ENVIRONMENTAL AND PERFORMANCE STUDIES OF R-123 AS A CHILLER REFRIGERANT — RESULTING RECOMMENDATIONS FOR ENVIRONMENTAL PROTECTION

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ABSTRACT

This paper reviews the introduction, importance, and uniqueness of R-123 as well as theoretical and practical performance comparisons for alternatives. It explains why a suitable replacement neither has been identified nor is anticipated. The paper summarizes detailed environmental studies of this refrigerant, leading to recognition that its phaseout will result in greater environmental detriment than benefit. It suggests a simple path to address this concern that is consistent with the preamble to the Montreal Protocol, which stipulates that "measures taken to protect the ozone layer from depletion should be based on relevant scientific knowledge, taking into account technical and economic considerations." The focal recommendation offered is based on environmental protection.

1. INTRODUCTION

The *Montreal Protocol on Substances that Deplete the Ozone Layer* is approaching its 20th anniversary with recognition as successful. This landmark treaty set in motion significant events, later intensified with amendments, to limit production (technically "consumption") and emissions of chemicals considered harmful to the global environment. The Montreal Protocol was complemented with the companion *Kyoto Protocol to the United Nations Framework Convention on Climate Change* to control emissions of additional substances that act as greenhouse gases.

The most significant impact to date for refrigerants has been nearly complete phaseout in new equipment of the widely used chlorofluorocarbon (CFC) refrigerants. The next steps for refrigerants focus on hydrochlorofluorocarbons (HCFCs), with shifts to hydrofluorocarbon (HFC) options – many of them blends – and alternatives such as ammonia, hydrocarbons (HCs), carbon dioxide, and water. The framers of the Montreal Protocol anticipated both development of environmentally safer alternatives and adjustments as warranted based on further scientific studies. Indeed, successive amendments added chemicals and adjusted phaseout measures. However, rigorous scientific evaluations now show that phaseout of one very important refrigerant, R-123 (an HCFC initially perceived to be a transition substitute for chillers), will result in greater environmental harm than benefit.

2. REFRIGERANT PROGRESSION

Figure 1 depicts the progression of refrigerants through four generations. Familiar solvents and other volatile fluids dominated the first hundred years – the first generation, for which the defining criterion was *whatever worked*. Ammonia and carbon dioxide were among the earliest refrigerants. Hydrocarbons were introduced later in small systems, but gained only limited acceptance despite promotion as safer than other more toxic and caustic choices.

The second generation was distinguished by a shift to fluorochemicals for *safety and durability*. Most were chlorofluorocarbons (CFCs) with later growth of hydrochlorofluorocarbon (HCFC) use, notably in residential and small commercial air conditioners and heat pumps. Ammonia continued as, and remains today, the most popular refrigerant for food and beverage processing, especially in large industrial-scale systems, and storage.

The third generation was driven by linkage of released CFCs – including CFC refrigerants – to depletion of protective stratospheric ozone. International agreement to the Montreal Protocol forced a shift to replacements with low ozone depletion potential (ODP) with loose concern for the looming, but then still unregulated, issue of global climate change. "Natural refrigerants" enjoyed renewed interest, particularly ammonia, carbon dioxide, and hydrocarbons along with expanded use of absorption and other not-in-kind approaches. Fluorochemicals retained the primary focus, with emphasis on HCFCs for interim (transitional) use and hydrofluorocarbons (HFCs) for the longer

