewhat larger. There will also be uncertainties in the precise overlap between CF_4 and the lines of CH_4 and N_2O, which we are unable to investigate in detail here.

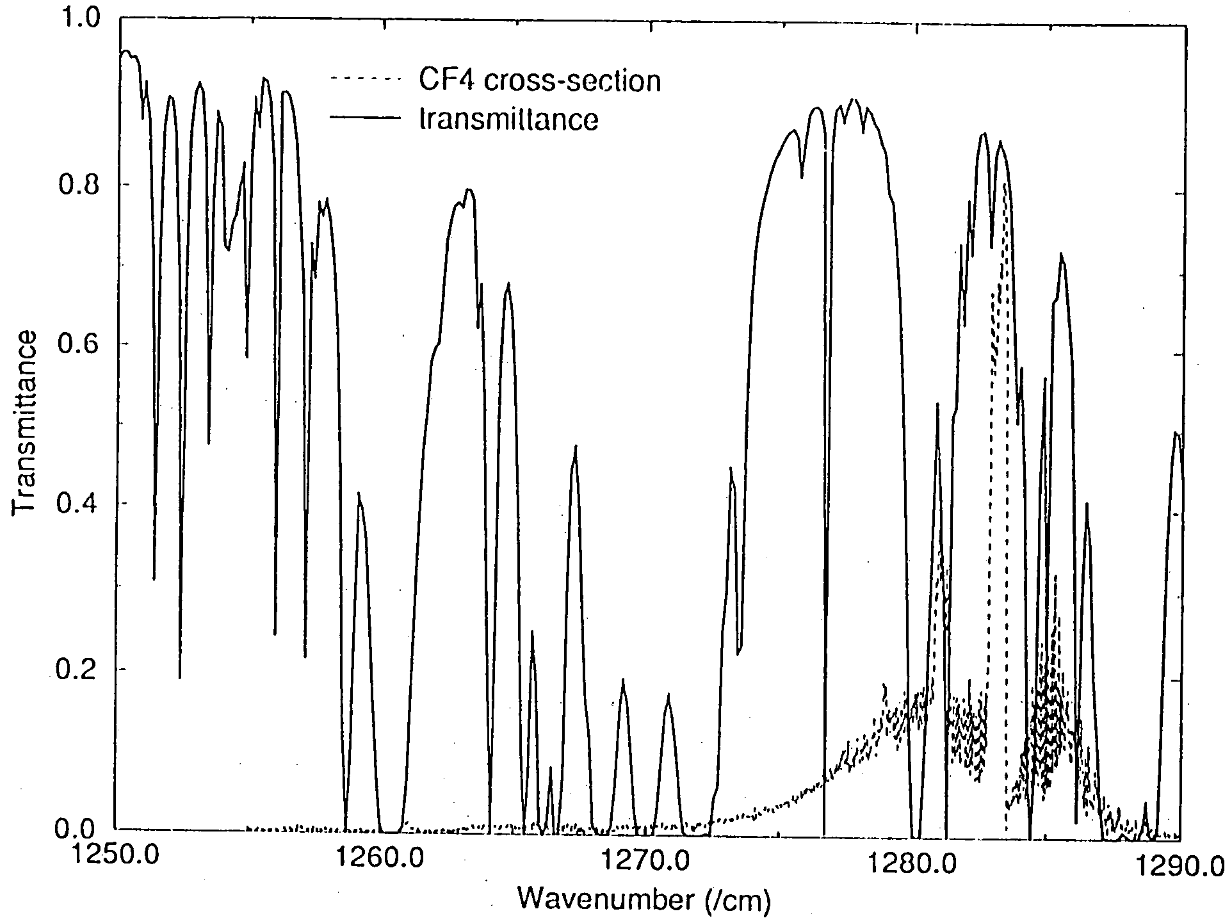

Figure 1: An approximate line-by-line transmittance calculation for a 1 km path at the surface, with typical mid-latitude concentrations, for water vapour (solid line), as a function of wavenumber. The dashed line shows the cross-sections of CF_4, in relative units, from McDaniel et al. (1991).

Case 4 was rerun with the UoR model with the CF_4 band strength increased and decreased by 10% to reflect the current spectroscopic uncertainties. The irradiance change was directly proportional, varying by $\pm$10% following the changes. Since some models spread the effects of CF_4 over a wider spectral interval, case 4 was also rerun with the UoR model with the cross-sections spread evenly over the 1250-1290 cm^{-1} region, instead of using the observed distribution shown in *Figure 1.* The irradiance change increased from 0.105 to 0.132 Wm^{-2}, indicating that spectral resolution is an important issue.

