

Interactive comment on “Analytical system for carbon stable isotope measurements of light non-methane hydrocarbons” by A. Zuiderweg et al.

Anonymous Referee #1

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The paper “Analytical system for carbon stable isotope measurements of light non-methane hydrocarbons” by Zuiderweg et al. presents an analytical technique to measure the stable carbon isotopic composition of atmospheric C₂-C₆ volatile organic compounds VOCs. Because the atmospheric chemistry of VOCs can be complicated by multiple sources (primary biogenic/anthropogenic, secondary biogenic/anthropogenic), and sinks (wet/dry deposition, biological uptake, photolysis, oxidation, etc.), this technique should prove very useful in understanding the individual processes and constraining their atmospheric budgets. As mentioned in the article, given the relatively short atmospheric lifetimes of several VOCs studied, this technique could potentially be used to characterize the age of an air mass and even estimate the concentration of

C1

atmospheric OH.

However, before a complete review of the presented technique can be done, increased organization of the manuscript and a more complete description of the analytical system is necessary. Below are a few comments.

1) From the description of the technique given, it is not clear what advancements have been made over other designs already described in the literature. For example, a recent application of GC-C-IRMS for the carbon isotopic characterization of low molecular weight compounds in the atmosphere with high accuracy and precision has been reported (Giebel et al. 2010). Although the precision of the analytical system reported by Zuiderweg et al. appears to be quite high, it is not stated in the abstract and little is done to characterize the accuracy of the isotope ratio measurements. This is important since sample fractionation can occur during gas sampling/analysis, particularly in high volume samples suggested in this paper. Even very small losses of compound can result in dramatic effects on the measured isotope ratios. Because extensive sample treatments with multiple cryotrap are used, fractionation cannot be automatically ignored.

2) The extremely high sensitivity of the technique presented by Giebel et al. 2010 allowed measurements of small volumes (1.0 L) of ambient air. What is the detection limit of the current technique? In other words, what is the minimum amount of sample needed for accurate and precise results? The authors briefly mention that high volume samples can be analyzed, but is this considered an advantage or a disadvantage? As written, it is not clear what the advantage (if any) there are of this technique over previous configurations. Ambient sampling required 20 L, which is more than an order of magnitude larger than Giebel et al. 2010. In addition, all testing was done with very high concentration standards with low volumes (50-200 mL). Since the dependence of sample volume up to the 20 L was not accessed with the standard, how can we be sure that the high volume ambient air samples were not affected by fractionation during processing/analysis?

C2

3) What is the humidity dependence of this technique?

4) The dependence of the isotope ratio on sample size (or lack thereof) should be explained in the abstract. "It was observed that, if the peak area of a given eluted compound was maintained above 0.5 Vs, IRMS nonlinearity is not a factor that needs to be corrected for, as for the compounds reported here it does not occur at peak areas above 0.5V s." What sample size does this correspond to (peak areas above 0.5 V s)? What is IRMS nonlinearity?

5) Surprisingly, the authors do not include a chromatogram showing the hydrocarbon sample peaks. This is necessary since extremely well separated chromatographic peaks are needed for isotopic studies by GC-C-IRMS.

6) Why is a separate column (SEP) needed for the removal of CO₂? Why can't the capillary GC column be used for separating CO₂ from VOCs?

This paper contains many incomplete sentences, sentences that make no sense and sentences that are so general that they carry very little meaning. For example, the second sentence of the abstract is an incomplete sentence, "This may be useful in particular for investigating the oxidative capacity of the atmosphere and studying long-range." Also in the abstract, the following sentence too broad and non-specific to be informative, "Results obtained agree well with previous research, but highlight the complex diurnal behavior of hydrocarbons in an urban environment."

Title: "...light non-methane hydrocarbons". The title is ambiguous: What is "light"? Instead, I would use low molecular weight (C₂-C₆) Abstract: "The inlet system is flexible and allows analysis of trace gases from medium size to very large ambient air samples (5–300 L) without loss of compounds of interest." What is medium size? Do you mean volume? The abstract is far too general without any quantitative information whatsoever on the results. Complex diurnal behavior of what? Concentrations or isotope ratios? The statement is vague and rather useless, "Results obtained agree well with previous research, but highlight the complex diurnal behavior of hydrocarbons in

C3

an urban environment."

Introduction What are the major gaps in our knowledge of VOCs in the atmosphere and how can measurements of isotope ratios help? Page 102, Line 25: A reference is needed after the statement, "The light NMHC, consisting of compounds with 2 to 7 carbon atoms (C₂ to C₇), account for the vast majority of anthropogenic emissions to the troposphere." What about biogenic VOCs? Page 103, Line 5: "Oxidative processes provide the atmospheric removal mechanism of NMHC compounds, mainly through reaction with OH, which is by far the dominant process (Conny and Currie 1996)". Do there are no other atmospheric removal mechanisms besides oxidation? What about wet/dry deposition, photolysis, and biological uptake? Page 103, Line 13: What about thermodynamic isotope effects (as opposed to kinetic)? Can they be important in the atmosphere? Page 103, Line 16: Briefly explain why isotopically lighter molecules react faster than heavier ones. Equation 2: Why is 1 subtracted from both sides of the equation? Simply this by removing this. Page 104, Line 10: The idea described here is not explained. How can isotope ratios be used as a tracer of transport and aging? This needs to be combined with later discussions of the isotopic clock concept. Page 108: Line 20, Improper reference: {Rockmann, 2003 #2132} Page 106: Line 25, What is the source of error in the extrapolation procedure described? "Mixing ratios of compounds not contained in the calibration gas were estimated by extrapolation based on the number of carbon atoms in the molecules of the species in question and can therefore contain a larger systematic error."

References Giebel BM, Swart PK & Riemer DD (2010) delta C-13 Stable Isotope Analysis of Atmospheric Oxygenated Volatile Organic Compounds by Gas Chromatography-Isotope Ratio Mass Spectrometry. *Analytical Chemistry* 82: 6797-6806.

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C4