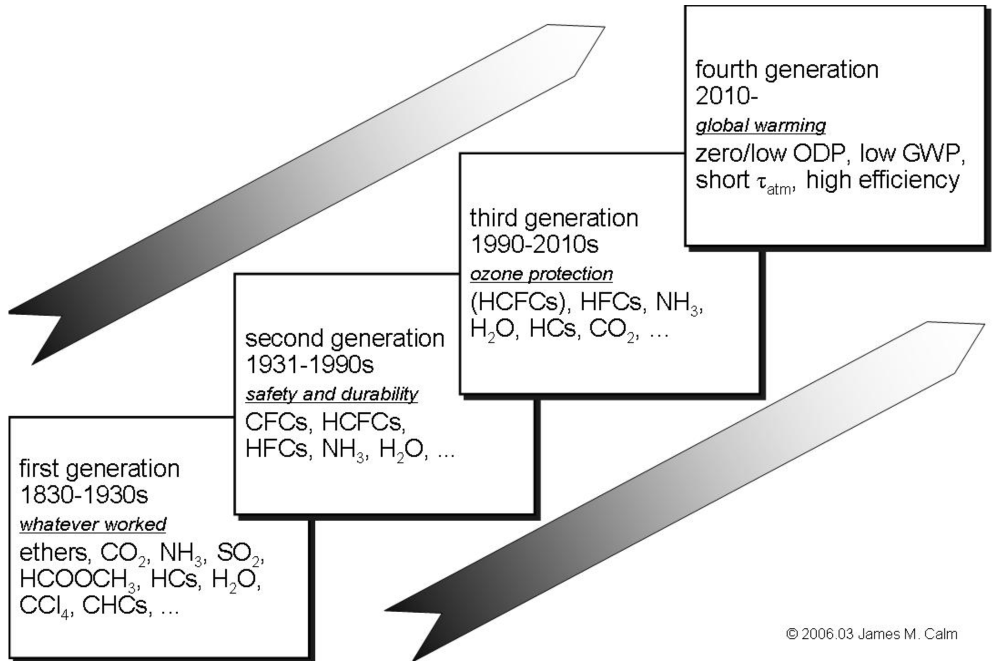

Figure 1: Refrigerant progression

term. A number of public and private research programs systematically examined both hydrofluoroether (HFE) and non-fluorochemical candidates, but yielded few promising options.

The pervasive expectation in the 1990s and even early 2000s was that the third generation alternatives (other than interim use of HCFCs) would be suitable for long-term use. Growing recognition of the severity of global climate change is forcing reconsideration and new measures to limit their global warming potential (GWP). This added criterion defines the fourth generation of refrigerants. The European Parliament set the timing with adoption on October 26, 2005, of measures to ban HFC refrigerants having GWP exceeding 150 in new air conditioners for automobiles effective 2011 and for all automotive use starting in 2017. The adopted "F-gas regulations" also require periodic inspection of stationery systems using HFCs. Although recommended by its Environment Committee, the Parliament rejected more stringent measures that would have banned HFC use as aerosol propellants by 2006, as foam blowing agents by 2009, and as refrigerants in stationery air conditioners and refrigeration by 2010. The contentious vote on the last item was 262-368, more than 40% in favor. The significant support level may result in future attempts at similar or compromise measures. The immediate effect of these measures is a ban on R-134a in its largest and, as a refrigerant, its most emissive application. The adopted GWP limit intentionally allows consideration of low GWP HFCs (notably R-152a even though flammable). The *F-gas* measures also sanction more stringent national regulations, some of which previously imposed bans on HFCs in large systems, explicitly banned HFC use in chillers, or imposed GWP-weighted excise taxes on HFC refrigerants.

The state of California also is deliberating proposed limits for refrigeration systems and for automobile air conditioners. At least eight other states are prone to follow California's lead if it regulates HFC uses or emissions.

Refrigerant manufacturers responded promptly with announcement of new classes of refrigerants. The largest such firm announced, on February 9, 2006, testing of new proprietary refrigerants to meet the GWP limit of 150 (DuPont, 2006). Another multinational manufacturer announced, one week later, a patented developmental refrigerant to meet the GWP limit (Honeywell, 2006). A patent issued several months earlier identifies zeotropic blends of R-1234yf (1,1,1,2-tetrafluoropropene) and R-13I1 (trifluoro-iodomethane) (Singh et al., 2005). Both the capacity and the efficiency are likely to be comparable to R-134a, though some initial tests showed reductions of approximately 5%. Both the first of these press releases and the patent clearly suggest potential to extend the new refrigerants into a broad range of applications, reinforcing expectation of a new generation of refrigerants defined by low GWP.

