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Assessing National Halocarbon Emissions Using Regional Atmospheric Measurements

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Abstract: To mitigate the environmental impacts of synthetic halocarbons it is crucial to quantify their emissions to the atmosphere on different spatial scales. For this, top-down modelling approaches were developed, relying on atmospheric concentration observations. However, increased sensitivity on a country-scale is needed, requiring a denser measurement network and models operating on a regional scale. In this light, we conducted an extensive study to assess Swiss halocarbon emissions, with high sensitivity to the regional emissions sources.

Keywords: Atmospheric measurements · Emissions · Halocarbons · Top-down modelling

Dominique Rust obtained her Bachelor's and Master's degree in Chemistry and Business Studies from the University of Zurich. During her Master's Thesis she worked on chiral liquid chromatography coupled to high-resolution mass spectrometry at the water research institute Eawag. She is currently a PhD student at the Laboratory for Air Pollution and Environmental Technology Department at Empa, focusing on atmospheric halocarbon measurements by gas chromatography coupled to mass spectrometry, and on assessing national halocarbon emissions.

1. Halocarbons in the Atmosphere and their International Regulation

Synthetic halocarbons are halogenated hydrocarbons which are widely used in industrial production processes and consumption-related applications. They are for example utilized as cooling agents in refrigeration and air conditioning, as foam blowing agents, solvents, or as fire extinguishing agents.[1] Once emitted to the atmosphere, many applied halocarbons have long atmospheric lifetimes and considerable global warming potentials (GWPs). Although being low-abundant in the atmosphere (in orders of ppt, parts per trillion, pmol mol^{-1}), human-made halocarbons contribute more than 10% to the radiative forcing caused by long-lived greenhouse gases (GHGs).[2] In addition, chlorine- or bromine-containing halocarbons contribute to the depletion of the stratospheric ozone layer in radicalic catalytic cycles. Therefore, in 1987, the production and consumption of the chlorofluorocarbons (CFCs) and halons (brominated alkanes), as well as the hydrochlorofluorocarbons (HCFCs), was regulated under the Montreal Protocol on Substances that Deplete the Ozone Layer, aimed at a global phase-out of these substances by 2010.[3] A down-scaling of the production and consumption of the highly global warming hydrofluorocarbons (HFCs) and perfluorocarbons (PFCs) was agreed upon in the Kigali Amendment to the Montreal Protocol, which entered into force in 2019. In addition, the HFCs and PFCs, together with other major GHGs, are included in the Kyoto Protocol which stipulates the annual reporting of national emissions inventories to the United Nations Framework Convention on Climate Change (UNFCCC). To answer the desired phase-down of the HFCs, a new class of fluorinated hydrocarbons has recently been introduced as replacement products in some applications, the hydrofluoroolefins (HFOs).[4] These substances contain an unsaturated C–C bond, which greatly reduces their atmospheric lifetimes and thus GWPs. However, a debate was sparked on the formed atmospheric degradation products, such as the environmentally persistent trifluoroacetic acid (TFA, CF_3COOH).[5–7]

2. Large-scale Measurement Networks

To assess and mitigate the impacts of synthetic halocarbons and monitor the efficacy of the measures agreed upon in international treaties, it is fundamentally important to, in a first step, monitor the atmospheric abundance and temporal and spatial distribution of halocarbons. This cause is taken up by the long-term measurement network Advanced Global Atmospheric Gases Experiment (AGAGE),[8] which goes back to 1978. Nowadays, the network consists of 15 globally distributed stations (Fig. 1), that are located at coastal or mountain sites, and which capture atmospheric background concentrations and regional pollution. For continuous *in situ* measurements, AGAGE operates identically constructed and fully intercalibrated analytical setups, consisting of specially developed Medusa pre-concentration units, coupled to gas chromatography and quadrupole mass spectrometry (GC-MS). In addition, AGAGE 'affiliate' stations operate different but compatible analytical setups.

