

Interactive comment on “A high volume sampling system for isotope determination of volatile halocarbons and hydrocarbons” by E. Bahlmann et al.

Anonymous Referee #1

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Overall:

This manuscript describes a method for sampling volatile halocarbons and hydrocarbons which is free of large power and liquid nitrogen/argon requirements, allowing the system to potentially be used at many sites inaccessible to previous systems. Furthermore, the authors describe laboratory measurements of the concentration and d_{13C} ratios of various hydrocarbons and halocarbons, and report these data for two field sites. The method described should be very useful for future work constraining the atmospheric budgets of various important organic compounds. It is relevant for the readers of AMTD, and thus I recommend that it be published after the following revisions are incorporated.

C487

sions are incorporated.

Suggested revisions:

The manuscript is light on figures, as it currently contains only two schematic diagrams and no figures depicting data. I recommend that the authors add a figure depicting the d_{13C} reproducibility results described in section 3.2.1 (see below). I would also suggest that a figure summarizing the field results be added. For example, a plot showing the range of ^{13}C values observed for each of the organohalogens (section 3.3.2) would be helpful.

I am also somewhat concerned that, in the authors' own words (page 2172, lines 8–9), “the reproducibility of the carbon isotope ratio determination was only tested for the analytical system.” While I agree that the recoveries of the sampling system were excellent, it is possible that biases in d_{13C} ratios could be present even when high recoveries are achieved. Did the authors not measure the ^{13}C ratios of the standard compounds during the recovery tests described in section 3.1? If so, they should be reported, as this data would represent a major improvement to the paper. If not, please justify this omission beyond the text quoted above.

The discussion of the d_{13C} measurement reproducibility vs. concentration in section 3.2.1 should be improved. CH_3Cl and CH_3Br were injected at concentrations varying from 0.2 to 20 nmol. The authors state that “[s]tandard deviations ($n=6$) for carbon amounts between 20 and 1 nmole were usually below 0.3%.” I assume this means that six injections at each concentration were performed, but this should be clarified. Also, I would prefer that authors be more specific, instead of stating that the standard deviations were “usually below 0.3%.” Furthermore, it is unclear if “ $n=6$ ” refers only to concentrations above 1 nmol, or to lower concentrations (i.e., 0.02 nmol). I think the paper would be improved if the data discussed in this section were presented in graphical form. That way statements like “The carbon isotope ratio determination was free of a systematic bias for carbon amounts down to 0.02 nmole” (p. 2171, lines 24–

C488

25) would be better supported, and the reader would be able to visualize the change in reproducibility that the authors report occurs at around 1nmol. Furthermore, since it does not appear that the authors found it necessary to correct $\delta^{13}\text{C}$ ratios for any blank effects, this figure would make it apparent that such a correction was not necessary.

Minor revisions:

p2164, lines 18-19, and p2165, lines 1-2: "Sampling times varied between 10:00 a.m. and 02:00 p.m. local time." This is confusing – does this mean the sample was collected starting at 10AM and ending at 2PM each day?

P2166, line 6 – shouldn't this read "behind valve 3" (not 2)? Also, text says this restriction flow was 50 mL min⁻¹, but Fig.1 says 70 mL min⁻¹. Please make consistent.

P2167, line 12: "3/3 inch"? Maybe the authors mean 3/4?

P2169, line 14: says desorption occurred at 350°C, but Fig. 2 says 330°C.

P2170, line 27: "The overall uncertainty of this procedure is estimated to $\pm 15\%$ on the 1σ level." Please provide a brief justification for 15%. Also, does this refer to the quantification or the purity control?

P2174 line 4: I recommend that the authors replace "paraffins" with "alkanes." Better to keep terminology consistent.

P2174 line 21: Replace "felt" with "fell"

P2176 line 7: "But own unpublished data. . ." Do you mean "But *our* own unpublished data. . ."?

P2181 lines 10-11: I don't think you can call this the "overall" reproducibility, since as stated on page 2172, lines 8-9, "the reproducibility of the carbon isotope ratio determination was only tested for the analytical system."

Interactive comment on Atmos. Meas. Tech. Discuss., 4, 2161, 2011.

C489