

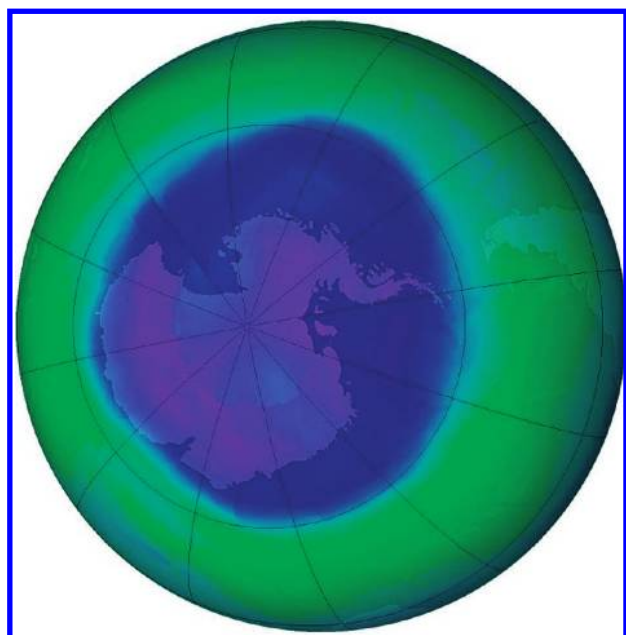
## A Bright Future for the Montreal Protocol

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Environmental policy of the 1980s could provide direction and solutions for 21st century debates.



In the early 1970s, scientists warned that anthropogenic chemicals containing chlorine (Cl) would lead to destruction of stratospheric ozone (O<sub>3</sub>), the protective veil that reduces the amount of harmful ultraviolet (UV) rays that reach the Earth's surface. A decade later, scientists working with the British Antarctic Survey described a seasonal "hole" (Figure 1) in the ozone layer over Antarctica (Farman, J. C., et al. *Nature* **1985**, 315, 207–210), resulting from the presence of Cl (species) in the stratosphere linked to anthropogenic emissions. These findings, and a growing realization that the entire planet was vulnerable to atmospheric pollutants, galvanized the international community and led to the formation of the Montreal Protocol, a global treaty aimed at phasing out O<sub>3</sub>-damaging compounds. Since its adoption in 1989, the Montreal Protocol has succeeded in eradicating production of many of the world's Cl- and bromine (Br)-containing molecules such as chlorofluorocarbons (CFCs)—organo-halogens that were once used universally in coolants, aerosols, solvents, and pesticides. "The Montreal Protocol is the best environmental treaty that the world has ever created," says Durwood Zaelke, president of the Institute for Gover-



**FIGURE 1.** The Antarctic ozone hole reached its maximum on September 12, 2008.

nance and Sustainable Development and an expert in international environmental law. The Protocol is a model for how international law can drive innovation and push the world toward sustainability, says Zaelke. Since the treaty is dynamic and evolving, scientists and policymakers are hoping that it can be strengthened to further protect the planet's sunshield while also doing more to prevent the dangerous buildup of greenhouse gases (GHGs).

At the time the Montreal Protocol was instated, climate change had not yet become a mainstream environmental issue. Nevertheless, replacing CFCs with more O<sub>3</sub>-friendly chemicals also had positive effects on the climate, because CFCs had a higher global warming potential (GWP; 1 GWP is how much CO<sub>2</sub> can warm the atmosphere) than their successors. In addition, the shift to new chemicals provided an opportunity for improved energy efficiency.

As CFCs were phased out, about 80% of the substitutes were more climate-friendly, says Zaelke. The other 20% were hydrochlorofluorocarbons (HCFCs), a class of compounds that functioned as drop-in replacements for CFCs. But as climate change has moved to the center stage over the last two decades (Figure 2), scientists have grown increasingly concerned about the contribution of HCFCs, themselves GHGs, to global warming. In 2007, the Parties to the Montreal Protocol agreed to accelerate the phaseout of HCFCs. The replacement of choice, hydrofluorocarbons (HFCs), has no impact on the ozone layer. But HFCs are powerful GHGs, with a GWP of about 1400.

