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Greenhouse Effect and Greenhouse Warming Potential for SF_6

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SUMMARY

Emissions of carbon dioxide from burning of fossil fuels have been known since the last century to have the potential to alter the earth's climate. Over the last decades increases in the concentration of other radiatively active trace gases have been observed. Such so-called climate gases include chlorofluorocarbons (CFC's), methane (CH_4) and nitrous oxide (N_2O), for which human activity is fully or partly responsible for the observed increase.

For various purposes it has been useful to evaluate the relative impact of each of the gases that can potentially lead to global warming. The Global Warming Potential (GWP) has been developed as a measure of the relative warming effect from emissions of each climate gas. Estimates of GWPs depend on the time period chosen for the analyses. Time horizons ranging from 20 to 500 years have been used, reflecting the different kinds of changes that may occur in various systems accompanying a climate change. A time horizon of 100 years has been assumed to represent a reasonable compromise.

Three fully fluorinated species have been measured in the atmosphere at enough locations to characterize global concentrations: tetrafluoromethane (CF_4), hexafluoroethane (C_2F_6) and sulphur hexafluoride (SF_6). All these species are relatively stable chemicals, with residence times in the atmosphere which are probably at least 500 years. Since they do not contain chlorine, they cannot to any significant degree deplete the ozone layer. As absorbers of infrared radiation they will contribute to an increase in the greenhouse effect.

The global concentration of the three fully fluorinated species are increasing due to the emissions in various industrial processes. SF_6 has been observed to increase by 7.4%/yr. The current concentration is 1-2 ppt (parts per 10^{12}, volume mixing ratio).

In this study the GWP value for SF_6 has been calculated by the use of a wide band infrared radiative transfer model. The work was carried out under contract from Norsk Hydro. SF_6 has been shown to be more efficient as a climate gas than the currently widely used $CFCl_3$ (CFC-11). The GWP value relative to $CFCl_3$ is 1.9 on a 100 year time horizon. Relative to CO_2, which is usually used as a reference molecule, the GWP value is 6800 for SF_6, also on a 100 year time horizon.

GREENHOUSE EFFECT AND GREENHOUSE WARMING POTENTIAL FOR SF_6

1 INTRODUCTION

It has been recognized from the middle of the 19th century, that carbon dioxide and certain other trace atmospheric gases are transparent to incoming solar radiation but absorb and reemit the long wavelength radiation emitted by the earth's surface, thereby warming the lower atmosphere. The term "greenhouse effect" used about this warming refers to the increased surface temperature of the earth due to the presence of radiatively active trace gases (now often labeled as climate gases) and clouds in the atmosphere.

The climate impacts of the carbon dioxide emitted by fossil fuel combustion, has received widespread attention over the last few decades. However, there has been a growing realisation that a number of other trace gases may also perturb the radiation balance of the earth (Ramanathan, 1975; Wang et al., 1976). Many human activities give rise to emissions of gaseous pollutants into the atmosphere. Some of these trace gases are able to absorb outgoing long wavelength radiation and have the potential to contribute directly to an increase in the greenhouse effect. Other trace gases are not radiatively active themselves, but may change the chemical composition of the atmosphere and thereby modify the concentrations of other radiatively active gases, altering the greenhouse effect indirectly.

Among the greenhouse gases which are naturally present in the atmosphere, water vapour and carbon dioxide are contributing most to the greenhouse effect. The increasing concentration of carbon dioxide since the industrial revolution is likely to have contributed more to global warming than have the changes in any other trace gases over this same period. However, some

of these other trace gases absorb long-wavelength radiation much more efficiently than carbon dioxide. As a result, over the last few decades, the balance between the effects of the increasing carbon dioxide consentrations and the effects of the other radiation-absorbing active gases may have changed. Recent analyses have indicated that the other radiation-absorbing active gases may now jointly contribute about as much to global warming as does carbon dioxide (Ramanathan et al., 1987).

Some of these trace gases are highly stable and may reside in the atmosphere for decades or even centuries. Their lifetimes may be tens, hundreds or even thousands of years, so that it is important to recognize that there is a long term greenhouse warming, once such pollutants have been released into the atmosphere.

The atmospheric concentrations of several gases other than CO_2 that contribute to the greenhouse effect directly or indirectly, are increasing due to human activities. Most attention has been paid to the gases methane (CH_4), nitrous oxide (N_2O), chlorofluorocarbons (CFCs) and alternative fluorocarbons (HFCs), which directly affect the radiation balance, and the gases which contribute to ozone formation in the troposphere, CO, NO_x and non-methane hydrocarbons. Since ozone is another infrared absorbing gas, these gases have an indirect effect on the radiation balance.

