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Radiative Forcing Calculations for CH₃Cl

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Abstract

Methyl chloride, CH₃Cl, is the major natural source of chlorine to the stratosphere. The production of CH₃Cl is dominated by biological sources from the oceans and biomass burning. Production has a seasonal cycle which couples with the short lifetime of tropospheric CH₃Cl to produce nonuniform global mixing. As an absorber of infrared radiation, CH₃Cl is of interest for its potential affect on the tropospheric energy balance as well as for its chemical interactions. In this study, we estimate the radiative forcing and global warming potential (GWP) of CH₃Cl. Our calculations use an infrared radiative transfer model based on the correlated k-distribution algorithm for band absorption. Global and annual average vertical profiles of temperature and trace gas concentration were assumed. The effects of clouds are modeled using three layers of global and annual average cloud optical properties. A radiative forcing value of 0.0053 W/m²/ppbv was obtained for CH₃Cl and is approximately linear in the background abundance. This value is about 2 percent of the forcing of CFC-11 and about 300 times the forcing of CO₂, on a per molecule basis. The radiative forcing calculation for CH₃Cl is used to estimate the global warming potential (GWP) of CH₃Cl. The results give GWPs for CH₃Cl of the order of 25 at a time of 20 years(CO₂ = 1). This result indicates that CH₃Cl has the potential to be a major greenhouse gas if significant human related emissions were introduced into the atmosphere.

I. Introduction

Methyl chloride, CH₃Cl, is the most abundant halocarbon in the earth's atmosphere (Elkins *et al.*, 1984), representing approximately 30 percent of the total chlorine content. Typical concentrations on the order of 600 parts per trillion have been determined (Rasmussen *et al.*, 1980, Singh *et al.*, 1983, WMO, 1991). Volcanic activity, biological production, automobile exhaust, and biomass burning have been considered to be CH₃Cl sources (Crutzen *et al.* 1979). The principal sink for CH₃Cl is the reaction with OH in the troposphere (Howard and Evenson, 1976). An atmospheric lifetime for CH₃Cl of about 1.5 years has been given by Prather (1989). According to Elkins *et al.* (1984), CH₃Cl has strong infrared absorption bands at 732, 1015, 1355, 1455, 2879, 2966 and 3042 cm⁻¹. The main purpose of this paper is to calculate the tropospheric radiative forcing of CH₃Cl using the line by line data in the HITRAN91 data base (Rothman *et al.*, 1991) and the spectroscopic line data of Brown (1994). The calculation will be done for a globally and annually averaged model atmosphere with a representative cloud distribution. GWP calculations for CH₃Cl will be made and compared to other trace gas GWP's given in IPCC (1992).

In a recent publication Grossman and Wuebbles (1992, "GW") a model for the calculation of the global warming potentials (GWPs) of trace gases in the atmosphere was described and used to calculate the GWP for SF₆. The GWP of a gas is defined as,

$$GWP(c_i) = \frac{\int_0^t \Delta F(c_i, t) dt}{\int_0^t \Delta F(c_{CO_2}, t) dt} \quad (1)$$

where ΔF is the change in radiative forcing with time as a function of the species concentration (c_i). The model for Equation 1 given by GW is,

$$GWP(C_i) = \frac{m_{CFC-11}}{m_i} \cdot \frac{a_i}{a_{CFC-11}} \cdot \frac{\tau_i}{\tau_{CFC-11}} \cdot \frac{(1 - \exp(-t/\tau_i))}{(1 - \exp(-t/\tau_{CFC-11}))} GWP(CFC-11) \quad (2)$$

where the a 's are the radiative forcing values at the tropopause in W/m² per ppbv, the m 's are the molecular mass, and the τ 's are the atmospheric lifetimes. The radiative forcing term a_i in Equation 2 is defined as the difference in the net radiative flux at the tropopause due to a change in the composition by 1 ppbv of a single molecular species while, at the same time, keeping the composition of all other species constant. In a recent publication Grant *et al.* (1992, G1) and Grossman and Grant (1992) a correlated k-distribution model for the absorption by the major atmospheric molecular absorption species (H₂O, CO₂, O₃, CH₄, and N₂O) was used to calculate the fluxes and heating rates in the 0–2500 cm⁻¹ wavenumber range. The fluxes and heating rates obtained for this model are accurate to within ten percent when compared to line by line calculations. The altitude range covered by these calculations was 0–60 km. The k-distributions were calculated using the HITRAN91 database (Rothman *et al.*, 1991) to obtain the line

parameters within each wavenumber sub interval, the FASCODE2 code (Clough, 1986) to calculate a grid of detailed line by line opacities, and the ABSORT code (G1) to calculate the cumulative probability distributions and the k-distributions for each atmospheric layer.

