Reply to reviewer comments

We thank the three referees! We appreciate their effort to review our paper. In the following we give detailed replies to their comments (in order of occurrence). The referee comments are reproduced for clarity.

Referee #1

Comment 1

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 cryotraps are used, fractionation cannot be automatically ignored.

Answer

The long term precision and stability has been evaluated to be 0.3-0.8 permil for all reported compounds. Since isotope ratio measurements are relative by definition we did not emphasize the discussion on accuracy, however, we point out that all our values are calibrated against the VPDB standard.
With respect to Giebel at al. (2010) our sensitivity is a factor 2-4 lower (i.e. 1.5-2.5 ng of collected Carbon). The main reason for this is the 1:1 splitting of the GC effluent between the quadrupole MS and the IRMS. The main innovation of our system is the sample treatment system which allows for huge sample volumes (>100L). This is ~100 times more that what is typically sampled by Giebel et al., so certainly both systems have their specific strengths.
All this information has been included in the abstract.

Comment 2

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?

Answer

The sensitivity of the instrument is 0.2-0.3 Vs/ngC. Usually an accurate detection of the peak is possible for signals larger than 0.5 Vs. This translates to a low detection limit of 1.5-2.5 ngC – not as outstanding as Giebel et al., but still better than most other existing systems!

Comment 3

2) 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.

Answer

The capability of treating large sample volumes is clearly an advantage. It allows for new applications such as measurements of firn air samples or high volume air samples from remote regions. We added these potential applications to the introduction section.

Comment 4

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?

Answer

We carefully designed the cryotraps to ensure virtually 100% efficiency under normal operation. We rely on other research (e.g. Archbold et al. 2005) and assume that no detectable fractionation is caused in such traps. We also did tests diluting the calibration standard into larger air volumes, which were subsequently sampled with the ambient air sampling unit. These tests did not reveal any fragmentation.

Comment 5
3) What is the humidity dependence of this technique?
Answer
We did not detect any dependence on humidity. Note that all bulk water is efficiently removed by the water-trap. This process did not cause fractionation for the compounds we report here. However, for other compounds (e.g. more polar and soluble compounds) this may be an issue.

Comment 6
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?
Answer
This information is not essential to assess the overall performance of the system and therefore we prefer to not include it in the abstract.
A signal of 0.5 Vs corresponds to 1.5-2.5 ngC, see answer to comment 2.
With IRMS nonlinearity we mean that the measured δ13C value depends on the sample volume below the threshold peak area of 0.5Vs. This is now made clear in the manuscript.

Comment 7
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.
Answer
This is now included.

Comment 8
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?
Answer
This is required if large volumes are sampled. Note that 300 liter of air contain more than 100 ml of CO2. This is physically too much to achieve decent chromatography with any capillary column.

Comment 9
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 longrange."
Answer
We apology for these shortcoming – this should not have happened. The revised version has been carefully proof read. The sentence should be "… longrange transport.".

Comment 10
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."
Answer
The corresponding section in the abstract reads now:

"The first application of this system was the analysis of 21 ambient air samples taken during 48 hours in August 2009 in Utrecht, the Netherlands. Results obtained are in line with previous research. The high time resolution highlights the complex diurnal behavior of hydrocarbons in an urban environment."

Comment 11
Title: "… light non-methane hydrocarbons". The title is ambiguous: What is "light"?
Instead, I would use low molecular weight (C2-C6)
Answer
We agree. Has been changed throughout the manuscript.

Comment 12
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?
Answer
With medium size we refer to the lower volumes in the given range. This has been made more clear.

Comment 13
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 an urban environment."
Answer
We have changed the wording (see above) but we prefer to give no quantitative information on these measurements in the abstract for two reasons: first, this is an instrument paper, and second, the sampling location at the university is too complex for a firm interpretation of the data. Their main purpose is to show the potential of the instrument.

Comment 14
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."
Answer
Reference is provided.

Comment 15
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?
Answer
Oxidation by OH is by far the dominant process. We adjust the statement accordingly:
"Oxidative processes provide the dominant atmospheric removal mechanism …"

Comment 16
Page 103, Line 13: What about thermodynamic isotope effects (as opposed to kinetic)? Can they be important in the atmosphere?
Answer
This paragraph discusses the kinetic isotope effect which is considered the most important atmospheric process for the compounds discussed here. Thermodynamic effects, however, may control the isotopic signatures of the sources.

Comment 17
Page 103, Line 16: Briefly explain why isotopically lighter molecules react faster than heavier ones.
Answer
Done:

“Isotopically lighter molecules usually react faster than isotopically heavier ones. In the case of hydrocarbons and carbon stable isotopes, this is because bonds in molecules containing solely ^{12}C atoms are weaker than those containing one or more ^{13}C atoms.”

Comment 18
Equation 2: Why is 1 subtracted from both sides of the equation? Simply this by removing this.
Answer
Equation 2 now defines KIE (see comment 25).

