Working Paper

Latitudinal and Altitudinal Distribution of Carbon Dioxide, Halocarbons, Nitrous Oxide, Methane, Carbon Monoxide and Hydroxyl in the Atmosphere

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WP-92-038
May 1992

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FOREWORD

IIASA, in collaboration with the National Institute for Public Health and Environment (RIVM; Bilthoven, The Netherlands), is adapting RIVM's global IMAGE model (Intergated Model to Assess the Greenhouse Effect) to provide regional values of temperature and, eventually precipitation change resulting from a variety of greenhouse gas scenarios. These regional values will be used as input to impact models such as those for vegetation and forest growth and also sea level rise that are being developed at IIASA and RIVM. This paper reports on today's latitudinal and altitudinal distribution of carbon dioxide, halocarbons, nitrous oxide, methane, carbon monoxide and hydroxyl in the atmosphere. Where possible, conclusions are drawn with regard to the preindustrial and future distributions of the gases. The availability of this knowledge will eventually become very important in the connection of the above regionalization attempt of IMAGE.

ABSTRACT

Due to human activities, atmospheric concentrations of several gases have been increasing during the past century. Some of these gases are so-called greenhouse gases and play an important role in the earth's climate. Increasing concentrations of greenhouse gases may ultimately result in global climate change. In order to investigate regional effects of the enhanced greenhouse effect, 1- to 3-dimensional computer simulation models are being developed. For the calculation of radiative transfer through the atmosphere, these models require basic information with regard to the latitudinal and/or altitudinal distribution of greenhouse gases in the atmosphere.

The purpose of this study is to give an overview of the spatial variations of atmospheric greenhouse gas concentrations. Data from several measurement programs are used to obtain first order estimates of latitudinal and height profiles of carbon dioxide (CO_2), several halocarbons (CFC-11, CFC-12, CFC-113, HCFC-22, CH_3CCl_3 and CCl_4), nitrous oxide (N_2O) and methane (CH_4). Also carbon monoxide (CO) and hydroxyl (OH) are considered, because these gases may influence CH_4 concentrations. An attempt is made to explain the observed gradients qualitatively. If possible, some conclusions are drawn with regard to the preindustrial and future distributions of the gases.

The results show that the present concentrations of all greenhouse gases at the earth's surface are higher in the northern than in the southern hemisphere. The main reason for this may be the fact that most emissions of these gases originate from the northern hemisphere. The profiles with height differ for the gases. In case the main sink is located in the stratosphere (for instance for CFCs and N_2O), a steep gradient with height is observed above the tropopause.

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1. INTRODUCTION

Since the Industrial Revolution, atmospheric concentrations of several greenhouse gases have been increasing (Table 1), and thus increasing the natural greenhouse effect. This could ultimately result in a global warming. Computer simulation models like IMAGE, the Integrated Model to Assess the Greenhouse Effect (Rotmans 1990), can be used to calculate the historical and future warming on a global scale.

To investigate regional impacts of an enhanced greenhouse effect, 1- to 3-dimensional climate models are being developed. For their calculations of radiative transfer in the atmosphere, these models require basic knowledge about atmospheric distributions of greenhouse gas concentrations. Several types of distributions can be examined. Concentrations may vary spatially with latitude, longitude or altitude. Next to this, there may be temporal variation, either short term (hourly, diurnal, weekly, monthly, seasonal or interannual), or long term (interannual or interdecadal). The purpose of this study is to give an overview of latitudinal and altitudinal variations of atmospheric greenhouse gas concentrations. The study focusses not only on today's spatial distribution of the gases, but if possible, some conclusions are drawn with regard to their preindustrial and future distributions as well. This background information can eventually be used for the atmospheric part of the IMAGE model which is presently being regionalized jointly by IIASA and the Netherlands' National Institute of Public Health and Environmental Protection (RIVM).

The spatial distribution of atmospheric gases is mainly the result of the spatial distribution of the sources, and the sinks, and transport in the atmosphere. Most of the gases considered are emitted into the atmosphere from the earth's surface. Atmospheric mixing then takes place. The main barriers for tropospheric mixing is the InterTropical Convergenze Zone (ITCZ), where warmer air due to solar heating ascends (Hadley cell). This is the latitude where the atmosphere is more or less divided into two hemispheres. Within one hemisphere, the atmosphere is mixed in about one to two months (Fabian 1989). Mixing between the hemispheres takes about one to two years (Fabian 1989). A second barrier for mixing is the tropopause, at a height of about 8-12 km. In the stratosphere air temperature increases with height. This temperature inversion reduces convection and, therefore, vertical mixing.

The gases considered here are
- carbon dioxide (CO_2),
- several halocarbons (CFC-11, -12, -113, HCFC-22, CH_3CCl_3, CCl_4).
- nitrous oxide (N_2O),
- methane (CH_4), and some gases that influence CH_4:
- carbon monoxide (CO),
- hydroxyl radical (OH),

Table 1. Tropospheric concentrations and the residence time of the major greenhouse gases. (Source: ^{1} Rotmans 1990, ^{2} Watson 1990).

Gas	Concentration in 1900^1	Present concentration^2	Present trend^2 (% per year)	Lifetime^{1,2} (year)
CO_2	285 ppmv	353 ppmv	0.5	50-200
CH_4	0.9 ppmv	1.7 ppmv	0.9	10
N_2O	285 ppbv	310 ppbv	0.25	170
CFC-11	0 ppbv	0.3 ppbv	4	75
CFC-12	0 ppbv	0.3 ppbv	4	125

2. METHODOLOGY

2.1 Data selection and processing

2.1.1 Data on concentrations of atmospheric trace gases

Atmospheric concentrations of gases have been investigated by many researchers in different ways. Concentrations of gases in ancient atmospheres can be investigated by analysis of air trapped in polar ice. The combination of both the age of the ice and the composition of the air found in the bubbles in the ice may reveal the atmospheric concentrations of gases prior to the Industrial Revolution. At present, concentrations are measured directly at either stationary or non-stationary monitoring stations.

There are, at present, several stationary monitoring networks, measuring concentrations in the atmosphere regularly on a long-term base. The main purpose of these programs is to obtain insight in the temporal variation of atmospheric trace gas concentrations at several locations. The measurement sites are almost always ground-based. The data sets provided by such programs are very useful for the present study, because they allow investigation of the latitudinal distributions at the earth's surface. An example of such a program is the Geophysical Monitoring for Climate Change (GMCC), a program of the National Oceanic and Atmospheric Administrator (NOAA). In this program concentrations of CO_2 and CH_4 are measuered regularly at up to 23 stations. At some of the GMCC stations also other gases (CFCs, N_2O, CO, O_3 etc) are measured. Other monitoring networks are described in the sections on the different gases.

Atmospheric concentrations can also be investigated using non-stationary monitoring. For instance, several data sets available are results of measurements taken aboard of ships, aircrafts and/or balloons. These data represent a detailed gradient (latitudinal or altitudinal) at a certain time. Unfortunately, it is often not possible to obtain annually averaged profiles from these data. However, with respect to distribution with height these are often the only data sets available. Several of these measurements are described in the sections on the specific gases.

Finally, concentrations of some gases are investigated by using satellites. Several satellites observe the earth's climate. The World Weather Watch Global Observation Satellite System comprises the follwing satellites: Meteosat (ESA), GOES EAST (USA), GOES WEST (USA), GMS (Japan) and a Russian satellite. In case these satellites record atmospheric concentrations, total column values are obtained. Satellite data have not been used in this study.

2.1.2 Selection of data

An important criterium for selection of data sets has been their completeness. Ideally data have to be obtained by measuring regularly during at least one year at enough representative sites. In case of the latitudinal distribution of CO_2 and CH_4 at the earth's surface, the data sets can be considered as complete. For most of the other profiles shown, however, the data sets are in some way incomplete. A second criterium for selection of data was the year of the measurement. In order to give an overview of the present situation the most recent data available are chosen. In some cases comparable data sets from the past are used to investigate the trends.

It can be questioned to what extent data sets obtained in different studies are comparable. For instance, data sets may include ship-, aircraft- and balloon-measurements, while other sets are from only land-based stations. Measurements performed some decades ago may include errors because of interlaboratorial differences. Finally, different mathematical procedures that are used to obtain annually averaged values might cause slightly different results. However, the purpose of this study is to give an overview of the first order spatial variation in concentrations. Investigating the main spatial concentration gradients it seems reasonable to assume that at least recent measurements are precise enough.

2.1.3 Data processing

Looking for first order effects only, we tried to find a linear relationship between atmospheric concentrations and sine of latitude, assuming that the best results are obtained by dividing the atmosphere in two areas (weighted linear regression with boundary condition).

Area 1:	90°S to X_k°N/S:	$Conc(X_i) = a_1 + b_1(X_i)$
Area 2:	X_k°N/S to 90°N:	$Conc(X_i) = a_2 + b_2(X_i)$

Boundary condition: $Conc(X_k) = a_1 + b_1(X_k) = a_2 + b_2(X_k)$, where

Conc = atmospheric concentration of a gas
Xi = sine of latitude i
X_k = sine of latitude where the atmosphere is divided

The least-squares fit of the calculated conc(X_i) to the available concentration conc(X) values depends on k. Therefore the results are, unless mentioned otherwise, presented for that k for which the result reveals the best least squares fit (described by the measure sqrt = $\Sigma(conc(X_i) - conc(X))^2$. The calculations are performed for data sets considering latitudinal and altitudinal distribution. In the latter case X_i refers to altitude (in km). In some cases, however, latitudinal and altitudinal distributions are adopted from others without recalculation.

2.2 Data on carbon dioxide

2.2.1 Carbon dioxide monitoring

Atmospheric concentrations of carbon dioxide have been measured at an increasing number of stations since 1958. In the following, a brief, far from complete, overview of the monitoring systems is given.

Latitudinal distribution of carbon dioxide

Data from the main stationary monitoring networks can reveal the latitudinal distribution of CO_2 at the earth's surface. For instance, NOAA's GMCC data are very useful (e.g. Komhyr et al. 1985, Conway et al. 1988, Thoning et al. 1989). Other data sets with regard to the latitudinal distribution are obtained using non-stationary monitoring, for instance aboard ships. An example is the Global Atmospheric Research Program 1979-1980, GARP (Keeling at al. 1984), or the First Global Geophysical Experiment, FGGE (Heimann and Keeling 1986, Keeling and Heimann 1986). Some other studies on the latitudinal distribution of CO_2 are: Pearman and Hyson (1981), Gilette and Hanson (1983), Fung et al. (1983), Pearman and Hyson (1986), Tanaka et al. (1987a), Tans et al. (1989, 1990, 1991), Enting and Mansbridge (1989, 1991), Keeling et al. (1989a, b) Heiman and Keeling (1989), Heiman et al. (1989), Nakazawa et al. (1991a), Boden et al. (1990).

Altitudinal distribution of carbon dioxide

Data with regard to the distribution with height are mainly those obtained using aircraft and balloons, for instance: Bishof (1971), Bishof et al. (1980), Fung et al. (1983), Tanaka et al. (1983, 1987b, 1988), Gamo et al. (1989), Pearman and Hyson (1986), Bolin and Keeling (1963), Nakazawa et al. (1991a).

Other variations in atmospheric carbon dioxide concentrations

Next to latitudinal and altitudinal variations, also longitudinal variations of carbon dioxide concentration have been reported (e.g. Keeling et al. 1989b) as well as short term temporal variations, like within-day variations (Navascuez et al. 1987, Tanaka et al. 1987b, Halter and Peterson 1988, Thoning et al. 1989), weekly to seasonal variations (e.g. Pearman and Hyson 1981, Cleveland et al. 1983, Gilette and Steele 1983, Gaudry et al. 1983, Heimann and Keeling 1986, Cliattaglia et al. 1987, Monfray et al. 1987, Robinson et al. 1988, Nakazawa et al. 1991b, Chan and Wong 1990) or short term interannual variations (e.g. Thompson et al. 1986, Gaudry et al. 1991).

2.2.2 Carbon dioxide data used in this study

Data used for latitudinal distribution of carbon dioxide

The data used for the latitudinal distribution of carbon dioxide are those reported by Keeling et al. (1989a), by Pearman and Hyson (1986) and by Tans et al. (1990). These data represent the latitudinal gradient at the earth's surface.

Data for the years 1962, 1968, 1980 and 1984 as reported by Keeling et al. (1989) are used here. Keeling et al. (1989) combine several data sets from stationary sources at the earth's surface (GMCC) and from ship-measurements. From SIO (Scripps Institute of Oceanography, University of Califronia) data they chose those from sites close to oceans or on barren ground, where local source/sinks are weak or absent. Furthermore, they used land-based data from the GMCC network, and cruise data from the FGGE project. They centered two-year portions of the atmospheric CO_2 data records on the years 1962, 1968, 1980 and 1984. Seasonally adjusted, trend corrected data from the land stations were derived by Keeling et al. from spline fits. Finally, concentration data from ships and ice floe stations were derived by averaging individual measurements, or by use of special functions. Data from the Mauna Loa Observatory were not used in this study, because these data refer to concentrations at a height of about 4 km.

Pearman and Hyson (1986) used several data sets to produce 1976 to 1982 averages in a similar way as Tans et al. (1990) (described below). Fraser et al. (1983a) pointed out that data from various observatories have not always been comparable. However, since 1984 several laboratories produced data which should be comparable. These include (1) the National Atmospheric and Oceanic Administrator's (NOAA) program Geophysical Monitoring for Climate Change (GMCC), (2) the University of California, Scripps Institute of Oceanograpy (SIO), and (3) the Australian Commonwealth Scientific and Industrial Research Organization (CSIRO) Division of Atmospheric Research. In order to obtain an extensive data set, Pearman and Hyson combined data obtained by these laboratories from land-based stations for the years 1976 to 1982. They calculated the mean annual average concentration for each year using the data from the eight flask sampling observatories which had produced data for the full seven years. Globally averaged year-to-year increases in CO_2 concentration were estimated from the mean annual averages. Subsequently, the annual mean concentration for all observatories and for all years were normalized to the 1982 concentrations, assuming that the rate of concentration increase is to a reasonable approximation the same everywhere. In this way, up to seven estimates of the normalized "1982" concentrations were obtained for the individual stations and averaged. These 1976-1982 averages are used in the present study. Data from elevated stations were excluded from the calculations, except those of the South Pole.

Finally, Tans et al. (1990) present annually averaged concentrations in dry air for selected (comparable) GMCC monitoring stations and for the years 1981 to 1987. The data used in the present study are the averaged values for the period 1981-1987. For calculating the 1981-1987 average, Tans et al. first normalized all years to 1987 by adding the globally averaged difference between 1987 and the year considered. These averages were calculated from third-degree polynomial curve fits to the available yearly data, in order to avoid biasing averages by the addition or omission of stations. Tans et al. did not use data from all GMCC sites. Records from the elevated sites Niwot Ridge, Colorado and Mauna Loa observatory were excluded from the calculations. At some other sites (e.g. Cape Meares, Oregon) the data appeares to be too noisy to extract annual averages with sufficient confidence.

Data for altitudinal distribution of carbon dioxide

For the purpose of the present study the data reported by Nakazawa et al. (1991a) appeared to be very useful. Nakazawa et al. measured 1984 and 1985 CO_2 concentrations systematically using commercial jet airliners between Anchora, Alaska and Sydney, Australia (via Tokyo) at 10-12 km height. About 640 samples were collected and analyzed within the two years. To obtain upper tropospheric concentrations, all data taken between Tokyo and Sydney were assigned to the troposphere, and about 70% of the data between Tokyo and Anchora to the stratosphere. For the area 40^o to 60^oN they could not present a complete set of the upper tropospheric data for every 5^o because the tropopause height was lower in high latitudes, especially in winter. Nakazawa et al. calculated annual average values by fitting and smoothing the observed data to a Fourier harmonics, Reinsch-type spline and the 26th-order Butterworth filter. The 1984 data reported by Nakazawa et al. are used here. For upper stratospheric concentrations August-September 1985 data of Gamo et al (1987) are used here, who measured CO_2 concentrations up to 25 km above Japan, using a balloon.

2.3 Data on halocarbons

2.3.1 Halocarbon monitoring

Halocarbon concentrations in the atmosphere have not been investigated as intensively as carbon dioxide concentrations. However, some very useful data sets are available with respect to latitudinal and altitudinal variations. Some publications dealing with latitudinal or altitudinal variation are listed below with respect to several halocarbons. The variations vary from interhemispheric or altitudinal differences for a single year to extensive long-term data sets at several monitoring sites. The list is not meant to be complete.

Latitudinal distribution of halocarbons

CFC-11: Sze and Wu (1976), Chang and Penner (1978), Singh et al. (1979a), Rasmussen et al. (1981), Rasmussen and Khalil (1982, 1983, 1986), Prinn et al. (1983a), Khalil and Ramussen (1988a), Cunnold et al. (1983a, 1986), Bodhaine and Rosson (1988), Delorey et al. (1988).

CFC-12: Singh et al. (1979a), Rasmussen et al. (1981), Rasmussen and Khalil (1983, 1986), Prinn et al. (1983a), Khalil and Ramussen (1988a), Cunnold et al. (1983b, 1986), Bodhaine and Rosson (1988), Delorey et al. (1988).

CFC-113: Singh et al. (1979a), Rasmussen and Khalil (1982, 1983), Khalil and Ramussen (1988a), Bodhaine and Rosson (1988), Delorey et al. (1988).

CFC-114: Singh et al. (1979a).

CFC-115: Singh et al. (1979a).

HCFC-22: Rasmussen and Khalil (1982, 1983), Khalil and Ramussen (1988a).

CH_3CCl_3: Chang and Penner (1978), Singh et al. (1979a), Rasmussen and Khalil (1981b, 1982, 1983, 1986), Prinn et al. (1983a), Khalil and Ramussen (1988a), Bodhaine and Rosson (1988), Delorey et al. (1988).

CCl_4: Singh et al. (1979), Rasmussen and Khalil (1981b, 1983, 1986), Prinn et al. (1983a), Khalil and Ramussen (1988a), Simmonds et al. (1983), Bodhaine and Rosson (1988), Delorey et al. (1988), Simmonds et al. (1988).

Altitudinal distribution of halocarbons

CFC-11: Heidt et al. (1975), Sze and Wu (1976), Robinson et al. (1977), Vedder et al. (1978, 1981), Goldan et al. (1980), Fabian et al. (1981), Rasmussen et al. (1981, 1982), Gallagaher et al. (1983), Fraser et al. (1983b), Golombek and Prinn (1986), Delorey et al. (1988).

CFC-12: Heidt et al. (1975), Sze and Wu (1976), Robinson et al. (1977), Tyson et al. (1978), Vedder et al. (1978, 1981), Goldan et al. (1980), Fabian et al. (1981), Rasmussen et al. (1981, 1982), Gallagher et al. (1983), Golombek and Prinn (1986), Delorey et al. (1988), Evans (1988).

CFC-113: Rasmussen et al. (1981, 1982).

CH_3CCl_3: Rasmussen et al. (1981).

CCl_4: Robinson et al. (1977), Vedder et al. (1978), Rasmussen et al. (1981).

HCFC-22: Rasmussen et al. (1981, 1982).

2.3.2 Halocarbon data used in this study

Data used for latitudinal distribution of halocarbon.

For the present study three data sets seem to be of special interest. 1) Useful data are reported by Khalil and Rasmussen (1988a). Concentrations of CFC-11, CFC-12, CFC-113, HCFC-22, CH_3CCl_3, CCl_4 and HCFC-22 data were obtained on an ocean cruise during the Soviet-American Gas and Aerosol Experiment (SAGA II). This experiment comprises an ocean cruise between about 50°N to 45°S in 1987. Annually averaged concentrations in 9 latitude bands are presented by Khalil and Rasmussen (1988a) for CFC-11, CFC-12, CFC-113, HCFC-22, CH_3CCl_3 and CCl_4.

2) CFC-11 and CFC-12 1977 to 1987 monthly averaged data obtained at 5 monitoring sites of National Oceanic and Atmospheric Administration's Geophysical Monitoring for Climatic Change (NOAA's GMCC) are reported by Bodhaine and Rosson (1988). CFC-11 and CFC-12 are measured at Mauna Loa Observatory (20°N), Niwot Ridge (40°N), Barrow (71°N), Samoa (14°S) and South Pole (90°S). Atmospheric concentrations are measured weekly. Monthly mean concentrations of the flask samples are presented by Bodhaine and Rosson (1988) for CFC-11 and CFC-12 for the period 1977 to 1987.

3) CFC-11, CFC-12, CFC-113, CH_3CCl_3 and CCL_4 monthly averaged concentrations were measured at five sites in the Atmospheric Lifetime Experiment (ALE) from 1978 to 1983 (Prinn et al. 1983a, 1983b, Cunnold et al. 1983a, 1983b, 1986, Simmonds et al. 1983, 1988). The Atmospheric Lifetime Experiment started in 1978. The experiment includes long-term measurements of the atmospheric concentrations of CFC-11, CFC-12, CH_3CCl_3 and CCl_4 at four sites since mid-1978, and at five sites since 1979. The air is sampled four times daily. The monitoring stations are land based at: Adrigole, Ireland (52°N, 10°W), Cape Meares, Oregon (45°N, 124°W), Ragged Point, Barbados (13°N, 59°W), Point Matalula, American Samoa (14°S, 171°W) and Cape Grim, Tasmania (41°S, 145°E). Concentrations are presented as monthly averages by authors mentioned above.

Data used for altitudinal distribution of halocarbons.

To investigate the variation in halocarbon concentrations with height, the data from northern mid-latitudes are used as described by Fabian et al. (1981). These data are the results of ten balloon flights. Large air samples were collected at eight different stratospheric heights, and tropospheric aircraft-measurements supplemented the data. Several vertical profiles in the years 1977, 1978 and 1979 were obtained for CFC-11 and CFC-12 in the months June to November. During the 1977 flight the height of the tropopause was measured between 12.1 and 13.1 km, during the 1978 flights between 10.5 and 16 km, and during the 1979 flights between 8.6 and 12.9 km.

2.4 Data on nitrous oxide

2.4.1 Nitrous oxide monitoring

Atmospheric nitrous oxide concentrations have been measured regularly since the late 1970's. The first measurements of N_2O showed variations between laboratories, because no method had been established as a reference against which the others could be compared. In 1977 there was still not even a general agreement on the absolute tropospheric mixing ratio (Pierotti and Rasmussen 1977). There may still be some interlaboratory differences, based on calibration differences or methodological precision.

N_2O concentrations in the atmosphere have often been measured in the same programs as halocarbons, for instance in the Atmospheric Lifetime Experiment (ALE) and its successor, the Global Atmospheric Gases Experiment (GAGE). Another important N_2O monitoring network is part of NOAA's GMCC. This program was described in the sections on carbon dioxide (2.2) and halocarbons (2.3). N_2O has been measured at the same sites as halocarbons since 1978. Monthly averaged GMCC results with respect to N_2O can be found in Bodhaine and Rosson (1988). Finally, the Soviet-American Gas and Aerosol experiment (SAGA II), also described in section 2.2.1, provides N_2O concentration in the midlatitudes and tropics. Results hereof are published, for instance, by Butler et al. (1989) and by Khalil and Rasmussen (1988a). Some other publications concerning the latitudinal and the distribution with height are listed below.

Latitudinal distribution of nitrous oxide:

Pierotti and Rasmussen (1977), Singh et al. (1979b), Weiss et al. (1981), Rasmussen et al (1981), Weiss (1981a,b), Levy II et al. (1982), Prinn et al. (1983a, 1990), Rasmussen and Khalil (1983), Khalil and Rasmussen (1983a), Rasmussen and Khalil (1986), Delorey et al. (1988), Khalil and Rasmussen (1988b), Butler et al. (1989).

Altitudinal distribution of nitrous oxide:

Pierotti and Rasmussen (1977), Tyson et al. (1978), Vedder et al. (1978, 1981), Roy (1979), Matthias et al. (1979), Goldan et al. (1980), Fabian et al. (1981), Ko and Sze (1982), Rasmussen and Khalil (1983), Gallagher et al. (1983), Golombek and Prinn (1986).

2.4.2 Nitrous oxide data used in this study

Data used in this study are the ALE/GAGE reported by Prinn et al. (1990) for latitudinal distribution. Atmospheric concentrations of N_2O have been measuered several times per day since 1978 at five locations (same as for CFCs). This program is described in more detail in the section on halocarbons (2.3). Monthly averaged data per station are published in e.g. Prinn et al. (1990). For the distribution with height data reported by Fabian et al. (1981) are used. This study is also described in the section on halocarbons (2.3).

2.5 Data on methane

2.5.1 Methane monitoring

Atmospheric concentrations of methane have been measured since 1978 (e.g. Rasmussen and Khalil 1981a,d, Blake and Rowland 1988). Measurements prior to 1970 indicated that CH_4 concentrations showed some variability with geographic location. However these data were generally not of enough precision or frequency to draw conclusions with regard to the existence of trends with latitude, season or year (Blake et al. 1982).

The latitudinal variation in methane concentration is investigated using land-based stations in, for instance, NOAA's GMCC network (e.g. Steele et al. 1987). Also ship measurements are used to investigate latitudinal concentration gradients (e.g. Ehhalt 1978, Singh et al. 1979a, Heidt et al. 1980, Cofer III 1982). CH_4 concentrations at different altitudes are measured using aircrafts and balloons (e.g. Fabian et al. 1981). A far from complete list of studies on spatial distribution follows.

