

Reply for Anonymous Referee #1

This study presents the first comprehensive dataset of 11 fluorinated greenhouse gases (F-gases) at Zhongshan Station (ZOS) in Antarctica throughout 2021, comparing results with other Antarctic and Southern Hemisphere stations. The manuscript is well-structured and provides valuable insights into F-gas variability and potential sources in a remote polar environment. However, several key aspects require clarification and improvement to strengthen the scientific rigor and impact of this work.

General comments

1. My main concern is about the data duality and working standards. The discussion on working standards (Section 2.1.2) lacks sufficient detail to assess calibration reliability. The authors may want to elaborate on how the samples got analyzed and how to trace back to AGAGE (or other) working standards.

Reply: Thank you for your comments, I have understood your concerns. Therefore, I have provided a detailed explanation in Section 2.1.2 on how the samples were analyzed and how to trace back to AGAGE (or other) working standards.

Ambient air was dried with a two-stage Nafion dryer and preconcentrated in a stainless-steel trap (1.60 mm ID, packed with HayeSep). Major background gases (N₂, O₂, Ar, Xe, CH₄, CO₂) were purged with high-purity helium under precise temperature control. The retained compounds were transferred to a second trap (0.51 mm ID, HayeSep) for reconcentration, then thermally desorbed, separated by GC (GasPro precolumn, PoraBOND Q analytical column), and detected by quadrupole MS. The GC temperature and pressure programs followed the Medusa GC-MS protocol (Miller, B. R. et al., 2008), with a total analysis time of 70 minutes. The modification section is added at *L110-115*.

Each air sample measurement was bracketed by a reference gas (working standard) measurement to detect and correct for drift in the detector sensitivity. The working standard gases used at measure instrument were compressed ambient air stored in high-pressure cylinders and calibrated against quaternary standards, which were calibrated by a tertiary standard from the Scripps Institution of Oceanography (SIO). Our measurements are reported on the derived calibration scale. The gases studied in this paper correspond to three types of SIO, namely: SIO-05 (CF₄, HFC-134a, HFC-152a), SIO-07 (PFC-116, HFC-23, HFC-32, HFC-143a), SIO-12 (NF₃), SIO-14 (HFC-125, HFC-227ea, HFC-236fa). The modification section is added at *L126-134*.

2. Another suggestion is to include the uncertainties in F-gas measurements, which are critical for later emission inversion studies but are only briefly mentioned.

Reply: Based on the concentration data of the AGAGE third-level working standard gas measured by the ODS5-pro system, we calculated the accuracy and precision of the instrument, which have been attached in the form of a table in the artical. The measurement precision of ODS5-pro system depends on the mole fractions of compounds. The precisions are around 0.5%, 0.5%–1%, 1%–4%, and 4%–11%, for

the species with mole fractions greater than 100, 20–100, 2–20, and 0.1–2 ppt, respectively. The specific content of the table which located at supplement material is as follows:

Table R1 Accuracy, limit of detection and quantitative method for each compound by ODS5-pro system. “A” means using the peak area for calculation, “H” means using the peak height for calculation.

Compound	Limit of Detection(ppt)	Accuracy(%)	Precision(%)	Quantify
HFC-134a	0.16	0.48	0.65	A
HFC-23	0.08	0.50	0.63	A
HFC-125	0.21	0.61	0.72	A
HFC-143a	0.18	0.84	1.10	A
HFC-32	0.59	0.55	0.72	A
HFC-152a	0.91	1.07	1.36	H
HFC-236fa	0.08	2.02	2.42	H
HFC-227ea	0.11	4.62	5.85	H
PFC-116	0.08	2.00	2.63	A
CF ₄	0.23	0.70	0.84	A
NF ₃	0.70	1.36	1.86	H

