# IMPACTS ON GLOBAL OZONE AND CLIMATE FROM USE AND EMISSION OF 2,2-DICHLORO-1,1,1-TRIFLUOROETHANE (HCFC-123)

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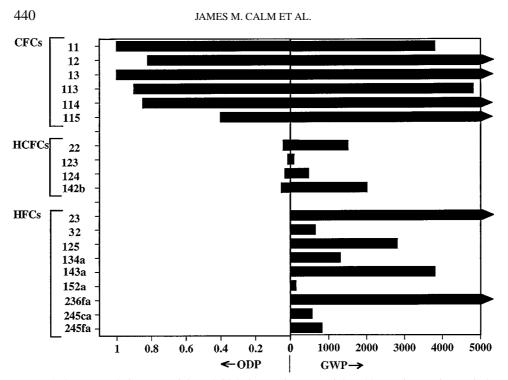
Abstract. Analyses of emissions, and consequent chlorine loading, show that projected use of 2,2dichloro-1,1,1-trifluoroethane (HCFC-123) will result in a virtually indiscernible impact on stratospheric ozone. Parametric scenarios uphold this conclusion, even for extreme levels of emissions far exceeding those of current technologies and practices. Additional scenarios reaffirm the conclusion for continued use - beyond the scheduled phaseout date - as a refrigerant in closed systems. By contrast, use of this compound offers unique opportunities to reduce global warming. Moreover, time-dependent analyses show that the minimal contribution to stratospheric chlorine from HCFC-123 emissions will not peak until more than a decade after the residual peaks of chlorine and bromine, from prior chlorofluorocarbon and halon releases, subside. While no single index exists to compare the relative demerits of ozone depletion and climate change, three conclusions are clear. First, reversal of the buildup of bromine and chlorine (i.e., healing of the 'ozone layer') is underway and progressing on target, while sufficient practical remedies for global climate change are far more difficult. Second, the analyses show that phaseout of all chlorinated, and conceptually - but much less probably - all brominated, compounds of anthropogenic origin targets some compounds that provide environmental benefits. Most chlorinated and brominated compounds do warrant phaseout; the exceptions are those with very short atmospheric lifetimes, and consequent low ozone depletion potential (ODP), that also offer offsetting environmental benefits. And third, since new global environmental concerns may, and probably will, be identified in the future, a more scientific approach is needed to determine environmental acceptability or rejection.

# 1. Introduction

Scientific assessments and regulatory actions usually group organohalides by their molecular composition. These broad distinctions imply degrees of relative concern with their potentials, upon emission, for depletion of stratospheric ozone. The chlorinated and fluorinated species are most commonly divided into the chlorofluorocarbon (CFC), hydrochlorofluorocarbon (HCFC), and hydrofluorocarbon (HFC) families (WMO, 1995; UNEP, 1993). These distinctions follow similarities in industrial applications and comparative magnitudes for ozone depletion potential (ODP) when released. As shown in Table I, which addresses the chemicals used and under consideration as refrigerants, the ODPs for these groups are of the order of 1 for CFCs, 0.01–0.1 for HCFCs, and less than 0.001 – approximately zero –



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*Figure 1.* Ozone Depletion Potentials and Global Warming Potentials (100 year integration period) for selected refrigerants.

for HFCs. Also shown in Table I are the global warming potentials (GWPs) as determined by Intergovernmental Panel on Climate Change (IPCC, 1995, 1996) for an integration period of 100 years. Figure 1 presents a summary of ODPs and GWPs in graphical form.

Simple chlorocarbons (CCs), such as tetrachloromethane (carbon tetrachloride), are generally considered with the CFCs based on both ODP and atmospheric lifetime ( $\tau_{atm}$ ). Likewise, hydrochlorocarbon (HCC) chemicals, such as 1,1,1-trichloroethane (methyl chloroform), usually are associated with the HCFCs. And, fluorocarbons (FCs, also identified as perfluorocarbons, PFCs, for emphasis), such as hexafluoroethane (perfluoroethane), are grouped with the HFCs, though higher concerns arise for their atmospheric persistence and global warming (IPCC, 1995, 1996). Based on the aggressive behavior of bromine for ozone depletion (e.g., see WMO, 1995), brominated compounds, including the halons and methyl bromide, generally are viewed as of similar or greater concern as CFCs. The remaining organohalides usually are discounted, as not posing a concern or having lesser industrial significance.

The HCFC group initially was perceived as acceptable, owing to reduced atmospheric stability linked to the hydrogen substituents (WMO, 1990). This perspective was tempered with further studies, which showed the need for more aggressive measures to return to targeted ozone levels. The revised perception recog-

Group	Chemical	$ au_{ m atm}$	ODP <sup>a</sup>	GWP <sup>b</sup>	
Fluorochemical number	formula	(yr)			
NONFLAMMABLE					
Bromofluorochemicals					
12B1	CBrClF <sub>2</sub>	20	5.1	Unknown	
13B1	CBrF <sub>3</sub>	65	12	5 400	
Chlorofluorocarbons (CFCs)					
11	CCl <sub>3</sub> F	50	1.0	3 800	
12	$CCl_2F_2$	102	0.82	8 100	
13	CClF <sub>3</sub>	640	$\sim 1$	11 700	
113	$CCl_2FCClF_2$	85	0.90	4 800	
114	$CClF_2CClF_2$	300	0.85	9 200	
115 <sup>c</sup>	CClF <sub>2</sub> CF <sub>3</sub>	1 700	0.40	9 300	
Hydrochlorofluorocarbons (HCFCs)					
22	CHClF <sub>2</sub>	13.3	0.04	1 500	
123	CHCl <sub>2</sub> CF <sub>3</sub>	1.4	0.014	90	
124 <sup>c</sup>	CHClFCF3	5.9	0.03	470	
142b <sup>c</sup>	$CH_3CClF_2$	19.5	0.05	1 800	
Hydrofluorocarbons (HFCs)					
23	CHF <sub>3</sub>	250	< 0.0004	11 700	
125 <sup>c</sup>	CHF <sub>2</sub> CF <sub>3</sub>	36	< 0.00003	2 800	
134a	CH <sub>2</sub> FCF <sub>3</sub>	14	< 0.000015	1 300	
236fa <sup>d</sup>	CF <sub>3</sub> CH <sub>2</sub> CF <sub>3</sub>	250	$\sim 0$	6 300	
245fa <sup>e</sup>	$CHF_2CH_2CF_3$	8.8	$\sim 0$	820	
Fluorocarbons (FCs) <sup>f</sup>					
14	CF <sub>4</sub>	50 000	$\sim 0$	6 500	
116 <sup>c</sup>	CF <sub>3</sub> CF <sub>3</sub>	10 000	$\sim 0$	9 200	
218 <sup>c</sup>	CF <sub>3</sub> CF <sub>2</sub> CF <sub>3</sub>	2 600	$\sim 0$	7 000	
Others					
744 (carbon dioxide)	CO <sub>2</sub>	>50	0	1	
FLAMMABLE <sup>g</sup>					
Hydrofluorocarbons (HFCs)					
32°	$CH_2F_2$	6.0	$\sim 0$	650	
143a <sup>c</sup>	CH <sub>3</sub> CF <sub>3</sub>	55	$\sim 0$	3 800	
152a <sup>c</sup>	CH <sub>3</sub> CHF <sub>2</sub>	1.5	$\sim 0$	140	
245ca <sup>h</sup>	CH <sub>2</sub> FCF <sub>2</sub> CHF <sub>2</sub>	7	$\sim 0$	560	

TABLE I
Atmospheric properties of refrigerants

	(Continued)			
<i>Group</i> Fluorochemical number	Chemical formula	τ <sub>atm</sub> (yr)	ODP <sup>a</sup>	GWP <sup>b</sup>
Others including hydrocarbons				
170 (ethane)	CH <sub>3</sub> CH <sub>3</sub>	0.39	0	Unknown
290 (propane)	CH <sub>3</sub> CH <sub>2</sub> CH <sub>3</sub>	0.048	0	Unknown
600 <sup>c</sup> (n-butane)	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	0.017	0	Unknown
600a (isobutane)	CH(CH <sub>3</sub> ) <sub>2</sub> CH <sub>3</sub>	0.018	0	Unknown
717 (ammonia)	NH <sub>3</sub>	0.32	0	Unknown
1270 <sup>c</sup> (propylene)	CH <sub>3</sub> CH=CH <sub>2</sub>	0.0031	0	Unknown

<sup>a</sup> Based on 2-D chemical-transport model analyses in WMO (1995).

<sup>b</sup> For 100-yr integration time horizon (ITH) (IPCC, 1996, and Orkin et al., 1994).

<sup>c</sup> Primarily used as a blend component.

<sup>d</sup> Replacement for CFC-114 for centrifugal chillers for naval use and for nuclear reactors.

<sup>e</sup> Candidate (not commercialized) to replace HCFC-123 in centrifugal chillers in larger capacities, but not suitable to retrofit CFC-11 and HCFC-123 equipment.

<sup>f</sup> Fluorocarbon (FC) without hydrogen, often identified as a perfluorocarbon (PFC) for emphasis. <sup>g</sup> For safety reasons, most uses are in very small systems to limit amounts, in blends with nonflammable components to suppress flammability, and in industrial settings. Use of isobutane and propane-isobutane blends has become the norm in domestic refrigerators in some countries, most notably Germany.

<sup>h</sup> Candidate (not commercialized) to replace HCFC-123 in centrifugal chillers, but not suitable to retrofit CFC-11 and HCFC-123 equipment.

nizes HCFCs as critical transition compounds, necessary to accelerate retirement of CFCs, but still warranting eventual phaseout (UNEP, 1991).

The progression in HCFC acceptability is mirrored in the Montreal Protocol and its amendments. This landmark international accord stipulates measures to protect the stratospheric ozone layer. Among its key provisions are requirements to halt production of compounds containing bromine and chlorine. The original provisions of the Montreal Protocol, signed in 1987, did not regulate HCFCs (UN, 1987). The 1990 (London) amendments set a nonbinding goal for their phaseout by 2040 or, if possible, by 2020 (UNEP, 1991). The 1992 (Copenhagen) amendments scheduled phased reductions and a binding halt to HCFC production in developed countries by 2030 (UNEP, 1993). The stepped reductions were adjusted and the *service tail*, a limited amount allowed for 2020–2030 to meet service needs of previously installed equipment, was reduced by approximately 10% in the 1995 (Vienna) amendments (UNEP, 1996). Some countries have proposed new amendments to further reduce production and accelerate the phaseout of HCFCs (UNEP, 1997a,b). While these amendments were rejected by the Parties (signatory countries to the

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Montreal Protocol) at a meeting in September 1997, they illustrate a desire by some nations for more aggressive actions to address ozone-depleting substances.

