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Atmospheric Measurement Techniques Discussions

Interactive comment on "An analytical system for studying the stable isotopes of carbon monoxide using continuous flow-isotope ratio mass spectrometry (CF-IRMS)" *by* S. L. Pathirana et al.

S. L. Pathirana et al.

supun22@gmail.com

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We thank the referee for the thorough and positive review of our manuscript and reply to the comments in detail below. Revised manuscript is attached as a supplement.

General Questions:

1. The best achievement in this study appears to be the short-time analysis and the small volume of air required, although the latter has been already achieved by Wang and Mak (2010). This could be more highlighted in the manuscript and preferably in introduction the authors might give what kind of solutions the achievement can provide in scientific viewpoint.

Conceptually, the key difference to the system by Wang et al is that our extraction system operates always under a flow of He; it is thus a conceptually different realization of the same idea of extraction and preparation of CO. The system is particularly well suited for routine operation and automated analysis of many samples. In terms of precision, the overall results are similar to the system described by Wang et al., and the main improvement is the strong reduction of the system blank. The above paragraph was added (page 5, from line 10) in the revised manuscript.

2. The authors can highlight and discuss what is new and advantages of the system compared to previously reported systems.

We have highlighted the achievements in the paragraph on page 5 starting on line 5 and a comparison to Wang and Mak, 2010 is included in the paragraph on page 5 starting on line 10.

3. The authors might describe time procedures of every step exactly. Only the total measurement time (18 min) is given, but almost no information is available for specific processes. I think this is helpful information for readers. For instance, flow rate and time (plus trapping efficiency) determines how much amount of the target gas is processed in a trap.

The below paragraph is included in page 8 starting from line 19, in the revised manuscript. In routine operation, the entire system is flushed for 425 seconds between runs, the Schütze regent is introduced into the main gas stream 425 seconds before injection of sample air, the sample processing takes 300 seconds, followed by another 300 seconds of flushing before the sample is transferred from trap T3 to T4. The cryogenic trap that removes the remaining traces of CO2 and N2O is warmed to room temperature for 302 seconds in between runs to remove the eluted gases and is cooled again for 123 seconds before the next sample is admitted.

4. Description of calibrations of both mole fraction and isotopic ratios is not given explicitly. Namely, the manuscript does not guide readers so that they can link the authors' reference gas ultimately to international standards. See specific comments.

The requested information is provided under the specific comments. Please see below.

5. Description of the measurement result (section 3) is far from complete. The section should be much more enriched. See specific comments.

The requested information is provided under the specific comments. Please see below.

Specific Question:

P2068 L6: for _13C and _18O "analyses"

This has been corrected in the revised version.

P2068 L13: I would delete "typical", because 185.4 nmol mol-1 is an CO concentration that can be observed in an urban area (rather than at clean background sites) and, in such an area, it may not be easy to determine a representative value due to high variability. Remind that the authors mention to 100 nmol mol-1 at the beginning of the introduction.

This has been corrected in the revised version.

P2068 L13: Here 0.7 nmol mol-1 is given, while 0.7% appears in the other places.

This has been corrected in the revised version.

P2068 L13: a suggestion "An automated single measurement is performed only in 18 min, and the achieved time efficiency (and small volume of sample air) allows repetitive measurements practically." In my opinion, the phrase "to improve precision" is misleading and I would leave it out. The multiple measurements do not improve precision (in a performance sense) of the measurement system, but improve standard error of the mean of measurements for one sample.

We have changed the sentence to (page 2, line 9 in the revised manuscript): An automated single measurement is performed in only 18 min, and the achieved time efficiency (and small volume of sample air) allows repetitive measurements practically.

P2069 L27: a range of overlap "in" _13C "signatures" – but the authors stated isotopic signatures are distinct in a few sentence before. It is unclear that which CO sources overlap in _13C signatures.

We have rewritten the sentence as follows (page 4, line 3): For CO sources that have a range overlap in δ13C values (vehicle emissions range $\sim$ -36 to -20 ‰ biomass burning range $\sim$-25 to -21 ‰ and NMHC oxidation range $\sim$-37 to -27 ‰, δ18O proves to be a better tracer. Also P2069 L20: The sentence "The two independent quantities... " is replaced by "The combination of the δ13C and δ18O values give a distinct isotopic signature for each individual CO source".

