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Reconstructed histories of the annual mean atmospheric mole fractions for the halocarbons CFC-11, CFC-12, CFC-113, and carbon tetrachloride

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Abstract. Annual mean mixing ratios for the halocarbons CFC-11 (CCl_3F), CFC-12 (CCl_2F_2), CFC-113 ($CClF_2CCl_2F$), and carbon tetrachloride (CCl_4) have been determined from their first year of industrial production through 1998. From the late 1970s (in the case of CFC-11 and CFC-12) or early 1980s (in the case of CFC-113 and carbon tetrachloride) the reported mixing ratios have been determined from experimental observations made by the Atmospheric Lifetime Experiment/Global Atmospheric Gases Experiment/Advanced Global Atmospheric Gases Experiment program. For years prior to these times we have used estimates of industrial emissions and atmospheric lifetimes to calculate historic concentrations. The likely error bounds of the annual mean values are also reported here. Errors in the annual mean mixing ratio may primarily be a result of incorrect industrial emissions data, an incorrect atmospheric lifetime, or uncertainty in the ALE/GAGE/AGAGE observations. Each of these possible sources of error has been considered separately. These results show that atmospheric concentrations for each of these compounds have experienced a rapid rise in the early part of their production. It is only within the past decade that rise rates have decreased sharply and (except in the case of CFC-12) in the past few years that atmospheric concentrations have begun to decrease. The uncertainties in the reconstructed histories are a similar proportion for each of the chlorofluorocarbons (<4% for most of the history). However, uncertainty in the history of carbon tetrachloride is much greater (up to 12%), and this is mainly the result of poor knowledge of CCl_4 emissions.

1. Introduction

The first chlorofluorocarbons (CFCs) were produced in the early part of the 20th century, and since that time their atmospheric concentrations have increased dramatically. Production of carbon tetrachloride (CCl_4) began ~2 decades before the first CFC production, and its atmospheric concentration has grown in a similar manner. It is only very recently that the World Meteorological Organization (WMO) Montreal Protocol [*WMO*, 1988] called for the gradual phase out of the use of these chemicals to reduce the threat to the Earth's protective ozone layer [*Molina and Rowland*, 1974], and their concentrations have begun to level off or even decrease [*Elkins et al.*, 1993; *Cunnold et al.*, 1994].

These halocarbons pass from the atmosphere into the ocean surface layer on a timescale of ~1 month through surface water gas exchange. Very low atmospheric halocarbon concentrations prior to the middle part of this century have meant that much of the ocean's deep water typically contains immeasurable quantities of these compounds. In contrast, more recently formed deep and intermediate waters tend to carry strong halocarbon signals characteristic of the atmospheric concentrations found at the time of their formation. In the past 15 years various studies have been carried out to resolve decadal timescale dynamic ocean processes and to determine water mass exchange rates from CFC measurements [e.g., *Weiss et al.*, 1985; *Wisegarver and Gammon*, 1988; *Doney and Bullister*, 1992; *Smethie*, 1993]. More recently, carbon tetrachloride has been measured and analyzed as a transient tracer [e.g., *Krysell*, 1992; *Wallace et al.*, 1994; *Meredith et al.*, 1996], although it is believed to be nonconservative under certain circumstances [*Krysell et al.*, 1994]. Ocean modelers have also begun to utilize these anthropogenic trace gases as diagnostic tools for assessing the validity of model flow fields and ventilation characteristics [e.g., *England et al.*, 1994; *Robitaille and Weaver,* 1995]. This type of analysis requires knowledge of both the solubility characteristics for each halocarbon and their historic atmospheric distributions.

Analytic functions have been determined that describe the solubilities of CFC-11 (CCl_3F) and CFC-12 (CCl_2F_2) [*Warner and Weiss*, 1985], of CFC-113 ($CClF_2CCl_2F$) [*Bu and Warner*, 1995], and of carbon tetrachloride [*Bullister and Wisegarver*, 1998] as functions of the water's temperature and salinity. Atmospheric measurements of CFC-11, CFC-12, CFC-113, and CCl_4 concentrations have been made by various groups around the world, and the earliest continuous measurement of CFCs and carbon tetrachloride concentrations were begun in the late 1970s to early 1980s. It is therefore necessary to use industrial production and emission data to determine atmospheric concentrations of these gases prior to these times. In this paper we present reconstructed annual mean atmospheric mole fractions for CFC-11, CFC-12, CFC-113, and carbon tetrachloride for the Northern and Southern Hemispheres. These histories have been compiled from a combination of direct atmospheric measurement and model calculation. All mixing ratios reported in this paper

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are dry air mole fractions relative to the Scripps Institution of Oceanography (SIO) 1993 calibration scale. For comparison with the SIO-1986 scale and the Oregon Graduate Institute (OGI) 1980 and OGI-1987 scales the reader is referred to the papers of Cunnold et al. [1994], Fraser et al. [1996], and Simmonds et al. [1998], wherein the ratios of these scales to the SIO-1993 scale are presented for each halocarbon. For comparisons with the National Oceanic and Atmospheric Administration (NOAA) Climate Monitoring and Diagnostics Laboratory (CMDL) calibration scales the reader is referred to the comparisons reported by *Prinn et al.*, 1999.

2. Atmospheric Measurements of CFC-11, CFC-12, CFC-113, and Carbon Tetrachloride

Measurements of the ambient atmospheric mole fractions of CFC-11, CFC-12, CFC-113, and carbon tetrachloride have been made by the Atmospheric Lifetime Experiment (ALE)/Global Atmospheric Gases Experiment (GAGE)/Advanced Global Atmospheric Gases Experiment (AGAGE) program. These measurements are made using electron capture detection gas chromatographs at frequencies up to every 6 hours in ALE, every 2 hours in GAGE, and every 40 min in AGAGE (R. G. Prinn et al., A history of chemically and radiatively important gases in air deduced from ALE/GAGE/AGAGE, submitted to *Journal of Geophysical Research*, 1999, hereinafter referred to as Prinn et al., submitted manuscript, 1999). If we exclude tropical latitudes (which are periodically subjected to air masses originating in the other hemisphere), then we observe that halocarbon gradients within each hemisphere are quite low. For example, comparing annual mean concentrations taken from California/Oregon with Ireland we note that Ireland is at most 2% higher than California/Oregon because of its proximity to major halocarbon sources in Europe. This gradient has decreased since the middle to late 1980s to <0.5% as source strengths have diminished. We have therefore used measurements from the ALE/GAGE/AGAGE stations in Ireland and California/Oregon to represent the Northern Hemisphere mole fractions. The Ireland station was located at Adrigole (52°N, 10°W) from 1978 to 1983 and then at Mace Head (53°N, 10°W) from 1987 to the present. The California/Oregon station was located at Cape Meares, Oregon (45°N, 124°W), from 1979 to 1989 and then at Trinidad Head, California (41°N, 124°W), from 1995 to the present. Measurements from the Cape Grim Tasmania station (41°S, 145°E) have been used to represent the Southern Hemisphere and it has operated from 1978 to the present.

These data have been filtered by the ALE/GAGE/AGAGE group to remove anomalously high values resulting from localized pollution events. Monthly mean mixing ratios for each compound and station have then been determined and are available from the Carbon Dioxide Information Analysis Center at Oak Ridge National Laboratory. However, there remain certain times in this filtered record where the reported monthly mean values are significantly higher than we would expect to see from the longer—term trends in these halocarbon concentrations. This was a particular problem with the Mace Head carbon tetrachloride record, as discussed by *Simmonds et al.* [1998]. This station is relatively close to the industrial centers of eastern Europe where heavy carbon tetrachloride use has continued until quite recently. We have therefore excluded all CCl_4 values recorded in Ireland prior to 1991. In addition, certain months in Ireland in late 1993 to early 1994 exhibit anomalously high CCl_4 values, and so, these too have been excluded from the analysis.

