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Releases of refrigerant gases (CFC-12, HCFC-22 and HFC-134a) to the atmosphere

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Abstract

Two of the gases, CFC-12 (dichlorodifluoromethane, CF_2Cl_2) and HCFC-22 (chlorodifluoromethane, CHClF_2) have long histories of emission from refrigeration and other uses. Production and sales records show the expected fall in the amounts of CFC-12 used in refrigeration after the Montreal Protocol came into effect but this does not seem to have been accompanied by significant substitution by HCFC-22, demand for which appears governed by organic growth. HFC-134a (1,1,1,2-tetrafluoroethane, CH_2FCF_3) is a relative newcomer that has partially substituted for CFC-12.

After developing a single data set for the global use of each substance in refrigeration, foam blowing and aerosol propulsion, and other promptly emissive uses, annual releases of the compounds were estimated by applying emission functions derived from surveying both the producers of the chemicals and the principal industrial users.

For CFC-12 and HFC-134a, atmospheric concentrations calculated from the emissions estimated here are in good agreement with observations, verifying that the emission functions adequately describe the relationship between the quantities in use, the atmospheric lifetimes of 100 and 14.6 years, respectively, and the extent of release into the atmosphere. The agreement between observation and calculation is poorer for HCFC-22, if its atmospheric lifetime is 12 years, but becomes much closer with a lifetime of 10 years.

An 80% reduction in CFC requirement has been substituted only to the extent of 25% by HFC-134a. This is consistent with improved technology to curtail leakage and so enable lower system charges that, in turn, translate into less demand. For the same reason, the refrigeration emission function for HFC-134a over the period 1990–2000 was not significantly different from that of CFC-12. The lower absolute rate of leakage and lower absolute charge sizes combining to maintain a similar relative rate of loss.

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1. Introduction

The title compounds are the most abundant of the chlorofluorocarbons (CFC), hydrochlorofluorocarbons (HCFC) and hydrofluorocarbons (HFC) in the atmosphere. The global average surface concentration of

CFC-12 in 2000 was $543 \text{ pmol mol}^{-1}$ (parts per trillion, or 1 in 10^{12}), more than double that of CFC-11, the next most abundant; HCFC-22 was present at ground level at $143 \text{ pmol mol}^{-1}$, over five times the concentration of all other HCFCs put together (Prinn et al., 2000; AGAGE, 2002). HFC-134a is similarly about five times as abundant as other HFCs, at 15 pmol mol^{-1} (AGAGE, 2002). All of these refrigerants are gases at ambient temperature with relatively low water solubility and so partition preferentially into the atmosphere (Ballschmiter,

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1992). All have sufficiently long atmospheric lifetimes to be well mixed, with small concentration gradients relative to, for example, carbon monoxide within each hemisphere, and a dynamically related concentration differential between Northern and Southern Hemispheres (Prinn and Zander, 1999; Kurylo and Rodriguez, 1999).

CFC-12 was developed as a refrigerant in the 1930s (Midgley, 1937) and subsequently found additional use as an aerosol propellant; the current level in the environment is a consequence of wide deployment in these uses and release from them over many decades. HCFC-22 became a significant new refrigerant in the 1960s and emissions have grown since then. Use of HFC-134a is a comparatively recent development, with no significant production before 1990 but, between then and 2000, the quantity produced grew rapidly. However, in no case is the emission of the compound directly related to current production; releases occur while the material is being used or on disposal of equipment at the end of its service life.

For the substances that contain chlorine, in this case CFC-12 and HCFC-22, the importance of their atmospheric burdens is in contributions to stratospheric chlorine loading, and hence ozone depletion, both now and in the future. Prediction of the trend in stratospheric chlorine based on emissions requires a rigorous method to relate emissions to the “bank” of non-released material that is still being used. Reliable estimation of future trends also implies good knowledge of production, particularly from the past to enable an accurate estimate of the size of the bank.

From political and scientific perspectives, chlorine loading dominates the need for data on CFCs and HCFCs. For the HFCs however, the environmental interest is in their potential future contribution to climate change. Because HFC-134a is such a new arrival in the market for refrigerant fluids (a market that is both long established and dominated by technical considerations), such prediction requires an insight into the extent to which it is substituting for CFC-12 and HCFC-22, the principal existing refrigerants.

In order to be of any value for these predictions, emissions inventories need to be global in scope and analytically based on long term production and consumption data.

2. Databases

2.1. Alternative fluorocarbons environmental acceptability study (AFEAS)

This database has been maintained by industry since the early 1970s and contains details of production of individual compounds, sales into emission-categorised

end uses and estimated emissions (AFEAS, 2001). The time span of the data is from first commercialisation of each compound and the substances included are: CFCs 11, 12, 113, 114 and 115; HCFCs 124, 141b, 142b and 22 and HFC-134a. The mechanism by which the database is assembled requires companies to submit their records of production, sales and transfers to an independent auditor who then reconciles the total to accountancy standards of accuracy. For the compounds of interest, the errors in the production totals are: 0.17% for CFC-12, 0.39% for HFC-22 and 0.9% for HFC-134a and this database sets the standard for product accounting (AFEAS, 1998).

Geographical coverage of production depends on the companies submitting data so that present and historic facilities in USA, Japan, European Union, Australia, Argentina, Brazil, Canada, Mexico, Republic of South Africa and Venezuela are covered but those in China, India, Korea and Russia are not. Up to 1990, this omission was barely significant, subsequently annual production of CFCs in the additional countries has exceeded that in the countries covered by the AFEAS data. Before the UNEP and other data became available in the early 1990s, informal estimates by producers were used to globalise the AFEAS database. The incorporation of real data from UNEP represents a significant improvement.

2.2. United Nations Environment Programme (UNEP)

In order to demonstrate compliance with the Montreal Protocol on Substances that Deplete the Ozone Layer, nations are required to submit their production and consumption of such substances, including CFCs and HCFCs, to the Secretariat to the Protocol. These data are assembled and published by UNEP as a database that is geographically categorised but where compounds are grouped as in the Protocol so that the national sum of CFCs is quoted separately from the sum of HCFCs. Units are ODP tonnes, the product of the defined Ozone Depletion Potential of each compound and the number of metric tonnes. The data are not audited and responsibility for accuracy rests with the nation submitting them. This has resulted in some significant changes in the data, for example, in UNEP (1998) Russian production of HCFCs for 1989 was entered at 437 ODP tonnes but, in the more recent database (UNEP, 2002), the value for that year had been increased to 1194 ODP tonnes. Being outside of the AFEAS database, this change affects the estimate of additional production, which is based on the annual mean from 1989 to 2000. There were somewhat smaller changes in the reports of CFC production in Argentina and Brazil over the period 1993–1996.