These developments raise interesting questions on the balance between conflicting environmental targets and between environmental goals and safety or compatibility. Although likely to be the minority component, R-13I1 is an

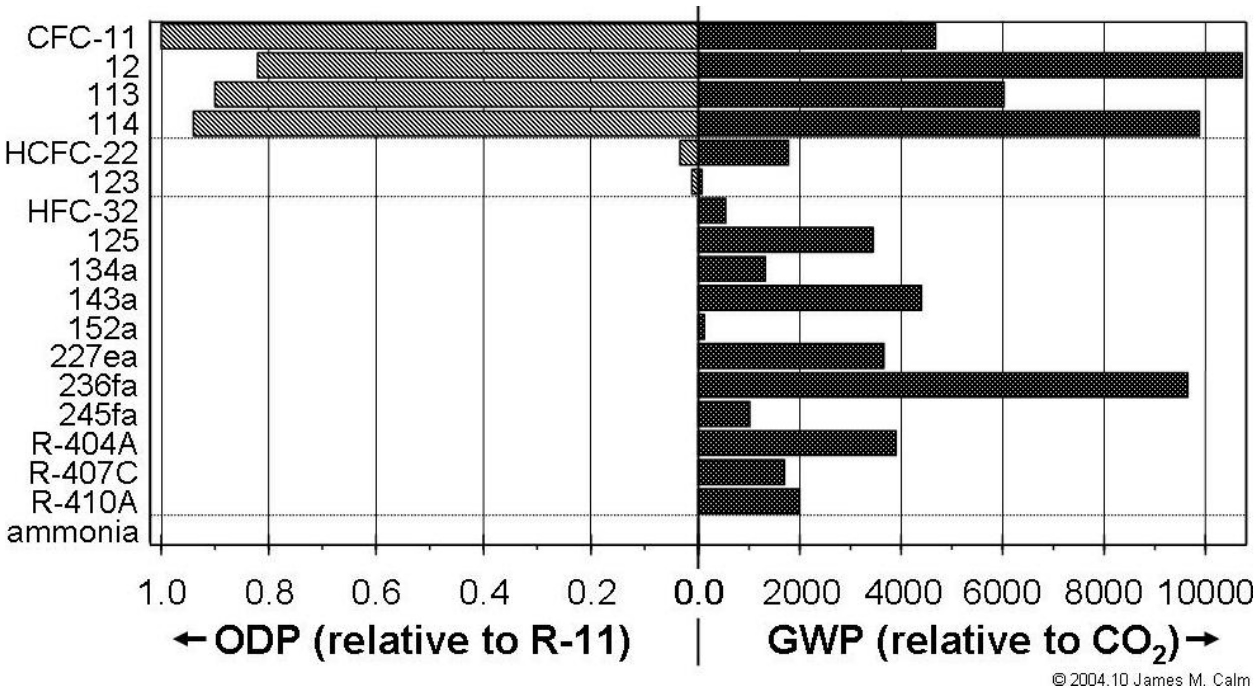

Figure 2: Ozone depletion potential (ODP) contrasted to global warming potential (GWP) for key refrigerants (based on data from IPCC 2001; WMO, 2003; and Calm and Hourahan, 2001). CFCs generally have high ODP and GWP. HCFCs generally have much lower ODP and GWP. HFCs offer near-zero ODP, but some have very high GWPs.

ozone-depleting substance with an ODP of <0.008, though not yet constrained by the Montreal Protocol since fluoro-iodocarbons (FICs) were not in commercial use when the controlled substances were enumerated. Likewise, the chemical is a potent cardiac sensitizer and may raise stability or compatibility questions in the presence of metals. Tetrafluoroprene is an HFC, but an unsaturated fluoro-alkene (a fluorinated olefin) rather than a fluoro-alkane. The generally higher reactivity of fluoro-alkenes leads to shorter atmospheric lifetime and lower GWP, but also higher toxicity and decreased stability. These points illustrate that perfect candidates cannot be found and that future refrigerant selections require a balance among different selection criteria.