A second long-term measurement program Halocarbons and other Atmospheric Trace Species (HATS) goes back to 1977 and is conducted by the National Oceanic and Atmospheric Administration (NOAA).[9] This research program, concentrated over North America (Fig. 1), includes flask sampling, airborne measurements, and *in situ* measurements. Analysis is based on GC coupled to electron capture detectors (ECDs) or MS.

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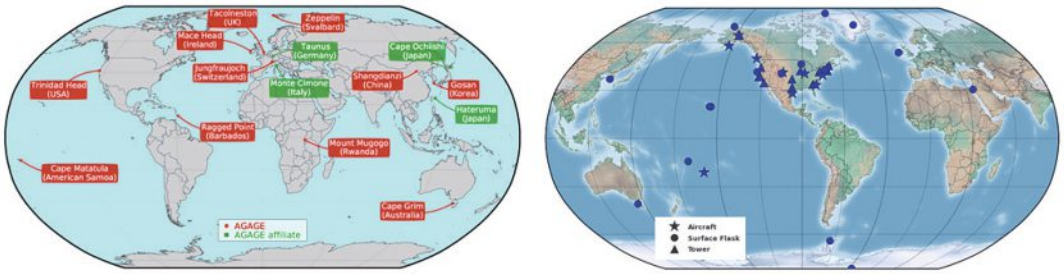

Fig. 1. Continuous *in situ* measurement sites of the Advanced Global Atmospheric Gases Experiment (AGAGE) network (left), and the flask sampling network operated by the National Oceanic Atmospheric Administration (NOAA, right). Figure taken from AGAGE and NOAA.

3. Approaches of Emissions Calculation and the Need for Down-scaling

To verify if countries comply with international treaties and to support policy making, it is important to accurately quantify the emissions of halocarbons to the atmosphere on a regional to national level. Countries commonly quantify their halocarbon emissions by the 'bottom-up' approach, accounting production, sales, and consumption statistics, and source-related emissions factors. However, the bottom-up approach bears an unknown level of uncertainty due to uncertainties in emission factors for many sources, lack or incomplete statistical data, or unconsidered sources. Moreover, annual GHG inventories are not available or complete for all countries, making it difficult to finalize the global picture.[10,11]

Therefore, 'top-down' box and inverse modeling methods are used to link the bottom-up emissions numbers with the observed atmospheric concentrations, to complement and verify, and to improve the quality of the bottom-up inventories. Top-down models can be operated to assess GHG emissions on different spatial scales, *i.e.* globally to regionally to nationally. The quality of top-down emissions modeling depends on the quality and density of input measurement data and the quality of the models. Models include 1-box and 12-box models, tracer-ratio approaches, or inverse methods combined with Eulerian or Langrangian transport models. They often rely on large-scale targeted atmospheric observations, for example from the AGAGE and NOAA networks. A variety of previous studies at different scale have confirmed the benefit of top-down emissions estimations to review the consistency between observed atmospheric concentrations and expected or reported emissions. In the following, only a few examples will be discussed.

A prominent example of top-down emissions assessment was recently published by Montzka *et al*.,[12] who, based on the measured atmospheric concentrations, reported resumed emissions of the globally phased out ozone-depleting substance CFC-11 (CCl_3F).

For sulfur hexafluoride (SF_6), the most potent greenhouse gas reported to the UNFCCC, considerable differences were found between the nationally published, in total lower bottom-up emissions inventories and higher, top-down derived global emissions budgets.[13] Two reasons were suggested, *i.e.* that developed (Annex-1) countries underreported their emissions by a factor of about 2, and that emissions from developing (non-Annex-1) countries, not obliged to report to UNFCCC, have increased significantly.