Although company production records should be a useful source of data for the national submissions, there

are subtle differences concerning accounting for stock-holding and transfers and the national data in UNEP (2002) are an independent record. Nevertheless, the values for production of CFCs in the countries that are covered in both AFEAS and UNEP data sets agree to within 0.6% over the period 1986–2000; a root mean square difference in the region of 3200 tonnes. For HCFCs the relative fit is poorer; AFEAS and UNEP data sets agree to within 4% over the period 1989–2000 and the RMS difference is between 6000 and 12,000 tonnes, depending on the ODPs of the product mix which itself is unknown.

The portion of CFCs not reported to AFEAS but included in the UNEP data set has risen steadily from 13% in 1986 to 75% in 2000, reflecting a much larger fall in the AFEAS values than any rise in the additional production. Over a similar period, the additional annual production of HCFCs has remained a relatively constant proportion, amounting to $10.3 \pm 4.6\%$ of the annual totals of production reported to AFEAS.

2.3. United Nations Framework Convention on Climate Change—the “Rio” Convention (UNFCCC)

The Subsidiary Body for Implementation (SBI) established under UNFCCC assembles data on emissions of greenhouse gases from submissions by parties to the Kyoto Protocol. No data on production and consumption are held and the emissions may be estimated in a variety of ways. While there are requirements for consistency (IPCC, 2000), the Parties can meet the requirements by submitting values for either the group of HFCs or individual compounds. The units are tonnes of CO₂ equivalent, calculated by multiplying the metric tonnes of estimated emission of each compound by its defined Global Warming Potential (at 100 year integration time horizon).

The resulting database (UNFCCC, 2000) is a mixture of values for greenhouse gas emissions, both of individual compounds and groups of compounds, that have been estimated by any one of three principal defined methodologies which can give dramatically different results for individual years (IPCC, 2000). Without production and consumption data, it is not capable of being audited in the same way as the database for ozone depleting substances, nevertheless it can provide useful points of comparison for HFC emissions calculated from independent data for sales combined with emission functions.

2.4. Country data for CFCs—Russia

Manufacture of CFCs within Russia and previously the USSR has been significant, but of uncertain scale. Production had apparently commenced in the USSR before 1968 and capacity there had grown to

80,000 tonnes yr⁻¹ by the early 1980s (Gamlen et al., 1986). However, according to Alperowicz and Cox (1987) the first two plants to make CFC-11 and 12 were commissioned in 1980 at Volgograd and 1983 at Yavan. Both could make up to 30,000 tonnes yr⁻¹ of CFC-11/12 mixtures but were dogged by operating problems and, in 1984, were reported to be working at only 25% capacity. If the statement by Alperowicz and Cox actually referred to imported technology and the plants replaced older, locally sourced technology, then the two perspectives on the history of Russian CFC production can be reconciled.

From 1986 onwards, Russia has reported production of CFCs to the Montreal Protocol database (as the total ODP tonnes), furthermore, the productive capacity and production sites have been declared to attract funding for assisted closure (World Bank, personal communication, 1999). Based on these values and assuming that the amount of CFC-11 relative to CFC-12 followed global trends, the estimated Russian production of CFCs is shown in Table 1.

2.5. Country data for CFCs—China, India and Korea

The primary source of information for these countries is the UNEP database. Indeed, for India and Korea it is the only source (UNEP, 2002). In the case of China the additional data from Bingfeng et al. (2000) is at odds with the values reported to UNEP. Table 2 shows the comparison. It is apparent that the values for total production and consumption are not the same in the two data sets. Furthermore, the split between compounds reported by Bingfeng et al. is far from complete (at 46%); their attributions covered only refrigeration and solvent cleaning, ignoring use in aerosols and foam blowing. The extent of domestic manufacture of individual compounds is completely unknown, although for many years Chinese consumption has outstripped domestic supply (see Table 2). Consequently China has been treated no differently from India and Korea and the production reported to UNEP has been assigned to CFCs 11 and 12 in the same annual proportions as reported in the AFEAS data.

2.6. Combined global database for production

After allowing for the estimated production of CFC-113 in Russia shown in Table 1, the remainder of the CFC total in the UNEP data was divided between CFCs 11 and 12 in the same ratio as in the AFEAS report. Over the period 1986–2000, the CFC-12 component rose from 53% to 66%. The CFC-12 production estimates are shown in Fig. 1 where the clear area shows production reported to AFEAS and the shaded area represents production derived from UNEP data—the “additional” production as described here.

Table 1
Estimated Production of CFCs within Russia

Year	Total CFC production	Calculated production (metric tonnes)		
	ODP tonnes	CFC-11	CFC-12	CFC-113
1986	105,296	43,700	49,800	14,800
1987	105,213	44,200	49,200	14,700
1988	105,130	44,000	49,300	14,700
1989	105,046	41,400	51,900	14,700
1990	103,696	46,200	45,800	14,500
1991	84,289	36,500	38,400	11,800
1992	62,127	25,500	29,600	8700
1993	40,580	14,100	20,600	7400
1994	42,526	10,900	24,300	9200
1995	39,322	8900	22,500	9900
1996	16,770	4400	9700	3300
1997	14,732	4500	7900	2900
1998	13,808	3500	7900	3000
1999	18,417	4900	10,300	4000
2000	25,536	6100	15,100	5500

Table 2
CFCs in China

Year	Data from UNEP (2002)		Data from Bingfeng et al. (2000)						
	Production	Consumption	Production	Consumption	Percentage of consumption attributed to				
	ODP tonnes	ODP tonnes	ODP tonnes	ODP tonnes	CFC-11	CFC-12	CFC-113	CFC-114/5	CFC-13
1986	11,540	29,237	—	—	—	—	—	—	—
1989	20,700	34,783	—	—	—	—	—	—	—
1990	20,688	41,829	—	—	—	—	—	—	—
1991	26,018	50,263	—	—	—	—	—	—	—
1992	24,941	57,045	—	—	—	—	—	—	—
1993	31,658	66,283	—	—	—	—	—	—	—
1994	50,809	70,779	—	—	—	—	—	—	—
1995	46,672	75,291	40,952	69,221	—	—	—	—	—
1996	44,016	47,089	43,878	46,976	—	—	—	—	—
1997	50,324	51,076	50,323	51,056	13	25	7	0.3	0.1
1998	55,402	55,414	—	—	—	—	—	—	—
1999	44,739	42,983	—	—	—	—	—	—	—
2000	58,000	—	—	—	—	—	—	—	—

HCFC data in the UNEP reports comprise annual production of all HCFCs weighted by their ODPs. The annual contribution from HCFC-22 was assumed to represent the same proportion of the total as in the AFEAS data. This amounted to 98% in 1989 but had fallen to 57% in 2000 with increased production of other hydrochlorofluorocarbons, particularly HCFC-141b ($\text{CH}_3\text{CCl}_2\text{F}$) and HCFC-142b (CH_3CClF_2). Annual production estimates for HCFC-22 are shown in Fig. 2, shaded similarly to Fig. 1.

