Revisions of egusphere-2025-4824
Global Observations and European emissions of the halogenated olefins HFO-1234yf, HFO-1234ze(E), and HCFO-1233zd(E) from the AGAGE (Advanced Global Atmospheric Gases Experiment) network
M. K. Vollmer et al.

Comments by the Referee 1 are in blue, replies in black.

Referee 1 Comment (24. Nov 2025, Isaac Vimont)

We thank the referee for his thorough review and address his comments (in blue) below (in black).

General Comments

"Global Observations and European emissions of the halogenated olefins HFO-1234yf, HFO-1234ze(E), and HCFO-1233zd(E) from the AGAGE (Advanced Global Atmospheric Gases Experiment) network" is an overview of measurements from the AGAGE network of 3 key haloolefins that are increasingly used in foam blowing and refrigeration, heating, and air-conditioning. The authors provide a nice overview of the global measurements, and provide more detailed analysis and emissions estimates for north western Europe. Additionally this paper easily meets every requirement set forth by ACP for publication in their journal.

This paper is excellent, and I have no major comments for the authors to address. I would like to thank the authors for providing such a well-written and thorough manuscript, it was a pleasure to read and review. This is a welcome change from many of the recent papers on halocarbons that I am asked to review. I further appreciate that the authors have taken the time to completely describe their calibration and uncertainty estimates (save for one small detail that I mention below). This is so often overlooked in manuscripts these days, and I found it a welcome change.

I did not find any issue with any of the modeling methods or results, however, the details of the models are outside my area of expertise and therefore I am not properly qualified to provide in-depth review of that portion of the text. It is a shame that these compounds are too short-lived for estimates of global emissions using traditional box modeling methods, as it would be nice to have global estimations of these species going forward as they are used increasingly throughout the world. However, an analysis of global emissions using more complex, full chemistry global models is outside the scope of this paper (indeed, likely a paper on its own).

In my opinion, the paper is nearly ready to publish in ACP. I have included a small number of minor, admittedly nit-picky, comments below, easily addressed, but overall, the paper is excellent and I look forward to its imminent publication.

Answer: We thank the referee for his positive review. We agree that global estimates of HFO emissions would be very useful. It seems that some independent efforts are underway by scientific groups using complex full-chemistry models for global estimates, so this is positive news.

Specific Comments

Line 35: This part of the sentence (...currently an intense debate…) is ambiguous (is the debate about banning PFA's or about adding HFO's to the ban?). To me, it doesn't add much to the paper nor the point being made in the paragraph. Suggest:

"Haloolefins are also within the scope of the definition of the very stable anthropogenic per- and polyfluoroalkyl substances (PFAS). In January 2023, authorities from Denmark, Germany, the Netherlands, Norway, and Sweden submitted a REACH (Registration, Evaluation, Authorisation and Restriction of Chemicals) dossier for a restriction proposal for PFAS in the EU to the European Chemicals Agency (ECHA, European Chemicals Agency, 2024) which suggests a wide-ranging ban of PFAS from usage in many applications. At the time of publication, this dossier is still being considered by the ECHA."

Answer: The debate is about both, the banning PFAS and whether HFOs should be included. We agree that it is ambiguous and have deleted this part. We also follow the suggestion and add another sentence at the end of the paragraph (slightly modified from the suggested sentence) about the status of the dossier. We also slightly changed the bibliography entry for the reference to ECHA to better encompass the topic.

Line 51: This paragraph seems out of place. We are 4 paragraphs into the introduction and only now are the three species listed and their uses explained. I suggest moving this up to be the second paragraph (currently the second paragraph starts at line 30). This would help clarify several points being made in the current second and third paragraphs.

Answer: Done, moved as suggested.

Line 56: "...and also difficult to reconstruct the temporal changes in regulations and applications in various parts of the world". To me, this sentence is unclear. What regulations do you refer to here? Above you have stated that haloolefins are up for consideration for regulation in the EU and that the MP does not restrict their use at this time. Or is this meant to say that it will be difficult in the future?

Answer: HFO are regulated differently in various countries and regions around the world, the EU case is listed as an example. Other examples are e.g. Switzerland, which initially did not allow HCFOs to be used, later they were allowed for specific applications only. Another example would be the USA, where e.g. only certain HFOs are permitted in MAC. We think that it is not appropriate (and difficult to reconstruct, as mentioned in the text) to list more specific regulations, so we kept the wording more general.
We hope to make this understandable now by changing the above sentence to
"*However, given the lack of reliable literature, it is difficult to evaluate the individual sectors in more detail, and also difficult to comprehensively reconstruct regulations and applications and the changes thereof for individual countries or regions*."
We then start the next sentence differently to show that the mentioning of the EU regulation is an (important) example.
In the EU for example, haloolefins are included in the ....."

Section 2.2: Monte Cimone has 5 years of data with a non-Medusa system, yet there is no description of any difference in measurement precisions for the three compounds, or detectability. From what I can see in the data presented here, there seems to be no change in the measurement quality, nor the detection limits, when the Monte Cimone site was switched to the Medusa system, which is excellent.
However, though this system is described in Maione et al., 2013), I suggest the authors provide a little bit more information on the comparability of these two instruments. Given the ~14 months of overlap, this may be easy and can be as little as to say that the measurement quality is comparable (assuming that it is), or a short mention in Section 2.4 if there is any small difference.

