

Recent changes in the production and global atmospheric emissions of chlorodifluoromethane (HCFC-22)

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Abstract

The atmospheric concentrations of chlorodifluoromethane (HCFC-22) have been continuously measured for over a decade in long-term monitoring experiments. Comparison of these data with the industrial and regulatory databases of production and sales indicates that containment of this material is improving and its rate of emission, relative to the quantities produced and in service, is falling. In this paper, we reconcile the results of long-term monitoring with emissions calculated from activity (as global sales into the categories of end-use) and identify the principal changes that have occurred in the overall emission functions.

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1. Introduction

HCFC-22 (chlorodifluoromethane, CHF_2Cl) is the most abundant of the hydrochlorofluorocarbons measured in the atmosphere, globally averaged concentrations reaching $140\text{--}145\text{ pmol mol}^{-1}$ in the year 2000 and growing at $5\text{ pmol mol}^{-1}\text{ yr}^{-1}$ (Montzka et al., 1999; Prinn et al., 2000; Sturrock et al., 2001; O'Doherty et al., 2004).

The principal use of HCFC-22 is as a commercial product in refrigeration and foam blowing applications, from which it is eventually released into the

atmosphere unless provisions are made to capture and destroy the material still in equipment at the end of its service life. HCFC-22 is also used as feedstock for the manufacture of fluoropolymers but is destroyed in this process, except for small fugitive emissions. There is an additional emission of byproduct HFC-23 (fluoroform, trifluoromethane, CHF_3) which is discussed in a companion paper (McCulloch and Lindley, 2005). HFC-23 is a greenhouse gas that falls within the provisions of the Kyoto Protocol. The HCFCs are also greenhouse gases but their production and consumption are controlled under the Montreal Protocol and will be reduced progressively towards phase out in 2040.

The accumulation of HCFC-22 in the atmosphere results from the quantities emitted but previous attempts to reconcile atmospheric concentrations

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with emissions have met with varying degrees of success (Miller et al., 1998; McCulloch et al., 2003; Montzka et al., 2003).

2. Global database—production

Since mid-1970s a database of production and use of fluorocarbons going back to 1931 has been maintained by industry (AFEAS, 2005). Production figures are audited against inter-company transfers and sales and the latter are reported for each compound separately into end-uses categorised by their emission functions. AFEAS provides data for the total production and sales in all fluorocarbon producing countries other than China, India, Korea and Russia. All parties to the Montreal Protocol, including these countries, report their production and consumption to the United Nations Environment Programme (UNEP) but on a different basis from the AFEAS values. The UNEP data are reported as the total for all HCFCs, expressed as ODP tonnes (metric tonnes of the substance multiplied by its ozone depletion potential) (UNEP, 2002, 2003). A previous study showed that, like-for-like, the two data sets for HCFCs agree to within a few percent (McCulloch et al., 2003) and so can be combined to provide a global database, after employing a suitable mechanism to deconvolute the aggregated UNEP data into values for individual substances. Production data for the countries not reporting into the AFEAS database were estimated separately.

2.1. Peoples Republic of China

HCFC-22 production in China is growing rapidly (IIR, 2003, 2004) and independent statistics for production from the 19 facilities were used for the actual Chinese production as shown in Table 1 (CCR, 2002; CAOFSMI, 2003).

2.2. India

CHF₂Cl is the sole HCFC produced in India and so the data in UNEP (2002, 2003) were interpreted as being wholly HCFC-22.

2.3. Korea and Russia

In the absence of other information, the total quantities reported in the UNEP databases were divided between HCFCs in the same annual ratios

Table 1
Production of HCFC-22 for dispersive uses

Year	Within countries not reporting to AFEAS					Global total
	Mg (kg × 10 ³)					
	China	India	Korea	Russia	Total	Mg (kg × 10 ³)
1989	10,716	2164	2240	20570	35,689	255,226
1990						242,899
1991						259,492
1992	5037	3745	3605	4395	16,781	261,891
1993	11,068	4818	3927	2724	22,537	260,423
1994	18,943	4836	3852	2867	30,499	263,741
1995	8204	5709	3661	2194	19,768	260,955
1996	8738	5091	4978	721	19,527	289,983
1997	13,138	6309	5192	620	25,259	276,088
1998	36,523	10,582	4875	594	52,573	313,748
1999	52,485	10,618	4083	1230	68,417	320,792
2000	63,788	14,055	4106	1432	83,380	327,227
2001	93,117	14,867	3228	5548	116,760	334,225
2002	111,225	16,929	3409	5397	136,960	335,168

as in the AFEAS data. The sensitivity to this assumption was tested by recalculation after changing the whole output from Korea to HCFC-22. The effect of this was to increase the total HCFC-22 production by 1% and to increase the standard error of the final result (as described below) from 0.11 to 0.12 pmol mol⁻¹.

