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Atmospheric Measurement Techniques
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Interactive comment on "Real-time analysis of δ¹³C- and δD-CH₄ in ambient air with laser spectroscopy: method development and first intercomparison results" *by* S. Eyer et al.

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General comments:

The study by Eyer and co-workers presents the first application of simultaneous analyses of mixing ratios as well as the stable carbon and hydrogen isotope ratios in methane by laser spectroscopy. This provides real-time data and allows for the resolution of events with duration of a few hours. I see two distinct uses for this technology: for quasi-continuous recording of atmospheric trends at select stations and for field studies to determine the isotopic signatures of methane emissions. Both are needed to improve our understanding of the notoriously under-determined changes in the atmospheric CH4 budget. The authors demonstrate that the technique has the necessary performance to serve these purposes (with the exception of clean air studies in remote locations) and is comparable to conventional mass spectrometry techniques. The presented tests seem comprehensive and the material is well presented. Minor changes in the structure of the manuscript and some clarifications on technical details would improve the paper, please see suggestions below. Overall, I consider the study to be a valuable contribution to atmospheric trace gas measurements.

Specific comments:

Abstract (8927; 19-23): I find the current wording confusing as the reader is not yet familiar with the details of the remaining offset between various examined techniques after correcting to a standard measurement. I suggest replacing “Thus, the intercomparison also reveals. . .” with “Remaining inter-laboratory differences reveal. . .” or similar wording.

Introduction: (8927; 26 – 8928; 2): The WMO/GAW newsletter is arguably not the best reference here as it does not provide citations for individual findings. For example, an appropriate citation for the pre-industrial CH4 concentration could be C. MacFarling Meure, et al., Law Dome CO2, CH4 and N2O ice core records extended to 2000 years BP. Geophysical Research Letters 33 (2006).

2.1.2.: (8931; 28) (also 8932; 12-13 and 8933; 24-25): please provide additional information on the geometry of the stand-off so that the reader can fully understand its function. From Fig. 1 it seems to be cylindrical. However, it is not clear whether it has a flat “bottom” surface that is pressed against the copper heat sink for better thermal contact. Also, the attachment of the spring and the position of the heat foil are unclear. A specific figure may be helpful; if the reader is referred to earlier methods papers for these details please do so explicitly.

(8932; 3): the trap temperature is considerably lower than Cryo-traps with the same absorbent (Hayesep D) that are used in pre-concentration units for IRMS measurements of CH4 isotopes (typically 130 – 150 K). The issue comes up again later when the co-desorption of O2 with CH4 is discussed. The wording in the paragraph here suggests that (break-through?) tests established the necessity for 100 K. It may be of interest to the reader to see details of such tests, given the fine balance between quantitative trapping of CH4 and avoidance of co-trapping of interfering gases, in this case particularly O2.

2.1.3.: What is the minimum duration of a trapping-desorption-conditioning cycle? I understand that an analytical cycle will take longer and include the measurements of standards as discussed later, but the length of the trapping cycle itself is still of interest.

2.1.4.: Are the described changes to the laser instrument made only to one custom-made instrument used in this study or did the development feed back to the manufacturer of the precursor model (Aerodyne Research Inc.)? That is, is an instrument as described commercially available (or will it be)?

2.2.1.: The first paragraph (8936; 9-13) is hard to follow because technical details on CG1 and CG2 are provided later. For example, it is not yet clear how two different tanks can yield “three different types of calibration gases” because the dilution system has not yet been introduced. The description of the calibration and target gases so far provided in 2.3. should be moved ahead of this paragraph because the reader needs that information to understand the design of the measurement cycle.

(8936; 10): Fig. 4 shows triplicate measurement of the analysed sample gas in one measurement cycle. Are the three individual results averaged?

2.2.5.: (8939; 21): Sperlich et al. (2013) describe an analytical set-up developed and used at the University of Copenhagen. That system differs markedly from the one described here for MPI. The reference therefore does not seem correct.

(8940; 16-20): Is it possible to provide a precision measured for 10 repeats of standard air? That way, the stated precision would be directly comparable to UU and RHUL.

2.2.6. (8941; 3): Can you provide either the volume of the container/bag that the sample is expanded from or the typical resulting pressure in the 75 cc sample loop? That would give a better estimate of the actually analysed sample volume.

2.3. As mentioned before, I recommend moving this paragraph ahead of 2.2.1. so that the reader can follow the design of the TREX-QCLAS cycles right away. Please also provide details on the dilution system for CG1 and CG2.