Next, using the MPI Mainz data, the weaker bands at 550-670 cm^{-1}, 1220-1250 cm^{-1} and 1420-1590 cm^{-1} were added to case 4 with the UoR model. The irradiance change increased by 2×10^{-3}, 4×10^{-3} and less than 5×10^{-4} Wm^{-2} respectively for these bands. Thus they increased the total change from 0.105 to 0.111 Wm^{-2}, or about 6%. Given the uncertainties in the calculation, this change is very small, although for completeness these bands are retained in Section 2.4.

Finally, for CF_4, the effect of changing the concentrations of the gaseous constituents was investigated by using the IPCC (IPCC, 1990) "business-as usual" values for 2025. These are: CO_2 437 ppmv; CH_4 2684 ppbv; N_2O 341 ppbv; CFC-11 0.488 ppbv; CFC-12 0.863 ppbv. Water vapour is increased by 5% at all levels and ozone and temperature are retained at their mid-latitude summer concentrations. The irradiance change decreased from 0.111 Wm^{-2} (case 7), to 0.101 Wm^{-2}, indicating a possible slight decrease in the effectiveness of CF_4 with time.

Table 4.3: Decrease in net tropopause irradiance in a clear sky mid-latitude atmosphere summer on adding 1 ppbv of C_2F_6

Band (cm^{-1})	Decrease in irradiance (Wm^{-2}) Mills et al.	Varanasi and Chudamani		MPI data
	UoR	UoR	NILU	MPI
210-230	<0.0005			
510-530	0.004			
700-730	0.005			
1100-1130	0.116	0.139	0.141	
1240-1260	0.177	0.216	0.186	
Total	0.302	0.364	0.336	0.331
		(incl Mills et al. weak bands)		

For C_2F_6 a much more limited set of calculations was performed because of the lack of detailed information on its spectra at the time when most of the calculations were performed. Again, the mid-latitude summer profile with the 1990 well-mixed gas concentrations were used. There is overlap with H_2O, CH_4 and, to a lesser extent than for CF_4, N_2O between 1240 and 1260 cm^{-1}, and weak overlap with H_2O between 1100 and 1130 cm^{-1}. *Table 4.3* presents the results from the UoR model for each band of C_2F_6 using both the Mills et al.(1958) and Varanasi and Chudamani (1988) data. Aditional calculations were performed with the NILU model using the latter data set,and with the MPI model using their own spectral data.

These results show that the two higher wave number bands dominate. The Varanasi and Chudamani values are about 20% greater, in almost exactly the same ratio as the spectroscopic strengths discussed in Section 4.2. C_2F_6 is about 3 times more effective, on a molecule-per-molecule basis, than CF_4. The forcing calculated by the MPI model is 15% larger if N_2O overlap is neglected.

4.3 Radiative Forcing

Whilst the results in Section 4.3 give a general indication of the radiative strength of CF_4 and C_2F_6, a proper assessment of the forcing requires the inclusion of clouds and, in principal, the inclusion of a process known as stratospheric adjustment (see Shine et al., 1990 and references therein). Briefly the conceptual model of the radiative forcing of climate change is that the surface and troposphere are tightly coupled and climate change is forced by variation in the irradiance at the tropopause. Thus the forcing should include changes in stratospheric temperature as a consequence of for instance trace gas changes.

In much earlier work, the radiative forcing is calculated using global mean conditions for temperature, H_2O, O_3 and cloudiness. Here the global mean is calculated by accounting for the latitudinal and seasonal variation of these quantities using available climatologies. Performing these latitudinally varying calculations with stratospheric adjustment requires the application of the assumption of fixed-dynamical heating (see Ramaswamy et al., 1992, for details).

The results from the UoR model are shown in *Figure 2* for a 1 ppbv increase of CF_4 and C_2F_6. In *Figure 2a* the effect of the stratospheric adjustment for CF_4 is shown to be very small (<5%). The same conclusion can be drawn from similar experiments with the NILU model. An increase in CF_4 leads to a warming of the stratosphere and a slight increase in the radiative forcing as the downward irradiance at the tropopause is increased. For CO_2 the effect is of the opposite sign and much bigger. Despite the smallness of this adjustment term, it is retained in further calculations for completeness.

