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News & Highlights Despite Effective Ban, Ozone-destroying Chemicals Still Up in the Air Chris Palmer

As reported in a study published in April 2023, some of the globally banned chemicals that decimated the Earth's ozone layer are still finding their way into the atmosphere [1]. While unlikely to greatly impact global ozone levels, the continuing pollution has scientists concerned for two reasons: the chemicals, called chlorofluorocarbons (CFCs), are potent greenhouse gases, and, perhaps more worrying, the sources of the surprising emissions remain unidentified.

Once widely used as refrigerants and in foam insulation, CFCs such as CFC-11 were first synthesized a century ago. But it was not until the 1970s that scientists determined that CFC-11 and numerous other CFCs, which were also, but less frequently, used as aerosol propellants and solvents, were depleting the highatmosphere ozone layer [2]. At its peak, the thinning ozone layer, which blocks deoxyribonucleic acid-damaging ultraviolet radiation from the sun, was estimated to contribute to nearly 2 million cases of skin cancer annually and other harms to people, animals, and plants [3]. Then, in the mid-1980s, researchers discovered a more than 2×10^7 km² hole in the ozone layer over the Antarctic (Fig. 1) [4], eliciting an urgent international effort to repair this gap. Under the Montreal Protocol, signed in 1987, the production of more than 100 first-generation ozone-depleting compounds began being phased out in 1989 and were completely banned beginning in 2010 [5]. Production of CFCs for use as feedstocks for other chemicals continues to be allowed.

The campaign to restore the ozone layer and fill the ozone hole has been a uniquely successful environmental undertaking, with every nation in the world adopting the treaty [6]. The protocol's ban forced manufacturers to find alternatives to CFCs and other ozone-depleting substances, resulting in a 99% reduction in their use [7]. Thanks to these changes, the ozone layer has been on the mend [7]. Still, scientists estimate that the global average amount of ozone 30 km high in the atmosphere will not return to circa 1980 levels until about 2040. And because the ozone layer remains so thin over Antarctica, a huge hole still appears there every year that will not be fully plugged until 2066 [2].

Researchers recently determined that by the end of this century the Montreal Protocol will have averted 63 million incidents of cataract damage and 443 million cases of skin cancer that would have resulted in about 2.3 million deaths, in just the United States [8].

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"The Montreal Protocol has been quite successful," said Jason West, professor of environmental sciences and engineering at the University of North Carolina in Chapel Hill, NC, USA. "It helps that it is a relatively small industry that creates CFCs, and there are replacement gasses available. Once the companies realized that they would not take a big hit financially, there has been a lot of cooperation."

There have, however, been a few interruptions in this trajectory to recovery. The April 2023 paper reported the unexpected finding that global atmospheric concentrations of five CFC chemicals have spiked between 2010 and 2020 [1]. Using data from 14 measurement sites around the world, a team of researchers from Australia, Germany, Switzerland, the United Kingdom, and the United States found that concentrations of CFC-112a, CFC-113, CFC-113a, CFC-114a, and CFC-115 have increased since 2010, reaching a record high abundance in the atmosphere in 2020 [1], albeit at still exceedingly small levels. CFC-112a, for example, is found in less than one-tenth of a part per trillion in the atmosphere.

"They are really low-concentration gases, but they are quite harmful," said Luke Western, a Marie Curie Research Fellow at the US National Oceanic and Atmospheric Administration (NOAA) and lead author of the 2023 report. "These long-term, high-precision measurements are really key to raising an early warning flag."

Depending on the source of emissions, the jump in ozonedestroying substances will barely hamper ozone-layer recovery, but the planet-warming impact of the gases is a concern. CFCs are potent greenhouse gases that trap heat up to 10 000 times more efficiently than CO₂. Regarding the five CFCs measured in the April 2023 paper, the amount emitted in 2020 would have an impact equivalent to the warming effect of Switzerland's total annual carbon emissions, Western said. "That is a big deal—if Switzerland went carbon-neutral, it would be headline news."