From the monthly mean values we have determined annual mean concentrations for each hemisphere. To minimize bias due to gaps in the data and variability in the confidence of each monthly mean when calculating annual means, we have used an empirical model to describe the monthly mean mole fraction for each gas. We have used similar methodology to that adopted by *Cunnold et al.* [1983] for their analysis of the ALE/GAGE/AGAGE record. The model used to represent the dry air mole fraction x of compound i in hemisphere j takes the form

$$\begin{aligned} x_{ij} = a_{ij} + b_{ij}\left(\frac{t}{n} - 1\right) + d_{ij}\left(\frac{t}{n} - 1\right)^2 + e_{ij}\left(\frac{t}{n} - 1\right)^3 \\ + f_{ij}\left(\frac{t}{n} - 1\right)^4 + c_{ij}\cos(2\pi t) + s_{ij}\sin(2\pi t) \\ + p_{ij}\cos(2\pi t/t_0) + q_{ij}\sin(2\pi t/t_0)\,. \end{aligned} \quad (1)$$

Here t is the time in years starting with the first observation, n is half the number of years fitted, and t_0 is the period of the quasi-biennial oscillation (=29/12 years). In this way we have fitted x_{ij} with up to a fourth-order curvature term and two modes of oscillation. In determining the likely values of the a_{ij}, b_{ij}, d_{ij}, e_{ij}, f_{ij}, c_{ij}, s_{ij}, p_{ij} and q_{ij} we have weighted each monthly mean observation by the inverse of its variance.

The growth rates of all x_{ij} have decreased markedly in the past several years, largely because of the phase out of CFCs demanded by the Montreal Protocol [*WMO*, 1988] and its subsequent amendments. We have therefore separated the data for each gas into discrete time periods and performed the fits in each period independently. For CFC-12 and CFC-113, two periods were used with data through December 1992 for CFC-12 and through December 1991 for CFC-113 being included in the first period. For CFC-11 and CCl_4, three separate time periods were selected. For CFC-11, data through June 1988 were included in the first period, and data from July 1988 through December 1993 were included in the second period. For CCl_4, data through December 1987 were included in the first period, and data from January 1988 through December 1990 were included in the second period.

The annual mean mole fractions calculated from the model fit are displayed in Plates 1, 2, 3, and 4 for CFC-11, CFC-12, CFC-113, and carbon tetrachloride, respectively. The monthly mean ALE/GAGE/AGAGE values for the Northern and Southern Hemispheres as used in this study are also plotted along with error bars representing ±1 standard deviation of the monthly mean values.

3. Model Reconstructed Histories

For years prior to ALE/GAGE/AGAGE atmospheric measurements the reconstructed concentrations for each compound have been determined from a two-box atmospheric model using estimates of annual atmospheric halocarbon release, following the work of *Bullister and Weiss* [1988]. The amount of each compound released to the atmosphere every year has been determined from industry estimates of annual halocarbon production. A certain fraction of each year's production is either lost to the atmosphere during manufacture or is released postproduction in the same year it was manufactured. The remainder is emitted over subsequent years or, in the case of carbon tetrachloride, is chemically converted during the manufacture of other compounds and so never released. The

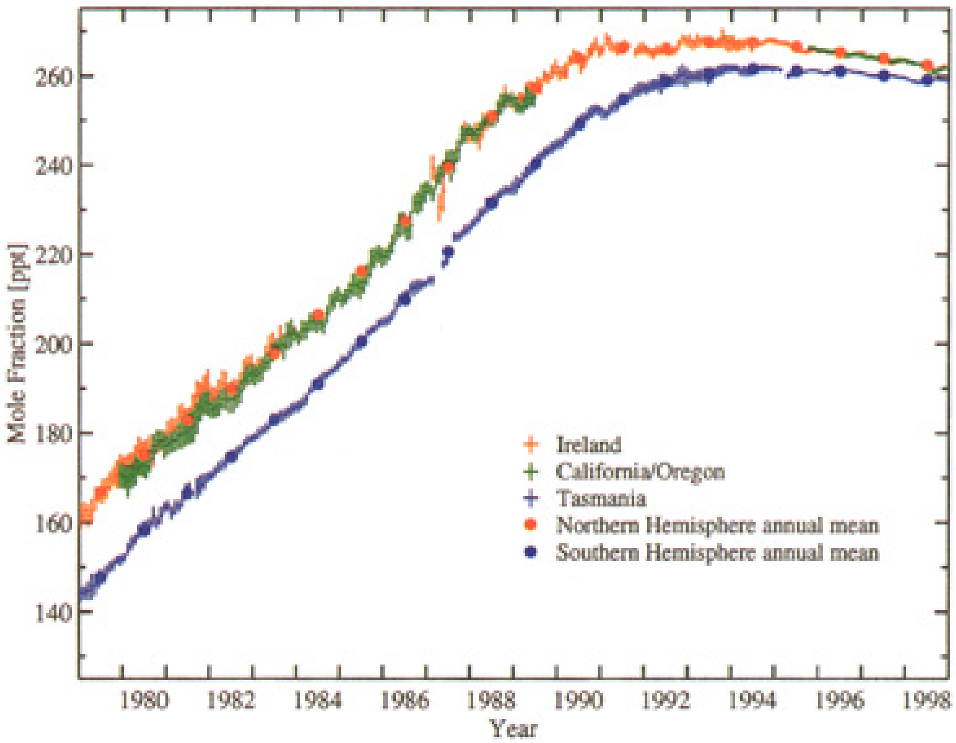

Plate 1. Annual mean dry air mole fractions for CFC-11 (CCl_3F) in the Northern and Southern Hemispheres (red and blue solid circles, respectively) as calculated from the model curve fit. Filtered monthly mean mole fractions from the Atmospheric Lifetime Experiment (ALE)/Global Atmospheric Gases Experiment (GAGE)/Advanced Global Atmospheric Gases Experiment (AGAGE) data set are also shown with vertical crosses representing the standard deviations. Red and green crosses represent monthly mole fractions from Ireland and California/Oregon in the Northern Hemisphere, respectively. Blue crosses represent monthly mean mole fractions from Tasmania in the Southern Hemisphere.

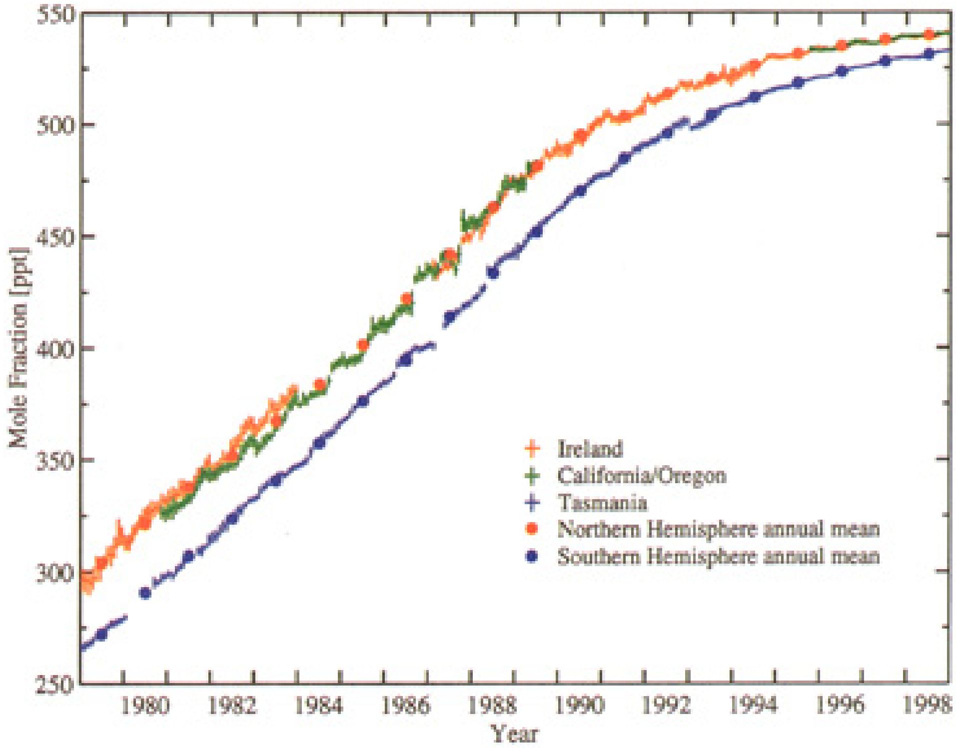

Plate 2. Annual mean dry air mole fractions for CFC-12 (CCl_2F_2) in the Northern and Southern Hemispheres (red and blue solid circles, respectively) as calculated from the model curve fit. Filtered monthly mean mole fractions from the ALE/GAGE/AGAGE data set are also shown with vertical crosses representing the standard deviations. Red and green crosses represent monthly mole fractions from Ireland and California/Oregon in the Northern Hemisphere, respectively. Blue crosses represent monthly mean mole fractions from Tasmania in the Southern Hemisphere.