Figures 2b and *Figure 2c* show the forcing for clear skies and average cloudy conditions for January and July respectively. Clouds generally act to reduce the outgoing infrared radiation and hence reduce the effect of adding greenhouse gases. The actual reduction is obviously dependent on the cloud amount and some uncertainty exists in this parameter. It is seen that the variation of forcing with latitude is greater in January *(Figure 2b)* than in July *(Figure 2c)*. In general as temperature decreases with latitude, the amount of energy in the strong CF_4 1280-1290 cm^{-1} band decreases. However, this is offset to some extent by a decrease in water vapour with latitude, which tends to increase the effectiveness of CF_4. These two effects are close to compensating for July, but the temperature effect dominates in January.

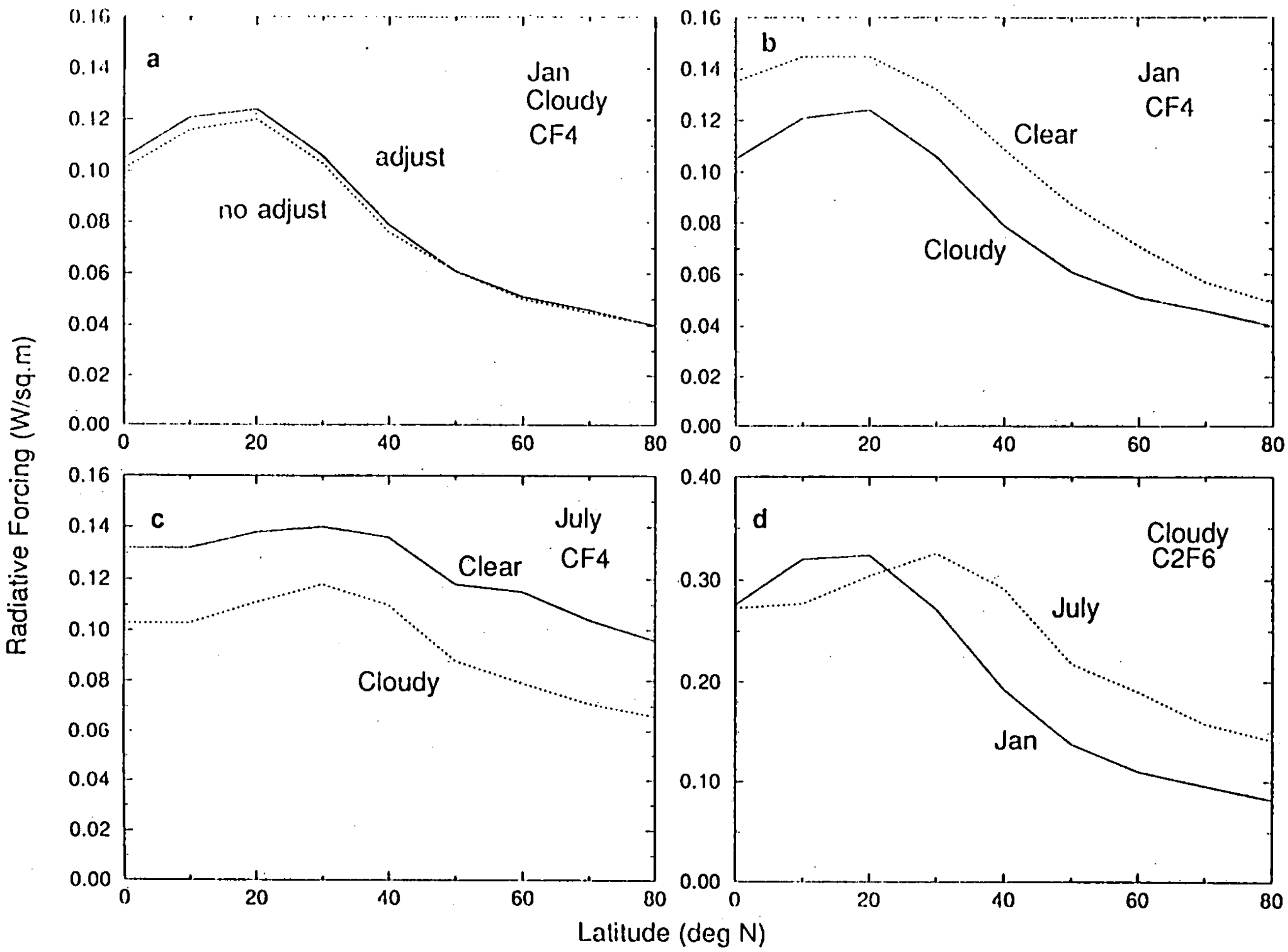

Figure 2: Latitudinal variation of radiative forcing (Wm^{-2}) for a 1 ppbv increase in fluorocarbon concentration as calculated with the UoR model. (a) CF_4 forcing with and without stratospheric adjustment for the January cloudy case. (b) CF_4 forcing with and without clouds for January, including stratospheric adjustment. (c) As (b) but for July. (d) C_2F_6 forcing for January and July assuming cloudy skies and including stratospheric adjustment.

The same effect can be seen for C_2F_6. *Figure 2d* shows the average cloudy calculations for January and July. The latitudinal effects for July is slightly larger than for CF_4, possibly because the C_2F_6 band at 1100-1130 cm^{-1} is less affected by H_2O overlap. Note also that the C_2F_6 forcing is 2 to 3 times stronger than CF_4.

Performing the above calculations with the UoR model for the whole globe for each month with such a high resolution radiation code was not practical. A "global mean" forcing is obtained by area-weighting the January and July results and taking their mean for the cloudy, adjusted calculations. The cruder but faster schemes used e.g. by Stordal and Myhre (1991) have a great advantage as it allows inexpensive calculations using a finer resolution in latitude and season. Calculations have been performed with the NILU model for the two hemispheres (resolution 10 deg. latitude), and for each of the 12 months. Observed climatological data for temperature, ozone and water vapour distributions are used. Representative global averages are then calculated. However, the experiments with the NILU model have been performed without clouds. The results from these two sets of experiments are discussed below.

4.4 Interpretation and comparison

The global-mean calculations of temperature change of Ramanathan et al. (1985) and Hansen et al. (1989) can be converted to radiative forcings by dividing the temperature change by a feedback parameter (0.52 for Ramanathan et al., see their Table 8; and 0.28 for Hansen et al., see Shine et al. 1990). These are compared with the values calculated here in *Table 4.4.*