P2070 L1: compared to 7–10‰ "for biomass burning (Röckmann et al., 1998; Tarasova et al., 2007)" and "an assumed value of 0‰ for NMHC oxidation (Brennikmeijer and Röckmann, 1997)".

This has been corrected in the revised version.

L2070 L2: What is assumed in assigning _18O signature of CO from NMHC oxidation?

The sentence has been modified as follows (page 4, line 8 of the revised manuscript): For NMHC oxidation no direct measurements are available and a δ18O value of 0 ‰ was indirectly derived from isotope budget considerations (Brenninkmeijer and Röckmann, 1997).

L2070 L14: "an" advantage "that mass spectrometry is based on CO2, which allows use of better standardized measurement techniques and calibration scales (Brenninkmeijer et al., 1999)." – I am not sure the position of the reference is correct (is the latter part of the sentence written in the paper?).

The reference was positioned at the end of the sentence.

P2070 L26: “spectroscopy” to “spectrometry”, same for every place

This has been corrected in the revised version.

P2070 L29: Same comment as that on P2068 L13.

This has been corrected in the revised version.

P2071 L18: Laboratory air intrudes in the lines when exchanging sample flasks. How is the laboratory air flushed or pumped away from the system?

The following information has been added to the revised manuscript (page 6, line 18): When starting an automated measurement sequence, first the 8 samples are connected to V1 and V2 is set in the direction of the samples. Then V3 is set to “evacuation” position and the membrane pump valve is opened, allowing the air from the point of the sample connection to the V3 to be evacuated. Following this procedure each sample position of V1 is evacuated and tested for leaks. After this leak test the sample bottle/can/cylinder valves are opened. From this point onwards the method is fully automated. The final pressure in the sample admission part of the system prior to the introduction of the sample is $\sim$1 mbar. To avoid contamination with remaining air when switching between samples via the multi-sample inlet system, V1 is first set to a “close” position between two sample ports and the system is evacuated for 60 sec. Afterwards the multi-sample inlet system is flushed with the new sample air for 55 seconds at a flow rate of 20 mL/min before it is injected via V3.

P2072 L1: How high is the flow rate and how long is it kept at the flow rate?

The flow rate is 20 mL/min, and it is kept for 5 min. This information has been added to the revised manuscript (page 6, line 13). The Sample is injected into the system at a flow rate of 20mL/min for 5 minutes.

P2072 L16: The authors might explain “Schütze blank” better – what it is, why it interfere the measurement, and why it is reduced by being flushed with He. How did you determine the He flow rate?

The following information has been added to the revised manuscript (page 12, line 12): The majority of the blank signal originates from CO2 that is released by the Schütze reagent. It is an accumulation of CO2 formed by the system CO blank or CO2 from the reagent itself, which are released in later measurements. The simple modification of adding a 6-port Valco valve to continuously flush the Schütze reagent with He at a flow rate of 8 ml/min reduced the blank to 1-3 %.

P2072 L20: Schütze reagent is probably commercially available. What is the advantage to produce it in your own laboratory? And is it a standard method in analyzing CO isotopes?

We have not used commercial Schütze reagent, but prepared highly reactive Schütze reagent with a simple setup in our own laboratory following methods that have been widely used in other laboratories (e.g. NIWA, New Zealand or MPI Mainz, Germany). We cannot comment on the quality of commercially available Schütze reagent.

P2072 L21: purified water?

CHROMASOLV® for HPLC graded water, filtered through a 0.2 μm filter.

P2073 L3: How high is the N2 flow rate?

The following paragraph has been added to the revised manuscript (page 7, line 22). The air exiting the reactor was passed through a molecular sieve and a large beaker of water. This was done to ensure that the H2SO4 vapor carried out with the N2 was removed before the N2 was released to the laboratory. The N2 flow rate was adjusted so that there was a slow release of bubbles visible in the beaker.

P2073 L12: “purification” is not a correct word. The sample is not “purified”, but the CO-derived CO2 is separated from the other residual component.