Latitudinal distribution of methane:

Ehhalt and Schmidt (1978), Ehhalt (1978), Singh et al. (1979a), Heidt et al. (1980), Rasmussen et al. (1981), Cofer III (1982), Khalil and Rasmussen (1983b), Rasmussen and Khalil (1983, 1984a,b, 1986), Blake and Rowland (1986, 1988), Isaksen and Hov (1987), Steele et al. (1987), Wahlen et al. (1989), Boden et al. 1990.

Altitudinal distribution of methane:

Ehhalt and Heidt (1973), Cumming and Lowe (1973), Ehhalt and Schmidt (1978), Reichle and Condon (1979), Rasmussen and Khalil (1981b, 1983), Newell et al. (1981), Fabian et al. (1981), Fraser et al. (1984), Isaksen and Hov (1987),

2.5.2 Methane data used in this study

Concentrations of CH_4 show seasonal variations in the troposphere. Moreover, the atmospheric lifetime of CH_4 is relatively short (about 10 years). To obtain annual average spatial profiles it is therefore necessary to use data measured throughout the year, and at several locations. Such a database is available for surface concentrations of atmospheric CH_4. In NOAA's GMCC program, concentrations of CH_4 have been measured for several years at 23 ground-based stations. Steele et al. (1987) present in their paper monthly averaged results for the years 1983, 1984 and 1985. Unfortunately, measurements at other altitudes are scarce. Several aircraft and balloon studies have been performed, but most of these studies only show altitudinal gradients at a certain time and a certain place. The CH_4 data used here are the GMCC 1984 data reported by Steele et al. (1987) for the latitudinal distribution, and the data of Fabian et al. (1981) for the distribution with height. These measurement programs are both described in the sections on CO_2 and CFCs (2.2 and 2.3).

2.6 Data on carbon monoxide

2.6.1 Carbon monoxide monitoring

Carbon monoxide concentrations show considerable spatial and temporal variability because of its short atmospheric lifetime (2-3 months). CO concentrations are not systematically measured, so that it is difficult to obtain reliable annual averages of latitudinally and altitudinally varying concentrations. Some articles concerning spatial distributions of CO are listed below.

Latitudinal distribution of carbon monoxide:

Seiler (1974), Newell et al. (1974), Heidt et al. (1980), Logan et al. (1981), Seiler and Fishman (1981), Rasmussen and Khalil (1983), Reichle et al. (1986), Isaksen and Hov (1987), Brasseur et al. (1991).

Altitudinal distribution of carbon monoxide:

Goldman et al. (1973), Reichle and Condon (1979), Rasmussen and Khalil (1981b, 1983), Logan et al. (1981), Newell et al. (1981), Seiler and Fishman (1981), Fabian et al. (1981), Isaksen and Hov (1987), Zander et al. (1990), Boatman et al. (1989), Brasseur et al. (1991).

2.6.2 Carbon monoxide data used in this study

For the latitudinal distribution of CO data from Seiler and Fishman (1981) are used. They measured atmospheric CO concentrations using aircrafts between 67^{o}N and 57^{o}S during July and August 1974. More than 60 vertical profiles with a latitudinal resolution of about 8 degrees were obtained making ascents and descents. The measurements were made between the earth's surface and 12 km height, and annually and zonally averaged values are reported for the free troposphere. In addition, latitudinal distributions as described by Logan et al. (1981) are used. For the distribution with height Logan's estimates are also used, and data obtained by Fabian et al. (1981). Fabian et al. report late summer altitudinal gradients for the year 1979, as described in the sections on CFCs and N_2O (2.3, 2.4).

2.7 Data on hydroxyl

2.7.1 Hydroxyl monitoring and data used in this study

Concentrations of atmospheric hydroxyl can be measured, but the data obtained are hard to interpret because of the large spatial and temporal variability of OH. The OH radical is one of the most reactive species in the troposphere. Its distributions are therefore calculated by models which simulate tropospheric chemistry. Some studies reporting spatial distribution of OH are those of Isaksen and Hov (1987), Prinn et al. (1987), Singh et al. (1979a), Hewitt and Harrison (1985) and Isaksen (1988). The study of Prinn et al. (1987) is used here. They base their estimate of the OH distribution on the CH_3CCl_3 distribution. CH_3CCl_3 is a gas with relatively well-known anthropogenic sources and only one sink: reaction with OH. However, in case it will appear that there are other sources or sinks of atmospheric CH_3CCl_3, the deduced OH distribution may turn out to be wrong.

3. RESULTS AND DISCUSSION WITH RESPECT TO CARBON DIOXIDE

3.1 Carbon dioxide in the atmosphere

Concentrations of atmospheric carbon dioxide have been increasing due to human activities. At present concentrations are measured to be 25% higher than before the Industrial Revolution, because of anthropogenic emissions. Human activities that lead to CO_2 emissions are known to be the use of fossil fuels, and land use changes.

Although the increase in both concentrations and emissions can be quantified, it is not easy to explain the observed concentration increase. Since preindustrial times concentrations increased less than the total amount of carbon dioxide emitted into the atmosphere. Slanina and Okken (1991) estimate the present fossil fuel related emissions of CO_2 to amount to 5.5 Gt C/yr and the emissions due to land use change to 1-2 Gt C/yr. The increase of atmospheric carbon reflects about 3 Gt C/year. Apparently, some of the anthropogenically emitted CO_2 is removed from the atmosphere. These removal processes, however, are only poorly understood. Slanina and Okken assume 1-2.5 Gt C/yr is removed by oceans, and 1-3 Gt/year by the terrestrial biosphere (so-called CO_2 fertilization of the biosphere). However, the question as to whether or not the biosphere absorbs more CO_2 as a result of CO_2 fertilization is still unanswered. At present there is little evidence for such an increase in CO_2 uptake by biota. Even if the CO_2 uptake by plants would have increased, this could have been counteracted by the global warming during the past century, which could have promoted additional releases of CO_2. Another reason to doubt the existence of CO_2 fertilization may be the fact that a lack of available nitrogen and phosphorus in soils might inhibit increased plant growth. On the other hand, the consistent evidence from oceanic models that the disappearing CO_2 cannot all be absorbed by the oceans leads some of the modelers to accept the hypothesis of plant stimulation. Some of the models that assume or try to calculate the existence of CO_2 fertilization are those of Tans et al. (1990), Keeling et al. (1989a,b), Siegenthaler and Oeschger (1985), Kohlmaier et al. (1987, 1989) and Enting and Mansbridge (1989). Keeling et al. (1989a,b) conclude that the present rates of fertilization and destruction may each be of the order of 5.10^{12} kg C/year, significantly more than those mentioned by Slanina and Okken, 1991. Also the models of Esser et al. (1991) and of Enting and Pearman (1987) indicate that at present the CO_2 release by deforestation more of less balances the CO_2 fertilization effect on a global scale. But even if the fluxes balance on a global scale, they might be important with respect to their spatial distribution.

The spatial variation of CO_2 in the atmosphere is mainly the result of spatial variation in sources and sinks, rate of emission increase and transport. However, seasonality may affect the spatial distribution of concentrations as well. Seasonal variation in concentrations is important to the overall mean annual field, because transport also varies with season. The role of seasonality and transport is described for instance by Keeling et al. (1989a,b).

3.2 Preindustrial carbon dioxide concentration

Carbon dioxide is one of the natural greenhouse gases. Its concentrations in the preindustrial atmosphere were the result of natural carbon fluxes between atmosphere, oceans and the (terrestrial) biosphere. Preindustrial concentrations of carbon are investigated analyzing ancient air, trapped in polar ice (for instance, Raynaud and Barnola 1985, Neftel et al. 1985, Pearman et al. 1986b, Staffelbach et al. 1991, Barnola et al. 1991). These studies indicate that the global average carbon dioxide concentration amounted to about 280 ppmv before the Industrial Revolution.

Another way of investigating natural carbon fluxes is to simulate the carbon cycle. For instance, Keeling et al. (1989a) calculated that CO_2 concentrations at the South Pole were higher than in the northern hemisphere by 0.82 ppmv before the industrial era. They suggest that oceans are likely to have been responsible. Wind-driven ocean currents and thermohaline circulation of deep water can transport CO_2 over great distances. The possibility of a natural imbalance amounting about 1 ppmv between the hemispheres has also been noted by Pearman and Hyson (1983). They, however, proposed that it arises from differences in the seasonal cycle of the terrestrial biosphere in the two hemispheres in combination with the interhemispheric mass flux.

3.3 1960-1990 Carbon dioxide concentration

3.3.1 Latitudinal distribution at the earth's surface.

Tables 2 and 3 and Figures 1, 2 and 3 show the results of calculations concerning CO_2 for the years 1962, 1968, 1980, 1984 (data from Keeling et al. 1989a) and for the 1976 to 1982 average scaled to 1982 (data from Pearman and Hyson 1986), and for the average of 1981 to 1987, scaled to 1987 (data from Tans et al. 1990). Table 2a shows the values for a_1, a_2, b_1 and b_2 for the best values of k (least mean square errors) and Table 2b for k's chosen as close as possible to the equator. The second Table is added because some studies suggest that the Intertropical Convergence Zone, located around the equator, is the main barrier for atmospheric mixing. In the following, however, values from Table 2a will be used, unless mentioned otherwise.

Figure 1 show the latitudinal variation for several years. The global average concentration increased during this period from 318 ppmv (1962) to 323 ppmv (1968), 337 ppmv (1980), 341 ppmv (1982), 342 ppmv (1984) and 348 ppmv (1987) (Keeling et al. 1989a,b, Tans et al. 1990).

The most obvious feature of atmospheric CO_2 at the earth's surface appears to be a south to north gradient (Figure 1 and 2). At present concentrations are found to be higher in the northern than in the southern hemisphere. This is different than in the preindustrial atmosphere, where southern hemispheric concentrations were higher (see section 3.2). Apparently, the latitudinal gadient reversed. To really understand the observed features, it is important to quantify carbon fluxes between land, atmosphere and oceans. However, current knowledge is not sufficient to explain all observed features of atmospheric carbon dioxide as described in section 3.1. About one conclusion, however, some studies seem to agree: by far the largest contributor at present to meridional variation in CO_2 concentrations is the combustion of fossil fuels 95% of which are injected into the northern hemisphere (Keeling et al. 1989a,b, Pearman and Hyson 1986). This seems to be in agreement with the profile for the year 1962 (Figure 1 and 2), which can be regarded as an intermediate between the preindustrial and the present latitudinal gradient.

Table 3 shows the calculated North-to-South Pole differences in CO_2 concentrations at the earth's surface. These differences are calculated to have been increasing from 0.95 ppmv in 1962 to 3.60 ppmv in 1984, while the average value for the period 1981-1987 amounts to 3.13 ppmv. The differences as calculated for the 1960's are in reasonable agreement with those reported by Pearman et al. (1983). For the 1980's the values are somewhat lower than, for instance, the high latitude-to-high latitude difference of 4-5 ppmv in 1980 reported by Pearman et al. (1983) and Fraser et al. (1983). Also Komhyr et al. (1985) calculated a higher mean North-to-South Pole difference of the period 1976-1982 of 3.4 ± 0.2 ppmv. Conway et al. (1988) present a pole-to-pole difference amounting to 2.9 ppmv in 1983, and 3.4 ppmv in 1981, while Gamo et al. (1987) measured a 3 ppmv difference between the mid-northern hemisphere and Antarctica in the mid-eighties. Keeling et al. (1989a,b) investigated the long term trend in the Mauna Loa (19.5 N) and South Pole (90 S) difference. Assuming both elevated stations reveal more or less their hemispheric average values, Keeling et al. show that the CO_2 gradient between the northern and the southern hemisphere increased from 1958 (0.3 ppm) to 1989 (2.2 ppm). More recent measurements indicate that the pole-to-pole difference is still increasing, although this trend was not obvious in the 1980's (Tans 1991). Comparing the results mentioned in Table 3 with data of others mentioned above, the 3.13 ppmv pole-to-pole difference for the period 1981-1987 (Table 3) seems a reasonable estimate of the present pole-to-pole difference in CO_2 surface concentrations. Table 3 suggests moreover that during the past two decades or so the relative pole to pole difference was about constant: 0.9 - 1.1% relative to the surface South Pole concentration.

Table 2a. Latitudinal variation in surface CO_2 concentration. Regression coefficients a_1, b_1, a_2, b_2, X_k and the least mean square (sqrt) as calculated for the data of Keeling et al. (1989a), Pearman and Hyson (1986) and Tans et al. (1990). See Section 2.1.3 for meaning of the symbols. Results are presented for the best value of k and refer to the annual average concentration (lat = sine of latitude).

year	a_1 ppmv	b_1 ppmv/lat	a_2 ppmv	b_2 ppmv/lat	X_k lat	sqrt $ppmv^2$
1962[1]	319.22	1.66	318.86	-0.35	-0.18	3.75
1968[1]	322.67	1.57	322.74	0.79	0.09	5.24
1980[1]	337.57	2.14	338.93	-0.38	0.54	1.68
1984[1]	342.52	0.23	343.77	2.12	-0.66	1.16
1976-82[2]	339.76	0.54	340.60	1.82	-0.66	9.38
1981-87[3]	346.79	-0.07	348.09	1.90	-0.66	2.67
1984[4]	344.35	1.51	344.61	-1.43	0.9	0.18

Table 2b. As in Table 2a, except for k chosen as close to the equator as possible.

year	a_1 ppmv	b_1 ppmv/lat	a_2 ppmv	b_2 ppmv/lat	X_k lat	sqrt $ppmv^2$
1962[1]	318.89	1.19	318.91	-0.43	0.01	4.12
1968[1]	322.69	1.58	322.69	0.91	0.01	5.32
1980[1]	337.69	2.33	337.69	1.21	0.00	1.89
1984[1]	344.03	2.27	343.90	1.59	-0.05	1.31
1976-82[2]	340.85	1.94	340.90	1.30	0.09	9.41
1981-87[3]	348.15	1.58	348.14	1.79	0.03	3.13
1984[4]	344.45	1.78	344.45	-1.04	0.00	0.25

[1] data from Keeling et al. (1989a)
[2] data from Pearman and Hyson (1986)
[3] data from Tans et al. (1990)
[4] data from Nakazawa et al. (1991) (upper troposphere)

Table 3. Pole-to-pole differences in surface CO_2 concentrations as calculated for the different data sets.

year	Pole-Pole difference (ppmv)[5]	Global concentration (ppmv)	Surface South Pole concentration (ppmv)	%[6]
(Preindustrial[1]	-1	280	280.5	0.4)
1962[2]	0.95	318	317.6	0.3
1968[2]	2.44	323	231.1	1.1
1980[2]	3.12	337	335.4	0.9
1984[2]	3.60	342	342.3	1.1
1976-1982[3]	3.20	341	339.4	0.9
1981-1987[4]	3.13	348	346.9	0.9

[1] See section 3.2 and estimated
[2] data from Keeling et al. 1989a
[3] data from Pearman and Hyson 1986, scaled to 1982
[4] data from Tans et al. 1990, scaled to 1987
[5] NP-SP, where NP = surface concentration at North Pole, SP = surface concentration at South Pole.
[6] percentage = 100*(NP-SP)/SP, where NP = surface concentration at North Pole, SP = surface concentration at South Pole.

3.3.2 Altitudinal distribution

Results of Nakazawa et al. (1991) indicate, that in 1984 and 1985, CO_2 concentrations in the Northern hemisphere decreased with altitude, while in the Southern hemisphere concentrations increased with altitude. Figure 4 shows the latitudinal variation in atmospheric CO_2 at ground level (data from Keeling et al. 1989a) and at the upper troposphere (10-12 km) for the year 1984. The 1984 surface data we used here are the same as shown in Figure 1 (Keeling's data). From Figure 4 it is clear that at about 13°N atmospheric CO_2 concentrations do not vary with height in the troposphere. This is in agreement with findings of Nakazawa et al. The absolute difference in CO_2 concentrations between the surface and the upper troposphere may amount to 0 - 2.7 ppmv (or 0 - 0.8%) of the surface concentrations.

One possible explanation for the distribution with height may be the fact that in the Northern hemisphere CO_2 sources most probably exceed sinks, while in the southern hemisphere sinks are dominant. Both sources and sinks are ground based, so that the altitudinal gradients may be opposite in the two hemispheres.

Lower stratospheric concentrations in the northern hemisphere, as measured by Nakazawa et al. equaled more or less the surface concentrations measured at the South Pole. Because of lack of data, we assume that in the stratosphere concentrations of atmospheric CO_2 do not vary with latitude. This would mean that the concentrations in 1984 in the upper troposphere are 0.5 - 2.2 ppmv higher than in the lower stratosphere. Gamo et al. (1987) show that, at least locally, concentrations in the upper stratosphere (25 km) are about 5 ppmv lower than in the lower stratosphere. Assuming that these data are respresentative for the global average, we obtain results as shown in Figure 4 and Table 4. The upper stratospheric concentrations are 5 - 8.6 ppmv (1.4 - 2.5%) lower than the surface concentration.

All above mentioned assumptions are highly simplified, so that these data must be regarded as estimates. The model results for the Northern hemisphere of Keeling et al.

(1989a,b) are in general agreement with the profiles shown in Figure 4. For the Southern hemisphere, however, they calculate almost no altitudinal variation in the troposphere, while Nakazawa et al. measured concentrations to be increasing with height. Although we use different data sets to obtain Figure 4, we prefer in this case the measured values over the simulated.

Tanaka et al. (1987c) used aircraft to measure CO_2 concentrations aloft between 1979 and 1987 above Japan. They concluded that the vertical profile was almost the same from year-to-year. The concentrations decreased gradually with height. Surface-upper tropospheric differences in concentrations were found to amount to about 2 ppmv on average. Tanaka et al. (1983) show that the yearly average values for the concentration decrease rapidly with increasing height above the ground in the lowest layer of the troposphere and rather slightly above it.

The vertical gradient of CO_2 amounts to at most 2.5% of the surface concentration. This is relatively moderate as compared to other gases. The reason may be that both CO_2 sources and sinks are ground-based and that CO_2 has a relatively long atmospheric lifetome (50-200 years).

The vertical profiles may have changed as well as a result of anthropogenic activities. As discussed by Keeling et al. (1989a,b) the vertical gradient may at least partly be the result of seasonally changing sources and transport. Because fossil fuel related emissions are land-based and also show a seasonal cycle (Rotty 1983, 1987), these emissions may influence the vertical gradient especially in the northern hemisphere. Vertical profiles in 1960, as reported by Bolin and Keeling (1963) are indeed different from the present. For the area between 0 and 40^oN they found tropospheric concentrations to be increasing with altitude, whereas nowadays concentrations are found to be decreasing with height.

Table 4. Latitudinal distribution of atmospheric CO_2 concentrations (in ppmv) at the earth's surface (based on Steele et al. 1987), at the top of the troposphere (based on Nakazawa et al. 1991), and in the lower and upper stratosphere (based on Gamo et al. 1989), estimated for 1984-1985.

	90S	60S	30S	0	30N	60N	90N
surface	342.3	342.3	342.7	343.8	344.8	345.6	345.9
upper trop.	342.8	343.0	343.6	344.4	343.9	343.4	343.2
lower strat.	342.3	342.3	342.3	342.3	342.3	342.3	342.3
upper strat.	337.3	337.3	337.3	337.3	337.3	337.3	337.3

3.4 Future carbon dioxide concentrations

Since preindustrial times, both the global average of, and the pole-to-pole difference in CO_2 surface concentration have increased. In this section we would like to answer the question how the latitudinal gradient, or the pole-to-pole difference might change in future.

The observed increase in global average concentration and in pole-to-pole difference can be explained to a large extent by fossil fuel emissions, as described earlier. If current trends continue fossil fuel emissions are likely to keep increasing in the near future. Because these emissions are all land-based, one may assume that the main location of emission will stay the northern hemisphere. Therefore, it seems reasonable to assume that both the global average concentration and the pole-to-pole difference keep increasing during the next decades.

Quantification of the future latitudinal gradient is difficult. In the following the future pole-to-pole difference is estimated in two different ways. It may be clear that, given the current state of knowledge, it is reasonable to assume that by the time the global concentrations amount to 420 ppmv, the pole-to-pole difference may be 4 - 7 ppmv.

One estimate on the future pole-to-pole difference may be based on the past growth of this difference, compared with the global increase in CO_2 concentrations. Since the Industrial revolution the global average CO_2 concentration increased by 70 ppmv. In the meantime the pole-to-pole difference increased by about 4 ppmv. In other words, the pole-to-pole difference increased 0.057 ppmv for each ppmv rise in the global average concentration. Continuing this linear relationship would yield a 7 ppmv pole-to-pole difference by the time the global concentration of CO_2 amounts to 420 ppmv. This situation is shown in Figure 5.

A second way to estimate the future latitudinal distribution might be based on the relative pole-to-pole difference. During the last two decades the pole-to-pole difference stayed at about 0.9 - 1.1% of the South Pole surface concentration. Assuming this percentage will remain constant in future, the pole-to-pole difference may be estimated to about 4 ppmv by the time the global concentration will have been risen to 420 ppmv.

To achieve a result as obtained in Figure 5, a linear relationships is assumed between global concentration and pole-to-pole difference. In the past this was not always the case. As shown in Figure 3, the rate of increase of the calculated North-to-South Pole difference seems to have increased in time. These observed nonlinearities are hard to explain, but may be related to the rate of increase of atmospheric carbon dioxide. Pearman and Hyson (1986) show that in years following low rates of increase, the north-south gradient tends to be lower than at other times. Also biospheric processes (for instance, changing CO_2 uptake or release by terrestrial vegetation) may be involved in the pole-to-pole gradient.

Another source of uncertainty is the role of the (terrestrial) biosphere. As discussed earlier, it is difficult to quantify carbon fluxes related to biospheric processes. Only if biospheric CO_2 uptake and release balance each other at a regional scale in future, may this have a small influence on the latitudinal distribution of atmospheric CO_2.

Finally, the role of climatic feedback processes, influencing atmospheric CO_2 concentrations, is unclear. When current trends continue, a global concentration of 420 ppmv may be reached by the year 2020 (IPCC's scenario A). The IMAGE model (Rotmans 1990) indicates that the temperature of the earth's surface increased by about 1.5 ^{o}C by that time (assuming a climate sensitivity $dT(2xCO_2)$ = 2.5 °C). Global warming may influence concentrations in several ways. For example Houghton et al. (1987) pointed out that terrestrial ecosystems may act as feedbacks in future; however, whether these feedbacks are positive of negative seems hard to tell. Kellogg (1983) gives an overview of five possible feedback loops, two of which are positive (amplifying the rate of concentration increase), two are weakly negative (damping the rate of increase) and one is indeterminate, but possibly positive. Kellog concludes that it is most likely that the global concentrations of CO_2 may increase faster when climate changes. These feedback processes are very likely to affect spatial concentrations as well, although it is highly uncertain in what way.

The gradient with height may change as well in future. However, even at present it is very difficult to explain the observed gradient. Therefore, the present study only deals with latitudinal variation of the future CO_2 concentration.

3.5 Conclusions

The latitudinal distribution of CO_2 in the present atmosphere may be best represented by the gradient based on data reported by Tans et al. (1990, see Figure 1 and Table 2a). This data set is relatively complete and recent (1981-1987 data), and shows the latitudinal gradient at the earth's surface. Concentrations of CO_2 increase with latitude from south to north. The main reason for this may be the fact that fossil fuels are burned mainly in the northern hemisphere. At present the pole-to-pole difference amounts to 3.13 ppmv or 0.9% of the surface South Pole concentration (Table 5). In the preindustrial atmosphere the latitudinal gradient was opposite, with the lowest concentrations in the northern hemisphere. This could be an indication that if future CO_2 emissions keep increasing, the pole-to-pole difference may also keep increasing. Based on trends during the last two decades it could be assumed that in future the pole-to-pole difference may at least amount to 1% of the surface South Pole concentration.

The altitudinal variation is somewhat smaller than the latitudinal. Based on data obtained by Nakazawa et al. (1991), Keeling et al. (1989a) and Gamo et al. (1989), the altitudinal variation for the year 1984/1985 is calculated to amount at most 2.5% of the surface concentration. This gradient is relatively moderate if compared to other gases because both sources and sinks of CO_2 are ground-based, and the atmospheric lifetime is relatively long (50-200 years).

Table 5. Approximate relative difference of CO_2 concentrations at the earth's surface relative to the (South Pole) surface concentrations in the present atmosphere.

Gas	latitudinal: pole-to-pole[1]	altitudinal: troposphere-to-surface[2]	altitudinal: stratosphere-to-surface[3]
CO_2	0.9%	0.1-0.8%	1.4-2.5%

[1] Pole-to-pole difference (surface values) given as percentage relative to the South Pole concentration: 100*|NP-SP|/SP, where NP = surface concentrations at North Pole, SP = surface concentration at South Pole. Data used are 1981-1987 average concentrations, scaled to 1987 (Tans et al. 1990).

[2] Altitudinal difference in the troposphere given as percentage relative to the surface value: 100*|UT-S|/S, where UT = upper tropospheric concentration, and S = surface concentration at latitude available. Data used refer to 1984-1985 (Keeling et al. 1989a, Nakazawa et al. 1991, Gamo et al. 1989).

[3] Altitudinal difference in the whole atmosphere (troposphere and stratosphere) given as percentage relative to the surface value: 100*|US-S|/S, where US = upper stratospheric concentration and S = surface concentration at latitude available. Data used refer to 1984-1985 (Keeling et al. 1989a,b, Nakazawa et al. 1991, Gamo et al. 1989).