(8941; 10-13): The fact that CG1 is a mixture of fossil and biogenic gas becomes clear only from Table 1. The resulting δ13C-CH4 value of the mix for CG1 is not ideal because it is more 13C-enriched than ambient air, i.e. CG1 and CG2 don't cover the range of measured δ13C-values (Fig. 9). Given that CG1 is very close in δ13C-CH4 to ambient air possible non-linearity problems are likely small or non-existent but the possibility of impacts on the results should be discussed. The same is true for δD (although in that case the atmospheric value cannot be achieved by mixing of fossil and biospheric sources).

(8941; 18): Sperlich et al. (2012) describe a method for producing exactly quantified CH4 isotope standards and Sperlich et al. (2013) describe an analytical set-up for δ13C-CH4 analysis. Both studies were conducted at the University of Copenhagen. Can you please clarify how the work described in these publications relates to the MPI isotope calibration scale? Are the very tanks produced by Sperlich et al. (2012) used at MPI or how is the MPI scale traced back to primary standards?

3.2. (8945; 20): the offset of the UU IRMS data is still within combined uncertainties, so arguably no more significant than differences between TREX-QCLAS and MPI IRMS. Is the purpose of this sentence (and of the preceding one) to present the applied offset? If so, were data sets with "insignificant differences" still offset corrected? Offset corrections for differences within combined uncertainties have the potential to create, or contribute to, offsets in the results discussed in Sect. 3.4. This is a minor point given that all offsets (except OA-ICOS) are small, but the authors may choose to clarify this issue.

(8947; 4-8): the sentence understates the discrepancy between CRDS and other measurements. The following sentence mentions specific times of CRDS drift relative to other values but no further comments are made. Even if the authors cannot provide further insight as to the reasons, this is not a trivial finding given that CRDS instruments are relatively cheap and easily deployed. The potential for erroneous results from more widely used CRDS analyses is something the community should be aware of.

(8947; 20-24): to verify if differences in sampling time affect the comparability of the various data sets it would be instructive to provide cross-plots or simply correlation coefficients between isotopic differences on one hand and sampling time or CH4 mole fraction on the other.

3.5. (8948; 12-20): this paragraph would benefit from some more detail, as it is the section that demonstrates the suitability of the new technique to capture emission events. I recommend labeling the CH4 mole fraction, δ13C-CH4 and δD-CH4 data points associated with the 19th-20th June emission event in Fig. 9. From the presented material it is not clear if the emission event (a single datum) is marked by extraordinary isotope values as well as high mole fraction. The datum in question should also be identified in Fig. 12. Assuming that this point is the one that falls within the isotopic range typical for landfills, a short discussion how that value may also be derived by mixing of biogenic and fossil fuel CH4 and why this is a more plausible scenario than pure landfill emissions is needed. It is also true that the source attribution for the 19th-20th June without the event data is distinct in δ13C-CH4 (more13C-depleted) from the other biogenic sources, which is not discussed. Finally, how do source reconstructions from CRDS data compare? Do they provide similar estimates as the other instruments for the periods when CRDS doesn't drift (e.g., 8th-9th June) and how far off are the results during drift periods? While the focus of this study is the new TREX-QCLAS technique, CRDS instruments are much more readily available and insights into their capabilities are therefore important.

Technical comments:

(8930; 2) please check the year of the WMO/GAW report, citations in text and reference list differ.

(8935; 4): style: “less abundant” instead of “lower abundant”?

(8937; 24-25): style: “Variations over the duration of the campaign were not significant and therefore. . .” (or similar wording) instead of “They varied not significantly. . .”.

(8939; 6): should this read “CarbonPLOT”?

(8939; 13): all other temperatures are reported in K, consider changing the value in degree Celsius to K for consistency.

(8940; 12): “CH4-derived CO2” would make it slightly easier to follow this sentence.

(8941; 4): Grammar/typo: “Individual sample analysis lasts. . .”

(8943; 17-20): Please check style/grammar of this sentence, i.e.: “. . .a fraction of O2 remained on the trap is desorbed. . .”

(8946; 27): this should read: “. . .as described in Sect. 3.2.”

(8948; 1-2): suggestion for style: “. . . when night-time CH4 mole fractions exceeded 2050ppb.”

(8949; 22): typo in “predominantly”

Fig. 1: please provide a legend; symbols for different types of valves and others (circled crosses or triangles) are not self-explanatory.

Fig. 6: typo in caption: remainder (or residual), not “reminder”.

Fig.12: the green field should be labelled “Biomass burning”, not just “Biomass”. Ar-

guably, introducing the term “thermogenic” would be more specific than “fossil” as well, given that biogenic CH4 can be emitted from natural gas sources or ancient reservoirs like methane hydrates or permafrost (admittedly the latter are not of concern for this study). Indicating a mixing path between microbial and thermogenic emissions would illustrate the argument that the event datum is the result of simultaneous emissions.

Interactive comment on Atmos. Meas. Tech. Discuss., 8, 8925, 2015.