For other halocarbons, discrepancies like this led to suggestions to identify yet unkown emission sources, revise assumed loss rates from industrial processes, amend lifetime estimates, or reconsider a number of assumed input factors used to calculate the bottom-up emissions.[14–18]

A large gap was also found between the total HFC emissions inventories reported to the UNFCCC and total global emissions modeled based on atmospheric measurements from the AGAGE and NOAA networks.[1] This is exemplarily shown for HFC-134a (CH_2FCF_3, Fig. 2), the most abundant HFC. Top-down modeling on regional scale confirmed the reported bottom-up numbers from Europe and the US, the largest emitters, and also all Annex I countries.[19–21] Like for SF_6, it was suggested that the discrepancy is mainly caused due to emissions from the non-Annex-1 countries, not obliged to report to UNFCCC. This presumption was supported by regional studies in East Asia.[22–24] However, on a country-level, various studies also reported considerable discrepancies between bottom-up and top-down derived emissions values for individual halocarbons[25–31] for the UNFCCC reporting Annex-1 countries (Fig. 3). For example, Brunner *et al*.[26] compared four inverse models over Europe for 2011. They emphasized that the existing European network included in their study had the potential to identify major shortcomings in the nationally reported emissions inventories, but that a denser measurement network sensitive to regional or national emissions would be needed for improved modelling on country scale.

4. National Top-down Emissions Quantification and a Switzerland Focused Study

Currently, the United Kingdom (UK), Switzerland, and Australia are the few countries complementing their UNFCCC reported emissions inventories with top-down derived national emissions numbers. The first top-down calculations of halocarbon emissions on country-scale were presented by Manning *et al*. in 2003.[32] In the most recent study, Manning *et al*.[15] highlighted the benefit of data from additional measurement stations to estimate the UK's HFC emissions and to get an improved insight into the spatial distribution of the emissions. For many investigated HFCs, the top-down emissions were lower than the UK's bottom-up inventory values.

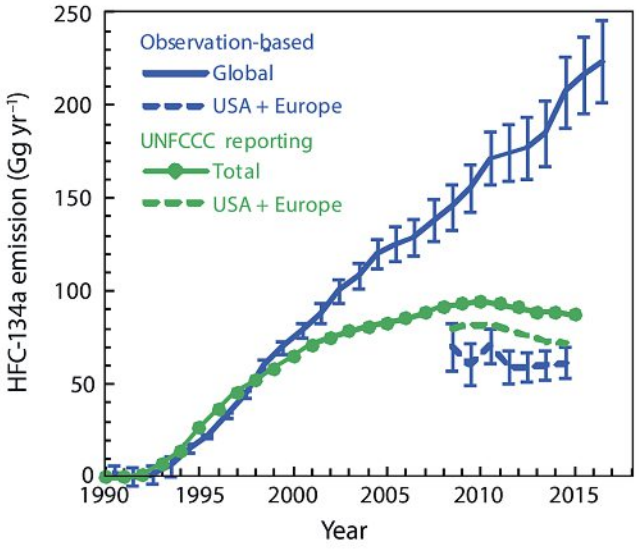

Fig. 2. Global, and US plus European HFC-134a emissions totals reported to the UNFCCC and derived from atmospheric observations. Figure taken from ref [1]. Copyright 2022 World Meteorological Organization (WMO).

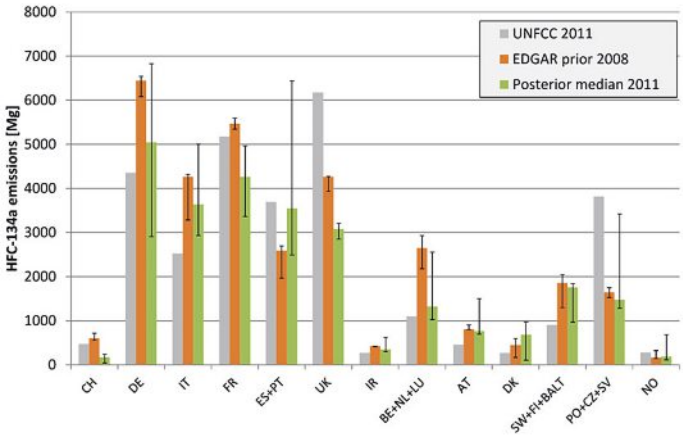

Fig. 3. Country-specific top-down modelled posterior emissions, compared to the prior emissions from the EDGAR inventory and to the UNFCCC reported numbers. Figure adapted from ref [26].