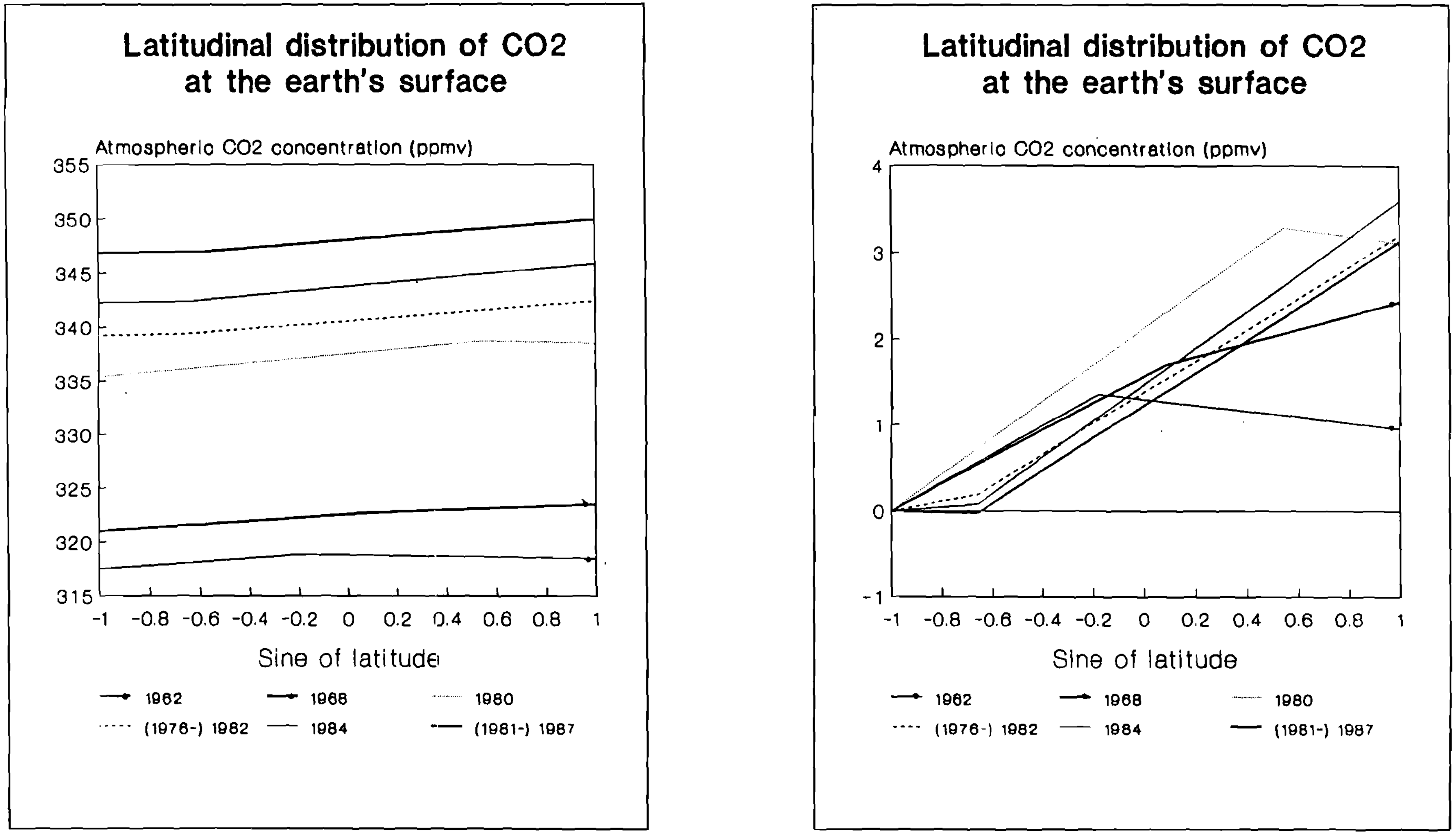


Figure 1. Latitudinal distribution of atmospheric CO_2 (ppmv) at the earth's surface (annual average), as calculated for the years 1962, 1968, 1980 and 1984 (data from Keeling et al. 1989), for the 1976-1982 average (data from Pearman and Hyson 1986) and for the 1981-1987 average (data from Tans et al. 1990). Graph on left hand side shows the absolute concentrations (ppmv), and the graph on the right hand side shows concentrations relative to the South Pole (ppmv, 0 at South Pole). Results refer to the best value of k.

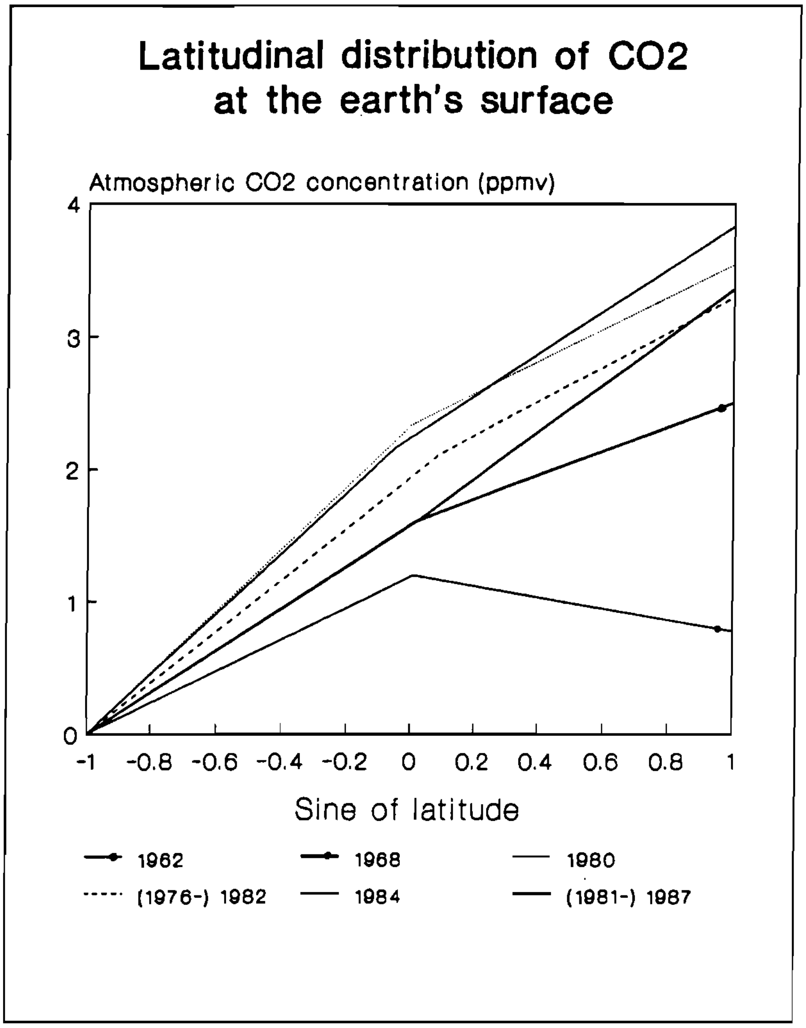


Figure 2. As in Figure 1 (right hand side), except for k as close to the equator as possible.

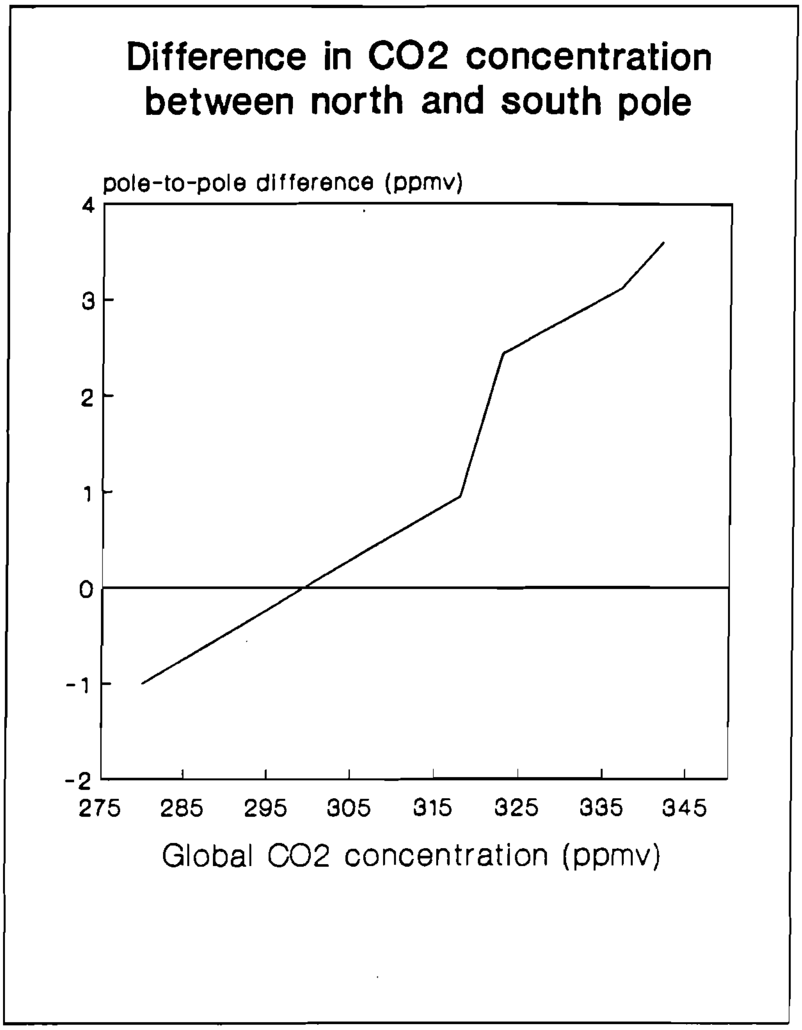


Figure 3. North-to-South-Pole differences of surface CO_2 concentrations (ppmv, annual average) for globally averaged concentrations of atmospheric CO_2 amounting to 280 ppmv (preindustrial situation), 318 ppmv (1962), 323 ppmv (1968), 338 ppmv (1980) and 342 ppmv (1984). Pole-to-pole differences are calculated from Table 2a, except for the 280 ppmv difference, which is adopted from section 3.2.

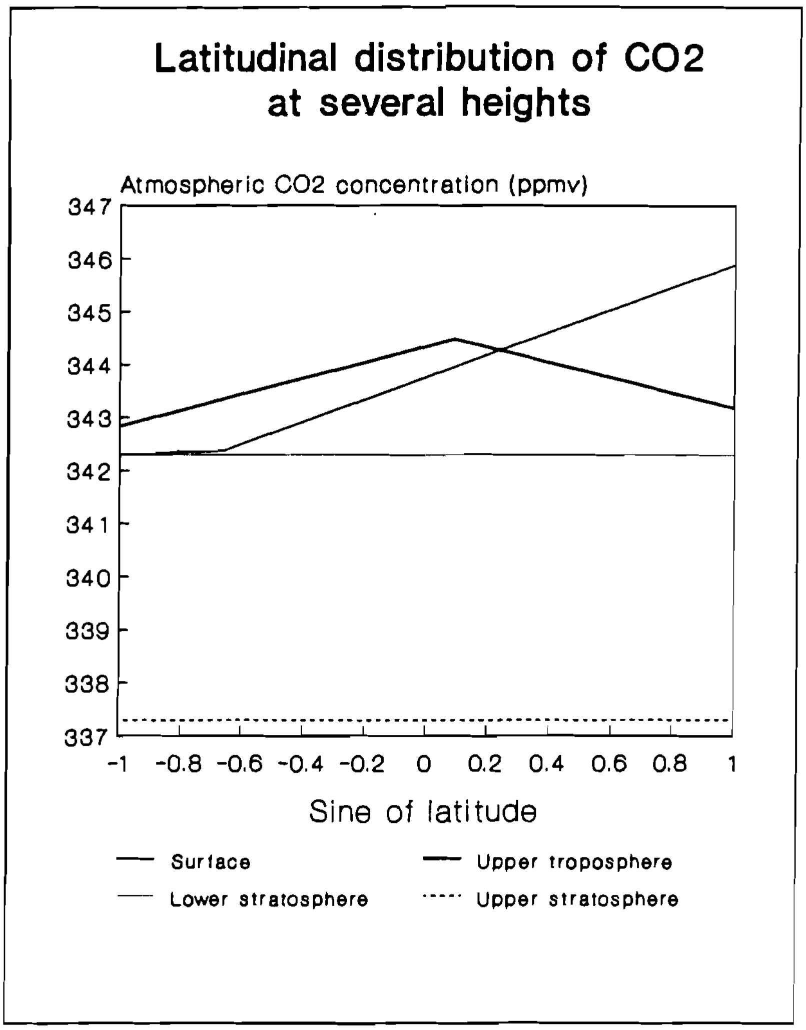


Figure 4. Altitudinal distribution of atmospheric CO_2 (ppmv) at several heights, as calculated for the year 1984 (data from Gamo et al. 1987, Keeling et al. 1989a and Nakazawa et al. 1991). Results use the best value of k.

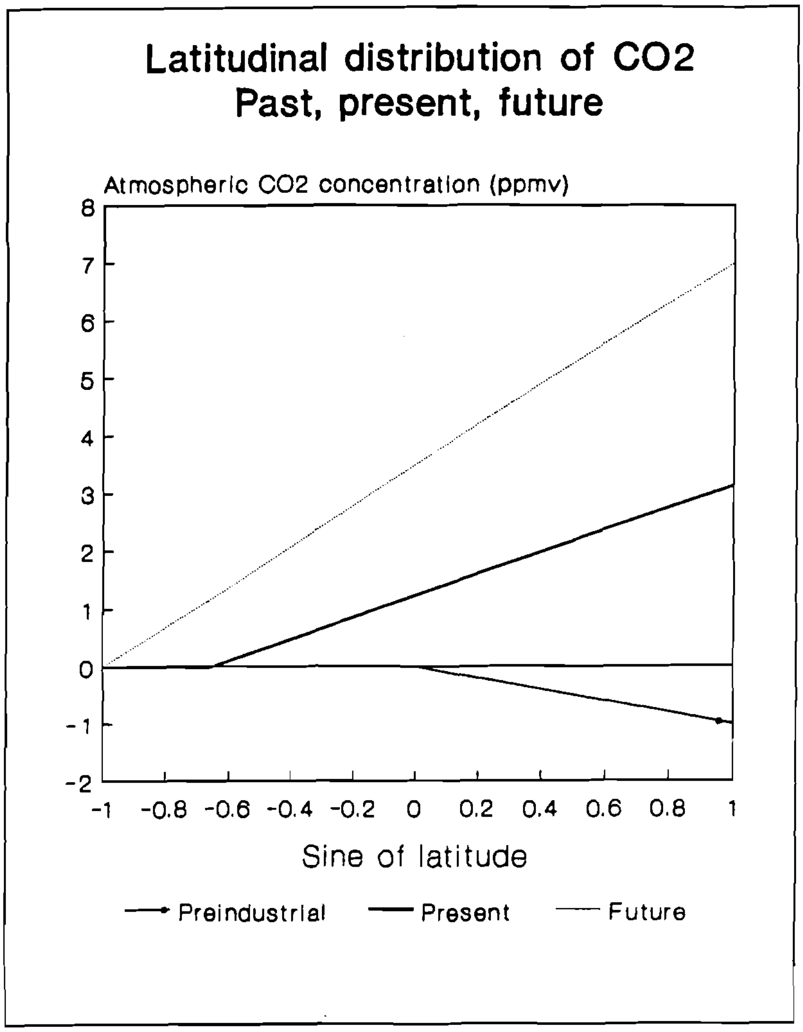


Figure 5. Latitudinal distribution of atmospheric CO_2 at the earth's surface (ppmv, annual average) for global average concentrations of 280 ppmv (preindustrial situation), 350 ppmv (1981-1987 average from Figure 2), and for 420 ppmv (future).

4. RESULTS AND DISCUSSION WITH RESPECT TO HALOCARBONS

4.1 History of man-made halocarbons

All halocarbons considered here, CFCs, HCFCs, CH_3CCl_3 and CCl_4, are man-made compounds. This means that preindustrial atmospheres were free of them. During the 1930's, when industries were looking for safe refrigerants, the first CFCs were produced. Since then production and emission of halocarbons have been increasing considerably.

At present the most widely used man-made halocarbons are the fully halogenated chlorofluorocarbons (CFCs). CFCs are used in a wide variety of purposes, the main applications being cooling agents, blowing agents, aerosol propellants and cleaning agents. In 1974 and 1975 the first scientific publications mentioned the possible environmentally negative effects of CFCs. CFCs were thought to attack the ozone layer (Molina and Rowland 1974) and to enhance the greenhouse effect (Ramanathan et al. 1975). After the discovery of the hole in the ozone layer in 1985 (Farman et al. 1985) production and use of CFCs became a serious issue of discussion. In 1987 the most important CFC producing countries agreed on a 50% reduction of CFC production by the end of the century (UNEP 1987). This so-called Montreal Protocol was strengthened in 1990 in London (UNEP 1990). When this London agreement will be implemented, production and use of CFCs, CCl_4 and CH_3CCl_3 will be virtually stopped from or short after the year 2000, and in a number of applications hydro(chloro)fluorocarbons (H(C)FCs) will most probably be used instead.

The halocarbon HCFC-22 is used at present, but the other H(C)FCs considered in this study have not yet been used in large quantities. Therefore, the man-made (hydro)chloro(fluoro)carbons detected in non-negligible amounts in today's atmosphere are CFCs, HCFC-22, CH_3CCl_3 and CCl_4.

Halocarbons have been emitted mainly from northern hemispheric land based sources. The only sink for halocarbons is photolysis in the stratosphere. Therefore, a north south gradient can be expected, with higher concentrations in the northern than in the southern hemisphere. The first measurements of halocarbon concentrations were made in 1970's (e.g. Lovelock 1973). Concentrations were indeed found to be higher in the northern hemisphere than in the southern.

4.2 Present halocarbon concentrations

4.2.1 Latitudinal distribution at the earth's surface

The man-made halocarbons that are abundant in the present atmosphere are mainly the CFCs, CH_3CCl_3, CCl_4 and HCFC-22. The latitudinal variation in these halocarbons is investigated using the SAGA II data. Khalil and Rasmussen (1988a) present an empirical fit to the average concentrations from the SAGA II measurements. The empirical relation they use is expressed as an a logistic equation. The solution of the equation is:

$$C = \frac{d + aKe^{lm}}{1 + Ke^{lm}}$$

where
C = atmospheric concentration (pptv)
m = sine of latitude
a, b, d and K are constants, and l = b(a-d)

Table 6a. Values of variables for the empirical logistic model, as reported by Khalil and Rasmussen 1988a (variables are fitted against the latitudinal data obtained during the 1987 SAGA II cruise).

Variable	CFC-12	CFC-11	CFC-13	CH_3CCl_3	CCl_4	HCFC-22
d	395	228	31	122	131	96
a	429	253	38	192	138	112
K	0.10	0.25	0.40	0.20	0.15	0.10
b	0.18	0.18	1.10	0.06	1.00	0.35

Table 6b. Latitudinal variation of annually averaged surface halocarbon concentrations at the earth's surface. Regression coefficients a_1, b_1, a_2, b_2, X_k and the least mean square (sqrt) as calculated for the 1987 SAGA II data (Khalil and Rasmssen 1988a). See section 2.1.3 for meaning of the symbols. Results are presented for the best value of k (lat = sine of latitude).

gas	a_1 pptv	b_1 pptv/lat	a_2 pptv	b_2 pptv/lat	X_k lat	sqrt $pptv^2$
CFC-11	215.13	-19.82	235.48	20.89	-0.5	18.82
CFC-12	401.29	11.18	398.57	38.41	0.1	28.06
CFC-113	32.84	2.95	33.30	7.59	-0.1	6.89
HCFC-22	98.55	10.89	95.66	20.54	0.3	0.75
CH_3CCl_3	133.25	17.30	126.08	88.98	0.1	50.82
CCl_4	131.77	1.36	132.46	8.27	-0.1	0.62

Table 6a summarizes values of the parameters a, b, d, and K, as given by Khalil and Rasmussen (1988a) while the concentrations which are calculated with the appropriate equations are shown in Figure 6. Figure 7 and Table 6a show the latitudinal variation as calculated from the 1987 SAGA II data using the linear regression technique mentioned in section 2. From Figures 6 and 7 it is clear, that CFC-11 and CFC-12 were the most abundant halocarbons in the 1987 atmosphere. Their global 1990 average concentrations are listed in Table 12. Figures 6 and 7 also show the calculated atmospheric halocarbon concentrations relative to the South Pole. It is clear, that northern hemispheric concentrations are higher than southern values for all halocarbons. This may be explained by differences in height of emissions, rate of emissions increase, latitudinally varying sinks and atmospheric lifetimes. Other factors that could influence latitudinal variation like latitudinal distribution of sources and transport are more or less the same for all halocarbons. From Figures 6 and 7 it is clear that the North-to-South Pole difference is most pronounced for CH_3CCl_3, and least for CCl_4. The CH_3CCl_3 pole-to-pole difference is considerably larger than the corresponding differences of the other halocarbons primarily due to large annual emissions in the northern hemisphere and loss of CH_3CCl_3 in the troposphere due to reaction with OH. This tropospheric sink is the reason that the atmospheric lifetime of CH_3CCl_3 is relatively short (6.3 years). A short lifetime is to promote spatial variation in atmospheric concentration. Moreover, there are indiactions that the OH concentrations show a north-south gradient opposite to the CH_3CCl_3 gradient, so that this sink is stronger in the southern hemisphere than in the northern. This is another factor increasing the CH_3CCl_3 gradient.

From Figure 6 and 7 and Tables 6a and 6b is clear that the linear regression method results in a higher North-to-South Pole ratio than the logistic method. Because no measurements were made north of 70^o in the SAGA II experiment, it is not possible to validate the methods. However, Khalil and Rasmussen conclude that their results are in agreement with high latitude land-based measurements. Moreover, the GMCC data (Bodhaine and Rosson 1988) indicate that the south-pole-to-arctic difference of CFC-12 is rarely higher than 40 pptv, indicating that Figure 6 (33 pptv difference) gives a better representation of reality than Figure 7 (45 pptv difference). Comparison of the two methods with interhemispherical concentration ratios reported in other studies (Tables 7 and 8) is not very easy because different methods are used to obtain the north-south ratios. For instance, vertically averaged values are somewhat lower than surface values, as will be discussed in section 4.2.2.

Table 9 and Figure 8 show the increase in CFC-11 and CFC-12 concentrations as calculated for both GMCC and ALE land-based stations. There is no clear latitudinal trend. These results may indicate that although emissions have increased, the latitudinal gradient has not been changing in time since the late 1970's. This may partly be due to the fact that the rate of CFC-11 and CFC-12 emission increase has slowed down since 1973. As discussed in the CO_2 section, a reduction in the rate of increase in emissions is to decrease the north to south gradient. This may hold for carbon dioxide as well as for halocarbons, because for both CO_2 and halocarbons the northern hemispheric anthropogenic emissions are the main reason for the observed latitudinal gradient.

Table 7. North-Pole-to-South Pole difference as calculated in the present study using the linear regression with boundary condition (Table 6b), and using the empirical fit as presented by Khalil and Rasmussen 1988a (see Table 6a). Pole-to-pole differences are given as percentage relative to the South Pole surface concentration: 100*|NP-SP|/SP, where NP = North Pole surface concentration and SP = South Pole surface concentration.

gas	This study	Khalil and Rasmussen 1988a
CFC-11	9.1%	10.5%
CFC-12	12.0%	8.4%
CFC-113	36.8%	22.5%
HCFC-22	32.6%	16.1%
CH_3CCl_3	85.5%	53.1
CCl_4	7.9%	5.3

Table 8. Difference between the hemispheric halocarbon concentrations (north/south ratios) as reported in literature.

gas	ratio	location	year	Reference
CFC-11	1.18	45°N/90°S	1975-80	1
	1.09	vertical/hemispherical average	1978	2
	1.08	vertical average Arctic vs. 30-40°S	1982 may	3
	1.09	45°N/90°S	1985	4
	1.05-1.07	vertical average,	1979-80,83	5
CFC-12	1.15	45°N/90°S	1975-80	1
	1.08	vertical/hemispherical average	1978	2
	1.07	vertical average Arctic vs. 30-40°S	1982 may	3
	1.08	45°N/90°S	1985	4
	1.03-1.06	vertical average,	1980	5
CFC-113	1.08	vertical/hemispherical average	1978	2
	1.25	vertical average Arctic vs. 30-40°S	1982 may	3
HCFC-22	1.18	vertical/hemispherical average	1978	2
	1.20	vertical average Arctic vs. 30-40°S	1982 may	3
CH_3CCl_3	1.58	45°N/90°S	1975-80	1
	1.3	vertical/hemispherical average*,	1978	2
	1.39	vertical average Arctic vs. 30-40°S	1982 may	3
	1.45	45°N/90°S	1985	4
	1.10-1.22	vertical average,	1976-80,83	5
CCl_4	1.11	45°N/90°S	1975-80	1
	1.04	vertical average Arctic vs. 30-40°S	1982 may	3
	1.12	45°N/90°S	1985	4
	0.99-1.04	vertical average,	1976-80,83	5

* above boundary layer

References:
1. Rasmussen and Khalil (1981b)
2. Rasmussen and Khalil (1983)
2. Rasmussen and Khalil (1982)
4. Rasmussen and Khalil (1986)
5. Delorey et al. (1988)

Table 9. Annual increase (pptv/year) in CFC-11 and CFC-12 concentration for the GMCC and ALE monitoring stations. GMCC values are based on 1978-1987 data, ALE values on 1978-1983 data (Bodhaine and Rosson 1988, Cunnold et al. 1986).