Since there is no evidence of significant production of HFC-134a before 2001 outside of the countries reporting to AFEAS, that database was considered to repre-

sent the global total for this compound (see Fig. 3). To place these values into context, the combined estimates of production of CFCs 11, 12 and 113, HCFCs 22, 141b and 142b and HFC-134a are plotted on the same scale in Fig. 4.

3. Refrigeration

3.1. Combined Global Database for Use in Refrigeration

Only the AFEAS data are subdivided by end use. Sales in that data set are reported separately for use

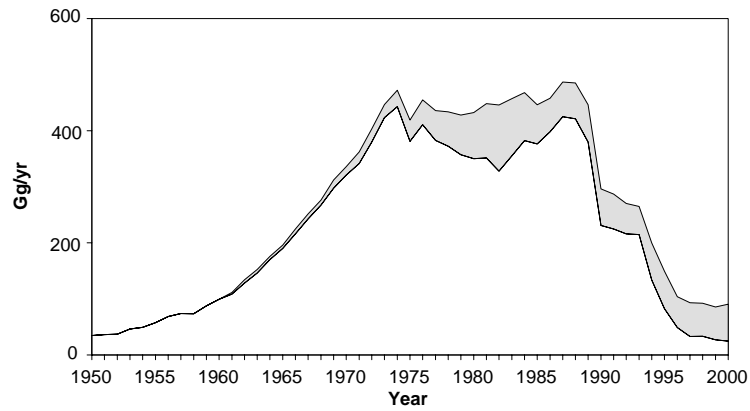


Fig. 1. Annual production of CFC-12. The open portion shows production reported in [AFEAS \(2001\)](#) and the shaded area the additional production calculated from [UNEP \(2002\)](#)

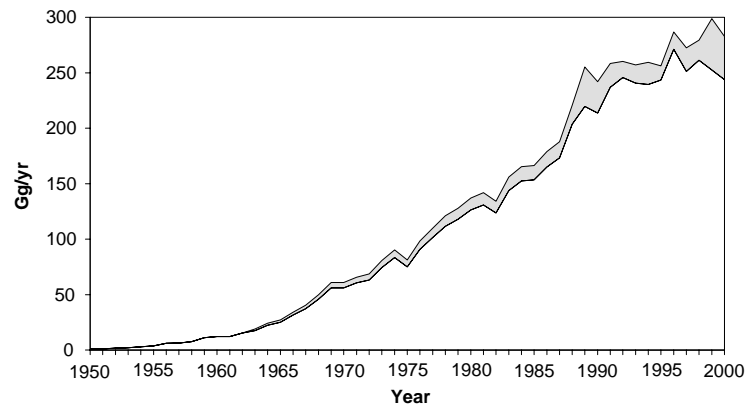


Fig. 2. Annual Production of HCFC-22. Shading as in [Fig. 1](#).

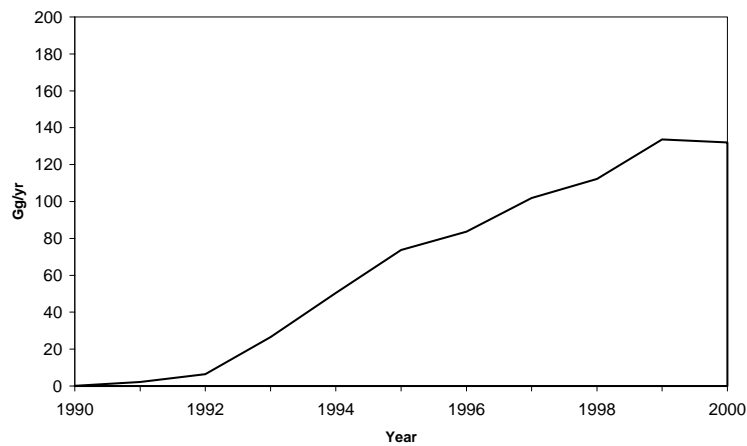


Fig. 3. Annual Production of HFC-134a. There was no additional production before 2000 and the values here are exclusively from [AFEAS \(2001\)](#).

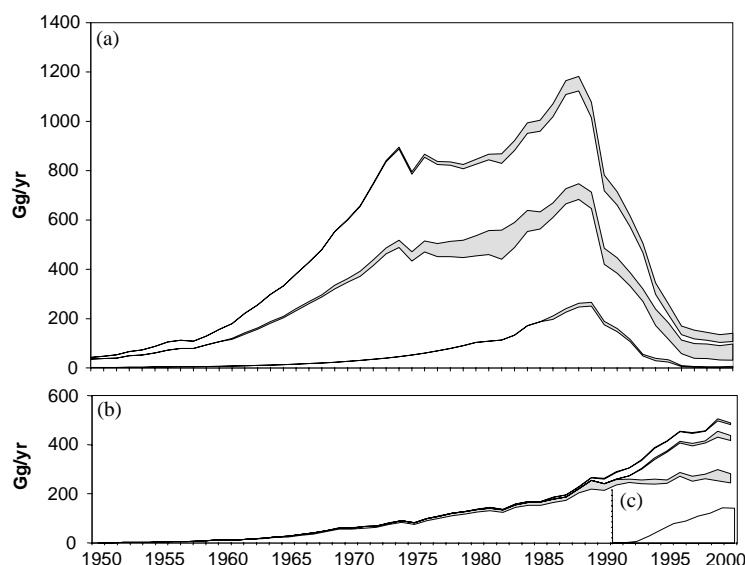


Fig. 4. Comparison of Production of Fluorocarbons: (a) CFCs; from the bottom CFC-113, then CFC-12, then CFC-11, shown as contributions to the annual total CFC production, shading as in Fig. 1; (b) HCFCs; from the bottom HCFC-22, then HCFC-141b, then HCFC-142b, shown in the same way as CFCs, and inset (c) HFC-134a on the same scale.