Many researchers and manufacturers turned to FCs and HFCs as long-term alternatives to ozone-depleting substances. As shown in Table I, most FC (the exceptions are those with unsaturated bonds) and some HFCs have very high GWPs and long atmospheric lifetimes. Indeed, these gases are among the six chemicals and chemical groups addressed in the subsequent international accord, the Ky-oto Protocol (UN, 1997), to control emissions of greenhouse gases. Attention to global warming is spurring renewed examination of hydrocarbons (e.g., propane, butane, and isobutane) and other nonhalogenated substitutes (e.g., ammonia, carbon dioxide, and water). Each of them, however, poses new concerns with regard to performance and/or safety as refrigerants.

Two additional dimensions complicate analyses of the environmental impacts of refrigerant releases. First, the global warming impact of those containing chlorine or bromine is partially offset by reduction of the greenhouse effect from destroyed ozone, itself a greenhouse gas. This effect is tied to the release rates and ODPs of individual compounds. It is pronounced for CFCs, reduced for the HCFCs, and negligible for the HFCs since they have near-zero ODPs. Second, refrigerant use requires energy use, to drive the refrigeration cycle, as dictated by fundamental thermodynamic principles. While a similar linkage exists for foam blowing agents when used to manufacture thermal insulation products, there is no or almost no energy linkage for chemical uses as aerosol propellants, fire suppressants, or solvents. The energy linkage is not addressed in many influential assessments (e.g., IPCC, 1995, 1996).

Multiple studies have shown that the radiative forcing (global warming effect) from refrigerant releases is small compared to that from greenhouse gas emissions (dominantly carbon dioxide) from related energy use (Calm, 1993; Fischer et al., 1991; March, 1997; Sand et al., 1997). These energy-related emissions depend on several factors, notably fuel selection (or generation mix for electricity), application operating conditions, and equipment efficiency (Calm, 1993). Where the first two are constrained, as usually is true, the emission levels are dominantly determined by efficiency, which is sensitive to the refrigerant selection. CFCs – and CFC-11 in particular – offered the highest attainable efficiencies for many applications, but their production has been stopped in developed countries (and will be stopped in most others) to protect the stratospheric ozone layer.

## 1.1. HYDROCHLOROFLUOROCARBON-123

One of the short-lived HCFCs, 2,2-dichloro-1,1,1-trifluoroethane (HCFC-123), offers efficiencies that approach those of CFC-11. HCFC-123 is unique for three reasons. First, its very short atmospheric lifetime of 1.4 years translates to one of the lowest ODPs among HCFCs. Moreover, its dominant use is in closed systems, for which containment technologies have greatly reduced emissions, to below 1%/y and to less than 0.5%/y in some equipment. The analyses presented below show its net impact on stratospheric ozone depletion to be less than 0.002% of the total from all natural and anthropogenic chemical emissions over the next century, even with continued use beyond its scheduled phaseout date. Second, HCFC-123's GWP is among the lowest for refrigerants and only 1-11% of identified alternatives. Third, its high thermodynamic efficiency and low GWP offer reductions in net greenhouse gas emissions, expressed in equivalent carbon-dioxide, of 11-17% compared to commercialized alternatives for its primary use, to cool large commercial and institutional buildings (Calm and Didion, 1997). Phaseout of HCFC-123 will force use of less-efficient alternatives that, as shown below, could increase greenhouse gas emissions by 0.7-1.1 million metric tons of carbon equivalent per year (2.5-4.1 million metric tons of carbon dioxide equivalent per year). These amounts correspond to approximately 0.5% of the emissions of the commercial sector in the United States. This fraction is not large as a percentage of total radiative forcing, but it is one that serves no purpose in view of the negligible impact on ozone depletion.

The majority of HCFC-123 use is as a refrigerant in large chillers, for airconditioning and process refrigeration systems, as a replacement for CFC-11.\* Much lesser amounts are used as components of fire suppressants, for both streaming and total-flooding uses, and as intermediates to make other chemicals. Despite thermophysical similarities, HCFC-123 has not replaced CFC-11 in the largest applications previously served by CFC-11, notably as a foam blowing agent or aerosol propellant. Rejection for these uses stems from regulations on HCFC substitution, concerns with limited chronic toxicity in open systems, differences in materials compatibility, higher cost, and existence of alternatives. Similar considerations as well as dissimilar solvency inhibit its use as a solvent to replace CFC-113. Very small amounts are used as precision solvents for special purposes, but the largest manufacturers of HCFC-123 no longer market it for this application. Current uses, therefore, are almost entirely in applications with extremely low emission rates.

The importance of HCFC-123 as a refrigerant stems from its thermodynamic efficiency, a factor that leads to energy savings and corresponding reductions in related greenhouse gas emissions. The theoretical advantage of HCFC-123 over current alternatives is 3–5% for an ideal cycle (Calm and Didion, 1997); the difference in efficiencies for the best available equipment is even higher, namely 9–20% (ARI, 1996). The theoretical difference reflects ultimate limits in basic vapor-

<sup>\*</sup> Chillers are refrigeration machines that cool water, brines, or process fluids by a vaporcompression (reverse Rankine), absorption, or other thermodynamic cycle. Their most common application is in central systems in large buildings or complexes, such as offices, campuses, shopping centers, hospitals, hotels, and military installations. The chilled water or brine is piped through the building or buildings to other devices, such as zoned air handlers, that use the cooled water or brine to air condition (cool and dehumidify) occupied or controlled spaces. By their nature, both efficiency and reliability are critical attributes of chillers.

compression, refrigeration cycles. The second range indicates achieved differences in an intensely-competitive market based on numerous engineering factors and attainable optimization (Calm and Didion, 1997). The only commercialized refrigerant offering higher performance is CFC-11, which is no longer manufactured in developed countries pursuant to the Montreal Protocol. Like CFC-11, HCFC-123 requires high displacement in vapor-compression (modified, reverse-Rankine) cycles, which are the mainstay based on performance and cost. This characteristic limits the practical suitability of HCFC-123 to large systems, using turbo (centrifugal) compressors. Negligible amounts – perhaps a tonne per year worldwide – are used in refrigerant blends where high glide is desired, but only in closed systems with comparatively small capacities.

#### **1.2. REPLACEMENTS**

When introduced, HCFC-123 was perceived as a transition refrigerant pending identification of alternatives with zero ODP. Among the most promising options, 2-(difluoromethoxy)-1,1,1-trifluoroethane (HFE-E245fa1) was found to react explosively with glass and to be unstable with fibrous-glass motor materials (Doerr et al., 1993). 1,1,2,2,3-Pentafluoropropane (HFC-245ca) was found to be flammable at some test conditions (Smith et al., 1993) and not suited for CFC-11 and HCFC-123 retrofits (Glamm et al., 1996). Blending it with other components to inert its flammability degrades its performance (Glamm et al., 1996).

Manufacturers have avoided flammable refrigerants for safety reasons, recognizing that the risk is higher with the pressurization necessary for vapor-compression cycles. Hydrocarbons and others have been used in low-charge systems, such as small refrigerators, that require no more than 0.5 kg of refrigerant, but compromise safety in larger systems. A large chiller would require several hundred kg, which would pose a significant risk. Carbon dioxide offers attractive environmental characteristics as a refrigerant, but its low critical temperature and very high pressures preclude effective use in chillers. It is being examined for automotive air conditioners and other small systems, but studies have found its efficiency to be unattractive in larger systems (Bullock, 1996). Ammonia is flammable, more toxic, and incompatible with some common fabrication materials, but it is widely used in industrial refrigeration. Its use in a centrifugal chiller would require eight or more stages of compression, a highly impractical option. High-pressure refrigerants and absorption cycles remain alternatives, and are commercially applied. The primary attractions to low-pressure, centrifugal designs, using HCFC-123 and CFC-11 before it, are higher efficiency - of growing importance in the specter of global warming – and lower life-cycle costs based on the energy savings.

1,1,1,3,3-Pentafluoropropane (HFC-245fa) remains a promising candidate, though its operating pressure is higher than for CFC-11 and HCFC-123, forcing the use of construction suitable for pressure vessels. Also, its performance is expected to be 2-3% lower in the most common capacities for centrifugal chillers, and it is

unlikely to be suitable for retrofit of equipment designed for CFC-11 or HCFC-123 (Calm and Didion, 1997; Hughes, 1997). Tests of HFC-245fa are underway, and cycle modifications may enable chillers using it to approach the efficiency of HCFC-123 in very large machines with multistage designs, but not in the most widely-used sizes. Tests show HFC-245fa to be nonflammable (Richard, 1967; van Dijck, 1996), but it approaches the flammability envelope and may become marginally flammable at extreme test conditions (Smith et al., 1994; Smith and Tufts, 1994).

While the possibility of as-yet undiscovered alternatives cannot be excluded, they remain elusive. Chemical producers, equipment manufacturers, governmental and independent researchers, environmental groups, and others have conducted exhaustive studies in search of a replacement. There are strong financial incentives that motivated repeated earlier searches in addition to the environmental motivation today. McLinden and Didion (1987) present a systematic search and recount efforts by predecessors to show that the candidates are limited. McLinden (1990) analyzes the implications of physical parameters on refrigeration cycle design. Calm and Didion (1997) examine the physical and thermodynamic traits of chemicals to show both that the qualifying candidates are constrained and that those already examined or in use are likely to offer the highest potentials. Calm (1993) and Fischer et al. (1994) show that identified not-in-kind technologies, namely those employing thermodynamic cycles other than the classic vapor-compression (modified reverse-Rankine) cycle to avoid the need for conventional and similar refrigerants, will increase greenhouse gas emissions.

## **1.3. STRATOSPHERIC OZONE DEPLETION**

Traditional analysis of the potential for ozone-depletion, by species, equates ultimate releases to initial production and multiplies that amount by a relative measure of the depletion potential, the ODP (Wuebbles, 1981, 1983). Recent assessments have integrated the effect over time to project coincident contributions from old releases, of long lived CFCs and halons, with recent releases of short-lived compounds (WMO, 1995; Solomon and Albritton, 1992). The present analysis examines projected HCFC-123 emissions as well as their timing and impact on ozone depletion. Three key differences are suggested from prior analyses and projections of emissions. First, the magnitude of expected HCFC-123 production is much lower than that assumed in earlier assessments (WMO, 1995; EPA, 1995). Second, the emission rates in closed systems, including all associated releases have been radically lowered, more than eight-fold in the last decade alone. Chillers installed in the last three years typically lose less refrigerant in their lifetime, including manufacturing and projected disposal, than those now being retired did in one year. Moreover, further technology changes are likely to halve one component of the remaining losses in the next year, as discussed below, though no credit is taken for such improvements in this study. And third, the lag between production

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#### TABLE II

## Scenarios analyzed

Na	me	Basis	Purpose		
1:	IPCC base case.	Assessment Table 2.5d(ii) (IPCC, 1996).	Consistency with accepted analyses.		
2:	Reference case (no HCFC-123 use).	Scenario 1 modified to exclude HCFC-123 emissions.	Base case for subsequent comparisons.		
3:	Projected HCFC-123 emissions.	Reference case (scenario 2) with forecast HCFC-123 refrigerant use added.	To examine impacts of probable HCFC-123 refrigerant use under the current Montreal Protocol phaseout schedule.		
4:	Worst-case HCFC-123 emissions.	Reference case with worst-case, HCFC-123 refrigerant emissions added.	To test sensitivity to a combination of extreme emission assumptions.		
5:	HCFC-123 reprieve.	Reference case with added HCFC- 123 emissions for continued refrigerant use.	To examine projected HCFC-123 emissions with continued use.		
6:	Worst case HCFC-123 reprieve.	Reference case with added worst- case HCFC-123 emissions for continued refrigerant use.	To test the sensitivity to a combination of extreme emission assumptions with continued HCFC-123 use.		
7:	Cap revision.	Scenario 1 with all HCFC emissions reduced by 9.7% after 2010.	Approximation (see text) to show the consequences of the lowering the HCFC cap from 3.1% to 2.8%.		
8:	CFC influence removed.	Scenario 1 with all CFC emissions removed after 1995 and all HCFC emissions stabilized at 2020 levels after that year.	Sensitivity analysis to test the influence of hypothetical, complete CFC phaseout; continued residual effects of prior releases; and continued, stabilized use of all HCFCs.		

and emission, inherent 'banking' or 'sequestering', defers most of the impact until residual CFC and halon effects have receded from their peak as shown below.