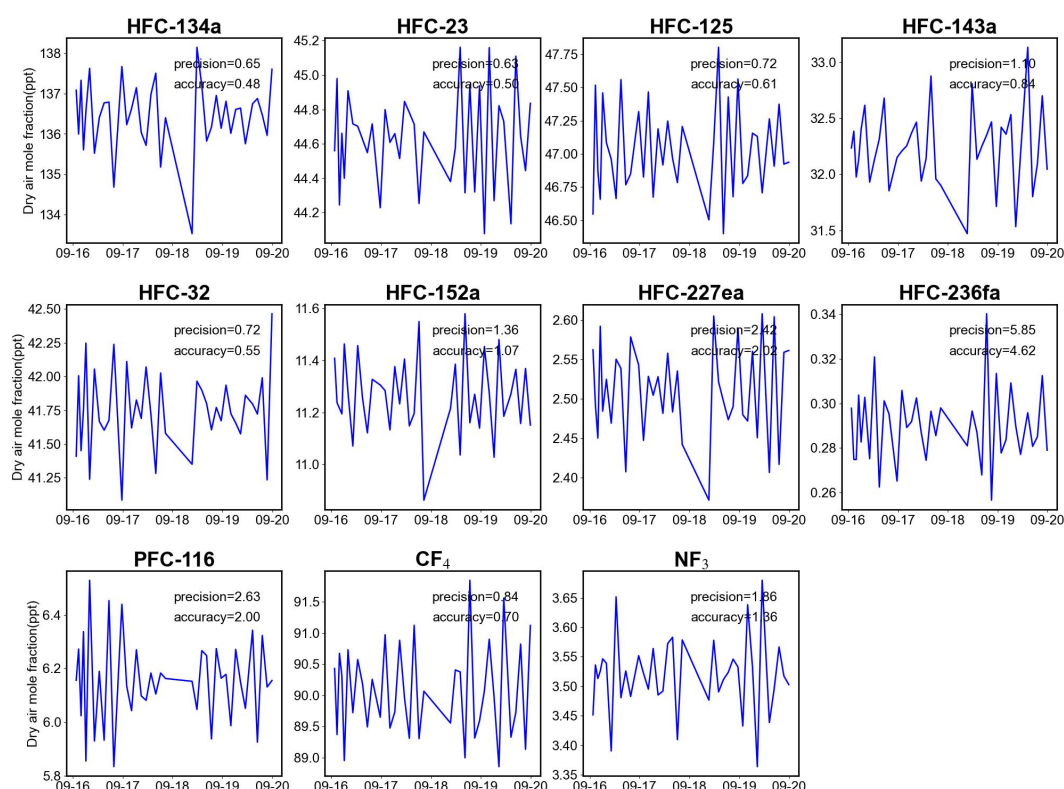


Figure R1. The precision and accuracy when ODS5-pro system measuring standard gas. *Please see: L135-138, Supplement material L26-33 and L43-45.*

3. Figure 2 and related discussion, I am not sure it's OK to discuss “trend” based on only one year of data. And consider showing error bars on this figure.

Reply: Thank you sincerely for your suggestion. The word "trend" may indeed not be

quite appropriate. It is generally based on data over multiple years. A more accurate description here should be the monthly changing characteristics. I have already made modifications to all the descriptions of "trend" in the text.

Regarding the suggestion of adding an error bar in Figure 2, we agreed with this improvement and have already added the corresponding error bar in the figure to more clearly demonstrate the uncertainty of the data. The following is the revised Figure.

