

Interactive comment on “Continuous and high precision atmospheric concentration measurements of COS, CO₂, CO and H₂O using a quantum cascade laser spectrometer (QCLS)” by Linda M. J. Kooijmans et al.

Anonymous Referee #1

Received and published: 21 March 2016

In their study, the authors have tested a recent model of the QCL Mini Monitor spectrometer (QCLS) from Aerodyne Research Inc. for its suitability to obtain continuous and high precision atmospheric measurements of COS, CO₂ and CO. They evaluated the performances of this instrument in the laboratory then in the field at the Lutjewad monitoring station in the Netherlands. The ultimate goal is to provide high-quality observations of COS needed to understand the seasonality, the long-term trend and the spatial distribution of sources and sinks of this trace gas because existing monitoring networks of CO₂ and CO make use of other instruments (e.g. cavity ring-down spectroscopy (CRDS) analyzers).

C1

General comments.

Although the QCLS was set up for continuous in situ measurements at different heights at the tall tower of the Lutjewad monitoring station, the authors do not demonstrate the suitability of the QCLS analyzer to perform profile measurements because data recorded at 7m height are not reported. I think that this question cannot remain open after having put much effort into assessing the performances of the instrument. If the authors consider that their data are not suitable for publication, they could instead make use of the hourly measurements of calibration standards conducted while the instrument was in the field in March-April 2015 to simulate the suitability of the QCLS analyzer to perform profile measurements (see below). The continuous COS, CO₂ and CO observations from Lutjewad are not even used to determine trace gas concentrations characteristic of air masses having either dominant continental or marine influence. Examples of diurnal variations could have been provided. Is there a seasonal change in the amplitude of the diurnal variations recorded by the instrument? Instead, the authors focus on COS seasonal variations reconstructed from incomplete records and compare QCLS daily averages with flask pair means from individual daytime sampling events (NOAA/ESRL data, see Fig. 11). If COS undergoes strong diurnal variations at Lutjewad, only daytime data should be compared with NOAA/ESRL data. My overall feeling is that the potential of the QCLS analyzer is not demonstrated in the field.

Thanks to rigorous testing in the laboratory, the authors clearly demonstrate that an appropriate direct water correction for COS is not possible with the combination of the standard spectral fit and the TDLWINTTEL software correction on. A potential solution to this is to modify the standard fit of the spectral bands (hardly achievable by a non-specialist) or to apply homemade water corrections with the TDLWINTTEL software correction on or off. One of the correction strategies (i.e., homemade water corrections with the TDLWINTTEL software correction off) was tested in the field against dry air flask sample QCLS measurements for COS. Data reported in Fig. 12 suggest that COS mole fractions are not well corrected for water interference yet. The upper panel

C2

(COS one) could benefit from having H₂O displayed.

The authors provide evidence that the baseline measurements typically done several times per hour by former users of QCLS analyzers (background measurements are determined with high purity nitrogen) are not recommended for continuous and high precision atmospheric measurements. They developed an optimal background and calibration strategy to ensure accurate field measurements and put much effort into stabilizing the temperature of the QCLS analyzer. Unfortunately, I found little evidence in the text and the figures that improving the temperature stability by actively cooling the electronics section and putting the analyzer in an enclosed box improved the precision and accuracy of field measurements. Plots showing the temperature dependency of COS, CO₂ and CO concentrations are missing. The histograms of standard deviations shown in Fig. 8 are not convincing because other parameters than temperature could have affected the noise of the instrument from August 2014 until February 2015 (instabilities of the laser for example that can be responsible for increases in SD). I noticed periods of higher stability before February 2015 (for example in September 2014) than after late March 2015 when the instrument was properly insulated.

The QCLS measurements of COS were not compared with that of other instrumentation except when four pairs of flasks filled with dry calibration gas were sent to NOAA/ESRL headquarters and analyzed there with GC/MS. Data shown in the top panel of Fig. 12 are misleading as the flasks shown are not analyzed with a different instrument.

Because this study is the first in-depth appraisal of the performances of the most recent model of the QCL Mini Monitor spectrometer (QCLS) from Aerodyne Research Inc., it should be published but after major revision. Improvements are necessary to demonstrate that this instrument is or is not suitable to obtain continuous and high precision atmospheric measurements of COS, CO₂ and CO. Since two representatives of the Aerodyne company are in the list of co-authors it would be interesting to know whether the TDLWINTTEL software will offer in the future the possibility to deselect the standard

C3

fit and use the new split fit (no more need to perform homemade water corrections). If the instrument drift between two backgrounds can be properly corrected using a reference cylinder, can the TDLWINTTEL software be updated to automatically correct for drift?