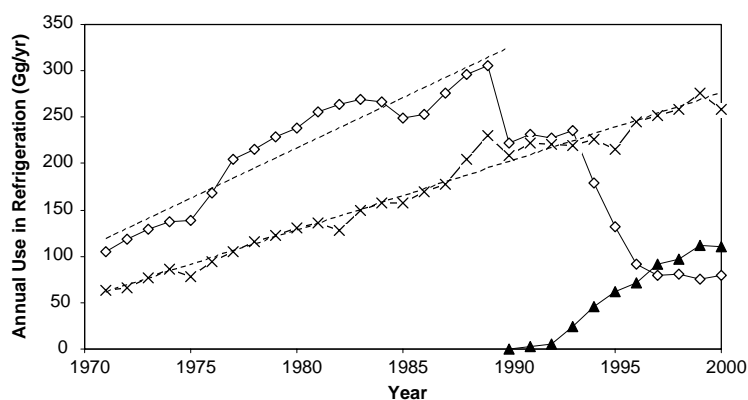


Fig. 5. Annual global use of refrigerant fluids: open diamonds—CFC-12; crosses—HCFC-22 and filled triangles—HFC-134a. The dashed lines represent the linear trends for CFC-12 (based on data to 1989) and HCFC-22 (based on the whole data set shown here).

categories where emissions are prompt, such as aerosols and solvents; categories that have slower emission rates, such as industrial and commercial refrigeration and categories where emissions occur over many years, such as hermetic refrigeration and air conditioning, and closed cell foams. The proportion used in each category was assumed to be applicable globally and the additional production was distributed in the same way.

Fig. 5 shows the quantities of each of the title compounds used annually for refrigeration throughout the world. Prior to 1990, when the Montreal Protocol took effect, the requirement for CFC-12 had been growing at a linear rate of nearly 11,000 tonnes yr^{-1} ,

which would have resulted in a demand of 435 Mg in the year 2000. However, the effect of the Protocol on CFC-12 use is clear; by 2000 it had fallen by 80% from the prior trend. For HCFC-22, the long term linear growth rate is 7400 tonnes yr^{-1} , with a coefficient of variance (R^2) of 0.97 from 1971 to 2000. If the phase out of CFC had affected demand for HCFC-22, one might have expected a significant change in growth rate during the early 1990s. The robust long term linear trend indicates otherwise and it could be concluded that substitution of CFC-12 by HCFC-22 has been insignificant.

There is clearly some substitution by HFC-134a but it amounts to about 25% of the requirement that would

have been expected for CFC-12 in the year 2000. It is too early to draw any conclusion from the levelling in demand in 2000.

3.2. Emission functions

The functions relating use of CFC-12 to its emissions from refrigeration and air conditioning are shown in Fig. 6. These were developed by Gamlen et al. (1986) from a survey of manufacturers of systems and producers of refrigerants. It was apparent from this survey that the major emission occurred from the systems that were not hermetically sealed. These are relatively few in number but contain 90% of the refrigerant fluid. They emit material in the short term; the losses occurring during operation and servicing. The sales data reported to AFEAS in this short term category comprise use in industrial and commercial refrigeration and air conditioning systems, and mobile air conditioning. In these systems service life of the refrigerant fluid is approximately normally distributed about a median of 4–5 years. The release function is actually biased slightly towards more rapid release to account for losses that occur on first filling the system. The average function represents a significant compromise. In general, mobile air conditioning and site constructed commercial systems have refrigerant fluid lifetimes that are less than the average; premature failure (accidental damage is a particular problem with mobile air conditioning), lower intrinsic system integrity and servicing practices that result in losses greater than standard would all result in more rapid emission.

Furthermore, the situation is evolving, with lower system charges and lower loss rates being features of current engineering. Large industrial refrigerators (for example cold storage systems) can have fluid lifetimes that are greater than the median but a single system failure can release many tonnes of refrigerant.

The resulting wide range of fluid lifetimes is represented by distributing emissions about the median using a standard deviation of 2 years, so that the statistical distribution of emissions is as shown in the open bars of Fig. 6. Expressed as a linear rate of release, averaged across all systems, this amounts to $10\% \text{ yr}^{-1}$ (Table 3). Loss rates of this size have been confirmed by more recent work. Using data from manufacturers of mobile air conditioning systems, Baker (1999) estimated that the best practice for systems that were operated using CFC-12 technology would give a system fluid lifetime of 3.4 years and, with the improvements in recovery during servicing and at end of life expected for newer systems, the fluid life would increase to 8 years (equivalent to $13\% \text{ yr}^{-1}$). Siegl et al. (2002) performed measurements of the actual release rates of HFC-134a from a range of vehicles and found that, allowing for losses during servicing, the system fluid lifetime would average 6 years (or about $8\% \text{ yr}^{-1}$).

Hermetically sealed units, typically domestic refrigerators, comprise the largest number of systems but contain only 10% of the CFC-12 used in refrigeration. They contain only a few hundred grams of fluid and leakage, when it occurs, is due to damage or corrosion. In developed countries, it is not economic to repair the refrigerator and it is scrapped. However, most emissions

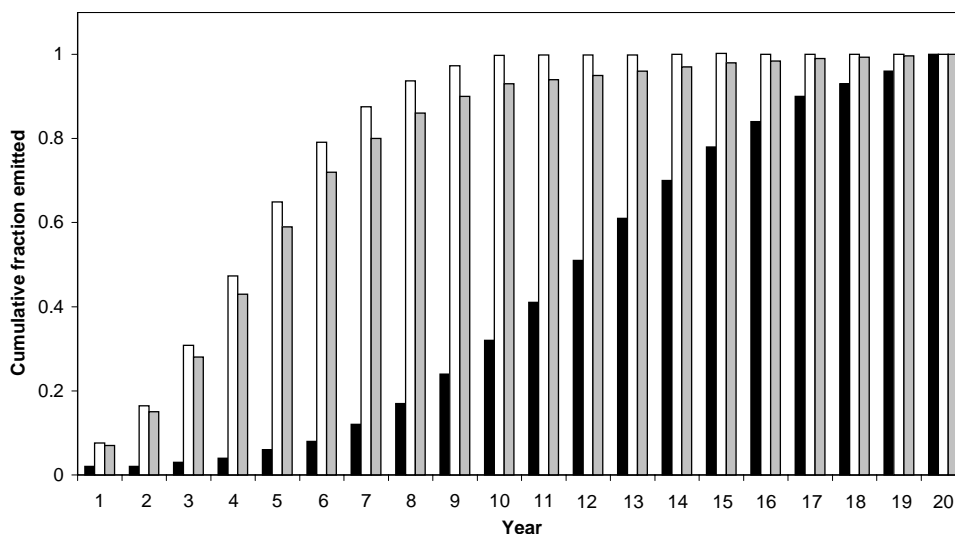


Fig. 6. Cumulative emission function for CFC-12 or HFC-134a from refrigeration: open bars—emission from short term category (see text); black bars—emission from hermetic refrigeration, and shaded bars—combined emission function, with a 10% hermetic component.