Station	latitude	network	increase CFC-11	increase CFC-12
SPO	90°S	GMCC	9.3 ± 0.5	16.8 ± 0.1
CGO	41°S	ALE	9.4 ± 0.2	16.5 ± 0.2
SMO	14°S	GMCC	9.7 ± 0.2	17.1 ± 0.1
SMO	14°S	ALE	9.4 ± 0.2	16.1 ± 0.5
RPB	13°N	ALE	9.2 ± 0.2	16.6 ± 0.2
MLO	20°N	GMCC	9.6 ± 0.1	16.0 ± 0.2
MWR	40°N	GMCC	9.4 ± 0.1	15.9 ± 0.2
CMO	45°N	ALE	8.1 ± 0.3	14.1 ± 0.7
ADR	52°N	ALE	8.5 ± 0.2	16.9 ± 0.2
BRW	71°N	GMCC	9.7 ± 0.1	16.7 ± 0.2

4.2.2 Altitudinal distribution

Table 10 and Figures 9 and 10 show the variation in CFC-11 and CFC-12 concentrations with height as calculated from the data given by Fabian et al. (1981). It is clear that concentrations in the stratosphere decrease with height to negligible levels at about 30 km. In the troposphere the altitudinal variation seems relatively moderate. The measurements by Fabian et al. refer to northern mid-latitudes. Although some studies indicate that in the stratosphere CFC concentrations show some variation with latitude, it may be assumed that this variation is negligible as compared to the altitudinal variation in the stratosphere.

Several studies indicate that the concentrations of CFCs decrease very little with height in the troposphere (e.g. Rasmussen and Khalil 1983). Therefore, the profiles for 1978 and 1979 may be the best representation for altitudinal variation in CFC-11 and CFC-12 concentrations. At other latitudes the variation with height may be different than those measured at midlatitudes, because the height of the tropopause may be different (see for instance Mahlman et al. 1986). However, the main features of altitudinal variation can be expected to be the same: a strong decrease with height in the stratosphere, and almost no altitudinal variation in the troposphere. For other gases with as long atmosphetic lifetimes (CCl_4, CFC-113, CFC-114, CFC-115) the altitudinal variation may be the same as for CFC-11 and CFC-12.

In the lower troposphere (0-4 km) altitudinal gradients are reported for CFC-11, CFC-12, CFC-113, HCFC-22 CH_3CCl_3 and CCl_4 by Rasmussen and Khalil (1981, 1982). Some of their results are summarized in Table 11. From this Table it is clear, that in case of CH_3CCl_3 and HCFC-22 this altitudinal gradient is relatively steep: at 0 km the atmospheric concentrations are 7.4 and 4.5% higher than at 3.4 km for CH_3CCl_3 and HCFC-22 respectively. For the other gases the difference between the concentrations in and above the boundary layer appear to be relatively small.

With respect to variation with height in the troposphere it can be concluded that, for halocarbons with long atmospheric lifetimes, the concentrations may not vary, or vary only slightly with height in the troposphere. At 9.9 km concentrations of CFC-11 and CFC-12 are calculated to be lower than surface values by 11.9 and 3.8 pptv, or 7.7 and 1.3% respectively for the year 1979. Concentrations of halocarbons with shorter lifetimes like HCFC-22 and CH_3CCl_3 may decrease somewhat more with height in the troposphere. In the stratosphere concentrations of all halocarbons decrease with height. At about 30 km stratospheric concentrations of all halocarbons considered are reduced to very low levels .

Table 10. Altitudinal variation in halocarbon concentration. Regression coefficients a_1, b_1, a_2, b_2, X_k and the least mean square (sqrt) as calculated for the 1977, 1978, 1979 data as reported by Fabian et al. (1981). Results are presented for the best value of k.

gas	a_1 pptv	b_1 pptv/km	a_2 pptv	b_2 pptv/km	X_k km	sqrt pptv^2
CFC-11						
1977	211.69	-7.96	-14.06	0.43	26.9	8916
1978	157.26	-2.39	197.95	-6.51	9.88	5609
1979	154.15	-1.20	218.94	-7.75	9.9	15340
CFC-12						
1977	354.78	-11.60	121.31	-3.26	28	17828
1978	293.53	-4.29	397.54	-12.42	12.8	8616
1979	294.58	-0.38	419.75	-13.02	9.9	24621

Table 11. Differences in halocarbon concentrations between 0 and 3.4 km (pptv) (Rasmussen and Khalil 1981). S.d. = standard deviation.

gas	difference (pptv)	s.d. (pptv)	difference (%)	s.d. (%)
CFC-11	3	1.2	1.6	0.6
CFC-12	2.8	2.3	0.7	0.7
CFC-113	2.7	0.7	3	3.15
HCFC-22	2.9	1.1	4.5	1.7
CH_3CCl_3	11	2.6	7.4	1.7
CCl_4	6	3	4	2

4.3 Future halocarbon concentrations

As described above, halocarbons were produced first in the 1930's. At present, annual global production and use of CFCs amounts to more than 1000 kton, as can be seen in Table 12. The phaseout of CFCs, CH_3CCl_3 and CCl_4 in the near future, as agreed upon in London in 1990 (UNEP 1990), does not mean that concentrations of CFCs will decrease in the near future. Model calculations show, that because of their long atmospheric lifetimes concentrations of CFCs will decrease only very slowly (den Elzen et al. 1990, Kroeze and Reijnders 1992, Kroeze and Reijnders in press). Nevertheless, a phaseout will have impact on the latitudinal distribution. As soon as anthropogenic emissions stop, the concentrations will probably more or less stabilize throughout the troposphere. The two hemispheres are relatively well mixed within one year, and interhemispheric mixing takes about 2 years. Therefore it can be expected that from the year 2010 the north-south gradient will have been disappeared for CFCs, CH_3CCl_3 and CCl_4. The altitudinal gradient in the troposphere, which is not very strong, may stay about the same.

Table 12. Global use and concentrations of halocarbons, and the resulting radiative forcing in 1990 and 2100 (Kroeze and Reijnders, in press). Class I H(C)FCs are H(C)FCs having a Global Warming Potential that is more than 10% of the Global Warming Potential of CFC-11, while Class II H(C)FCs have a Global Warming Potential that is less than 10% of the Global Warming Potential of CFC-11. Future estimates are based on a scenario which assumes that H(C)FCs will be used unrestrictedly to replace CFCs and halons, while no emission control in terms of better housekeeping, recycling or destruction of halocarbon waste is to be implemented.

Gas	Use (kton/year)		Concentration (pptv)		Radiative forcing (W/m^2)		Atmospheric lifetime (years)
	1990	2100	1990	2100	1990	2100	
CFCs							
CFC-11	351	11	266	97	0.06	0.02	60
CFC-12	450	13	466	318	0.13	0.09	120
CFC-113	172	8	53	46	0.01	0.01	90
CFC-114	15	0.5	7	8	<0.01	<0.01	200
CFC-115	23	0.7	5	13	<0.01	<0.01	400
Class I H(C)FCs							
HCFC-22	304	1520	106	1254	0.02	0.24	15.3
HCFC-142b	0	109	0	90	0	0.02	6.6
HFC-125	0	471	0	432	0	0.11	28.1
HFC-134a	0	1693	0	1205	0	0.20	41.0
HFC-143a	0	380	0	625	0	0.09	19.0
Class II H(C)FCs							
HCFC-123	0	997	0	57	0	0.01	1.6
HCFC-124	0	19	0	4	0	0.01	6.6
HCFC-141b	0	675	0	230	0	0.03	2.0
HFC-152a	0	48	0	7	0	<0.01	1.7
Other							
CH_3CCl_3	563*	16*	135	4	0.01	<0.01	6.3
CCl_4	76*	2*	103	17	0.01	<0.01	50

* Emissions (kton/year)

As CFCs and halons are phased out, new halocarbons will be used to replace the fully halogenated CFCs and halons. The most important substitutes will be the hydro(chloro)fluorocarbons: HCFCs and HFCs. These substitutes have a low Ozone Depleting Potential. However, they all have some Global Warming Potential (GWP). Based on current use and market trends, future use of H(C)FCs can be estimated. The most widely used H(C)FCs will be Class I H(C)FCs, as can be seen in Table 12, especially HCFC-22 and HFC-134a in cooling appliances. These model calculations show, that in case H(C)FCs will be used to replace CFCs and halons, equilibrium warming by halocarbons could be 1 degree Celsius by 2100, despite the CFC phaseout. The equilibrium warming by CFCs alone following a phaseout is calculated to amount to about 0.1 degree Celsius by 2100. It is, therefore, important to include H(C)FCs in a study on future global warming.

The latitudinal distribution of these HCFCs and HFCs to be used can not be predicted without a three dimensional atmospheric model, including emissions, sinks and transport.

4.4 Conclusions

Table 13 summarizes the best estimates for latitudinal and altitudinal distributions of halocarbons, as discussed in this study. The north-south differences are found to vary between 5 and 53% of the South Pole surface concentrations. It can be extpected that the north-south gradients of CFCs, CH_3CCl_3 and CCl_4 will disappear a few years after the expected phaseout.

The altitudinal gradient is found to be relatively small in the troposphere, but steep in the stratosphere for CFC-11 and CFC-12. For halocarbons with shorter lifetimes, such as H(C)FCs and CH_3CCl_3 the tropospheric gradient may be somewhat steeper. In case halocarbons are to be phased out, the altitudinal gradients will most probably qualitatively stay the same, but the altitudinal gradient in the stratosphere may decrease as concentrations decrease.

Table 13. Approximate relative difference of halocarbon concentrations at the earth's surface relative to the (South Pole) surface concentrations in the present atmosphere.

Gas	latitudinal: pole-to-pole[1]	altitudinal: troposphere-to-surface[2]	altitudinal: stratosphere-to-surface[3]
CFC-11	10.5%	7.7%	100%
CFC-12	8.4%	1.3%	100%
CFC-113	22.5%		100%
HCFC-22	16.1%		100%
CH_3CCl_3	53.1%		100%
CCl_4	5.3%		100%

[1] Pole-to-pole difference (surface values) given as percentage relative to the South Pole concentration: 100*|NP-SP|/SP, where NP = surface concentrations at North Pole, SP = surface concentration at South Pole. Results refer to 1987 SAGA II data reported by Rasmussen and Khalil (1988).

[2] Altitudinal difference in the troposphere given as percentage relative to the surface value: 100*|UT-S|/S, where UT = upper tropospheric concentration, and S = surface concentration at latitude available. Results are based on the 1979 data from Fabian et al. (1981). Upper troposphere is chosen to be the altitude of the best value of k (9.9 km).

[3] Altitudinal difference in the whole atmosphere (troposphere and stratosphere) given as percentage relative to the surface value: 100*|US-S|/S, where US = upper stratospheric concentration and S = surface concentration at latitude available. Results are based on the 1979 data from Fabian et al. (1981). Upper stratosphere is chosen to be where concentrations are calculated to be zero.

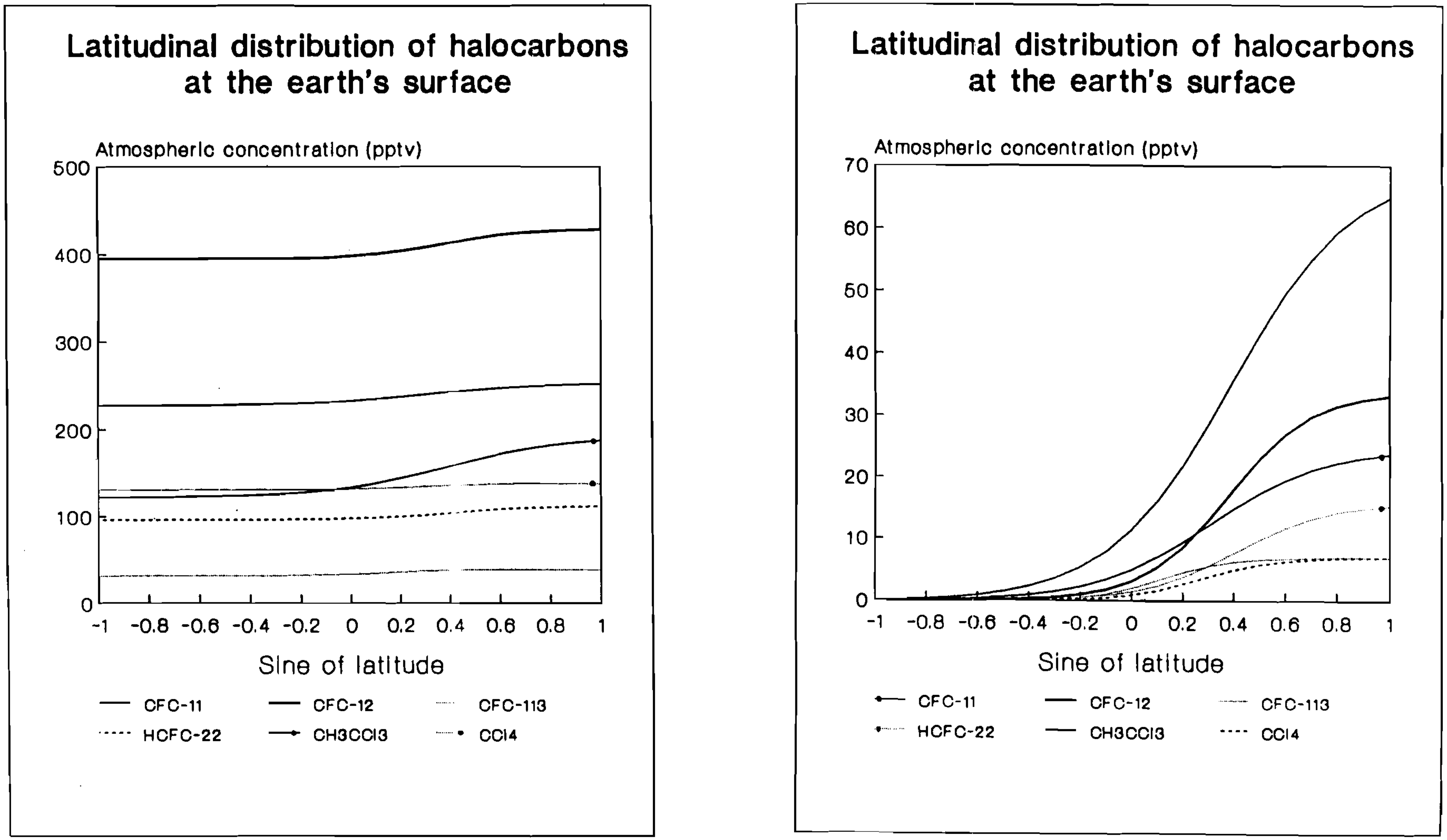


Figure 6. Latitudinal distribution of atmospheric halocarbons (pptv) at the earth's surface (annually averaged) for the year 1987 (adopted from Khalil and Rasmussen 1988). Graph on left hand side shows the absolute concentrations (pptv), and the graph on the right hand side shows concentrations relative to the South Pole (pptv).

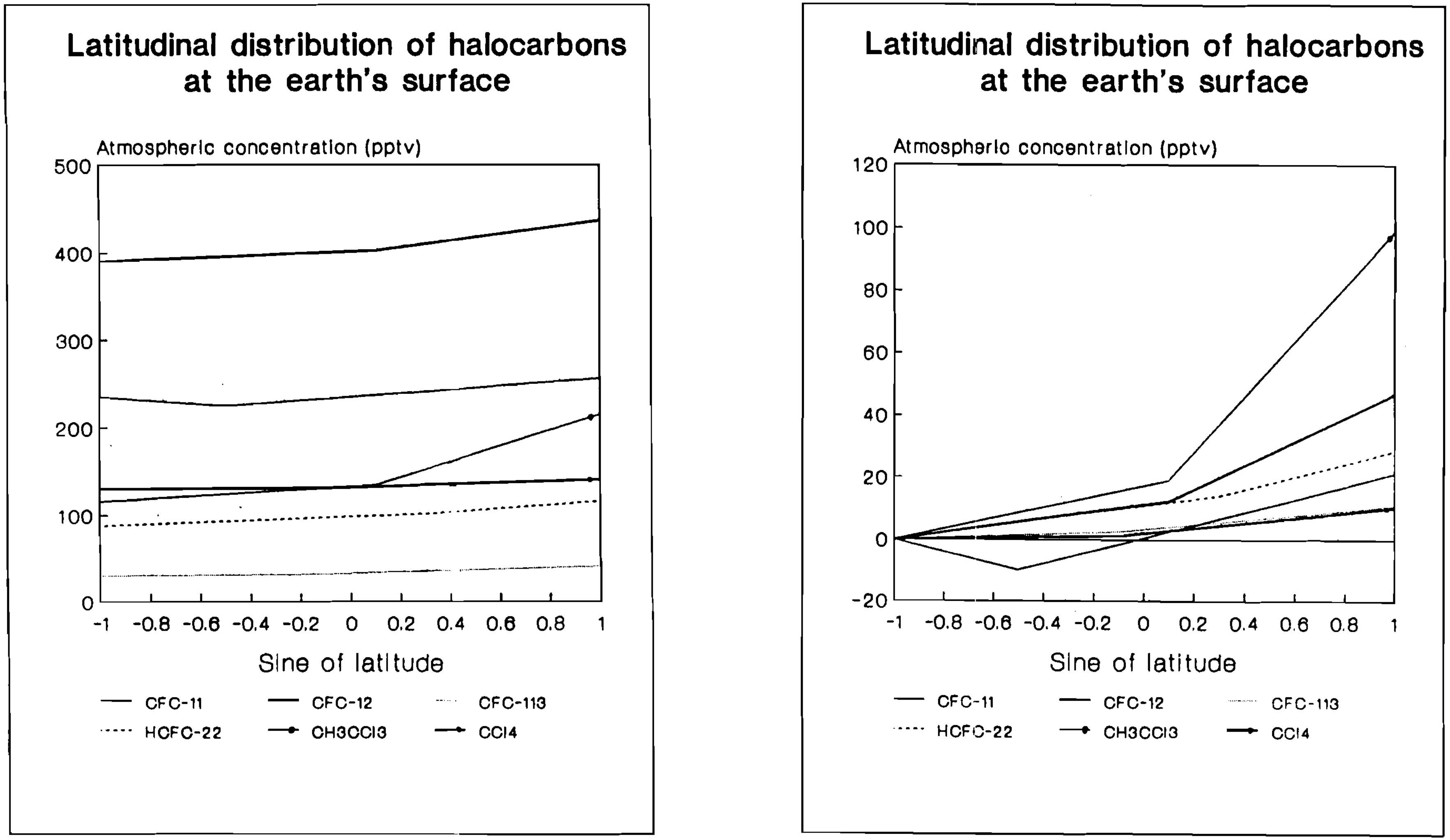


Figure 7. As in Figure 6, except latitudinal distribution is calculated using linear regression with boundary condition. Results use the best value of k.

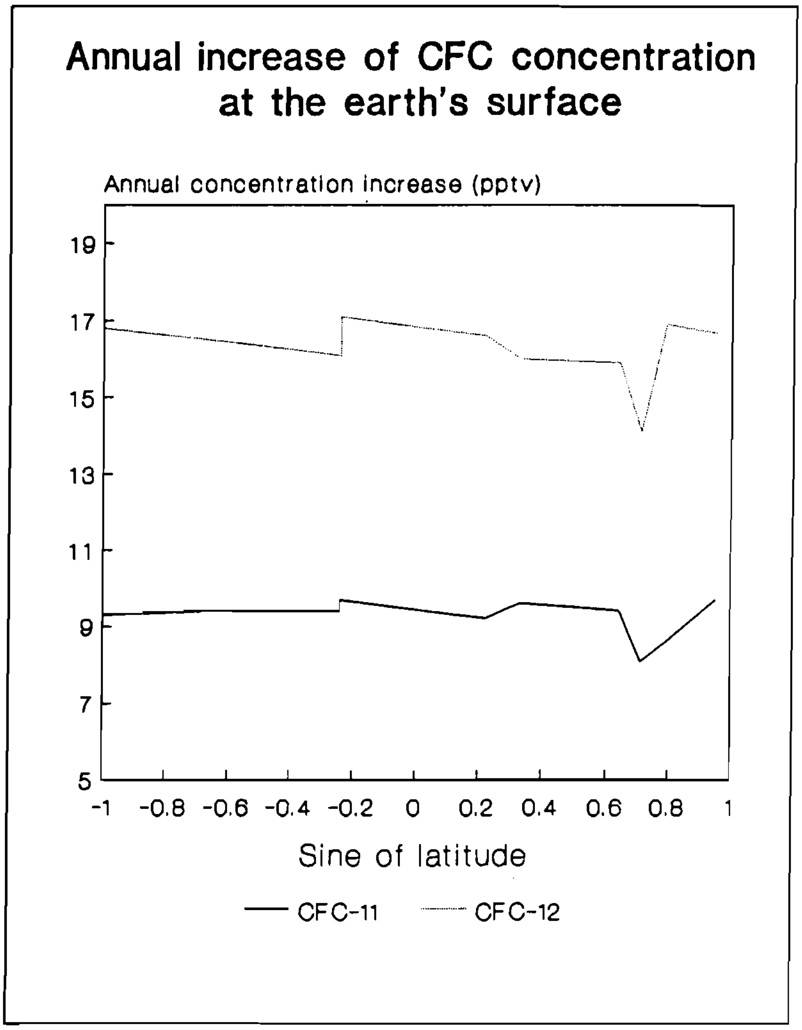


Figure 8. Annual increase of atmospheric halocarbon concentrations (pptv/year) as measured at the GMCC and ALE sites (1978-1987 GMCC data from Bodhaine et al. 1988, and 1978-1983 ALE data from Cunnold et al. 1986).

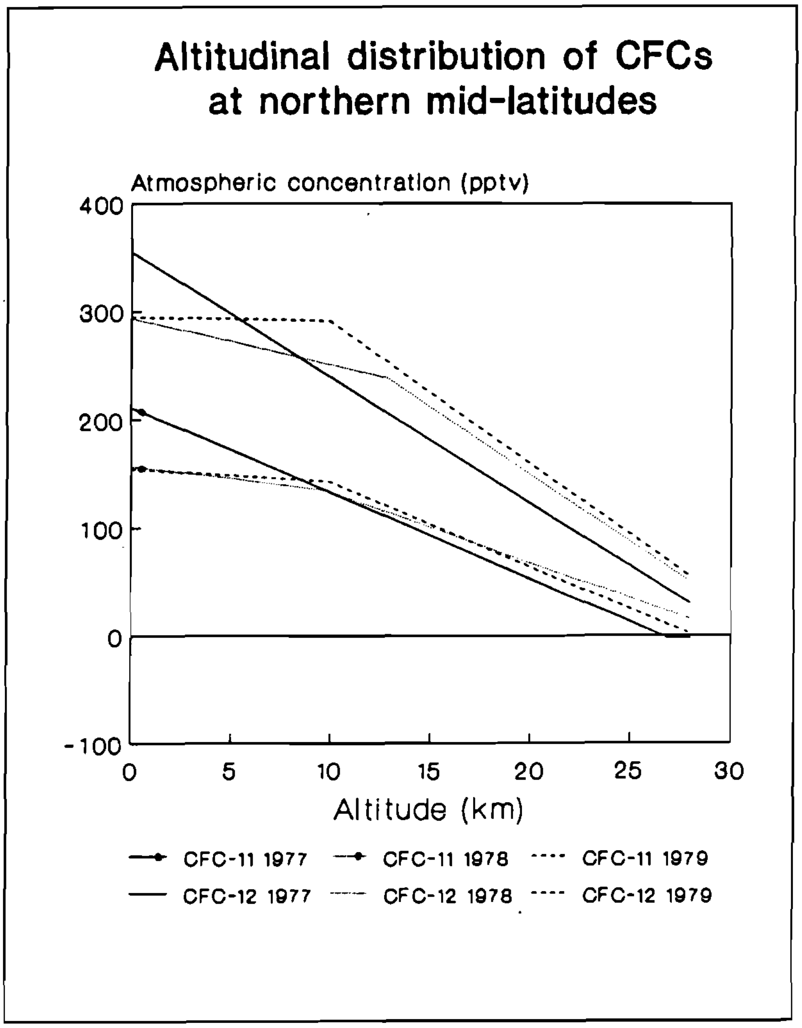


Figure 9. Altitudinal distribution of CFC-11 and CFC-12 (pptv) as calculated for the 1977, 1978 and 1979 data reported by Fabian et al. (1981). The graphs shown are those calculated for the best value of k.