In 2009, the U.S. Environmental Protection Agency (EPA) ruled that six compounds that contribute to climate change are also human health hazards, including CO<sub>2</sub> and HFCs.

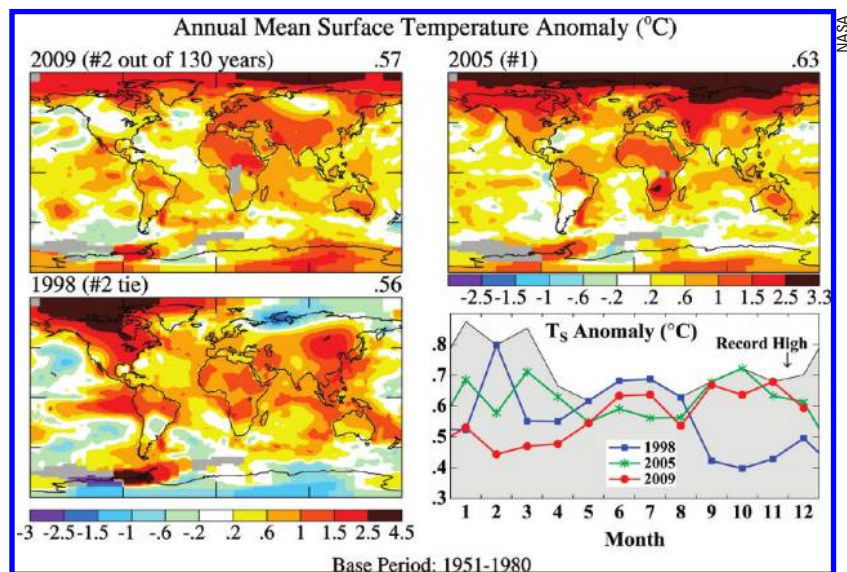


FIGURE 2. As more CO<sub>2</sub> is released year after year, the atmosphere warms ever more, inducing climate change.

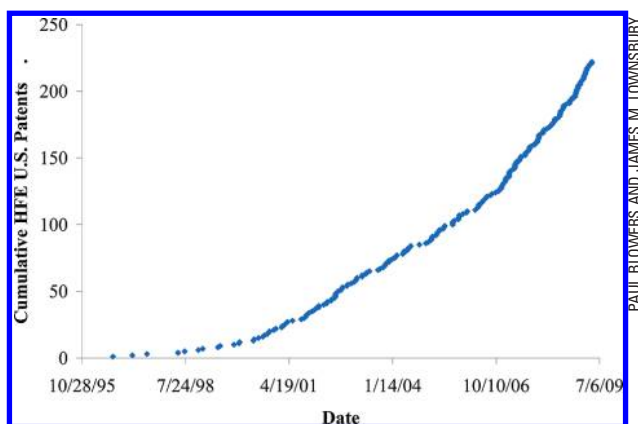


FIGURE 3. The increasing availability of HFEs warrants assessment of their potential environmental impact(s).

Now it appears that solving more complex problems like global climate change while continuing to protect the ozone layer will require greater sophistication and a deeper understanding of the whole lifecycle of a chemical, from its production and use to its end life.

If HFCs do not become regulated, their emissions are predicted to rise substantially in the next few decades due to a growth in demand for refrigeration and air conditioning as well as foam-insulating products. A different class of compounds, hydrofluoroethers (HFEs) is now being considered as the primary candidate to replace HFCs should the latter become regulated (Figure 3). Since the two classes have very similar physicochemical properties, HFEs could substitute for HFCs across the full range of applications. Yet there are significant gaps in the physical data for HFEs, so their potential impact on the environment has not yet been assessed. This led Paul Blowers and James Lownsbury, of the University of Arizona, to perform a lifecycle assessment (LCA) on an emerging HFE, trifluoromethoxy methane (CF<sub>3</sub>OCH<sub>3</sub>), which could replace HFCs for use as a refrigerant, to determine potential emissions. They report in a recent article in *Environmental Science & Technology* (*Environ. Sci. Technol.* **2010**, DOI: 10.1021/es9023354), that unless new air conditioning and refrigeration systems are upgraded for higher energy efficiency, this HFE could lead to higher GHG emissions and therefore increased global climate change compared to HFCs (specifically R-12 [dichlorodifluoromethane, CCl<sub>2</sub>F<sub>2</sub>], a Montreal Protocol predecessor, and R-134a [1,1,1,2-tetrafluoroethane, CH<sub>2</sub>FCF<sub>3</sub>]).