This has been corrected in the revised version.

P2073 L20: Same as the comment on P2073 L12.

This has been corrected in the revised version.

P2073 L20: The dehydration of sample air should be given in a separate sentence, because it is totally a different process from GC separation. For what purpose the Nafion dryer ("trap" is not a suitable word) is installed here? Where is the source of water in the upstream part?

Nafion trap has been corrected to Nafion dryer. There is no direct source of water in the part prior to the Nafion dryer. However, there are always traces of water in analytical systems, and this Nafion dryer is installed to protect the IRMS in case a leak causes a surge of water vapour into the system. Over long times, traces of water may accumulate in the GC. This accumulated water is regularly removed by baking the GC at 180oC and this water is then also removed via the Nafion dryer.

P2073 L22: Here readers can understand the system is connected to vacuum pumps.

As I commented on P2071 L18, this description could appear earlier, for instance in section 2.1 (before section 2.1.1), and the authors might write how and when the lines are evacuated. An additional sentence (page 5, line 24 of the revised manuscript) has been added on the evacuation steps as described above.

P2073 L26: a custom-made open-split interface "(Röckmann et al., 2003)". Here the authors might briefly describe how the open-split interface was modified and improved.

We think that the description of this open split interface is not warranted in this manuscript, since similar systems are now also commercially available. As the system was not modified, referring to the original publication is considered sufficient.

P2073 L28: The authors might describe how long does it take to process every step (extraction, conversion, collection of CO-derived CO2 and cryofocus). See general comment.

Extraction, conversion and collection of CO-derived CO2 are performed in one step, so we cannot give specific times for each step. To indicate timing, we have now added

the following information (page 8, line 19, in the revised manuscript): In routine operation, the entire system is flushed for 425 seconds between runs, the Schütze regent is injected into the main gas stream 425 seconds before injection of sample air, the sample processing takes 300 seconds, followed by another 300 seconds of flushing before the sample is transferred from trap T3 to T4. The cryogenic trap that removes the remaining traces of CO2 and N2O is warmed to room temperature for 302 seconds in between runs to remove the eluted gases and is cooled again for 123 seconds before the next sample is admitted.

P2073 L28: Does the 18 min include the all process described from section 2.1.1 to 2.1.4? Then I would bring this sentence in section 2.1 (just before 2.1.1).

Yes, the 18 min includes the whole process described from section 2.1.1 to 2.1.4. This has been included in the revised manuscript.

P2074 L1: I do not get what "reduction" means.

Title changed to "Data processing and calibration".

P2074 L8: It is the case if the conversion efficiency from CO to CO2 is 100

The possibility of complete conversion using Schütze reagent has been established in Brenninkmeijer, 1993. We verified the conversion completeness in this system by adding a second reactor filled with Schütze reagent, and comparing the results.

P2074 L14:. . . the area of the sample peak "of signal m/z=44 on the mass spectrometer?"

It is the combined area signal of m/z=44, 45 and 46 taking into account the different amplification factors for the different ion signals.

P2074 L17: I do not find the reason of this sentence. Does it mean that you set the sample and reference at the same flow for the same flow time when a sample to analyse is expected to be at an ambient mole fraction level? Are there any cases you set differently?

Yes, when the sample is expected to have a similar mole fraction as the reference the flow rate and the injection time applied to both runs (sample & reference) are the same. However if the sample mole fraction is expected to be considerably lower or higher the flow rate or a combination of the flowrate and the injection time can be adjusted accordingly.

P2075 L5: : : :the international standard “VPDB or VSMOW” –to clarify the reason of the subscript “V”.

This has been corrected in the revised version.

P2075 L7: CO2 “is generated” when the CO from sample air “is” oxidized by the Schütze reagent.

This has been corrected in the revised version.

P2075 L13: Here readers may wonder how the last term can be obtained, because it is not measureable. The authors might mention to that it is described later.