Table 3
Release functions from fluorocarbon applications

Application	Material	Linear release function				Distributed release function Years	Service life	
		Fraction released		Fraction released			Median years	Uncertainty
		Initially	Uncertainty	Annually	Uncertainty			
Refrigeration (non-hermetic)	CFC-12							
	HCFC-22							
	HFC-134a	—	—	—	—	4.5	10	4
Refrigeration (hermetic)	CFC-12							
	HFC-134a	—	—	—	—	12.5	20	8
Extruded polystyrene foam	CFC-12							
	HCFC-22							
	HFC-134a	0.325	0.0375	0.03	0.005	—	50	10
Polyethylene pipe	CFC-12							
	HCFC-22	1	—	—	—	—	—	—
Polyethylene block	CFC-12							
	HCFC-22	0.9	0.025	0.05	0.02	—	2	1
Polyurethane integral skin	HCFC-22	0.95	0.0125	0.025	0.00625	—	2	1
Polyurethane continuous panel	HCFC-22							
	HFC-134a	0.15	0.025	0.0075	0.00125	—	25	2.5
Polyurethane appliance	HCFC-22							
	HFC-134a	0.075	0.0125	0.005	0.001	—	15	2.5
Aerosol propellant	CFC-12							
	HFC-134a	0.5	—	0.5	—	—	—	—
Open cell foam	CFC-12							
	HCFC-22	0.83	—	0.17	—	—	—	—

occur at equipment disposal which generally happens before it has failed mechanically. The resulting average distribution of emissions is shown as the black bars in Fig. 6. It comprises complete emission within 20 years, with a distribution skewed around 12.5 years (Table 3). For CFC-12, most of the releases from this sector are historic, having occurred before the 1990s, so that recovery of the fluid on disposal has not made a significant impact. Furthermore, such recovery is far from complete (Baker, 1999). Nevertheless, recovery on disposal should significantly reduce potential emissions in the future and will have to be taken into account in future emission functions.

In this work, the same emission function is used for HFC-134a and CFC-12. This would seem to ignore the technical developments that have been made in the design of systems. However, these developments embody parallel improvements in fluid containment and reductions in the quantity of fluid circulating in each system (Preisegger, 1999). The consequence is that, while the absolute rate of loss has decreased, the relative rate of loss has remained similar.

The pattern of emissions from HCFC-22 refrigeration is not the same as that from CFC-12 and HFC-134a. The major difference is a much larger allowance for initial loss (totalling 38% in the first year) due to widespread use in commercial systems that are site

constructed (Midgley and Fisher, 1993). These are intrinsically less robust than factory built units, with non-welded connections and long pipe runs, and so commissioning losses can be high (Bivens, 1999).

4. Closed Cell (Rigid) Foams

Comparatively little CFC-12, HCFC-22 and HFC-134a is used to blow plastic foams (Gamlen et al., 1986; Midgley and Fisher, 1993; Ashford, 2000) and the matrices are polystyrene and polyethylene that, unlike the polyurethane blown using CFC-11, have relatively rapid emission profiles. Nevertheless, it is important to quantify emissions from foams so that the balance between emissions and atmospheric concentrations can be calculated. It was assumed for each compound that the fraction used annually to blow foam was a global constant, so that the distribution reported in AFEAS (2001) could be applied to the additional quantities calculated here and shown in Figs. 1 and 2. Then, in the manner described in McCulloch et al. (2001), these annual estimates for use in closed cell foams were further subdivided into use in extruded polystyrene, polyethylene pipe and polyethylene block which have the emission functions shown in Table 3 (Ashford, 2000).

5. Prompt Emission Categories

Applications such as aerosol propulsion and the blowing of open cell plastic foams result in relatively prompt emissions of the working fluid. In the case of aerosols, the emission function allows for 50% emission in the year in which the fluid is sold for this use and 50% in the following year. Since most of the aerosols were sold retail, this allows for delays that arise from stock holding at the aerosol product manufacturer and in the distribution chain. In the case of open cell foams, emission is even more rapid (because it is used industrially) and 83% is considered to be emitted in the year in which the fluid is produced (Gamlen et al., 1986; Midgley and Fisher, 1993). Historical use of CFC-12 in aerosols was large; in the mid-1970s on an annual basis it exceeded use in refrigeration and overall it accounts for almost 30% of the total quantity of CFC-12 sold. On the other hand, use in promptly emissive categories amounts to only 8% of total production in the case of HCFC-22 and 10% for HFC-134a (AFEAS, 2001).

6. Emissions

Annual emissions of each of the fluorocarbons were calculated by multiplying the matrix of categorised global production and sales by the matrix of cumulative emissions derived from the emission function for each category. Uncertainties were quantified by Monte Carlo combination, as described in McCulloch et al. (2001), of the uncertainties in the total quantity used, the distribution between end uses, the quantity and timing of refrigerant emissions, the quantity used in aerosols and open cell foams and the magnitude of the initial loss, annual rate of emission and service lifetime of closed cell foams. For all of these fluids, the largest single effect arose from the uncertainty in the timing of refrigerant emissions in the short term category. Results are shown in Table 4 for the complete history of production and emission of all three compounds.

7. Comparisons with atmospheric determinations

7.1. CFC-12

In order to verify the estimates of CFC-12 emissions, the time series of atmospheric concentrations was calculated using a single box model (SORG, 1990) and an atmospheric lifetime of 100 years (Prinn and Zander, 1999). There are obvious limitations to such a simple atmospheric model for a single compound. However, the model, and its counterpart with two hemispherical boxes, fits observations for all the compounds discussed

here relatively well, with few significant differences. Results are plotted in Fig. 7 in comparison with the observations recorded in Prinn et al. (2000), updated with information from AGAGE (2002). Also shown in the figure are the concentration estimates obtained by propagating the uncertainty in emissions shown in Table 4 in the same direction through the whole time series.

