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 2 are green, replies in black.

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:

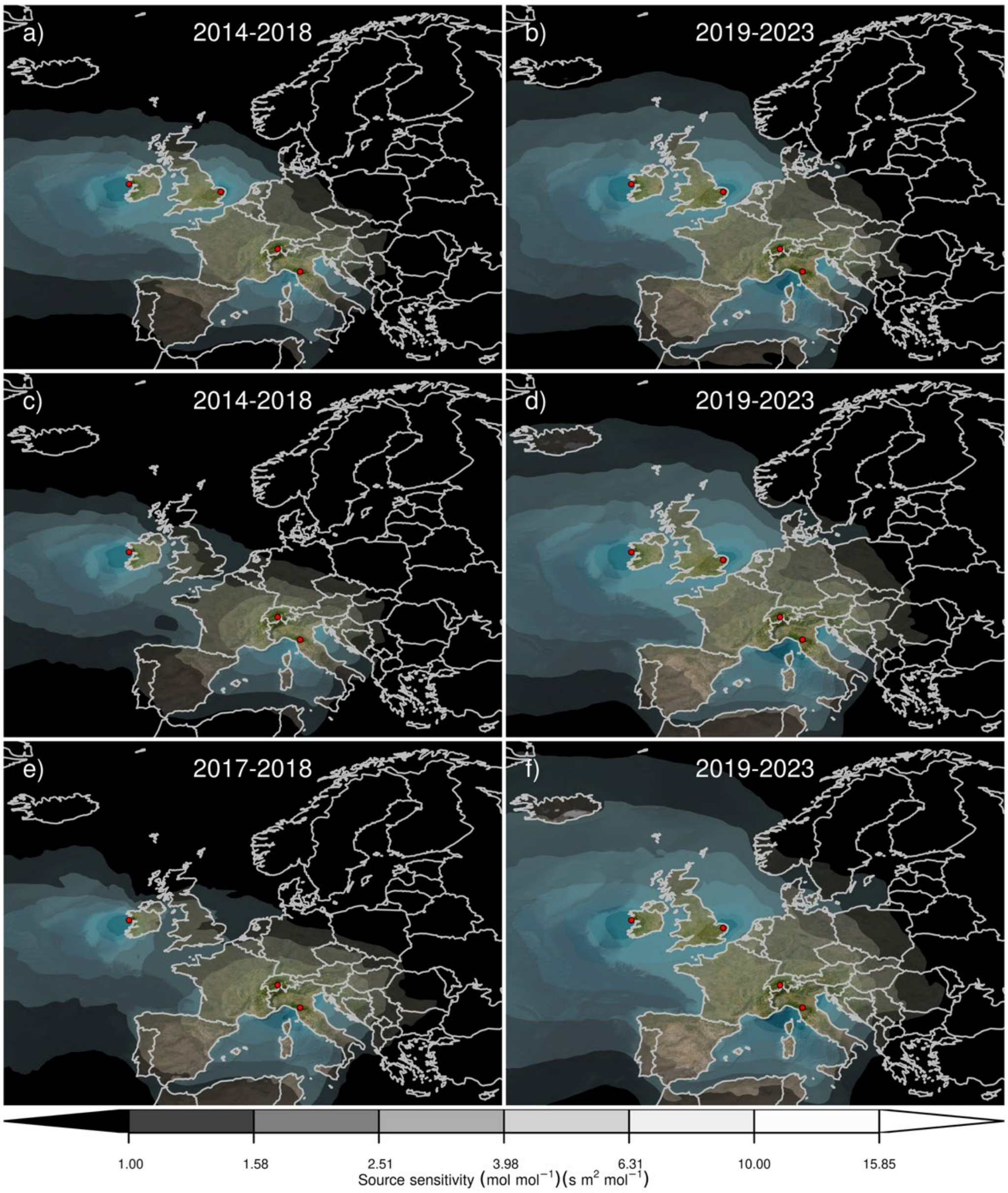

Figure S7: Average source sensitivity to HFO-1234yf (a,b), HFO-1234zeE (c,d), and HCFO-1233zdE (e,f) emissions as calculated by the NAME transport model for the years 2014-2018 (a,c,e) and 2019-2023 (b,d,f). For HCFO-1233zdE the earlier period only includes sensitivities from 2017 and 2018 since no observations 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.