# 2. Evaluation Scenarios to Examine Ozone Depletion Consequences

Eight scenarios are analyzed to assess the global environmental impact of HCFC-123 use as summarized in Table II. The last two are not unique to HCFC-123, but are examined because of their possible impact on broader HCFC policy issues.

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Scenario 1, which essentially corresponds to the base case of the most recent international assessment on climate change (IPCC, 1996), establishes consistency with accepted approaches. Only the halocarbon portion of that study is considered here. The scenario is a modified version of the earlier IS92a scenario, developed by the IPCC, to better account for halocarbon production and emissions based on the 1992 (Copenhagen) amendments to the Montreal Protocol. Scenario 2 then backs out the HCFC-123 component to provide a reference case for subsequent analyses. As discussed below, our analyses suggest that the assumptions for HCFC-123 in the IPCC scenario significantly overestimate those emissions.

Scenarios 3–6 sequentially add projected HCFC-123 emissions back in for four cases summarized in Table II. They examine the probable and worst-case release estimates both for the scheduled phaseout and for a test case, to evaluate the impact of continued use of HCFC-123 as a refrigerant. This use offers unique environmental benefits, as discussed above, that suggest a need to examine resulting advantages and disadvantages. There are other reasons to consider retention of individual chemicals such as costs or effectiveness, but we chose to limit the present comparisons to offsetting environmental benefits.

The two reprieve scenarios (5 and 6) examine the impacts of hypothetical exemption from phaseout under the Montreal Protocol for refrigerant use. Other limits still will restrict HCFC-123 application as discussed below.

Scenario 7 approximates the cap reduction, from 3.1% to 2.8%, based on the 1995 (Vienna) amendments to the Montreal Protocol. The 'cap' refers to the calculated (ODP-weighted) level of HCFC consumption plus the stated multiplier times the calculated level of CFC consumption, both based on 1989 data. It serves as the base amount, to determine stepped-reduction levels leading to the phaseout of HCFCs. No attempt was made to factor in increased resistance to HCFCs before 2020 based on the lowered cap. As a consequence, scenario 7 slightly overstates chlorine loading to the atmosphere expected with the cap reduction. Similarly, no intra-HCFC shifting is made to account for intensified regulations, likely to target high-ODP HCFCs to preserve allowances for HCFCs with low ODPs.

The final scenario, number 8, is a strictly hypothetical case with no relationship to existing international agreements, to explore the consequence of HCFC use had full CFC phaseout occurred by 1996. HCFC levels are stabilized in 2020, on the arguable premise that technologies will have advanced sufficiently to allow either stabilized levels of use, or growth in use with offsetting advances in emissionreduction technologies and practices.

Scenarios 7 and 8 go beyond the stated focus of this paper in order to examine the sensitivity of projected chlorine/bromine loading (CBL), as explained below, to the effect of all HCFCs, not just HCFC-123.

## 3. Emission Projections

Although aggregate production data are published for the most widely used fluorochemicals (AFEAS, 1997), HCFC-123 is not included. The data aggregation effort does not publish the reported statistics for chemicals for which less than three manufacturers meet threshold quantities, to avoid the opportunity to determine production data for individual manufacturers.

The estimated emission rates for HCFC-123 that were used in prior ozonedepletion assessments exceeded 23 kt/y in 2010 (WMO, 1995; EPA, 1995), but they are believed to be incorrect. Discussions with the investigators who supplied the projections indicate that they were coarse estimates, resorted to in the absence of rigorous data. They were predicated on assumed use of HCFC-123 to replace CFC-11 as a foam blowing agent and aerosol propellant, which has not occurred and is not likely based on the existence of less expensive, more suitable alternatives. An assessment of greenhouse gas emissions discusses the difficulty in obtaining emissions data (EIA, 1994). More recent government reports for U.S. releases in 1995 indicate 50 t/y – not kt/y – (EPA, 1997).

Sidebottom and Franklin (1996) observed that 'no data are yet available on HCFCs-123 and 124, but the production of these compounds is believed to occur on a much smaller scale than for the other three HCFCs listed above', namely HCFCs are 22, 141b, and 142b with 1994 emissions of 219, 23.1, and 11.9 kt/y, respectively. The HCFC-142b production rate and emission flux from the source cited by Sidebottom and Franklin were since revised to 38.4 and 10.7 kt/y, respectively, for 1994 and to 38.7 and 12.0 kt/y for 1995 (AFEAS, 1996 and 1997). For HCFC-123 'production to occur on a much smaller scale' implies rates well below those. Indeed, ECETOC (1996) estimates worldwide production of HCFC-123 to be only 'several kt/y'.

Historical estimates and future projections were developed, as detailed below, based on forecasts of uses and engineering analyses. These estimates have the advantage of allowing sensitivity studies for different emission scenarios. The resulting release fluxes are consistent with both the limited indications cited (Sidebottom and Franklin, 1996; ECETOC, 1996; EPA, 1995) and with data and forecasts obtained from manufacturers on a confidential basis.

The predictions include *projected* and *worst-case* estimates of worldwide HCFC-123 emissions for both the current phaseout schedule and for a limited exemption, for HCFC-123 use as a refrigerant in closed systems. The estimates were based on analyses of the market for chillers, in which HCFC-123 competes, and releases associated with such chillers. The worst-case scenario combines all assumptions leading to higher aggregate emissions. Moreover, significant multipliers (based on the emission components) are factored in to assure confidence that it would not be exceeded. The four consequent cases are:

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- *Projected emissions* based on the current phaseout schedule (Montreal Protocol with amendments through 1995).
- *Worst-case emissions* for the same case.
- *Projected emissions with continued HCFC-123 use*, solely as a refrigerant in closed systems, assuming removal of phaseout restrictions by 2000.
- Worst-case emissions with continued HCFC-123 use for the same case.

Despite the descriptor used, the data and assumptions used for the *projected-emissions* scenario take no credit for future release-reduction technologies and practices. As such, the resulting estimates are conservative, since some improvements are foreseen. Advances are likely in sealing technologies, including gaskets and seals. Reduced refrigerant charge is expected with further improvement and use of surface enhancement in heat exchangers, leading to reduced service, disposal, and accidental losses. Technologies are being developed that would completely eliminate the small losses associated with lubricant changes (i.e., from refrigerant dissolved in the lubricant). Although less certain, increased use of hermetic motor drives, with associated emission reductions, may result from long-term introduction of hydrostatic bearings. Purge advances are likely, but current designs are so close to zero-emission that further improvements would materially lower only the worst-case scenarios. A near-term opportunity to reduce HCFC-123 emissions, through packaging changes, is discussed below.

## 3.1. CHILLER PROJECTIONS

Although industry statistics are kept for chiller production, the reported data are not disaggregated by compressor type or refrigerant selection. The four manufacturers of centrifugal chillers in the United States, two of which manufacture products using HCFC-123, were contacted to obtain projections on market outlooks. The aggregate statistics and estimates obtained on market shares, by refrigerant and manufacturer, were used to forecast future HCFC-123 chiller use. The forecast beyond 2010 for scenarios 5 and 6 disregards cyclical market swings and simply shows growth as proportional for forecasted economic growth. Figure 2 summarizes expected HCFC-123 chiller production; this forecast accounts both for new construction and replacements in existing facilities. The figure also shows projected CFC-11 to HCFC-123 conversions on a worldwide basis, based on the industry forecasts (ARI, 1997) and projections obtained in the manufacturer interviews. Retrofit to HCFC-123 of chillers using CFC-113, medium-pressure refrigerants (e.g., CFC-12, CFC-114, and R-500 which is a binary blend of CFC-12 and HFC-152a), and high-pressure refrigerants (e.g., HCFC-22) generally is impractical; it requires complete replacement of the compressor and drive as a minimum. HCFC-123 use for such retrofits is not allowed in the United States (GPO, 1994, 1996) or other countries with similar regulations. The conversion potential for HCFC-123, therefore, is effectively limited to remaining CFC-11 chillers. International surveys suggest that 110,000 CFC-11 chillers were in use 1993, or 64% of remaining CFC

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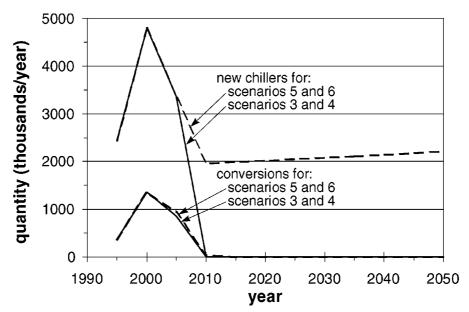


Figure 2. Projected worldwide production of new and converted chillers for HCFC-123 use.

chillers, but very few are being converted outside the United States (UNEP, 1994). The CFC-11 fraction in the U.S.A. is slightly higher, indicating 39,000 (ARI, 1995, 1997) to 47,000 machines (this study) at the start of 1997.

The two reprieve scenarios (5 and 6) examine the impacts of hypothetical exemption from phaseout under the Montreal Protocol for refrigerant use. Other limits still will restrict HCFC-123 application. Physical factors limit its suitability to large machines, using specific (centrifugal) compressor types. The demand for such machinery is constrained by new construction and replacement rates. The market-size and HCFC-123 penetration projections used are based on optimistic rates of economic growth and construction in developing nations. New measures to encourage efficiency improvement, in order to reduce energy-related greenhouse gas emissions, will favor HCFC-123 use. Related measures (e.g., higher insulation levels and more-efficient lighting) to reduce building and process cooling loads will curtail the demand for all chillers and shift the capacities needed to smaller sizes, in which centrifugal machines are less competitive economically.