This has been corrected in the revised version. “δ18OR vs. V:CO is obtained using Eq. 6 as described in Section 2.2.2 ” (starting at page 11, line 13 in the revised manuscript)

P2075 L19: Almost no information on the calibration is given. The authors should mention to, for instance, the origin of air (when and where the air is pressurized into the bottle), size and material of the bottle, and the initial inner pressure. Such information might be given at the beginning of the section (where the reference air appears for the first time). Which method is used to analyze air in the cylinder and relative to what types of standards? On which scale is the mole fraction? Also, it is known that CO mole fraction in a cylinder could fluctuate during storage (e,g, Novelli et al. 2003, JGR). Did you make any experiments to examine stability of the reference air in the bottle? Otherwise accuracy of the mole fraction measurement would not be guaranteed, thinking that 5 years has passed already since the time of calibration.

Novelli et al. (2003), Reanalysis of tropospheric CO trends: Effects of the 1997–1998 wildfires, J. Geophys. Res., 108, D15, 4464, doi:10.1029/2002JD003031.

Sect. 2.2.1 has been modified as follows: The reference air bottle (Ref) is a Luxfer 30-L Aluminum cylinder with Rotarex- Ceodeux brass valve, used with a Scott Specialty Gases type 51-14C pressure regulator. The Ref bottle was filled with dry atmospheric air at the Max Plank Institute for Biogeochemistry (MPI-BGC) in Jena, Germany, in 2009. The initial filing pressure was 130 bar. A mole fraction of 185.4 nmol mol-1 was assigned by MPI-BGC, and is linked to the WMO X2004 calibration scale. The Ref bottle is regularly measured against other gas cylinders, for isotope calibration (see Sect. 2.2.2) and for checking the system stability. No significant drift in CO mole fraction relative to other gases has been observed since the measurements described here were started.

P2076 L4: “values of”

This has been corrected in the revised version.

P2076 L5: What is the gas (e.g. CO in synthetic air or nitrogen)? How is the Cal bottle labeled? The authors might give this information so that readers can match it to one of bottles listed in Brenninkmeijer (1993). At least I cannot find the match. Also, the authors should give at least briefly how the Cal gas was calibrated originally relative to what types of standard in the description so that you can clearly state your reference gas is ultimately referenced to VPDB. Is there any uncertainties given by Brenninkmeijer?

The gas is CO in nitrogen. The bottle was labelled as AP57. The uncertainty for 18OCal vs. VPDB-CO2 has been given: 11.43 ± 0.3 ‰Ẇe do not think that a full description on absolute referencing is warranted in this paper. No international standards are available for CO isotopes. Many of the available measurements, also the measurements we present here, are linked to international standards via a calibration that was presented in Brenninkmeijer (1993). The original calibration of that calibration gas bottle was verified with an independent method in Brenninkmeijer and Röckmann, (1997).

P2076 L8: The Cal bottle had been stored for 20+ years. Is it assumed that the gas stayed identical in CO isotopic ratios?

Yes, it is assumed that the CO isotopic ratios remained identical. An independent calibration of the reference bottle was published in 1997 (Brenninkmeijer and Röckmann, 1997), which confirmed the originally assigned values after a long period of storage. This has been added in the revised manuscript (page 11, line 2).

P2076 L9: How was this mole fraction determined?

The mole fraction of the diluted cylinder was determined by a Peak Performer 1 reduction gas analyser, relative to the calibration bottles that were referenced to the WMO CO X2014 scale. (Note that we only use the DiCal cylinder for calibration of isotopic values and not for calibrating mole fractions). .

P2076 L10: Is there any evidences to support this assumption? As described earlier, CO mole fraction in a cylinder could fluctuate, but isotopic ratios of CO could stay same?

We do not have direct evidence and therefore state this clearly as an assumption. No international reference materials are available for CO for comparison.

P2076 L12: : : :vs. the lab CO2 working gas “using the present measurement system” and the averages were used for calibration, “by which isotopic ratios of CO in Ref is referenced to those in DiCal.”

This has been corrected in the revised version.

P2076 L14: is done “in the same manner as equation (5):”

This has been corrected in the revised version.

P2076 L24: “However, : : :” as suggested above, I would discuss possible uncertainties where relevant information is given.