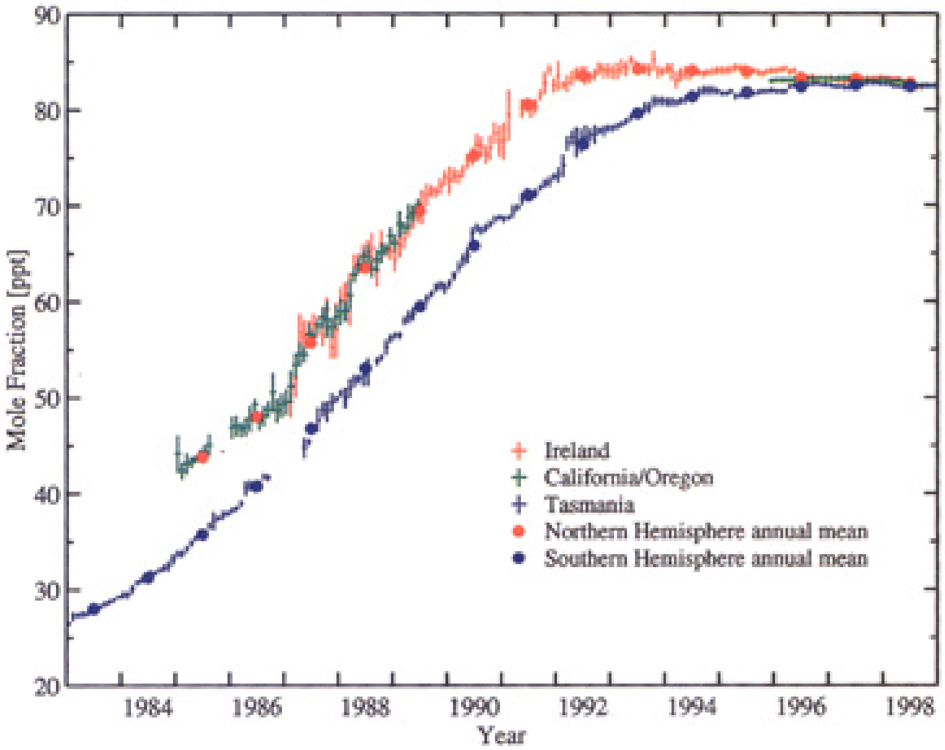

Plate 3. Annual mean dry air mole fractions for CFC-113 ($CClF_2CCl_2F$) in the Northern and Southern Hemispheres (red and blue solid circles, respectively) as calculated from the model curve fit. Filtered monthly mean mole fractions from the ALE/GAGE/AGAGE data set are also shown with vertical crosses representing the standard deviations. Red and green crosses represent monthly mole fractions from Ireland and California/Oregon in the Northern Hemisphere, respectively. Blue crosses represent monthly mean mole fractions from Tasmania in the Southern Hemisphere.

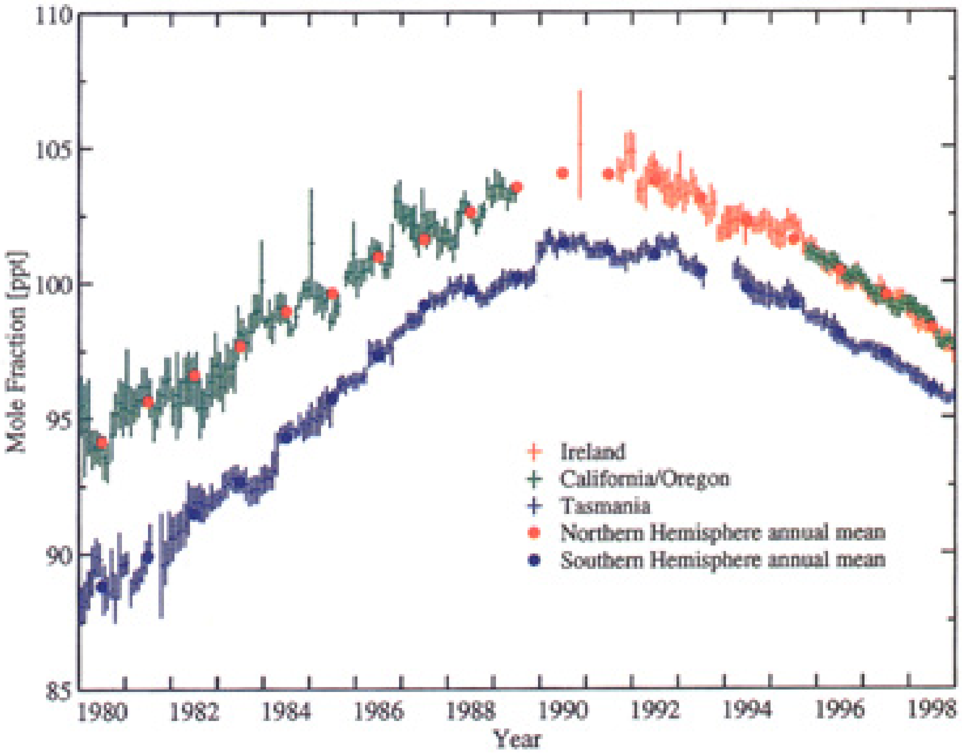

Plate 4. Annual mean dry air mole fractions for carbon tetrachloride (CCl_4) in the Northern and Southern Hemispheres (red and blue solid circles, respectively) as calculated from the model curve fit. Filtered monthly mean mole fractions from the ALE/GAGE/AGAGE data set are also shown with vertical crosses representing the standard deviations. Red and green crosses represent monthly mole fractions from Ireland and California/Oregon in the Northern Hemisphere, respectively. Blue crosses represent monthly mean mole fractions from Tasmania in the Southern Hemisphere.

exact temporal pattern of atmospheric emission is strongly dependent upon the specific use to which each halocarbon is put. For example, CFCs used in air-conditioning typically have a 12 year lag between production and atmospheric emission, whereas those used as propellants or solvents are released to the atmosphere almost immediately after production. Accurate knowledge of annual emissions therefore requires an analysis of the quantity of each halocarbon sold in each end use category.

3.1. Industrial Production and Emissions of CFC-11 and CFC-12

Annual production totals for CFC-11 and CFC-12 have been compiled by the Chemical Manufacturers Association (CMA) and the *Alternative Fluorocarbons Environmental Acceptability Study (AFEAS)* [1995] since 1975. Quantities sold in the short-lifetime usage category (aerosols, cleaning/drying, and open cell foam blowing) and in the long lifetime usage category (refrigerant, closed cell foam blowing, and heat transfer fluid) were also recorded. These data from the CMA reporting companies encompass manufacture by the majority of the world's CFC-producing companies. However significant quantities of both CFC-11 and CFC-12 have been produced by companies not reporting to the CMA, the most notable of which are in the former Soviet Union or eastern Europe. *McCarthy et al.* [1977] estimated total world annual production and subsequent world atmospheric emission of these CFCs from the time of their first significant industrial manufacture in the early 1930s. The slightly modified world annual atmospheric release estimates as tabulated by *Kaye et al.* [1994] were used in the box model as they include improved Soviet and eastern European production estimates and updated temporal emission patterns.

3.2. Industrial Production and Emissions of CFC-113

Annual production of CFC-113 was not reported to the CMA until 1980. Prior to that time the CMA compiled a cumulative total of 706.83Gg [*AFEAS*, 1995] for all reporting companies' CFC-113 output up to and including 1979. To determine annual industrial production levels of CFC-113 before 1980, we assumed that significant synthesis began in 1960 (P. Midgley, personal communication, 1997), and that annual production for the CMA reporting companies (P_{CMA}) followed the exponential growth model until 1980, as described in equation (2):

$$P_{\mathrm{CMA}} = A\left[e\left(\frac{t-1959}{m}\right)-1\right]. \qquad (2)$$

Equation (2) satisfies the AFEAS cumulative production total to 1979 and the 1980 annual production figure (103.7 Gg [*AFEAS*, 1995]), with A=17.54 Gg/yr and with an e-folding timescale of M=10.86 years. Since 1980 the CMA and AFEAS have kept records of the annual production of CFC-113, with sales totals for long- and short-lifetimes categories again recorded. Non-CMA reporting companies' production of CFC-113 is believed to be quite small relative to the reporting companies' totals. In the early 1990s it was estimated that the nonreporting companies' production of CFC-113 was only about ~15% of world production [*Fisher and Midgley*, 1993], and it is very likely that in early years the nonreporting share was much smaller than this, as observed for the other chlorofluorocarbons. We assumed that there was no production of CFC-113 in the rest of the world prior to 1970 and that from that time, production in non-CMA reporting countries grew by 1% of the reporting countries production per year to a maximum of 15% (P. Midgley, personal communication, 1997).