Gases like CF_4, C_2F_6 and SF_6 have also been indicated as possible direct climate gases. While halocarbons containing chlorine are known to contribute to depletion of the stratospheric ozone layer, no significant ozone depletion will be caused by the fully fluorinated components CF_4, C_2F_6 and SF_6, as fluorine is much less efficient than chlorine in the catalytic destruction of ozone in the stratosphere.

The greenhouse effect for most of the direct climate gases mentioned above has been quantified in several numerical studies, as compiled e.g. in the report of the Intergovernmental Panel on Climate Change (IPCC, 1990). Calculations of the greenhouse effect of the component SF_6 have been performed in this study, and results are described in this report.

2 THE GLOBAL WARMING POTENTIAL CONCEPT

For various purposes it has been useful to formulate a simple methodology which allows the ranking of climate gases to indicate their relative contributions to the greenhouse effect. The global warming potential (GWP) has been developed as a measure of possible warming effect from emissions of each climate gas. It is based on the radiative forcing due to a perturbation in the concentration of a gas. This radiative forcing is defined as the net radiative flux change at the tropopause, keeping all the tropospheric parameters (including moisture and temperature) fixed. The GWP of a greenhouse gas takes into account both the radiative forcing effects of a single pulsed emission of the gas and its lifetime in the atmosphere.

Following work of Fisher et al. (1990), Lashof and Ahuja (1990), Rodhe (1989), and Derwent (1990), the IPCC (1990) report defined the GWP as the time integrated contribution to radiative forcing from the instantaneous release of 1 kg of a trace gas expressed relative to that from the release of 1 kg of carbon dioxide:

$$GWP = \frac{\int_0^n a_i \; c_i \; dt}{\int_0^n a_{CO_2} \; c_{CO_2} \; dt} \qquad \text{(Eq 1)}$$

where a_i is the instantaneous radiative forcing due to a unit increase in the concentration of trace gas, i, c_i is concentration of the trace gas, i, remaining at time, t, after its release and n is the number of years over which the calculation is performed. The corresponding values for carbon dioxide are in the denominator.

Although another gas or surrogate would have a simpler atmospheric decay rate as compared to CO_2, an ongoing revised evaluation of GWPs, within IPCC, continues to use CO_2 as the reference gas of choice, reflecting the importance of CO_2 as the gas of primary concern to future climate change.

The GWP index is a direct function of radiative forcing and residence time, and only an indirect indicatior of the potential climatic response. While it must be mentioned that it has serious limitations, the GWP is considered the best practical tool for assessing the relative impact of emissions.

3 TIME HORIZONS FOR GWPs

Estimates of GWPs depend on the time-period of integration chosen for the analyses. There is no given choice of integration time for determining GWPs that is ideal and covers all the uses of this concept.

Possible future climate change is associated with different kinds of changes in various (e.g. geophysical and biological) systems. For example, rapid climate change over successive decades may have adverse impacts to biological systems as climate zones shift more quickly than natural systems can migrate. Likewise, a temperature increase of $2\text{-}5^0$ C over a somewhat longer time horizon, such as the next century or next two centuries,, could have adverse effects on both human communities and natural ecosystems. Each type of system has its own characteristic sensitivity to different types of damage. The choice of time horizon for assessing the risks of climate change depends on the type of changes that are of greatest interest.

The GWPs evaluated over the 100 year period appear generally to provide a reasonable compromise between the various time horizons for climate response. In addition, carbon cycle models also indicate that this time period broadly represents the time

scale over which a significant fraction of CO_2 is removed from the atmosphere. GWP values for the 100 year time horizon are therefore likely to by emphasized in future policy analyses.

4 SOURCES AND ATMOSPHERIC DECOMPOSITION OF FULLY FLUORINATED SPECIES

Three chemicals in this category have been measured at enough locations to characterize global concentrations: tetrafluoromethane (CF_4, CFC-14), hexafluoroethane (C_2F_6, CFC-116), and sulphur hexafluoride (SF_6). These three man-made species are relatively stable chemicals with atmospheric residence times over 500 years. These species are not chemically involved in atmospheric processes below about 50 km. The main sources on a global scale of CF_4 and C_2F_6 are not at all clear. A temporal increase of about 2%/yr in CF_4 concentrations has been measured (R.J. Cicerone et al, unpublished manuscript, 1985). This rate of increase is less than that deduced by Cicerone (1979). SF_6 is a dielectric gas used in electrical equipment as well as in the magnesium industry, and its concentration is also currently increasing in the atmosphere. The current concentration is 1-2 ppt (parts per 10^{12}, volume mixing ratio), and the rate of increase has recently been estimated to be 7.4%/yr in the 10 year period from 1979 to 1989 (Rinsland et al., 1990a).