The 14 sites that contributed measurements to Western and colleagues' results represent about half of the just 30 or so such monitoring sites around the world—most of which are in the Northern Hemisphere. Earlier research found that while monitoring coverage was robust enough in North America and Europe to effectively rule out those regions as sources of increased levels, there was enough signal to identify East Asia as the source of three of the increasing CFCs—CFC-113a, CFC-114, and CFC-115 [9,10].

Western said it was not possible to further pinpoint the cause or source of the pollution due to the limited number of monitoring sites. Such sites, he said, are expensive to build, hard to maintain,



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Fig. 1. Ozone column amounts in Dobson units (the number of ozone molecules required to create a layer of pure ozone 0.01 mm thick at a temperature of 0 °C and a pressure of 1 atmosphere (the air pressure at the surface of the Earth). Lower ozone column heights (blue to yellow), such as those measured in Antarctica in 2007, represent thinning or holes in the ozone layer. Ozone levels in Antarctica during springtime (September–October) are not expected to return to pre-1980 levels until 2066. Credit: Wikimedia (CC BY-SA 3.0).

and need local personnel to operate them. "When we look at global trends, measurements tend to come from sites in remote locations—like mountaintops and remote islands like Samoa and Tasmania, far away from any polluting sources," Western said. "Almost by definition, we do not really see pollution happening at those sites. You really have to be within a couple hundred miles of a polluting source to locate it."

Stephen Montzka, senior scientist at NOAA's Global Monitoring Laboratory, said the parties to the Montreal Protocol have expressed a renewed interest in building new monitoring stations. "Their interest has increased substantially since the CFC-11 issue," Montzka said, referring to new accumulations of CFC-11 emissions first observed beginning after 2012 [11]. "We do not have a dense regional network that can identify and quantify emissions for all the important regions of the world and that makes it difficult to rapidly locate and address problems."

As reported in 2019 [12], readings from monitoring stations in the Republic of Korea and Japan showed the CFC-11 emissions appearing to originate from eastern China. A follow-up study reported in 2021 showed that the emissions—likely related to the use of CFC-11 as a blowing agent in the production of foam insulation [12]—had declined, suggesting successful curbing of the practice by the Chinese government [13]. "There was pressure by the parties to the Montreal Protocol, and China laid out a plan for how they were going to respond—it appears to have made a difference," said Montzka, who was a co-author of the 2018, 2019, and 2021 reports as well as the more recent April 2023 report.

As for the other CFCs found in the atmosphere between 2010 and 2020, two of them, CFC-112a and CFC-113a, have no known current uses and the researchers are unsure about what their sources might be, although CFC-112a had previously been used

in the production of fluorovinyl ether or solvents. Western said the other three chemicals—CFC-113a, CFC-114a, and CFC-115 are likely being released by manufacturing plants during the production of hydrofluorocarbons (HFCs), which are widely used as replacements for CFCs in air conditioners, refrigerators, and fire extinguishers [14]. "Either they are not being fully converted during chemical reactions, and there are leakages in that process, or they are byproducts that manufacturers are not destroying as they should," Western said.

HFC levels are typically monitored at the same sites that track CFCs, Western said. While harmless to ozone, HFCs, like CFCs, are extremely potent greenhouse gases that can heat the planet hundreds to thousands of times more efficiently than CO_2 . Because of this, their use is also subject to a negotiated international agreement, the 2016 Kigali Amendment to the Montreal Protocol [15]. The agreement mandates an 85% reduction in HFC use by 2047, a "phase-down" projected to avert 0.3–0.5 °C of additional global warming [2]. However, even production of some next-generation refrigerant chemicals that are replacing HFCs—hydrofluoroolefins (HFOs)—can emit some CFCs [14].

While the Montreal Protocol has been highly successful, it has little direct parallel to other climate accords aimed at reducing emissions of other greenhouse gases, such as the Paris Agreement [16]. For the banned ozone-destroying and subject to phase-down chemicals, the corporations that manufacture them can still profit by making their replacements. "Producing refrigerant gases involves a relatively small sector of the economy, but energy is fundamental to driving our world economy," West said. "It is much harder to get the fossil fuel megacompanies and their vested interests onboard to accept changes that might mitigate climate change."

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