CFC-113 has been sold mainly as a cleaning and drying agent with only 1-3% of each year's sales since 1980 being in the long-lifetime categories. This predominance of sales for short lifetime uses is expected to be valid for years prior to 1980, so we have assumed that 75% of each year's production was released to the atmosphere in the year of manufacture, with the remainder released the following year (this is release Scenario A of *Fisher and Midgley* [1993]). The CMA and total world annual production and atmospheric release values derived in this way are listed in Table 1.

Table 1. Reconstructed Chemical Manufacturers Association (CMA) and Total World Production and Atmospheric Emission of CFC-113

	CMA		World	
Year	Production, Gg	Emissions, Gg	Production, Gg	Emissions, Gg
1960	1.7	1.3	1.7	1.3
1961	3.5	3.1	3.5	3.1
1962	5.6	5.1	5.6	5.1
1963	7.8	7.2	7.8	7.2
1964	10.3	9.6	10.3	9.6
1965	12.9	12.3	12.9	12.3
1966	15.9	15.1	15.9	15.1
1967	19.1	18.3	19.1	18.3
1968	22.6	21.7	22.6	21.7
1969	26.5	25.5	26.5	25.5
1970	30.7	29.7	31.0	29.9
1971	35.4	34.2	36.1	34.8
1972	40.5	39.2	41.7	40.3
1973	46.1	44.7	47.9	46.4
1974	52.2	50.7	54.8	53.1
1975	59.0	57.3	62.5	60.6
1976	66.3	64.5	71.0	68.9
1977	74.4	72.4	80.4	78.0
1978	83.3	81.1	90.8	88.2
1979	93.0	90.6	102.3	99.4
1980	103.7	101.0	115.1	111.9

Data were calculated assuming that CMA production grew exponentially and that non-CMA production grew by 1% of the CMA production per year since 1970; 75% of each year's production is assumed to be released to the atmosphere in the year of manufacture with the remainder released in the following year.

3.3. Industrial Production and Emission of Carbon Tetrachloride

Significant production of carbon tetrachloride began in 1908, and release estimates up to 1930 have been compiled by the *National Research Council (NRC)*, [1978]. Initially, CCl_4 was used mainly as an industrial solvent, dry cleaning agent, fire extinguisher, grain fumigant, and pesticide. All of these may be thought of as short-lifetime uses, with the majority of the compound being emitted to the atmosphere within 1 year of manufacture. Estimates of the total annual world production (and therefore also the emission) of carbon tetrachloride are less certain than for either CFC-11 or CFC-12. *Simmonds et al.* [1983] compiled world production and emission statistics that encompass likely upper and lower bounds for these values. We have used the mean of these two estimates to give an expected value for the total world annual emission of CCl_4 up to the time of the first atmospheric measurements. However, we recognize here that this assumption potentially introduces a significant error in our model, and this is discussed further in section 4.2.

3.4. Box Model

A box model has been used to determine historic atmospheric mole fractions from the annual atmospheric release figures described above. The model consists of two boxes, with one box representing each hemisphere. The hemispheres are assumed to be well mixed, with an exchange time τ_e of 1.25 years. Each gas i degrades in the boxes with characteristic e-folding lifetime τ_i.

The atmospheric concentration for each species i in the Northern Hemisphere (x_{iN}) can be expressed as:

$$\frac{dx_{iN}}{dt} = F_{iN} - \frac{x_{iN}}{\tau_i} - \frac{x_{iN} - x_{iS}}{\tau_e}. \tag{3}$$

Here F_{iN} is the monthly emission of compound i to the Northern Hemisphere obtained by dividing the annual atmospheric releases for each compound between the 12 months equally. Almost all halocarbon use is believed to have occurred in the industrialized nations of the Northern Hemisphere, so it was assumed that 95% of each gas emission occurred in that box. A similar equation relates x_{iS} to the monthly emissions in the Southern Hemisphere (F_{iS}) and to τ_i, τ_e, and x_{iN}:

$$\frac{dx_{iS}}{dt} = F_{iS} - \frac{x_{iS}}{\tau_i} - \frac{x_{iS} - x_{iN}}{\tau_e}. \tag{4}$$

The tropospheric lifetimes for each gas have been taken from the literature. For CFC-11 and CFC-12 these lifetimes are 45 and 100 years, respectively [*Prinn et al.*, 1999]. The lifetimes for CFC-113 and carbon tetrachloride are 85 years and 35 years respectively [*Prinn et al.*, 1999].

The mixing ratios determined from the box model calculation for each compound and hemisphere have been normalized to match the first ALE/GAGE/AGAGE annual mean concentration. The normalization factor applied, R, was determined so as to minimize (in a least squares sense) the sum of misfits between the box model mixing ratio and the first ALE/GAGE/AGAGE ratio for the two hemispheres. The values of R for each compound and the years at which the normalization factors were determined for each hemisphere and compound are listed in Table 2. It can be seen that the best agreements between the box model and observation are achieved for CFC-11 and CFC-12. The greatest correction has been applied to the CFC-113 concentrations, where it appears that our box model has overestimated the hemispheric concentrations by ~11%. *Fraser et al.* [1996] observed a similar (~10 percent) discrepancy between the industry estimates of emissions and observed CFC-113 tropospheric mixing ratios. They suggested that perhaps up to 10% of emissions had in fact not been released. Our normalization of the box model results in effect indirectly applies the assumption that about 11% of the emissions listed in Table 1 were in fact not released.

Table 2. Normalization factor R as Applied to the Box Model Portion of the Reconstructed History

Compound	Normalization Year		R
	Northern Hemisphere	Southern Hemisphere	
CFC-11	1979	1979	1.07
CFC-12	1979	1979	1.04
CFC-113	1985	1983	0.89
CCl_4	1980	1980	1.08

R is the ratio of the measured Atmospheric Lifetime Experiment (ALE)/Global Atmospheric Gases Experiment (GAGE)/Advanced Global Atmospheric Gases Experiment (AGAGE) mean concentration to the calculated box model value at the year of normalization listed for each compound.

Table 3. Annual Mean Atmospheric Dry Air Mole Fractions and Estimated Uncertainty for CFC-11 (CCl_3F)

	Northern Hemisphere		Southern Hemisphere	
Year	Value, ppt	Error, ppt	Value, ppt	Error, ppt
1944.5	0.0	0.0	0.0	0.0
1945.5	0.1	0.0	0.0	0.0
1946.5	0.1	0.0	0.1	0.0
1947.5	0.1	0.0	0.1	0.0
1948.5	0.2	0.0	0.1	0.0
1949.5	0.4	0.0	0.2	0.0
1950.5	0.7	0.0	0.4	0.0
1951.5	1.0	0.0	0.7	0.0
1952.5	1.5	0.1	1.0	0.0
1953.5	2.2	0.1	1.5	0.1
1954.5	3.0	0.1	2.2	0.1
1955.5	4.0	0.2	3.0	0.1
1956.5	5.3	0.2	4.0	0.1
1957.5	6.7	0.2	5.2	0.2
1958.5	8.1	0.3	6.5	0.2
1959.5	9.3	0.3	7.7	0.3
1960.5	11.0	0.4	9.1	0.3
1961.5	13.2	0.4	10.8	0.3
1962.5	16.0	0.5	12.9	0.4
1963.5	19.4	0.6	15.7	0.4
1964.5	23.5	0.7	19.0	0.5
1965.5	28.2	0.8	22.9	0.6
1966.5	33.3	0.9	27.4	0.7
1967.5	39.1	1.0	32.4	0.8
1968.5	45.6	1.1	38.0	0.9
1969.5	53.2	1.3	44.4	1.0
1970.5	61.9	1.4	51.8	1.2
1971.5	71.4	1.5	60.1	1.3
1972.5	81.9	1.7	69.3	1.4
1973.5	94.0	1.9	79.7	1.6
1974.5	107.4	2.1	91.4	1.8
1975.5	120.3	2.2	103.8	1.9
1976.5	132.8	2.3	116.1	2.1
1977.5	144.6	2.4	128.2	2.3
1978.5	155.2	2.4	139.5	2.4
1979.5	166.7	1.2	147.6	1.0
1980.5	175.1	1.7	158.1	1.0
1981.5	182.8	2.3	166.5	1.0
1982.5	189.9	1.9	174.7	0.8
1983.5	197.7	1.8	183.0	0.9
1984.5	206.3	1.8	190.9	0.9
1985.5	216.1	2.0	200.5	0.9
1986.5	227.5	1.9	209.8	1.1
1987.5	239.7	2.5	220.6	1.4
1988.5	250.9	1.6	231.5	0.8
1989.5	257.2	1.5	240.3	0.8
1990.5	263.8	1.5	249.1	0.9
1991.5	266.2	1.2	254.7	0.9
1992.5	266.1	1.0	258.8	0.9
1993.5	267.5	0.7	260.5	0.5
1994.5	267.4	0.5	261.6	0.3
1995.5	266.4	0.3	261.1	0.4
1996.5	265.2	0.3	261.1	0.4
1997.5	263.8	0.3	260.1	0.1
1998.5	262.3	0.4	259.1	0.3