The calculated production of HCFC-22 in these four countries is shown in Table 1. Note that UNEP (2002) does not contain data for the years 1990 and 1991. However, in the final column of Table 1 which shows the total of global production (including that reported to AFEAS), these years have been interpolated for the non-AFEAS countries.

Only the AFEAS sales data are explicitly categorised by end use according to the emissiveness of the use, and so the additional sales arising from production not reported to AFEAS were allocated to the end-use categories using the same fractional distribution as the AFEAS values.

3. Emissions calculated from historical functions

Sales data are reported into the AFEAS database in three categories corresponding to end uses with short, medium and long time scales (“banking time”) before the substance is emitted (AFEAS, 2005). “Short” in this context means aerosols and open cell foam blowing, where emissions are prompt, with 83% of the sales into this category

being released in the year of production and the remainder in the following year. This category also includes fugitive emissions from production. Refrigeration uses dominate the medium banking time. Material in applications with long banking times, for e.g. foamed polyurethane and phenolic thermoset resins, is released at the rate of 2% per year.

Emissions are calculated using a “vintaging” model in which the sales for each year and each category are treated separately. In previous work (Midgley and Fisher, 1993; Midgley and McCulloch, 1997; Aucott et al., 1999; McCulloch et al., 2003) a single emission function was used for refrigeration and air conditioning. This had an initial loss of 30% of the fluid with the remainder released over the next 10 years. No provision was made for hermetically-sealed systems. However, the vintaging model provides the possibility for initial releases, operational losses and decommissioning losses to be varied separately and so reflect changes in equipment and servicing practices.

The historical emission functions were applied to the annual totals in each category, making no distinction between sales reported by AFEAS and those calculated from the UNEP consumption. “Global” concentrations of HCFC-22, calculated using a single box model of the atmosphere, as described in SORG (1990), are shown in Fig. 1 compared with the mean global measured concentrations reported in Montzka et al. (2003). This model treats the atmosphere as a single box in which concentrations are increased by emissions and reduced by atmospheric decomposition. Values for

emissions are calculated as the total during a calendar year and the time-step for the calculated decomposition (parameterised as an atmospheric lifetime of 12 years Montzka et al. (2003)) is also 1 year. Consequently, the date on the x-axis of Fig. 1 corresponds to 1 January of each year and the calculated concentration then depends on the emissions up to and including the previous year. The observed yearly average concentrations are plotted half way through each year. The model uses an independent estimate of atmospheric lifetime, which was derived from gas kinetic data and the mass balance of 1,1,1-trichloroethane (methyl chloroform) in the atmosphere (Prinn et al., 1995, 2001).

The concentration calculated from historic emissions and the observations are similar in 1980 but it is clear that subsequently the calculated concentrations are significantly larger than the measurements when the original refrigeration emission function is used. This emission function had a high initial release that reflected the major use of HCFC-22 in site-fabricated commercial refrigeration applications where commissioning losses were significant (Midgley and Fisher, 1993), with the rest of the system charge being emitted over 10 years.

The discrepancy could be removed using an atmospheric lifetime of 10 years (Miller et al., 1998) but with little justification for the shorter lifetime. Another possibility is that the emissions are overstated in the historical model, which fits with a recent reanalysis of fluorocarbon emission sources that suggests that containment of refrigerants in general has improved significantly (Ashford et al., 2004). Consequently, the effect of revised emission functions has been examined.