For Switzerland, emissions are annually calculated top-down (with a tracer-ratio method) based on the measurement data from the high-Alpine research station at the Jungfraujoch, incorporated into the AGAGE network.[33] However, Jungfraujoch is located at a topographically complex site, only periodically capturing air masses from the polluted Swiss boundary layer. This induces significant uncertainty to the top-down quantified emissions. Therefore, we recently conducted another extensive study to assess Swiss halocarbon emissions with increased sensitivity to the most important emissions regions.[34] A dedicated measurement campaign was carried out at the Beromünster tall tower, being sensitive to the most populated and industrialized area of Switzerland, the Swiss Plateau (Fig. 4). Emissions were assessed by Bayesian inverse modelling, based on atmospheric transport simulations produced with FLEXPART-COSMO. A tracer-ratio method was applied as a second independent top-down approach. The continuous *in situ* measurements were fully intercalibrated within the AGAGE network, implying a valuable asset for improved Bayesian inverse modeling. Emissions were quantified for the major halocarbon classes, *i.e.* CFCs, HCFCs, HFCs, and, for the first time, for three recently phased-in HFOs. Among others, this diversity of investigated halocarbons presented some challenges for the top-down calculation approaches, such as defining appropriate prior values, determining impacts of used lifetime numbers for the short-lived HFOs, or confrontation with assumed spatial and temporal similarity of emissions sources of the halocarbons and the tracer used for the tracer-ratio method. The top-down calculated emissions results were compared to the Jungfraujoch-based emissions, and, if possible, to the UNFCCC reported bottom-up inventory. For the major CFCs and HCFCs, the calculated emissions were consistent with the release from remaining banks. For most of the major HFCs, the top-down results compared well to the reported inventory numbers. However, similar to the study from the UK,[15] for HFC-134a, the top-down derived emissions were consistently lower than the latest UNFCCC reported inventory (Fig. 5). For SF_6, the most potent GHG investigated, top-down derived emissions were somewhat higher than, but within the uncertainty of the UNFCCC reported inventory. As mentioned earlier, first national emissions were also assessed for the HFOs. The impacts of degradation products like TFA and possible adverse effects on local scale are highly debated, underlining the wish to monitor these substances on a regional scale.

In addition to the studies focusing on Switzerland and the UK, efforts were already previously undertaken to carry out devoted field campaigns with continuous *in situ* halocarbon measurements in Hungary,[28] Crete[35] and France[36] in order to assess emissions from different European countries. Moreover, a new long-term observation site has recently been established in Central Germany.[37] For the US, national emissions were quantified based on the extensive flask sampling program of NOAA.[19]

Modeling methods are also constantly being improved. For example, in the context of the same project under which the above-described Switzerland focused study was conducted,[34] the spatial resolution of the atmospheric transport model FLEXPART-COSMO will be increased from 7 km to 1 km, to test the improvement for emissions characterization.

5. Conclusions

Observation-based top-down modeling has been developed into a valuable approach to independently quantify halocarbon emissions to the atmosphere. From the existing measurement in-