Table 4.4: Radiative forcing ($Wm^{-2}/ppbv$) for CF_4 and integrated CF_4 band strengths: a comparison of calculations from the present work and earlier studies. The earlier calculations were performed with clouds, whereas the present calculations are performed with as well as without clouds.

	Radiative Forcing ($Wm^{-2}/ppbv$)	Integrated band strength ($x10^{-16}$ cm^{-1} /($molec.cm^{-2}$)
Present work:		
UoR, with clouds	0.097	1.66
UoR, without clouds	0.123	1.66
MPI, with clouds	0.085	1.66
NILU, without clouds	0.103	1.66
Ramanathan et al. (1985)	0.115	1.57
Hansen et al. (1989)	0.150	1.73

It can be seen that the values of Ramanathan et al. (1985) are about 25% higher than those derived here with the UoR model, whilst the Hansen et al. (1989) values are 55% higher. The total band strengths could explain 5% of the difference for Hansen et al. (1989), but the difference with

Ramanathan et al. (1985) is of the wrong sign. Since the earlier studies effectively used calculations of forcing with globally averaged profiles, whereas the current work averages the forcing, the effect of the order of this averaging process was calculated with the UoR model; the difference was found to be less than 1%. A further possible source of the difference is that the current calculations, and those of Ramanathan et al. (1985), are for a 1 ppbv increase from zero, whilst Hansen et al. calculate the change for an increase from 0.07 to 0.09 ppbv (their estimate of the increase in concentration of CF_4 between 1980 and 1990). A repeat of the present calculations for the same change gave a forcing 5% higher than would be deduced from a 1 ppbv change.

A likely source of a large difference seems to be the radiative treatment including the spectral resolution and the overlapping gases. Indeed, it is not absolutely clear whether Hansen et al. (1989) have included CH_4 and N_2O in the calculations presented in their Table 1, or what concentrations have been used. We assume that they will have included them at near present day concentrations. It was found in section 4.3 that the CF_4 strength was increased by 25% if it was spread equally across the 1250 to 1290 cm^{-1} spectral interval, which is close to the spectral resolution used in the calculations by Hansen et al. (1989). Thus the effects of different band strengths, different concentration changes, and the degraded spectral resolution would increase the present values by 40%, bringing them closer to the values obtained by Hansen et al. (1989). On the other hand, results obtained with the broad band NILU model are lower than the ones from the UoR model (cloud free case), which could possibly be explained by different values for the climatological data used, especially temperature and water vapour.

