

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

**E. Bahlmann et al.**

enno.bahlmann@zmaw.de

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We agree with referee 2 that peak overlap is an important source of bias and appreciate the suggestion to add a chromatogram to the paper. This will surely help the reader to assess the quality of the method presented here. Anyhow, we find it more appropriate to provide a chromatogram including a detailed description in the supplementary. As this would truly go beyond the scope of this paper, we would suggest add it to the supplementary material.

Referee 2 further has expressed his concerns about the length of the discussion in par-

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ticular the discussion of the results by compound and location. Due to the complexity of ambient air samples and the multiple sources for bias such as peak overlaps, changing water backgrounds, interferences from sulfur containing compounds as reported here and incomplete combustion especially of fluorinated compounds- we think that the reliability of d13C determination cannot solely rely on comparison with standard mixtures. Thus, the main purpose of our discussion is to compare the results of our study with those from previous studies in order to assess the reliability of our data. For this reason a discussion of possible systematic dependencies between mixing ratios and isotope ratios as the referee has done exemplarily for chloromethane is beyond the scope of our paper. Furthermore, we also think that the data set is too small for such a discussion.

Pointing towards the differences in the isotope ratios between the urban and the coastal site, which have been observed for some of the long-lived compounds, the referee makes a very important point. We would like to pick up his comments for a more detailed discussion of the reliability of d13C measurements of atmospheric halocarbons. We fully agree with the referee that there are good reasons for the assumption that the variability of the d13C values of long-lived (H)CFCs reflect the methods reproducibility. This implies that these compounds could serve as a kind of internal standard. Given this, with exception of the dichlorodifluoromethane measurements at the coastal site, both the within-site variability and the variability between the two sites exceed what one might expect for such an inert tropospheric trace gas. If we compare our data with those of Redeker et al. (2007) and Mead et al. (2008), it becomes obvious that the repeatability (reproducibility within a lab) reported of all three studies is comparable. However, the average d13C values reported in our study for several (H)CFCs show substantially larger variations pointing towards a low reproducibility. For instance, the average d13C values for dichlorodifluoromethane vary from  $-33.5\%$  to  $-41.2\%$  those for chlorodifluoromethane vary from  $-33.9\%$  to  $-53.2\%$ . If the assumption that these trace gases are inert in the troposphere is valid we can currently state only a low reproducibility for these compounds, which underlies the need for an even more rigid valida-

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tion of the method. On other hand we can currently not rule out that CFCs and other long-lived organohalogens are degraded in ocean surface waters (see Yvon & Butler 1996; Yvon-Lewis 2002). For chloromethane and trichloroethane the oceanic lifetime has been estimated to 70 and 95 days, respectively (Yvon-Lewis 2002). For carbon tetrachloride the oceanic lifetime driven by hydrolysis has been estimated to 2599 days and is reduced to 94 days due to (micro)biological activity as suggested by Butler et al (1997). The estimates of oceanic lifetimes of chlorofluorocarbons that showed an isotopic enrichment in our study range from 1100 days to more than 120000 days without considering an additional biological sink in the oceans. As already pointed out by Yvon Lewis (2002), there is substantial evidence for a microbial degradation of chlorofluorocarbons from different environmental settings. If such degradation processes also occur in the surface ocean and is assigned with a substantial large fractionation factor as for instance described for bromomethane, they should considerably imprint the isotopic composition of these trace gases in the atmosphere. Thus, in our opinion there is a clear need for more investigations covering these aspects in the future

Reviewer 2 suggests presenting the individual data in table 2 rather than averages and standard deviations. As pointed out before the main scope of this table is to make the data from our study comparable to those from previous studies. We think that in this context the presentation of individual data in table 2 will make this table confusing and thus would refuse this. Anyhow an additional table with the individual data will be provided in the supplementary material. We could skip the CAS-Nr in tables 1 and 2 as suggested by referee 2 to increase readability. We think that with a chromatogram added to the supplementary material the ordering of the compounds by retention time is the most appropriate one and thus should not be changed.

The minor revisions are eglible and will be accounted for. Page 2178-2179 This will be corrected to both sites.

Page 2179, line 27.. trifluoroethane. This will be changed.

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Page 2186 (Table 2): The table will be checked for decimal points and meaningful digits. For propene this should indeed be -25.0.

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