We do mention here possible sources of uncertainty. However it is very difficult to quantify them, therefore we think that it is sufficient to mention them so that the reader is fully aware of them.

P2077 L3: : : :when calculating “_13C and _18O values from measured m/z ratios 45/46 and 46/44.” This has been corrected in the revised version.

P2077 L4: “However, : : :” hard to understand this sentence and the following sentences. Might be better elaborated.

This has been elaborated in the revised version. “However, atmospheric CO possesses mass independent oxygen isotope anomaly with Δ17O values (Δ17O ≡ ïĄď17O – 0.52 Âů δ 18O) between 2.5 ‰ and 7.5 ‰ (Röckmann and Brenninkmeijer, 1998; Röckmann, 1998). Both 13C16O16O and 12C17O16O contribute to the ion signal at m/z = 45. This means that, when assuming MDF, the contribution of 17O to the ion beam at mass 45 is underestimated, leading to an overestimation in the ïĄď13C. Röckmann and Brenninkmeijer (1998) calculated this overestimation (error) of ïĄď13C to be 0.08 - 0.25 ‰ for a Δ17O range of 2.5 - 7.5 ‰Ṡince the current method does not resolve the contribution from 17O, we report the δ 13C and δ 18O values calculated assuming MDF.” (page 11, line 25).

P2077 L7: “e/m” to “m/z”

This has been corrected in the revised version.

P2077 L11: : : : “the _13C and _18O” values: : :

This has been corrected in the revised version.

P2077 L16: The injection time “5 min” should be given earlier in section 2.1.1.

This has been corrected in the revised version.

P2077 L16: peak area of m/z=44?

The mentioned peak area is Area All (Vs), which is the sum of the peak areas of ion masses 44, 45 and 46.

P2077 L18: I would delete “has to be manually integrated and”

This has been corrected in the revised version.

P2077 L22: : : : a 6-port Valco valve “to continuously flush” the Schütze reagent: : :

This has been corrected in the revised version.

P2077 L22: What is the origin of CO2 when the Schütze reagent trap was not flushed by He? Does it mean that small amount of CO2 is generated in the trap with a compound contained in laboratory room air that could not be completely removed from the other parts of lines? If so, where is the “leaky” place? Otherwise any other explanations?

This is very hard to positively identify, but we assume that it is an accumulation of very small amounts of CO2 from small leaks or CO2 released from the reagent itself.

P2078 L1: Trapping (or removal) “efficiency” of CO2 and N2O

This has been corrected in the revised version.

P2078 L9: the “CO2 and N2O traps” means both the Ascarite and T1 traps? Please clarify.

This has been clarified in the revised version. CO2 is removed by the Ascarite trap and T1. N2O is removed by T1.

P2078 L10: What is the actual result? I suggest that this section should be rewritten so that readers can understand the trapping efficiency of the traps clearly. The blank tests show CO2 is not eluted from the traps and perhaps you might present difference between with and without the traps.

The result of such runs is the same as a blank run without the Schütze reagent trap. This has been adjusted accordingly (page 13, line 3).

P2078 L18: The text tells 2000 nmol mol-1, while Table 1 gives 2 nmol mol-1. Please clarify, although the former is likely. How was this gas produced? “Adding 2000 nmol mol-1 N2O” sounds strange. For instance, “adding 2000 nmol N2O” is understandable. “nmol mol-1” represents mole fraction and the mole fraction of the product gas is determined by relative fractions of the two gases of mixture (namely the gas’s mole fraction should be between 2000 nmol mol-1 and ambient level that Ref has depending on fraction of mixture). Again, the authors should give the origin of the reference gas air, and the N2O mole fraction should be given preferably. If the reference gas was not calibrated for N2O, “approximately” 2000 nmol should be given.

Approximately 15 μL of pure N2O was admitted to a 2.5 L steel can, which was then filled with reference gas (which already includes atmospheric levels of N2O) until the pressure inside the bottle was 3 bar. This has been clarified in the revised manuscript (page 13, line 9).

P2078 L20: : : :the cryogenic trap “(T1)”: : : same for the other places

This has been corrected in the revised version.

P2078 L20: What gas was analyzed for this experiment? The reference gas?

