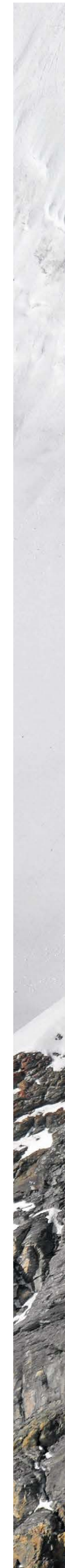
The pollution detectives

Someone, somewhere, is producing banned ozone-destroying chemicals. Meet the researchers tracking down the rogue polluters who are putting the planet at risk. **By Jane Palmer**



High in the Swiss Alps, scientists in a small research station are busy fingerprinting the atmosphere.

Perched on a mountain ridge at around 3,450 metres altitude, the Jungfraujoch centre boasts five laboratories, a workshop, a library, a tiny kitchen and ten small bedrooms. Day and night, funnels suck in the thin mountain air and channel it into a series of instruments designed to separate, identify and measure the chemicals swirling through this pristine locale. "We are scanning the whole spectrum of thousands and thousands of molecules," says atmospheric chemist Martin Vollmer. "It is like we are taking the DNA of the atmosphere."

Vollmer, who works at the Swiss Federal Laboratories for Materials Science and Technology (EMPA) in Dübendorf, specializes in sniffing out newly emerging trace gases, which make up less than 1% by volume of the planet's atmosphere. Some of the most notorious are the chlorofluorocarbon (CFC) coolants used for refrigeration and foam production. These destroy the ozone layer, the shield that protects life on Earth from damaging ultraviolet light. In 1987, after researchers demonstrated the threat posed by CFCs, nations banded together to adopt an international agreement known as the Montreal Protocol, to control and eventually phase out CFCs. Updates to the treaty have outlawed some of their replacements, which also turned out to damage the ozone layer, climate or both.

Behind the scenes, scientists such as Vollmer are keeping watch over the health of the atmosphere – in part to make sure nations are honouring their promises. "This is detective work," says Stephen Montzka of the US National Oceanic and Atmospheric Administration (NOAA) in Boulder, Colorado. "Our remit is to understand if things are changing as expected."

For many years, the news coming from these air-monitoring campaigns was good. Concentrations of CFCs and several other dangerous compounds were declining steadily. It was the biggest win in environmental policy the world has ever seen, say researchers.

Then, in May 2018, Montzka reported a disturbing blip: levels of one of the most harmful chemicals, trichlorofluoromethane, known as CFC-11, weren't dropping as fast as expected[1], suggesting that companies were producing this compound somewhere, in violation of the protocol. "It was the most surprising and shocking thing I've seen in my entire career," Montzka says.

Montzka's research pointed to eastern Asia, and a follow-up study last May pinpointed the source of a significant fraction of the emissions to two provinces in China[2]. The discovery of these rogue CFC-11 emissions has highlighted just how much the Montreal Protocol relies on the vigilance of scientists. But it has also raised questions about whether researchers can keep up with an ever-growing list of damaging compounds – some so new that their impacts remain unknown.

For the moment, they hope they are winning. Last November, nations that are parties to the Montreal Protocol gathered in Rome, where Montzka presented some positive news about the illegal CFC emissions.

Fresh start

It all starts with fresh air. Every week, come rain, shine or, more typically, snow, Jen Morse makes the trek up to a small green shack on Colorado's Niwot Ridge, which lies on the Front Range of the southern Rocky Mountains. In summer, she can drive part of the way and has to hike only the final kilometre of the 6-kilometre trip; in winter, she has to ski the entire distance to the remote, wind-swept spot at 3,523 metres altitude, carrying four large gas canisters in her backpack.

Once in the shack, Morse, who is a climate technician at the University of Colorado, Boulder, connects each flask to an inlet and waits for them to fill. She then heads back down and delivers the snapshots of mountain air to NOAA's Global Monitoring Division in Boulder, just 40 kilometres away. At the lab, Montzka and his colleagues run the flasks' contents through three separate gas chromatographs to determine what resides in the 'background' atmosphere, which doesn't have any nearby contamination and therefore provides a reading of chemicals circling the entire globe. "We have to pick special locations far away from local sources of pollution to do that," Montzka says. "These are desolate areas that are hard and expensive and difficult to be at."

Flasks are shipped to the lab from 16 sites around the world, including the South Pole, the top of Greenland's ice cap and the tip of Tasmania in Australia.

The NOAA team runs samples through its instruments to determine the levels of 50 trace gases in the atmosphere. The Jungfraujoch lab is part of a second, NASA-sponsored network called the Advanced Global Atmospheric Gases Experiment (AGAGE), which has 13 active stations in a dozen nations.

