**Atmospheric
Measurement
Techniques
Discussions**

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

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Received and published: 13 June 2011

The paper describes an improved methodology for sampling, processing and compound specific isotope ratio analysis of atmospheric Volatile Organic Compounds (VOC) at the low ppt level. While there are a few published related methods for sampling large air volumes for VOC analysis (not necessarily all connected to isotope ratio analysis), this paper presents significant improvements in practicability and in several aspects of performance and thus is a significant step towards isotope ratio measurements as an established tool to gain new insight into atmospheric VOC chemistry. The authors provide sufficient information on performance criteria and tests of the method

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to provide reasonable confidence in the results of the measurements. A detail missing is a chromatogram for an atmospheric sample with the most important peaks identified (ideally a mass 44 trace and a trace for the 45/44 ratio). An important source for bias and uncertainty in GC-IRMS measurements is peak overlap. In the context of the discussion of results, the authors mention that in several cases peak overlap does not allow determination of isotope ratios. This indicates that the authors indeed were thorough in evaluating their results. Nevertheless, I think it is only fair if the reader is allowed to form an own opinion about possible interference due to peak overlap.. There is a useful discussion of the small set of measurements, although I feel that the separate discussions by compound and by location are adding unnecessary length. Moreover, the data sets are small, at most three measurements for each of the two locations and in this case many of the differences between locations may have limited statistical significance. There is one, very interesting aspect which is not considered in detail in the discussion: Possible systematic dependence between mixing ratios and isotope ratios. Due to the complex interaction of atmospheric mixing and reactions in the atmosphere, the dependence between mixing ratio and isotope ratio can be extremely complex for reactive, short lived compounds, which makes meaningful interpretation of small data sets very difficult. However, for compounds with atmospheric residence times in the order of years or longer the current atmospheric chemistry knowledge justifies development of hypothetical dependencies between isotope ratio and mixing ratio which can be compared with observations even if the available data set is small. The basic assumption here is that the atmospheric background is reasonably uniform and well established, which is justifies for many of the long lived trace gases. A comparison of the urban and coastal chloromethane mixing ratios suggests that chloromethane at the coastal site is enriched in 13C. This is consistent with other published findings. Already the cited paper by Thompson et al. (2002) presents evidence that chloromethane in background air is slightly enriched in 13C compared to samples influenced by terrestrial emissions. This may be explained by an enrichment of 13C resulting from atmospheric loss reactions or a systematic difference in isotope ratios between marine

and terrestrial chloromethane emissions. However, the urban chloromethane mixing ratios (Table 2) are slightly lower while the δ13C values are nearly 4‰ lighter compared to marine background air. While atmospheric removal may explain the slightly lower mixing ratio in continental or urban air, this does not explain the lower isotope ratio since atmospheric reactions of chloromethane are expected to result in an increase of δ13C (see cited paper by Keppler et al. and references therein). In the paper by Keppler et al. it is suggested that there are substantial terrestrial sources and sinks for chloromethane, which to a significant extent compensate each other. In this case the impact of terrestrial sources and sinks on mixing ratio and isotope ratio on chloromethane in continental air would be visible as a net effect of terrestrial sources and sinks. The slightly higher mixing ratio and the 13C enrichment in chloromethane in marine air may be qualitatively explained by a small marine source enriched in 13C compared to the net effect of terrestrial sources and sinks. However, the cited paper by Keppler et al. references a poster presentation by Komatsu et al. (2004) indicating that chloromethane in the ocean has a δ13C value in the range of -38‰ very close to that of marine atmospheric background. It cannot be ruled out that the similarity in isotope ratio between background air and oceanic chloromethane is a coincidence resulting from a combination between sources with different isotope ratios and isotope fractionation due to atmospheric removal, but such a coincidence seems not very likely. A more likely explanation is that ocean-atmosphere exchange of chloromethane is the reason for the similarity of isotope ratios in these two coupled reservoirs. In this case the effective isotope ratio of a net oceanic source and its impact on the isotope ratio of atmospheric chloromethane would not necessarily be identical to the isotope ratio of oceanic chloromethane. This is just one example for potentially very important implications, that can be derived from a combination of isotope ratio and mixing ratio measurements of atmospheric VOC. However, there are some caveats. One, which already has been mentioned, is the limited size of the data set. This can, and very likely will be remedied in the near future since presently there are more and more research groups interested in studies of VOC isotope ratios. A far more serious problem is ex-

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perimental bias. The presented ambient data suggest that in some cases there may be a possible bias between measurements in marine and urban air. The presented data include a range of substances with atmospheric residence times in the range of several years or even decades. Moreover, for several of these long-lived compounds such as CFC and carbon tetrachloride present day emissions are, as consequence of the Montréal Protocol and its amendments, marginal compared to the atmospheric reservoir. In these cases variability of isotope ratios and mixing ratios will be most likely dominated by measurement uncertainties. Indeed, for quite a few of the CFC, HCFC and halogenated hydrocarbons the variability in mixing ratio and isotope ratio is similar to the variability observed in repeat measurements of test mixtures (Table 1). However, there are also compounds, such as some CFC and carbon tetrachloride, with atmospheric residence times of several decades and variability in isotope ratio substantially exceeding the reproducibility of repeat measurements. While it cannot be excluded that this may point towards some deficiencies in our current understanding of the atmospheric cycles of these trace gases, a very detailed study of possible interferences and bias is needed to justify such far reaching conclusions. Nevertheless, I understand that when presenting a method that allows measurement of isotope ratios and mixing ratios for a very wide range of VOC, a detailed analysis of accuracy and bias for each of the VOC is beyond the scope of a single paper. I expect, and hope, that due to the ongoing development of more and more routine techniques for VOC isotope ratio measurements there will be more publications concentrating on specific VOC, which will not only provide larger data sets, but also allow detailed analysis of possible bias and measurement error.

Some details:

Page 2174, line 21: fell, (instead of felt) Page 2178-2179: . . . the two sites.. or . . . both sites.. (not "the both sites") Page 2179, line 27.. trifluoroethane.. Page 2186 (Table 2): 3,27, change to 3.3 (decimal point instead of comma, meaningful significant digits). Line with "propene, other studies:-25.0 (I assume, a +25.0 ‰ value would be

very extreme).

I would also suggest presenting the individual data instead of averages and standard deviations. For the very small data sets (2 or 3 data points) this is far more useful for the reader and would fit well into the table, especially if the numbers are rounded according to the number of meaningful significant digits. The CAS numbers should be removed from the table; they are redundant with the substance name and can in any case easily be found for these relatively simple compounds. The retention times in Table 2 are only useful for the reader if chromatograms are presented. I also find that listing of the VOC by retention time is only useful for the very experienced GC specialist. Ordering by name or a more traditional CAS ordering may better serve the reader.

Komatsu D.D., Tsunogai U., Yamaguchi J., Nakagawa F., Yokouchi Y. and Nojiri Y. The budget of atmospheric methyl chloride using stable carbon isotopic mass-balance. Poster A51C-0784, AGU Fall Meeting, San Francisco, 2004.

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

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