Given the uncertainties in the precise spectral overlap (case 6 versus case 4 in *Table 4.1*) it is possible that the values calculated here should be some 10% higher than shown in *Table 4.3*.

For C_2F_6, *Table 4.5* shows the values calculated with UoR models using the Mills et al. (1958) data, along with a comparison with the two earlier studies (Hansen et al. (1989) provide insufficient decimal places in their table for a more accurate computation). The three studies, which use the same spectral data, can be seen to be in good agreement. *Table 4.5* also shows the results obtained with the MPI and NILU models are somewhat different from the result obtained with the narrow band model.

However, more recent data for C_2F_6 indicate that the integrated band strength should be about 20% higher than the Mills et al. (1958) value. The recommended value for adoption here is therefore increased by 20% above that shown in *Table 4.5* computed by the UoR model, to 0.30 Wm^{-2}/ppbv, which is in good agreement with the results of the MPI and NILU models.

Table 4.5: Radiative forcing ($Wm^{-2}/ppbv$) for C_2F_6: A comparison of calculations from the present work and earlier studies.

Model	Band strength data	Radiative Forcing $Wm^{-2}/ppbv$
Present work		
UoR, with clouds	M	0.25
MPI, with clouds	MPI	0.24
MPI, without clouds	MPI	0.33
NILU, without clouds	M	0.30
NILU, without clouds	VC	0.35
Ramanathan et al. (1985)	M	0.25
Hansen et al. (1989)	M	0.22 (approx)

M: Mills et al.
MPI: Max Planck Institute
VC: Varanasi and Chudamani

4.5 Recommended values for radiative forcing

The recommended values for use in radiative forcing calculations are 0.10 $Wm^{-2}/$ ppbv for CF_4 and 0.30 $Wm^{-2}/ppbv$ for C_2F_6. The error due to uncertainties in spectral resolution, the effect of overlapping gases and band strengths are, rather qualitatively, estimated to be about $\pm$ 20%.

We recommend these values in estimates of the global warming potential of the fluorocarbons. Their strength relative to CO_2 and CFC-11, using the values of CO_2 and CFC-11 in IPCC (1990, table 2.3), are given in *Table 4.6*, on both a per molecule and a per mass basis.

Table 4.6: Relative strength of CF_4 and C_2F_6 compared to the IPCC values of CO_2 and CFC-11 (only direct radiative effects included), on a per molecule and a per unit mass basis

	relative strength per molecule		relative strength per unit mass	
Gas	CO_2	CFC-11	CO_2	CFC-11
CF_4	5430	0.44	2710	0.69
C_2F_6	16900	1.37	5360	1.37

4.6 Recommended values for Global Warming Potentials (GWPs)

There has been a need for a simple methodology which allows the ranking of climate gases to describe the relative contribution of their emissions to the greenhouse effect. The GWP has been developed as such a tool. GWPs, although there are serious limitations that constrain their practical utility, are still used by the IPCC (IPCC, 1990; 1992).

As described in detail by IPCC (1990; 1992) the GWP measures the warming potential of emissions of a climate gas relative to that of a reference gas. As one given number, it is meant to give the global and annually-averaged warming effect. It is further a cumulative measure of warming over a specified time horizon, taking into account the decay of the atmospheric concentration following the emission of the compound.

The GWP is defined by the relation

$$GWP = {}_0\int^{t_h} a_i\, c_i\, dt \;/\; {}_0\int^{t_h} a_r\, c_r\, dt$$

where a_i is the instantaneous radiative forcing due to a unit increase in the concentration of trace gas i, c_i is its concentration remaining at a time, t, after its emission. The corresponding values for the reference gas is given in the denominator. The time horizon, t_h, is the time period for the integration.