Some of these sites have been monitoring CFCs and related compounds since the 1970s. When these compounds were invented in the 1920s, chemists regarded them as safe. But by the 1970s, researchers recognized that CFCs could drift up to the stratosphere and erode the protective ozone layer. This realization – along with the shocking discovery in 1985 of a hole in the ozone layer over Antarctica – led nations to adopt the Montreal Protocol.

NOAA and AGAGE researchers meet regularly to discuss their findings, which they summarize in reports for the parties to the Montreal Protocol. These reports document the decline in the concentrations of CFCs in the atmosphere and they have identified other

The Jungfraujoch research station in Switzerland is part of a global network that monitors the atmosphere.

ozone-damaging chemicals. As such, scientists have continued to provide input into the protocol, which nations have updated to limit the production of other harmful gases. "It wasn't a one-stop scientific treaty," says David Fahey, an atmospheric chemist with NOAA, and one of the four co-chairs of the Scientific Assessment Panel of the Montreal Protocol.

The teams monitoring the air are forever playing catch up as new compounds appear in the skies. Even before CFCs were banned, manufacturers developed substitute coolants such as hydrochlorofluorocarbons (HCFCs). But researchers quickly found that these compounds also damage the ozone layer, and a 2007 amendment to the protocol called for the complete ban of production and consumption of HCFCs by 2030. Next came a third generation of coolant, the hydrofluorocarbons, or HFCs. These don't contain chlorine or bromine, and so they don't damage the ozone layer. But they turned out to be powerful greenhouse gases; most have a warming power between 1,400 and 5,000 times greater than that of carbon dioxide.

Consequently, in 2016, delegates agreed on the Kigali Amendment to the Montreal Protocol, which calls for cutting the production and use of HFCs by 80–85% by the late 2040s. The amendment entered into force at the start of 2019 with the goal of avoiding warming by up to 0.5 °C.

Monitoring stations such as Jungfraujoch track progress towards those goals in different parts of the world; sometimes they find problems. Scientists at the station found that northern Italy had emitted between 26 and 56 tonnes of HFC-23 per year in 2008–10, yet the official Italian inventory had estimated only 2.6 tonnes for the whole country.

Blindsided

Until a few years ago, it seemed that the main threats to the ozone layer were on their way out and scientists could focus on the newer gases. Then came the first hints of trouble.

One day in 2013, Montzka ran the air from his weekly delivery of flasks through the mass spectrometer he had designed nearly 30 years earlier. But when he looked at the output of these routine measurements from the previous few months, he noticed something odd: the levels of CFC-11 were not declining as fast as before.

To Montzka, the observation made no sense — production of CFCs had been phased out worldwide three years earlier. Before 2012, the concentration of CFC-11 had dropped by about 0.8% per year, but Montzka's flask data suggested the decline rate had slowed substantially. "I was totally amazed, I couldn't believe it," Montzka says. "Then I thought to myself

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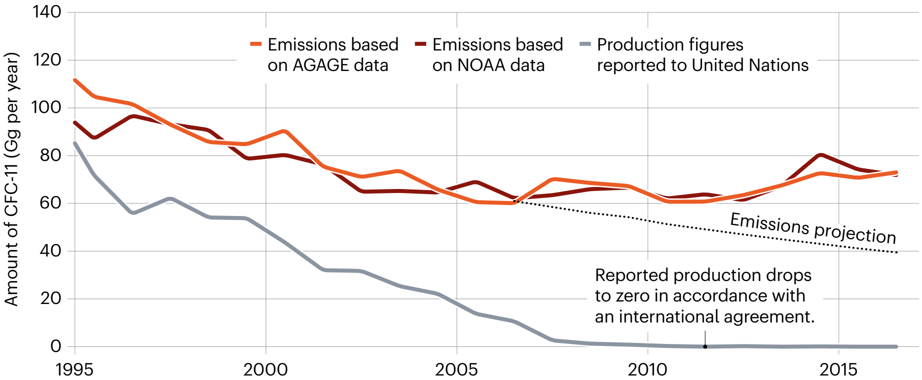
SECRET STOCKS

Researchers use data from two air-monitoring networks to calculate emissions of CFC-11, which can come from new production or leakage from older products. Emissions declined as expected until 2005, but then plateaued and started to rise because of rogue manufacturing.



that it was just some blip that will go away next year — something weird has happened in the atmosphere, or in my instrument."

Montzka double-checked his measurements and then, for the next few years, he and the international team searched for possible explanations. Eventually, the trail of evidence led to a single conclusion: emissions of CFC-11 were going up rather than down, pointing to a violation of the Montreal Protocol (see 'Secret stocks'). "It did take a while to unravel the story in a way that I thought would be useful to the international community," Montzka says.