Blowers and Lownsbury found that when *only* the GWP of the individual chemicals is considered, switching to the HFE would be favorable for preventing global climate change. But their assessment of the overall lifecycle of the chemicals, from use through disposal, indicates that replacement with the HFE would result in increased indirect CO<sub>2</sub> emissions due to this particular refrigerant's compressor and cooling water requirements. In refrigeration systems, the compressor accounts for 69–72% of the electricity needs, according to the authors. "What's often hidden is the indirect emissions due to the efficiency of the equipment and the chemical, and the need for electricity to run compressors or pumps, or to deliver water," says Blowers.

Blowers points out that the geographic location where the refrigerant is used also plays a role in a chemical's impact on GHG emissions. In regions of the world where electricity is primarily produced from coal, the existing HFC is friendlier on the climate than the HFE. But in places where renewable or nuclear power is prevalent, the HFE results in lower greenhouse gas emissions than the HFC. These results illustrate why a "one-size-fits-all approach" is no longer sufficient for regulating chemicals and achieving sustainability, says Blowers. He further emphasizes that in some cases, as with HFEs, the dearth of physical data means the necessary calculations cannot be made to determine impact. He notes that another key factor in considering which chemical might have less impact on the climate is how much energy is required to manufacture the chemical. "What if making the HFE used up 100 times more energy than making up the HFC? Or what if it's the opposite?"

These findings also apply to the automobile industry, which is working to lower its carbon footprint by phasing out HFC from vehicle air conditioning. Studies have shown that vehicle air conditioning systems are responsible for up to 7% of fuel use in motor vehicles in the U.S. and up to 20% in vehicles in hot and humid climates, such as in China and India. Vehicle air conditioning also accounts for a third of the HFCs used in the world. Due to tightening regulations and a concern for climate change, the global automotive community is evaluating potential substitutes for the current refrigerant used in automobile air conditioning systems, R-134a, which has a GWP of 1430. However, the EU has adopted legislation that will require all new vehicles to contain a refrigerant of 150 GWP or less by 2017. (By comparison, R-12, the refrigerant used in vehicles before the compound was phased out by the Montreal Protocol, was 10,000 GWP.)



Climate legislation pending in the U.S. Congress will phase down HFC production and reward reductions in GHGs.

In a recent study in *Environmental Science & Technology*, (*Environ. Sci. Technol.* **2009**, DOI: 10.1021/es902124u), Stella Papasavva, an independent environmental consultant, and her EPA colleagues developed an inventory of the future emissions of the proposed alternative compound, HFC-1234yf (2,3,3,3-tetrafluoropropene, CH<sub>2</sub>CFCF<sub>3</sub>), from the U.S. vehicle fleet by state in 2017, in order to get a complete picture of its potential environmental impacts. HFC-1234yf is the main candidate under consideration due to its 4.4 GWP and relatively short atmospheric lifetime. Choice of that chemical, however, will require better refrigerant containment and recycling to avoid the potential of increased chemical breakdown products such as trifluoroacetic acid (TFA, CF<sub>3</sub>COOH) and volatile organic compounds (VOCs) that could contribute to smog formation.

To carry out their analysis, the researchers applied a program called GREEN-MAC-LCCP (Lifecycle Climate Performance), which Papasavva and a colleague developed with the support of an international team of experts and introduced in 2006. GREEN-MAC-LCCP assesses the climate performance of refrigerant technologies for mobile air conditioning systems (MACS), taking into account all of a chemical's emissions from the time it is produced, to its usage in a vehicle, and its final resting place in a landfill. The program, which has become a globally recognized standard in the automobile industry, also accounts for emissions from "leaks" that occur regularly through hoses and compressors as well as leaks resulting from damage to parts by road debris, for example. "The breakthrough of the GREEN-MAC-LCCP program is to introduce the lifecycle analysis thinking into the engineering community, the policymaking community, and the scientific and business communities—all of the sustainability legs you can think of—in a very transparent way," says Papasavva. They found that because HFC-1234yf emissions constitute a small portion of the VOCs in the atmosphere, they will likely not contribute significantly to ground-level O<sub>3</sub>, a constituent of smog. They also concluded that without emissions reductions, HFC-1234yf would lead to production of about five times more TFA than its predecessor refrigerant. Zaelke notes that reducing emissions of refrigerants to zero is not merely a concern for automobile manufacturers and regulators: anyone who conducts maintenance on a vehicle, from a professional mechanic to someone in their driveway, could introduce cracks that result in release of refrigerant GHGs.