3. CONFLICTING ENVIRONMENTAL GOALS

Figure 2 contrasts the ODPs and GWPs of candidate refrigerants for chiller use. No inference should be drawn that a unit of ODP on the left is equivalent in impact to a unit of GWP shown on the right; the two metrics are dissimilar and cannot be equated numerically. However, the figure is useful to show which chemicals are offensive based on ODP, GWP, or both. The Montreal Protocol only addresses protection of the stratospheric ozone layer. The left (ODP) side of Figure 2 reveals the logic of phasing out high-ODP CFCs quickly, moving to zero ODP solutions such as ammonia (or similarly hydrocarbons, carbon dioxide, or water) or to HFCs with practically zero ODP, and allowing interim use of low or very low ODP HCFCs. The right (GWP) side of Figure 2 – momentarily covering the ODP side on the left – suggests a very different outcome had global warming been addressed first. The GWPs of some HFCs (and perfluorocarbons, PFCs) are comparable or even higher than those of CFCs. Had climate change been addressed first, the terminology CFCs, HCFCs, and HFCs might not have come into popular usage, since the right side of the figure shows high GWP variability within these composition families. That variation would have forced selection based on the specific attributes of individual candidates rather than by family.

Now return to both sides of Figure 2 together. It is clear that ammonia (or similarly hydrocarbons, carbon dioxide, or water) offer zero ODP and near-zero GWP. Likewise, R-152a and R-32 are attractive based on near-zero ODP and very low GWP. All three are flammable, though R-32 and ammonia (R-717) burn less readily. The figure reveals clear advantages for R-123, with both very low ODP and very low GWP. Additional awareness of its very high thermodynamic efficiency, low pressure (hence reduced leakage) of operation, and short atmospheric lifetime increase its environmental appeal. Its fire suppression ability further enhances its attraction as a refrigerant.

4. RATIONAL FOR R-123 RETENTION

Three important considerations provide a clear rationale to retain R-123 as an allowed chiller refrigerant:

- Its impact on stratospheric ozone is negligible.
- It offers important offsetting environmental benefits.
- There neither are nor can be ideal refrigerants – trade-offs are necessary.

4.1. Impact on Stratospheric Ozone is Negligible

Calm, Wuebbles, and Jain (1997) analyzed the impacts on stratospheric ozone with the same model as that used to determine many of the ODP values adopted by international scientific consensus. They examined eight scenarios, starting with reconstruction of the accepted international emission projections for all known ozone-depleting substances using consistent data and other inputs. They then backed out the R-123 component to create a base case, to enable parametric analyses for different scenarios. The analyses then examined R-123 releases from use in new chillers and from retrofit conversions of existing R-11 chillers for four cases, namely projected and worst-case emissions each with and without scheduled phaseout of R-123. The worst-case scenarios combined increased usage with extreme increases for each of the emission components. The "cradle to grave" approach included emissions during manufacturing and related handling, installation, operation and service, and ultimate removal and disposal. Finally, the investigators tested additional scenarios of HCFC caps, CFC phaseout acceleration, and HCFC stabilization. The robust study found that exempting R-123 from phaseout for use as a chiller refrigerant would increase total chlorine-bromine loading of the stratosphere by 0.001%, an indiscernible impact. Even the worst case (for which the parametric variations then examined now appear too extreme based on later data) amounted to only 0.004%, still negligible. The identified study was rigorously reviewed before and after submission for journal publication, and has been widely cited in the pertinent scientific literature.

4.2. Offsetting Environmental Benefits

In contrast to its indiscernible impact on stratospheric ozone, R-123 use offers multiple, significant environmental benefits:

1. It offers <u>higher efficiency than other fluorochemicals, hydrocarbons, and ammonia</u> as a refrigerant for centrifugal chillers (Calm, 2005). Its thermodynamic efficiency is exceeded – but just slightly – only by R-11 (a CFC) and R-141b (also an HCFC), both of which have much higher ODP and GWP and longer atmospheric lifetime. R-141b also is flammable. In contrast, R-123 offers a 3-5% thermodynamic advantage over additional candidates and an even greater improvement for practical systems, as discussed below.
2. The higher efficiency translates to <u>significantly reduced greenhouse gas emissions, primarily carbon dioxide, from associated energy use</u>.
3. Its <u>GWP of 76 is one of the lowest among fluorochemicals</u> and its net-GWP (Daniel, Solomon, and Albritton, 1995), with adjustment for its impact on ozone (a potent greenhouse gas), of -43 to +53 (midpoint of 5) is comparable and even lower than for most hydrocarbons (IPCC and TEAP, 2005).
4. Its <u>atmospheric lifetime of 1.3 years is one of the shortest among fluorochemicals</u> (WMO, 2003), enabling rapid atmospheric elimination in contrast to the much longer atmospheric elimination periods of CFCs and most HFCs in the event of discovery of future global environmental concerns.
5. Its low operating pressure results in <u>much lower leakage and other releases than for higher-pressure alternatives</u>, with documented emission levels on an annualized life-cycle basis of 0.5%/yr based on extended monitoring of more than 4000 new and converted chillers in three independent studies (Calm, Wuebbles, and Jain, 1999). This loss rate includes releases from manufacturing, packaging, repackaging, transport, storage, leakage, service, catastrophic accidents, decommissioning, and ultimate disposal. Typical operating leakage and service releases, verified in monitoring of large numbers of chillers for as long as seven years, were effectively zero for the majority. In contrast, medium- and high-pressure chillers are prone to loss of the majority or full charge loss in the event of a rupture or catastrophic refrigerant handling or chiller accidents (including building disasters).

