

## Media communiqué

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*Empa develops an “early warning system” to detect new halogen-containing air pollutants*

### First evidence of new fluorocarbons in the atmosphere

***Just about as soon as they are manufactured and released into the atmosphere, new air pollutants can be identified and measured by Empa researchers. Ever more sensitive environmental analysis instrumentation make this possible, as two recently published studies show very impressively. Environmental scientists from Empa were able to demonstrate for the first time the presence of two new halogenated foaming agents in the air above the Jungfrauoch, data which will allow estimates to be made of the worldwide emissions of these climate-changing substances. This information is essential for a better understanding of chemical processes in the atmosphere, and the role played by these chemical in global warming. The two substances under investigation currently show relatively low concentrations in the atmosphere but the levels are increasing rapidly.***

The Montreal Protocol, which came into force in 1987, led to an incremental ban on certain halogenated hydrocarbons responsible for damaging the earth's ozone layer, in particular the infamous “ozone killing” chlorofluorocarbons or CFCs. Among other applications, these were commonly used as foaming agents in the manufacture of plastic packaging and insulation materials. Manufacturers were compelled to find and use alternatives according to a fixed schedule. As substitutes for the CFCs came the HCFCs (hydrochlorofluorocarbons) with reduced chlorine content, which in the meantime have also been banned in Europe. Currently the “third generation” of foaming agents is being marketed; hydrofluorocarbons (HFCs), fluorinated hydrocarbons which contain no chlorine and therefore do not attack the ozone layer at all. There is one major problem, however, with HFCs – they act as classic greenhouse gases, causing global warming like carbon dioxide (CO<sub>2</sub>), though in this respect some HFCs are up to 10,000 times more effective than CO<sub>2</sub>.

### A good nose for air pollutants on the Jungfrauoch

In order to better understand both the contribution made by HFCs to global warming and their chemical life cycle in the air, reliable estimates are necessary of the amount of these substances in the atmosphere. This is not an easy task, particularly at the beginning of the marketing cycles of such products when production quantities are small and therefore emission levels are low. This is the case for the two foaming agents pentafluoropropane (technically known as HFC-245fa) and pentafluorobutane (HFC-365mfc). “We know that these chemicals have been in production since 2002 and 2003 respectively. The question is, will we see traces of them in the atmosphere, and if yes, then when?” says Empa researcher Martin Vollmer.

This is a task for Empa's highly sensitive instruments in the research station on the Jungfrauoch. Because of its location – simultaneously at high-altitude in the Alps and yet in the middle of the heavily industrialized European continent – and the very low level of local contamination, this research station is perfectly placed for research into atmospheric emissions. But Vollmer and his colleague Stefan Reimann have also analyzed air samples for traces of the new HFCs from partner stations belonging to the world-wide AGAGE (Advanced Global Atmospheric Gases Experiment) measurement network, such as those at Cape Grim in Tasmania and Mace Head on Ireland's west coast, working together with their Australian and European collaborators. At the same time the Empa team also analyzed the air samples for CFC-11, a first generation foaming agent which has been banned in Europe since 1995, and for HCFC-141b, its erstwhile second generation substitute, also banned since 2003.

The results of the study, which was partially financed by the Swiss Federal Office for the Environment (FOEN), were recently published in the scientific journals "Geophysical Research Letters" und "Environmental Science and Technology". The conclusion the papers reach is that practically as soon as these substances are manufactured Empa researchers are able to detect them in the atmosphere, and in the minutest quantities imaginable. The concentrations of the two HFCs are in the parts per quadrillion, or "ppq", range. This means one molecule of substance X to a quadrillion (i.e. a million million!) "molecules" of air. "Not many laboratories can measure that sensitively, and to do so we have to work extremely carefully to avoid even the slightest external contamination", says Reimann, not without a certain degree of pride. The pollutants are also to be found in the air around Tasmania, even though they are produced and used industrially exclusively in the northern hemisphere. "If something is blown into the atmosphere here in the northern hemisphere, a year or so later it will be detectable in the air in the southern hemisphere," according to Reimann.

### **Small quantities of CFCs – but a steeply rising trend**

All told the global emissions of both substances at present are still relatively minor. "In the quantities currently seen, they are of negligible significance in climatic terms compared to CO<sub>2</sub> or methane," says Martin Vollmer. This is despite the fact that both chemicals have a greenhouse effect which is between eight hundred and a thousand times stronger than that of CO<sub>2</sub>. However the emissions of both HFCs increased massively over the last few years, and if this trend continues they could in future play a more significant role in the global warming phenomenon. For example, in 2002 HFC-245fa could not be detected in the atmosphere. Just one year later Empa measurements showed that global emissions of this substance had reached about 2200 tonnes, and by 2005 it had reached 5500 tonnes. HFC-365mfc measurements tell a similar tale, with an increase from 600 tonnes in 2002 to about 3200 tonnes in 2005. "This is the first time that we have been able to observe newly appearing air pollutants in quasi real time," explains Reimann. "We now have available an excellent early warning system which allows us to identify trends very early on so we can take remedial action as soon as possible."