Comment 19
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.
Answer
This is actually an application of the isotopic clock concept. We re-located the paragraph accordingly.

Comment 20
Page 108: Line 20, Improper reference: {Rockmann, 2003 #2132}
Answer
Corrected.

Comment 21
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.”
Answer
We can only speculate about the source. However in Fig. 4 it can be seen that the sensitivity generally stays in the range 0.2-0.32 Vs/ngC. So we expect that the systematic error of this method is of order +/- 30%. Note that the relative uncertainty between individual measurements is smaller (~10%) because all individual measurement are affected in the same way.

Referee #2

Comment 22
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.
Answer
Title is changed. See comment 11.

Comment 23
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.
Answer
This information is now included in the abstract.

Comment 24

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.

Answer

We tried to improve style and readability.

Comment 25

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

Answer

We agree. These definitions are not important here. We only define the KIE in equation 2 and leave out ε and α.

Comment 26

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.

Answer

This paragraph has been moved and is now used as an example of how the isotopic clock concept can be applied.

Comment 27

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.

Answer

We apology for this mistake. Figure 1 is corrected. The order has been adjusted in the Figure caption.

Comment 28

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?

Answer

This information is provided now: liquid nitrogen and electrical heating, respectively.

Comment 29

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.

Answer

All these suggestions were thankfully accepted.

Comment 30

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.

Answer

We moved the discussion of Fig. 2 towards the end of this section. We changed the text to make clear that the QMS at the tail end of the SEP column. Pg 107, line 23-27 has been improved. The other suggestions given here are interesting, however, we chose for the conservative approach to use liquid nitrogen for all cryotraps in order to avoid fractionation effects. Cryo-trapping at higher temperatures may result in not-perfect (<100%) trapping efficiencies for some compounds.

Comment 31

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?

Answer

See answers to comments 4. The SAMP, REC and FOC traps were all included.

Comment 32

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?

Answer

Liquid nitrogen is used in all cryo-traps and all traps are heated electrically (unless mentioned otherwise). We made this clear in the revised manuscript. The water trap works very efficiently and only small traces of water need to be removed with the scrubber. This grants that we can indeed analyze multiple samples without having to replace the chemicals in the scrubber.

Comment 33

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?

Answer

All information will be provided. Carrier gas is He at a flow rate of 2.1 ml/min which is held constant by a MKS flow controller. There is a flow-rate drop at the open split: approximately 0.5mL/min is admitted to the IRMS (which is the maximum allowed), so about 0.5mL/min of the sample stream is lost at the open split.

Comment 34

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

Answer

The QMS was used for all analyses and yielded additional data that has been used for quality control (e.g. to identify overlapping peaks). Also the split ratio in the open split could be further optimized. Without QMS and an optimized split ratio we would probably achieve similar sensitivities as Giebel et al. 2010, however, because we can easily acquire large samples we choose to operate with parallel QMS and IRMS measurements. As mentioned above (answer comment 33), 0.5 mL/min is admitted to the IRMS, i.e. approximately 25% of the effluent of the GC column. At our defined limit of 0.5Vs, the injected amount of sample is approximately 1.5-2.5 ngC, thus about 0.4-0.6 ngC are transferred into the IRMS.

Comment 35
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.
Answer
It was not included. We decided to describe the ambient sampling system separately because it needed only for in situ sampling of ambient air. For most other applications (e.g. firn air samples, CO2 concentrates) the sample is already very dry and a much simpler system can be used to deliver the sample to the preconcentration system. On the other hand the preconcentration system is always operated as described.

Comment 36
Have you tried performing your calibrant tests using wet air instead of tank (synthetic air)?
Answer
Any humidity is removed by the chemical scrubbers, so no effect is observed. However, if the sample introduces substantial amounts of humidity the scrubber chemicals need to be replaced quite frequently. Normally, samples are already dried before introduction to the system, so this is rarely necessary.

Comment 37
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?
Answer
The detection limit is about 1.5-2.5 ngC collected amount of substance, and 0.5 Vs is indeed the threshold defining the detection limit. Also see answer to comment 2. For lower signals the integration of the peaks becomes difficult and inaccurate.

Comment 38
Pg 110, lines 21-28 – awkward, grammar revision needed, past and present tense used in same sentence/paragraph.
Answer
Improved.

Comment 39
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?
Answer
This panel is indeed simply showing that the behavior of the system with respect to stability is fairly consistent over time. The peak area limit (0.5Vs) that we describe is appropriate to the $\delta^{13}C$ measurement stability. Below this limit there is non-linearity with peak area: there is enrichment as the peak area decreases. Correction for this behavior is diffcult at best in order to obtain reliable $\delta^{13}C$ values. The sensitivity parameters shown here relate to measurement of mixing ratio exclusively. The data points are indeed from the m/z 44 trace.

Comment 40
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‰?