#### 3.2. EQUIPMENT LIFE

Data for equipment longevity also are sparse. Chiller retirements cannot be estimated by component and material lives, since the parts that wear are replaced with scheduled maintenance. The primary impetus for replacement is to reduce operating costs, since current chiller designs use as little as half the energy of the older machines being retired. One widelycited reference estimates the service life of centrifugal chillers to be 23 years (ASHRAE, 1995). Correlation of equipment shipments, adjusted for commercial construction rates, with historical shipment statistics indicates a life of approximately 25 years. That number was used in the present analysis, although there are reasons to believe that the service life will increase for current equipment. One is that the margin for further efficiency increases is much smaller, since newer machines are closer to theoretical performance limits, removing the primary future motivation to replace current equipment as it ages. Another is that modern lubricant and vibration analyses allow earlier identification of problems, before failures occur. Any increase in service life would lower the forecast emissions, by reducing the frequency of the initial and disposal losses discussed below.

Parametric studies show low sensitivity of emissions to assumed equipment life. A small delay is introduced in the peak emission timing with increased life, but the impact on emission amplitude is small for two reasons. First, the largest component of near-term emissions is associated with losses from older equipment, converted from CFC-11 to HCFC-123. That equipment does not match the performance of optimized HCFC-123 designs, and will not share the cited justification for longer retention. Second, the highest losses, on an annualized basis, are the operating and intermittent ones rather than initial and disposal. Within a credible range, therefore, equipment life has only a minor impact on the findings reported herein.

## 3.3. CHILLER INVENTORIES

The service life estimates address only the mean duration of use. Actual retirements are distributed around the mean for a number of reasons. They include the quality of maintenance, accidents such as fires, failures, changing load requirements, space constraints, and the economics as the machines age. An attempt was made to calculate a standard deviation and to fit a Gaussian distribution to the limited data available. Insufficient historical data were obtained to substantiate or refute this approach, particularly since current trends are perturbed by shifts to alternative refrigerants, for environmental reasons or as hedges. The emissions presented were calculated using the Gaussian distribution; future refinement may be possible with better data.

Consequent inventories of chillers were determined by year by cumulative summation of new chillers less retirements or of conversions less retirements. The two inventories are separately analyzed based on dissimilar emission estimates, as outlined below. Figure 3 shows the projected inventory of new and converted chillers using HCFC-123. The projection is based on the current stock, additions shown in Figure 2, and projected retirements. Table III summarizes projected additions, retirements, and inventories for both new and converted chillers for HCFC-123 use with phaseout under the Montreal Protocol (scenarios 3 and 4). Table IV provides the same information with allowed future use (scenarios 5 and 6).

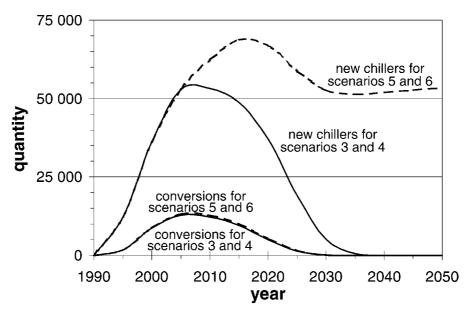


Figure 3. Projected inventory of new and converted chillers using HCFC-123.

TABLE III
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Projected chiller quantities, with HCFC-123 phaseout as mandated by the Montreal Protocol including the 1995 (Vienna) amendments  $^{\rm a}$ 

Years	New HCFC-123 chillers				Retrofits from CFC-11 to HCFC-123		
	Annual	Annual	Ending	-	Annual	Annual	Ending
	production	retirements	inventory		conversions	retirements	inventory
1991–1995	2 4 4 0	0	12 200		360	0	1 800
1996–2000	4 7 90	0	36100		1 360	0	8 700
2001-2005	3 360	0	53 000		850	10	12 800
2006-2010	0	80	52 600		0	130	12 200
2011-2015	0	720	49 000		0	520	9 600
2016-2020	0	2 370	37 100		0	930	5 000
2021-2025	0	3610	19 100		0	730	1 300
2026-2030	0	2780	5 200		0	240	130
2031-2035	0	930	530		0	30	0
2036-2040	0	100	20		0	0	0
2041-2045	0	0	0		0	0	0
2046-2050	0	0	0		0	0	0

<sup>a</sup> The production, retirement, and conversion projections shown are the average annual quantities for the periods indicated. The inventory projections are the installed quantities at the end of those periods.

Years	New HCFC-123 chillers			Retrofits from CFC-11 to HCFC-123		
	Annual Annual Ending Annual Ann		Annual	Ending		
	production	retirements	inventory	conversions	retirements	inventory
1991–1995	2 4 4 0	0	12 200	360	0	1 800
1996-2000	4 790	0	36 100	1 360	0	8 600
2001-2005	3 360	0	53 000	930	10	13 200
2006-2010	1 960	80	62 400	40	130	12 800
2011-2015	1 990	720	68 700	0	520	10 200
2016-2020	2 0 2 0	2 370	67 000	0	950	5 500
2021-2025	2 0 5 0	3 670	58 900	0	780	1 600
2026-2030	2 0 8 0	3 370	52 800	0	280	200
2031-2035	2110	2380	51 400	0	40	0
2036-2040	2 1 4 0	2030	52 000	0	0	0
2041-2045	2 1 8 0	2 0 2 0	52 700	0	0	0
2046-2050	2 2 1 0	2 0 5 0	53 500	0	0	0

TABLE IV Projected chiller quantities, without HCFC-123 phaseout

## **3.4. REFRIGERANT REQUIREMENTS**

The quantities of refrigerant (*charge* quantities) required for each chiller were determined from equipment selections for ranges of representative efficiencies and capacities. There is no preset amount, since large tonnage chillers are customized assemblies of components (heat exchangers, compressors, motors, and accessory devices) produced in discrete-sizes. Two chillers with the same cooling capacity might have different internal volumes based on design temperatures and flow rates, which are determined by location, load factor, and other application factors. Different combinations of heat exchangers and compressors, number of compressor stages for some designs, gear selections for some designs, and other options might be selected to achieve higher efficiency or lower cost for the same capacity and operating conditions. Likewise, the heat exchanger size would vary for a given capacity, based on use of highly enhanced heat transfer surfaces or different tube-bundle arrangements.

Optimized equipment selections were obtained for actual equipment by refrigerant, based on representative operating conditions and capacities. The charge sizes were normalized by capacity and then correlated with efficiency. The resulting regression was used to calculate a weighted average based on industry sales statistics and projections. The range for HCFC-123 was found to vary from approximately 0.2 to more than 0.4 kg/kW<sub>t</sub> (charge mass per unit of cooling capacity), with a weighted average of 0.24 kg/kW<sub>t</sub>. This average is 9% higher than that reported in an earlier study that used a similar approach (Calm, 1991). The earlier study reflected older equipment designs and lower efficiencies than now are prevalent; these difference support the higher charge quantity.

Confidential estimates of current and projected production were obtained from refrigerant manufacturers, to validate these estimates. While a single company manufacturers the majority of HCFC-123 used, market forecasts obtained from its competitors were in reasonable agreement. Adjusted for the initial losses discussed below and for stocking of service inventories, reasonable agreement was found between 1995 sales for refrigerant use and the calculated demand. Precise comparison is not possible, since no data exist on the amount stocked. Whereas HCFC-123 is still a comparatively new refrigerant, inventories by wholesalers, distributors, contractors, and users are still being built up for service and emergency needs.

## 3.5. RELEASE RATES

Refrigerant emissions were divided into four categories, to allow examination of the timing of emissions. These categories and the loss rates used in this study, expressed as a fraction of the operating refrigerant quantity, or *charge*, are as follows:

- *Initial*: This group includes all losses associated with making equipment functional, and specifically those associated with manufacturing, performance and leak testing, transportation, installation, initial charging, field testing, and *shakedown*. While measured data are not available, these losses are very small, except in cases where a significant leak is discovered or a failure occurs during start up. As an average, such losses were estimated at 0.7% based on communications with manufacturers, observations of plant and site tests, and discussions with technicians. A high multiplier, 500%, was applied for the *worst-case* scenario, to insure an adequate margin for uncertainties. Most of the manufacturers and technicians contacted strongly felt that this multiplier was excessive.
- *Operating*: Unlike the initial losses, which occur once in the life of a machine, the operating losses are recurring. They include both leakage and purge releases. Portions of the refrigerant circuit operate below atmospheric pressure in HCFC-123 chillers, and the entire circuit is subatmospheric at some operating conditions. Most leaks, therefore, result in air being sucked in rather than loss of refrigerants. Purge devices remove this air, which would lower performance by acting as a noncondensible gas. Older purges resulted in CFC-11 losses of 8–10% per year, and in extreme cases 15–30% per year, in venting the air. Current designs use condensing systems and charcoal canisters, which are periodically replaced and then reprocessed to recover any trapped refrigerant, to reduce purge losses to near-zero emissions. Whereas the combined leakage and purge make-up rates exceeded 10% annually in the past (Calm, 1993), the four U.S. manufacturers of centrifugal chillers (high- and low-

pressure) all claim to have lowered operating losses to less than 0.5% per year. Test and field data support this claim, which has become a competitive selling point to reduce refrigerant costs and environmental effects. The rate was doubled for the worst-case estimate, to test sensitivity while reflecting confidence in the data.

- Intermittent: Also recurring, these releases include those from maintenance (e.g., in disconnecting hoses and opening systems for major service procedures), accidents, failures, unintentional venting, technician errors, and non-specific causes. The loss rates used herein were based on manufacturer and technician communications as well as anecdotal data. The averaged intermittent losses were modeled as 0.5% per year for projected losses and 2.5% for the worst case analyses. The higher multiplier for this group reflects greater dispersion in the available data from different sources. Not all refrigerant additions (*make-up*) to operating systems imply emissions. Examples include additions to correct initial undercharging and replacement amounts for contaminated refrigerants, recovered for reclaim or disposal, from motor burn-outs or high acid levels.
- *Disposal*: This amount accounts for the refrigerant lost at equipment retirement, a one-time event per machine. It typically is less than 0.5%, with current recovery approaches, but was raised to 1.5% for the analyses, to amortize catastrophic equipment losses. Such incidents are rare, and the refrigerant charge often is not lost or fully lost, when they occur. The *worst-case* scenario was increased to 4.5%. Field observations for appliances and residential equipment suggest higher rates, but differences are linked to the economics of scale. High recovery rates were common for large chillers for economic reasons, long before environmental concerns were raised with refrigerant venting.

The combined *operating* and *disposal* loss rates presented above exceed the average make-up rates calculated from the service histories obtained for more than 400 operating chillers. Conservative values were deliberately chosen, even for the 'projected emissions' scenarios (3 and 5), since these machines are still comparatively young; small emission increases are likely when they undergo major maintenance and also may occur with age.

Two primary sources of fugitive emissions, affecting both the initial and intermittent losses, are being addressed. They include leakage from refrigerant containers and venting with their disposal. HCFC-123 typically is shipped in drums (*barrels*), which are accessed by opening a bung. Bung and joint leakage are not uncommon; technicians indicate that a small fraction of barrels received at job sites are noticeably light and, in very rare cases, empty. Similarly, the tops of emptied barrels must be removed before disposal, resulting in loss of the remaining refrigerant. These drums are not fabricated to withstand the deep evacuation needed for complete vapor removal. Motivated by costs and environmental concerns, the industry is switching to returnable cylinders that will result in lowered leakage and venting. Whereas the loss rates for this study reflect current practice, they are higher than anticipated with a shift to the new container technologies during the next year.