Values from 1979 onwards have been determined from the ALE/GAGE/AGAGE data set. Values prior to 1979 have been determined from the box model reconstruction. Here, ppt is parts per trillion.

Table 4. Annual Mean Atmospheric Dry Air Mole Fractions and Estimated Uncertainty for CFC-12 (CCl_2F_2)

Year	Northern Hemisphere		Southern Hemisphere	
	Value, ppt	Error, ppt	Value, ppt	Error, ppt
1935.5	0.0	0.0	0.0	0.0
1936.5	0.1	0.0	0.0	0.0
1937.5	0.1	0.0	0.1	0.0
1938.5	0.2	0.0	0.1	0.0
1939.5	0.2	0.0	0.2	0.0
1940.5	0.4	0.0	0.3	0.0
1941.5	0.5	0.0	0.4	0.0
1942.5	0.7	0.0	0.5	0.0
1943.5	0.9	0.0	0.7	0.0
1944.5	1.2	0.0	0.9	0.0
1945.5	1.6	0.0	1.2	0.0
1946.5	2.3	0.1	1.7	0.0
1947.5	3.4	0.1	2.4	0.1
1948.5	4.7	0.1	3.4	0.1
1949.5	6.1	0.1	4.6	0.1
1950.5	7.6	0.2	5.9	0.1
1951.5	9.2	0.2	7.4	0.2
1952.5	10.9	0.2	9.0	0.2
1953.5	12.8	0.3	10.7	0.3
1954.5	14.9	0.3	12.5	0.3
1955.5	17.3	0.4	14.6	0.3
1956.5	20.1	0.4	17.0	0.4
1957.5	23.3	0.5	19.8	0.4
1958.5	26.7	0.6	22.8	0.5
1959.5	30.3	0.6	26.1	0.6
1960.5	34.7	0.7	29.9	0.7
1961.5	39.8	0.8	34.2	0.7
1962.5	45.5	0.9	39.1	0.8
1963.5	52.2	1.1	44.8	1.0
1964.5	60.0	1.2	51.4	1.1
1965.5	68.9	1.4	59.1	1.3
1966.5	78.7	1.6	67.7	1.5
1967.5	89.7	1.8	77.4	1.7
1968.5	102.1	2.0	88.2	1.9
1969.5	116.0	2.3	100.4	2.2
1970.5	131.2	2.6	114.0	2.4
1971.5	147.4	2.9	128.8	2.7
1972.5	165.1	3.2	144.7	3.1
1973.5	184.5	3.6	162.2	3.4
1974.5	205.8	4.0	181.3	3.8
1975.5	226.7	4.3	201.6	4.2
1976.5	246.4	4.5	221.7	4.6
1977.5	265.2	4.7	241.1	4.9
1978.5	282.4	4.9	259.5	5.2
1979.5	303.8	2.6	272.1	2.2
1980.5	321.3	4.0	290.7	1.8
1981.5	337.8	3.2	307.1	2.2
1982.5	351.7	4.4	323.7	1.9
1983.5	367.1	5.3	340.7	2.1
1984.5	383.8	2.8	357.4	2.1
1985.5	401.4	2.5	376.2	2.0
1986.5	422.0	3.8	394.4	2.5
1987.5	441.8	4.3	414.1	3.2
1988.5	462.9	2.9	433.5	2.8
1989.5	481.2	2.9	452.0	2.1
1990.5	495.3	2.8	470.2	2.1
1991.5	503.5	2.9	484.7	2.4
1992.5	513.6	2.3	495.9	2.3
1993.5	520.4	1.5	504.2	1.5
1994.5	526.2	1.4	512.1	0.3
1995.5	531.4	0.5	518.5	0.2
1996.5	534.9	0.4	523.5	0.3
1997.5	537.7	0.4	528.0	0.2
1998.5	539.7	0.7	531.2	0.3

Values from 1979 onwards have been determined from the ALE/GAGE/AGAGE data set. Values prior to 1979 have been determined from the box model reconstruction.

Tables 3, 4, 5, and 6 contain the combined annual mean dry air mole fractions in parts per trillion (ppt or parts in 10^{12}) for the Northern and Southern Hemispheres for CFC-11, CFC-12, CFC-113, and carbon tetrachloride, respectively. These data are plotted on Figures 1, 2, 3 and 4. The error bars in figures 1-4 give an indication of the estimated uncertainty in each point (see below).

4. Uncertainties in the Annual Mean Mole Fractions

The mole fractions listed in Tables 3-6 and displayed in Figures 1-4 contain some uncertainty as a result of measurement and/or model error. In this section we attempt to set a bound on the likely error in each year's reconstructed mole fraction. Errors in the observed ALE/GAGE/AGAGE atmospheric mole fractions (E_{OBS}) and in the model reconstructed mole fractions (E_{MODEL}) are considered.

Table 5. Annual Mean Atmospheric Dry Air Mole Fractions and Estimated Uncertainty for CFC-113 ($CClF_2CCl_2F$)

Year	Northern Hemisphere		Southern Hemisphere	
	Value, ppt	Error, ppt	Value, ppt	Error, ppt
1959.5	0.0	0.0	0.0	0.0
1960.5	0.0	0.1	0.0	0.0
1961.5	0.1	0.1	0.1	0.1
1962.5	0.3	0.1	0.1	0.1
1963.5	0.5	0.1	0.3	0.1
1964.5	0.8	0.2	0.5	0.1
1965.5	1.1	0.2	0.8	0.2
1966.5	1.5	0.2	1.1	0.2
1967.5	2.0	0.2	1.5	0.2
1968.5	2.6	0.3	2.0	0.2
1969.5	3.3	0.3	2.6	0.2
1970.5	4.2	0.3	3.3	0.3
1971.5	5.1	0.3	4.1	0.3
1972.5	6.2	0.3	5.0	0.3
1973.5	7.5	0.3	6.1	0.3
1974.5	8.9	0.4	7.3	0.3
1975.5	10.6	0.4	8.8	0.4
1976.5	12.4	0.4	10.4	0.4
1977.5	14.5	0.5	12.2	0.4
1978.5	16.9	0.5	14.3	0.5
1979.5	19.6	0.5	16.6	0.5
1980.5	22.6	0.6	19.2	0.5
1981.5	25.8	0.6	22.1	0.6
1982.5	29.1	0.7	25.2	0.7
1983.5	32.9	0.8	28.0	0.4
1984.5	37.8	0.9	31.3	0.4
1985.5	43.9	0.9	35.8	0.4
1986.5	48.0	1.3	40.8	0.7
1987.5	55.8	1.6	46.8	0.9
1988.5	63.5	1.1	53.1	0.7
1989.5	69.5	1.2	59.5	0.7
1990.5	75.2	1.0	65.8	1.1
1991.5	80.5	1.5	71.0	0.8
1992.5	83.5	0.9	76.4	1.1
1993.5	84.2	0.5	79.6	0.3
1994.5	84.1	0.4	81.3	0.2
1995.5	84.2	0.3	81.8	0.2
1996.5	83.5	0.4	82.4	0.2
1997.5	83.2	0.1	82.6	0.2
1998.5	82.8	0.3	82.4	0.2

Values from 1985 in the Northern Hemisphere and 1983 in the Southern Hemisphere have been determined from the ALE/GAGE/AGAGE data set. Values prior to these times have been determined from the box model reconstruction.