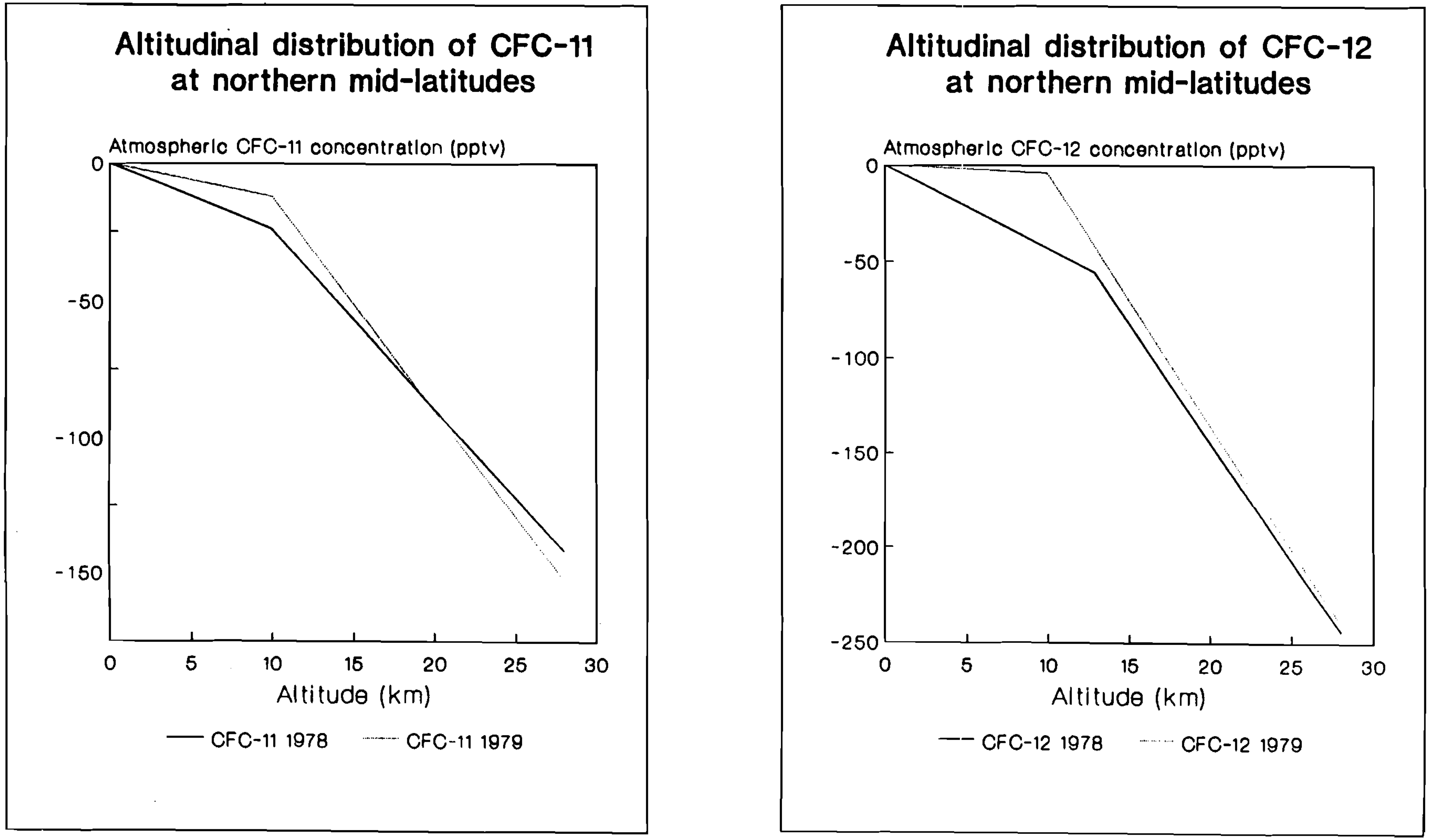


Figure 10. As in Figure 9, but only for 1978 and 1979 data. The data are reduced by the concentration at the earth's surface (pptv).

5. RESULTS AND DISCUSSION WITH RESPECT TO NITROUS OXIDE

5.1 Preindustrial nitrous oxide concentration

In preindustrial times the concentrations of N_2O amounted to about 285 (280-290) ppbv, according to analysis of ancient air in polar ice bubbles. Natural sources of N_2O are mainly the result of biological processes. Bacteria in soils, oceans and freshwater produce N_2O as end-product or by-product of nitrification and/or denitrification. Next to this there may be N_2O release from soils as a result of chemodenitrification. Also biomass burning, especially in tropical regions, may contribute to N_2O emissions. Finally there are some indications that N_2O may be formed in the atmosphere under specific conditions. Although the relative importance of the distinguished sources is still a matter of discussion, some data are described in Section 5.2. The main sink of N_2O is photolysis in the stratosphere.

Natural sources and sinks of N_2O are widely distributed over the earth. This and the relatively long atmospheric lifetime are the reasons that in the preindustrial atmosphere a latitudinal or altitudinal gradient was not well established in the troposphere. For instance, Weiss et al (1981b) indicate that the preindustrial interhemispheric difference may be neglegible. Some researchers, on the other hand, conclude from model calulations that there was a latitudinal gradient before the Industrial Revolution, with northern hemispheric concentrations were somewhat lower southern hemispheric. The interhemispheric difference might have amounted to about 1 ppbv (Levy et al (1981). Analysis of ancient air trapped in polar ice by Khalil and Rasmussen (1988) indicated, however, that the preindustrial southern hemispheric concentration was 1.9 ± 2.5 ppbv higher than the northern.

5.2 Present nitrous oxide concentration

5.2.1 Present concentrations, sources, sinks.

Nitrous oxide is a gas with a relatively long atmospheric lifetime of 150 years (Watson et al. 1990). Prinn et al. (1990) report the results of 10 years of N_2O measurements. They conclude that during the period 1978-1988 the average concentration amounted to 302.9 ppbv, while the concentration increased at a rate of 0.25 - 0.31% per year. Like CFCs the only well known sink for atmospheric N_2O is photolysis in the stratosphere. An increase of atmospheric N_2O concentrations therefore not only enhances the greenhouse effect, but also attacks the ozone layer. In 1990 the atmospheric N_2O concentration amounted to about 310 ppbv. Reasons for the increase in atmospheric N_2O are still matter of discussion. Up to 1987 fossil fuel combusition was believed to be the most important anthropogenic source of N_2O. However, Kramtlich et al. (1987) showed that these emissions were overestimated as a result of measurement artefacts. At present, there seems agreement among scientists that fossil fuel combustion contributes only small amounts to the global N_2O burden. Other anthropogenic sources of N_2O are mainly the stimulation of biological processes by human activities. For instance land use change and use of fertilizers could alter the micro-environment in such a way that denitrifying and nitrifying bacteria are favoured, leading to increasing emissions of N_2O. The same holds for addition of mineral nitrogen to soils by atmospheric deposition. Also, biomass burning is believed to be an important source of N_2O. And, finally, there are some indications that N_2O may be emitted from nylon production.

The increase of atmospheric N_2O at present amounts to about 3-4.5 Tg N/year and the stratospheric sink amounts to 7-13 Tg N/year (Watson et al. 1990). Therefore a total emission of 10-17.5 Tg/year is necessary to explain the observed increase in atmospheric N_2O. According to Watson et al. the known emissions of N_2O amount to 4.4-10.5 Tg N/year (Table 14). Watson et al. conclude that there is a 'missing source'. Table 14 also shows the emission estimates of Prinn et al. (1990). They use these estimates in a computer model which simulates the spatial N_2O distribution in the atmosphere. Table 15 summarizes the locations of these emissions as used in their study. Although the spatial distribution obtained by the simulation of Prinn et al. is realistic, this is no proof that their emission estimates are correct. However, the calculations indicate that at least the locations of emissions (Table 15) may be realistic. Prinn et al. concluded from their calculations that the N_2O latitudinal gradient can be simulated in case anthropogenic emissions are located in the tropics (most probably biomass burning and land use change), and in the northern mid-latitudes (industrial sources and fertilization).

Another explanation of the 'missing source' may be increased natural N_2O emissions as a result of global warming. During the last century the global temperature increased by about 0.5°C. Rasmussen and Khalil (1989) estimate that this warming may have produced about 20% of the increase of N_2O between preindustrial times and present. It may be possible that this feedback is not completely included in current emission estimates.

Several studies tried to answer the question whether or not atmospheric N_2O concentrations show temporal variation. This could be expected because natural emissions related to microbial acticity may be sensitive to temperature and humidity. So far, no clear seasonal cycle has been observed. Although Khalil and Rasmussen (1983) reported seasonally changing N_2O concentrations based on 3 years ALE/GAGE data, analysis of 10 years of ALE/GAGE data showed no indications for a seasonal cycle (Prinn et al. 1990). Matthias et al. (1979) found a diurnal variation at ground surface, decreasing with height.

Table 14. Sources and sinks of N_2O as reported by Watson et al. (1990) and Prinn et al. (1990).

	Watson et al. (1990) Tg N/yr at present	Prinn et al. (1990) Tg N/yr in 1982
SOURCE		
Natural		
ocean	1.4 -2.6	2.5
soil tropical	2.2 -3.7	3.8
soil temperate	0.7 -1.5	0.6
total	4.3 -7.8	6.9
Anthropogenic		
fossil fuel	0.1 -0.3	≤ 1.6
land disturbance*	0.02-0.2	1.9-4
fertilized soil	0.01-2.2	≥ 1.0
total	0.13-2.7	5.8
SINK		
removal by soils	?	
stratosphere	7 -13	
atmospheric increase	3 -4.5	

* biomass burning included

Table 15. Approximate fraction of sources of N_2O in four latitude belts (Prinn et al. 1990)

Source	90°-30°N	30°N-0°	0°-30°S	30°-90°S
Natural				
ocean	0.18	0.25	0.27	0.30
soil tropical	0	0.55	0.45	0
soil temperate	0.92	0	0	0.08
Anthropogenic				
fossil fuel	0.86	0.089	0.024	0.027
land disturbance	0	0.57	0.43	0
fertilized soil	0.52	0.37	0.1	0.01

5.2.2 Latitudinal distribution at the earth's surface

Early measurements of atmospheric N_2O indicated that concentrations were relatively homogenuously distributed in the troposphere. Pierotti and Rasmussen (1977) and Singh et al. (1979) concluded from their measurements in the early 1970's that there was no latitudinal gradient observed. A 1.000 ratio (approximate 90% confidence limits: 0.999 - 1.002) between average northern and southern hemisipheric concentrations was reported by Rasmussen et al. (1981), based on 1975-1980 measurements at two monitoring stations (45°N and 90°S).

More recent measurements, however, indicate that there is a north to south gradient: current concentrations are measured to be higher in the northern than in the southern hemisphere. For instance Weiss (1981a,b) reported a 0.83 ± 0.15 pbbv difference between average northern and southern hemispheric concentration based on 1967-1980 measurements from both land-based stationary stations and ship measurements. A relatively flat north south ratio was reported by Delorey et al. (1988): 0.997 ± 0.013 to 1.004 ± 0.02 as the result of six aircraft flights and one oceanic cruise between 1976 and 1983. Measuring N_2O concentrations from 1978 to 1981 at Cape Meares (45°N) and Cape Grim (42°S) Khalil and Rasmussen found average concentrations in the northern hemisphere to be 0.8 ppbv higher than in the southern. Moreover, they measured the increase in concentrations in the northern hemisphere to amount to 0.9 (0.6-1.1) ppbv/year and in the southern hemisphere to be 0.7 ± 0.2 ppbv/year. Khalil and Rasmussen (1983a) report a north-south difference amounting to 1.1 ± 0.4 ppbv. Although Watson et al. (1990) report a 1 ppbv interhemispheric difference, we think that the ALE/GAGE 0.75 ppbv difference (Prinn et al. 1990) may be a good estimate. Figure 11 and Table 16 show the approximate latitudinal N_2O distribution as Prinn et al. (1990) derived from ten years of ALE/GAGE data. The 1978-1988 pole-to-pole difference amounts to 0.9 ppbv, according to these data, which is 0.3% of the South Pole surface concentration. Concentrations of N_2O have not been investigated enough to determine a detailed latitudinal gradient.

The latitudinal gradient shown in Figure 11 is different from the one in the preindustrial atmosphere. As discussed in section 5.1 there are indications that prior to the Industrial Revolution, N_2O concentrations were highest in the southern hemisphere. At present, concentrations are highest in the northern hemisphere. This could be due to the location of anthropogenic emissions, that are mostly land-based and therefore located mainly in the northern hemisphere.

Compared with CFCs the N_2O latitudinal gradient is relatively moderate, although both CFCs and N_2O have comparable locations of sinks, anthropogenic sources, and comparable atmospheric lifetimes. This may be caused by the fact that N_2O is emitted by nature as well, and, as can be seen in Table 16, the natural sources are found all over the world. Therefore the northern hemispheric anthropogenic sources have less impact on the latitudinal gradient than in case of CFCs.

Table 16. Differences between the 10-year mean mixing ratio (in ppbv) in four latitudinal regions (sine of latitude) and the global average of the four means (302.90 ppbv in 1978), and the difference between the northern and southern hemispheric averages of these means (adapted from Prinn et al. 1990).

Sine of lat.	1.0 to 0.5	0.5 to 0	0 to -0.5	-0.5 to -1.0	NH-SH
Difference	0.40	0.35	-0.25	-0.50	0.75
Range	0.18-0.62	0.18-0.52	-(0.36-0.14)	-(0.37-0.63)	0.59-0.91

5.2.3 Altitudinal distribution

Figure 12 shows the distribution of N_2O with height at mid-latitudes, as derived from data reported by Fabian et al. (1981). From this figure it is clear that in the troposphere the N_2O concentrations decrease only slightly with height. We think the best estimate is given by the year 1979, where a moderate latitudinal gradient is visible. These results are in general agreement with measurements made by Pierotti and Rasmussen (1977) and Roy (1979), who found no altitudinal gradient in the troposphere. Also Ko and Sze (1982) and Roy (1979) found no altitudinal variation up to 15 km, both in the mid-latitudes and in the tropics. As can be seen in Figure 12, surface concentrations are calculated too high. However, differences relative to the surface may be used. At 15.1 km the 1979 N_2O concentration is calculated to be 23.4 ppbv (7.0%) lower than the surface concentration.

In the stratosphere concentrations decrease with height. At a height of about 45 km, concentrations drop to negligible levels in the year 1977 and 1979. This is in agreement with Ko and Sze (1977) and Roy (1979), who reported that at 50 km virtually no N_2O was measured. Although some studies indicate that in the stratosphere N_2O concentrations show some variation with latitude, it may be assumed that this variation is neglegible as compared to the altitudinal variation in the stratosphere. Therefore, the first order variation in N_2O concentrations with height may be no or little variation in the troposphere, and a linear decrease of N_2O concentration between tropopause and 45 km.

Table 17. Altitudinal variation in nitrous oxide concentration. Regression coefficients a_1, b_1, a_2, b_2, X_k and the least mean square (sqrt) as calculated for the 1977, 1978, 1979 data as reported by Fabian et al. (1981) Results are presented for the best value of k. See Section 2.1.3 for meaning of the symbols.

year	a_1 pptv	b_1 pptv/km	a_2 pptv	b_2 pptv/km	X_k km	sqrt pptv^2
1977	327.08	-0.04	508.66	-13.98	13.03	58683
1978	368.64	-4.30	563.89	-16.58	15.9	36184
1979	335.27	-1.55	548.63	-15.68	15.1	21329

5.3 Future nitrous oxide concentrations

As pointed out earlier, the reasons for increases in atmospheric N_2O concentrations are not clear. However, it seems reasonable to assume that the anthropogenic emissions are somehow related to food production, and may therefore be hard to control. Moreover, when climate changes, several feedback mechanisms may influence natural N_2O emissions. The net feedback may be a positive one, resulting in increasing emissions as the global temperature increases (Khalil and Rasmussen, 1989). It can therefore be expected that atmospheric N_2O concentrations will continue to increase in future.

In what way the latitudinal distribution may change in future is difficult to say, depending mainly on location and rate of increase of N_2O emissions. In case anthropogenic emissions from the northern hemisphere will show a fast increase in time, the north-south gradient may continue to increase. In case natural emissions (also located in the southern hemisphere) or anthopogenic emissions from the southern hemisphere will rise, the latitudinal gradient may stay the same or even decrease. Finally, a changing atmospheric or oceanic transport as the result of climate change may alter the latitudinal distribution.

At present, N_2O concentrations vary little with altitude in the troposphere. As emissions increase, a tropospheric altitudinal gradient may be developed (concentrations decreasing with height). In the stratosphere the distribution with height may also change as tropospheric concentrations increase. It seems, however, reasonable to assume that also in future stratospheric concentrations may decrease to neglegible levels at about 45 km.

5.4 Conclusions

In the present atmosphere concentrations of N_2O vary relatively moderately with latitude. Table 18 shows that the pole-to-pole difference amounts to about 0.9 ppbv, or 0.3% of the South Pole surface concentration at present, with highest concentrations in the northern hemisphere. The present latitudinal gradient is most probably caused by high northern hemispheric emissions as compared to southern. There are indications that in the preindustrial atmosphere the latitudinal gradient was opposite, showing concentrations to be highest in the southern hemisphere. Assuming that the latitudinal gradient is reversed due to human activites, the north-south difference may change in future as well.

The altitudinal gradient in the troposphere is calculated to be 7% of the surface values. In the stratosphere concentrations decrease with height to neglegible levels at about 45 km. Photolysis in the stratosphere is the main removal mechanism of atmospheric N_2O.

Table 18. Approximate relative difference of N_2O concentrations at the earth's surface relative to the (South Pole) surface concentrations in the present atmosphere.

Gas	latitudinal: pole-to-pole[1]	altitudinal: troposphere-to-surface[2]	altitudinal: stratosphere-to-surface[3]
N_2O	0.3%	7.0%	100%

[1] Pole-to-pole difference (surface values) given as percentage relative to the South Pole concentration: 100*|NP-SP|/SP, where NP = surface concentrations at North Pole, SP = surface concentration at South Pole. Data adapted from Prinn et al. (1990).

[2] Altitudinal difference in the troposphere given as percentage relative to the surface value: 100*|UT-S|/S, where UT = upper tropospheric concentration, and S = surface concentration at latitude available. Based on 1979 data reported by Fabian et al. (1981). Upper troposphere is chosen to be the altitude of the best value of k: 15.1 km.

[3] Altitudinal difference in the whole atmosphere (troposphere and stratosphere) given as percentage relative to the surface value: 100*|US-S|/S, where US = upper stratospheric concentration and S = surface concentration at latitude available. Based on 1979 data reported by Fabian et al. (1981). Upper stratosphere is chosen to be where concentrations are calculated to be zero.

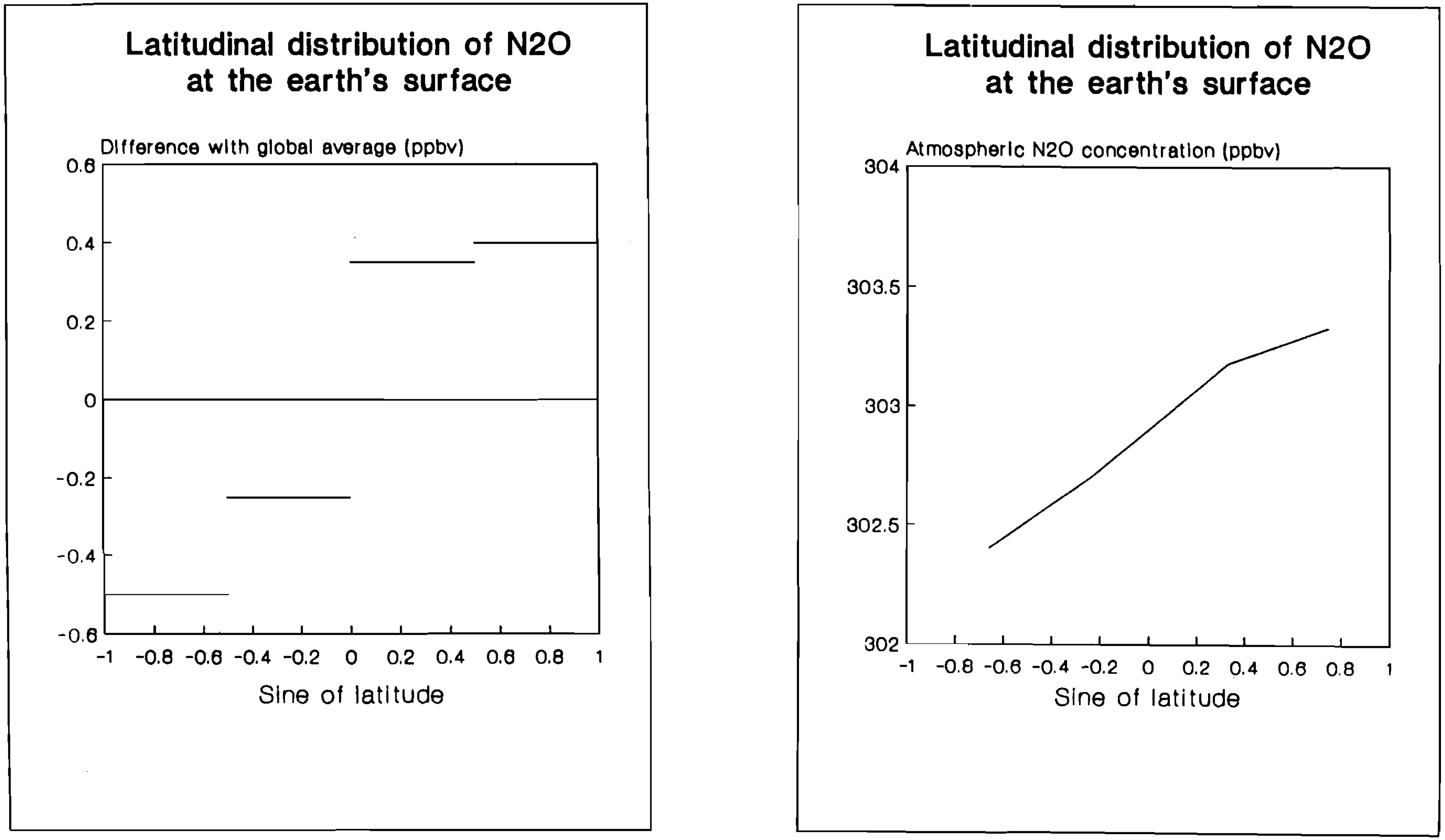


Figure 11. Latitudinal distribution of atmospheric N_2O (ppbv) at the earth's surface (annual average) as presented by Prinn et al. (1990) based on 10 years of ALE/GAGE measurements. Graph on right hand side shows the absolute concentrations for the year 1978. Graph on the left hand side shows concentration as difference with the global average value.

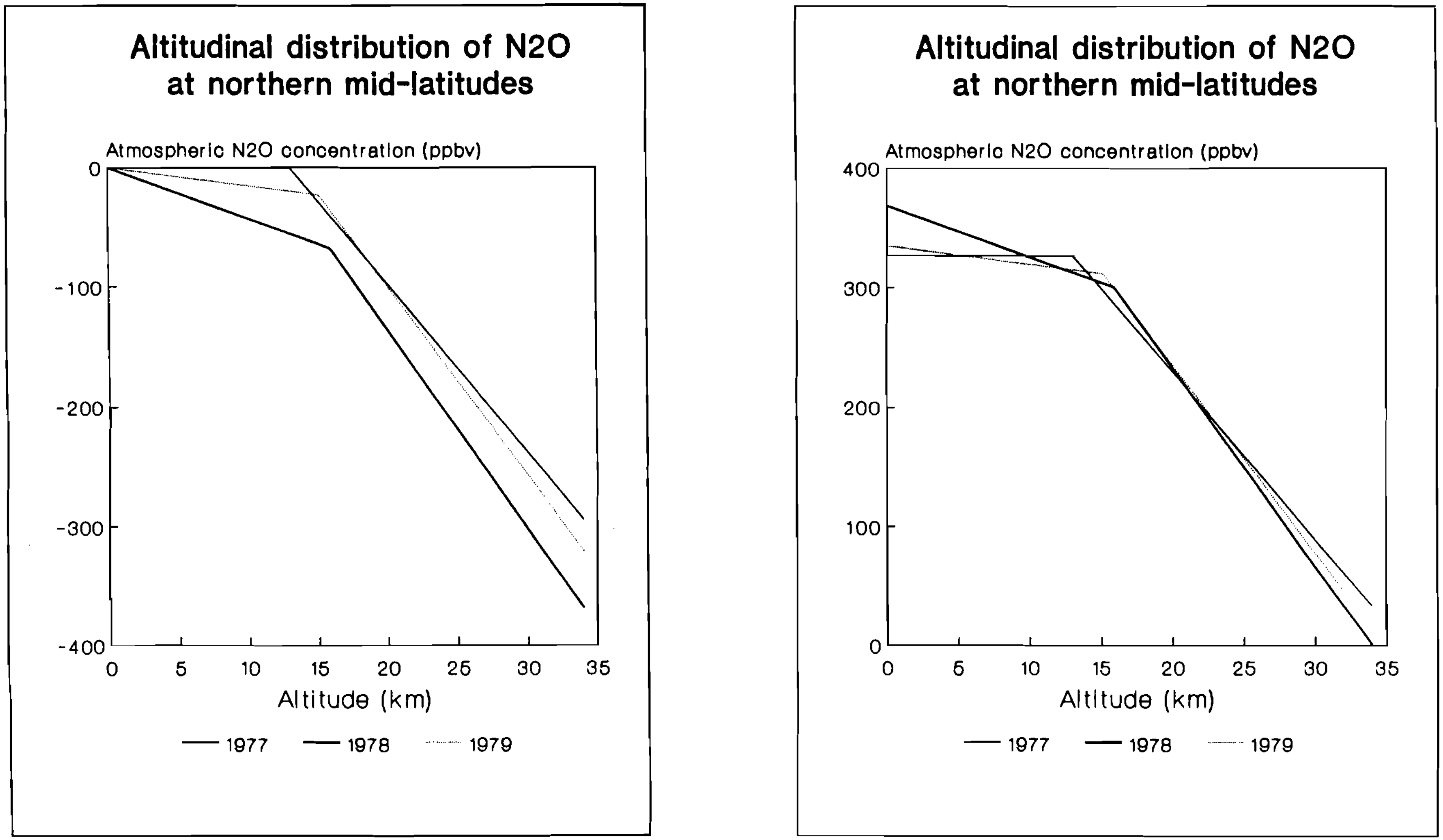


Figure 12. Altitudinal distribution of atmospheric N_2O (ppbv), based on measurements in 1977, 1978, 1979 (June-November) by Fabian et al. (1981). Graph on right hand side shows the absolute concentration (ppbv). Graph on left hand side shows the concentrations reduced by the concentrations at the earth's surface.