Answer: This is a good point. It is now extensively discussed in the Supplement. In summary, most of the observed differences fall within the combined measurement uncertainties, indicating that the two instruments are statistically consistent within their reported errors. Some deviations that exceed the expected uncertainty range are reported, particularly at higher concentrations, most likely due to some fast (short term) pollution transport events that the different instruments weren't able to track because of the non-perfect synchronisation (here we used 10-min matching windows) of the two sampling systems.

Section 2.4: What are the uncertainties for clean air samples? Unless misread here, I see an excellent detailing of polluted sample uncertainty, but no mention of unpolluted background air uncertainties? I would expect that the uncertainty will increase somewhat as the chromatographic peak approaches the detection limit.

Answer: We are very thankful for spotting this. We originally had included a description on this, but it got lost when re-arranging information in this section with the modeling section. We are now including this description again. As the referee states correctly, the uncertainty is large in percentage terms for small peaks, difficult to quantify and dependent on instrument (MS) status. It now reads:

"The uncertainties directly associated with the air sample measurements on the Medusa-GCMS are highly mole-fraction dependent. For individual air samples with mole fractions up to 0.5--1 ppt, we conservatively estimate these at 0.020 ppt or 10\%, whichever is greater. For more polluted air masses with mole fractions greater than ~1 ppt, the precisions are ~2% for HFO-1234yf and HFO-1234ze(E), and ~1% for HCFO-1233zd(E) as determined from repeated measurements of working standards of similar mole fractions."

We now also improved our description and definition of detectable mole fraction:
"We define detection limit' for these measurements as the mole fractions that correspond to the smallest integrated chromatographic peaks. These vary over time and among the instruments, mostly reflecting the performance status of the GCMS. Reliable detection of the peaks is estimated at mole fractions larger than ~0.005 ppt (parts-per-trillion, picomol mol-1), which we refer to as `detectable levels' in the Results Section."

The above analytical description is later extended in the modeling section to describe how the low/zero abundance samples were treated in the modeling:

"Because of the occasionally low abundance of the haloolefins in air samples, chromatographic peaks were frequently not integrated (Subsection 2.2), so the reported mole fraction was zero (despite occasional positive but not integrated above-baseline detector responses). For the purpose of inverse modeling, all observations with reported mole fractions below 0.0025 ppt (i.e. half the limit of detection) were set to 0.0025 ppt."

Line 338: "...large magnitudes of pollution…" is awkward. Suggest changing to "...large enhancements relative to background…"

Answer: We changed this now to the suggested wording.

Sections 3.1.1 and 3.1.2: I have some minor skepticism of the conclusions drawn in these two sections relating to the slower adoption of HFO's in the region of influence for the Gosan

station relative to the European stations, particularly with respect to 134a. The Gosan Station has significant influence from both the DPRK, the Republic of Korea, and Eastern China. Both the Korean and Chinese automobile industries have exploded in the last 10 years, with Korea's beginning even before this. Though my experience with specific vehicles is quite limited, both modern Chinese and Korean vehicles are coming with haloolefin refrigerants, and have been for some time. Despite the DPRK, China, and the Republic of Korea being A5 countries and thus having longer phase down times, both the Korean and Chinese automobile manufacturers are targeting non-A5 countries for sales, including the US, Europe, and Australia. They would be prevented from selling vehicles in these regions with 134a, and from a manufacturing perspective, it is difficult to see how they would tool their manufacturing plants differently depending on whether the vehicle was to be sold domestically or internationally.
If we assume the conclusions drawn here are true, it would be good to discuss why the vehicle fleets in China and Korea would be expected to be largely running 134a despite their new vehicles being produced with HFO-1234yf. Unlike the US, Europe, Australia, etc… where the vehicle fleets might be expected to contain significant numbers of older vehicles (though from this paper it is clear that Europe's fleet is changing over), China's fleet is likely quite a bit newer, as evidenced by their historically low, but rapidly increasing, vehicle ownership statistics (e.g. https://doi.org/10.1007/s11356-024-34344-0). I think the authors could expand a bit on this, as while their conclusions are certainly plausible, to me they have not addressed this additional factor which could run counter to their hypothesis.

Answer: It is likely correct that the newer fraction of the Asian car fleet is equipped with HFO-1234yf in replacement of HFC-134a even though the regulations foresee a ban of GWP>150 by 2029 (potentially, the transition has started a while ago). However, HFC-134a is also used extensively in stationary refrigeration. The turn-over and replacement of these stationary units is likely not as fast as in the MAC sector in Asia, we are seeing a combination of these two timescales in the observations.. It is possible that the potentially largely replaced refrigeration in MAC (as suggested by the reviewer) is seen already in the HFO-1234yf/HFC-134a ratio at Gosan compared to the HFO-1234ze(E)/HFC-134a ratio, the former being only about twice as large. We have now inspected the 'above-pollution' ratios for these refrigerants a bit more in detail, also following some suggestions of reviewer 2, and find that these are still robust after applying some corrections for decay of the shorter-lived haloolefins during transport from sources in the Asian region to Gosan (which is likely longer than the transport time in Europe). These findings have led us to keep our statements about the delayed transition from HFC-134a to the HFOs in the Asian region.