# Response to Reviewers

"Short-term variability of atmospheric helium revealed through a cryo-enrichment method"

### Referee #1

*The group of Birner has developed new techniques to analyse with high precision helium in atmospheric samples in order to resolve a long-standing question: the potential rise of crustal 4He in the atmosphere since the beginning of large-scale hydrocarbon exploitation, i.e the 20th century. Results have been published elsewhere but here authors present an improved system to measure atmospheric variability of helium and associated gases (CO2) in urban area air samples to check possibly short and long-term variability and its association to natural (i.e., gas transport and degassing from oceanic breeze) and anthropogenic sources (urban traffic and other related sources). The paper is well organized and first results interesting, I suggest some improvement to clarify a few technical points and scientific ones.*

We thank the reviewer for these kind words and taking the time to review our manuscript. We greatly appreciate the feedback and will respond to the suggested improvements below.

*Now to explain the improvements done on their system to analyse with precision variations in He, the previous system should be explained a little bit better (lines 35-40). Sentences as "The observed changes in He/M are then converted to equivalent changes in helium to nitrogen ratio (He/N2) using separate observations of CO2, O2, and Ar" are not really clear for people unaware of the previously developed system and this paper should be read as a "stand-alone". The previous sentence means that you measure variations in CO2, O2, Ar and then use constant atmospheric ratios with N2 to extrapolate N2 data? It is unclear to me, likely worst for a non-specialist.*

Thank you! We now explain this conversion from He/M to He/N2 in the introduction more clearly and added a reference to section 2.6 where the equation is given. The He-mole fraction measurements can be mathematically converted to a He-to-nitrogen ratio given knowledge of changes in the major components of air (N2, O2, Ar, CO2). Notably, the conversion is not critical to any of our results as illustrated by the strong correlation between He/M and He/N2 evident in Figure 3.

*Everywhere the analytical system is indicated as MS (Mass spectrometer). At lines 79 is indicated as a GV Isoprime 100 magnetic sector mass spectrometer, which is unusual for measuring He, while in previous papers of Birner a MAT253 was used, also unusual for measuring helium. Can clearly state from beginning which MS was used in the older system and which one is now used in the improved system (possibly adding it into Figure 1' caption)? Helium is historically measured by quadrupole MS or noble-gas-MS (NGMS). Can you briefly explain the advantages and disadvantages of using an Isoprime compare other magnetic sector gas-source MS usually used by noble gas geochemists?*

We thank the reviewer for the suggestion. In response, we now clarify in the introduction that the getter and cryo-enrichment methods both rely on a continuously pumped magnetic sector MS. In our method, the GV Isoprime 100 functions identically as the MAT253 used by Birner et al (2022). Because we believe a more detailed discussion of the differences between dynamic (i.e., continuously pumped) and static MS is somewhat off-topic for our paper, we will only provide a short discussion here:

As explained by the reviewer, "static" MS have been used historically for He analysis. In a static MS a sample is introduced once and then analyzed for an extended period of time. Standards are measured by the same method before and after the sample to correct for instrument drift on long time scales. We instead use a "dynamic" MS which allows for continuous introduction of new sample and reference gas that is eventually pumped away by a turbo molecular pump. This not only allows for the analysis of much larger samples with higher ion beams but in our method also enables rapid comparison of the sample to a reference gas every 20 seconds. This dynamic mode of operation is needed to interface with the cryo-enrichment system we developed which provides large gas streams and greatly improves precision compared to historical noble gas measurements with a static MS.

*At lines 207-210 the diurnal variations in He and CO2 are presented. During day marine breeze would bring natural He and CO2 from the ocean, while during night, reverse air circulation would bring anthropogenically enriched He+CO2 mixtures. I suppose that the mechanism is diffusive degassing of dissolved He and CO2 at ASSW conditions. Can the CO2/He ratios sufficiently precise to support this mechanism? Or eventually can you slightly develop this point air-seawater noble gas exchange has been the focus of several papers (Seltzer et al., 2019; Hood et al., 1997) but not all community is aware about.*

Marine air is low in $CO_2$ and He compared to air coming of the land and serves as a "background" reference in our study. Terrestrial air masses typically see larger respiration signals as well as emissions of $CO_2$ and He, in contrast. As such, marine sources and sinks do not enter the comparison made in the paper. This is now clarified in the section on the diurnal cycle. We note here that Helium is nearly insoluble in water and that $CO_2$ gas exchange is a slow process (timescale 1 month), thus oceanic fluxes are presumably negligible on short timescales.

