Scouring the atmosphere for pollutants

CFCs are still harming the ozone layer; industrial gases with a high greenhouse potential heat up the atmosphere. The polluters don't go undiscovered, though. Empa atmosphere scientists are tracking the trace gases with highly sensitive instruments and identify the sources of pollution with the help of meteorological data.

TEXT: Rainer Klose / PICTURES: iStockphoto, Empa, Nasa

Praying and hoping for improvements wouldn't have done any good. In 1987 the dwindling ozone layer could only be saved through an international agreement – the Montreal Protocol. 197 countries have since ratified the treaty and banned the worst ozone killers: greenhouse gases in spray cans and synthetic foams, cooling agents and fire extinguishing gases. The most recent model calculations show that the earth's protective shield is slowly starting to recover. By around 2050 the ozone layer above the southern hemisphere will probably be as thick as in 1980 – if we continue to be on our guard.

Stefan Reimann along with his team is monitoring which substances are particularly damaging for the ozone layer right now. The Empa scientist sits in a rather quiet room in the basement of the laboratory building on Empa's Dübendorf campus. The computer is his tool. This is where the data from the AGAGE network are collated – Advanced Global Atmospheric Gases Experiment. Around the world ultrasensitive scientific instruments literally keep their noses in the wind to identify trace gases that shouldn't be there. The Swiss nosy parker is located 3,580 meters above sea level at Jungfraujoch, the Irish one at Mace Head on the Atlantic coast and the Norwegian one at Ny-Ålesund on Spitzbergen.

Every two hours these devices "breathe" in two liters of air from their environs and draw it through an activated carbon filter cooled to -170 degrees Celsius. At the end of the measurement the filter is

