The manuscript submitted by Zuiderweg et al. (Titled: Analytical system for carbon stable isotope measurements of light non-methane hydrocarbons) describes techniques and a "new automated system" for the carbon isotope ratio measurement of C2-C6 atmospheric hydrocarbons after extraction from high volume air samples. Stable isotopic data is unique because it provides additional information about a compound's source(s) and removal mechanism(s) that concentration measurements alone cannot provide. With that in mind, the analytical system developed by Zuiderweg et al. can provide new knowledge with regard to the dynamic action of non-methane hydrocarbon sources and sinks, a hydrocarbon's overall budget, and the extent of atmospheric processing an atmospheric hydrocarbon has undergone. This paper will be beneficial to the atmospheric science and isotope community.

Despite the usefulness of the technique, some questions linger and need to be addressed. This critique will be organized following the sections of the manuscript.

Title:

I would suggest modifying the word "light" within your title, and identify the carbon range you are focusing on (i.e. C2-C6). While reading the title, I mistook the word "light" to signify material isotopically depleted in 13C.

Abstract:

The abstract lacks information. A few sentences about the setup, tests, and results are desirable. Provide the readers with this information here so they can decide if the paper is useful to their needs and so they can determine where to find the information they need within the main text. Name the compounds that you are studying, C2-C6 does not provide enough information. What is/are the advantage(s) of a "flexible inlet system"? It appears that one of the intentions of this system is to analyze "clean samples" from remote locations and stratospheric samples. Perhaps this should be mentioned here, as this may partially explain why high volume samples may be needed.

Intro:

General remark: Many sentences are long and attempt to say too much (i.e. Intro pg 102 lines 17-20; pg 102 line 26 starting with "Acetylene" and continuing to pg 103 lines 1-4). Long sentences tend to lose their meaning, so try to break them up into two or more.

In the first paragraph you begin two successive sentences with the word "These". Maybe you can use this as an opportunity to name the actual compounds you are studying.

Regarding isotope terminology and equations: I understand the terminology within the fields and subfields of stable isotope geochemistry is inconsistent, however I do not think it is appropriate to define ε and α as "fractionation constants". As you show in equation 3, α is considered to be the inverse of the KIE (k13/k12) and typically defined as a 'fractionation factor'. Whereas, ε is a convenient way of expressing the isotopic enrichment (on the per mil delta scale) that would be observed for the remaining pool of compound after a removal process occurred. In this regard, ε is often defined as an 'enrichment factor'. I must ask, is the discussion of either term necessary since the manuscript does not discuss atmospheric loss processes in depth? Perhaps it would be better to omit these terms and explain the idea in more general terms? (When an atmospheric hydrocarbon is oxidized, the remaining pool becomes enriched in 13C, and that a larger KIE is accompanied by a higher degree of isotopic fractionation?) If you wish to define these terms as constants, than you should explain that these are

constant for a particular hydrocarbon, under a specific set of conditions, for a single removal process (i.e. chemical oxidation by OH and O3 would have different values associated with the fractionation).

Can you add some additional depth/explanation on how these measurements can be used as tracers of transport and aging? This idea currently stands alone as single paragraph containing a single sentence.

In the last paragraph of the introduction it is suggested that high volume samples provide the capability of analyzing stratospheric samples where mixing ratio for NMHCs might be low. Maybe this information should be added to the abstract?

Experimental

Preconcentration system

This section requires significant reorganization. The first item that needs correcting is Figure 1. The terms: SAMP, SEP, REC, and FOC are not labeled on the figure; yet the reader is directed to their presence in the manuscript text and figure caption. The order listed in the figure caption is not the same as the order listed in the first paragraph of the preconcentration system section. This caused some confusion during the review of the manuscript.