Answer
We did not observe any trends with respect to sample size. This has been clarified in section 2.2 with an example. The variation around the mean is better evaluated in Figure 5.

Comment 41
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.
Answer
We have done this and there is no trend with respect to sample size. Therefore we decided to include all data in this evaluation. In the revised version, however, we report values (standard deviation and mean) for the same analysis based on 50, 100, and 200 mL samples, respectively, in section 2.2.

Comment 42
Please see Table 3 Caption – Figures 8-10 do not exist
Answer
Corrected.

Comment 43
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.
Answer
Clarified:
The maximum observed in acetylene is more enriched than previous measurements reported in urban environments, but is within the range of daytime summer values reported from rural/marine environments (Redeker et al. 2007).

Comment 44
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 $\delta 13C$ 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)?
Answer
We understand the point, however, we decided to keep the Figure in its current form because it looks too busy otherwise. The corresponding intercepts are presented in Table 5 anyway.
The interpretation of these data must remain somewhat speculative because of the complex location of the sample site (University building). The example of ethylene fits best into what we would expected. The measured source signature (~-27 permil) agrees well with fossil fuel primary emissions. The atmospheric lifetime is short (a few hours), so we expect to see a kinetic isotope effect because samples were taken on hot summer days. The enrichment observed for lower concentrations agrees well with this.
The interpretation for the other compounds is more complicated because their lifetimes is longer and the concentrations may be controlled by transport and mixing of different sources. The source signature of butane suggests that fossil fuels are the dominant local source. However, the reversed slope may indicate that background concentrations of butane originate mainly from other sources. The discussion in the manuscript has been clarified.

Comment 45
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) .
Answer
This is a misunderstanding. Table 4 reports results from ambient air samples. A larger standard deviation here actually shows that we are detecting a 'real' signal.

Comment 46
The system is reported to allow high volume ambient air sampling without the loss of compounds of interest; have you really shown this?
Answer
This statement refers to the performance of the SEP trap and we have shown this in the paper. Furthermore we have carefully tested all our cryotraps (this was a dedicated bachelor thesis project) but we do not report these results here; instead we refer to these well established matters have been discussed in greater detail (e.g. Archbold et al. 2005).

Comment 47
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.
Answer
We added a short section on the automation.

Referee #3

Comment 48
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.
Answer
Done.

Comment 49
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?
Answer
Title has been changed. "carbon stable isotope ratios" has been changed to "stable carbon isotope ratios".

Comment 50
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.
Answer
All these questions have been taken into account and helped improving the manuscript.

Comment 51
Some discussion of why isotope ratio methods are useful in comparison to standard methods of VOC ratios to determine aging would be useful.
Answer
Done. We emphasize the isotopic clock concept and the potential of isotope ratio measurements to disentangle different sources of airborne trace gases.

Comment 52
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.
Answer

The reference to CFCs has been deleted. Examples are given for "samples of varying origin".

Comment 53
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).
Answer
Again we apologize for the confusion. All this has been fixed.

Comment 54
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 CH_3Cl 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?
Answer
We tested different flow rates and there is almost no difference between a flow of 50 and 70 ml/min. Once the best conditions had been defined, we kept using this set of flow rate and cut-off time. The 2 permil shift seems to be a persistent feature for which we do not have an explanation at this point.
The referee's guess sounds reasonable (we thought this as well). If this was the case, we would expect this mechanism to cause enrichment of the sample, however, we observed a 2 permil depletion (see Table 1).

Comment 55
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 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?
Answer
The CO2/H2O scrubber has been used. This has been specified in the revised version. For the other questions we refer to our answers to comments 4, 30 and 31.

Comment 56
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.
Answer
Improved/corrected.

Comment 57
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?
Answer
All this information is given now. See answers to comments 2 and 34. The 1:1 split between QMS and IRMS could be changed if the sensitivity needs to be increased.

Comment 58

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.

Answer

The mixing ratio was calculated from mass 44. A chromatogram has been added.

Comment 59

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?

Answer

The sentence has been improved the required discussion/information is given.

Comment 60

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."

Answer

Horizontal lines are no trends but set at the average value. All suggestions implemented.

Comment 61

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.

Answer

Figure 6 has been improved. The dashed lines are indeed running averages, black for both days, orange and blue for day 1 and the other for day 2.

Comment 62

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

Answer

We discuss some values in the text but we want to keep this section short because this is not the main purpose of the work presented here.

Comment 63

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 13C 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.

Answer

Reference corrected. We discuss all these processes for ethylene. As for acetylene the measurements of d13C and VMR cannot be interpreted as straightforwardly because of the complexity of the sampling location.

Comment 64

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.

Answer

We shortened the discussion and focus only on the most prominent features.

Comment 65

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 (â˘A´c) represents a radical. I believe these should be dots, not asterisks.
4. P. 104, line 16: necessary should have only one “c”.
5. P. 106, lines 5-6 and elsewhere: “preconcentration” 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.

Answer

All points corrected.