Table 6. Annual Mean Atmospheric Dry Air Mole Fractions and Estimated Uncertainty for carbon tetrachloride (CCl_4)

	Northern Hemisphere		Southern Hemisphere	
Year	Value, ppt	Error, ppt	Value, ppt	Error, ppt
1910.5	0.0	0.0	0.0	0.0
1911.5	0.1	0.0	0.0	0.0
1912.5	0.1	0.0	0.1	0.0
1913.5	0.1	0.0	0.1	0.0
1914.5	0.2	0.0	0.1	0.0
1915.5	0.3	0.0	0.2	0.0
1916.5	0.5	0.1	0.3	0.0
1917.5	0.8	0.1	0.5	0.1
1918.5	1.0	0.1	0.7	0.1
1919.5	1.1	0.1	0.9	0.1
1920.5	1.2	0.1	1.1	0.1
1921.5	1.3	0.1	1.1	0.1
1922.5	1.4	0.2	1.2	0.1
1923.5	1.6	0.2	1.4	0.1
1924.5	1.9	0.2	1.6	0.2
1925.5	2.1	0.2	1.8	0.2
1926.5	2.5	0.2	2.1	0.2
1927.5	2.8	0.3	2.4	0.2
1928.5	3.0	0.3	2.6	0.2
1929.5	3.6	0.3	3.0	0.3
1930.5	4.2	0.4	3.5	0.3
1931.5	4.8	0.5	4.0	0.4
1932.5	5.4	0.5	4.6	0.4
1933.5	6.0	0.6	5.2	0.4
1934.5	6.8	0.6	5.8	0.5
1935.5	7.7	0.7	6.5	0.5
1936.5	8.8	0.8	7.5	0.6
1937.5	10.2	0.9	8.6	0.7
1938.5	11.5	1.1	9.8	0.8
1939.5	12.8	1.2	11.0	0.9
1940.5	14.3	1.3	12.3	1.0
1941.5	16.1	1.4	13.8	1.1
1942.5	18.3	1.7	15.6	1.3
1943.5	21.1	1.9	17.8	1.5
1944.5	24.0	2.2	20.4	1.7
1945.5	26.5	2.4	23.0	1.9
1946.5	27.9	2.4	25.1	2.0
1947.5	29.9	2.5	26.9	2.0
1948.5	32.2	2.6	28.9	2.1
1949.5	34.0	2.6	30.9	2.2
1950.5	35.3	2.6	32.6	2.2
1951.5	37.0	2.6	34.1	2.2
1952.5	38.1	2.5	35.5	2.2
1953.5	39.0	2.4	36.6	2.1
1954.5	39.3	2.3	37.5	2.0
1955.5	39.7	2.1	38.0	1.9
1956.5	40.0	2.0	38.4	1.8
1957.5	40.3	1.9	38.7	1.7
1958.5	41.1	1.6	39.2	1.6
1959.5	42.2	1.3	39.9	1.4
1960.5	43.3	1.1	40.9	1.2
1961.5	44.3	1.0	41.9	1.0
1962.5	45.5	0.9	42.9	0.8
1963.5	47.2	0.8	44.2	0.8
1964.5	48.9	0.9	45.7	0.7
1965.5	50.5	1.0	47.3	0.8
1966.5	52.5	1.2	48.9	0.9
1967.5	55.3	1.3	51.0	1.0
1968.5	58.6	1.5	53.6	1.2
1969.5	62.9	1.6	56.9	1.2
1970.5	68.7	1.9	61.2	1.3
1971.5	74.2	2.3	66.4	1.4
1972.5	77.0	2.3	70.8	1.6
1973.5	79.1	2.1	73.7	1.6
1974.5	82.5	2.0	76.5	1.5
1975.5	84.5	1.9	79.4	1.4
1976.5	86.3	1.8	81.4	1.3
1977.5	89.0	1.7	83.6	1.3
1978.5	91.1	1.5	86.0	1.2
1979.5	92.5	1.2	87.8	1.1
1980.5	94.2	0.9	88.8	0.8
1981.5	95.6	0.7	89.9	0.7
1982.5	96.6	1.0	91.5	0.5
1983.5	97.7	1.0	92.7	0.6
1984.5	99.0	0.6	94.3	0.6
1985.5	99.6	0.9	95.8	0.6
1986.5	101.0	0.9	97.3	0.6
1987.5	101.6	0.9	99.2	0.6
1988.5	102.6	0.7	99.7	0.5
1989.5	103.5	0.6	100.2	0.5
1990.5	104.0	0.8	101.5	0.5
1991.5	104.0	1.0	101.2	0.5
1992.5	103.8	0.7	101.0	0.6
1993.5	103.1	0.4	100.4	0.1
1994.5	102.2	0.2	99.8	0.4
1995.5	101.6	0.3	99.2	0.2
1996.5	100.4	0.2	98.1	0.2
1997.5	99.5	0.2	97.4	0.2
1998.5	98.3	0.2	96.1	0.2

Values from 1980 onwards have been determined from the ALE/GAGE/AGAGE data set. Values prior to 1980 have been determined from the box model reconstruction.

4.1. Atmospheric Measurement Uncertainty

The standard deviations of the monthly mean mole fractions (with pollution events filtered), as reported by the ALE/GAGE/AGAGE group, primarily reflect regional variability due to proximity to emissions. These standard deviations are thus greater for the Northern Hemisphere stations than for the Cape Grim station and have declined as emissions have declined. In addition, monthly mean standard deviations are influenced by instrumental precisions which have improved significantly over the evolution of ALE/GAGE/AGAGE instrumentation (Prinn et al., submitted manuscript, 1999). Thus as emissions have declined in recent years, instrumental precisions have improved and have generally remained a smaller component of the monthly mean standard deviation.

To determine how well our empirical model represents the annual means for the ALE/GAGE/AGAGE data set, we have calculated the standard deviation of the model fit from the monthly mean ALE/GAGE/AGAGE observations for each year. This standard deviation is used to represent the uncertainty in each year's atmospheric mixing ratio for the ALE/GAGE/AGAGE portion of the reconstructed data set (E_{MEAS}).

All ALE/GAGE/AGAGE measurements that were originally made against OGI-1980 and OGI-1987 calibration scales have been adjusted to the SIO-1993 calibration scale [*Cunnold et al.*, 1994; *Fraser et al.*, 1996; *Simmonds et al.*, 1998]. The uncertainty in the adjustment factor that has been applied to each of the two earlier calibration scales introduces an additional error (E_{STAND}) to each measurement which has been adjusted. We have added the standard error of comparison of the calibration standards as reported by *Cunnold et al.* [1994] for CFC-11 and CFC-12, *Fraser et al.* [1996] for CFC-113, and *Simmonds et al.* [1998] for carbon tetrachloride. These errors have been converted to ppt for each compound and have been applied to measurements made against the OGI standards until 1993.

The total estimated uncertainty in the annual mean mole fraction determined from the monthly ALE/GAGE/AGAGE data set (E_{OBS}) has been calculated using the sum of squares as:

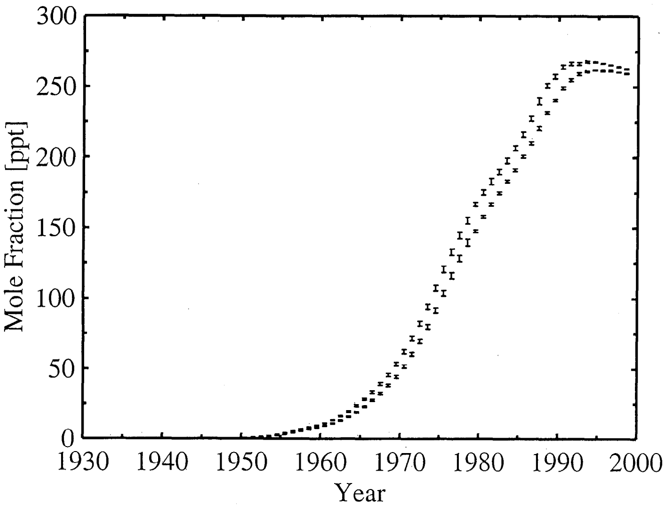

Figure 1. Reconstructed annual mean dry air mole fractions for CFC-11 (CCl$_3$F) in the Northern (upper curve) and Southern (lower curve) Hemispheres. Values from 1979 onward have been determined from the ALE/GAGE/AGAGE data set. Values prior to 1979 have been determined from the box model reconstruction. The size of the vertical error bar represents the estimated uncertainty (±68% confidence limit) in that year's mole fraction (see text).