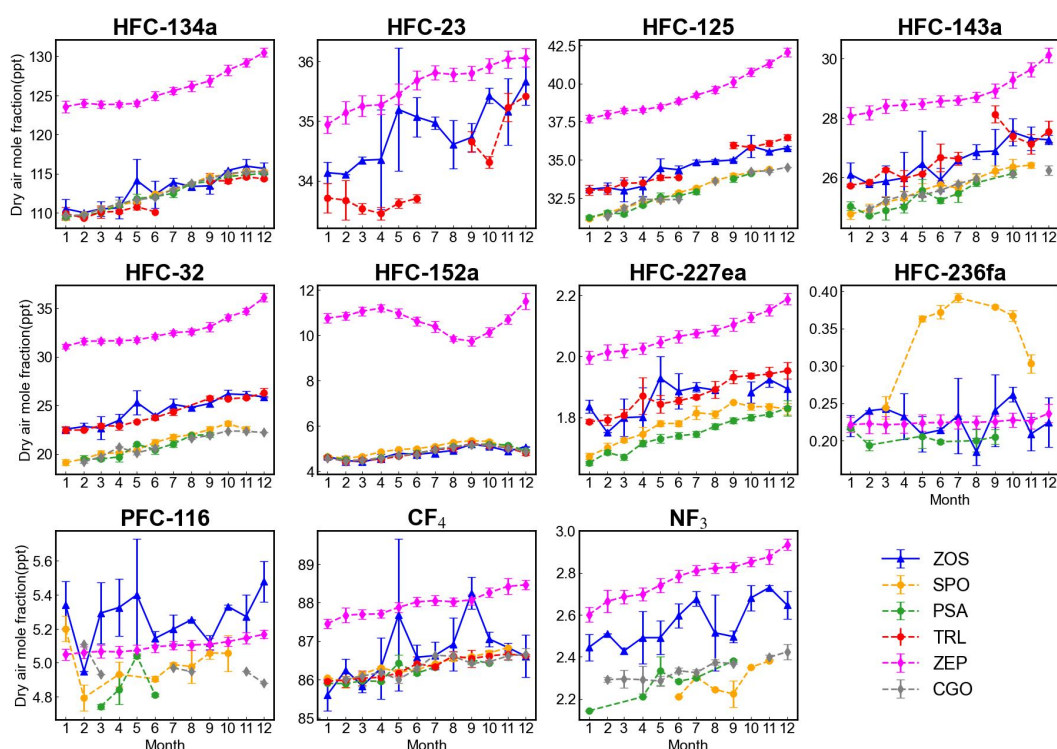


Figure R2. Monthly concentrations of F-gases at the six stations in 2021.

4. On a different note, do you see the impact of polar day and night on F-gases?

Reply: Thank you for the innovative questions you raised for us, which have triggered a lot of our thinking and data analysis comparisons. However, we are very sorry. Based on the current time resolution and uncertainty of our data, it is difficult to compare the differences in concentration increase among polar day, polar night and normal dates. At present, the Zhongshan Station in Antarctica is still using tank sampling. In the future, online observation will be set up. It is expected that the online observation data in the future can be used for related research. This limitation has been pointed out at the end of artical. *Please see: L406-409.*

5. About the HYSPLIT trajectory clustering (Section 4.2), it appears superficial to me and may oversimplify transport dynamics. I am not sure how polar singularities may impact the trajectory results and thus clustering.

Reply: Sorry, I admit that this article has such limitations. Due to the relatively low temporal resolution of this data, there are few methods available for trajectory

traceability. In addition to the HYSPLIT model, we also attempted the FLEXPART model to simulate the source receptor relationship on the high-concentration date on May 28 in 2021 at ZOS (see the figure below, the triangular symbol represents ZOS), and obtained consistent research results. There was no significant increase in the concentration at the stations by high-concentration air masses, and the air masses did not move too far from the Southeast Polar region on May 20. So the concentration at Zhongshan Station reflects to some extent the background concentration at the Southeast Pole. HYSPLIT trajectory clustering provides initial insights into the potential transport paths of F-gases in Antarctica

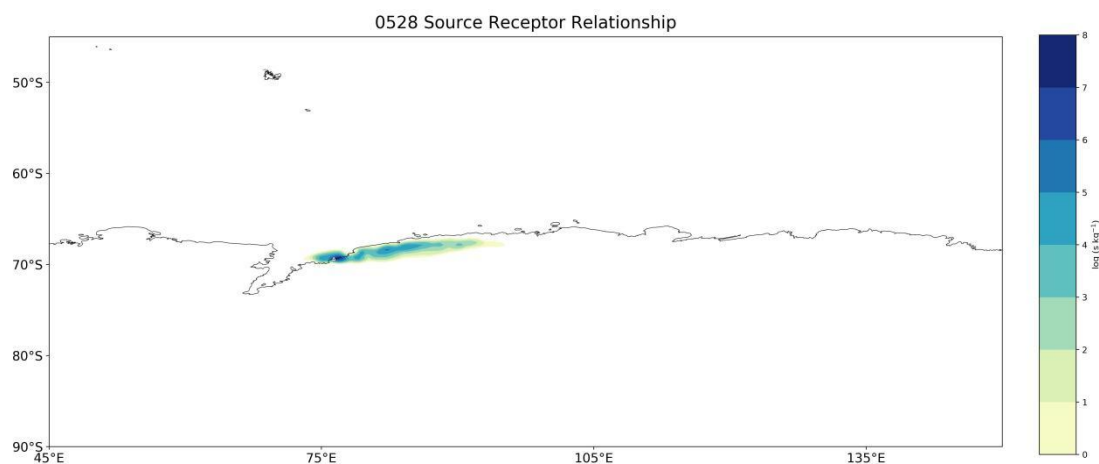


Figure R3. Source receptor relationship at ZOS on May 28, 2021 using FLEXPART model.