The GWP for a climate gas depends not only on its radiative properties, but also on its lifetime in the atmosphere. For example a short lived climate gas has a relatively larger GWP on a short time horizon than on a longer time horizon. The cumulative effect of very stable gases, like CF_4 and C_2F_6, is larger for longer time horizons. This can clearly be seen from the expression for the GWP, which can be simplified when the lifetime is much larger than the time horizon. As discussed in section 3, the lifetime for both CF_4 and C_2F_6 is very likely to be at least 10 000 years, which is much longer than any time horizon for which GWPs are useful. The simplified expression for the GWP is then

$$GWP = a_i c_i t_h / {}_0\int^{t_h} a_r c_r dt$$

The reference gas used is usually CO_2 which is the dominant anthropogenic contributor to the greenhouse effect. Since CO_2 is removed from the atmosphere by several processes, for which the time constants are uncertain, the value of the denominator in the expressions is connected with uncertainties. In *Table 4.7* we therefore also specify GWPs with CFC-11 as a reference gas. It has the advantage that CFC-11 has an atmospheric lifetime which is given by an exponential decay. However, as pointed out in IPCC (1992), the CFCs could have strong indirect effects, through their impact on the stratospheric ozone (also a greenhouse gas) on a global scale. The indirect effect will probably lead to a cooling of similar size to the warming from the CFC-11 molecule itself (Ramaswamy et al., 1992). Therefore, if both direct and indirect effects of the CFCs are considered, the GWPs for these compounds could be substantially less than the values obtained if only the direct effects are considered. In fact, estimates of the GWPs when both direct effects and indirect effects are taken into account, suggest that the indirect effect nearly balance the direct CFC effect (IPCC, 1992). CF_4 and C_2F_6, on the other hand, do not affect ozone (although there will be a very weak effect via changes in stratospheric temperatures), and are therefore believed to have no indirect effect on global warming. The comparisons in *Table 4.7* With $CFCl_3$, are based on calculations where only the direct radiative effects of CFC-11 are considered. Some sensitivity runs made with the MPI model showed that the values may increase substantially if indirect effects from CFCs are included.

As there is no single time horizon that is ideal for calculations of GWPs, we follow IPCC (1992) and use 20, 100 and 500 years as time horizons in the calculations of GWPs. These time horizons should cover the main range of interest for climate change. The 100 year time scale is often used as a compromise between short time effects and chronic long time effects.

Table 4.7: Global Warming Potentials (GWPs) for CF_4 and C_2F_6 (mass basis). Numbers are given relative to CFC-11 (only direct radiative effects included) and CO_2. Radiative forcing and lifetimes (loss rates) for CFC-11 and CO_2 are taken from IPCC (1992).

Time horizon (years)	20	100	500
Relative to CO_2:			
CF_4	3700	5100	8800
C_2F_6	7300	10000	17300
Relative to CFC-11:			
CF_4	0.8	1.5	6.3
C_2F_6	1.6	3.0	12.4

4.7 Conclusions on the GWP calculations

The radiative transfer models which have been used to calculate the radiative forcing due to CF_4 and C_2F_6 show that the effect of spectral overlap with other atmospheric species is of great importance for the calculation of radiative forcing of CF_4; exploratory line-by-line calculations indicate that even a 10 cm^{-1} spectral resolution may be inadequate for an accurate calculation, given the sharpness of the absorption features of CF_4. Recommended values for CF_4 and C_2F_6 are 0.10 Wm^{-2}/ppbv and 0.30 Wm^{-2}/ ppbv respectively. The error in these figures is estimated to be about 20%. Global Warming Potentials (GWPs) have been estimated based on the Intergovernmental Panel on Climate Change methodology. The estimates for GWPs relative to CO_2 are for CF_4 3700, 5100, and 8800, and for C_2F_6 7300, 10000, and 17300 on the 20, 100 and 500 years time horizons respectively.

The GWP values for CF_4 in this report are lower than the ones calculated by Stordal and Myhre (1991). The numbers presented here represent an improvement to the earlier numbers, especially since the overlap between CF_4 and H_2O has been more properly treated. The present GWPs for C_2F_6 are somewhat larger than those of Stordal and Myhre (1991), reflecting simply the larger values used here for the band strength (see Section 4.1), again representing an improvement compared to the earlier work.