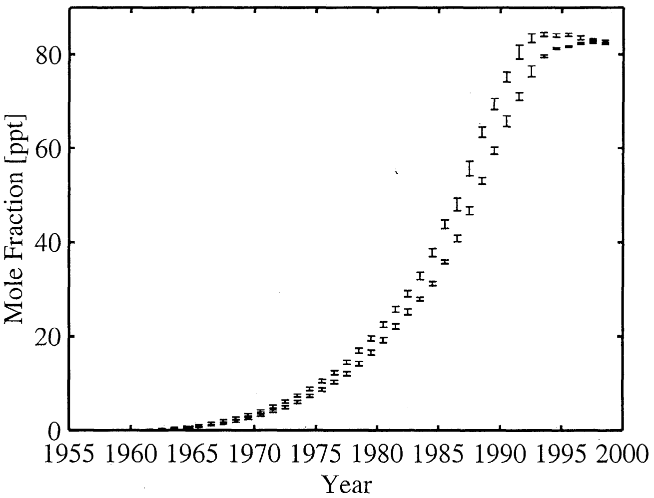

Figure 3. Reconstructed annual mean dry air mole fractions for CFC-113 (CClF$_2$CCl$_2$F) in the Northern (upper curve) and Southern (lower curve) Hemispheres. Values from 1985 in the Northern Hemisphere and 1983 in the Southern Hemisphere have been determined from the ALE/GAGE/AGAGE data set. Values prior to these times have been determined from the box model reconstruction. The size of the vertical error bar represents the estimated uncertainty (±68% confidence limit) in that year's mole fraction (see text).

$$E_{\mathrm{OBS}}^2 = E_{\mathrm{MEAS}}^2 + E_{\mathrm{STAND}}^2 \qquad (5)$$

These estimates (in ppt) are listed in columns 3 and 5 of Tables 3, 4, 5, and 6 for CFC-11, CFC-12, CFC-113, and carbon tetrachloride, respectively.

4.2. Model Reconstruction Uncertainty

Uncertainties in the atmospheric lifetime and in the annual atmospheric emission totals for each compound will affect the mole fractions calculated from the box model. The industrial emission uncertainties may result from errors in either the total industrial annual production figure (CMA reporting companies' plus nonreporting companies) or from an incorrect assumption of the temporal release to the atmosphere of each year's production. Generally speaking, the CMA reporting companies' annual production statistics are believed accurate to ~±0.5% so that errors in these data do not contribute significantly to the overall error.

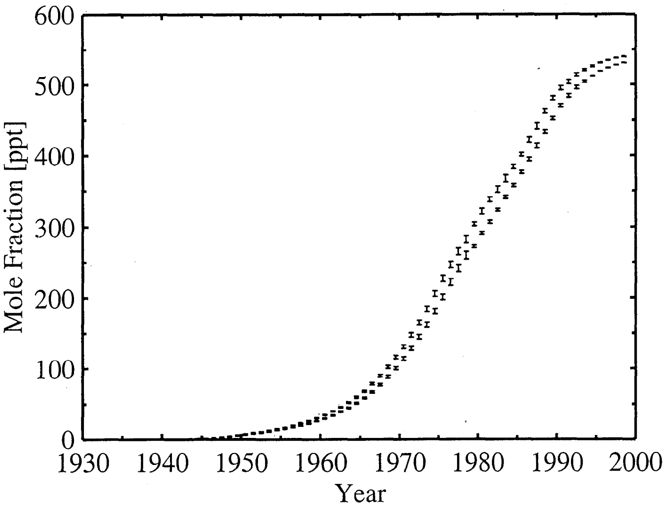

Figure 2. Reconstructed annual mean dry air mole fractions for CFC-12 (CCl$_2$F$_2$) in the Northern (upper curve) and Southern (lower curve) Hemispheres. Values from 1979 onward have been determined from the ALE/GAGE/AGAGE data set. Values prior to 1979 have been determined from the box model reconstruction. The size of the vertical error bar represents the estimated uncertainty (±68% confidence limit) in that year's mole fraction (see text).

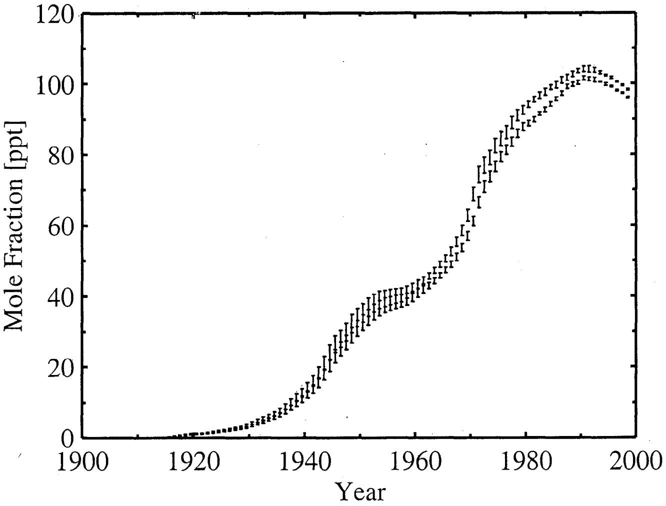

Figure 4. Reconstructed annual mean dry air mole fractions for carbon tetrachloride (CCl$_4$) in the Northern (upper curve) and Southern (lower curve) Hemispheres. Values from 1980 onward have been determined from the ALE/GAGE/AGAGE data set. Values prior to 1980 have been determined from the box model reconstruction. The size of the vertical error bar represents the estimated uncertainty (±68% confidence limit) in that year's mole fraction (see text).

Errors induced by uncertainties in the lifetime and annual halocarbon emissions were considered separately. The mole fractions determined for each gas have been recalculated using maximum and minimum lifetime estimates taken from the literature and again using upper and lower bounds on the industrial emission data. These modified mole fractions were subtracted from those calculated with the standard parameter estimates described in section 3 to give an estimated uncertainty due to the halocarbon atmospheric lifetime uncertainty (E_{LIFE}) and due to uncertainties in the industrial emission data (E_{EMISS}).

There is an uncertainty in the first ALE/GAGE/AGAGE annual mean mole fraction ($x_{\mathrm{OBS}}(1)$), which has been used to normalize the box model results. This normalization error ($E_{\mathrm{OBS}}(1)$) propagates backward in time to introduce an uncertainty in all the normalized box model results (E_{NORM}) which is given by

$$E_{\mathrm{NORM}} = \frac{x_{ij} E_{\mathrm{OBS}}(1)}{x_{\mathrm{OBS}}(1)}. \tag{6}$$

The total estimated error in the model reconstructed history for each year (E_{MODEL}) was then determined from a sum of squares combination of the lifetime, emission, and normalization errors:

$$E_{\mathrm{MODEL}}^2 = E_{\mathrm{LIFE}}^2 + E_{\mathrm{EMISS}}^2 + E_{\mathrm{NORM}}^2. \tag{7}$$

While the error bounds presented here cannot all be defined statistically as 2σ limits, we assume that the upper and lower bounds for the lifetimes and emission values are ~95% confidence limits of the true values of these parameters [cf. *Fisher and Midgley*, 1994].

4.2.1. CFC-11 and CFC-12 lifetime and emission uncertainties. *Prinn et al.* [1999] have recently compiled estimates for the lifetimes of both CFC-11 and CFC-12 including the confidence ranges for the lifetimes. These values are based upon both stratospheric gradient measurements and inverse modeling techniques, whereby observed tropospheric growth rates and industrial emission estimates are used to determine the lifetime. We have used the extreme lifetime estimates of 29-76 years for CFC-11 and 77-185 years for CFC-12 [*Prinn et al.*, 1999] to recalculate the box model concentrations and determine E_{LIFE}.