6. RESULTS AND DISCUSSION WITH RESPECT TO METHANE, CARBON MONOXIDE AND HYDROXYL

6.1 Atmospheric chemistry

Methane is a gas that plays an important role in the chemistry of both troposphere and stratosphere. It is beyond the scope of this study to review the chemical processes involved; however, some important features are highlighted here. Very useful articles with regard to atmospheric (photo)chemistry are those of Hameed et al. (1979), Logan et al. (1981), Callis et al. (1983), and Thompson and Cicerone (1986).

In the troposphere concentrations of CH_4, CO, OH, NOx, O_3 and NMHCs (Non-Methane HydroCarbons) are interrelated. The chemistry involved is extremely complicated and not completely understood. Nevertheless, it seems clear that especially emissions of CH_4, CO and OH affect each others concentrations. Therefore, OH and CO are included in this study although they are no radiatively active gases themselves.

Hydroxyl (OH) radicals are formed in the troposphere as result of a reaction of $O(^1D)$ atoms released by the ultraviolet photolysis of ozone with wavelengths < 295-314 nm with H_2O. Therefore, the amount of OH produced depends on water vapor content of the atmosphere, the amount of irradiance and temperature. Next to this the concentrations of NMHC's (non methane hydrocarbons), NOx and O_3 also influence the OH production.

Hydroxyl radicals play a central role in atmospheric chemistry. For CH_4, CO and many other gases oxidation by OH is the main sink. Because of their reactive nature, OH radicals have only a very short lifetime. Model studies indicate that increasing emissions of CO and CH_4 may result in decreasing concentrations of OH. Subsequently, the atmospheric lifetime of CH_4 may increase, causing its concentrations to also increase. This positive feedback may have accounted for some of the observed concentration increase. On the other hand concentrations of NO_x, tropospheric ozone and NMHC's are influenced by anthropogenic activities as well. This influence may have counteracted the OH decrease. Unfortunately, it is not possible to validate the model results with observational data. Thompson et al. (1989) conclude from their model calculations that in most regions increasing emissions of NO, CO and CH_4 will suppress OH and increase O_3, but also that these trends may be opposed by stratospheric O_3 depletion (increasing tropospheric photooxidation) and climate change. According to Isaksen (1988) it is difficult to judge how much OH has changed over the last decades.

An increase of atmospheric CH_4 in the atmosphere may have several effects. First of all, CH_4 is a greenhouse gas, and increased concentrations may result in a radiative forcing. Another important effect of increasing CH_4 concentrations may be an increase of tropospheric O_3 in clean non-urban air. Tropospheric O_3 is considered to be harmful because it is highly reactive, and one of the strongest greenhouse gases. Finally, in the stratosphere CH_4 provides water vapour by reacting with OH and terminates the chlorine atom catalysed destruction of O_3 by reacting with Cl atoms to form HCl (Rasmussen and Khalil 1982). Therefore, an increase of stratospheric CH_4 concentrations may mitigate stratospheric O_3 depletion by CFCs.

6.2 Preindustrial concentration of methane, carbon monoxide and hydroxyl

6.2.1 Methane

Methane is one of the natural components of the atmosphere of the earth. Analysis of ancient air, trapped in polar ice revealed that the concentration of atmospheric methane prior to the industrial era was about 0.8 ppmv (800 ppbv), about half of the present-day concentration (e.g. Robbins et al. 1973, Rasmussen and Khalil 1984a,b, Pearman et al. 1986, Khalil and Rasmussen 1982, 1987, Stauffer et al. 1988).

Rasmussen and Khalil (1984b) found that CH_4 concentrations 250 years ago and earlier was 10% (± 4%) higher in the Arctic as compared to the Antarctic. They concluded that this finding is consistent with the expected ratio of about 1.07-1.11 obtained from a global mass balance model. A few hundred years ago, only natural processes resulted in CH_4 emissions to the atmosphere. These natural sources are mainly the result of biological activity. In particular, microbial processes under anoxic conditions, for instance in natural wetlands or enteric fermentation in animals may result in CH_4 emissions. Natural emissions of CH_4 are mainly from land and therefore mainly from the northern hemisphere. This may partly explain the preindustrial north-south gradient.

6.2.2 Carbon monoxide

Carbon monoxide concentrations in polar ice bubbles have been investigated by Robbins et al. (1973). They concluded that the background concentrations of carbon monoxide in the atmosphere has been about 0.1 ppmv for many centuries.

6.2.3 Hydroxyl

As discussed before, concentrations of OH are investigated using models that simulate the atmospheric chemistry. Some of these models indicate that concentrations of OH may have decreased during the past century. For instance the model of Khalil and Rasmussen (1985) indicates that concentrations of OH may have been 10^6 molecules/cm^3 several hundred years ago, about 30% higher than the present concentration.

Because the production rate of OH depends on water vapor content, temperature and solar irradiance, it can be expected that in preindustrial atmospheres the concentration of OH was highest in tropical regions. The complex nature of tropospheric chemistry, however, makes it difficult to quantify the latitudinal and altitudinal variation.

6.3 Present concentration of methane, carbon monoxide and hydroxyl

6.3.1 Present concentrations, sources, sinks.

6.3.1.1 Methane

At present, the global concentration of methane amounts to about 1.7 ppmv (1700 ppbv). The increase of CH_4 concentrations began about 250 years ago as the result of anthropogenic activities, but most of the increase dates from the 20th century. Watson et al. (1990) report that 30% of the increase in atmospheric methane has taken place during the last 40 years.

The increase of atmospheric methane concentrations may, as discussed above, have two reasons. Khalil and Rasmussen (1985) calculate that 70% of the observed increase of atmospheric CH_4 is the result of increased CH_4 emissions. The remaining 30% may be the result of decreased OH concentrations, caused by increased emissions of CO and to a lesser extent of CH_4. Anthropogenic activities that lead to CH_4 emissions are, for instance, agriculture (cattle, rice paddies), natural gas and coal mining, landfills and biomass burning. These emissions are, like natural emissions, mostly land-based. The emissions from rice paddies take place in the tropics, but the other land based sources are primarily located in the northern hemisphere.

Tropospheric concentrations of methane show a seasonal cycle (Rasmussen and Khalil 1981a,d, Steele et al. 1987). Steele et al. (1987) found that some features of the seasonal cycle change with latitude. In the southern hemisphere a concentration maximum was found in winter, while in the northern hemisphere two concentration maxima were found in spring and fall. The reasons for the seasonal cycle may be seasonally changing sources, sinks and atmospheric transport. As discussed above, most of the sources are located in the northern hemisphere. In summer emissions may increase as the result of a temperature increase. But also the sinks (reaction with OH) may increase in summer as the result of a more water vapour in the atmosphere and more solar irradiance. A complicated interaction of these seasonally changing processes may account for the complicated seasonal cycle in the northern hemisphere. In the southern hemisphere the seasonal cycle is determined mainly by the seasonal cycle of OH.

Atmospheric methane may also show a longitudinal variation, because most of the sources are land-based and because of the relatively short atmospheric lifetime (8 years). Steele et al. (1987), however, assume that this longitudinal variation is relatively small compared to latitudinal or altitudinal variation.

6.3.1.2 Carbon monoxide

Concentrations of carbon monoxide show considerable spatial and temporal variation, especially in the lower troposphere. Concentrations at the earth's surface can be up to a factor of two higher than in the free troposphere (Zander et al. 1989). Measurement data within the lowest layers of the atmosphere are mostly very noisy as a result of local sources and transport. It is therefore difficult to obtain an annually averaged value of atmospheric CO concentrations in a certain region. In the free troposphere the variability is somewhat smaller. Zander et al. (1989) estimated that in 1950-1951 the vertically and annually averaged concentration above 3.58 km amounted to 67 ± 15 ppbv at 47^{o}N, and 100 ± 18 ppbv in 1985-1987.

Also the rate of increase is not easy to estimate without long term measurements from several sites. Several studies indicated that concentrations of carbon monoxide have been increasing. The reported rates of increase in the northern hemisphere vary between 1 and 10% per year (e.g. Graedel and McRae 1980, Zander et al 1989). The most recent estimates suggest a 1% per year increase of atmospheric carbon monoxide in the northern hemisphere (Watson et al. 1990). It is not clear what the trend of CO is in the southern hemisphere.

The total source of carbon monoxide is estimated to amount to about 2400 Tg/year. About half of this may be emitted directly as the result of human activities (incomplete combustion of both fossil fuels and biomass). The other half may be the result of oxidation of atmospheric methane and NMHCs, of which concentrations increased during the past decade due to anthropogenic activities.

The main sink for atmospheric CO is oxidation by OH (see Section 6.1). The seasonal variability of OH causes concentrations of CO to vary with season. Its concentrations are observed to be lowest in the late summer and highest in late winter. The modulation in total column CO may amount to 25% (Zander et al. 1989).

6.3.1.3 Hydroxyl

Atmospheric concentrations of OH are calculated to amount to 7.7×10^5 radicals per cm^3 (Prinn et al. 1987). These measurements are based on the spatial distribution of CH_3CCl_3. This is a gas with a known source (anthropogenic only), and with OH being the only sink, so that the OH concentration can be calculated in case concentration and emission of CH_3CCl_3 are known.

Khalil and Rasmussen (1985) calculated that the OH concentrations to amount 7×10^5 molecules/cm^3 at present. These calculations assume that the concentrations of OH have decreased during the past century.

Concentrations of OH may change with seasons. This is the result of changing temperature, water vapor content and solar irradiance. Because of insufficient experimental data available the seasonal variation is hard to quantify. Model calculations suggest that concentrations of atmospheric OH are 3-4 times higher in summer than in winter (Hewitt and Harrison, 1985).

6.3.2 Latitudinal distribution at the earth's surface.

6.3.2.1 Methane

Figure 13, and Table 19 show the latitudinal variation in surface concentrations of CH_4 as calculated using the 1984 data of Steele et al. (1987). From these results it is clear that CH_4 concentrations are higher in the northern than in the southern hemisphere. The calculated annual pole-to-pole difference amounts to 153 ppbv. This is 9.7% of the 1984 CH_4 South Pole surface concentration. Prior to the industrial era the pole-to-pole difference may have amounted about 10% as well (see Section 6.2.2). The absolute pole-to-pole difference has apparently increased from 70 ppbv to 153 ppbv since preindustrial times. This may be an indication that the doubling of the CH_4 concentration resulted in a doubling of the pole-to-pole difference, but that the North-to-South Pole ratio has stayed about constant.

Table 20 summerizes some reported interhemispheric differences. Most of the values presented consider hemispherically averaged surface concentrations. These values are somewhat lower than the pole to pole differences presented above, because the latitudinal gradient extends from pole to pole. Nevertheless the results in Table 20 seem to be in general agreement with the 0.153 ppmv (153 ppbv) pole-to-pole difference we found. Blake et al. concluded in 1982 from several studies that a concentration gradient exists of approximately 6% between the NH and the SH.

Furthermore, Figure 13 shows that the latitudinal gradient is more pronounced in winter than in summer. This is the result of the seasonal cycle. Cofer III (1982) found the hemispheric gradient to be very sharp between 14°N and 10°N latitude, the intertropical convergence zone.

Table 19. Latitudinal distribution of annually averaged surface CH_4 concentration. Regression coefficients a_1, b_1, a_2, b_2, X_k and the least mean square as calculated for the NOAA/GMCC 1984 data (Steele et al. 1987) See section 2.1.3 for meaning of the symbols. Results are given for annually averaged data, and for the averages of the months November, December, January (NDJ) and June, July, August (JJA) (lat = sine of latitude).

year	a_1 ppbv	b_1 ppbv/lat	a_2 ppbv	b_2 ppbv/lat	X_k lat	sqrt pptv^2
annual	1597.46	24.01	1609.51	116.77	-0.13	604.09
NDJ	1598.24	35.76	1610.55	130.51	-0.13	1375.68
JJA	1592.01	11.61	1610.69	89.45	-0.24	76.55

Table 20. Reported north-south differences of CH_4 concentrations at the earth's surface.

N-S (ppmv)	N/S ratio	
0.1	1.08	Dec/Nov 1972 hemispheric average concentration[1]
0.04	1.03	Sep/Dec 1977 hemispheric average concentration[2]
0.09	1.06	Oct/Noc 1980 hemispheric average concentration[3]
0.14	1.09	Jan 1980 45°N - 90°S[4]
0.11	1.07	1980, hemispheric average[5]
0.1	1.06	Apr/May 1978, hemispheric average concentration[6]
0.15	1.09	May 1982, arctic - 30-40°S average concentration[7]
0.14	1.09	Jan 1985, 45°N - 90°S concentration[8]
0.09		1980, late spring, hemispheric average concentrations, model results/input[9]

1. Ehhalt (1978)
2. Singh et al. (1978)
3. Cofer III (1982)
4. Ramussen and Khalil (1981)
5. Khalil and Rasmussen (1983)
6. Heidt et al. (1980)
7. Rasmussen and Khalil (1983)
8. Ramussen and Khalil (1986)
9. Isaksen and Hov (1987)

6.3.2.2 Carbon monoxide

As discussed above, the spatial and temporal variability of atmospheric CO concentrations in combination with an insufficient measuring network makes it difficult to give a reliable latitudinal or altitudinal gradient. Moreover, Reichle et al. found that concentrations of CO are a strong function of longitude. Nevertheless, in some studies assumptions are made about the spatial distribution of CO. For instance, in their atmospheric chemistry model Logan et al. (1981) used broad estimates of latitudinal and altitudinal variations of annually averaged CO concentration. Figure 14 shows the estimated latitudinal distribution of CO at the surface and in the mid-troposphere, based on this study. From this figure it is clear that concentrations of CO are assumed to be higher in the northern than in the southern hemisphere. Moreover, it is assumed that concentrations of CO are more or less constant in the southern hemisphere (65-70 ppbv at the surface and 70-75 ppbv in the mid-troposphere). In the northern hemisphere surface concentrations of CO are estimated to amount to 145 ppbv between the equator and 30°N (sine of latitude = 0.5), and 200 and ppbv in the region 30°N-60°N (equivalent = 0.5 - 0.87 in sine of latitude). In the mid-troposphere these values are 100 and 120 ppbv, respectively.

Figure 14 shows also the results of the linear regression, using the free troposphere data of Seiler and Fishman (1981). These data were obtained aboard an airplane during the months July and August in 1974. These data are free tropospheric average values, and may be compared with the mid-tropospheric gradient based on Logan's study. From this comparison it may be concluded that with regard to the northern hemisphere the results are in reasonable agreement. However, the measurements by Zander et al. (1989) discussed in section 6.1.2.1. show free tropospheric concentrations in the northern hemisphere that are lower than those of Figure 14. Zander et al. concluded that the estimates of Logan et al. (1981) were too high for the free troposphere of the northern hemisphere. Therefore, we assume that the best guess for the northern hemispheric concentrations may lie somewhere between the free-tropospheric gradient based on Seiler and Fishman, and Logan's 15°N estimate (100 ppbv). This 'best guess' is shown at the right hand side in Figure 14.

Furthermore, the left hand side graph in Figure 14 shows that in the southern hemisphere the free and mid-tropospheric gradients show some differences. The free tropospheric data result in increasing concentrations with latitude, whereas the mid-tropospheric estimate assumes concentrations to be more or less constant with regard to latitude. Because most studies indicate that annually averaged CO concentrations vary only slightly with latitude in the southern hemisphere (e.g. Seiler 1974), we think that here the estimates of Logan are a better representation.

The right hand side graph in Figure 14 shows what we think is the best guess for the annually averaged latitudinal distribution of CO. For the northern hemispheric gradient based on the data given by Seiler and Fishman the results are given for k as close as possible to the equator (sine of latitude = -0.03). The pole-to-pole difference may amount to 43-97% of the surface South Pole concentration; however, it must be realized that these conclusions are very tentative.

Table 21. Latitudinal variation of free tropospheric CO concentration. Regression coefficients a_1, b_1, a_2, b_2, X_k and the least mean square as calculated for data reported by Seiler and Fishman (1981). See section 2.1.3 for meaning of the symbols. Results are given for the best value of k and for k chosen as close to the equator as possible (k equ.) (lat = sine of latitude).

	a_1 ppbv	b_1 ppbv/lat	a_2 ppbv	b_2 ppbv/lat	X_k lat	sqrt pptv^2
best k	94.70	29.14	71.29	66.89	0.62	9747.99
k equ.	100.14	45.38	99.65	29.15	-0.03	9952.46

6.3.2.3 Hydroxyl

Because the rate of OH production depends (among other things) on temperature, atmospheric water vapor content and solar irradiance, concentrations of OH are calculated to be greatest at low latitudes. This can be seen in Figure 15, where the altitudinal OH distribution according to Prinn et al. (1987) is shown. Their study is based on the observed distribution of CH_3CCl_3, as discussed in Section 6.2.1.3.

Figure 15 shows that at mid-latitudes the concentrations of OH are higher in the southern than in the northern hemisphere. Several studies suggest an interhemispherical difference, although this difference seems difficult to quantify. Singh et al. (1979) calculated, based on the latitudinal distribution of CH_3CCl_3, an interhemispherical difference in OH concentrations of 1.5, higher than that shown in Figure 15. They argue that one possible reason for the interhemispherical gradient may be the high concentrations of CO in the northern hemisphere if compared to the southern. They furthermore suggest that in case the interhemispheric difference of CO is caused by anthropogenic activities, the OH gradient may increase in future if CO emissions increase.

Hewitt et al. (1985) conclude that southern hemispheric concentrations may be twice those in the northern hemisphere. On the other hand, model studies by Logan et al. (1981) and Isaksen and Hov (1987) suggest a much smaller interhemispherical difference. Because the results of Figure 15 are (indirectly) based on observations, we think that this may be the best representation of the latitudinal distribution of OH. The pole-to-pole difference is 9.3% of the surface South Pole concentration according to these data.

Table 22. Latitudinal distribution of atmospheric OH (10^5 radicals/cm^3) at two altitudes as calculated by Prinn et al. (1987).

sine of lat.	-1.0 to -0.5	-0.5 to 0	0 to 0.5	0.5 to 1.0
Pressure:				
500-1000 mbar	5.4 ± 1.0	9.8 ± 1.8	10.4 ± 1.9	4.9 ± 0.9
200-500 mbar	6.0 ± 1.1	10.4 ± 1.9	9.9 ± 1.8	4.8 ± 0.9

6.3.3 Altitudinal distribution

6.3.3.1 Methane

Figure 16 and Table 23 show the altitudinal variation of atmospheric methane from data obtained in the summers of 1977, 1978 and 1979 at northern mid-latitudes (data from Fabian et al. 1981). It is clear that CH_4 concentrations decrease with height both in the trospophere and in the stratosphere. In the tropsophere the decrease with height is found to be smaller than in the stratosphere. The value for best value of k is found at the top of the troposphere: at 12.0, 13.2 and 15.9 km. At these altitudes CH_4 concentrations are found to be respectively 111, 278 and 330 ppbv or 6, 15.8 and 19.5% lower than at the surface. In the stratosphere concentrations drop to almost neglegible levels at 40 km.

These profiles may be different at other latitudes, and other seasons. Our results will be compared below with other studies which indicate that the profiles as shown in Figure 16 may be representative for the annual profiles in stratosphere and in the northern hemispheric troposphere. In the troposphere in the southern hemisphere it may be assumed that concentrations do not vary with height.

Troposphere

Early measurements of tropospheric methane concentrations showed no altitudinal gradient (for instance, Heidt et al. 1980, Newell et al. 1981, Reichle et al. 1978, Ehhalt and Heidt 1973). This may be partly due to the fact that early measurements lacked required precision to measure the relatively small altitudinal gradients in the troposphere.

Several more recent studies indicate that CH_4 concentrations decrease with altitude in the northern hemisphere. For instance, Boatman et al. (1989) found a concentration difference between 1300-1700 meter and 2300-2600 meter amounting to 20 - 30 ppbv between 29°N and 41°N latitude. Rasmussen and Khalil (1873) found that in May 1982 CH_4 concentrations decreased slightly with altitude (0-4 km) at high latitudes in the northern hemisphere. In the boundary layer concentrations were found to be about 27 ppbv higher than above the boundary layer (Rasmussen and Khalil 1981a). Isaksen and Hov (1987) simulated the latitudinal and CH_4 distribution with height. Their results indicate that at the end of May 1980 the upper tropospheric concentrations were about 80 ppbv lower than surface concentrations in the northern hemisphere, and that this is a general feature throughout the northern hemisphere.

Boatman et al. (1989) investigated concentrations of atmospheric CH_4 between 29°N and 41°N at two altitudes in the troposphere. They concluded from samples taken during 6-day periods in all four seasons that a seasonal cycle was observed. Concentration maxima were found in spring and fall. The average amplitude of the seasonal cycle was found to amount 40 ppbv at both altitudes. This may be an indication that the altitudinal gradient in northern mid-latitudes may be about the same in all seasons. Assuming this to be the case, the results as presented in Figure 16 may be regarded as annually averaged values. This conclusion has to be thought over again once new databases with more altitudinal profiles will become available.

From the above it may be concluded that the results as shown in Figure 16 are in general agreement with recent studies and that they may be assumed to be representative of the northern hemispheric annual altitudinal gradient in the troposphere.

In the southern hemisphere the situation is different. While in the northern hemisphere tropospheric concentrations of methane are found to decrease with height, they were measured to increase with height in the southern hemisphere. This increase, however, is relatively moderate. For instance, Fraser et al. (1984) measured between September 1980 and March 1983 concentration differences between 10 km and the surface. They observed a difference of 16 ppbv in December 1981, a maximum difference of 24 ppbv in March, and a minimum of 8 ppbv in September/October. Some other studies conclude that concentrations of atmospheric CH_4 do not vary with height in the southern hemisphere. For instance, in the model of Isaksen and Hov (1987) concentrations are calculated to be more or less constant in the southern troposphere.

The difference between the two hemispheres with regard to altitudinal CH_4 distribution may be partly caused by the spatial distribution of sources and sinks. Most CH_4 sources are located on northern hemispheric continents, while the main sink (OH) is more pronounced in the southern hemispheric low troposphere. This low altitude sink in the southern hemisphere, combined with transport of CH_4 enriched air via the descending arm of the Hadley cell may result in CH_4 concentrations increasing with height.

Fraser et al. (1984) concluded that during the three years of measurements the altitudinal gradient in the southern hemisphere diminished. It is not clear if this is a ongoing trend. Also the reasons for the decrease are unclear.

In the southern hemisphere the amplitude of the seasonal cycle was found to decrease with altitude (Fraser et al. 1984). At the surface the amplitude was measured to amount to 28 ppbv, in mid-troposphere 9 ppbv, while in the upper troposphere no seasonal cycle was observed.

From the above it may be concluded that as a first order estimate concentrations could be assumed not to vary with altitude in the southern hemispheric troposphere.

Stratosphere

In the stratosphere the concentration decrease with height is more pronounced than in the troposphere. As can be seen in Figure 16, concentrations fall to neglegible levels at about 40 km. This is in agreement with model calculations and observations as presented by Jones and Pyle (1984). Their results also show that the variation with height in northern and southern hemisphere is more or less the same. The only region where altitudinal variations are somewhat different are the tropics. Because of upward transport and a higher tropopause, the concentrations in the tropical region are a little higher than in other areas of the same height. However, we think that as first order estimate the profile as presented in Figure 16 may be of enough precision for the whole globe.

Table 23. Altitudinal variation of CH_4 concentration at northern mid-latitudes. Regression coefficients a_1, b_1, a_2, b_2, X_k and the least mean square as calculated for the 1977, 1978 and 1979 data as reported by Fabian et al. (1981). See section 2.1.3 for meaning of the symbols. Results are presented for the best value of k.

	a_1 ppmv	b_1 ppmv/km	a_2 ppmv	b_2 ppmv/km	X_k km	sqrt ppmv^2
1977	1.6941	-0.0275	2.1880	-0.0459	12.01	1.1342
1978	1.7559	-0.0175	2.3941	-0.0576	15.9	0.5736
1979	1.7280	-0.0084	2.3157	-0.0529	13.2	0.6519

6.3.3.2 Carbon monoxide

Figure 17 shows an estimate of the distribution with height of tropospheric CO as estimated from Logan et al. (1981). To obtain this graph it is assumed that there is no altitudinal variation between 2 and 12 km. The figure shows that only in the lowest 2 km concentrations are assumed to vary with height. In the northern hemisphere CO concentrations are assumed to decrease to 100-120 ppbv, while in the southern hemisphere CO concentrations are estimated to increase up to 70-75 ppbv.

The assumption that concentrations of CO do not vary with height in the free troposphere of the southern hemisphere seems to be supported by measurements and calculations (e.g. Isaksen and Hov 1987). In the northern hemisphere, however, measurements seem to reveal ambiguous results. Figure 17 shows at the right hand side the gradient obtained from Fabian's data (Fabian et al. 1981) for the year 1979. From this graph it is clear that for the best value of k concentrations decrease with altitude up until 18 km and are more or less stable in the stratosphere. More studies indicate concentrations to decrease with increasing height throughout the troposphere. For instance, Goldman et al. (1973) found CO concentrations to decrease gradually between 4 and 14 km in January 1972. Reichle and Condon (1979) concluded that at 45°N CO concentrations were found to be decreasing with increasing height up to the altitude of the highest measurements (8 km). Other studies that indicate an altitudinal gradient are those by Zander et al. (1989), Crutzen et al. (1985), Isaksen and Hov (1987) and Rasmussen and Khalil 1983. Most of the studies indicating an altitudinal gradient in the northern hemisphere are measumenent experiments performed over continents. Sources of CO are mainly land-based, what may explain at least partly why concentrations are found to decrease with height. However, over sea the altitudinal gradient may be different. Without additional data it is very difficult to draw conclusions with regard to the altitudinal gradient. Figure 18 shows what we think might be the best guess with regard to the altitudinal variation of CO concentrations. It shows that despite all indications of an altitudinal gradient in the northern hemisphere concentrations are assumed to vary in agreement with the profiles of Logan et al. (1981). This means a relatively steep gradient in the lowest two kilometers, and no altitudinal variation between 2 and about 11 km. In the stratosphere the altitudinal gradient based on Fabian's data is adopted. A difference between Figure 18 and Logan's estimates is that in the southern hemisphere the 45°S profile is assumed to be the best, and in the northern hemisphere the 15°N profile. This results in profiles at mid-latitudes that are in better agreement with other studies like, for instance, Zander et al. (1989) and Isaksen and Hov (1987). As with the latitudinal distribution of CO, these conclusions must be regarded preliminary.

