

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

Anonymous Referee #3

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The manuscript by A. Zuiderweg et al. titled “Analytical system for carbon stable isotope measurements of light non-methane hydrocarbons” presents a new system for measuring the stable carbon isotope ratios of C₂-C₆ hydrocarbons and halocarbons in samples ranging between 5 and 300 L of ambient air. Isotope measurements of VOCs can be used to extract valuable information regarding the source origin and photochemical processing of an air mass, and thus the methodology and instrumentation presented in the paper are valuable and will contribute greatly to the scientific community’s understanding of atmospheric processes affecting VOCs. However, the authors must first address a number of questions regarding the instrumentation and make some serious amendments to the presentation and defense of the method in the

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paper.

General Comments

The manuscript could benefit strongly from a careful overhaul of sentence structure, grammar, and punctuation. Many sentences are unreadable, and many are awkward in style, structure and meaning.

Specific Comments

Title

The title is somewhat misleading, because it mentions light non-methane hydrocarbons, but in reality the methodology includes C2-C6 NMHC and halogenated species. As well, “light” implies isotopically light. Also, this may just be my personal preference, but I think “carbon stable isotope ratios” is awkward, and I prefer “stable carbon isotope ratios”. Are we referring to stable isotope ratios of carbon, or the stable carbon isotope ratios of VOC?

Abstract

The abstract is very brief, and does not actually address many details of the instrument or the results of the instrument’s first measurements. What it does suggest is very vague. What about this instrument makes this measurement new? What is different between it and previous instruments? How is the inlet flexible - physically or metaphorically? Regarding how much sample can be collected, what is “medium” sized? How is the range of sample sizes a benefit to the measurement? What typically controls the sample size? In what situations is such a wide range useful? In what ways do the results agree with previous research? What is the complex diurnal behavior you are referring to? Many of these questions are not just for the abstract, but should highlight why this instrument is important to the atmospheric community, and how it improves upon previous capabilities.

Introduction

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Some discussion of why isotope ratio methods are useful in comparison to standard methods of VOC ratios to determine aging would be useful.

In the last paragraph, you say “samples of varying origin” – varying in what way? And you mention CFCs, and yet you show no measurements of CFCs in your analysis.

Experimental, Precon System

The preconcentration system that you refer to is not labeled in Fig. 1: “System diagram”. Is the entire system the preconcentration system? If not, label the preconcentration region, or at least describe which parts the preconcentration system includes. Further, the caption for Fig. 1 refers to a number of items that are not labeled on the plot: SAMP, SEP, REC, FOC. Label these. Also, 3 traps are labeled Trap 2, Trap 3 and Trap 4, but there is no Trap 1. In the text regarding Fig. 1, the order is not the same for the regions mentioned above, and the numbering (i), (ii), and (iii), but is abandoned before (iv).

You say that typically the SAMP trap is operated at a flow of 50 standard liters per min (SLM), but why does Fig. 2 show a chromatogram demonstrating the separation at 70 SLM? How much of a difference does this make? Did you try to use different carrier gas flow rates or heating rates and different “cut-off” times for the venting of the CO₂ peak to establish whether or not this is the explanation for the -2 permil CH₃Cl fractionation? Just mentioning that this fractionation exists and then stating that it is unclear why it exists appears careless. Did you do any tests to explore this? What are the uncertainties on the -2 permil? (i.e., what is the variability? Does it depend on the sample concentration?) If I had to guess, I'd say that it is likely that you are losing a small amount of one carbon isotopomer of methyl chloride when you vent the CO₂ peak, and that if you changed when the column is reversed that the -2 permil will change slightly. Is there a humidity dependence?

For the above test, when you say “only” the LN₂ traps, does that mean that you aren't using the residual CO₂/H₂O scrubber? Does the presence of the scrubber make a

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difference in your results? How confident are you that none of the other traps create a fractionation? Have you done any tests to prove this?

The caption for Fig. 2 is very awkward and needs editing, in particular the first sentence. I assume that methane and nitrogen are both in “A”? This is not immediately clear. Also, the x-axis is labeled in seconds, while the text implies that the CO₂ peak takes 10 minutes to vent completely.

GC Separation

What are the specifics of the GC separation? I.e, what is the carrier gas? What is the carrier gas flow rate? Why is so much of the effluent (1:1 split) being used for peak identification? What is the detection limit (you say 0.5 Vs, but don't quantify what this is in terms of ng of carbon.) Can you change the ratio that is being injected into the IRMS? What is the open split ratio?

Using which IRMS peak area are the mixing ratios calculated? Mass 44? There should really be a small discussion regarding the IRMS 13C detection, and the paper would benefit from a chromatogram showing the mass 44, 45 and 46 traces. The separation of these peaks is crucial for a good isotope ratio measurement, and this is not addressed at all.

Performance and stability

P. 110, lines 21-23. This sentence/paragraph is awkward and needs to be rewritten. Explain how this was observed or give evidence for it. What does nonlinearity refer to? What sample size does this require?

In Fig. 4, change “better” to “more”. Are the horizontal lines in 4b the trends or are they set values? If they are trends, then state this. If they are set values, explain what they are and how they were decided upon. Also, the x-axes are not really “Day of year” since Jan. 1, 2009, but rather “Day since Jan 1, 2009.”

Mixing ratio

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For Fig. 6, what are the dashed traces? Are they running averages? Also, the notation on the plots is a bit much: “A). compound” – remove the parenthesis or the period. And it should be n-Pentane, not n.Pentane, for example.

In the second paragraph, it seems that it should be common knowledge that afternoon peaks are rarely as large as morning traffic-related peaks because of boundary layer breakups. You mention this later as a possibility, but seem surprised and confused by it here.

Carbon stable isotope composition

It would be useful to show a table of previously measured ambient ^{13}C values for the VOCs you measured alongside your findings for comparison.

You reference Anderson et al. (although you show 2003, and it should be 2004) for the ethylene OH-KIE, but an acetylene OH-KIE has also been published: Rudolph et al., J. Geophys. Res., 105, D24, 29,329–29,346, 2000. It would make sense to consider the KIE of such a fast-reacting VOC with, as you say, “a large daily variation” in isotope ratios, and not just an average range of ^{13}C values from the literature. For that matter, a discussion on what you would expect for the diurnal variation of all the compounds measured would likely give significant credibility to your measurements, using known OH rate constants and either measured or estimated OH-KIEs.

Source signatures

This section seems weak, and poorly described. Someone who is not familiar with Keeling Plots would not at all understand how to interpret the plots.

Technical Corrections

1. Abstract: p. 102, lines 3–5: this is not a complete sentence: “studying long-range” what? 2. Introduction: p. 102, line 25: delete “The”. 3. Reaction (1) and other uses of OH^* and R^* : conventionally, * indicates a high energy species, whereas a dot ($\dot{}$) represents a radical. I believe these should be dots, not asterisks. 4. P. 104, line

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16: necessary should have only one “c”. 5. P. 106, lines 5-6 and elsewhere: “pre-concentration” or “preconcentration”? Be consistent. 6. P. 108, line 20: the Rockmann reference is still a field code. 7. P. 110, line 4: you should state “Apel-Riemer, AiR. . .” here (where it is first mentioned, instead of in figure captions). Also, Inc. should be capitalized. 8. P. 111, line 17: is it 4-6 Aug or 6-8 Aug? See Table 3. 9. P. 111, line 18: change “within 500 m to a high traffic. . .” to “within 500 m of a traffic. . .” 10. P. 112, line 4: change “assure” to “ensure” 11. Table 3: change Fig. 8-10 to Fig. 6-8.

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