Searching for coolant traces in the atmosphere

March 24 2015

The Jungfraujoch station

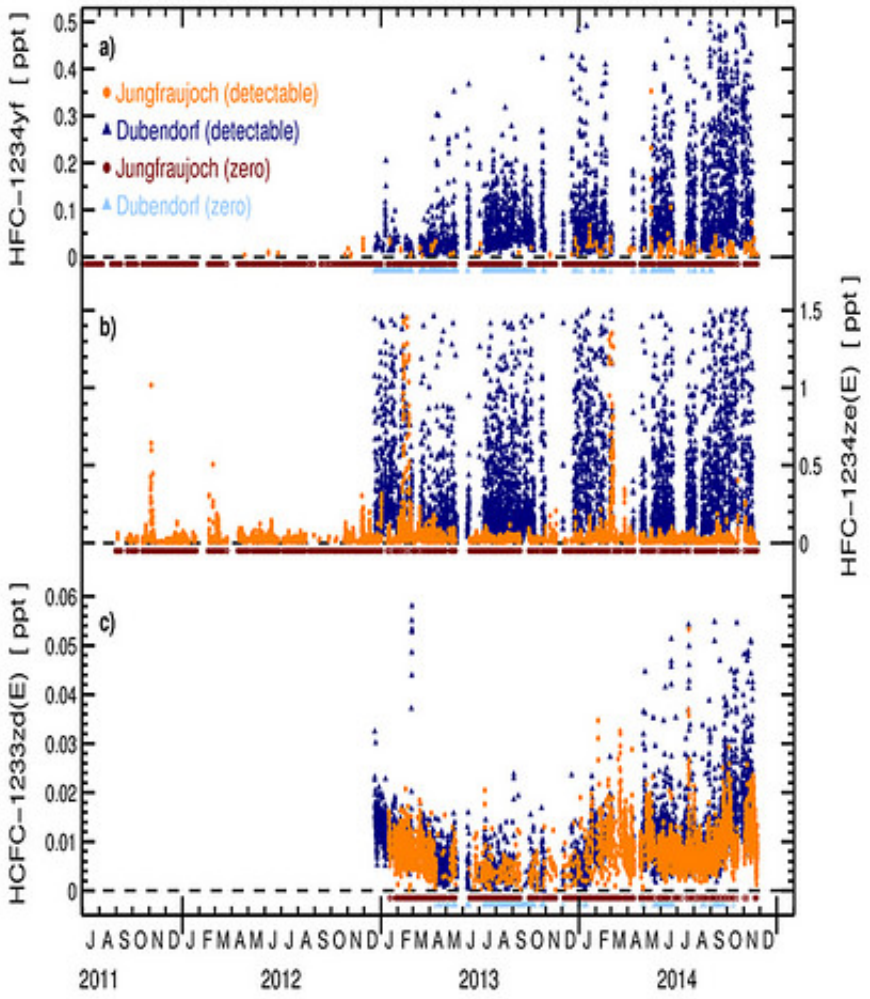
Fourth generation halogenated coolants and foaming agents have only been in use for a few years. They have replaced persistent greenhouse gases such as R134a, which were used in (car) air conditioning units, refrigerators and in a variety of foams. Empa researchers have now published first measurements on the atmospheric distribution and

abundance of these new substances. They show that the new coolants are frequently used in Europe - and that their use is increasing.

The latest generation of halogenated coolants is a big step forward: these substances decay more quickly in the atmosphere hence their lifetimes are considerably shorter. That is why they do not add nearly as much to the greenhouse gas effect as their stable predecessors. These new substances, with names like HFC-1234yf, HFC-1234ze(E) and HCFC-1233zd(E), are now also more frequently used, as evidenced by the first measurements made by Empa at the Jungfraujoch and in Dübendorf. Since the start of the measurements in 2011, at the same time as the market launch of the new substances, the number of events in which these three substances could be traced has steadily increased. This indicates that a growing number of manufacturers are choosing to replace 3rd generation coolants with the new generation of coolants in their products.

The team led by Empa researcher Martin Vollmer is the first to analyse the traces of the latest generation of coolants in the atmosphere. "The first generation coolants arrived on the market in the 1930s. The process of taking measurements to trace these substances in the air began much delayed, 40 years later. The gap between market introduction and first measurements gets narrower with every generation," said Vollmer.

Measurements from Day 1



The measurement values show steady increases in all three of the new coolants and foaming agents. Depending on the air currents and wind directions, high concentrations of these even reached the Jungfraujoch in places - whereas in Dübendorf very high concentrations could be observed constantly. The diagram also shows that HCFC-1233zd(E) occurs at roughly the same concentrations both in Dübendorf and on the Jungfraujoch. This indicates that the foaming agent is used in tiny amounts or not at all in Europe - but its likely source is in North America or Asia. Credit: Empa

Researchers have been tracing the distribution of the latest refrigerants in the atmosphere since their introduction onto the market. What is

interesting is that the substance HFC-1234yf did not appear at the start of the test series at the Jungfraujoch. It is evident that the substance is anthropogenic – it is man-made. "Zero values are nothing negative. Quite the contrary. This way, we could prove that the substances do not occur in nature. That is also an important finding," explains Vollmer. It took two years until the concentrations of the new substances in the atmosphere were high enough to be detected at Jungfraujoch. Vollmer sees the investigations as a fully functioning early warning system. As soon as a new substance is on the market, researchers can monitor it and identify precisely when the substances appear in the atmosphere for the first time - and how long they persist. While, for example, the first generation of coolants remain in the atmosphere for decades (and even now traces of them can still be detected), the new coolants "survive" for only a few days or weeks before decaying in the atmosphere.