The steel can with approximately 2000 nmol mol-1 of N2O in the reference gas was measured for this experiment.

P2078 L26: The average peak area of a 100 mL “aliquot of Ref” is : : : Presenting the mole fraction is redundancy. The number of measurements (N=?) should be given. And the period of the measurements might be given to indicate longer-term reproducibility.

This has been corrected in the revised version. This is the reproducibility of 46 reference runs made overnight.

P2078 L27: : : :, which “is translated” to repeatability of 0.7

This has been corrected in the revised version.

P2079 L1: How were the repeatabilities of _13C and _18O determined? Elaborate clearly.

The repeatabilities of δ13C and δ18O were determined by calculating the standard deviations of the δ13C and δ18O, for the same 46 reference runs made overnight.

P2079 L2: This daily-basis test yielded the repeatability given in the previous sentences? Otherwise you might give result of this test (probably with larger number of measurements), which better represents reproducibility of the system?

The repeatability values given are based on occasional overnight runs in which typically 10-50 measurements of the reference air cylinder were performed. Since the reference air cylinder is measured often (several times / day) and all the samples are measured relative to this reference air cylinder, this repeatability on short term (hours to days) is the most important. This is clarified in the revised manuscript (page 13, line 22).

P2079 L3: “After an idling period (how long is it?), at least 5 measurements are made to stabilize the system.” What is the difference of status of the system between the measurement and idling mode and what causes the worse reproducibility after an idling period?

Idling periods can be from a few days to a few weeks. The first runs may produce strange results as there could be blank accumulation in the system. The other runs are mostly done to confirm the reproducibility of the system.

P2079 L15: “the number of seconds” to “time in seconds”

This has been corrected in the revised version.

P2079 L13: The “injection time” for usual measurements is 300s? This should be given somewhere in this paragraph and the peak area observed for this injection time

corresponds to what amount (in nmol mol-1) of CO2 (or originally CO)?

Yes, the injection time is 300 s. The peak area of $\sim$0.1 Vs corresponds to about 4 nmol mol-1.

P2079 L19: I do not get what the subsentence “which is basically: : :” means.

This has been changed to: Figure 4b shows the dependence of δ13C and δ18O on the injection time. Since the various injection times give different peak areas, Figure 4b shows the δ13C and δ18O dependence on peak areas from Fig. 4a.

P2079 L21: Is the origin of the CO2 the Schütze reagent trap?

The origin of CO2 is mainly the Schütze reagent trap. It could also be from small leaks.

P2080 L4: Delete “and” after “glass flask”

This has been corrected in the revised version.

P2080 L10: Please give how much mole fraction the 1.5 Vs corresponds to.

1.5 Vs correspond to 60 nmol mol-1. This was included in the revised version (page 14, line 26).

P2080 L10: The small decreasing trend is visible in Figure 5. Please discuss if it is significant or not.

This decreasing trend is not significant, and the data is still within the reproducibility mentioned in this manuscript.

P2080 L11: What is the “linear data”? I do not think this is a correct term. If there is a significant decreasing trend in _18O measurements, the average would not make sense.

This has been reworded. The “decreasing trend” is not significant and these data are still within the method’s reproducibility.

P2080 L14: It appears that the authors show data that have been already presented in a paper published from their group. This might not be against the journal's policy (please double-check), but it would be even preferable if any other dataset analysed by the present system could be shown. Otherwise clearly state that the data presented is identical to those in Popa et al. (2014).

As this paper describes the development of the analytical system, we do not attempt any deep discussion of data and we show this figure as illustration of an application like it is custom in method papers. We do clearly state that these are the data from Popa et al., 2014.

P2080 L14: Start a new section (3.5). This section does not give enough description so that readers can judge performance of the measurement system. Rigorous description of the data is lacking, which is, in my opinion, not allowed if the authors would like to convince readers for performance of the system. First, no data of CO mole fraction are presented. Readers cannot find whether the present system yield reasonable measurement result or not. This is also a reason why readers cannot identify which air samples are considered to be background. Second, quantitative discussion on the measured mole fraction and isotopic values is missing. Discuss whether the "background" values indeed represent clean air values by reviewing previously papers. Discuss whether the estimated isotopic signatures of vehicle's exhaust are in agreement with previous reports or whether they are new findings.