For almost all of the data record, the calculated concentrations are consistent with observations at 95% significance based on emissions. However, in recent years there appears to be a sharper inflexion in observed concentration than in that calculated from emissions. This may indicate that actual emissions are lower than the estimates, which would agree with the expectation of better containment (Baker, 1999), but the values are well within uncertainty limits and a longer series of data would be required to substantiate lower emissions.

7.2. HCFC-22

The calculation is not as good a match with observations as CFC-12; in particular, the slope of the calculated concentration is different from the observations when using a 12 year lifetime (Kurylo and Rodríguez, 1999). Furthermore, while agreement between observations and calculation is well within 95% confidence limits up to 1990, by 1996 the lower boundary of the 95% confidence of concentration from the calculated emissions exceeded observations. However, if the environmental lifetime of HCFC-22 is 10 years (as reported in Prinn et al., 2000), observations and calculation match well (Fig. 8).

7.3. HFC-134a

In the absence of global concentration data, hemispherical values from AGAGE (2002), Montzka et al. (1996) and Oram et al. (1996) were used and compared to hemispherical concentrations calculated using the two box model described in McCulloch and Midgley (1996), with an atmospheric lifetime of 14 years (Kurylo and Rodríguez, 1999). Figs. 9 and 10 show that the match between calculated concentrations and observation is good in both hemispheres. The apparent systematic difference in the Northern Hemisphere up to 2001 may be an artefact of the emission function or the model. For example, release 6 months earlier would promote a far better match but there is no evidence to suggest more prompt release. However, there is exceptionally close agreement in the Southern Hemisphere and, at this point, especially because the data record is very short in comparison with the other two fluorocarbons, there is no rationale to change the emission function. This seems to be describing the relationship between production (or use) of HFC-134a and emissions adequately.

Table 4
Estimated emissions of fluorocarbons

Year	Annual CFC-12 emission, (Mg)			Annual HCFC-22 emission, (Mg)			Annual HFC-134a emission, (Mg)		
	Mean	+2 σ	−2 σ	Mean	+2 σ	−2 σ	Mean	+2 σ	−2 σ
1930	0	0	—	—	—	—	—	—	—
1931	0	100	—	—	—	—	—	—	—
1932	0	100	—	—	—	—	—	—	—
1933	100	200	—	—	—	—	—	—	—
1934	200	400	—	—	—	—	—	—	—
1935	300	600	—	—	—	—	—	—	—
1936	500	1000	—	—	—	—	—	—	—
1937	800	1700	—	—	—	—	—	—	—
1938	1100	2200	0	—	—	—	—	—	—
1939	1700	3100	200	—	—	—	—	—	—
1940	2200	3900	500	—	—	—	—	—	—
1941	3000	5100	800	—	—	—	—	—	—
1942	3600	5900	1400	—	—	—	—	—	—
1943	4500	7200	1800	0	0	0	—	—	—
1944	6100	11,000	1100	0	0	0	—	—	—
1945	7900	14,600	1300	0	0	0	—	—	—
1946	13,900	19,100	8700	0	0	0	—	—	—
1947	21,300	25,800	16,800	0	0	0	—	—	—
1948	24,700	28,100	21,300	100	100	0	—	—	—
1949	26,600	28,900	24,200	100	200	100	—	—	—
1950	29,400	31,700	27,200	300	500	200	—	—	—
1951	32,300	35,000	29,700	500	700	300	—	—	—
1952	33,600	36,400	30,900	800	1100	500	—	—	—
1953	37,800	41,700	34,000	1200	1600	700	—	—	—
1954	42,800	47,500	38,200	1600	2200	1000	—	—	—
1955	48,100	53,900	42,400	2100	2900	1300	—	—	—
1956	56,100	63,500	48,700	3400	4500	2200	—	—	—
1957	63,800	71,800	55,800	3900	5400	2500	—	—	—
1958	66,900	75,400	58,300	4800	6500	3100	—	—	—
1959	74,700	83,300	66,200	6800	91,00	4600	—	—	—
1960	89,000	97,400	80,600	8000	10,700	5300	—	—	—
1961	100,000	108,400	91,700	8700	11,500	5900	—	—	—
1962	115,400	123,600	107,300	10,700	13,900	7500	—	—	—
1963	135,600	143,600	127,600	13,100	16,700	9600	—	—	—
1964	157,800	165,600	149,900	16,300	20,500	12,200	—	—	—
1965	177,900	187,200	168,500	19,000	23,900	14,200	—	—	—
1966	199,500	211,000	188,100	23,300	29,000	17,600	—	—	—
1967	225,100	238,300	211,900	27,800	34,700	20,900	—	—	—
1968	252,500	266,500	238,500	33,800	42,200	25,500	—	—	—
1969	281,800	297,200	266,300	41,100	51,400	30,800	—	—	—
1970	307,800	324,800	290,800	44,700	56,000	33,400	—	—	—
1971	331,600	349,800	313,500	49,600	61,400	37,700	—	—	—
1972	362,100	382,500	341,800	54,200	66500	42,000	—	—	—
1973	401,100	424,500	377,800	62,200	75,100	49,400	—	—	—
1974	435,100	459,400	410,700	70,300	84,400	56,300	—	—	—
1975	423,700	445,400	402,100	71,100	84,500	57,700	—	—	—
1976	413,600	437,900	389,300	80,100	93,800	66,500	—	—	—
1977	401,300	434,300	368,400	89,300	104,100	74,500	—	—	—
1978	376,700	413,300	340,200	97,600	113,300	81,900	—	—	—
1979	375,900	413,500	338,300	104,700	121,500	87,800	—	—	—
1980	379,900	415,400	344,300	113,000	130,600	95,400	—	—	—
1981	394,000	427,000	361,100	119,500	137,700	101,300	—	—	—
1982	403,100	430,200	376,100	121,200	138,000	104,400	—	—	—
1983	417,000	441,300	392,600	133,100	150,100	116,000	—	—	—
1984	439,200	464,100	414,300	142,800	160,500	125,000	—	—	—

Table 4 (continued)