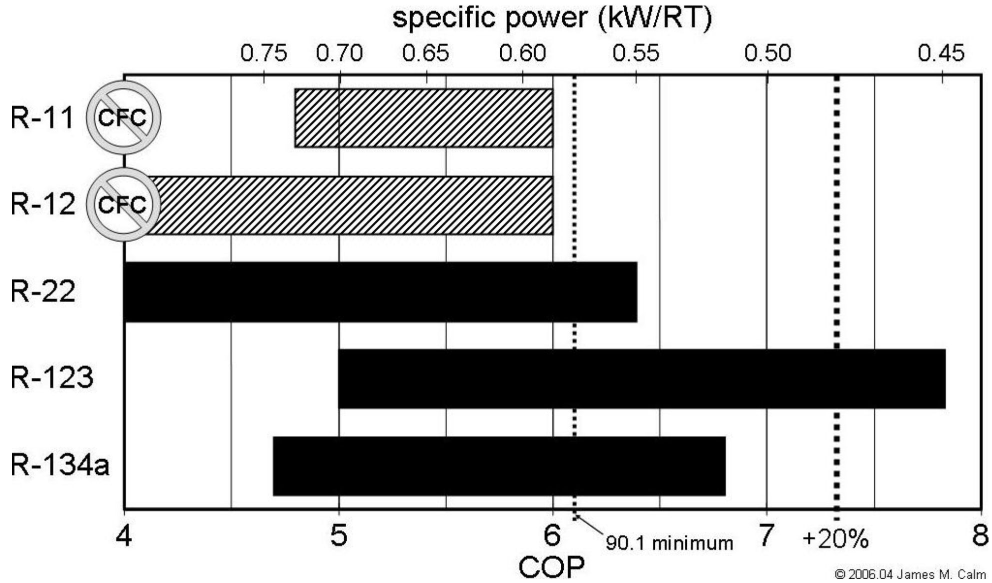

Figure 3: Efficiency ranges by refrigerant in centrifugal chillers

Figure 3 depicts the ranges of rated efficiencies for the five refrigerants most-widely used in centrifugal chillers. While R-11 and R-12 can exceed the efficiencies of R-123 and R-134a, respectively, manufacturers ceased improvement for the CFCs in developed (and in most developing) countries in the late 1980s in anticipation of their phaseout. R-123 and R-134a are the most common choices today with lesser use of R-22. All three can achieve the minimum efficiencies allowed in the most widely adopted energy standards (ASHRAE, 2004, and derivative codes and regulations). The minimum COP labeled as the "90.1 minimum" is for water-cooled chillers of 1055 kW (300 RT) capacity or larger. The figure shows that R-123 is critical to achieve 20% improvement (actually any improvement exceeding 12%) to address greenhouse gas emissions from associated energy use. For perspective, air conditioning amounts to 26% – the largest single component – of commercial building energy use in the USA; the sum of all thermal services including cooling, refrigeration, ventilation, and space and water heating amount to 48% of the total, overshadowing even the sum of lighting, office equipment, and other plug loads (EIA, 2005). These statistics highlight the large opportunities for resource conservation and for emission reductions by increasing efficiency.