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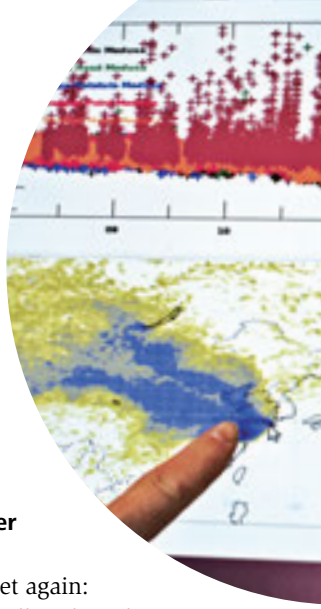
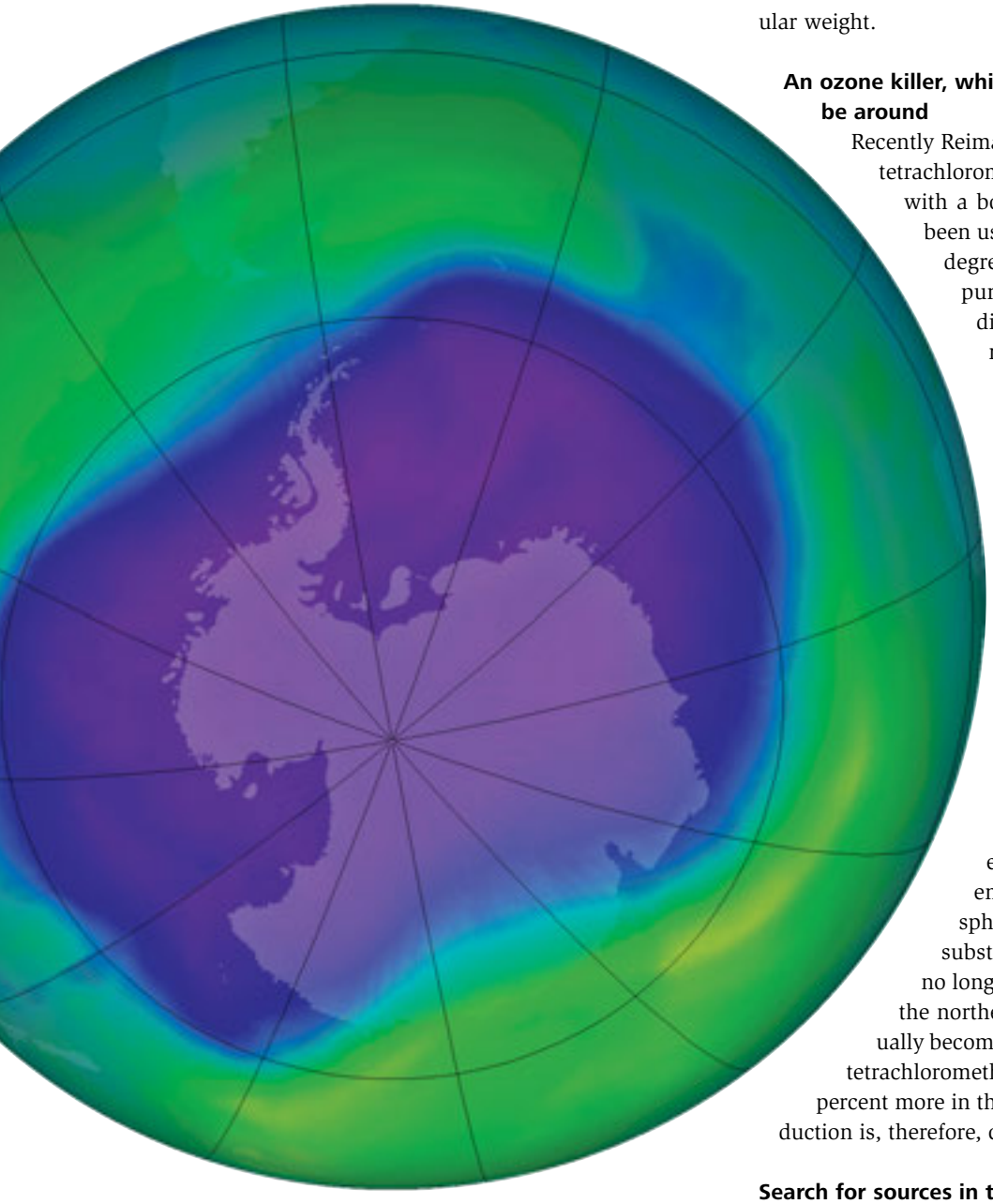


heated to more than 100 degrees and the captured chemical substances are placed in a GC-MS, a gas chromatograph with an attached mass spectrometer. There each individual substance can be identified thanks to its signature molecular weight.



An ozone killer, which should no longer be around

Recently Reimann was surprised yet again: tetrachloromethane, a sweet-smelling liquid with a boiling point of 77 degrees, which had been used in the past in fire extinguishers and as a degreasing agent in workshops and chemical purification (it is globally banned today), is disappearing far more slowly from the atmosphere than expected. Normally, the substance would gradually degrade in the atmosphere – the concentration should fall by about four percent every year. But this isn't happening as Reimann could see from his data. It is only falling by around one percent a year. This means that new tetrachloromethane is being emitted somewhere. The researchers estimate a volume of 39,000 tons a year. The substance may still be used by industry as an intermediate product for chemical syntheses – but small leaks in a few factories here and there still don't go far enough to explain such an emission level.

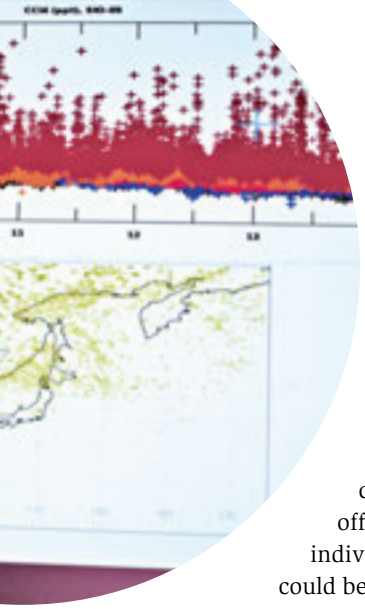
And another clue in Reimann's data points to ongoing tetrachloromethane emissions. "Around 90 percent of global emissions come from the northern hemisphere", explains the atmospheric chemist. If a substance – for instance after a global ban – were no longer to be emitted, then the concentrations in the northern and southern hemispheres would gradually become aligned. Reimann: "This is not the case for tetrachloromethane. We consistently measure one to two percent more in the north than in the south. In the north production is, therefore, continuing."