*Lines 284-296. This last part of the future applications is less clear. I don't understand the interest of measuring neon isotopes or concentrations in the atmosphere except the fact that atmospheric Ne should be constant and thus help, if I well understand, separated atmospheric N2 variability by some geological source. Why not Kr, is mostly constant in the Universe and has no problems of double charges which could hamper your measurements in dynamic mode. About H2 would be more interesting, but authors do not relay expand this part. I would suggest stopping at line 284 their future application considerations.*

We agree this paragraph is not a suitable wrap-up of the paper. Nevertheless, we believe the possible relevance of the method for other measurements, particularly $H_2$ and Ne isotopes in the atmosphere at unprecedented precision is worth mentioning briefly. He/Ne measurements may for example be needed in special geological samples where $N_2$ can vary ($N_2$ in the atmosphere is however extremely stable globally and hence serves as the reference for our proposed flask measurements). This content is now presented under a separate heading. We also added some clarification to the paragraph to hopefully make it more accessible to the reader and in response to the reviewer suggestion now conclude the paper with a new summary statement featuring a more holistic review of the topics discussed in the paper.

**Referee #2**

*Variations in the abundance of atmospheric helium have the potential to trace the anthropogenic cycle of CO2. Radiogenic helium-4, generated as an alpha particle by the decays of U and Th in the crust, is readily released to the atmosphere together with carbon during exploitation of natural gases. The flux rate of C is well constrained from mining statistics but the potential sinks of CO2 are less known, and using an independent tracer of carbon release le 4He can help to better understand the carbon cycle over the last decades. The Scripps group has developed a novel analytical method to measure variations in the amount of atmospheric helium by measuring at high precision the 4He/N2 ratio in air sampled at different periods during the Anthropocene. The rationale is that, assuming that N2 is constant, secular increase of the ratio should be the result of release of hydrocarbon-related 4He from the crust. The group has validated the method by reporting an evolution curve of 4He/N2 since 1974 that fits well the expected flux of 4He released by hydrocarbon exploitation. This remarkable achievement, which constitutes a world premiere, required processing large quantities of air and long duration measurements. It was not possible to investigate short-term variations over short periods of time like weeks or months that could have a potential interest for tracing local sources ort air mass movements.*

*To circumvent this problem, the group has improved the analytical method by concentrating the amount of 4He with a cryogenic trap and by automatizing the whole process including regeneration of the trapping mechanism. This contribution describes in detail the new system and reports validation tests in terms of analytical precision, reproducibility, and short term variation of 4He concentration in air daily sampled on the Pacific coast.*

*This is a well written technological paper that opens new areas of research in atmospheric chemistry and climate change monitoring. The paper is well suited for publication in Atmospheric Measurement Techniques and I recommend its acceptance after minor corrections.*

Thank you very much for your kind words!

*The overall rationale of the method is somewhat difficult to follow in the first part as it is based on a diagram (Figure 1) where the reader has to guess the significance of the acronyms, and the essence of the method becomes clear only in the second part of the paper. I suggest the authors to add a paragraph explaining clearly the method and the use of the different devices displayed in Fig. 1.*

We thank the reviewer for raising this point. We added a brief overview at the beginning of the methods section to provide better orientation for the reader before diving into the details. The acronyms in Fig. 1 are now all defined in the legend of the figure.

*The conversion of He/M to He to N2 needs to be better explained. It is not clear to me why the direct measurement of the 4He/N2 ratio (4/28 peak ratio) cannot be done. I suspect that there are some mass spectrometric issues (e.g., magnet hysteresis) that should be explained.*

That is correct! In response this this and other comments we restructured parts of the introduction, and the relevant section now reads:

 "The "getter-helium" method pioneered by Birner et al. (Birner et al., 2021, 2022) measures changes in the $^4$He mole fraction (He/M) of dry air by stabilizing the flow of an air sample and air-like reference gas to a continuously evacuated magnetic sector mass spectrometer (MS). By holding the air flow constant

regardless of the gas source, changes in $^4He^+$ ion beam intensity reflect changes in the helium mole fraction between the sample and reference. Directly upstream of the MS, the He is concentrated by removing ("gettering") the non-noble gases using a hot titanium sponge. The observed changes in He/M are subsequently converted to equivalent changes in He/N$_2$ by taking account of changes in the major components of air constrained by separate observations of $CO_2$, $O_2$, and Ar (see section 2.6). The He preconcentration step is necessary to achieve strong He$^+$ beams and highest precision but precludes a direct measurement of He/N$_2$. However, reporting changes in terms of He/N$_2$ has the advantage that N$_2$ is present at near-constant levels in the atmosphere while denominator M – the total moles of dry air – may change from a variety of different processes that affect the overall composition of air (Keeling and Shertz, 1992; Keeling et al., 1998; Birner et al., 2022, 2021). In any case, for most air samples the correction from He/M to He/N$_2$ is small because changes in $CO_2$ and $O_2$ partially cancel."