Vendors of centrifugal chillers using R-134a, the primary alternative to R-123, and of refrigerant R-245fa, developed chiefly for foam-blowing use, insist for marketing reasons that R-123 is not needed. They argue that R-134a chillers driven by adjustable-speed drives (ASDs, primarily inverters) can achieve high annual performance. This argument overlooks the opportunity to apply ASDs with R-123 to realize even higher corresponding efficiencies. Moreover, near-universal use of drive gears for R-134a impellers reduces actual efficiency by 3-4% beyond the 3-5% thermodynamic advantage of R-123. Inverters characteristically degrade full-load efficiency by an additional 3% or more, taxing peak-loaded power transmission and distribution systems and, similarly, requiring more power plants to meet peak air-conditioning demands. Despite aggressive marketing, only one manufacturer – in Japan – has opted to use R-245fa as a chiller refrigerant, and that as a complement to its primary R-123 line for higher capacities with similar equipment. Although R-245fa offers higher efficiency than R-134a, but still lower than R-123, manufacturers remain concerned with R-245fa's (1) long-term availability based on potential regulation due to its GWP of 1020, (2) significantly higher cost, and (3) potential flammability, despite classification as nonflammable, since it closely approaches the flammability envelope and is marginally flammable at some test conditions.

R-134a use has increased in recent years, especially in low-cost, low-efficiency chillers, displacing some R-123 chiller use. The R-123 market share may erode further as its Montreal Protocol phaseout dates approach, unless exempted from phaseout based on the environmental justification summarized herein. For now, R-123 remains the primary selection in nearly half of all centrifugal chillers sold, with greater penetration in high-efficiency selections and especially those for extended operation, such as in the warmest climates and for process cooling (for example, for semiconductor and electronics manufacturing).

R-123 also offers important safety advantages beyond its global environmental benefits,. First it has low acute inhalation toxicity, hence is fairly safe in the event of accidental release. Second, it is nonflammable – in fact it has been used as a fire suppressant – an important consideration for large equipment. And third, its low volatility limits release rates in the event of a system rupture or a container left open inadvertently.

Kroeze and Reijnders (1992a and 1992b) analyzed the impacts of CFC alternatives on earth's equilibrium temperature. Their analyses divided these radiatively active chemicals into two groups, by GWPs. They concluded that uncontrolled use of HCFCs and HFCs from the high-GWP group can increase the equilibrium temperature by 0.28-0.66 °C (0.5-1.2 °F) by 2100 compared to substitution of HCFCs and HFCs from the low-GWP group. They also found that phaseout of HCFCs by 2035, to protect the ozone layer, could increase temperature forcing by 0.46-1.16 °C (0.8-2.1 °F) if replaced by HFCs. 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 R-123 studies identified below illustrate a specific case with consistent conclusions.

4.3. Absence of Ideal Refrigerants

Foiled by erroneous data in published references, Midgley and colleagues developed fundamental insights for the molecular makeup of refrigerants as early as 1928. Using a periodic table of the elements, Midgley quickly eliminated the inert gases based on their very low boiling points, elements yielding compounds with insufficient volatility, those resulting in unstable and toxic compounds. He determined that only eight elements (carbon, nitrogen, oxygen, sulfur, hydrogen, fluorine, chlorine, and bromine) clustered at an intersecting row and column of the periodic table offered promise as refrigerants (Midgley, 1937). Interestingly, all of the first generation refrigerants comprised just seven of them, namely all but fluorine. The first publication on fluorochemical refrigerants shows how chlorination and fluorination of hydrocarbons can be varied to provide desired boiling points (Midgley and Henne, 1930). This paper also shows how the composition influences relative flammability and toxicity.

Other investigators repeated Midgley's search with newer methods and modern databases, but reached similar findings. McLinden and Didion (1987) documented an extensive screening of industrial chemicals. Of the chemicals meeting their criteria, all but two — both highly reactive and toxic — consisted of the eight Midgley elements.