4. Emissions calculated using a series of functions for refrigeration

In constructing the original emission function, it was assumed that much of the equipment containing HCFC-22 was fabricated on site and filled there, so that there was a high initial loss as a consequence of both filling losses and leaks that occurred during start-up and first operation. This appeared to reflect the situation in the 1960s and 1970s when much of the HCFC-22 was used in medium-scale commercial systems, such as supermarket freezer cabinets. At that time, relatively few units were self-contained. However, since then, the proportion of hermetically sealed units has increased significantly and there has

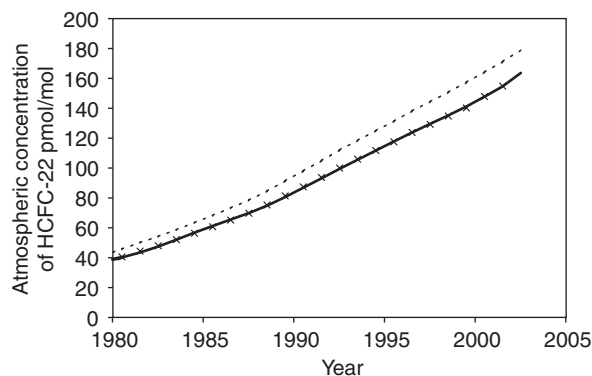


Fig. 1. Atmospheric concentrations of HCFC-22. Crosses indicate globally averaged measurements (Montzka et al., 1999). The dotted line is the concentration calculated using the historical (AFEAS) emission function and the solid line was calculated using the variable emission function as described in the text.

also been a change towards self-contained systems that require a minimum number of connections to be made on-site at installation. Frequently, these are pre-charged with refrigerant under factory conditions, so avoiding the losses that arise from filling on-site. Re-analysis of the data in a recent survey of the global air conditioning market (BSRIA/JARN, 2002) indicates that, in the developed world now, one quarter of the demand for filling new equipment is in hermetic and self-contained units, one quarter in systems that might require to be filled on site and the remaining half in systems that are already charged when they are delivered to site. In the developing world, typified by China, only 3% of systems are hermetic or self-contained and the remainder may potentially be charged or connected on-site.

Each of these has a different pattern of the extent of emissions in time. Hermetic and self-contained units, such as window air conditioners, are expected to have service lifetimes of about 20 years. Leaks will occur from a relatively few initial failures, from equipment that is damaged and on disposal of the system. Little, if any, servicing of the actual refrigeration system is carried out and the end of service life is often dictated by external considerations, such as renewal of the building. The distribution of emissions is shown in Fig. 2 (black bars); all of the refrigerant is lost within 20 years and the rate of loss is highest in the middle of the time period. The same release pattern was used for HFC-134a from hermetic systems (McCulloch et al., 2003).

For modern split systems, that have far fewer site-fabricated connections than those installed in the

1960s and 1970s, an emission function the same as that used for HFC-134a in general refrigeration was used. This is shown in Fig. 2 (as grey bars) and reflects an emission rate that averages 10% per year, again with the highest rates in the middle of the time period around 4 to 5 years.

Where there is significant site fabrication and filling, the emission function allows for an initial loss averaging 30% of the amount charged and subsequent losses that are evenly spread through the service life of the system (including the first year). The distribution is shown as the unfilled bars in Fig. 2.

In order to apply these to the historic production of HCFC-22, a series of emission functions was derived that allowed for different fractions of the total demand being used in hermetic (or self-contained) equipment and in systems with emissions similar to HFC-134a equipment and systems with the highest initial emissions shown in Fig. 2. In addition to the original emission pattern, with high initial losses, four other regimes were considered, designed to reflect the transition towards increased hermetic equipment, better containment in the non-hermetic equipment and the situation of the developing world where significantly more systems are fabricated on site with higher initial emissions. The extent to which demand fell into each category is shown in Table 2 and the resulting cumulative emission pattern is shown in Fig. 3.

Each regime typifies the emissions arising from equipment installed during a particular time period. Atmospheric concentrations were calculated following the sequence shown in Fig. 4:

Firstly, total global sales were subdivided into uses with short-term (prompt) emissions, uses with

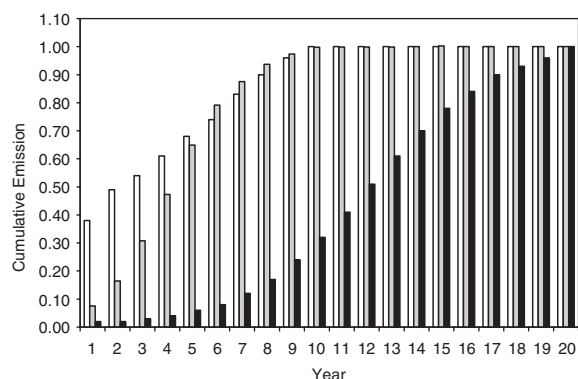


Fig. 2. Emission patterns from individual categories of use in refrigeration and air conditioning. Unfilled bars show the average loss from site-fabricated equipment, grey bars show the loss from equipment that is not self-contained and black bars show the loss from hermetic and self-contained units.