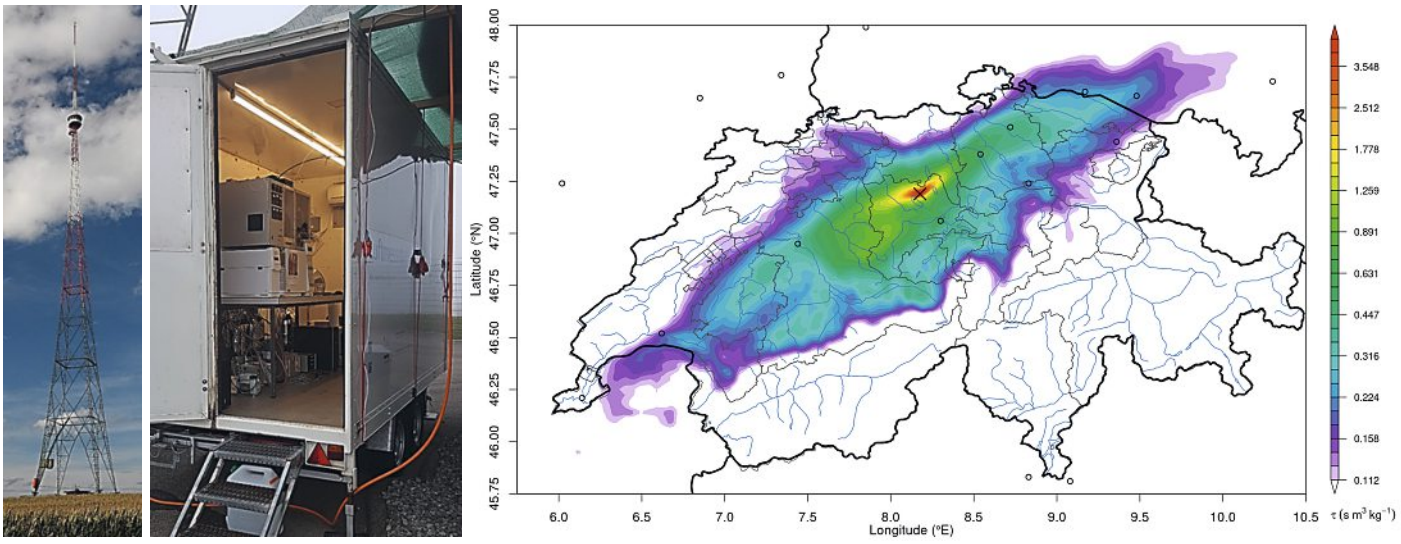

Fig. 4. The Beromünster tall tower in Switzerland (left), and the analytical instruments used for the atmospheric measurements in ref. [34] placed in a trailer beneath the tower (center). Modelled surface sensitivity over the Swiss Plateau for the measurement site at Beromünster (black cross). Figure taken from ref [34].

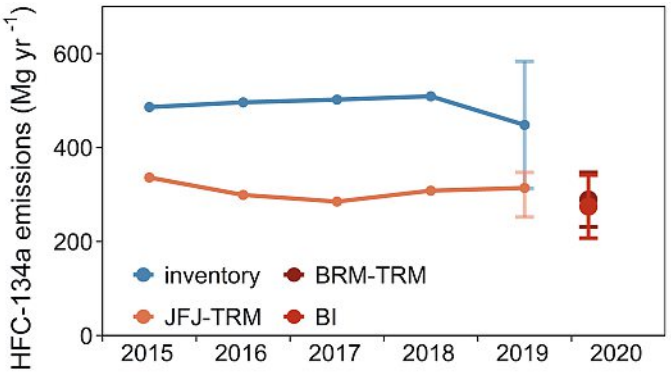

Fig. 5. Swiss HFC-134a emissions derived from the measurements at Beromünster (BRM) by the tracer-ratio method (TRM) and Bayesian inverse (BI) modelling, and compared to the national bottom-up inventory reported to UNFCCC, and to the Jungfraujoch (JFJ)-based emissions. Figure adapted from ref [34].

frastructure and modeling techniques, global emissions can be adequately assessed. However, it showed that top-down emissions quantification on regional to country scale is fundamentally important and revealing. This requires much higher spatially and sufficiently temporally resolved atmospheric measurements, and robust modelling techniques representing similar scales. A substantial limitation is that needed infrastructure and model development is costly and operation must be carried out by well-trained staff. Nevertheless, efforts in this direction have already been undertaken, for example in Switzerland, and should be extended in the future.

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