Search for sources in the atmosphere

Whenever high concentrations are measured at Jungfraujoch, the Empa researcher compares the noticeable peaks in his measurements with meteorological data. The air currents during the measurement reveal at which location the substance was blown into the air. "The source of tetrachloromethane is not in Europe", comments Reimann, "that's for sure". As the European measurement stations on their own are not capable of pinpointing any exact location in the rest of the world, the Empa scientist looked into the dataset from the AGAGE network. And in fact: one station in South Korea identified major peaks, which means some of the emissions are likely to come from Asia.

To ensure that politicians and the public also take note of the most recent findings about the condition and chemistry of the at-

Video
What would have happened if CFCs hadn't been banned in 1987? An animation by NASA provides the answer.



mosphere, Stefan Reimann and his international colleagues regularly publish articles in scientific journals and pass on the data to the Federal Office for the Environment (BAFU) and other national authorities. There the Empa observations are compared with estimates based on the official emission data reported by the individual countries. These findings could be included in the next round of negotiations about adjustments to the Montreal Protocol. Reimann also regularly writes reports for the World Meteorological Organization (WMO) in Geneva. His latest report is brand-new, dating back only to September 2014: Scientific Assessment of Ozone Depletion. In this report he warns about the growing indirect influence of climate gases such as laughing gas, methane and carbon dioxide on the ozone layer. Furthermore, increasing levels of fluorinated hydrocarbons (HFCs) are already beginning to reverse the progress of the Montreal Protocol in countering global warming. So the problem hasn't been solved for good.

Greenhouse gases from northern Italy

The researchers not only catch ozone killers but also classical greenhouse gases (regulated under the Kyoto Protocol) in their "dragnet operation". One particularly harmful greenhouse gas is HFC-23 (trifluoromethane). The substance is formed as a by-product during the manufacture of HCFC-22, which is used amongst other things to make Teflon. The manufacturers are obliged to report HFC-23 emissions. But it seems they only do this sporadically. Italy, for example, reported an annual emission of 2.6 tons for 2009 – the measurements at Jungfraujoch showed, however, that, during the period in question, between 26 and 56 tons were released into the atmosphere over northern Italy, to be more precise from just one factory. What makes this situation so critical: HFC-23 has a climate impact about 15,000-fold stronger than that of carbon dioxide (CO_2). In other words: in just one year this factory's emissions contribute the equivalent of 50,000 Italian mid-range cars that each travel 10,000 kilometers to global warming.

According to Reimann these measurements are – unfortunately – not yet being used to verify the Kyoto Protocol for imposing international limits on the greenhouse effect. The reason: his analytical method that compares trace gas measurements with weather data was only validated ten years ago. The Kyoto Protocol, however, was already negotiated in 1997 and entered into force in 2005 before the negotiators were familiar with today's skills of the "atmosphere detectives". And so it is left to each individual country to correctly report its emissions (or not) until the next climate summit. //

