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 reviewers are in blue (referee 1) and green (referee 2), replies in black. Both referees' comments and replies are given in this document for easier handling by the coauthors. I will probably split this for re-submission (depending on the journal's procedure).

Referee Comment 1 (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.

Referee Comment 2 (7 Jan 2026, anonymous)

We thank the referee for their thorough review and will address their comments (in green) below (in black).

Overview: This paper reports on global observations of two HFOs and one HCFO that are being increasingly used as replacements for HFCs. Further, the authors use multiple inverse modeling frameworks to estimate emissions and emissions trends in NW Europe. Authors report increasing prevalence of detectable levels of these gases since 2011, with increasing levels observed in pollution plumes (normalized to a HFC observation). Inverse modeling suggests increasing emissions for these gases in NW Europe, with somewhat rapid increases inferred in the time series. Haloolefins are being increasingly used worldwide, but emission magnitudes and environmental and health impacts are poorly known. Given the reactive nature of these gases, they are harder to observe and track with sparse global networks. This paper nicely present important measurements of these gases and infers reasonable conclusions. The multi-method inverse assessment of Europe is a strong addition to the paper, and illustrates the need to consider more measurements near emissions regions to truly characterize HFO's moving forwards. The paper is appropriate for ACP. I have some modest concerns and suggestions for the authors, which should be straightforward to address and would strengthen the manuscript.

Answer: We thank the reviewer for their comments. We have now addressed these comments which we believe have improved the manuscript. Below are the individual points and answers.

General comments:
Add uncertainties: In reporting concentrations, enhancements, and flux numbers, please add uncertainties. For example, in the abstract when stating the increase in ppt's, or when stating estimated emissions, confidence intervals or uncertainties should be added. This shouldn't be overly complicated to add, as you have uncertainty assessments on measurements you can apply, and you could create confidence intervals on fluxes in a number of different statistical ways leveraging the multiple inverse model methods.

Answer: We have now selectively added uncertainties. We have added uncertainties to the estimated emissions (in text and abstract). As for the concentrations (and their rates of change), we have not added uncertainties; we have added the 'approximate' symbol before these, as these are ballpark numbers to give an approximate understanding to the reader. The measurement uncertainty on the annual averages is small compared to the atmospheric variability of these gases. In the abstract we prefer not to go into these details and instead provide approximate values to support the qualitative point that the mole fraction of these species is increasing in the atmosphere. We have also added the following to the Calibration and Measurement Uncertainties section (see also response to reviewer 1): "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."

Consider/address OH and lifetimes in both ratios of pollution magnitudes (e.g. Fig. 3) and slopes of pollution ratios (e.g. Fig B1, B2). As discussed elsewhere in the paper, and included in the inverse modeling, the lifetime of some of these gases for some times of year is sufficiently short to potentially significantly impact observe ratios/slopes, which could

strongly impact these values and interpretations. For example, is Gosan lower because it is sampling after greater chemical loss? Please consider doing addition calculations/corrections to account for OH loss and/or consider sensitivity studies.
Regarding the slope analysis, this is not a case where OLS regression is appropriate (Fig. B1,B2). A Type II model regression should be conducted as variance (uncertainty) on both axes are large and comparable (if the y-axes variable variance was 3x> than x, than OLS would be ok, but here that isn't the case). Further justification would also be needed for forcing the intercept thru 0. I don't think updating the regression approach will impact the conclusion, but would improve the analysis. Also please include uncertainty/significance/CI for the slopes as well.

Answer: We have now addressed these comments in our revised manuscript. With regard to the question, whether the slopes for Gosan are smaller because of potential decay on the transport to the site: We have made a first approximation of this effect by estimating the decay of the three haloolefins for a conservative transport time of four days on the travel time to Gosan and using the yearly mean lifetimes (from supplement Table S1). This effect is now shown in Figure 3 by adding a color band to the ratio determined for Gosan. The estimates show that, for HFO-1234yf, there is a small effect (for HFO-1234ze(E) and HCFO-1233zd(E) significantly smaller than HFO-1234yf) but overall, the differences between the JFJ/MHD and the GSN ratios remain large. It also remains to be noted that we have not made a similar correction for the MHD and JFJ observations. A correction to these observations would, even though the transport time is probably shorter than in the case of Gosan, enhance the ratios for MHD and JFJ as well (for HFO-1234yf).

We have now also adapted the regression (Figs S4 and S5) to orthogonal distance regression, by also scaling the delta values between 0 and 1. As for the 0,0 intersection, we are plotting the delta above baselines of joint pollution samples only. The 0,0 in our graphic is where both compounds are at their baseline. What we are interested in is how the pollution behaves above the baseline, thus fitting a linear regression through 0,0 makes sense.