II. CH₃Cl Data

Inspection of the HITRAN91 database reveals that only the lines of the ν_1 , ν_4 , and $3\nu_6$ bands of CH₃Cl between 2907 and 3173 cm⁻¹ have been included in the compilation. According to Elkins et al. (1984) the strength of these bands represent approximately 40 percent of the total line strength of all CH₃Cl bands. Furthermore this spectral region contains water vapor bands and the CH₃Cl contributions to the radiative forcing may be small due to overlapping water vapor absorption. A database for the properties of the CH₃Cl lines in the ν_2 , ν_3 , and ν_5 bands has been developed by Brown (1994) and Brown et al. (1987) in the wavenumber regions 661 to 772 cm⁻¹ (ν_3) and 1261 to 1646 cm⁻¹ (ν_2 , ν_5). This is an IR window region and thus these bands should contribute the majority of the radiative forcing. According to Elkins et al. (1984) the ν_2 , ν_3 , and ν_5 bands represent approximately 55 percent of the total line strength of the CH₃Cl bands. The ν_6 band at 1015 cm⁻¹ is not presently tabulated on any database and cannot be included in the radiative forcing calculation. The effect of the ν_6 band omission would be on the order of 5 percent. According to Elkins et al. (1984) the combined strength of the ν_2 , ν_3 , and ν_5 bands should be approximately 1.34 times the combined strength of the ν_1 , ν_4 , and $3\nu_6$ bands. The ratio of the combined line strength of the ν_2 , ν_3 , and ν_5 bands in the Brown (1994) to the combined line strength of the ν_1 , ν_4 , and $3\nu_6$ bands in the HITRAN91 data base is 3.92, indicating that the HITRAN line strengths may be too low by a factor of 2.92. Radiative forcing calculations will be done for the HITRAN91 line strengths as given and for the case where the line strengths have been multiplied by a factor of 3. A technique has been developed to merge both the Brown (1994) and the HITRAN91 databases into the calculation of the k-distributions outlined in G1 in order to calculate the complete radiative forcing of CH₃Cl.

III. Parameters of the Calculations

Flux and radiative forcing calculations were made for the following model atmosphere parameters.

A. Globally and seasonally averaged model atmosphere, (Wuebbles et al., 1994):

1. Altitude resolution;
 - a. 1 km, 0–20 km altitude,
 - b. 2 km, 20–60 km altitude.
2. Temperature–pressure–mixing ratio vertical profiles given in Figures 1 and 2.
3. A ground temperature of 291 K.
4. Tropopause at 166 mb.
5. Cloud Distribution;
 - a. Cloud thickness of 1 km.
 - b. Cloud bases at 2 km, 4 km, and 10 km altitudes.

- c. Fractional cloud cover amounts of 0.31 (low), 0.09 (middle), 0.17 (high).
- 6. Outgoing terrestrial radiation of 239 W/m².
- 7. A wavenumber range of 500 to 3200 cm⁻¹ in 25 cm⁻¹ subintervals
- 7. CH₃Cl mixing ratio of 0.0 (ambient), and 100 ppbv (forced), constant with altitude.

IV. Results and Discussion

The globally- and annually-averaged altitude profiles for water vapor, ozone, and methane (Wuebbles et al., 1994) are depicted in Figure 1. Carbon dioxide is constant at 350 ppmv throughout the model atmosphere. Nitrous oxide decreases monotonically from 308 ppbv near the surface to 1.2 ppbv at 59 km. The pressure-temperature profile for the model atmosphere is shown in Figure 2. The tropopause in the globally-averaged atmosphere, based on the temperature gradient in the troposphere decreasing to a value of 2K/km, indicated in Figure 2, occurs at 166 mb (~13.2 km).

The tropospheric radiative forcing calculations for CH₃Cl are shown in Table 1.

Table 1. Tropospheric radiative forcing calculations for CH₃Cl

INCLUDED BANDS	RADIATIVE FORCING(W/M ² /ppbv)
$\nu 1, \nu 2, \nu 3, \nu 4, \nu 5, 3 \nu 6$ (100 ppbv forcing)	5.31×10^{-3}
$\nu 1, \nu 2, \nu 3, \nu 4, \nu 5, 3 \nu 6$ (1 ppbv forcing)	5.90×10^{-3}
$\nu 1, \nu 4, 3 \nu 6$ (HITRAN91)	2.71×10^{-6}
$(\nu 1, \nu 4, 3 \nu 6) \times 3$	7.15×10^{-6}

The results of Table 1. show that the tropospheric radiative forcing of CH₃Cl is due entirely to the $\nu 2, \nu 3$, and $\nu 5$ bands. The contribution of the $\nu 1, \nu 4$, and $3 \nu 6$, bands, even with a factor of 3 increase in the line strengths, is most likely heavily overlapped by water vapor lines. It appears that the radiative forcing is linear to within approximately 10 percent in the abundance of CH₃Cl between 1 and 100 ppbv. Using the radiative forcing formulae given in IPCC (1990), the radiative forcing of CH₃Cl is about 2 percent of that of CFC-11 and about 300 times that of CO₂, on a per molecule basis. Table 2 shows the results of a calculation of the GWP for CH₃Cl at times of 20, 100, and 500 years (c.f. Equation 2).

Table 2. Global warming potential for CH₃Cl

20 YEARS	100 YEARS	500 YEARS
25.5	7.0	2.4

The lifetime, 55 years, and GWP's for CFC-11 at 20, 100, and 500 years, 4500, 3400, and 1400, are taken from IPCC (1992). The GWP's of CH₃Cl given in Table 2 are of the same order as CH₄, on a per kilogram basis (IPCC, 1992). Of course the actual abundances of CH₃Cl are so small, approximately 600 parts per trillion, that serious greenhouse problems are not a current problem and will not become a problem unless large releases of this gas occur.

Acknowledgments

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Figure Captions

- Figure 1. Globally and annually averaged profiles of water vapor, ozone, and methane as a function of altitude for the ambient atmosphere.
- Figure 2. Pressure-temperature profile for the ambient atmosphere. The temperatures are globally and annually averaged.

Figure 1 Globally- and annually-averaged profiles of water vapor, ozone, and methane as a function of altitude for the ambient atmosphere.

Figure 2 Pressure-temperature profile for ambient atmosphere. The temperatures are globally- and annually-averaged.

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