Calm and Didion (1997) extended these approaches to show how chlorination and fluorination of hydrocarbons impacts ODP and GWP. They further analyzed candidate refrigerants to relate molecular properties to performance and molecular makeup to properties, stability, reactivity, toxicity, and other key refrigerant considerations. They concluded that the probability of finding an ideal refrigerant, particularly with the exhaustive searches performed to date, is practically zero based on conflicting composition goals to achieve ideal attributes. Simply put, compromise – or trade-offs – among target attributes is unavoidable since different performance, environmental, and safety criteria impose conflicts on molecular makeup. They noted that "indiscriminate elimination of entire classes of compounds, without regard to offsetting benefits for those of low concern, may force less desirable compromises later."

Wuebbles and Calm (1997) similarly concluded that "use of single-measure ODP controls places excessive emphasis on the process rather than the objectives. To the extent that low ODP compounds have indiscernible impact, their phaseout serves no purpose." They also concluded that "phaseout of compounds based on GWPs will not resolve global warming concerns unless related emissions of greenhouse gases, from associated energy use, also are addressed. Further, "careless elimination of options can be more harmful than beneficial." Wuebbles and Calm (1997) also noted that "it is highly probable that HCFC-123 and several other CFC replacements would have survived compound-specific restrictions, had the global warming restrictions occurred first. With keener awareness of the more-limited options remaining, the framers of the Montreal Protocol might then have been more cautious in rejecting chemicals with minimal impacts and offsetting benefits."

In the specific case of R-123, once promising replacements such as R-245ca and HFEs have since been rejected after detailed evaluations, some progressing as far as full-scale tests before elimination based on unexpected findings.

5. INTERNATIONAL ASSESSMENTS

The environmental advantages of R-123 are documented in the 2002 assessment "Report of the Refrigeration, Air-Conditioning, and Heat Pumps Technical Options Committee" (UNEP, 2003b):

> "HCFC-123 has a favourable overall impact on the environment that is attributable to five factors: (1) a low ODP, (2) a very low GWP, (3) a very short atmospheric lifetime, (4) the extremely low emissions of current designs for HCFC-123 chillers and (5) the highest efficiency of all current options."

This international assessment cites studies showing that "continued use of HCFC-123 in chillers would have imperceptible impact on stratospheric ozone while offering significant advantages in efficiency, thereby lowering greenhouse gas emissions from associated energy use." The importance of these findings is highlighted by the UNEP *Annual Report* (UNEP, 2004):

> "Global production and consumption of most ozone-depleting substances (ODS) has peaked and is declining, leading scientists to cautiously predict a gradual recovery of the Earth's ozone shield by the middle of the century. … International efforts to achieve the same kind of success in tackling global climate change – which represents an even greater threat to human health and sustainable development – have been less successful."

6. RECOMMENDED CHANGE TO THE MONTREAL PROTOCOL

There are many ways to amend or adjust the Montreal Protocol (UNEP, 2003a) to enable continued or limited continued use of R-123 based on the justification summarized herein. The simplest approach, because it entails only an annex and not the actual provisions, would be to:

> Add a note in annex C where R-123 is identified as a *controlled substance* in group 1 to indicate "excluding for use as a refrigerant in centrifugal chillers based on offsetting environmental benefits."

An alternative approach would expand Article 2F, *Hydrochlorofluorocarbons*, with insertion of:

> "9. HCFC-123 is excluded from these provisions for application as a refrigerant in chillers."

Another approach would adjust Article 2F to add an *essential use exemption* for substances in Group I of Annex C predicated on documentation of greater environmental detriment unless exempted. Decision IV/25 on *Essential uses* allows qualification based on absence of "technically and economically feasible alternatives or substitutes that are acceptable from the standpoint of environment and health," though Article 2F currently has no exemption provisions.

7. CONCLUSIONS

The important environmental benefits of R-123, which eclipse its negligible impact on stratospheric ozone, provide clear and strong justification to allow its future use as a unique chemical substance, even though an HCFC. Recognizing that there neither are nor can be ideal refrigerants and that R-123 phaseout would exacerbate global climate change, its phaseout defeats rather than supports the underlying objective of protecting the environment. Further recognizing that the associated adverse impacts on climate change from R-123 phaseout contribute to what UNEP describes as a "greater threat to human health and sustainable development," the scientific findings justify revision or adjustment of the Montreal Protocol to allow continued use of R-123 based on its comparative environmental merits and indiscernible impact on stratospheric ozone.

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