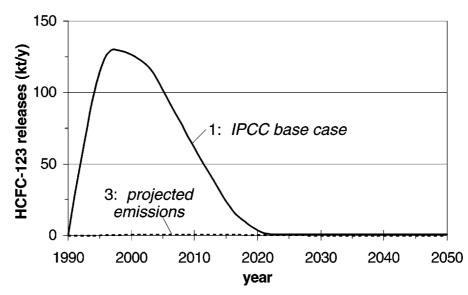
Initial losses were modeled as occurring in the year of installation. Losses related to manufacturing usually precede installation by one to four months. Losses from initial charging and field testing are part of the installation process, which normally occurs shortly after delivery or within one to two months, depending on the status of other construction elements.

Both operating and intermittent losses were treated as continuous, uniform releases. Intermittent losses actually occur periodically or at random for individual machines; the approximation reflects stochastic occurrence for the full population. Any error would be conservative, since major overhauls and repair frequency would be skewed toward the end of equipment life.

Disposal losses were modeled as occurring upon retirement.

No data were found to compare releases for new HCFC-123 chillers and those converted from CFC-11 to HCFC-123. Estimates obtained from technicians were inconsistent, possibly based on the extent of conversions normally performed. The simplest conversions include replacement of incompatible materials and refrigerant changeout. More extensive conversions replace older purges, with condensing purges, and fittings prone to leakage with tighter seals, or brazed connections, to reduce emissions. Full conversions also modify or replace impellers, and drive gears in applicable designs, to maximize performance (capacity and/or efficiency) with HCFC-123. Most manufacturers and technicians reported that the initial losses in conversions are slightly higher to approximately twice those for a new installation; they were doubled for this study. There was general agreement that leakage and purge losses would be higher in converted equipment, and especially so without a purge upgrade. Inclusion of the latter would be almost automatic with most models, but might be omitted where the original purge already was a highly efficient design. Operating losses were increased to 10% for conversions in the projected releases scenario, approximating a purge upgrade and some leakage (mostly air into the chiller, hence longer purge run time) reduction. They were increased to 20% for the worst-case scenario, considering the leakage rates of older, CFC-11 chillers. No adjustment was made to intermittent and disposal losses, since the factors driving them are not substantially different between new equipment and retrofits.

While we believe that the projected and worst-case release scenarios are probable and extreme estimates, respectively, the absence of reliable data is a concern. The probability of exceeding the results for the *worst-case* scenario is very remote for two reasons. First, quite high multipliers were applied to the *worst-case* emission rates, to insure a conservative analysis. And second, even if some loss components did approach the extreme scenario, it is highly unlikely that all would. Nevertheless, the above discussion identifies a number of voids; reliable data for them would enable reduction of the *worst-case* loss scenario to a less extreme increase.



*Figure 4*. Emissions assumed for HCFC-123 in the IPCC (1996) modified IS92a scenario (scenario 1 in this paper) in contrast to the emissions derived for scenario 3.

Purge frequency, purge operating time, refrigerant purchases, and refrigerant use by machine are starting to be logged at many sites. Future collection and analysis of sample data should provide much of the missing data. This sample may be biased, however, since those carefully logging the data probably are the ones most committed to emission reduction.

## 4. Calculated Releases and Time Dependence

Figure 4 contrasts the extremely high emissions assumed for HCFC-123 in the IPCC (1996) modified IS92a scenario (scenario 1 in this paper) to the emissions derived for scenario 3, *projected emissions*. Emissions derived for scenarios 3 through 6 are shown in Figure 5. As discussed above, the HCFC-123 emissions by the IPCC were radically higher, by more than a factor of 50 compared to the *worst-case* scenarios developed here. Scenarios 3 and 5 have a maximum emission of HCFC-123 of less than 0.2 kt/y while the worst-case scenarios have maximum emissions of roughly 0.5 kt/y. In contrast, the peak emission in the IPCC case, scenario 1, is more than 125 kt/y and peaks almost a decade earlier than the scenarios derived here. Note that the IPCC analyses did not address the timing of chiller emissions.

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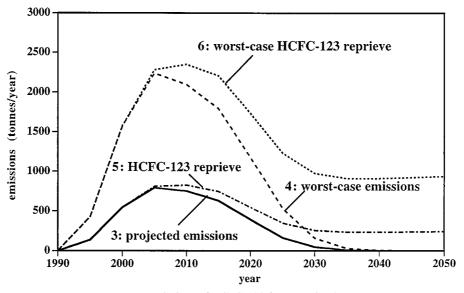


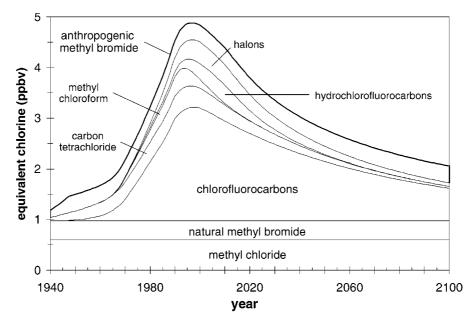
Figure 5. Emissions of HCFC-123 for scenarios 3 to 6.

# 5. Chlorine-Loading Model

Chlorofluorocarbons such as CFC-11, CFC-12, CFC-113, halons such as 1211 (BCFC-12B1) and 1301 (BFC-13B1), plus several other chlorine- and brominecontaining halocarbons appear to be largely responsible for the significant decrease in stratospheric ozone observed over the last few decades (WMO, 1995). Most were released as foam-blowing agents, solvents, aerosol propellants, fire suppressants, and other emissive uses rather than by refrigerant releases or other losses from closed systems. The primary environmental concern from use of these halocarbons has been the potential for chlorine and bromine released from these compounds to destroy significant numbers of ozone molecules in the stratosphere. Atmospheric measurements have linked ozone depletion in the Antarctic and Arctic to emissions of these compounds, while the weight of the evidence on ozone depletion at midlatitudes also appears to be related to anthropogenic halocarbon emissions (WMO, 1995).

Along with model calculations, the concept of chlorine loading, or more conventionally chlorine/bromine loading (CBL), a measure of the chlorine and bromine loading in the atmosphere, has been a powerful tool to analyze policy options to protect the stratospheric ozone layer (Prather and Watson, 1990; WMO, 1995; Wuebbles and Kinnison, 1996). As part of the search for and examination of replacement compounds, CBL is being used in evaluating the potential effects on ozone from potential production and emissions of these replacements.

The concept of CBL combines the knowledge gained from atmospheric observations with analyses from atmospheric models, to evaluate the total amount of

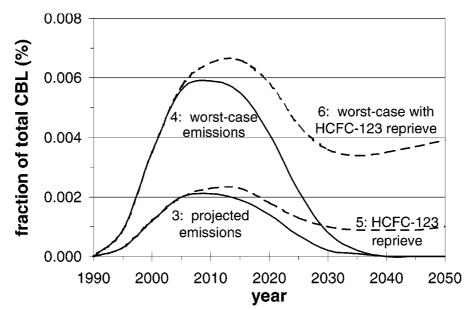


*Figure 6.* Chlorine-Bromine Loading (CBL) for scenario 1. Similar to earlier analyses presented in WMO (1995).

chlorine and bromine reaching the stratosphere, where these halogens can react with ozone. CBL is directly proportional to the surface emissions of the halocarbons, their reactivity as reflected in their atmospheric lifetimes, and the number of chlorine and bromine atoms released per molecule. Model calculations and laboratory measurements indicate that bromine is much more reactive with ozone than chlorine (WMO, 1995). In order to account for both chlorine and bromine, CBL includes a multiplicative factor,  $\alpha$ , on the amount of bromine released into the stratosphere to account for its larger reactivity with ozone. The bromine was multiplied by an  $\alpha$  value of 40 in the earlier WMO (1995) ozone assessment. The CBL values presented here assume that  $\alpha = 60$ , to account for the greater reactivity of each bromine emitted with stratospheric ozone compared to chlorine. This value is based on integration of the relative effects of chlorine and bromine on ozone from a zonally-averaged, chemical-radiative-dynamical model of the global atmosphere (Wuebbles et al., 1991, 1997; Kinnison et al., 1994).

The changes in CBL with time suggest the amount of ozone change expected from past and projected emissions of halocarbons based on consideration of the ozone changes that have occurred already as a result of chlorine and bromine in the atmosphere. This equivalent chlorine is used only for nonsoluble gases, as aerosols such as sea salt (NaCl) and soluble gases like hydrochloric acid (HCl) will be rained out of the atmosphere almost in their entirety, before they can reach the stratosphere and affect ozone.

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*Figure 7*. Percentage difference in CBL due to HCFC-123 for scenarios 3 to 6 relative to total chlorine loading from scenario 2.

# 6. Findings

Figure 6 shows the contribution of the various source gases containing chlorine and bromine to the total CBL. Future emissions assume global compliance with the Montreal Protocol, as represented by scenario 1 based on IPCC (1996). As was discussed for a similar analysis in WMO (1995), this figure indicates that the anthropogenic sources of chlorine and bromine from CFCs, halons, HCFCs, and other ozone-depleting substances have contributed most of the equivalent chlorine in today's atmosphere. Natural sources of CH<sub>3</sub>Cl and CH<sub>3</sub>Br, primarily from the oceans, are only a minor source of current levels of chlorine and bromine reaching the stratosphere. Figure 6 also indicates that the CBL is expected to peak by 1998 or 1999 and then to slowly recover, to levels observed before human-related emissions. Although production of the CFCs and halons have decreased greatly under the Montreal Protocol, the long atmospheric lifetimes of these compounds created a large reservoir of chlorine and bromine, already released but awaiting eventual dissociation in the stratosphere. The smaller effect on projected CBL from HCFCs is related both to their much shorter atmospheric lifetimes and to the halt in their production by 2030. The HCFC-123 component of the equivalent chlorine for scenario 1 is negligible compared to the other sources of chlorine and bromine; it is less than 0.1% of the total CBL at any given time. It is also less than 0.25% of the natural source of chlorine in the stratosphere from CH<sub>3</sub>Cl.

Figure 7 summarizes the relative effects of emissions from HCFC-123 for scenarios 3 to 6, the scenarios based on the analyses of HCFC-123 sources presented in this paper, on the CBL. These effects are shown as a percentage difference relative to scenario 2, the reference case. Projected emissions of HCFC-123 following the Montreal Protocol, scenario 3, reach peak HCFC-123 concentration and corresponding peak in equivalent chlorine in the atmosphere by about 2010 and then decrease slowly to zero by 2040. Continued production and emissions under the reprieve case, scenario 5, allow for slightly higher and later chlorine amounts than scenario 3, while resulting in additional emissions and CBL at later times in the scenario. However, the additional loading beyond 2030 is less than 0.0004% of that in scenario 1 (from Figure 6). The worst-case scenarios (4 and 6) are three to four times larger in the effect of HCFC-123 on CBL than scenarios 3 and 5, but are still small in comparison with scenario 1.