However, this degradation poses new problems for science. The coolant HFC-1234yf, for example, is not exactly unproblematic. Although it degrades faster in the air than its predecessor, it decomposes into a new harmful substance: trifluoroacetic acid, an extremely stable molecule that does not naturally degrade any further. It accumulates in water and living organisms, and it is also toxic for certain plants, especially certain types of algae. So in terms of the atmosphere the problem is solved, but now other kinds of ecosystems face new challenges – and so does research. It is increasingly important for researchers to consider not only the half-life of the new substances in the atmosphere, but also the effects of their decay products.

Molecules from all over the world

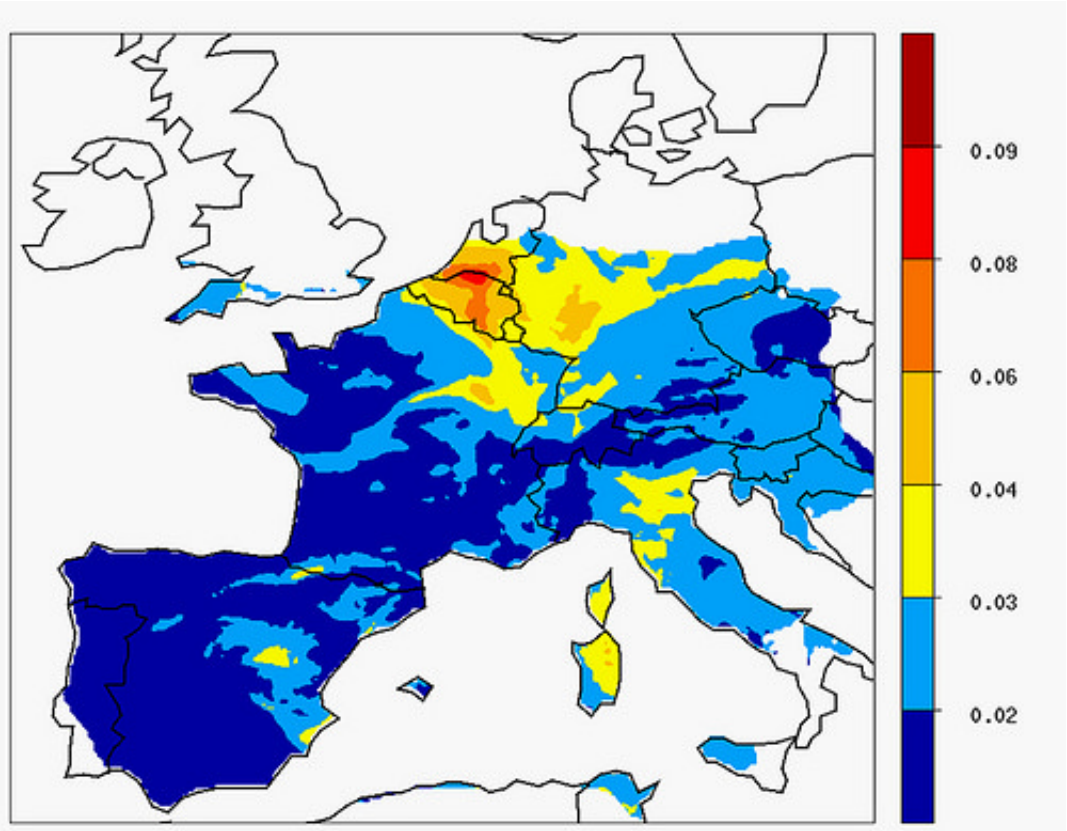
The Jungfraujoch station

The measurements and models from Switzerland not only show whether and to what degree certain substances are present in the region, but also give indications on their source regions. In the case of the foaming agent HFC-1234ze(E), the "epicentre" of the emissions lies on the border between Belgium and the Netherlands. Empa's researchers identified this by combining their data with meteorological data on air movement.

Anaesthetics in the air

During surgery patients are often anaesthetised using inhalation anaesthetics. They are inhaled via a breathing mask and then exhaled by the body in virtually unaltered form. These substances then enter the atmosphere via the operating theatre's ventilation system. The problem is

that anaesthetics belonging to the group of halogenated ethers (fluranes) are powerful greenhouse gases. The industry is keeping a low profile as to the quantities in production. With the aid of air analyses, Empa researchers, in collaboration with international research groups, have been able to gather initial data on emission of the anaesthetics Desflurane, Isoflurane and Sevoflurane. Flurane emissions across the world correspond to around 3 million tonnes of CO2. In comparison, Swiss automotive traffic emits around three times that amount every year. The study is due to be published in the science journal *Geophysical Research Letters*.



The map clearly shows a single European emissions source of HFC-1234ze(E) on the border between Belgium and the Netherlands. Credit: Empa

More information: "First Observations of the Fourth Generation Synthetic Halocarbons HFC-1234yf, HFC-1234ze(E), and HCFC-1233zd(E) in the Atmosphere" *Environ. Sci. Technol.*, 2015, 49 (5), pp 2703–2708 DOI: 10.1021/es505123x

"Modern inhalation anesthetics: Potent greenhouse gases in the global atmosphere" *Geophys. Res. Lett.*, 42, DOI: 10.1002/2014GL062785

Provided by Swiss Federal Laboratories for Materials Science and Technology

Citation: Searching for coolant traces in the atmosphere (2015, March 24) retrieved 27 April 2024 from https://phys.org/news/2015-03-coolant-atmosphere.html

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