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Atmospheric Measurement Techniques
Discussions

Interactive comment on "Comparison of cavity enhanced optical–feedback laser spectroscopy and gas chromatography for ground-based and airborne measurements of atmospheric CO concentration" *by* Irène Ventrillard et al.

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We are grateful to Referee#1 for his/her careful reading and the helpful criticisms to our manuscript, which will help improving it.

Besides revisiting the manuscript with several minor corrections and reformulations, we list below our responses to the individual issues raised by the reviewer.

Attached is a pdf file of the revised version of the manuscript.

1) Page 2, line 10: though based on an "old" spectroscopical technique, an in-situ diode laser based CO analyzer has been deployed on board of the Geophysica aircraft since 2005, with performances comparable to those of the described device: S. Viciani, F. D'Amato, P. Mazzinghi, F. Castagnoli, G. Toci, P.W. Werle: "A cryogenically operated laser diode spectrometer for airborne measurement of stratospheric trace gases", Appl. Phys. B 90, pp. 581-592 (2008). Moreover, analyzers by different firms, (Aerodyne, for instance), use direct absorption in the middle infrared, as very often in this spectral region, and at the target concentrations, few tens of meters are sufficient for measurements at the same level of LOD, resolution and accuracy of the submitted paper. In principle, a good advantage of OF-CEAS, with respect to the above work, is the possibility of using lasers emitting closer to the near infrared, despite the weaker absorption bands. In this wavelength region all the components are generally more user-friendly (and cheaper) than in the middle infrared. Yet, in page 10, lines 5-10, the authors claim (correctly) that any kind of laser (including QCL and ICL, both in the middle infrared) can fit this technique. This reviewer would appreciate a short, further discussion about the motivation for the use of OF-CEAS, in order to provide a clearer picture of the field of application of this technique.

In the introduction section we now more clearly write that the aim of the paper is to compare OFCEAS measurements to the well established GC technique in order to demonstrate for potential new users that this technique is reliable. This is essential to extend the use of OFCEAS beyond the spectroscopist community, for example to atmospheric chemistry, geophysics or medicine. In particular it is relevant to note that OFCEAS instruments are now commercially available (we move this point to the introduction section while it was mentioned at the end of the OFCEAS section, page 5). The comparison of the OFCEAS technique with the numerous other spectroscopy techniques is beyond the scope of this paper. But as advised by the referee, in the introduction we now underline the advantages of the OFCEAS technique. We compare OFCEAS CO analyzers (that are commercially available) to different commercial instruments: we moved here references to Picarro and Los Gatos instruments (previously at the end of the OFCEAS section p5) and added Aerodyne. These instruments operate in the MIR to reach a sub-ppb LOD. This lead us to present the discussion on the NIR or MIR spectral region in the introduction part.

The introduction part was modified (parts underlined) : Page 2 line 11- page 3 line 6

Among them, Optical–Feedback Cavity Enhanced Absorption Spectroscopy (OF-CEAS) (Morville et al., 2005) exploits a high finesse optical cavity in which is coupled a laser source to enhance the interaction of photons with gas molecules present inside the cavity (Morville et al., 2014). OF-CEAS offers many advantages for quantitative and selective trace gas analysis: it allows real-time absolute measurements with a smallest detectable absorption coefficient in the range of a few 10-10/cm for 1 s acquisition time (Landsberg et al., 2014), it does not require calibration with certified gas mixtures, its sampling volume is small (20 cm3), its response time can be faster than 1 s, and it enables the development of compact instruments to be operated by non-specialists.