Halocarbons released at the ground can generally be removed from the atmosphere by reaction with the hydroxyl radical (OH) in the troposphere (0-ca. 15 km), by dissociation by ultraviolet (UV) radiation or reaction with an exicited oxygen atom ($O(^1D)$) the stratosphere (ca. 15-50 km) and the mesosphere (50-90 km), or by extreme UV radiation or electron capture in the ionosphere (above 90 km). The longer the residence time, the more of the decomposition will take place at high altitudes. CF_4, C_2F_6 and SF_6 are removed predominately in the ionosphere. Although their lifetimes have not been calculated explicitly, from the process known to decompose them it can be

inferred that the lifetimes are at least 500 years, probably several thousand years. As discussed above, GWPs are usually considered for 100 years, or at most 500 years. For practical purposes, one can therefore neglect the decomposition of SF_6 when the GWP is calculated. By doing so, one will slightly overestimate the GWP, as discussed below.

5 THE MODEL USED IN THE PRESENT STUDY

Detailed calculations of the infrared radiative effects of climate gases require use of models that treats the radiative transfer of each spectral line. Such so called line-by-line calculations are computationally very expensive, and have not been used for GWP calculations. They do, however, form the basis for comparison with more coarse models used in GWP calculations as well as in climate models. For such purposes models treating the radiation transfer within relatively broad spectral bands are used . All GWP estimates published so far are based on calculations with broad-band models similar to the model used in this study.

This model (Stordal, 1988) calculates the radiatiative transfer of infrared radiation in the troposphere and the stratosphere. Gases that are taken into account are CO_2 , O_3 and H_2O, all of which are part of the natural atmosphere. Further, effects of several CFCs, N_2O and CH_4 have been included, and for this study also SF_6 . Absorption data for the latter component has been taken from Rinsland et al. (1990b).

The effect of clouds have been neglected in this study. Although clouds do influence the radiative balance, it has been shown to be a reasonable approximation to neglect this when only relative effects of various greenhouse gases are considered (WMO/UNEP, 1990), as in calculations of GWPs.

In the present study, calculations have been performed for all latitudes (increment of 10 deg) and all times of the year

(every month). A better measure of the radiative effects of the greenhouse gases is then obtained. Usually GWP values are estimated assuming globally and yearly averaged conditions.

6 MODEL RESULTS

GWPs have not been reported in the literature for SF_6. The absorption efficiency of UV radiation by various halocarbons vary considerably, yielding a wide range of atmospheric residence times, as explained above. However, absorption of infrared radiation by many of the most widely used halogenated species, and also SF_6, does not vary to a large extent from one species to another. GWP values therefore seem to be within a factor of about 10, at least for time horizons of 100 years or less. For the extreme long-lived species, the influence of the estimated lifetimes become more important when calculating the GWP's under long time horizons. This leads to increased GWP's of these components compared to CFC's and CO_2 under long time horizons (e.g. 500 years). Their GWP values therefore increase when going to very long time horizons.

GWP values calculated in this study for SF_6 are given in two tables. Results have been given relative to $CFCl_3$ (CFC-11) (Table 1) as well as the conventional compound CO_2 (Table 2).

Table 1: GWP values for SF_6 relative to $CFCl_3$ (CFC-11).

	Time horizon		
	20 yrs	100 yrs	500 yrs
SF_6	1.1	1.9	8.0

Table 2: GWP values for SF_6 amd $CFCl_3$ relative to CO_2.

	Time horizon		
	20 yrs	100 yrs	500 yrs
$CFCl_3$	4 500	3 500	1 500
SF_6	5 000	6 800	12 000

Since the present study has been based on calculations for various latitudes and seasons, one is allowed to study latitudinal and seasonal effects. In Figure 1 the radiative forcing at the tropopause level resulting from increases in SF_6 and $CFCl_3$ are given for various latitudes and seasons. The results are given relative to the similar radiative forcing of CO_2. For both species, the radiative forcing is substantially stronger in the tropics and weaker at high latitudes compared to the CO_2 forcing. The resulting climate change resulting from increased levels of e.g. SF_6 and $CFCl_3$ can therefore be somewhat different from the climate change due to CO_2 increase, even if amounts are released of the gases that yield equal globally averaged radiative forcing. Even between the two above mentioned species there are slight differences, with SF_6 giving somewhat less contrast between radiative forcing at low and high latitudes than $CFCl_3$.