The performance of the system is actually shown in the main part of this paper, and this section only gives an illustration of an application, as it is often done in method papers. We chose a different representation of the data that have been described and scientifically discussed in detail by Popa et al., 2014. We do not think that a rigorous scientific discussion of this short application example is warranted in a method paper.

P2080 L16: I suggest to leave out words after "as a contribution to: : :".

This has been corrected in the revised version.

P2080 L18: Please give size of the flasks and pressure at the sample collection.

The samples were in 1 L glass flasks under a ~1.8 bar pressure. The information has been added in the revised version (page 15, line 6).

P2080 L19: Were the CO mole fraction not analyzed? Otherwise the results should be given.

The CO mole fraction was analysed by the Peak Performer 1 reduction gas analyser. As described above, we do not intend a detailed interpretation of these data and therefore only show the isotope values as an illustration.

P2080 L21: Delete "many" if the authors cannot give anything quantitative (counts, frequency etc.)

This has been corrected in the revised version.

P2080 L22: "very high CO concentrations" Please give the CO mole fraction explicitly (be quantitative). Change "concentration" to "mole fraction" to be consistent in the whole text. Changed "concentration" to "mole fractions" and added "(2 – 10 ppm)" after "very high. . ." The CO mole fractions have been already published in Popa et al., 2014 and we think that a qualitative discussion is adequate for this application example in a method paper.

P2080 L23: I do not get what "essentially" means. Please be quantitative and discuss in numbers.

"Essentially" was removed. The quantitative values are given in P2080 L25.

P2080 L24: Move (Popa et al., 2014) to the end of the sentence.

This has been corrected in the revised version.

P2080 L25: If the entrance air varied in CO mole fraction influenced by vehicles' emission, I would not consider that the air represents "background". And this "background" contradicts the following sentence in which the authors write that the entrance data are between "background" and "fossil fuel combustion" signatures.

The sentence has been changed to "The entrance data has been influenced in varying proportions by the emissions of vehicles on the highway".

P2081 L3: This section should be rewritten after revision of the whole manuscript.

Section 4 has been revised.

P2081 L4: Insert "-" between "flow" and "isotope" to be consistent with other places. "method" to "system".

This has been corrected in the revised version.

P2081 L8: Perhaps these compounds cannot be removed "completely", although the level of elution was lowered so that they negligibly interfere the measurement of the targets.

This has been corrected in the revised version.

P2081 L9: "that" to "which"

This has been corrected in the revised version.

P2081 L10: Delete "in this method"

This has been corrected in the revised version.

P2081 L11: Please give how much nmol mol-1 the 0.7

The sentence will be rephrased to "The repeatability for the mole fraction measurement is 0.7 nmol mol-1 for a reference air cylinder with a CO mole fraction of 185.4 nmol mol-1. This corresponds to a relative error of 0.4 %" (page 15, line 24 in the revised manuscript).

P2081 L11: I do not get what "on a single sample" means.

This has been removed in the revised version. We wanted to implicate that precision can be increased statistically by averaging multiple measurements.

P2081 L12: Please give relative fraction of the blank with respect to the sample measurement with air at ambient CO mole fraction level.

The system blank is $\sim$1-3 % in respect to a sample measurement with air at ambient CO mole fraction.

P2081 L12: delete "values"

This has been corrected in the revised version.

Figure 3 caption: Large part of the sentences (after "During a normal measurement, : : :), should be given in the text (in the second paragraph of section 3.2), not in caption.

This has been included in Section 3.2 (starting page 12, line 25).

Figure 6: How did you determine the position and the size of the ovals? Readers cannot judge the representativeness. Elaborate clearly in the text.

The ovals were drawn by hand to indicate the respective end members but now they have been removed.

Please also note the supplement to this comment:
http://www.atmos-meas-tech-discuss.net/8/C1739/2015/amtd-8-C1739-2015-supplement.pdf

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Interactive comment on Atmos. Meas. Tech. Discuss., 8, 2067, 2015.