The greatest uncertainty in the industrial emissions statistics for CFC-11 is the rate of CFC release from closed cell foams [*Gamlen et al.*, 1986; *Fisher and Midgley*, 1994]. The standard release pattern [*Gamlen et al.*, 1986] assumes that 10% of each year's CFC-11 production used in closed cell foam manufacture is lost during manufacture and that the remainder is lost evenly over 20 years. The fast release scenario assumes again that 10% is lost during manufacture and the remainder is lost over 10 years. The slow release scenario assumes an 11% initial loss, followed by 1% per year diffusion loss and disposal/destruction losses as given by *Little* [1980].

For CFC-12 the most significant emission uncertainty is the level of production assumed in the former Soviet Union and eastern Europe [*Gamlen et al.*, 1986; *Fisher and Midgley*, 1994]. We have modified the global emission estimates of *Kaye et al.* [1994], giving upper and lower bounds to this non-CMA reported production as proposed by *Gamlen et al.* [1986]. For the high Soviet/eastern European production scenario we have assumed that CFC-12 production in the former Soviet Union continued to compound by 18% per year from 1975 as it had done between 1968 and 1975. Eastern European production was assumed to be 30% of Soviet production. For the low Soviet/eastern European production scenario it was assumed that former USSR production compounded at only 3% per year and that eastern European production was zero during this period. In both cases the atmospheric emission for each year was calculated in the same manner as for the CMA reporting countries.

4.2.2. CFC-113 lifetime and emission uncertainties. *Prinn et al.* [1999] have determined that the tropospheric lifetime for CFC-113 is 85 years, with a 95% confidence range of between 54 and 143 years. We have therefore used these values to determine E_{LIFE} as outlined above.

We have used the release scenario adopted by *Fraser et al.*, [1996] as the fast release limit, whereby 99% of each years' CFC-113 production is released in the year of manufacture and the remaining 1% is released over the next 12 years. For the slow release scenario we have used scenario E of *Fisher and Midgley* [1993], where 50% is released in the year of manufacture, 40% is released the second year, and the remainder is released over 12 years.

The degree of uncertainty in our assumption that nonreporting production grew at 1% of reporting production per year since 1970 is difficult to estimate. However, if we instead allow the nonreporting production to compound at 2% and 0.5% per year, this will encompass by a comfortable margin the industry estimate that 85% of total world CFC-113 manufacture came from the reporting companies in 1985.

In addition to the emission, lifetime, and normalization uncertainties discussed above, the reconstructed history for CFC-113 is also subject to uncertainty because of imprecise knowledge of the first year of its industrial production (E_{START}). In the above analysis it was assumed that significant industrial CFC-113 production began in 1960. However, we allow for some error here by recalculating the atmospheric release history for CFC-113 starting in 1958 and 1962. Thus the total estimated error for CFC-113 is given by

$$E_{NORM}^2 = E_{LIFE}^2 + E_{EMISS}^2 + E_{NORM}^2 \tag{8}$$

4.2.3. Carbon tetrachloride lifetime and emission uncertainties. The most recent estimates made by *Prinn et al.* [1999] place the tropospheric lifetime of carbon tetrachloride at 35 years, with a 95% confidence range of between 21 and 43 years. We have therefore used these values to calculate E_{LIFE}.

Uncertainty in the total production and emission of carbon tetrachloride is quite large as it is known that large scale production has occurred outside of the United States and that reliable records of this production are not available. As has been stated already, significant production of CCl_4 began in 1908, but since the early 1930s it has been used as a feedstock for the manufacture of chlorofluorocarbons. In this process the majority is stoichiometrically converted to CFCs, but a small portion (~3%) is lost to the atmosphere. Many of the other uses of carbon tetrachloride (such as use in dry cleaning and as a fire extinguisher) have decreased as a result of concerns over its toxicity, so that until recently, an increasingly dominant portion of carbon tetrachloride output has been used as a feedstock for CFC production. Thus the ratio of carbon tetrachloride used in CFC manufacture to total carbon tetrachloride sales is a very significant factor to consider in estimating atmospheric emissions from annual CCl_4 production. It is known that the U.S. share of the global production of chlorofluorocarbons has decreased steadily over the years, having fallen from ~80% to 30% of world production between 1958 and 1980. Non-U.S. production of CCl_4 must, of course, have increased dramatically to account for this sharp rise in non-U.S. CFC output, and world production of

CCl_4 for uses other than CFC manufacture has probably increased in a similar manner.

Simmonds et al. [1983] assumed that the rest of the world used a similar proportion of their carbon tetrachloride production for CFCs as did U.S. industry. Since we know the ratio of U.S. to world CFC production, we can estimate the total world output of CCl_4. However, as it is quite likely that many countries continued to use a larger proportion of CCl_4 for cleaning and extinguisher uses, this first estimate was considered to be a lower limit on total world production. An upper estimate that gives cumulative world CCl_4 production ~15% higher than this in 1980 was also proposed, and we have used these upper and lower limits as tabulated by *Simmonds et al.* [1983] to determine E_{EMISS}.

5. Conclusions

The reconstructed annual mean mole fractions for CFC-11, CFC-12, CFC-113, and carbon tetrachloride are listed in Tables 3, 4, 5, and 6 and plotted on Figures 1, 2, 3, and 4 for the Northern and Southern Hemispheres. The uncertainties listed in tables 3, 4, 5, and 6 are the ±68% confidence limits of the annual mean mole fractions.

The temporal variation of atmospheric concentrations of all four halocarbons exhibit the general growth and decay patterns that we may expect to see given the history of their industrial use. In general, the mixing ratio of each gas has initially increased exponentially for several years, followed by a period of more linear growth. In the past 2 decades the rate of increase has declined sharply as industrial production has been curtailed. Since the early 1990s, the Northern Hemisphere concentrations of CFC-11, CFC-113, and CCl_4 have begun to decrease, and at the same time the hemispheric gradients have diminished. In contrast, CFC-12 concentrations are continuing to rise. This is most likely due to the fact that most CFC-12 production has been used in comparatively long lifetime applications such as in refrigeration. We may therefore expect a significant continued flux of CFC-12 into the troposphere even though the majority of CFC-12 production has ceased.

Comparison of the error bars shown in Figures 1-4 reveals that the relative uncertainty in the reconstructed carbon tetrachloride history is far greater than that for any of the three CFCs. Specifically, if we exclude the ALE/GAGE/AGAGE section of each reconstruction, then we observe that the uncertainty in the CCl_4 concentration is between ~4 and 12% for most of its history, whereas for the CFCs the uncertainty is <4%. The comparatively large errors in the carbon tetrachloride annual means are mainly a result of the large uncertainties in the industrial emission figures. The emissions for carbon tetrachloride have basically been determined from the difference between the total CCl_4 production and the amount of CCl_4 converted in CFC manufacture. These two quantities are of very similar size so that relatively small errors in either one inevitably leads to a disproportionately large error in both the carbon tetrachloride emissions and tropospheric concentrations. The smaller percentage uncertainties for CFC-11 and CFC-12 are due to their industrial emissions being relatively well known. In contrast, there are significant uncertainties in the rate of release of CFC-113 to the atmosphere. However, as industrial production of CFC-113 began only in 1960, the atmospheric history for this chlorofluorocarbon is also relatively well constrained.

Appendix

ASCII versions of the annual mean mixing ratios and associated errors presented in Tables 3-6 are available via the World Wide Web at http://gaslab.ucsd.edu/pub/cfchist. The individual histories and uncertainties are stored in files named cfc11atmhist.m, cfc12atmhist.m, cfc113atmhist.m, and ccl4atmhist.m for CFC-11, CFC-12, CFC-113, and carbon tetrachloride respectively. It is anticipated that we will continue to update these files with the latest annual mean mixing ratios as new data become available from the ALE/GAGE/AGAGE program.

We expect that ALE/GAGE/AGAGE measurements will soon be reported on an updated SIO-1998 calibration scale. At that time the histories stored at the above location will also be updated to SIO-1998 so that conversion factors will be required to relate SIO-1993 to SIO-1998. References to the papers containing these conversion factors will be included with the atmospheric histories after the new scale has been published.

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