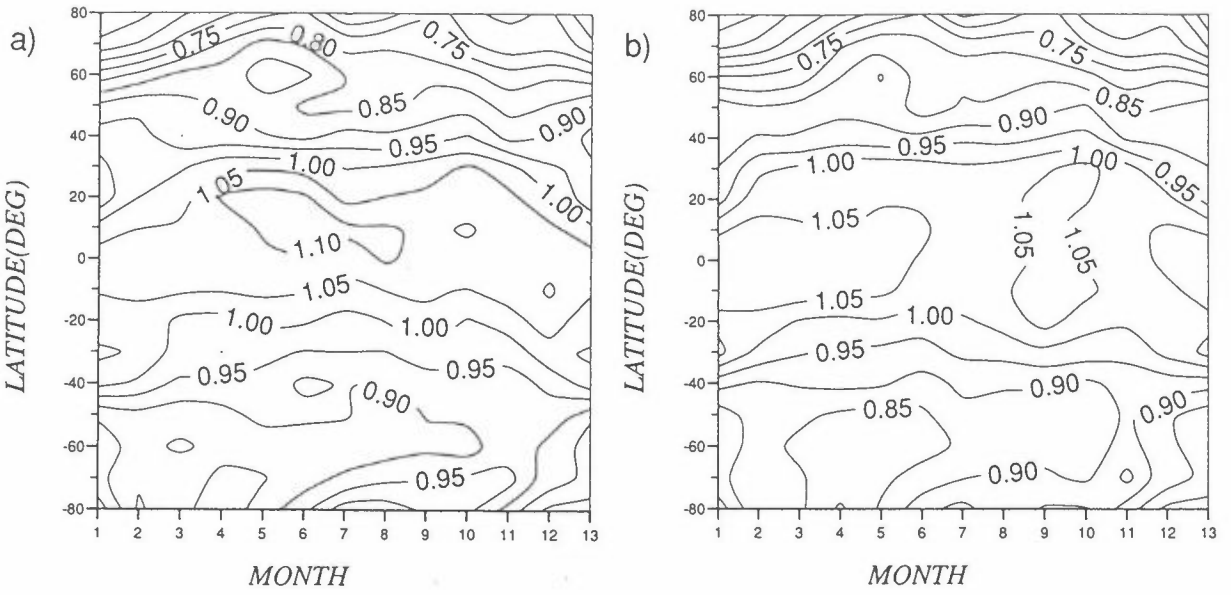

Figure 1: Radiative forcing at the tropopause level due to addition of (a) $CFCl_3$ and (b) SF_6, relative to the forcing from CO_2 at a given latitude (40 N) and time of the year (February).

As discussed above the GWP values given here are based on the assumption that SF_6 is not decomposed in the atmosphere (an infinite lifetime). This leads to a systematic overestimation of the GWP values. This effect is however modest, and probably small compared to other uncertainties in the calculations. The ratio between the correct GWP and the GWP estimated according to the infinite lifetime assumption depends on the real lifetime of the species in question. It can be explicitely specified from Equation 1, and yields:

$$r = \frac{1}{n} \int_0^n e^{-t/\tau} \, dt \qquad \text{(Eq. 2)}$$

where τ is the residence time. Table 3 shows that the infinite lifetime assumption yields and overestimate of 10.4% of the GWP for a species with 500 years lifetime on the 100 years time horizon. As the lifetime of SF_6 is most likely as least 1000 years, the error is probably less than 5%.

Table 3: Overestimate (%) of the GWP for a species with various lifetimes (τ) assuming an infinite lifetime.

τ (yrs)	Error (%), time horizon 100 yrs
500	10.4
1 000	5.0
10 000	0.5

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Rapporten beskriver drivhuseffekten forårsaket av komponenten SF_6 som brukes i magnesiumindustrien. GWP-verdier er beregnet med en bred-bånd modell som beskriver overføring av infrarød stråling.

TITLE
Greenhouse effect and greenhouse warming potential for SF_6

ABSTRACT

The report describes the greenhouse effect caused by the species SF_6 which is used in the magnesium industry. GWP values are calculated with a broad band infrared radiation transfer model.

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