Figure 7 indicates that any of these four scenarios, even those allowing future use of HCFC-123, would produce negligible impact – much less than 0.002% of the total from all sources – on CBL and therefore on ozone over the next century. A similar statement can be made even with the much larger, overstated, emissions for HCFC-123 from the IPCC assessment used in scenario 1. Scenarios 5 and 6 also suggest that an exemption allowing continued use of HCFC-123 in closed refrigeration systems would have minuscule effects on chlorine loading or on stratospheric ozone. Further, the four scenarios for HCFC-123 also add insignificantly to atmospheric chlorine relative to the natural sources, giving a CBL that is less than 0.02% of that for CH<sub>3</sub>Cl.

A sensitivity analysis for the conditions of scenario 6, adjusted by a 50% increase to projected chiller production after 2000, shows an increase in peak chlorine loading to 0.356 pptv from 0.324 pptv, a difference of 0.032 pptv, in the year 2011. This increase demonstrates that the conclusions do not change even with levels of population growth and international economic development that far exceed expectations.

Figure 8 compares the HCFC component of the CBL for scenario 1 with the cap revision case, scenario 7. The reduced cap gives essentially the same equivalent chlorine due to HCFCs, to within 0.006 ppbv, at all times compared to scenario 1. This change in the cap will have negligible effect on the equivalent chlorine and, therefore, negligible effect on the expected ozone response.

Full phaseout of CFC emissions by 1996 while allowing HCFC emissions stabilized at 2020 levels after that year, scenario 8, would have a small effect on the total equivalent chlorine relative to scenario 1, as shown in Figure 9. The differences in these two scenarios are about 0.2 ppbv or less, suggesting that allowing controlled use of HCFC emissions after 2020, while more strictly limiting CFC emissions, would not significantly impact on the projected changes in ozone. Overall, there would be a slight benefit through reduced effects on ozone.

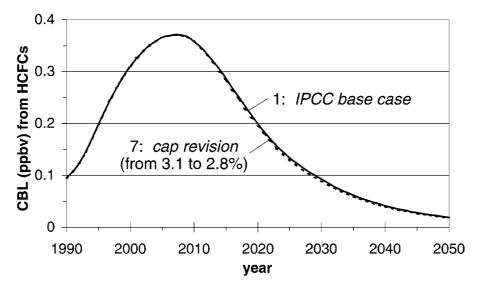
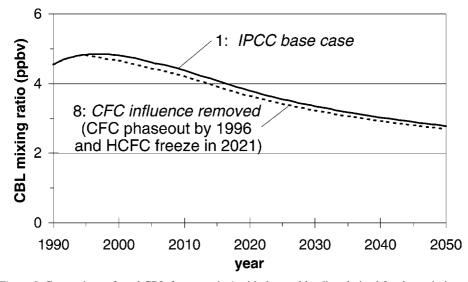


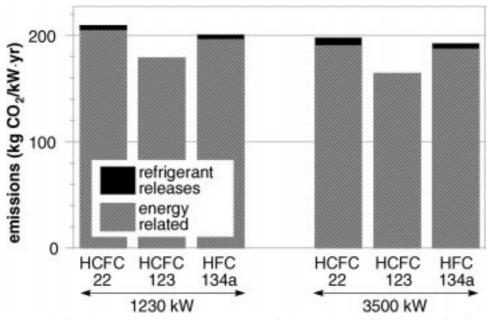
Figure 8. Comparison of the HCFC component of CBL for scenario 1 with the cap revision case, scenario 7.



*Figure 9.* Comparison of total CBL for scenario 1 with the total loading derived for the emissions in scenario 8.

# 7. Global Warming Impact

HCFC-123's importance as a refrigerant, for which it is used in more than half of all new centrifugal chillers, is attributable to several factors. The primary one, as stated above, is that it offers higher efficiency than all commercialized refrigerants except CFC-11. High performance translates to reduced carbon dioxide and other



*Figure 10.* Greenhouse gas emissions (expressed as equivalent carbon dioxide) per unit of cooling per year for the best available chillers in two representative capacities.

greenhouse gas emissions to power the equipment and lowers operating costs. It also reduces other resource requirements, such as the water needed for prevalent cooling towers to reject the heat removed by cooling, in addition to fuel use.

Figure 10 summarizes the net greenhouse gas emissions from chiller operation for the refrigerants currently used in centrifugal chillers for two representative capacities. Similar designs for CFC-11, CFC-12, CFC-113, CFC-114, and R-500 (a blend of CFC-12 and HFC-152a) are still in use, but they are no longer manufactured based on phaseout of the CFCs. The details of and underlying data for the engineering calculations are presented in Calm (1993), except that the GWP values from Table I (based on the latest IPCC assessment, IPPC, 1996) were applied, newer release rates were used (discussed above), electricity generation mixes and heat rates were updated to 1995 projections, and newer performance data were incorporated (Calm and Didion, 1997).

The figure shows that switching from the best HCFC-123 chillers to HFC-134a chillers will increase net annual emissions of greenhouse gases by more by than 12–17%, depending on the chiller capacity. For physical reasons, specific refrigerants tend to have optimal capacity ranges for specific designs. Plots of chiller performance suggest that the penalty would be even higher for intermediate capacities. The penalty for switching to HCFC-22 would be more than 17–20%, again depending on capacity; but phaseout of HCFC-22 chillers will precede that of HCFC-123 based on its higher ODP (and GWP) as well as national regulations pursuant to the Montreal Protocol. These increases include the emissions from energy

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required for heat rejection equipment (cooling towers) and associated pumping, both of which are needed for chiller operation (Calm, 1993). They also account for the direct effects of refrigerant releases converted to equivalent  $CO_2$  using the GWPs from Table I. The higher chiller efficiency of HCFC-123, namely 9–20% as discussed above, lowers the energy needed for auxiliary devices. The significantly lower GWP, 90 compared to 1300 or 1500 for HFC-134a and HCFC-22, respectively, amplifies its benefits.

These differences in emissions were extrapolated to worldwide projections of radiative forcing impacts by use of the chiller installation, conversion, retirement projections summarized in Table IV. Chiller inventories were calculated by year for the next half century by cumulative summation of installations plus conversions less retirements. The average HCFC-123 inventory for the next half century was determined to be 57,200 chillers manufactured for HCFC-123 use and 4,350 converted to HCFC-123 use. Overall reductions in radiative forcing were then estimated by interpolating between the two capacities analyzed for a representative chiller capacity of 1750 kW. The estimated difference in greenhouse gas emissions between the best available HCFC-123 and HCFC-22 chillers calculates to 4.0 million tonnes of CO<sub>2</sub> per year or 1.1 million tonnes of carbon equivalent (MTCE) per year. Similar comparison of HCFC-123 to HFC-134a calculates to 2.4 million t/y of CO<sub>2</sub> or 0.7 MTCE. Comparison to 1996 estimates for the United States (EIA, 1997) indicates that these amounts equal approximately 0.5% of total greenhouse gas emissions by the commercial sector, including those from other energy uses such as heating, lighting, and unrelated equipment. This fraction increases severalfold if only the segment of the commercial sector for which chillers are pertinent is considered.

The HCFC-22 comparisons are more indicative of the next several years based on existing equipment. The HFC-134a comparisons are more indicative of later years, based on anticipated phaseout of HCFC-22. HFC-134a already exceeds HCFC-22 use in new centrifugal chillers in the capacities corresponding to those for HCFC-123. Other refrigerants, including ammonia, hydrocarbons, water and other non-fluorocarbons, were examined by Calm and Didion (1997). That work shows that the efficiencies of these alternatives also would be lower. Moreover, most of the candidates offering both zero ODP and very low GWP would compromise safety with higher flammability, toxicity, or both. Although the possibility of finding a superior alternative in the future cannot be excluded, Calm and Didion (1997) review prior search efforts and show – based on chemical and thermophysical properties – that the prospects are not encouraging.

No adjustment is made in Figure 10 for the offset in warming impact from ozone loss from releases of HCFC-22 or HCFC-123. Because ozone also is an important greenhouse gas, ozone destruction results in a loss of greenhouse effect often described as *cooling* (relative to the natural equilibrium) or *negative radiative forcing*. While uncertainty remains in the magnitude of the resulting cooling, the direction is clear. Table V, based on data from IPCC (1966) and Daniel et al. (1995),

Refrigerant	$ au_{ m atm}$	Direct	Net GWP 1990–2020		
	(yr)	GWP <sub>100 yr</sub>	Minimum	Maximum	
BFC-13B1	65	5 400	-30 700	-14 100	
CFC-11	50	3 800	540	2 1 0 0	
CFC-12	102	8 100	6 200	7 100	
CFC-113	85	4 800	2 600	3 600	
HCFC-22	13.3	1 500	1 300	1 400	
HCFC-123	1.4	90	20	50	
HCFC-124	5.9	470	390	430	
HCFC-142b	19.5	1 800	1 600	1 700	

TABLE V
Net GWP with cooling effects <sup>a</sup>

<sup>a</sup> Based on data from IPCC (1996) and Daniel et al. (1995).

shows the net GWP values for ozone-depleting refrigerants. Comparison to the atmospheric lifetimes shows that chemicals with shorter lifetimes tend to induce more of an offsetting cooling effect. The result significantly reduces the GWP for HCFC-123, from 90 to an uncertainty range of 20–50. The lower net GWP brings HCFC-123 into the range commonly associated with hydrocarbons. Inclusion of the net GWPs would reduce the refrigerant-related impact for chillers using HCFC-123 by 44–78% and for those using HCFC-22 by 7–13%. High ODP chemicals, as illustrated by BFC-13B1 (halon 1301), actually have a net cooling impact due to aggressive ozone depletion.

# 8. Discussion

There is no single index to compare the combined effects of ozone depletion and global warming. Likewise, the ODP and GWP of a substance do not reflect the probability of emissions, including either the differences between use in open and closed systems or, for the latter, leak-prone and tight designs. The severe consequences of ozone depletion are being averted through the Montreal Protocol. As the emissions cease, the ozone layer is expected to recover, though the process will take time due to effects of previously released CFCs and other long-lived halocarbons. As seen in Figure 6, the CBL peak is imminent and recovery will soon be underway.

However, the prospects to resolve the global warming threat and the severity of its consequences are far less favorable. Even if global emissions of greenhouse gases are reduced on a per capita basis, these reductions will be partially or totally offset by projected population growth. Moreover, targeted economic advances in developing countries, with attendant increases in energy use, suggest a more daunting prospect. Whereas the role of net carbon dioxide emissions overshadows the effects of other greenhouse gases, reduction in energy demands and efficiency improvement in meeting them have to be key measures. Improved energy efficiency also leads to conservation of other resources.