In contrast to the two newcomers, emissions of the banned substances CFC-11 and HCFC-141b are dropping. The astonishing thing is that even twelve years after the ban was introduced, about 3000 tonnes of CFC-11 escape annually into the atmosphere over Europe alone, for example by diffusing out of aging foamed plastics. "This just shows what enormous quantities of CFC-11 were once produced!" says Vollmer.

### **And where do the pollutants come from?**

The scientific station on the Jungfrauoch offers yet another advantage. When the Empa scientists combine the data collected there over many years with meteorological models, they are able to trace pollutants to their source. When they did so, they had “the greatest surprise we have had since we’ve been measuring up there”, as Reimann put it. According to the trajectory model used by the Empa researchers, the main source of HFC-365mfc emissions was smack in the middle of France. A quick glance at the map confirmed the finding – at exactly the location pinpointed by the computer model was the only factory producing the chemical. The simulation also reliably identified the second most significant source of emissions, the Po valley in northern Italy, where a large proportion of the substance is used in the production of foamed plastics. “About a third of the HFCs used escaped into the atmosphere during production”, say Empa colleague Vollmer.

Ideally, one would use only foaming agents which had no effect on the earth’s climate. Alternatives are available – pentane and nitrogen are examples – but most do not possess all the required characteristics; some are not such good thermal insulators as HFCs. These latter gases will therefore continue to appear in the air above the Jungfrauoch and driving the Empa instruments off scale. Currently Reimann’s team is working on the development of an analyzer which can measure even more substances even more accurately.

[www.empa.ch/climate\\_gases](http://www.empa.ch/climate_gases)

### **Publications**

Vollmer, M. K., Reimann, S., Folini, D., Porter, L. W. and Steele, L. P. (2006). First appearance and rapid growth of anthropogenic HFC-245fa (CHF<sub>2</sub>CH<sub>2</sub>CF<sub>3</sub>) in the atmosphere. *Geophysical Reserach Letters* 33 L20806 doi:10.1029/2006GL026763.

Stemmler, K.; Folini, D.; Ubl, S.; Vollmer, M. K.; Reimann, S.; O'Doherty, S.; Greally, B. R.; Simmonds, P. G.; Manning, A. J., European Emissions of HFC-365mfc, a Chlorine-Free Substitute for the Foam Blowing Agents HCFC-141b and CFC-11, *Environ. Sci. Technol.*; (Article); 2007; ASAP Article; DOI: 10.1021/es061298h

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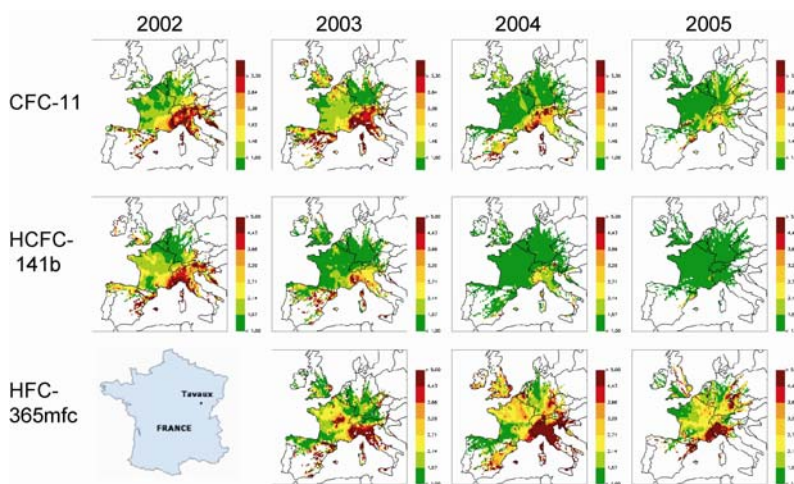
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The High-Alpine Research Station on the Jungfrauoch is 3580 meters above sea level and ideally suited to determining the concentrations of atmospheric pollutants. It serves as the so-called “background station” within the National Air Pollution Monitoring Network (NABEL) operated jointly by the Swiss Federal Office for the Environment (FOEN) and Empa.



Tracing air pollutants: differing trends shown by three halogenated foaming agents whose emission levels and regions of origin were identified by Empa staff through measurements made at the Jungfrauoch. While emission levels of the now banned CFC-11 and HCFC-141b have dropped over the last four years, the concentration of the substitute chemical HFC-365mfc has increased. With the help of meteorological models, it is even possible to identify the source of the emissions – the manufacturing plant in Tavaux, France, and the processing factories in the Po valley where the chemical is used.

High quality images are available from [remigius.nideroest@empa.ch](mailto:remigius.nideroest@empa.ch)