Table 24. Altitudinal variation in CO concentration at northern mid-latitudes. Regression coefficients a_1, b_1, a_2, b_2, X_k and the least mean square as calculated for the 1979 data as reported by Fabian et al. (1981). See section 2.1.3 for meaning of the symbols. Results are presented for the best value of k.

	a_1 ppbv	b_1 ppbv/km	a_2 ppbv	b_2 ppbv/km	X_k km	sqrt ppbv^2
1979	151.06	-7.70	4.21	0.50	17.9	12029.44

6.3.3.3 Hydroxyl

Figure 15 shows not only the latitudinal distribution of OH in the lower troposphere, but also at higher altitudes. From this figure it is clear that in most cases the surface concentrations of OH are lower than the upper tropsopheric. An exception is the region 0-30°N, where concentration of OH are found to be higher at higher altitudes.

6.4 Future concentration of methane, carbon monoxide and hydroxyl

Future concentrations of CH_4 will depend on emissions of CH_4 and concentrations of OH, and therefore on emissions of CO, water vapor content of the atmosphere, solar irradiance, temperature, and concentrations of gases like NMHCs, NO_x, O_3, etc. What exactly will happen in future is very difficult to predict because of the complex nature of tropospheric chemistry. However, some preliminary conclusions may be drawn.

The main causes of the past increase in atmospheric CH_4 are probably related to the increase in human population (Khalil and Rasmussen 1989). Therefore it seems realistic to assume that concentrations of CH_4 may continue to increase in case the human population continues to increase.

Some positive feedbacks, causing concentrations to increase faster at a certain rate of emissions may be expected in case climate changes (higher temperature, humidity) and in case the deterioration of the ozone layer is not halted (increased photooxidation). For example, emissions from arctic and boreal wetlands may change as humidity and temperature change (e.g. Sebacher et al. 1986), and in case temperatures increase, CH_4 emissions from permafrost may increase (Nisbet 1989).

The north/south ratio of CH_4 has been more or less the same in the past, despite the global increase in concentrations. This may lead to the assumption that also in future the north-south difference may stay about 10% of the South Pole surface concentration. In case of CO and OH this is not clear.

6.5 Conclusions

Table 25 summarizes the spatial distributions of CH_4, CO and OH. Surface concentrations of CH_4 and CO are at the North Pole 9.7 and 43-78% higher than at the South Pole. South Pole concentrations of OH are found to be 9.3% lower then at the North Pole. The altitudinal profiles for CH_4 are moderate in the tropophere, and steep in the stratosphere.

In case of CH_4 there are indications that the north-south ratio has not changed since preindustrial times. This may lead to the assumption that also in future the surface North Pole concentrations may be about 10% higher than the surface South Pole concentration.

Table 25. Approximate relative differences of CH_4, CO and OH concentrations at the earth's surface relative to the (South Pole) surface concentrations in the present atmosphere.

Gas	latitudinal: pole-to-pole[1]	altitudinal: troposphere-to-surface[2]	altitudinal: stratosphere-to-surface[3]
CH_4	9.7%	0-6%	100%
CO	43-97%*	7.7-31.0%	67-85%
OH	9.3%	2.0-11.1%	

* free troposphere

[1] Pole-to-pole difference (surface values) given as percentage relative to the South Pole concentration: 100*|NP-SP|/SP, where NP = surface concentrations at North Pole, SP = surface concentration at South Pole. CH_4 results based on 1984 data from Steele et al. (1987). CO results based on Logan et al. (1981) and Seiler and Fishman et al. (1981). OH results based on Prinn et al. (1987).

[2] Altitudinal difference in the troposphere given as percentage relative to the surface value: 100*|UT-S|/S, where UT = upper tropospheric concentration, and S = surface concentration at latitude available. CH_4 results based on 1979 data from Fabian et al. (1981). CO results based on Logan et al. (1981). OH results based on Prinn et al. (1987).

[3] Altitudinal difference in the whole atmosphere (troposphere and stratosphere) given as percentage relative to the surface value: 100*|US-S|/S, where US = upper stratospheric concentration and S = surface concentration at latitude available. Upper troposphere is chosen to be where concentrations are calculated to be zero. Results based on 1979 data reported by Fabian et al. (1981).

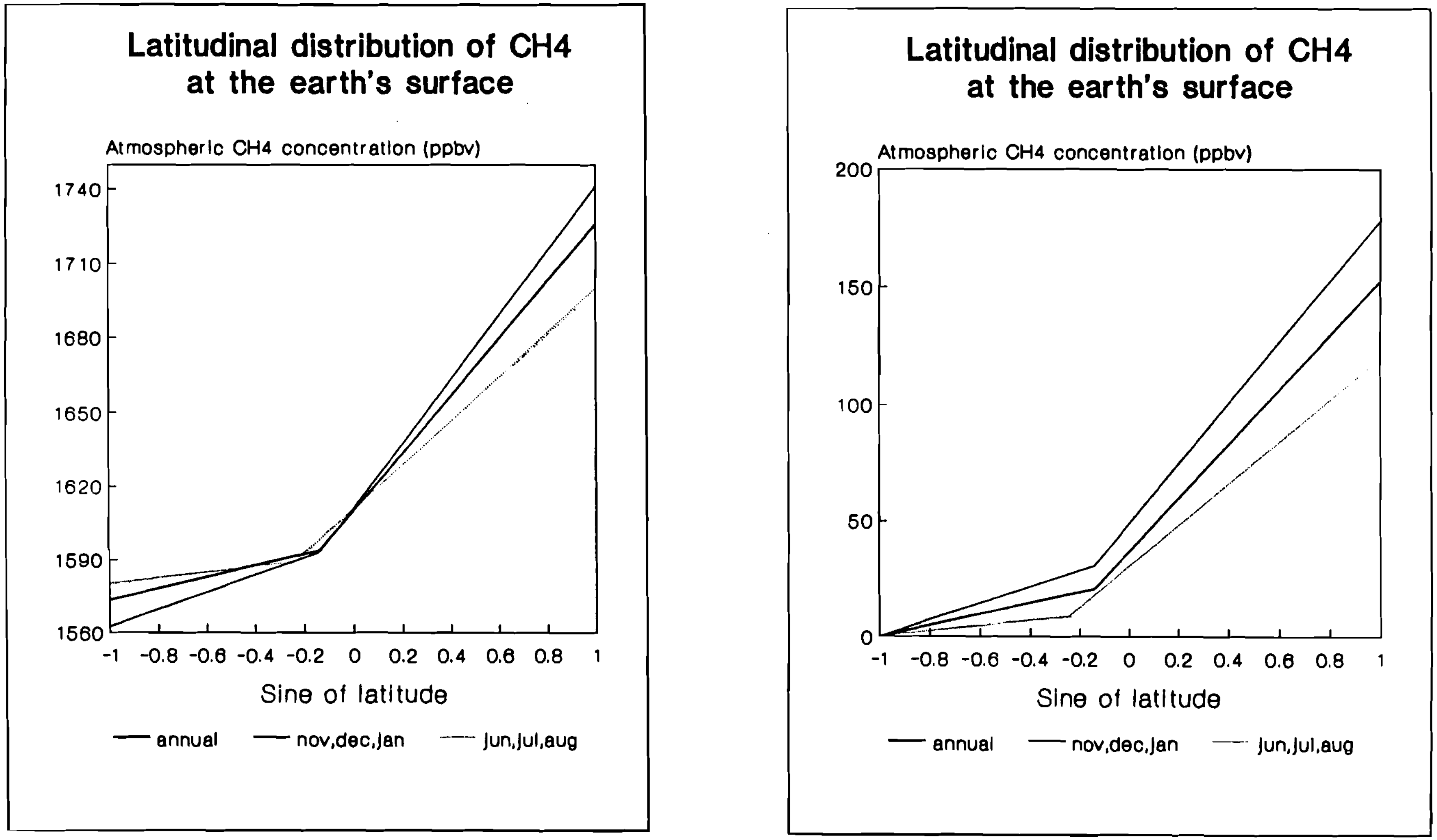


Figure 13. Latitudinal distribution of atmospheric CH4 (ppbv) at the earth's surface (annual average), based on 1984 data reported by Steele et al. (1987). Graph on left hand side shows the absolute concentrations (ppbv). Graph on the right hand side shows concentration as difference with the surface South Pole value.

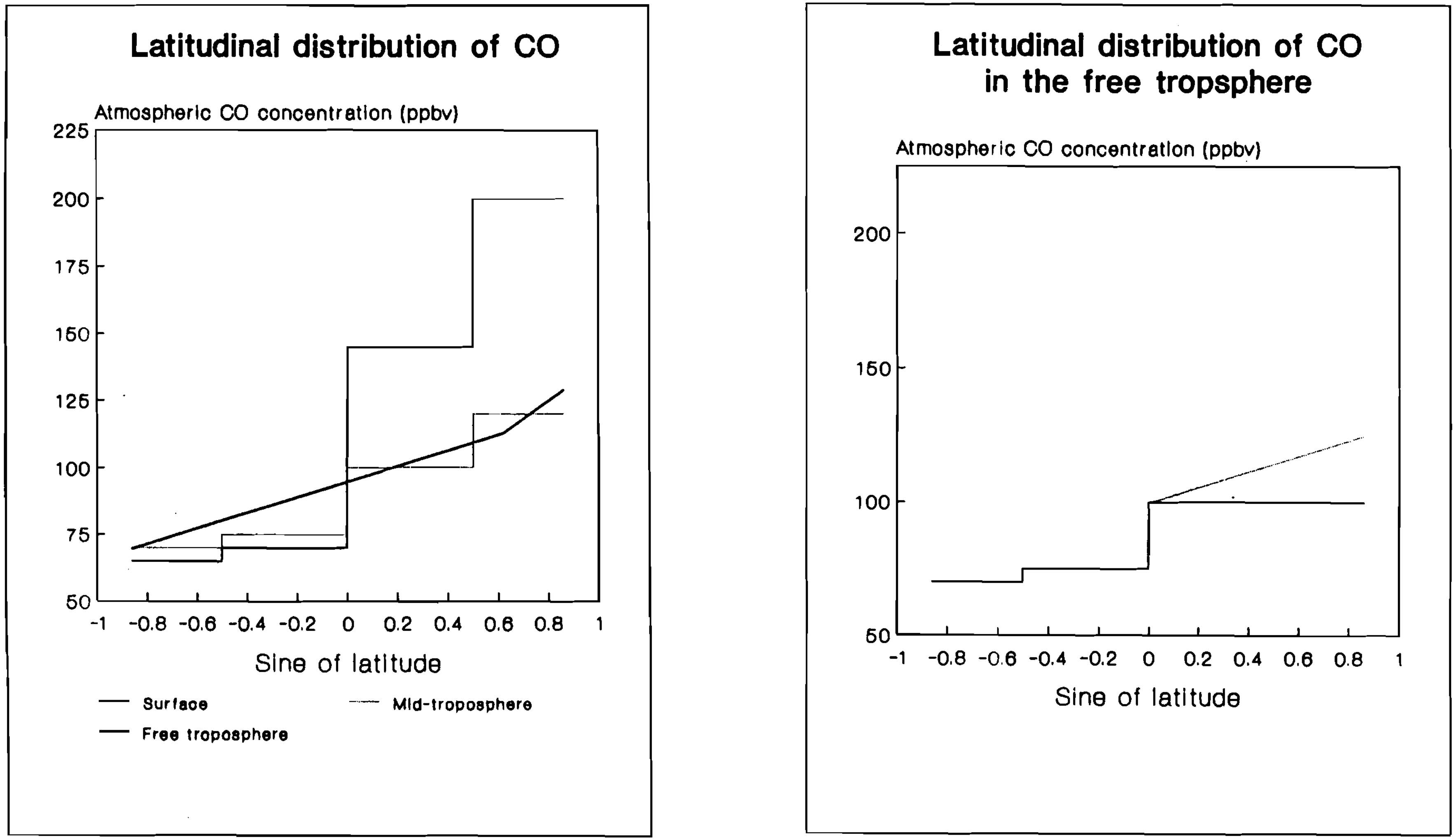


Figure 14. Latitudinal distribution of atmospheric CO (ppbv) at the earth's surface (annual average). Graph on left hand side is partly (surface and mid troposphere) adopted from Logan et al. (1981) and partly (free tropsophere) based on 1974 data reported by Seiler and Fishman (1981). Graph on the right hand side shows the best guess of the present latitudinal distribution of CO.

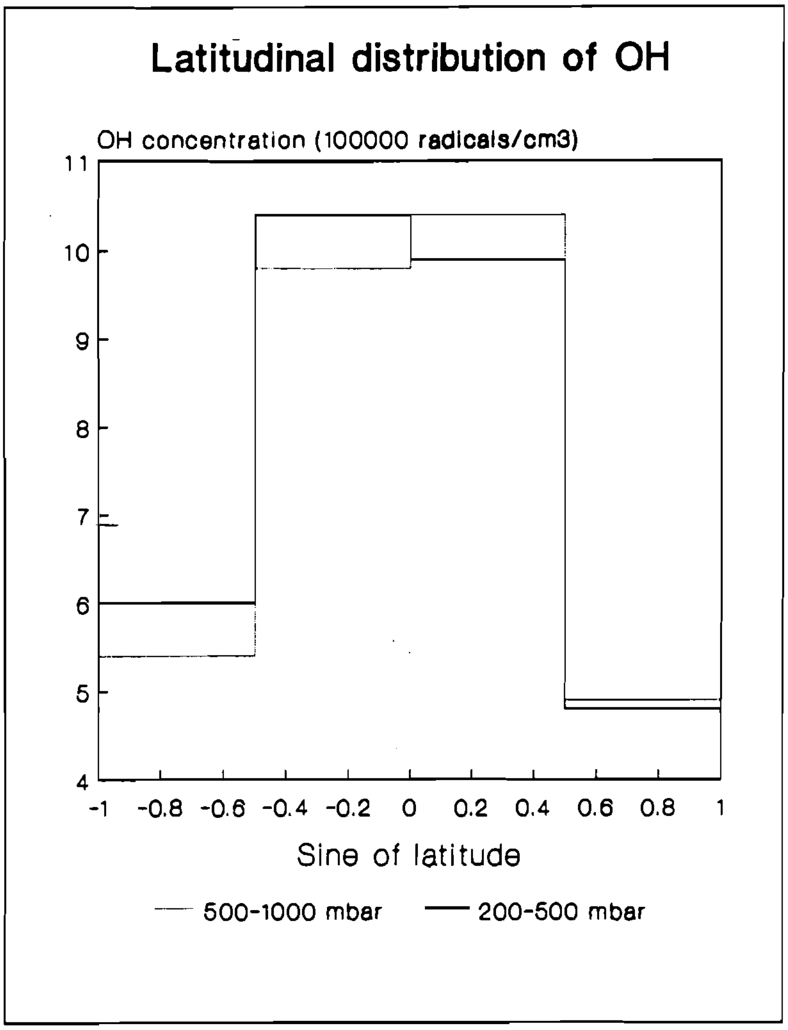


Figure 15. Latitudinal distribution of atmospheric OH (10^5 radicals per cm^3) at the earth's surface, adopted from Prinn et al. (1987).

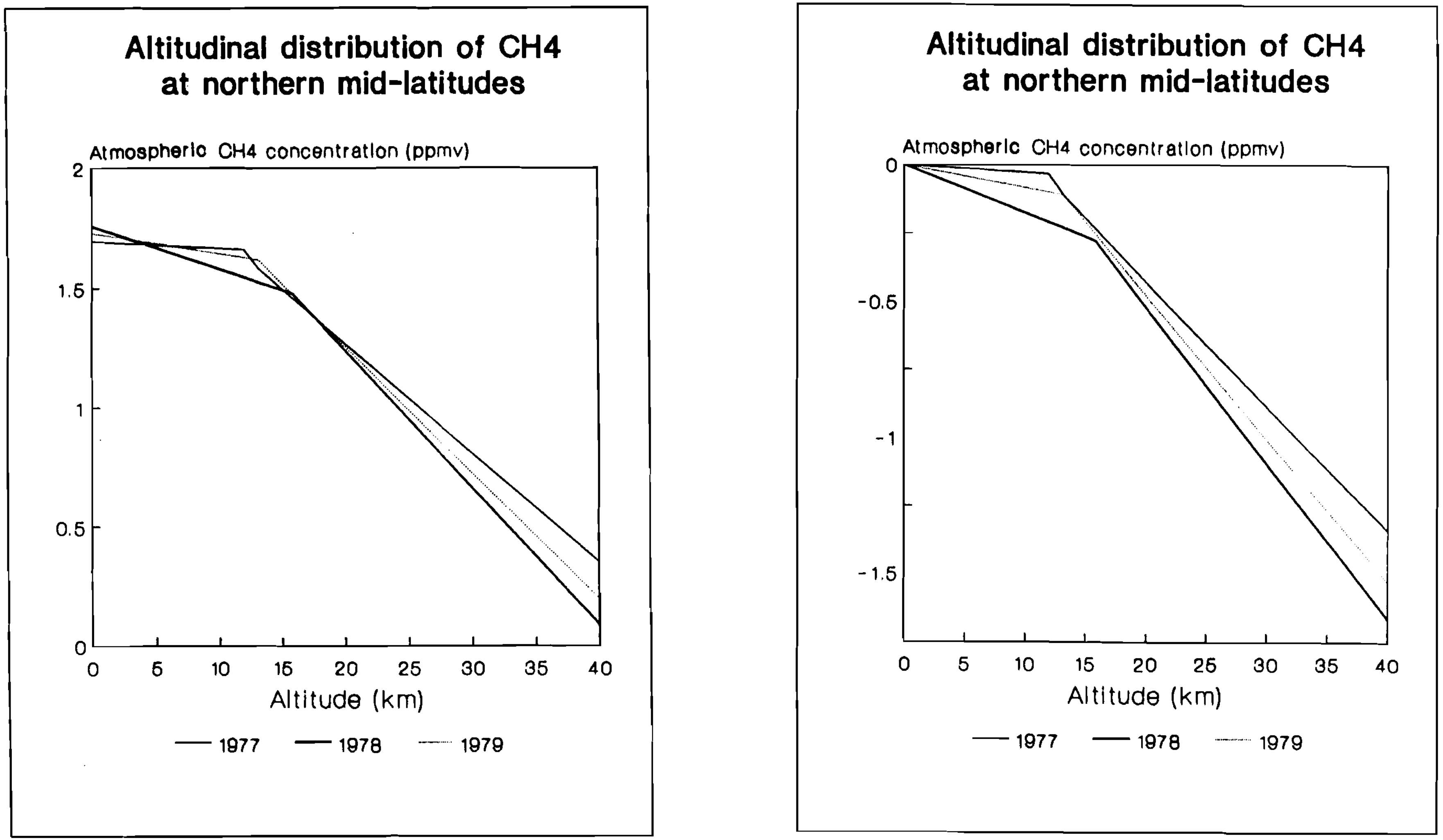


Figure 16. Altitudinal distribution of atmospheric CH4 (ppbv), based on measurements in 1977, 1978, 1979 (June-November) by Fabian et al. (1981). Graph on left hand side shows the absolute concentration (ppbv). Graph on right hand side shows the concentrations reduced by the concentration at the earth's surface.

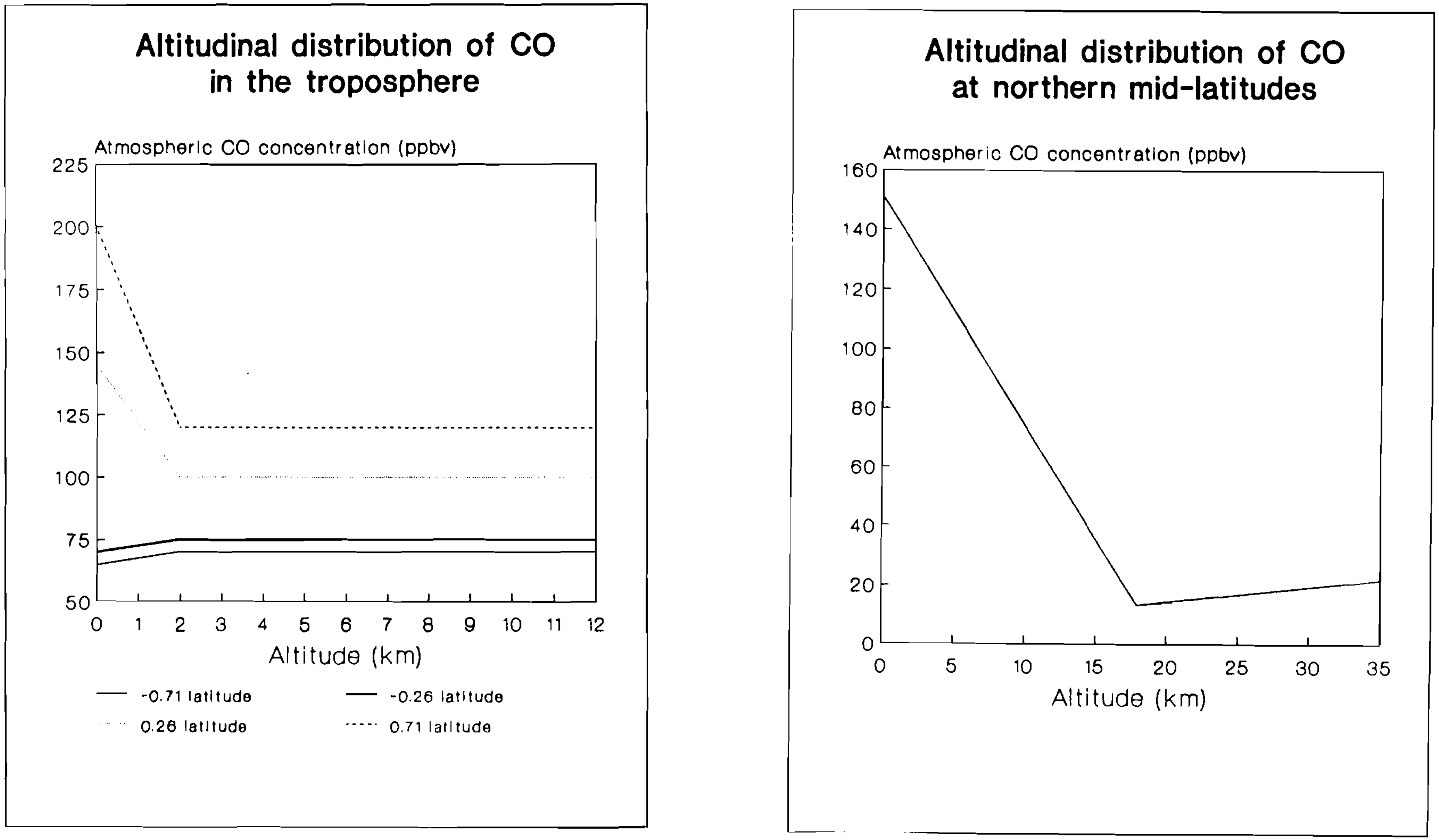


Figure 17. Altitudinal distribution of atmospheric CO (ppbv) (annual average). Graph on left hand side is adopted from Logan et al. (1981). Graph on the right hand side is based on northern mid-latitude measurements in 1977, 1978, 1979 (June-November) by Fabian et al. (1981).

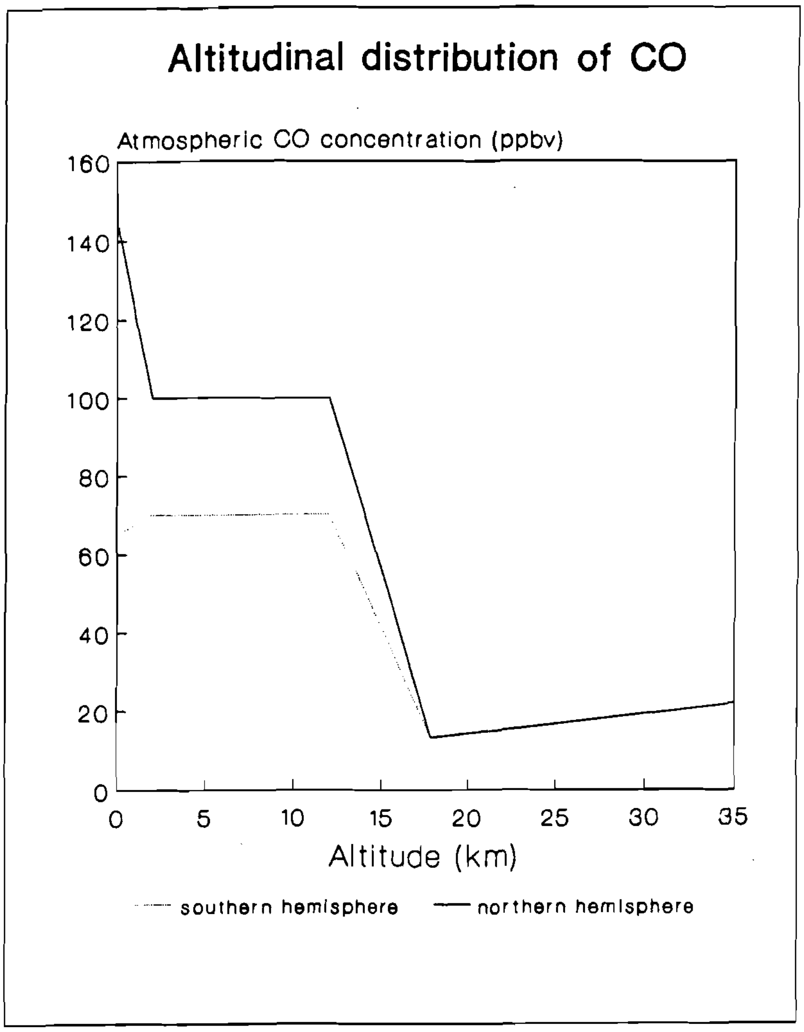


Figure 18. Distribution with height of CO. Best guess, based on Figure 17.