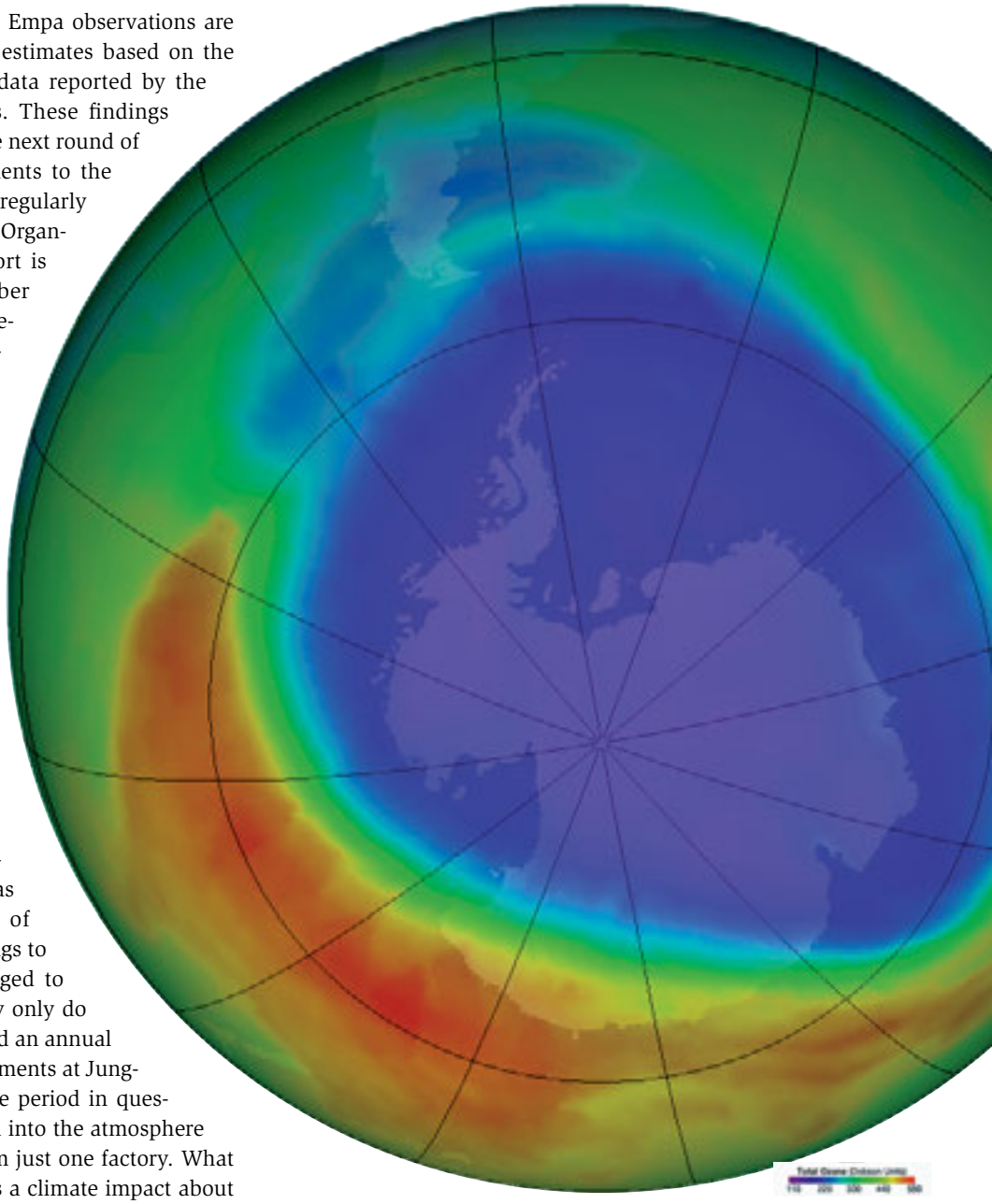


Photo left: On September 24, 2006, the hole in the ozone layer was at its biggest to date.

Photo right: The hole in the ozone layer over the Antarctic measured on September 18, 2014.
Source: http://ozonewatch.gsfc.nasa.gov/
(The Dobson Unit scale reveals the total amount of ozone from the Earth's surface into the empty cosmos.
Bluish-purple: lowest ozone levels; red: highest levels.)

Photo top: The ozone killer tetrachloromethane is still produced in large amounts in Asia. Thanks to the global AGAGE monitoring network, the region where the pollutant comes from can be identified.