Comment on egusphere-2022-830
Anonymous Referee #2

Referee comment on "A UAV-based sampling system to analyse greenhouse gases and volatile organic carbons encompassing compound specific stable isotope analysis" by Simon Leitner et al., EGUsphere, https://doi.org/10.5194/egusphere-2022-830-RC2, 2022

Review of the paper

A UAV-based sampling system to analyse greenhouse gases and volatile organic carbons encompassing compound specific stable isotope analysis

by Leitner et al.

This paper describes the development of air samplers for the analysis of CO₂ and methane as well as some selected VOC, in this case light chlorinated hydrocarbons. The samplers can be mounted on a small UAV. The samples are then analyzed in the laboratory. In general, the approach is very interesting because such unmanned aerial vehicles can be used where the collection of air samples is difficult to perform, e.g., directly at certain sources such as smokestacks, volcanoes, or at low altitudes over rough terrain. Therefore, the development of such methods is very welcome. This work certainly makes an important contribution to this field and is of great interest to the scientific community. The functionality of the system is proven at the end by some measurements, mainly mixing ratios and isotope ratios of CO₂ and CH₄. The results of the VOC measurements, on the other hand, are less convincing.

In principle, the paper is worth publishing, but not in its present form. It needs to be completely revised linguistically. Also some explanations and descriptions should be formulated more clearly.
General comments:

The paper is not easy to read, firstly because the English is not particularly good, and secondly because many sentences are completely incomprehensible. Some sentences have to be read several times to understand what is meant. Often enough, the sentences are grammatically incorrect and lack periods and commas.

Examples are the sentences on page 1, line 11: “Both samplers can be mounted to an unmanned aerial vehicle (UAV), the targeted compounds were greenhouse gases (e.g. CO$_2$, CH$_4$) and volatile organic compounds (VOC, i.e. chlorinated ethenes), for all compounds mole fraction and the stable carbon isotope ratio were measured.” or on page 2, line 50: “However, sampling methodology is attendant on the target measurement precision sample pre-requisites for GHG measurements are similar to those of VOCs, often relying on large and heavy sample containers (International Atomic Energy Agency, 2002).”

Cryptic sentences can be found throughout the paper. Numerous imprecise statements considerably reduce the value of this paper. A thorough proofreading and a substantial revision are necessary here.

In the introduction, a lot of information is given in a general way. However, some explicitly refer to the measurement of CO$_2$ with high mixing ratios, while others refer to measurements of VOCs with extremely low mixing ratios. A clearer distinction should be made here, since the prerequisites are completely different, especially for the isotope measurements.

Why was the focus set to CE, which are maybe not the most important VOC as suggested?

In the title, “volatile organic carbons” should be changed to “volatile organic compounds”.

Specific comments

Page 1, line 19: nmol should read nmol mol$^{-1}$
Page 1, line 20: What is a triplicate measurement of a replicate? Do you really mean 7.3 mmol mol\(^{-1}\)? To be able to assess the data, it would be necessary to know how large the sample volume was. Was the sample partitioned and if so, why? Was each sample measured three times? There are more questions than answers here.

Page 2, line 41: Reference is made here to the additional information that measurements of the ratios of stable (carbon) isotopes can provide. Works by Keeling (1958 and 1979) are cited, which refer exclusively to CO\(_2\). There is a lot of more recent literature on isotope ratios of CO\(_2\), but also especially of VOC. Current and especially specific literature should be cited here.

Page 3, line 80: I think local sampling provides information about the emissions at the time of sampling, but not about inventories.

Page 3, line 93 ff.: Did you test the criteria that led to the selection of Tenax GR yourself or does the selection refer to the cited literature? What problems were encountered with the other adsorbents? And what was the recovery rate? Which ghost peaks occurred?

Page 5, line 131: PBT must be PET.

Page 5, line 151: “We recommend ... “. This sentence makes no sense.

Page 5, line 155: Delete “developed”

Page 6, line 161: What is a “negative pressure”?

Page 6, line 162 ff.: “The dead-volume ...” Did you measure the influence on the results? What does “significant” mean here? How large is the influence? What do you mean by “follow-up measurement set-up”?

Page 6, line 183: Here a sampling time for the adsorption tubes of 600 s is given. With a flow rate of 50 mL/min as given in chapter 2.1.3 an air volume of 500 mL is sampled. As an example, assuming a DCE mixing ratio of some 100 pptV, this would result in some 10 ng of the compound and only a few ng of carbon per sample. Usually about 50 ng of carbon are needed to measure isotope ratios with a GC-C-IRMS with a suitable precision. I am not sure, if this method is well suited to measure isotope ratios of VOC.
Page 7, line 211: “electronic ionization” must be “electron ionization”.

Page 7, line 239: “CH$_4$, which was ....”  This sentence is another example of imprecise wording. Methane is not “oxidized” to H$_2$, but pyrolized. Did you really measure the isotope ratio of $^{2}$H/H? If not, this information is unnecessary here.

Page 9, line 273 ff.: “vegetation crown”, better: “canopy height”. And I think, not the field campaign was overcast, right? What do you mean by “decoupling from atmospheric background”? CO$_2$ profiles are not generated, but measured. With the described system mixing ratios or isotope ratios can be measured, but no fluxes.

Page 10, line 29: “Injected amounts ...“. Again a cryptic sentence.

Page 10, line 303: “Volutilization of light isotopes ...“ I think you mean “volatilization of molecules containing no $^{13}$C atoms ...”

Page 10, line 315: The minimum quantification level is quite different for the measurement of mixing ratios and isotope ratios. The “sufficient sensitivity” may hold for ambient air monitoring but not necessarily for isotope ratio measurements. Maybe, a more specific discussion is needed here.

Page 12, line 363 ff.: The mixing ratios of heptane and toluene seem to be rather high. If these values are correct, I wonder why they are only given as approximate values. Since a GC-IRMS system was used (by the way, there is no information about the chromatography such as columns, temperature program, etc.), I wonder why only the two compounds were measured. With the comparatively high mixing ratios, I would expect that a large number of other compounds should be measurable. Are the isotope ratios given for the calibration standard or for the ambient measurements?

Page 13, line 380 ff.: In this section it is not clear to me when exactly which sample was taken. First, it states that the manual samples were taken two hours before the UAV samples. Then it states the samples were taken at the launch of the UAV along with the UAV samples. What is meant by "chilled center"? What is meant by "rotor off"? My understanding is that the UAV would crash if the rotors were turned off. How were the samples collected with the UAV, in the ascent or in the descent phase? That has a significant impact on the air samples collected, as is implied in the text. I think a clearer description of the sampling process is needed here.

Figure caption, Fig. 1: What is A, what is C? There's not really anything discernible at D.
Figure 2: If you look at the results of the gas standards, there are data points with large error bars of almost 1 per mil, which I think is realistic, but also data points with practically no errors, which is quite unrealistic. Here I lack a more detailed explanation.

Figure 5: I suggest to show here an actual "vertical profile", namely the height on the y-axis. Beyond that, the axis label is quite odd.