*The use of two mass spectrometers, if I understand well, is also unclear. Maybe the authors could add a flow chart diagram of the method.*

Thanks for the excellent suggestion. We prepared the following flowchart and now include it in the Supplementary Information.
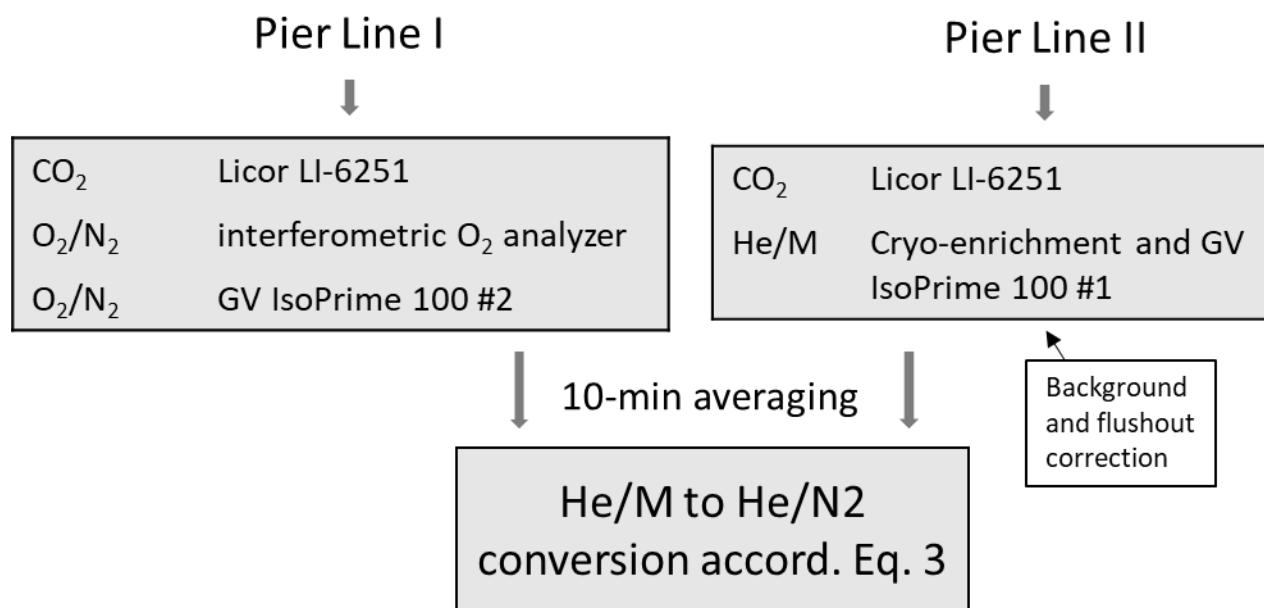
*Figure 1. Flow chart of the analysis carried out to obtained He/N2 data from the two separate gas streams of Pier Line I and Pier Line II.*

*What are the use of the different calibration tanks and what are their composition?*

Thanks! We now clarify in the methods section that these are air-like standard gases. The exact composition of these reference gases is unknown in absolute terms, but that is unnecessary because they are used only as references to detect relative changes.

*There are a few typos, e.g. "reference" in Fig. 1*

We are not sure which typo precisely the reviewer is referring to, but we reviewed the manuscript once more for typos.

*Explain meg in abstract*

Thanks, we added a definition of per meg in terms of per mille to the abstract which is more commonly used in geochemistry.

*Why not using the mu notation for 1E-6 like "solid" isotopists ?*

Is the reviewer perhaps suggesting using mu instead of per meg? Per meg is the established unit in the atmospheric community for small changes reported in delta notation. To ensure continuity with previous literature, we used the unit here as well.

*Is it possible to have C3+ and 04+ contributing to mass 4 ?*

The reviewer raises an interesting question. We believe $C^{3+}$ and $O^{2+}$ (or $O_2^{4+}$) don't contribute significantly to the mass 4 signal. The MS is unable to resolve $^4He^+$ from $C^{3+}$ and $O^{2+}$ (or $O_2^{4+}$) but levels of these non-He species are vanishingly small and identical during sample and reference gas analysis. The vast majority of C and O is removed from the gas stream during cryo-trapping. The residual C and O is not commonly present at such a high charge state. To estimate the contribution to the $^4He$ peak, we suggest a scaling calculation based on the signal intensity of the peak at m/z=8 (i.e., $O^{2+}$): The m/z=8 peak is about 2 orders of magnitude smaller than the peak at m/z=16 (i.e, $O^+$). Assuming at least similar reductions in abundance going to the higher charge states of $O^{2+}$ at m/z = 4, the contribution of $O^{2+}$ to the m/z=4 peak is presumably $<5*10^4$ cps, or < 0.1%. We also see no reason that this small signal would vary between sample and reference, so the impact on the detected variations in $He/N_2$ would be even smaller. For such a small contribution, no background correction is needed as it falls within our uncertainty (i.e., 0.1% of 2000 per meg would yield a 2 per meg correction). Contributions from $C^{3+}$ are likely smaller because no peak is visible at m/z=6.

*What are the compositions of reference gas, and what is the composition of the standard?*

Thanks for the question! As stated above, all our reference tanks for the He measurement are air-like. We now explain in the manuscript that "$He/N_2$ data are reported in delta values (Eq. 1) relative to the instrument reference gas which contains unpolluted air collected on 10th Feb. 2022."