Another advantage that follows from the high sensitivity of the OF-CEAS technique is the ability to work in the near infrared region (NIR) where widely used optics are commercially available together with room temperature lasers and detectors. Traditional near infrared (NIR) OF-CEAS instruments reach limit of detection (LOD) at the sub-ppb level for CO(Faïn et al., 2014) that is comparable to other instruments exploiting the mid infrared (MIR) spectral region where absorption coefficient are typically two orders of magnitude higher. Indeed, commercial MIR laser spectrometers based on different laser spectroscopy techniques offer CO sub ppb LOD, such as Picarro instruments by CRDS with a resonant cavity or instruments exploiting a multipass cell like Aerodyne and Los Gatos products. The performance of the OF-CEAS technique in the NIR led a private company (AP2E, Aix-en-Provence, France) to exploit the patent for commercially available analyzers (namely ProCEAS). Exploiting the MIR with OF-CEAS instruments allows to reach sub-ppb levels for several species of interest in trace detection and ppm levels for isotopic ratio measurements (Maisons et al., 2010; Gorrotxategi-Carbajo et al., 2013; Manfred et al., 2016; Richard et al., 2016).

OF-CEAS based measurements of CO have been conducted before around various applications, for example for in-situ trace measurements on geothermal gases (Kassi et al., 2006), for continuous and high resolution measurement of air extracted from ice cores drilled out of polar glaciers (Faïn et al., 2014) or for breath analysis in different medical settings (Ventrillard-Courtillot et al., 2009; Maignan et al., 2014). ProCEAS analyzers are now commercialized in the domains of industrial and air quality monitoring, with some very stringent applications such as air quality control onboard nuclear submarines. In order to further establish for different user communities that OF-CEAS can become a work-horse in many CO applications, which demand robust and compact instrumentation with ppb sensitivity and a fast response time, this paper reports on the comparison of CO measurements performed by OF-CEAS against those obtained by the well established gas chromatography technique. GC measurements were done with a high performance gas chromatograph equipped with a mercuric oxide reduction gas detector (Yver et al., 2009). First, the atmospheric CO concentration in Gif-sur-Yvette, France, was continuously analyzed at ground level over one week. Then, the OF-CEAS instrument was set aboard a small aircraft employed for periodic tropospheric air measurements over the French Orléans forest area. Airborne in-situ CO measurements by OF-CEAS were then compared with flask samples later analyzed with the GC at LSCE.

One sentence at the end of the conclusion section was removed to avoid repetition (previously p2 line 22-25) : With this comparison we demonstrate that OF-CEAS can become a work-horse in many CO applications for environmental (including atmospheric) applications, which demand robust and compact instrumentation with ppb sensitivity and a response time faster than 1 s

2) Page 5, line 11: it would be useful to show here Fig. 1 of Kassi et al. (2006), as many readers probably would not go and check that reference, and could ask themselves how to fit a 50 cm cavity (plus some optics) in a 48.26 cm wide rack. Since 2006, the mechanics has been improved. We prefer not to show again the set-up used for the

measurements reported here and previously published in Kassi et al 2006. We added a mention to the geometry inside the 19" rack : Now page5, line 5-6 : ...fit inside a 19" chassis where the V-shaped cavity is placed in the diagonal as shown in figure 1 of Kassi et al. (2006)

3) Page 7, line 8: the volume of a 3/8" pipe, 20 m long, is about 1400 cm3. With a flow of "250 sccm" it would take more than 5 minutes to cross the entire pipe length. Could the authors explain their statement? It was a mistake, we replaced " about 1 min" by " about 6 min". We clarify the point that the delay between the two instruments (14min deduced from measurements as shown in Figure 2) is mainly due to the cold trap of the GC.

now page 7 Line 15-19 : The estimated sample propagation delay along the tube from the roof to the OF-CEAS instrument is about 6 min (with a gas flow of 250 sccm). A larger delay is observed on the GC data due to the use of the cold trap. The volume of this trap corresponds to the sample volume collected over about 15 min by the GC, inducing a smoothing of the signal of the semicontinuous injections. To eliminate the time delay between both instruments, the time shift wasfixed to 14 min (Fig. 2).

Please also note the supplement to this comment:
http://www.atmos-meas-tech-discuss.net/amt-2016-386/amt-2016-386-AC1-supplement.pdf

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