

Recently discovered halogenated greenhouse gases HCFC-31 and HCFC-133a in the atmosphere

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HCFCs (hydrochlorofluorocarbons) are a class of ozone depleting halogenated greenhouse gases whose temporary use was allowed by the Montreal Protocol to facilitate the phaseout of more potent ozone-depleting substances. HCFCs are primarily used in refrigeration, foam blowing, air conditioning and solvent applications. Even though HCFCs are currently phased out in developed countries for the above mentioned applications, they are still allowed to be used in developing countries.

Advances in measurement techniques recently led to the discovery of HCFC-31 and HCFC-133a in the atmosphere, two so far unmonitored HCFCs, for which no purposeful end-product usage is known to date. To assess their atmospheric history and the evolution of their global emissions, archived air samples from 2000 – 2014 and in situ observations were combined with a chemistry-transport model. First results show increasing emissions of up to $\sim 1 \text{ kt yr}^{-1}$ for HCFC-31 and $\sim 3 \text{ kt yr}^{-1}$ for HCFC-133a until 2012, followed by a rapid decline afterwards.

Both HCFCs are used as intermediates in the synthesis of widely used refrigerants, which for HCFC-133a are HFC-134a (CH_2FCF_3), HFC-125 (CHF_2CF_3) and HFC-143a (CH_3CF_3) and for HCFC-31 is HFC-32 (CH_2F_2). Given this knowledge and the finding of the rapid decline in emissions of both substances, we conclude, that the major global emission reductions are related to the prevention of emissions from activities which are under direct human control (e.g. release of intermediates during the production process).

The discovery, the temporal emission evolution and the proposed emission sources of these two substances highlights the necessity of a continuous top-down monitoring of products as well as intermediates and feedstock, even if production processes are designed not to lead to such emissions. Furthermore, this example illustrates the value of an ongoing search for previously unidentified chemicals in the atmosphere.