Table 2
Demand patterns for the mass quantities of HCFC-22 used in equipment

Regime shown in Fig. 3	Extent of hermetic and self-contained systems (%)	Extent of non-hermetic systems	
		With high initial losses (%)	With low initial losses (%)
1	0	100	0
2	10	10	80
3	20	0	80
4	30	0	70
5	3	40	57

long-term emissions and refrigeration and air conditioning. Annual emissions from the first two categories were calculated using the AFEAS emission functions (AFEAS, 2005). These were not changed during the subsequent fitting steps.

Secondly, annual emissions from global sales into refrigeration and air conditioning were calculated using the appropriate emission functions derived from the BSRIA/JARN (2002) study applied over a time period that was varied during the fitting steps.

Thirdly, atmospheric concentrations were calculated from the total calculated annual emissions using the one-box model described in SORG (1990).

Although the approximate duration can be assumed for the time period over which each set

of emission functions for refrigeration and air conditioning is valid, the periods that gave the best statistical fit were estimated empirically by adjusting their duration to minimise the standard error between the series of measured atmospheric concentrations and the calculated values. The time periods that gave the best fit are shown in Table 3 and the calculated atmospheric concentration is shown by the solid line in Fig. 1. The difference between this line and the measured points, expressed as the standard error over all 23 pairs of data is $0.1 \text{ pmol mol}^{-1}$. The emissions so calculated are shown in Table 4. The sensitivity of the calculated emissions to change in the time periods is such that a displacement in the periods by one year results in a 70% increase in the standard error.

Table 4 also includes the uncertainty range at two standard deviations. In this case, uncertainty was calculated by Monte Carlo simulation, as described in McCulloch et al. (2001), of the uncertainties in the total quantity used, the distribution between end

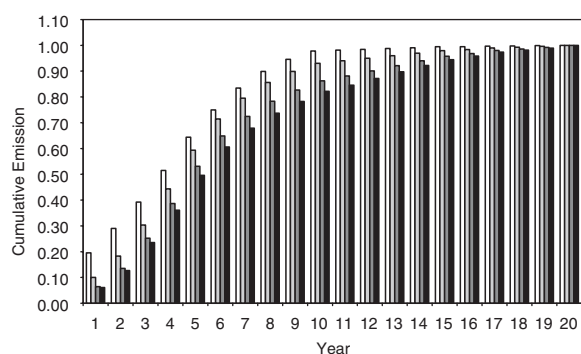


Fig. 3. Composite emission functions from refrigeration and air conditioning following the regimes shown in Table 2. Black bars: regime 2; dark-grey bars: 3; light grey: 4 and unfilled: 5. Regime 1 is the same as the average loss from site-fabricated equipment shown in Fig. 2 and is not shown again here.

Table 3
Durations of emission regimes

Regime	Duration	
	Start	End
1	1943	1977
2	1978	1984
3	1985	1993
4	1994	Continuing
5	1963	Continuing