These studies illustrate the complexity of trying to regulate chemicals to protect the ozone layer while also reducing the impact on climate change. "This is the kind of research that we should do before we make any fundamental systemic changes," says Braden Allenby, a professor of civil and environmental engineering and law at Arizona State University. Allenby points to corn-based ethanol as an example where the whole lifecycle was not sufficiently considered before implementing environmental regulations. Because corn-based ethanol was deemed a renewable fuel, the U.S. government threw its support behind it, offering subsidies to producers. Farmers began growing corn for fuel, rather than for food, which hiked up food prices worldwide. "It's not that corn-based ethanol is a bad technology or a bad material. It's just that the scale that we ramped up to had huge disruptive effects in a number of coupled systems, such

as food," says Allenby. "These papers show that there's a very powerful danger in focusing on only one dimension."

Arguably, there may not be a problem more in need of multidimensional thinking than climate change. Efforts to negotiate an international treaty to regulate GHGs have fallen far short of the successes of the Montreal Protocol. The recent global climate summit in Copenhagen, in December 2009, disappointed many within the international climate community who had hoped to strike a strong, binding agreement to replace the Kyoto Protocol, which expires in 2012. But negotiators reached an impasse and made only modest steps for the Copenhagen Accord, leaving some to question whether a global treaty is the best way to tackle climate change. "The whole structure that was feasible politically in Montreal just has proved enormously problematic [for] climate change," says Daniel Bodansky, a professor of international law at the University of Georgia who specializes in climate change. One reason is that regulating climate change has far greater economic implications than did phasing out O<sub>3</sub>-depleting chemicals. Bodansky believes that the best way forward in managing climate change will be for individual countries to develop national policies that will form the basis for international policies. "If the international policies try to dictate what your domestic policies are going to be, countries just get scared off."

Still, the Montreal Protocol offers some important lessons for how climate change policy might be achieved. Stephen O. Andersen, an environmental consultant retired from the EPA who cochairs the Montreal Protocol Technology and Economic Assessment (TEAP), says that one of the greatest strengths of the Montreal Protocol is it began with modest reductions of CFCs that were gradually ratcheted up by adding new chemicals and accelerating the phaseouts of each of them. "It's kind of a learning by doing and it took away all the trepidation people had," says Andersen, a coauthor with Papasavva on the study comparing automobile refrigerants. "People learned to be enthusiastic about finding alternatives. That's a big difference."

Zaelke agrees and says that huge gains can be made in the climate arena by focusing on compounds other than CO<sub>2</sub>. "By focusing obsessively on CO<sub>2</sub>, we picked a fight with the biggest bully in the schoolyard—the fossil fuel industry," says Zaelke. By looking at ways to reduce other warming agents such as HFCs, black carbon, soot, methane (CH<sub>4</sub>), and tropospheric O<sub>3</sub>, we can break the problem down into smaller, more manageable parts and make significant progress in delaying climate change, he says. In October 2009, Zaelke and his colleagues published a study (Molina, M. et al. *PNAS*, **2009**, www.pnas.org/content/early/2009/10/19/0902568106.abstract) showing that cutting non-CO<sub>2</sub> pollutants while continuing to pursue reductions in CO<sub>2</sub> emissions could delay climate change by about 40 years.

Fortunately, the Montreal Protocol already has the mechanisms to phase down HFCs and to make further significant strides toward reducing global climate change. Further, the treaty has the flexibility and agility to consider the entire lifecycle and climate performance of individual compounds. "As we regulate for more variables to achieve sustainability, we need to be more sophisticated," says Zaelke. "We've got to start, we've got to learn, and we've got to get better. But we've got to start."

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