Secondly, we appreciated the reviewer's comment regarding the potential influence of polar singularities on trajectory simulations and clustering analysis. Polar singularities arise from the convergence of longitudes at the poles, which may lead to numerical instabilities or interpolation uncertainties in trajectory models. To address this concern, we have consulted relevant reference materials and the technical documentation of the models applied in this study. HYSPLIT supports the use of polar stereographic grids, and since February 2018, polar concentration grids for particles and puffs have been officially supported. Moreover, NOAA technical documentation confirms that meteorological data can be preprocessed onto a user-selected polar stereographic grid. Additionally, we examined the analyzed trajectories and identified no abnormal patterns with significant mutations. Finally, the purpose of applying the HYSPLIT model was to obtain the general transport path of air masses entering four Antarctic stations, which facilitates the dynamic tracing of F-gases from anthropogenic emission sources.

When the accumulation of F-gases concentration data at ZOS in the future is sufficient or online observation is achieved, we will use the REA5 dataset with higher spatiotemporal resolution to calculate backward trajectories. And we will have an in-depth discussion on the questions you raised, from the aspect of wind direction and speed to the limitations of the backward trajectory analysis area (such as not involving the range $>85^{\circ}\text{S}$). This limitation has been pointed out at the end of artical. *Please see: L406-409.*

6. Finally, some sections are overly verbose or lack logical progression. For example, the introduction (Section 1) could be streamlined by focusing on F-gas relevance to Antarctica rather than the general climate context. Results in Section 4.1.3 ("Discrete daily concentration") are fragmented; consider merging with Section 4.1.1 or using subheadings. The PMF source apportionment (Section 4.3) overlaps with Table 3; consolidate for brevity.

Reply: Thank you for your suggestion. The introduction has been simplified according to your suggestions, with redundant descriptions such as halogenated gases and the relationship between F-gases and ODSs. The focuses are placed on the F-gases in Antarctica and the current observation status of F-gases in the Antarctic region, thereby leading to the research ideas of this paper. *Please see: 1 Introduction(L34-81).*

The section "Discrete daily concentration" and "Monthly concentrations" have been merged, and the recurring conclusions have been removed. *Please see: 4.1.2 Monthly and discrete daily concentration(L253-304).*

"Table3 Main applications of 8 types of F-gases" is an introduction to the main applications of gases, and Section 4.3 elaborates on the quantitative results of PMF source apportionment; There are minor differences between the two part, but the description in the previous version did have too much repetition.

Minor Comments:

1. Page 2, line 34, remove "the issue of"

Reply: It has been modified.

2. Page, line 43, change "include" to "including"

Reply: It has been modified.

3. Page 2, line 60, change "reaction" to "reactions"

Reply: It has been modified.

4. Page 2, line 60, change "atoms" to "radicals"

Reply: It has been modified.

5. Page 3, line 55, clarify why F-gases have "zero ozone depletion potential" when some (e.g., HFC-23) are byproducts of HCFC-22 production.

Reply: It has been modified.

6. Page 3, line 74, you never define "MP"

Reply: I have provided the full form of MP, "Montreal Protocol on Substances that Deplete the Ozone Layer", when it first appeared in the article.

7. Page 7, line 150, specify how AGAGE-NOAA intercalibration offsets were corrected (e.g., scaling factors).

Reply: I'm extremely sorry for that I only found the scaling factors(NOAA/AGAGE) of HFC-134a and HFC-152a in the article published by R. G. Prinn et al. In 2018 published in the ESSD, which were 1.0015 ± 0.0048 and 0.9976 ± 0.0227 respectively. And the HFC-134a and HFC-152a of the two NOAA sites, SPO and PSA, were

calibrated to the AGAGE level. The remaining F-Gases have not completed AGAGE-NOAA intercalibration. However, the errors caused by AGAGE-NOAA intercalibration have a relatively small impact on the variation characteristics and site differences, and do not affect the main conclusion of the article. In the future, we will also conduct more in-depth research on the AGAGE-NOAA intercalibration of the remaining F-gas based on the latest Antarctic observation data to make up for this regret.

8. Figure 3, improve readability by using distinct symbols for stations or separating into panels.

Reply: Thanks, the figure has been modified.

9. Table 2, include detection limits for each F-gas to contextualize variability.

Reply: Thank you. This question is very professional and very helpful for my article. I inserted a **Table S3** in the article(as same in reply of comment 2), which contains the detection limits of each F-gas. The detection limit of the ODS5-pro system was determined using a signal-to-noise (S/N) method(Yi et al., 2023). The LOD of the ODS5-pro system was calculated by a signal-to-noise ratio (S/N) approach. S/N can be obtained by comparing the measured signals from ambient samples with known low mole fraction of target compounds with those from blank samples. The LOD was defined as the mole fraction of the target compound when the S/N=3. *Please see: Supplemant material L26-33.*