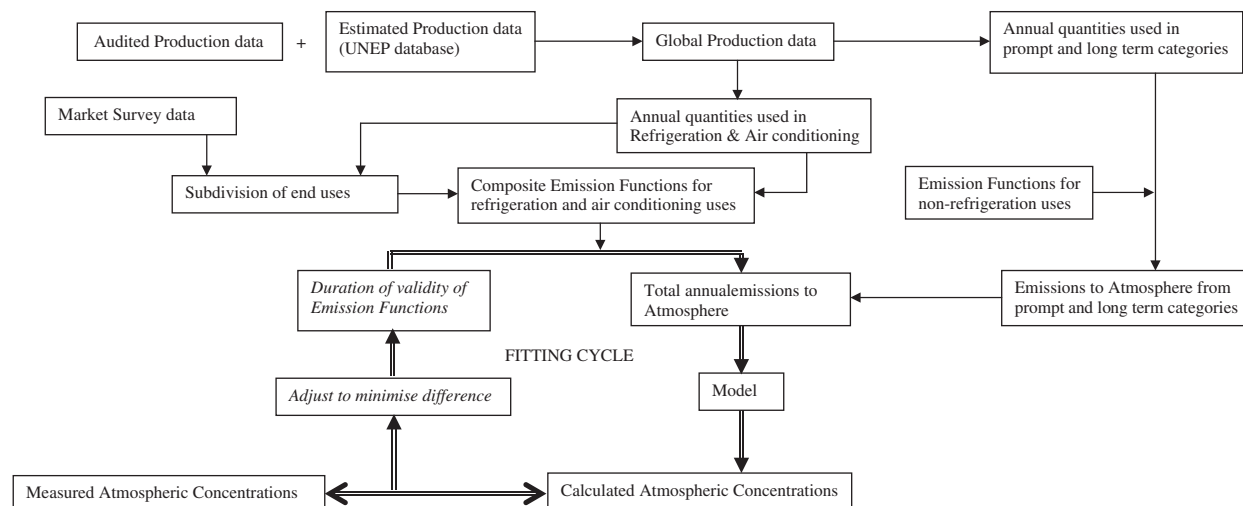


Fig. 4. Sequence of fitting calculated atmospheric concentrations to measurements. Steps indicated by single lines and arrows are performed only once. Steps indicated by double lines and arrows are iterated within the fitting cycle.

Table 4
Annual emissions of HCFC-22

Year	Emission Mg ($\text{kg} \times 10^3$)			Year	Emission Mg ($\text{kg} \times 10^3$)		
	Mean	+2 SD	−2 SD		Mean	+2 SD	−2 SD
1943	40	53	27	1974	70,800	85,200	56,400
1944	51	74	28	1975	71,500	85,300	57,800
1945	64	91	37	1976	80,600	94,600	66,700
1946	65	96	34	1977	89,800	105,000	74,700
1947	67	95	39	1978	66,600	77,500	55,700
1948	126	167	85	1979	68,900	80,000	57,600
1949	168	225	110	1980	83,000	96,000	69,700
1950	385	507	263	1981	96,000	111,000	81,400
1951	549	753	344	1982	110,000	125,000	94,400
1952	849	1150	544	1983	125,000	141,000	108,500
1953	1210	1660	758	1984	132,000	148,000	115,000
1954	1650	2260	1040	1985	133,000	148,000	117,000
1955	2180	2990	1380	1986	136,000	152,000	121,000
1956	3400	4570	2220	1987	142,000	157,000	127,000
1957	3980	5440	2510	1988	156,000	173,000	139,000
1958	4860	6530	3180	1989	174,000	193,000	155,000
1959	6860	9100	4610	1990	189,000	208,000	170,000
1960	8060	10,700	5380	1991	195,000	214,000	176,000
1961	8740	11,600	5930	1992	205,000	224,000	186,000
1962	10,800	13,900	7570	1993	208,000	226,000	190,000
1963	13,200	16,800	9640	1994	216,000	234,000	199,000
1964	16,500	20,700	12,300	1995	223,000	238,000	207,000
1965	19,200	24,100	14,300	1996	229,000	244,000	214,000
1966	23,500	29,300	17,600	1997	232,000	248,000	216,000
1967	28,000	35,100	21,000	1998	238,000	254,000	222,000
1968	34,100	42,600	25,600	1999	248,000	264,000	232,000
1969	41,400	51,900	30,900	2000	264,000	280,000	247,000
1970	45,000	56,500	33,500	2001	278,000	297,000	259,000
1971	49,900	62,000	37,800	2002	316,000	337,000	295,000
1972	54,600	67,100	42,100	2003	275,000	293,000	257,000
1973	62,600	75,800	49,500				

uses, the quantity and timing of refrigerant emissions, the quantity used in aerosols and other promptly emitting categories and the annual loss rate from closed cell foams. Uncertainties in the atmospheric modelling parameters, such as atmospheric lifetime, were not considered.

5. Conclusion

The emissions calculated here are substantially different from those reported elsewhere and the quantities of HCFC-22 released are estimated to be much less than those calculated in our previous paper (McCulloch et al., 2003) and in Montzka et al. (2003). The previous work assumed that there had been no change in containment but it is now clear that the audited production and sales can match with atmospheric concentrations only if there

has been a significant shift towards better containment. This would result both from the change towards use in systems that are more intrinsically self-contained and from reducing the leakage from all systems. While the fit with atmospheric concentrations does not indicate a single or unique set of emission parameters, the functions used are consistent with the change in the market towards greater use of HCFC-22 in hermetic and self-contained air conditioning systems and also indicate that site-fabricated systems now have much smaller initial leakage.

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