> SAMP Trap: This was described as a cryotrap, yet the cryogenic was not disclosed? The method used to heat the trap and release the material was not mentioned. Are you using electrical devices or hot water to achieve 120 degrees C?
>
> SEP Column & Figure 2: (pg 106, line 23 – awkward sentence, consider revising). It is understood that chemical sorbents were not the primary means to remove CO2, but the description as written was confusing, "GC-based removal" was listed as the method by which CO2 was removed. I would consider removing this statement and keep it simple by saying something like 'a packed GC-column acted as a trap for NMHCs and allowed unwanted CO2 to pass'. I would also consider replacing the term "SEP Column" with 'SEP Trap', even though CO2 is separated from the NMHCs, you are in fact trapping the NMHCs. Discussing/labeling this as a "column" and telling the reader you chose "GC-based removal" made me think I was reading the chromatography section of the paper.
>
> The location within the text where you discuss figure 2 and the eluting CO2 and NMHCs is awkwardly placed. I think you would be better served discussing the rest of the preconcentration system first and then describing your use of a quadruple mass spec to test the retention of NMHCs and elution of CO2, CH4 etc from the SEP Column. Also, was the Quad MS for this test used past the GC or immediately at the filtering column? This test seems to be a good idea for characterizing your entire preconcentration system, not just the SEP column individually. Suggestion: did you consider using a cryogenic slurry of dry ice in either acetone or ethanol to trap the NMHCs and allow the CO2 to pass? Perhaps this would not work considering the large sample sizes? After the flow through the SEP column was reversed and reduced to 11.2 ml/min, how was this flow controlled? Pg 107, line 23-27 needs revision for grammar and organization.
>
> The SEP column is reported to have no effect on the NMHCs' measured isotopic signature, is this true for the all traps upstream and downstream of the SEP column? In other words, how was the preconcentration system plumbed to the IRMS for this test? Was the REC and FOC trap included between the SEP and GC?

REC and FOC Trap: The large volume samples you intend to collect will undoubtedly contain lots of water, the majority of which is trapped in the ambient air sampling unit (described below). Does the chemical CO2/water scrubber have the ability to collect large amounts of water from multiple samples without being replaced? Is liquid nitrogen being used at the FOC trap? How is the REC and FOC trap heated?

GC separation, combustion, and detection

Is a chromatogram available? Can you provide the column flow rate? What is the carrier gas? Is the flow through the column maintained as constant flow or pressure? Is there a significant flow rate drop at the open split in front of the IRMS?

Exactly half of the sample is lost at the quadruple mass spec split, is the quadruple mass sepc used during every analysis or only to help identify peaks on a single sample? What is the slit ratio between the open split and the IRMS? How much sample (ng carbon or compound) is being transferred to the IRMS?

Ambient air sampling unit

It is not clear if the ambient air sampling unit was included during tests of the two calibration gases (Table 1 and 2). I would guess it was not. It would probably be better to discuss this unit in your preconcentration system section since it appears to attach to the front end of the preconcentration system. Have you tried performing your calibrant tests using wet air instead of tank (synthetic air)?

Performance and Stability

How much sample (ng Carbon or ng Compound) is associated with 0.5Vs? Should I to assume this is your lower limit of quantitation? If you go below this value, to what degree are your isotopic values affected? What is the detection limit?

Pg 110, lines 21-28 – awkward, grammar revision needed, past and present tense used in same sentence/paragraph.

Figure 4B: What is the point you are trying to make about sensitivity? I understand it may change with filament use. What you show here looks fairly stable. If the displayed stability is btw ~0.2-0.33 Vs/ngC, why is nonlinearity observed below 0.5Vs? Are these data point for the mass-44 trace?

Figure 4A: Is the observed variation in δ13C influenced by sample size/volume? Are 50ml samples enriched or depleted in 13C compared to 200ml samples? In general, what is the variation for each compound around the mean? Between ~0.5-2‰?

Figure 5: Is it possible to identify sample volumes? It would be interesting to see if too little or too much sample is contributing to one side of the tail or the other.

Please see Table 3 Caption – Figures 8-10 do not exist.

Carbon stable isotope composition

Page 114, lines 5-7 – I do not understand what you are saying. Do your results agree with Redeker et al.? Are the results made by Redeker et al unreasonable? This needs clarity.

Source Signatures

Figure 8: This section uses a Keeling Plot to determine the potential source isotopic signature of ethylene, butane, and pentane. Since these results are determined by the y-axis intercept of δ13C vs inverse concentration, it seems appropriate to extend each regression to the y-axis. Why does ethylene appear to have a different slope compared to the other two hydrocarbons? (Page 116, Lines 1-3 needs revision). The slope is determined mainly by reaction kinetics rather than dilution, how does this affect the slope? Can you explain how the isotopic signature of ethylene is changed, what specifically causes the reversal in slope compared to the other compounds (butane and pentane)?

Conclusion

I understand that during the calibrant tests measurement errors were below 1‰; however I think it would be appropriate to also mention that your measurement errors are between approx. 0.6 to 4‰ (See Table 4) for ambient samples, with the exception of ethylene (which is higher due to its high reactivity and KIE) . The system is reported to allow high volume ambient air sampling without the loss of compounds of interest; have you really shown this?

General Remarks

This was described as an automated system, yet no discussion was provided about how and what was automated? Please provide further details or remove this statement.

The manuscript contains many instances where grammar, clarity, and general organization suffer. In some cases, a single sentence may benefit from being separated. In other instances, words are missing. Finally, more detail can be used to help fully express the ideas and discussion the authors are trying to present.