While policies for ozone protection and climate change are currently being addressed separately, rejection of a key mitigation measure for global warming, based on minuscule ozone depletion, warrants reconsideration (Wuebbles and Calm, 1997). Kroeze and Reijnders (1992a,b) analyzed the impacts of CFC alternatives on the earth's equilibrium temperature. Their analyses divided these radiatively active chemicals into two groups, based on their GWPs. They concluded that uncontrolled use of HCFCs and HFCs from the high-GWP group could increase the equilibrium temperature by 0.28-0.66 °C by 2100 compared to substitution of HCFCs and HFCs from the low-GWP group (Kroeze and Reijnders, 1992a). They also found that phaseout of HCFCs by 2035 to protect the ozone layer could increase temperature forcing by 0.46–1.16 °C if these HCFCs are replaced by HFCs and no emission-reducing measures are implemented (Kroeze and Reijnders, 1992b). They concluded that restricted use of low-GWP HCFCs with containment measures and phaseout of those with high GWPs could reduce global warming compared to total HCFC phaseout with HFC replacement. The study presented herein illustrates a specific case with consistent conclusions.

Analyses of emissions, and consequent chlorine loading, show that projected use of HCFC-123 would result in almost no impact on stratospheric ozone. Comparisons between phaseout of this compound and its continued use as a refrigerant, in closed systems, show a negligible difference in impact. Parametric scenarios uphold this conclusion, even for extreme levels of emissions, far exceeding those of current technologies and practices.

By contrast, phaseout of HCFC-123 will increase global warming effects unless a more efficient alternative is discovered, which is highly improbable. Repeated searches have shown that only CFC-11 offers superior efficiency, but with an ODP and GWP that are more than 70 and 40 times higher, respectively. Moreover, timebased analyses show that the minimal contribution to stratospheric chlorine from HCFC-123 emissions will peak more than a decade after the residual effects of prior CFC and other halocarbon releases subside. While no single index exists to directly compare chemical ODPs and GWPs, several conclusions are clear. First, reversal of the buildup of bromine and chlorine (i.e., healing of the 'ozone layer') is underway and progressing on target, but sufficient practical remedies for global climate change are far more elusive. Second, the analyses show that continued use of HCFC-123 will cause indiscernible ozone depletion, even for a combination of 'worst-case' conditions, but that its future use offers important environmental benefits. Although the present study focused on HCFC-123, the findings suggest that there may be additional chlorinated or brominated compounds with very shortatmospheric lifetimes that also warrant re-examination. And third, since new global environmental concerns may, and probably will, be identified in the future, a more scientific approach is needed to determine environmental acceptability or rejection.

One critical question to conclude this analysis is whether a reprieve from phaseout for HCFC-123 would promote broader use than addressed herein, and specifically use in other applications? As with CFC-11 before introduction of HCFC-123, its physical properties limit its attraction as a refrigerant to machines employing centrifugal compressors and then to a well defined range of capacities. The volumeflow rates are too high for the positive displacement compressors that dominate smaller capacities. Similarly, denser gases are required for larger capacities to avoid unwieldy equipment sizes. The range for which it is suitable, however, is the one for which centrifugal chillers are most widely used.

Will that demand grow, for example in developing countries? The projections used in this study anticipate future measures to limit greenhouse gas emissions in both developed and developing countries. Notwithstanding their efficiency advantage, chillers – including those using HCFC-123 – still use large amounts of energy. Accordingly, efficiency improvement is insufficient and ultimately limited by the laws of thermodynamics. Cooling – and other – load reductions will be needed to stabilize or reduce greenhouse gas emissions, particularly with anticipated population growth and economic development. These reductions will shift demand to chillers with smaller capacities for which HCFC-123 is not suited.

Will HCFC-123 use blossom if those reductions do not occur? The need for the high efficiency of HCFC-123 and related mitigation of radiative forcing will become more critical if those reductions are not realized. As discussed above, a doubling or even a ten-fold increase in the use of HCFC-123 chillers still will have a negligible consequence on stratospheric ozone. However, these inconceivable increases imply an energy intensity and a radiative forcing scenario in which the efficiency and GWP advantages of HCFC-123 become essential.

Would allowed future use of HCFC-123 open the door for more emissive uses, for example as a foam blowing agent, aerosol propellant, or solvent? Better, less expensive foam blowing agents have been identified, so the answer is no for this use. HCFC-123 is a liquid at normal temperature and pressure, so it is not effective as an aerosol propellant for most applications. Identified chronic (long-term, repeat exposure) toxicity concerns hinder consideration of HCFC-123 in highly emissive applications. Although these concerns are not limiting for closed systems such as chillers, they inhibit use as a blowing agent, aerosol propellant, or solvent. In any case, provisions for future use of HCFC-123 should specify that production will be allowed only for refrigerant use as justified by environmental benefits.

#### 9. Conclusions

The study presented herein conclusively demonstrates that phaseout of HCFC-123 provides a negligible advantage to protect stratospheric ozone. In contrast, use of HCFC-123 as a chiller refrigerant offers clear benefits to address global warming. Taken together, there are compelling environmental reasons to continue use of this compound. The analyses presented suggest that elimination of compounds based on molecular composition alone, without regard to consequent impact and offsetting benefits, will have a net adverse rather than beneficial impact on the environment.

These analyses reveal several additional findings. First, use of single measure ODP controls or chemical composition alone places excessive emphasis on the process rather than the objectives in controlling future production. Phaseout serves no purpose for compounds with very low ODP in applications with very low emissions. This finding is especially apt for chemicals that offer offsetting environmental benefits, for which emissions could have been sufficiently addressed – from a scientific perspective - by containment, recovery, or distinction between prohibited and allowed uses. Second, the Montreal Protocol does not provide for exemptions based on inconsequential ozone impacts or offsetting environmental benefits. The criteria for essential-uses, adopted as decisions of the parties, deal with necessity and the availability of alternatives. They stipulate that 'use of a controlled substance should qualify as "essential" only if it is necessary for the health, safety, or critical functioning of society (encompassing cultural and intellectual aspects)' (UNEP, 1996). While a broad reading would view 'environmental protection' as inherent to 'health and safety', a specific mention would provide a better signal. Third, prior assessments have significantly overstated past and projected emissions of HCFC-123. Examination is needed to determine whether other emissions have been similarly inflated considering current and projected demands and practices. And fourth, phaseout of compounds based on GWPs alone, as some countries have proposed, will not avert global warming - and may exacerbate it by eliminating efficient options - unless related greenhouse gas emissions arising from associated energy use also are addressed.

# Appendix

Three sets of chiller emission data were obtained after completion of the study herein. The additional data corroborate those used and even show it to be slightly conservative.

Data were obtained from manufacturing records on refrigerant use and recovery for a period covering production of nearly 1700 chillers using HCFC-123 (Bartley and Wettstein, 1998). The losses associated with manufacturing operations, factory tests, and elective 'witness' tests of performance by purchasers amounted to 0.87% of the total refrigerant charge. This fraction includes an estimated 0.25% of the refrigerant that is dissolved in the lubricant or otherwise trapped in the chiller. This amount stays inside the chiller and offsets the required refrigerant amount when the system is recharged upon installation (the factory test charge is removed before shipping). The dissolved fraction was included in the intermittent losses for periodic lubricant changes, though technologies are being tested that could completely eliminate such releases. The manufacturer that provided these data has identified ways to further reduce the initial losses that will be implemented in the next year. Overall, these new data suggest that the release rates used in the present study for both initial and disposal losses were very close to those being achieved today without credit for future technology improvements.

The second set comprises field data gathered by the U.S. Environmental Protection Agency, in the form of service summaries for 189 chillers installed since July 1992 (Sheinson, 1997). Analysis of these data show net HCFC-123 makeup rates of 0.4%/yr. These losses are estimated to represent 80–90% of the sum of *operating* and *intermittent* losses – the largest components on an annualized basis – as defined herein.

The third set is from an analysis by a major chiller manufacturer of service records for 3,888 chillers installed since 1991, 2,768 of them manufactured for HCFC-123 use and 1,120 converted from CFC-11 to HCFC-123 (Trane, 1997). The data were collected from 83 franchised and company-owned field offices for all HCFC-123 chillers for which complete service records were available since installation or conversion. The study found average net makeup rates of 0.46%/y for original HCFC-123 chillers and 0.62%/y for conversions. The sample size in this study is quite large and the data quality are judged to be very reliable based on two factors. First, the approaches used for selection and data collection appear to be sound. Second, there was agreement between the reported make-up amounts obtained by the authors and those from the new study for several chillers that were included in both data sets.

There are different levels of conversion, ranging from simple replacement of incompatible materials and recharge to replacement or modification of components to approach the performance and tightness of new equipment. Anecdotal data from other conversions indicate that the quality of the conversions covered by the second set of new data exceeds the average and more closely reflects what is attainable rather than the global average.

The majority of chillers, new and converted (provided they were retrofit with a condensing purge unit), represented in both the earlier and new data sets required no refrigerant make-up. The authors plan to examine the consolidated data further and to seek explanations for the few machines that required significant refrigerant additions. There was some overlap in the chillers examined in the two new sets and between them and the earlier set, but there was enough independence to provide corroboration. The overlap was inevitable based on the separate efforts to obtain data from as many chillers as possible. Further data are being sought both to in-

crease the net sample size and to investigate potential changes as the equipment ages and undergoes major overhaul cycles.

The new refrigerant loss and make-up data are slightly lower for original HCFC-123 machines, and notably lower for chillers converted to HCFC-123, than those from other installations, which were used in the study. Both the new data and those used in the study show that the overwhelming majority of HCFC-123 chillers require no refrigerant additions even after several years of operation. An undetermined share of the 'make-up' reflects initial undercharging rather than refill for losses. Overall, the new data validate the conservative approach used in this study and reinforce the conclusions presented.

#### References

- Air-Conditioning and Refrigeration Institute (ARI): 1995, 'ARI Chiller Survey Confirms Pace of CFC Phaseout', *Koldfax*, Arlington, VA, April 1.
- ARI: 1996, Inputs for AFEAS/DOE Phase 3 Study of Energy and Global Warming Impacts, November.
- ARI: 1997, Slower than Expected CFC Chiller Phaseout Requires Huge Number of Replacement Units, press release, April 9.
- Alternative Fluorocarbons Environmental Acceptability Study (AFEAS): 1996, Production, Sales and Atmospheric Release of Fluorocarbons Through 1994, Washington, D.C.
- AFEAS: 1997, Production, Sales and Atmospheric Release of Fluorocarbons Through 1995, Washington, D.C.
- American Society of Heating, Refrigerating, and Air-Conditioning Engineers (ASHRAE): 1995, 'Owning and Operating Costs', *ASHRAE Handbook – Heating, Ventilating and Air-Conditioning Applications*, Atlanta, GA, 33.4.
- Bartley, J. and Wettstein, M.: 1998, Private communication, February 6.
- Bullock, C. E.: 1996, 'Assessment of Carbon Dioxide as a Refrigerant', Tech. Update 5(5), 1.
- Calm J. M.: 1991, *Refrigerant Charge in Air-Conditioning Equipment with Selected Alternative Refrigerants*, Report JMC/AFEAS-9106C, AFEAS, Washington, D.C.
- Calm J. M.: 1993, Comparative Global Warming Impacts of Electric Vapor-Compression and Direct-Fired Absorption Equipment, Report TR-103297, Electric Power Research Institute (EPRI), Palo Alto, CA.
- Calm, J. M. and Didion, D. A.: 1997, 'Trade-Offs in Refrigerant Selections: Past, Present, and Future', *Refrigerants for the 21st Century*, Proceedings of the ASHRAE-NIST Conference, Gaithersburg, MD, October 1997, ASHRAE, Atlanta, GA, *Int. J. Refrigeration* 21 (4), 308–321.
- Daniel, J., Solomon, S., and Albritton, D.: 1995, 'On the Evaluation of Halocarbon Radiative Forcing and Global Warming Potentials', J. Geophys. Res. 100, 1271–1285.
- Doerr, R. G., Lambert, D., Schafer, R., and Steinke, D.: 1993, 'Stability Studies of E-245 Fluoroether, CH<sub>3</sub>-CH<sub>2</sub>-O-CHF<sub>2</sub>', Paper DE-93-20-3 (Annual Meeting, Denver, CO, June 1993), American Society of Heating, Refrigerating, and Air-Conditioning Engineers (ASHRAE), Atlanta, GA, *Transactions* 99 (2), 1137–1140.
- Energy Information Administration (EIA): 1994, Emissions of Greenhouse Gases in the United States, 1987–1992, Report DOE/EIA-0573, U.S. Department of Energy (DOE), Washington, D.C.
- EIA: 1997, *Emissions of Greenhouse Gases in the United States, 1996*, Report DOE/EIA-0573, U.S. Department of Energy, Washington, D.C., October.