Year	Annual CFC-12 emission, (Mg)			Annual HCFC-22 emission, (Mg)			Annual HFC-134a emission, (Mg)		
	Mean	+2 σ	−2 σ	Mean	+2 σ	−2 σ	Mean	+2 σ	−2 σ
1985	449,900	472,900	427,000	148,600	165,800	131,500	—	—	—
1986	460,200	484,200	436,200	157,700	175,300	140,100	—	—	—
1987	463,100	492,900	433,300	166,500	184,200	148,700	—	—	—
1988	451,800	488,100	415,500	185,600	205,400	165,800	—	—	—
1989	418,700	458,100	379,300	210,500	232,800	188,300	—	—	—
1990	367,100	396,300	337,800	217,100	238,600	195,700	0	0	0
1991	336,600	363,700	309,600	226,500	248,200	204,800	200	500	0
1992	319,900	342,800	296,900	235,400	257,300	213,500	800	1900	0
1993	300,500	317,900	283,000	236,200	256,500	215,800	3600	8200	0
1994	277,000	—	239,800	241,300	260,500	222,200	90,00	19,400	0
1995	255,500	—	187,800	247,600	264,800	230,400	19,700	36,800	2700
1996	233,100	—	140,300	263,700	280,900	246,500	31,900	55,300	8600
1997	207,700	—	99,800	257,300	274,300	240,200	41,800	72,400	11,200
1998	182,000	—	74,000	256,500	273,500	239,600	53,800	88,800	18,800
1999	155,200	—	53,600	266,700	282,700	250,800	69,800	108,500	31,100
2000	134,100	—	29,300	267,600	282,400	252,900	85,200	123,600	46,800

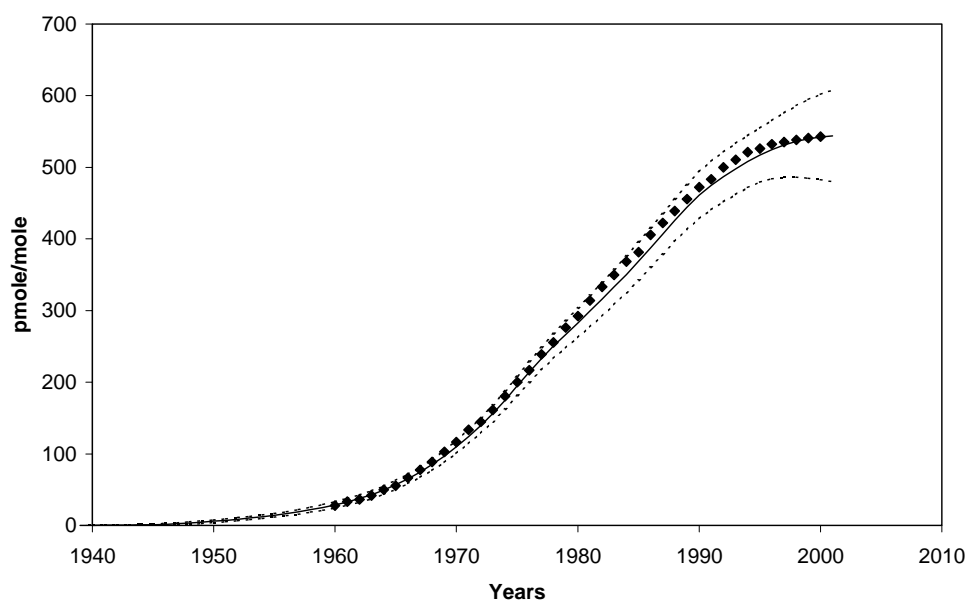


Fig. 7. Atmospheric Concentrations of CFC-12. Filled diamonds—observations reported in [Prinn et al. \(2000\)](#) with newer data from [AGAGE \(2002\)](#). Solid line—concentrations calculated from mean estimated emissions and 100 year atmospheric lifetime ([Prinn and Zander, 1999](#)); dotted lines—95% confidence limits based solely on uncertainty in emissions.

Agreement between the emissions of HFC-134a calculated here and the values reported by Parties to the Kyoto Protocol in [UNFCCC \(2000\)](#) is less good. In 1990, the total of the latter was 810 Mg (compared to less than 100 Mg from this work). The Parties reported 22,338 Mg in 1995 and 44,846 in 1998 (19,700 and 53,800 from this work). Emissions reported under the Kyoto Protocol can be derived in several ways: annual

emissions can be set equal to annual consumption; emissions can be derived from an estimate of the number of systems using the substance and emission factors from each system (“bottom-up” methodology) or they can be derived from overall sales into particular categories of system and emission functions that account for the proportions used to fill new equipment and to service existing systems (“top-down” methodology)

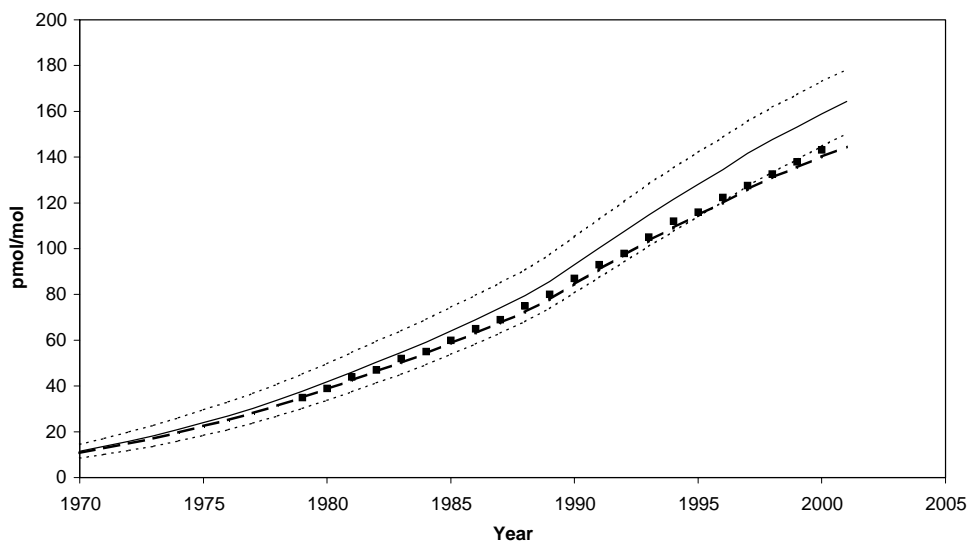


Fig. 8. Atmospheric concentrations of HCFC-22. Filled squares—from [Prinn et al. \(2000\)](#) and [AGAGE \(2002\)](#). Solid line—concentrations calculated from mean estimated emissions and 12 year atmospheric lifetime ([Kurylo and Rodríguez, 1999](#)), with its 95% confidence limits based only on emission uncertainty (dotted lines). Dashed line—concentrations calculated from mean estimated emissions and 10 year atmospheric lifetime ([Prinn et al., 2000](#)).