Between 2002 and 2012, CFC-11 emissions averaged 54,000 tonnes per year, owing to gradual leakage of old stores of the compound contained in foam insulation and appliances made before the mid 1990s. But the researchers found that between 2014 and 2016, average emissions grew to 67,000 tonnes a year — an increase of roughly 25%[1]. They also noted that, in 2013, the flask data at the Mauna Loa Observatory in Hawaii suddenly showed increased levels of CFC-11 in the pollution plumes regularly recorded at the site. On closer investigation, they found that the sources of those plumes, and the uptick in CFC-11 emissions, came from eastern Asia.

A team of scientists immediately began to look for clues in an independent set of measurements, in particular those from the AGAGE stations on Jeju Island in South Korea, and Hateruma in Japan. Data from these stations revealed spikes in CFC-11 whenever plumes of pollution passed by. And the spikes had grown since 2013.

With this information, the scientists ran computer models using atmospheric circulation data and the monitoring-station measurements to determine where the pollution was coming from. Four independent modelling groups worked on solving the puzzle, and all came back with the same answer: about 7,000 tonnes per year were coming from the Chinese provinces of Shandong and Hebei[2].

The newly discovered emissions will not significantly delay recovery of the ozone layer, says Matthew Rigby, an atmospheric chemist at the University of Bristol, UK. "But if they carry on, we could be seeing delays of years or more," he says.

A close call

On 4 November 2019, Tina Birmpili, executive secretary of the UN Ozone Secretariat, delivered her opening speech at the 31st Meeting of the Parties to the Montreal Protocol in Rome. She began by praising the success of the treaty so far and the decisive action taken by China to address its emissions of CFC-11, including setting up a national monitoring network and increased penalties for companies that violate production bans. "CFC-11 was an alarm for all parties to ensure that they address illegal production swiftly and send a clear message to those who would break the law," Birmpili says.

Then Birmpili turned her attention to some unanswered questions around the unexpected CFC-11 emissions. The researchers' most recent published findings estimate that CFC-11 emissions from China account for 40–60% of the global increase between 2014 and 2017, but that leaves 4,000–10,000 tonnes unaccounted for[2].

Right now, the researchers aren't in a position to say whether there are other sources of illegal emissions or whether uncertainties in their models can account for the remaining percentage of the global trend, Rigby says. In the future, they will try to improve their models to see if they can glean a more accurate picture of the CFC-11 changes, he says. Montzka thinks that this time the monitoring community was lucky: researchers were able to detect the global trend change fairly early and happened to be making measurements near the region where at least some of the new emissions were coming from. But if CFC-11 had emanated from India, Russia or South America, the existing networks wouldn't have been able to identify the location of the source because no regional stations exist nearby.

When Montzka stepped up to the podium in Rome, he presented some fresh observations from the global monitoring data. In 2018, the rogue emissions seemed to slow or disappear. The decline of the global concentrations of CFC-11 accelerated, and the amount of the gas in plumes reaching the monitoring stations in Hawaii and Jeju Island substantially decreased. Although researchers have yet to fully check the latest measurements, they take heart from the trend. "The evidence suggests that the Montreal Protocol is being effective in yet another set of circumstances — in this case, unprecedented circumstances," Fahey says.

If the CFC-11 concentrations continue to decline over the next few years, it will mark a significant victory for the scientists and their monitoring networks. "There's always the discussion of whether it is really important that we are still here," says Stefan Reimann, an atmospheric chemist at EMPA. "And, yes, history proves that we still have to be here."

The rogue-emissions incident highlights weaknesses in the current system, which was developed to investigate the science of how the atmosphere is changing, not to track emissions, says geochemist Ray Weiss at the University of California, San Diego. "We never expected to see a violation, which is a lesson in itself really."

In response to the latest challenge, NOAA added a flask-collection site on the west coast of South Korea to gather more information from eastern Asia. And this year, the parties will continue to discuss what is needed to ensure a similar violation doesn't happen again, Birmpili says.

Meanwhile, the scientists are maintaining their strategy of watching, waiting and investigating. At Jungfraujoch, Vollmer is paying close attention to the latest generation of coolants: hydrofluoroolefins (HFOs). As those break down, some of them, such as one known as HFO-1234yf, can decompose into trifluoroacetic acid, which is toxic to some plants and soil organisms. The German and Norwegian environment agencies have recommended more research on the HFOs.

Measurements at Jungfraujoch show a rapid rise in these compounds. In 2011, HFO-1234yf appeared in none of Vollmer's samples. By 2018, it was in 71% of them.

Currently, industry produces only a small amount of HFOs because the phase-out of HFCs has just begun. "But if you make a back-of-the-envelope calculation and you replace all the compounds that we've been using previously by the HFOs, there are going to be huge quantities of these gases," Vollmer says.

So he makes the journey each month to the high, glaciated saddle between two peaks in the Alps, where Jungfraujoch's instruments hum away day and night. "We have to keep watching," he says.

Jane Palmer is a freelance writer based in Colorado.

1. Montzka, S. A. *et al. Nature* **557**, 413–417 (2018).
2. Rigby, M. *et al. Nature* **569**, 546–550 (2019).

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