We have revised the main text slightly, it now reads:

"This is illustrated in Fig. 3a and Fig. 3b where we compare the pollution magnitudes of the two HFOs in relation to those for HFC-134a. We determine linear fits for the above-baseline pollution events of HFO-1234yf (ΔHFO-1234yf) against those of HFC-134a (ΔHFC-134a) for each year of observations using linear regression based on least-square methods (Fig. S4) and show these as timeseries in Fig. 3a and Fig. 3b. The linear fit slopes (ratios) increase strongly over the observational period, and are higher for Jungfraujoch and Mace Head compared to Gosan. This is indicative of a faster transition from HFC-134a to HFO-1234yf and HFO-1234ze(E) for Europe compared to the footprint regions of Gosan, in line with the stringent HFC phase-out regulations in Europe."

We are therefore staying with our statement of a delayed transition from HFCs to HFOs/HCFOs in the Asian region compared to Europe.

For the gridded flux output (such as in Fig. 7), please also provide a spatial figure that shows where the inverse modeling work has sensitivity/constraint. This could be a footprint type figure with contours, or a uncertainty reduction type figure, or Fig. 7 could have regions not constrained left in white or gray. It is important to show where observations are constraining emissions and where not (to prevent false impressions that say the Iberian Peninsula has no emissions when it is simply not observed by this network).

Answer: To discuss to which areas the current observing network is most sensitive we added an additional figure (new S7) that shows the source sensitivity simulated by the transport model separately for the three compounds and split into the same periods as discussed in Figure 7. The following text (in section 2.5) and figure (S7) were added:

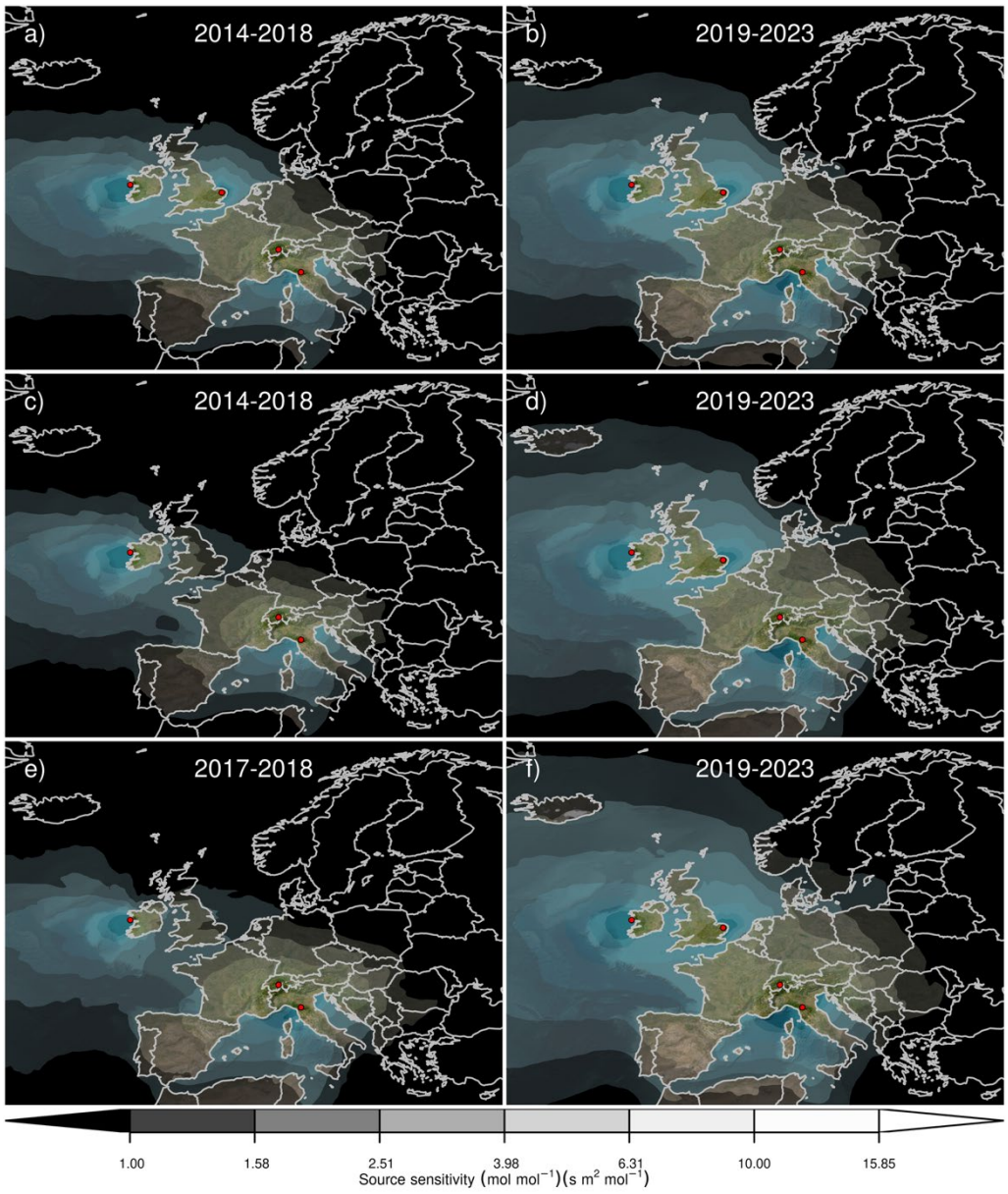

Figure S7: Average source sensitivity to HFO-1234yf (a,b), HFO-1234zeE (c,d), and HCFO-1233zdE (e,f) emissions as calculated by the NAME transport model for the years 2014-2018 (a,c,e) and 2019-2023 (b,d,f). For HCFO-1233zdE the earlier period only includes sensitivities from 2017 and 2018 since no observations were available before. Observing stations active in each period are marked as red dots. Areas with visible land surface represent regions for which emissions can be observed well from the network. Shaded or dark areas represent regions for which limited emission information can be obtained from the network. The text now reads:

"The selection of countries for which emissions are reported was based on the country-level error reduction for the inversion posterior emissions. This depends on the spatial sensitivity of the

observation network, which can be seen in Supplement Fig. S7, showing the average simulated source sensitivity for times when observations were available from the network. Sensitivities somewhat increased over time after the onset of observations at CMN in 2017. In addition to this footprint sensitivity, the error reduction for a given country also depends on the ability to discriminate between emissions from that country and emissions closer to the observing sites. For example, while emissions from Spain do result in enhancements at the measurement sites, these can often not be separated from enhancements due to emission from closer sources. Hence, the inversion lacks sufficient information to accurately spatially allocate these emissions and the country-level error reduction is low."

Detailed comments:
Lines 205-208: It is unclear how this release height adjustment was determined to be appropriate – please explain further/justify.

Answer: We agree with the reviewer that the sentence "*Release heights of 1000 m and 500 m above ground level were found to be appropriate for Jungfraujoch and Monte Cimone, respectively."* is too simplistic. We have now revised the text to:

"*The release heights of particles from the high-altitude stations (1000 m agl for JFJ and 500 m agl for CMN) is a mechanism to address the influence of substantial sub-gridscale changes in topography. There is no practical way to estimate, hour by hour, what the most appropriate model release height should be from these stations as it is constantly changing as the observations respond to, to varying degrees, the impact of the surrounding ground or, conversely, the free troposphere. In addition, the resolution of the under-pinning meteorology, both vertically and horizontally, has improved over the years of this analysis, thereby changing the surface height in the model. The given heights were chosen following a multi-year analysis comparing modelled and measured carbon monoxide, assuming a known emission distribution.*"

This solution has obvious limitations but was considered to be a pragmatic solution.

Lines 211-212: Please at some point discuss the possible impact of this simplified chemical loss approach.

Answer: Utilised average lifetimes will tend to destroy more HFO during the night, overcast days and the further north we go as compared to reality, as these are situations/regions for which we can expect lower than average OH. The first two situations should average out over time and we don't expect any biases in the inverse estimates. The last point could lead to positive emission biases further north. However, these will be considerably smaller than what we obtain in the sensitivity inversions for an inert tracer (Supplement S5). The following text was added to the manuscript (section 2.5.1):

"*Applying average monthly lifetimes will overestimate atmospheric decay during the night and overcast conditions. We assume that over time and during the transport to the observational sites this lifetime variability is averaged out. Furthermore, there may be a general overestimation of atmospheric decay the further north we go in the domain. However, such regional differences in lifetime will have smaller effects than not considering atmospheric degradation at all, which is discussed for all three compounds in the Supplement S-5."*

Line 340: I'm not sure you can conclude this means delayed replacement. Could you simple be further away in a warmer wetter environment where HFO's are thus not seen at the site as well? Could you have growth in both HFOs and HFCs here?

Answer: We believe that we have addressed this point as part of the earlier comment by the reviewer. While lifetime is short, the 'pollution' ratios of HFOs/HFCs are smaller at Gosan even when correcting for lifetime and a conservative transport time during which the substances could have undergone decay. As for the question of having growth both in HFCs and HFOs, yes that is possible, but that would also be part of a delayed transition.

Line 346-7: I'm not sure this has been established, particular since chemistry was not accounted for in this analysis.

Answer: We have now added decay to our analysis as specified in an earlier comment by the reviewer. We have shown that decay may change the ratio of pollution events of HFCs vs HFO-1234yf for Gosan to some degree, the overall clear differences between MHD/JFJ and Gosan are however still present.

Fig 3.: Perhaps also do this considering decay of the substances during transport.

Answer: As stated above, we have now added a mean decay of the HFOs/HCFO for an estimated transport time to the Gosan station. As stated earlier, the effect is not very big and does not change our conclusions.