Specific comments.

Abstract.

Page 1 - line 15. Hope that the authors will be able to demonstrate the suitability of the QCLS analyzer to perform profile measurements too.

Page 1 - line 27. The comparison of in situ QCLS measurements with measurements from flasks is not adequate for COS. See also page 9 – line 24, page 12 – line 7 and page 16 – line 9. Data reported in Fig. 12 suggest that COS mole fractions are not well corrected for water interference yet.

Introduction.

Page 2 - line 11. The past study of Belviso et al. (2013) relied on in situ samples analyzed on-line (not flasks) with GC/MS. I am aware of other on-line measurements of COS with GC/MS using the MEDUSA instrument (AGAGE network).

Page 2 - line 30. Please clarify your calculations. How can you jump from LRU ratios (the ratio of the deposition velocities of COS and CO₂) to measurement precisions of COS better than 0.3-0.8%?

Page 3 - line 12. First clear indication that you are interested in profile measurements. See also page 10 – line 8, Fig. 5 and the legend of the figure. Again see page 10 – line 17. The goal was to provide high-quality observations of COS needed to understand the vertical distribution of this gas at Lutjewad but may be the authors consider that their data are not suitable for publication.

Experimental setup.

C4

Page 3 - line 13. Not sure that the first prototype of QCLS required little operator attention. I think that the recent one still requires operator attention and manual post processing of data. Stimler et al. 2010a is in fact Stimler et al. (2009). See also page 4 line 17.

Page 3 - line 17. Unfortunately not for COS.

Page 3 - line 27. Please use the same terms throughout the manuscript. Are primary standard, secondary standard and target gas more appropriate terms? In general, it would be valuable to know how long was the duration of injections of standards.

Page 7 - lines 8-10. The statement "The frequency of reference cylinder..." is not sustained with data. Show plots of COS vs T for example as in Berkelhammer et al. (2014). See also the discussion about temperature stability page 10 – line 25.

Page 8 - line 13. Here you mention the existence of instabilities of the QCLS. It is important to know whether instabilities of the QCLS occurred when the instrument was deployed in the field (see Fig. 8). See also page 12 – line 31. Factors such as alignment and laser instabilities influence the precision as well.

Result and discussion.

Page 13 – line 1. How was the overall uncertainty calculated? Please clarify the method.

Conclusions.

This is a nice summary but what are the main conclusions of the study? Is the instrument suitable for tower profile measurements? What perspectives can you draw?

Table 1. Three cylinders are mentioned in the text but results of two cylinders are reported in Table 1. I suggest to trace the cylinders throughout the whole manuscript.

Table 5. It is impossible to reconstruct the overall uncertainty from data gathered in Table 5.

C5

Figure 1. Mention in the legend the existence of a small water band at about 2050.4 cm⁻¹.

Figure 2. Explain why response curves for CO₂ and CO were corrected for drift using a reference cylinder. How important was the drift and how many response curves were corrected. The residuals were averaged isn't it?

Figure 7. It is possible to simulate a nocturnal gradient of COS and CO₂ from the assigned cylinder values corresponding to the green and orange samples. During the day the atmosphere is rather well mixed so COS is high and CO₂ is low (green dots). During the night the atmosphere is stratified. Assuming that the ecosystem removes COS from the atmosphere and respire CO₂, COS will decrease (- 41.2 ppt) and CO₂ will increase (+ 9.2 ppm, orange dots). It is difficult to visualize the COS gradient because the signal is very noisy. I suggest to zoom in and check the difference between a series of consecutive orange and green dots. Is the difference about 40 ppt? You can also calculate daily averages and check again that the difference approaches 40 ppt. For CO₂ it looks fine.

Figure 8. I think you should compare what is comparable. The leaky valve was removed January 7, 2015 so my suggestion is to redraw the transparent dark histograms using data collected after this date.

Figure 9. It seems that the grey dots (upper left panel) have turned to black in the upper right panel.

Figure 10. This is a poorly informative figure. I suggest to focus on diurnal variations and land-ocean differences rather than on seasonal variations.

Figure 11. This is also a poorly informative figure because the new dataset is incomplete (see also general comments above).

Figure 12. The upper left panel should be removed and the upper right panel should be presented after figure 4. I think it is more interesting to display the temporal difference

C6

between CRDS and QCLS data, the standard deviation of the difference and to look for temporal trends than to plot one against the other and calculate a slope. Ordinates are missing.

Interactive comment on Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2016-50, 2016.