7. SUMMARY AND CONCLUSIONS

The purpose of this study is to give an overview of the latitudinal and altitudinal distribution of atmospheric gases that are greenhouse gases or that may influence concentrations of greenhouse gases. The gases considered in the study are: carbon dioxide (CO_2), several halocarbons (CFC-11, -12, -113, HCFC-22, CH_3CCl_3 and CCl_4), nitrous oxide (N_2O), methane (CH_4), carbon monoxide (CO) and hydroxyl (OH). This information can eventually be utilized by 1- to 3-dimensional models when calculating the radiative transfer through the atmosphere in order to investigate regional impact of an enhanced greenhouse effect.

Long-term measurement programs show that the atmospheric concentrations of several gases have been increasing during the past century due to anthropogenic activities. For instance, concentrations of the greenhouse gases CO_2, halocarbons, methane and nitrous oxide are observed to be higher than in preindustrial times. Also, concentrations of carbon monoxide and hydroxyl, not radiatively active themselves but influencing concentrations of methane, have changed. Carbon monoxide concentrations are observed to be increasing, at least in the northern hemispheric troposphere. The concentrations of hydroxyl on the other hand have probably been decreasing as the result of anthropogenic activities. The result of increasing CO and decreasing OH concentrations may be an increase of the CH_4 concentration.

Annually averaged profiles of latitudinal and altitudinal distribution should be based on extensive data sets, obtained by regular measurements during at least one year at sufficient representative locations. An example of such an extensive network is the Geophysical Monitoring of Climate Change program of the National Oceanic and Atmospheric Administration (NOAA's GMCC), where concentrations of carbon dioxide and methane have been measured at more than 20 sites for several years. These data enable one to get a good impression of the latitudinal distribution of these gases at the earth's surface. However, data sets with regard to altitudinal profiles are far less complete, mostly based on a number of individual flights with airplanes or balloons. For the other gases considered in this study data sets are usually smaller than those of CO_2 and CH_4. In case concentrations are known to show only small temporal variations during a year (for instance CFCs), small data sets may be sufficient. However, in case concentrations show large spatial and temporal variabilities, (for instance, in case of carbon monoxide and OH), it is difficult to present reliable profiles that are representative for the current spatial distribution.

Despite uncertainties and incomplete data sets, for each of the gases mentioned two profiles are chosen to be the best representation of the current latitudinal and altitudinal distribution in the present atmosphere. These profiles are shown in Figures 19 to 22. Although several of the profiles are based on summer data these gradients may be regarded as first order estimates of annually averaged spatial distributions. Table 26 summarizes the relative importance of the spatial distributions. From this Table it is clear that for the different gases the spatial variation in the concentration is of differing importance. The amount of spatial variation is determined by the spatial distribution of sources and sinks, rate of change in emissions, atmospheric lifetime and transport.

From the figures it is clear that for most of the gases concentrations are higher in the northern than in the southern hemisphere. For most of the gases emissions from the northern hemisphere exceed those of the southern. This may be the main reason for the observed latitudinal gradients. In general, the north-south differences in concentrations increase with the spatial variation or the rate of increase of emissions, and with a decrease of atmospheric lifetime.

Carbon dioxide concentrations vary with latitude and altitude ($\leq$2.5% of surface concentration). At present the surface concentrations at the North Pole are 3.1. ppmv higher than at the South Pole (the north-south difference amounts to 0.9-1.1% of the surface South Pole concentration). This latitudinal variation is caused mainly by the fact that most of the fossil fuel related emissions originate in the northern hemisphere. In preindustrial times concentrations were probably greatest at the South Pole. The present latitudinal gradient can therefore be regarded as being caused by anthropogenic activities. This implies that in case anthropogenic emissions change in future, the latitudinal gradient might change as well. A best guess of the future north-south difference may be at least 1% of the South Pole surface concentration. The CO_2 gradient with height is relatively moderate as compared to some other gases (see Table 26). The reason for this is that both sources and sinks of CO_2 are ground based, and the atmospheric lifetime of CO_2 is long enough for mixing in atmosphere.

Halocarbons are man-made gases and were not present in the atmosphere prior to 1930. These gases are mainly emitted from the northern hemisphere, and, therefore, show a north-south gradient, as shown in Figure 20. The present north-south difference is 5 to 53% of the South Pole surface concentration. Within the coming decade emissions of CFCs, CH_3CCl_3 and CCl_4 will most probably decrease considerably, when the revised Montreal Protocol (UNEP 1991) is implemented. This will most probably result in a flattening of the latitudinal profile. If emissions become virtually zero at the beginning of the next century, it can be expected that the latitudinal gradient will disappear after a few years. The altitudinal gradient, caused by the fact that photolysis is the only sink for CFCs and CCl_4 in the stratosphere, may disappear more slowly. Emissions of HCFC-22 and other H(C)FCs will continue to increase. In case these gases are emitted from the northern hemisphere mainly, the concentrations of these gases may show similar profiles as shown for the other halocarbons. However, most H(C)FCs have shorter lifetimes than CFCs because they are broken down in the troposphere as well as in the stratosphere. Therefore the future altitudinal profile of H(C)FCs may be different from that of today's CFCs.

Figure 21 shows the spatial distribution of nitrous oxide. Like CFCs, N_2O is emitted from the surface and destroyed only in the stratosphere. Emissions are somewhat higher in the northern hemisphere than in the southern, which explains the observed latitudinal gradient (north-south difference is 0.75 ppbv, or 0.3% of South Pole surface concentration). There are some indications that the north south gradient was opposite in the past: concentrations might have been higher in the southern hemisphere. This could mean that, as was the case with CO_2, the latitudinal gradient reversed as the result of human activities. If this trend continues, the north-south difference might keep increasing. Therefore, despite uncertainties with regard to future N_2O emissions, it might be assumed that the future north-south difference will remain at 0.3% of the South Pole surface concentration. The distribution with height is similar to those of CFCs.

Figure 22 shows the spatial distributions of CH_4, CO and OH. At the earth's surface concentrations of CH_4 are observed to be 153 ppbv (9.7% of South Pole surface concentration) higher in the northern than in the southern hemisphere. This is partly caused by the higher emissions from the northern hemisphere as compared to the southern. CH_4 removal takes place in both troposphere and stratosphere, mainly by reaction with OH. There are indications that concentrations of OH haven been decreasing, and at present OH concentrations seem to be higher in the southern hemisphere than in the northern. Although the interhemispheric difference in OH is difficult to quantify, it may be another reason for the observed north-south CH_4 profile. CO concentrations are higher in the northern hemisphere (north-south difference amounts to 43-97%) for the same reasons as CH_4, and because of the fact that one of the sources of CO is oxidation of CH_4 in the atmosphere, a process probably more pronounced in the northern hemisphere at present. The altitudinal gradient of CH_4 is shown in Figure 22. In the southern hemispheric troposphere the gradient might be different from that shown in the figure: not varying with height. The altitudinal and latitudinal profiles of CO and OH must be regarded as approximate. The latitudinal gradient of CH_4 has increased since the Industrial Revolution: the pole-to-pole difference amounted to about 10%

of the surface South Pole concentration both in the preindustrial and the present atmosphere. This may lead to the assumption that the pole-to-pole difference will keep increasing in future, while the relative north-south difference may stay at about 10%.

Table 26. Approximate relative differences of (greenhouse) gas concentrations at the earth's surface relative to the (South Pole) surface concentrations in the present atmosphere.

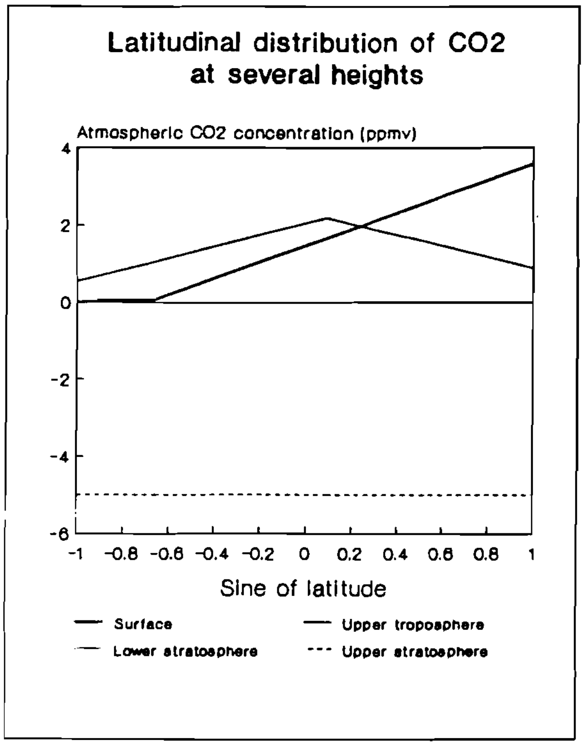
Gas	latitudinal: pole-to-pole[1]	altitudinal: troposphere-to-surface[2]	altitudinal: stratosphere-to-surface[3]
CO_2	0.9%	0.1-0.8%	1.4-2.5%
CFC-11	10.5%	7.7%	100%
CFC-12	8.4%	1.3%	100%
CFC-113	22.5%		100%
HCFC-22	16.1%		100%
CH_3CCl_3	53.1%		100%
CCl_4	5.3%		100%
N_2O	0.3%	7.0%	100%
CH_4	9.7%	0-6%	100%
CO	43-97%*	7.7-31.0%	67-85%
OH	9.3%	2.0-11.1%	

* free troposphere

[1] Pole-to-pole difference (surface values) given as percentage relative to the South Pole concentration: 100*|NP-SP|/SP, where NP = surface concentrations at North Pole, SP = surface concentration at South Pole.

[2] Altitudinal difference in the troposphere given as percentage relative to the surface value: 100*|UT-S|/S, where UT = upper tropospheric concentration, and S = surface concentration at latitude available.

[3] Altitudinal difference in the whole atmosphere (troposphere and stratosphere) given as percentage relative to the surface value: 100*|US-S|/S, where US = upper stratospheric concentration and S = surface concentration at latitude available.



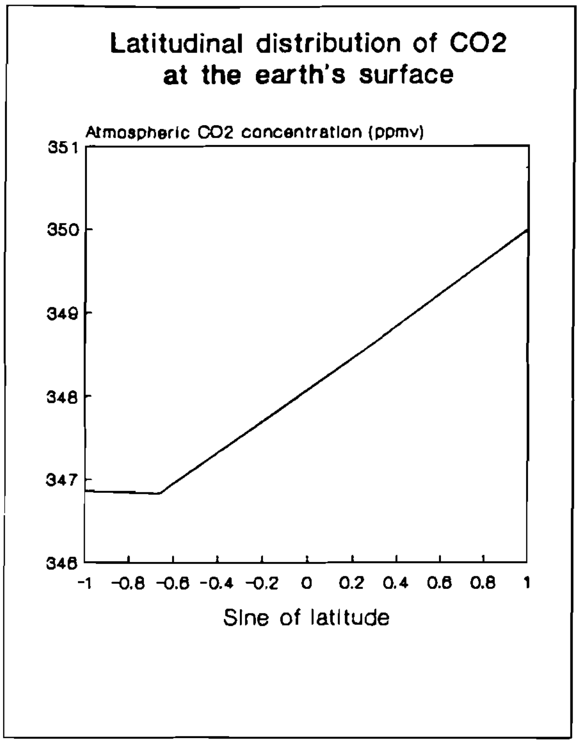
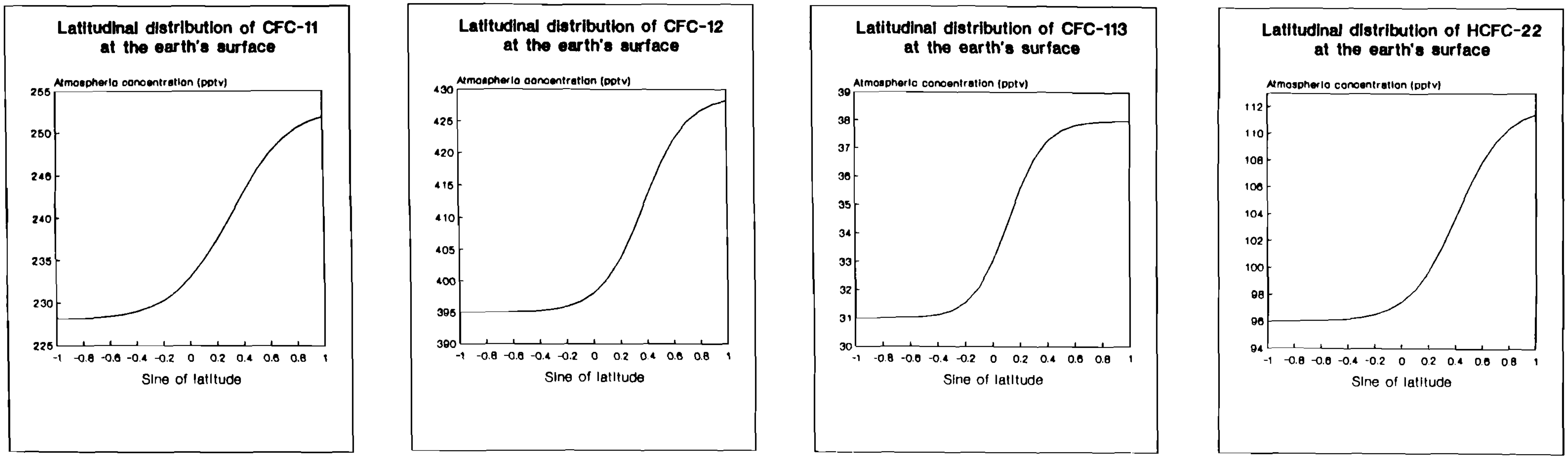


Figure 19. Latitudinal and altitudinal distribution of carbon dioxide in the atmosphere. Latitudinal distribution is based on 1981-1987 average data, scaled to the year 1987 (Tans et al. 1990). Altitudinal distribution is shown relative to surface concentration at the South Pole based on annually averaged 1984 data as reported by Keeling et al. (1989) and Nakazawa et al. (1991), and August/September 1985 values as reported by Gamo et al. (1989).



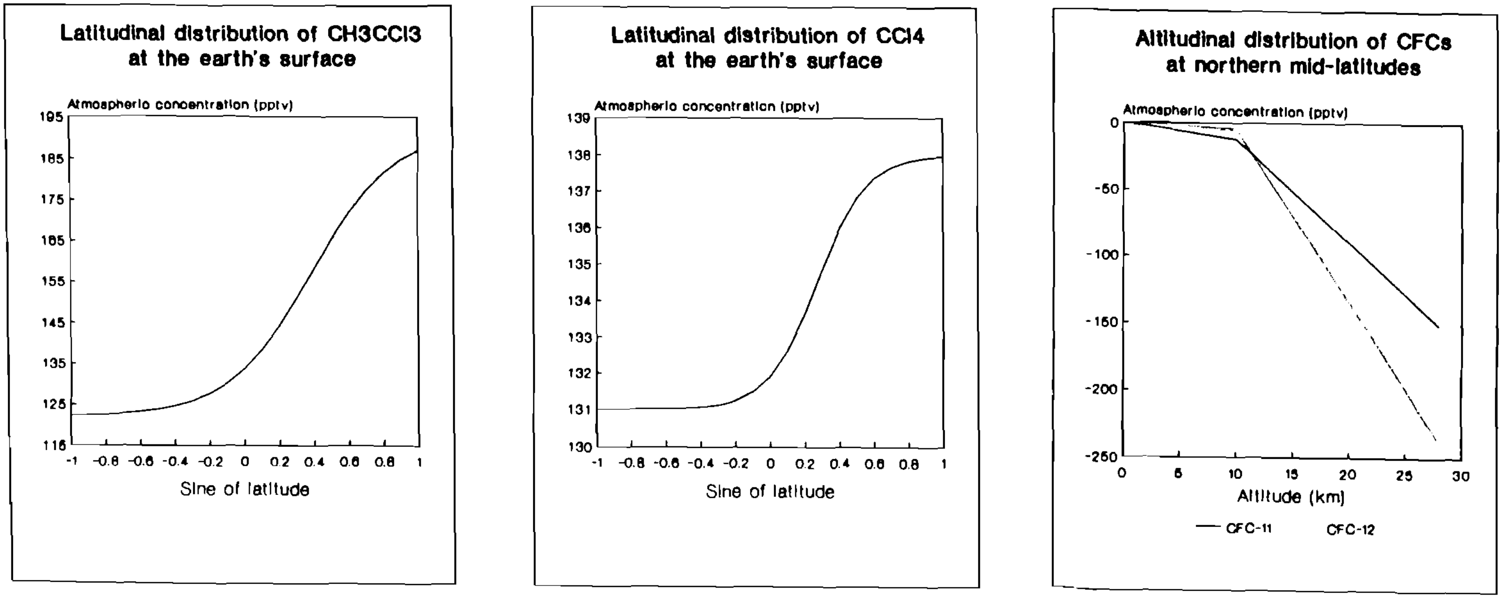


Figure 20. Latitudinal and altitudinal distribution of halocarbons in the atmosphere. Latitudinal distributions refer to 1987 values and are adopted from Khalil and Rasmussen (1988). Altitudinal distribution is based on 1979 summer data as reported by Fabian et al. (1981). The altitudinal distribution is reduced by the concentration at the earth's surface.

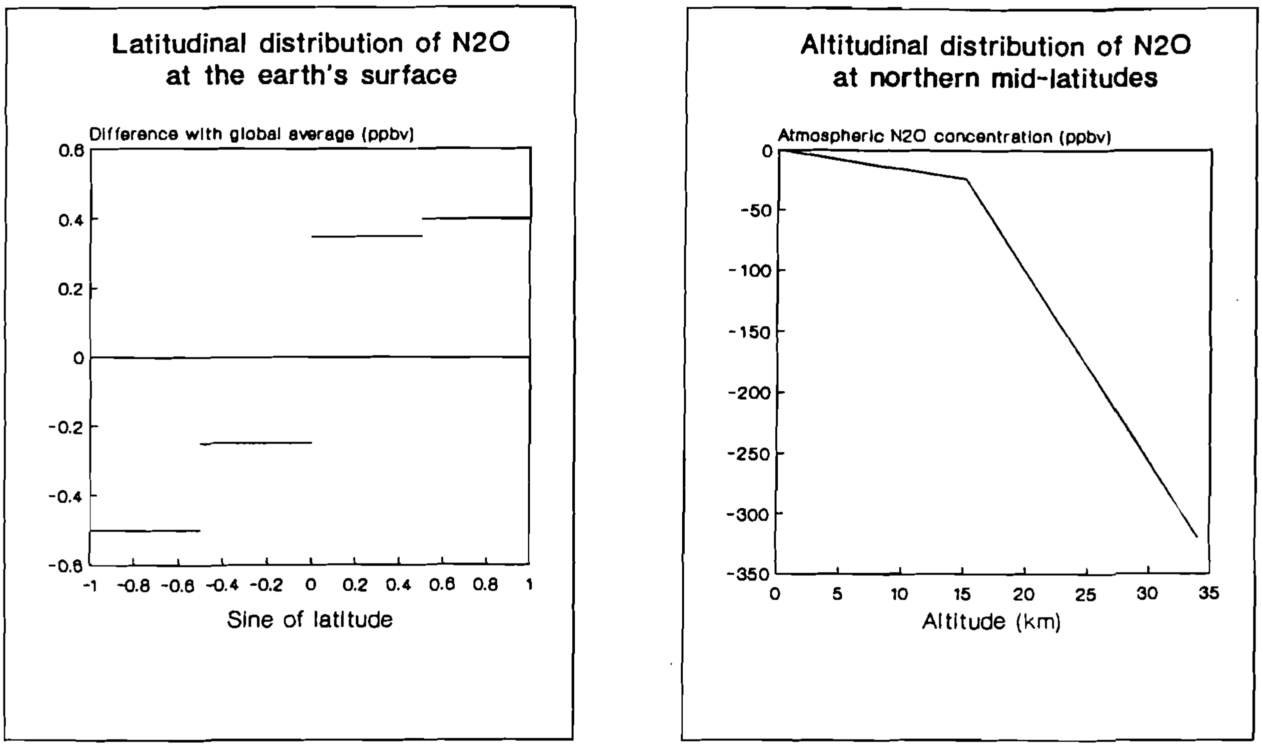
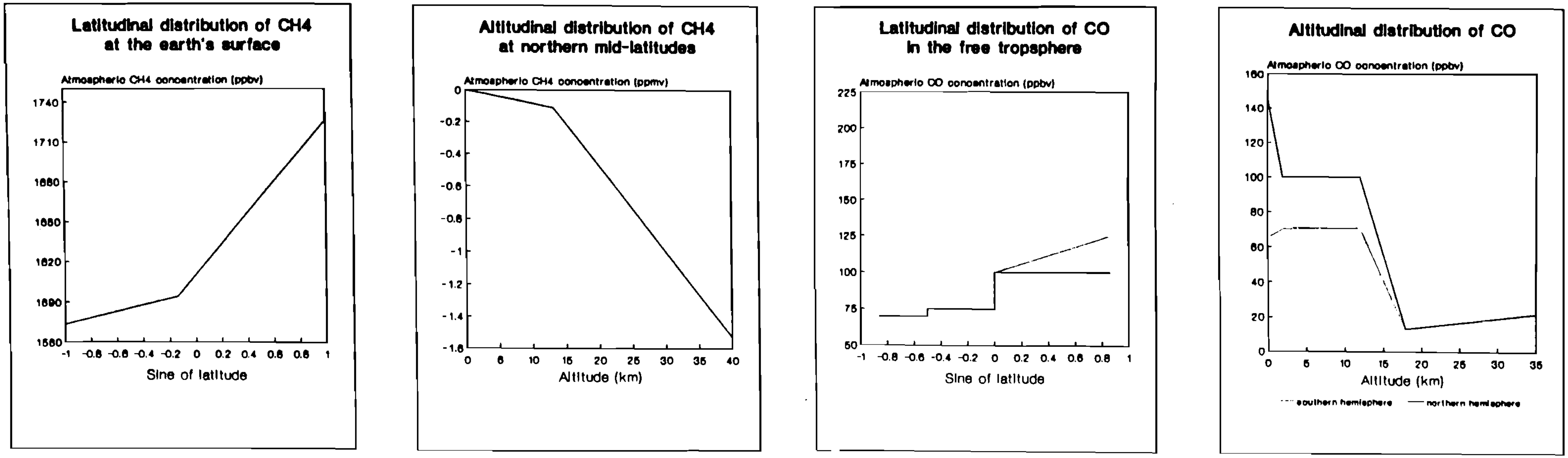


Figure 21. Latitudinal and altitudinal distribution of nitrous oxide in the atmosphere. Latitudinal distribution is adapted from Prinn et al. (1990) and based on 10 year averaged data (1978-1988). Latitudinal distribution is shown relative to the global average concentration. The altitudinal distribution is based on 1979 summer data as reported by Fabian et al. (1981) and is reduced by the concentration at the earth's surface.



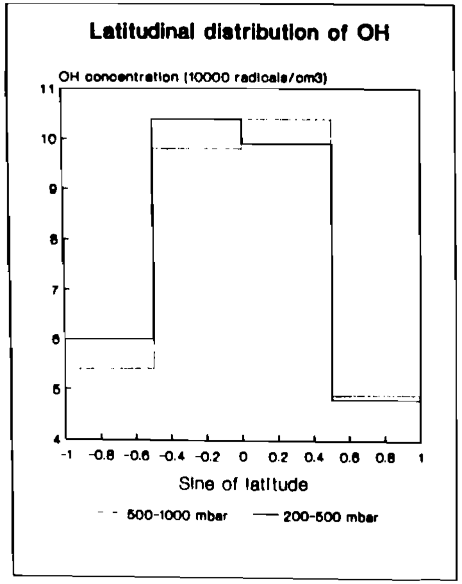


Figure 22. Latitudinal and altitudinal distribution of methane, carbon monoxide, and hydroxyl in the atmosphere. Latitudinal distribution of methane is based on the 1984 annually averaged data as reported by Steele et al. (1987). The altitudinal distribution, reduced by concentration at the earth's surface is based on 1979 summer data as reported by Fabian et al. (1981). Carbon monoxide's latitudinal distribution as shown by the solid line is based on Logan et al. (1981) and refers to annually averaged data in the 1980's. The dotted line is the northern hemispheric latitudinal distribution abased on 1974 summer data as reported by Seiler and Fishman (1981). The altitudinal distribution of CO refers to the period 1967-1978, and is based on Logan et al. (1981) and on 1979 summer data as reported by Fabian et al. (1981). The OH profiles are adopted from Prinn et al. (1987) and refer to annually averaged data for the period 1967-1978.

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