- Environmental Protection Agency (EPA): 1995, Unpublished data, as cited in Tromp, T. K., Ko, M. K. W., Rodriguez, J. M., and Sze, N. D.: 1995, 'Potential Accumulation of a CFC-Replacement Degradation Product in Seasonal Wetlands', *Nature* 376, 327–330.
- EPA: 1997, *1995 Toxics Release Inventory: Public Data Release*, Washington, D.C., pp. 76–80, April (as cited in EIA, 1997, above).
- European Centre for Ecotoxicology and Toxicology of Chemicals (ECETOC): 1996, Joint Assessment of Commodity Chemicals Number 33: 1,1-Dichloro-2,2,2-Trifluoroethane (HCFC-123) CAS No. 306-83-2, February.
- Fischer, S. K., Hughes, P. J., Fairchild, P. D., Kusik, C. L., Dieckmann, J. T., McMahon, E. M., and Hobday, N.: 1991, *Energy and Global Warming Impacts of CFC Alternative Technologies*, AFEAS and DOE, Washington, D.C.
- Fischer, S. K., Tomlinson, J. J., and Hughes, P. J.: 1994, Energy and Global Warming Impacts of Not-in-Kind and Next Generation CFC and HCFC Alternative Technologies, AFEAS and DOE, Washington, D.C.
- Glamm, P. R., Keuper, E. F., and Hamm, F. B.: 1996, Evaluation of HFC-245ca for Commercial Use in Low Pressure Chillers, Report DOE/CE/23810-67, Air-Conditioning and Refrigeration Technology Institute (ARTI), Arlington, VA.
- Government Printing Office (GPO): 1994, *Protection of Stratospheric Ozone; Final Rule*, Federal Register, Washington, D.C.
- GPO: 1996, Protection of Stratospheric Ozone; Acceptable Substitutes for the Significant New Alternatives Policy (SNAP) Program, 40 CFR 82, Washington, D.C.
- Hughes, H. M.: 1997, 'Contemporary Fluorocarbons', *Refrigerants for the 21st Century*, op. cit., 117–121.
- Intergovernmental Panel on Climate Change (IPCC): 1995, in Houghton, J. T., Meira Filho, L. G., Bruce, J., Lee, H., Callander, B. A., Harris, N., Haites, E. F., Harris, N., and Maskell, K. (eds.), *Climate Change 1994: Radiative Forcing of Climate Change and an Evaluation of the IPCC IS92 Emission Scenarios*, Cambridge University Press, Cambridge, U.K.
- Intergovernmental Panel on Climate Change (IPCC): 1996, in Houghton, J. T., Meira Filho, L. G., Callander, B. A., Harris, N., Kattenberg, A., and Maskell, K. (eds.), *Climate Change 1995 – Contribution of Working Group I to the Second Assessment Report of the Intergovernmental Panel on Climate Change*, Cambridge University Press, Cambridge, U.K.
- Kinnison, D. E., Grant, K. E., Connell, P. S., Rotman, D. A., and Wuebbles, D. J.,: 1994, 'The Chemical and Radiative Effects of the Mount Pinatubo Eruption', J. Geophys. Res. 99, 25705– 25731.
- Kroeze, C. and Reijnders, L.: 1992a, 'Halocarbons and Global Warming,' Sci. Total Environ. 111, 1–24.
- Kroeze, C. and Reijnders, L.: 1992b, 'Halocarbons and Global Warming, II,' Sci. Total Environ. 112, 269–290.
- March Consulting Group: 1997, *Refrigeration and Global Warming*, European Chemical Industry Council, Brussels, Belgium, September.
- McLinden, M. O. and Didion, D. A.: 1987, 'Quest for Alternatives', ASHRAE J. 29 (12), 32-42.
- McLinden, M. O.: 1990, 'Optimum Refrigerants for Nonideal Cycles An Analysis Employing Corresponding States', in Tree, D. R. (ed.), *Proceedings of the 1990 USNC-IIR-Purdue Refrigeration Conference and ASHRAE-Purdue CFC Conference*, Purdue University, West Lafayette, IN, July, pp. 69–79.
- Orkin, V. L., Khamaganov, V. G., Guschin, A. G., Huie, R. E., and Kurylo, M. J.: 1994, *Rate Constants for the Reactions Between Hydroxyl Radicals and Fluorinated Ethers*, Abstract D55, 13th International Symposium on Gas Kinetics, University College Dublin, p. 359.
- Prather, M. J. and Watson, R. T.: 1990, 'Stratospheric Ozone Depletion and Future Levels of Atmospheric Chlorine and Bromine', *Nature* 344, 729–734.
- Richard, R. G.: 1997, Private communication, AlliedSignal Incorporated, Buffalo, NY.

- Sand, J. R., Fischer, S. K., and Baxter, V. D.: 1997, *Energy and Global Warming Impacts of HFC Refrigerants and Emerging Technologies*, AFEAS and DOE, Washington, D.C.
- Sheinson, B.: 1997, Refrigerant loss data, Private communication from R. Forte, U.S. EPA, Washington, D.C.
- Sidebottom, H. and Franklin, J.: 1996, 'The Atmospheric Fate and Impact of Hydrochlorofluorocarbons and Chlorinated Solvents', *Pure Appl. Chem.* 68, 1757–1769.
- Smith, N. D., Ratanaphruks, K., Tufts, M. W., and Ng, A. S.: 1993, 'R-245ca: A Potential Far-Term Alternative for R-11', *ASHRAE J.* **35** (2), February, 19–23.
- Smith, N. D., Ng, A. S., Tufts, M. W., Drago, A. M., and Ratanaphruks, K.: 1994, 'Evaluation of HFC-245fa as a Potential Alternative for R-11 in Low-Pressure Chillers', in *Stratospheric Ozone Protection for the 90's*, Proceedings of the International CFC and Halon Alternatives Conference, Alliance for Responsible Atmospheric Policy, Arlington, VA, pp. 894–901.
- Smith, N. D. and Tufts, M. W.: 1994, 'Flammable Properties of HFC Refrigerants Some Fundamental Considerations', in ARI Flammability Workshop – Summary and Proceedings, ARI, Arlington, VA, Section 2.2.
- Solomon, S. and Albritton, D. L.: 1992, 'Time-Dependent Ozone Depletion Potentials for Short- and Long-Term Forecasts', *Nature* 357, 33–37.
- Trane Company, The: 1997, Private communication of unpublished study and data files from the *HCFC-123 Refrigerant Management Study*, November 24, La Crosse, WI.
- United Nations (UN): 1987, *Montreal Protocol on Substances that Deplete the Ozone Layer*, New York, NY.
- United Nations (UN): 1997, Kyoto Protocol to the United Nations Framework Convention on Climate Change, New York, NY.
- United Nations Environment Programme (UNEP): 1991, *Handbook for the Montreal Protocol on Substances That Deplete the Ozone Layer* (second edition), Ozone Secretariat, Nairobi, Kenya.
- UNEP: 1993, Handbook for the Montreal Protocol on Substances that Deplete the Ozone Layer (third edition), Ozone Secretariat, Nairobi, Kenya.
- UNEP: 1994, Report of the Refrigeration, Air Conditioning, and Heat Pumps Technical Options Committee, 1995 Assessment, Ozone Secretariat, Nairobi, Kenya.
- UNEP: 1996, Handbook for the International Treaties for the Protection of the Ozone Layer, 4th edn., Ozone Secretariat, Nairobi, Kenya.
- UNEP: 1997a, 'Proposal by the European Community', in *Consideration and Consolidation of the Amendments and Adjustments Proposed by the Parties, Addendum*, Document UNEP/OzL.Pro/WG.1/15/2/Add.3, February 20, Ozone Secretariat, Nairobi, Kenya.
- UNEP: 1997b, 'Proposal by Switzerland', in Consideration and Consolidation of the Amendments and Adjustments Proposed by the Parties, Addendum, Document UNEP/OzL.Pro/WG.1/15/2/Add.6, March 4, Ozone Secretariat, Nairobi, Kenya.
- van Dijck, P. G. J. M.: 1996, Test Report 96D2/2344, Prins Maurits Laboratory, TNO, Rijswijk, The Netherlands.
- World Meteorological Organization (WMO): 1990, Scientific Assessment of Stratospheric Ozone: 1989, Report 20, Geneva, Switzerland.
- WMO: 1995, *Scientific Assessment of Ozone Depletion: 1994*, Global Ozone Research and Monitoring Project, Report 37, Geneva, Zwitzerland.
- Wuebbles, D. J.: 1981, The Relative Efficiency of a Number of Halocarbons for Destroying Stratospheric Ozone, Report UCID-18924, Lawrence Livermore National Laboratory (LLNL), Livermore, CA.
- Wuebbles, D. J.: 1983, 'Chlorocarbon Emission Scenarios: Potential Impact on Stratospheric Ozone', J. Geophys. Res. 88, 1433–1443.
- Wuebbles, D. J., Kinnison, D. E., Grant, K. E., and Lean, J.: 1991, 'The Effect of Solar Flux Variations and Trace Gas Emissions on Recent Trends in Stratospheric Ozone and Temperature', J. *Geomagnet. Geoelect.* 43, 709–718.

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- Wuebbles, D. J. and Kinnison, D. E.: 1996, 'Prediction of Future Ozone Changes', *Int. J. Environ. Stud.* **51**, 269–283.
- Wuebbles, D. J. and Calm, J. M.: 1997, 'An Environmental Rationale for Retention of Endangered Chemicals', *Science* 278, 1090–1091.
- Wuebbles, D. J., Wei, C-F., and Patten, K. O.: 1998, 'The Distribution of Stratospheric Ozone and Temperature During the Maunder Minimum', *Geophys. Res. Lett.* 25, 523–526.

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