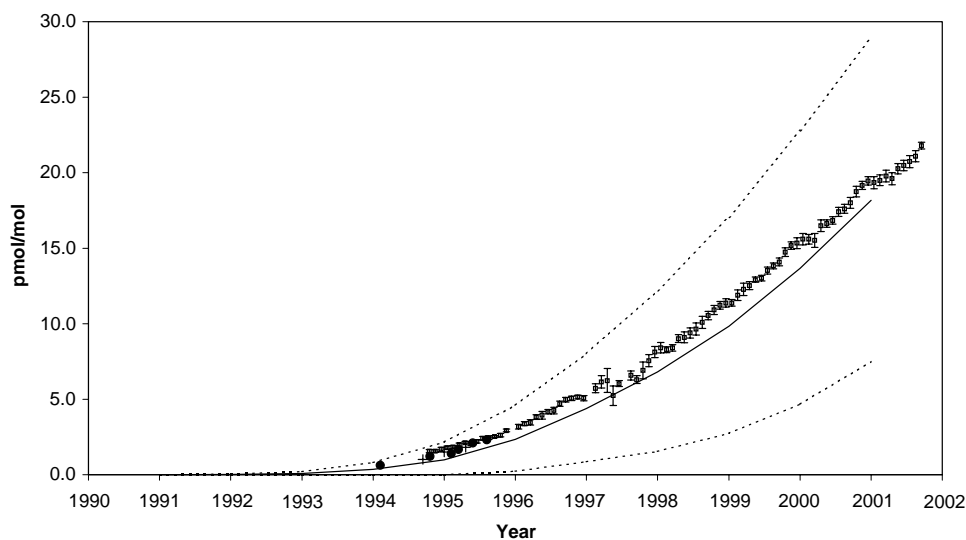


Fig. 9. Northern hemispherical concentrations of HFC-134a: filled circles—from [Montzka et al. \(1996\)](#); crosses—from [Oram et al. \(1996\)](#); points with error bars—monthly data for Mace Head, Ireland from [AGAGE \(2002\)](#); solid line—concentrations calculated from mean estimated emissions and 14 year atmospheric lifetime ([Kurylo and Rodríguez, 1999](#)), with its 95% confidence limits based only on emission uncertainty (dotted lines).

([IPCC, 2000](#)). There is no requirement for consistency between Parties and emissions may be reported as aggregates of all HFCs, or there may be no report of HFCs at all. Hence it is all the more remarkable that the values for 1995 and 1998 lie within the uncertainty of the annual estimates for those years calculated in this work.

8. Conclusions

For CFC-12 and HFC-134a, atmospheric concentrations calculated from the emissions estimated here are in good agreement with observations and it would appear that the emission functions adequately describe the

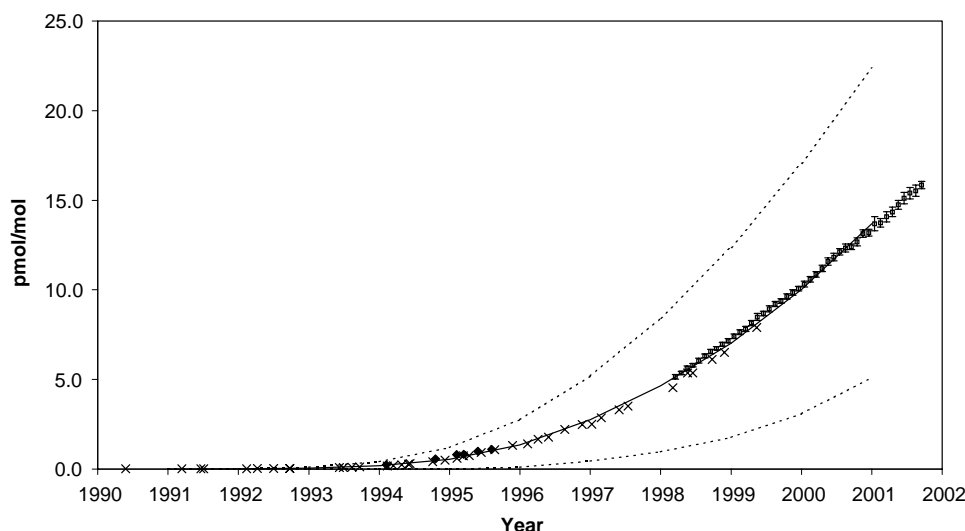


Fig. 10. Southern hemispherical concentrations of HFC-134a: filled diamonds—from Montzka et al. (1996); crosses—measurements at Cape Grim, Tasmania (*personal communication*, P. Fraser); points with error bars - monthly data for Cape Grim from AGAGE (2002); solid line—concentrations calculated from mean estimated emissions and 14 year atmospheric lifetime, with its 95% confidence limits based only on emission uncertainty (dotted lines).

relationship between the quantity in use and the extent to which it is released into the atmosphere. It is therefore surprising that the agreement between observation and calculation is poorer for HCFC-22. Assuming that there are no errors of calibration or analysis in the observed concentrations, the calculated values could be made to fit either with progressively lower emissions over 20 years or by using a lifetime of 10 years (as in Prinn et al., 2000). The first alternative is not impossible but it is highly unlikely that there has been a linear improvement in containment; such improvements tend to be stochastic, leading to curvature in the atmospheric concentration record (McCulloch et al., 2001).

The production and sales records for the three compounds show the expected fall in the amounts of CFC-12 used in refrigeration after the Montreal Protocol came into effect. This does not seem to have been accompanied by significant substitution by HCFC-22, for which demand in refrigeration grew linearly at 7400 Mg yr^{-1} over the whole period from 1971 to 2000 (with a coefficient of variance, R^2 , of 0.97). This is consistent with the properties of the two refrigerants; given the greater volatility of HCFC-22, direct substitution in existing systems is unlikely and other technical considerations have meant that the two fluids were used in different applications. The time series for use of HCFC-22 indicates that demand is governed by organic growth rather than substitution for CFC-12.

On the other hand, the values for use of HFC-134a in refrigeration are consistent with substitution for CFC-12, albeit at much lower rate; an 80% reduction in CFC

requirement has been substituted only to the extent of 25% by HFC-134a. This is consistent with improved technology to curtail leakage and so enable lower system charges which, in turn, translate into less demand. For the same reason, the emission function for HFC-134a over the period 1990–2000 was not significantly different from that of CFC-12. The lower absolute rate of leakage and lower absolute charge sizes combining to maintain a similar relative rate of loss.

Finally, it is likely that the bank of CFC-12 in existing equipment is essentially exhausted and that most of the emissions are sourced from current production. Thus the emissions of CFC-12 should respond sharply to any further drop in its production and use. HCFC-22 and HFC-134a have significant banks in existing equipment and so their emissions would not demonstrate such an immediate connection with use.

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