5. CONTRIBUTION TO GLOBAL WARMING

The calculated radiative forcing, combined with the observed increases in atmospheric concentrations can be used to estimate the global impact on climate by CF_4 and C_2F_6. The increase in the latter compound is not known, however, its atmospheric abundancy is small comparerd to the abundancy of CF_4; it is expected to have a much smaller climate effect than CF_4. Although, the estimated increase in CF_4 also is connected with uncertainties, the observations indicate an increase of approximately 2% per year in the the beginning of the 1980s. If the trend continued throughout the decade, CF_4 mixing ratios could have increased by 15 ppt during the 1980s. If we compare this increase to the increase in $CFCl_3$ of approximately 100 ppt (WMO,1992) in the same time period, and take into account the relative band strength of 0.44 *(Table 4.6)* compared to $CFCl_3$, we obtain a contribution to the greenhouse warming from CF_4 that is approximately 6% of the direct contribution from $CFCl_3$. Since the direct contribution from $CFCl_3$ to the total greenhouse warming from man made sources in the same period is approximately 6%, the contribution from CF_4 and C_2F_6 together to the greenhouse warming is less than 0.5%. However, CF_4 could contribute significantly to the national greenhouse budget in countries where the aluminium production pr. capita is large (e.g. Norway, Iceland).

6. RECOMMENDED FUTURE WORK

6.1 Calculations of GWPs

These studies have shown that calculated GWPs still are connected with uncertainties, and that more work needs to be done to decrease the uncertainties.

* Firstly, the sharp spectral features of these gases indicate the need for detailed line-by-line calculations, as the degree of overlap with other species can only be resolved properly with this method.

* Secondly, further measurements of the overall strength and the detailed spectra is required, especially for C_2F_6. It is known that such measurements are in progress in some laboratories.

* Finally, a new version of the HITRAN spectral data base is just becoming available; this will have updated strengths and positions of H_2O, N_2O and CH_4. Calculations with this new data would be desirable.

6.2 Estimates of the emission of CF_4 and C_2F_6 from the aluminium industry

The observational data discussed here are not conclusive with regards to the question of: a) The trends in atmospheric abundancies of CF_4 and C_2F_6, or b) the contribution of the aluminium industry to the atmospheric abundancies. There are indications that other sources may exist. It is suggested that both analysis of temporal trends in the atmospheric abundancies, and improved measurements of the emission rates per tonne of aluminium produced are done to estimate global emissions. New analytic techniques exists to perform the analysis with sufficient accuracy and time resolution.

* The trends in the atmospheric concentrations can be determined by analysis of stored air samples, which are available from 1980. With new analytical techniques that are used in analysis of air samples, only a negligible amount of the stored air samples are needed to perform accurate analysis of the abundancies and the trends of CF_4 and C_2F_6. Changes in annual concentrations during periods when annual production showed relatively unusual changes are of particular interest.

* A unique way to answer the question of whether there is a natural source or not will be to measure the CF_4 and C_2F_6 content in air trapped in ice cores which are more than 100 years old. If industry is the sole source such cores should contain virtually none of this gas. If, on the other hand, the conclusion drawn by Fabian et al. (1987) is correct, then 100 yrs old air should contain about 65% of the current level. Although a substantial larger amount of ice core is required to get the necessary amount of air for the

analysis, the new analytic technique which requires smaller amounts of air, limit the demand for large quantities of ice. Ice core samples that could provide this information are currently available.

* A more direct approach in estimating emissions from the aluminium industry will be to compare the ratio of C_2F_6 to CF_4 in the ambient air to the ratio from aluminium industry emissions. The latter should be measured directly in the stacks from a variety of cells operating under different conditions. As it is unlikely that this ratio would be the same either from natural sources or from other industrial sources such as comparison could provide a useful method. The usefulness of this method could, however, be limited, as the ratio could in emissions from the same plant, let alone in emissions from different smelters. The Tunabel Diode Laser Absorption Spectrometer method has sufficient specificity and sensitivity to make the measurements.

* In order to follow future development in the emission of CF_4 and C_2F_6 the two gases should be measured regularly at a few of the existing background stations for trace gas measurements that are in operation.

* National emission scenarios should be collected after improved estimates of emission factors have been obtained.

6.3 Studies of height distributions

One study (Fabian et al., 1987) indicate a faster drop in the mixing ratio with height of C_2F_6 in the stratosphere than in CF_4. If this drop indeed is real, it could indicate a a faster growth in emission of the former compound. However, it could also indicate an unknown upper atmospheric sink of C_2F_6. In order to clearify this, two studies are suggested:

* Firstly, new analysis of stratospheric air samples should be performed. Such samples have been collected in connection with the Arctic campaign this winter (EASOE). Arctic samples from the stratosphere will give the best opportunity to study vertical gradients, as these air masses are likely to have the largest vertical gradients.

* Model studies of the time dependent distribution of the gases in the stratosphere. New and improved emissions, based on the studies suggested above will be input to the model studies. Analysis of the result will be made based on comparisons with observed profiles.

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