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Atmospheric Measurement Techniques Discussions

Interactive comment on "Field inter-comparison of two high-accuracy fast-response spectroscopic sensors of carbon dioxide" *by* B. A. Flowers et al.

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The manuscript is listed as a contribution to the special issue "Carbon dioxide, other greenhouse gases, and related measurement techniques - 16th WMO/IAEA meeting (GGMT-2011)" and describes a comparison of two gas analyzers based upon different spectroscopic techniques: The Picarro 1301 is a CH4/H2O/CO2 fast analyzer, while the Campbell TGA-100 applied in this study is designed for the measurement of stable CO2 isotopes. The title puts the focus on the important issues "field inter-comparison", "accuracy" and "fast response" and the paper has the character of an evaluation and may even be understood as a recommendation, especially in the context of the WMO special issue. The purpose of this comment is to show how complex data interpretation

can be and what additional or even different conclusions can be drawn from the data.

Both the TDL and the CRDS sensor under investigation were operated in a laboratory at the Los Alamos National Laboratory Environmental Research Park for the ambient carbon dioxide inter-comparison study. The analysis of outdoor ambient air in a lab is not really a "field study", at least it might be misleading for the reader, who may expect measurements at remote sites and/or under harsh environmental conditions. It is mentioned that the CRDS had been coarsely calibrated with less precise standards ($\pm$7–8 ppm uncertainties – is this precision or accuracy?) prior to the cross-calibration, but unfortunately there is nothing said about accuracy. The word "accuracy" appears only in the title and abstract, but is not defined or even used anywhere else in the text. Furthermore, the title suggest "fast" response analyzers, but the 1-min temporal response used for the time series is not really "fast", as for the measurement of trace gas fluxes for example 10 Hz are used and meanwhile state-of-the-art. It is emphasized in the abstract that the TDL requires frequent calibrations that limit its time resolution. In general, frequent calibrations do not limit the time resolution - they may interrupt a time series. Also the mentioned use of liquid nitrogen is not a technical limitation, even though at some remote sites liquid nitrogen supply may be a practical or logistical problem. Throughout the text the isotopic notation is used. This makes the paper difficult to read and as the paper does not deal with isotopes the conventional notation CO2 should be preferred.

Detailed investigations of the linearity before and after the measurement have been performed. Linearity is an inherent feature of Beer′s law at low absorbance and, therefore, any well designed trace gas sensor should be linear for the monitored low concentrations, especially in the specified range of the instrument from 350 to 550 ppmV CO2. This has now been confirmed as during 12 months of operation the authors have not observed non-linear behavior for either the CRDS or TDL sensors in a wide variety of applications. However, as discussed below it is more important to monitor drift of zero (ambient air devoid the target gas) and span (calibration) during that period.

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For field applications the instruments thermal and opto-mechanical stability and the corresponding background fluctuations during the time of the measurements are the critical issue. Therefore, manufacturers like Los Gatos Research, Inc. and Aerodyne Research, Inc. put a lot of effort in active thermal stabilization of field instruments. It is important to avoid a time dependent superposition of background effects and other interfering structures like optical fringes. The impact of fringes and atmospheric turbulence on accuracy and precision of laser spectrometers for trace gas sensing have been discussed recently and practical guidelines how to interpret instrument stability data and how to design measurement cycles have been provided [1, 2].

The authors use a laboratory inter-comparison study based upon 16 hours of time series data from a reference gas to establish the precision and instrument stability as a function of signal integration time. This is an important task and its relevance cannot be overemphasized. Such an analysis can help to identify problems related to the instrument itself or the instrument as it is embedded at a measurement site. There is nothing wrong with the analysis provided, but the interpretation and discussion is incomplete and therefore can be misleading. It is mentioned that the CRDS sensor exhibits stability at considerably longer integration times than does the TDL sensor, the minimum detection limit is observed at 3500 s (58 min) signal integration time, opposed to 30 s for the TDL. The CRDS detection limit at 58 min is reported to be in close agreement with the prototype CRDS sensor from the manufacturer with a reference to van Pelt (2011) and it is said to be independently verified (unfortunately, van Pelt 2011 is not in the references list). However, for the TDL the 58 min time constant should not be mentioned as the instrument is only specified up to 60 sec according to the given stability analysis and the measurement sequence recommended by the manufacturer. Much more important is the missing discussion of the "slopes" in the plot of the Allan variance versus integration time. It is written that the "overall noise is dominated by random noise and increasing signal integration time, T, decreases the variance until a time at which instrumental noise begins to dominate and the variance begins to increase again". But: Under stable conditions the variance is inversely pro-

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portional to the integration time. Only under such stationary conditions the variance decreases (precision gets better) without affecting accuracy [1]. Any deviation from the expected behavior due to instrumental noise (which is typically a drift) affects the accuracy of the measurement. The author′s analysis has been modified in Fig. 1, where the expected slopes now are included to illustrate the following discussion: The TDL instrument starts at 15 sec and then follows the expected 1/T relationship until at about 60 sec an instrumental drift starts to dominate the system performance. This is a “classical” behavior. Anything that happens beyond that point is not relevant as during the measurement phase there is a frequent recalibration applied to compensate for those longer term disturbances. The CRDS in contrast starts at 1 sec and almost immediately after about 2 seconds the instrument deviates from the expected 1/T behavior. With respect to accuracy, the minimum is rather at 2 seconds than at 58 min. At the 30 sec time scale, which is used for the comparison of the time series, the variance for the CRDS is already about an order of magnitude higher than it should be according to the prediction of the 1/T dependence. There is no explanation given for this and it is not clear whether this behavior is characteristic for the fast analyzer under investigation or whether it has to be attributed to the measurement setup and operating conditions. The authors force a zero y-intercept in their final analysis because “both sensors should respond to a sample absent of carbon dioxide with zero concentration”. Besides the span calibration, the zero measurement is an important part of a calibration procedure [3]. It might be important to allow the concentration offset as a degree of freedom as there was no calibration of the CRDS for 19 days and a significant deviation from the expected behavior for integration times longer than 2 seconds can be observed. This indicates immediate loss of accuracy, which would have required further investigations to decide about modifiied operting procedures for example. In order to see any deviations it would have been interesting to show the differences of the time series plotted as residuals. As a result of the present analysis it turns out that the TDL works correct within its specifications, while the CRD exhibits unexplained characteristics. The question is even more important as the analysis of van Pelt (2011) seems

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to show the same characteristics. As long as these deviations from expected behavior are not understood any comparison and judgment remain very difficult.

In the last decade tremendous progress has been made by manufacturers of trace gas analyzers and now such devices are increasingly available for atmospheric research, ecological studies and the greenhouse gas monitoring community. The selection of an appropriate sensor is still a challenge and the currently available spectroscopic trace gas analyzers should not be considered as turn-key instruments, which operate in plug and play mode. In order to assure data quality even state-of-the-art laser-optical gas analyzers still require a basic understanding how these systems work and what has or may have an impact on instrument performance and data quality.

Instrument evaluations and inter-comparisons require a lot of care and attention by experienced users, when interpreting data, especially when direct or indirect recommendations will be given. Instrument inter-comparisons are important, but they need a clear focus on a given application. Even though a general reference to a WMO meeting in 2005 is mentioned, it is not explained, why the authors make an inter-comparison for CO2 with a slow TDL CO2 isotope analyzer and a fast CRDS CH4 analyzer with an additional CO2/H2O channel (added for spectroscopic corrections of humidity effects)? There exist a fast CH4 analyzer from Campbell Scientific, Inc. and a CO2 isotope analyzer from Picarro, Inc. as well. As the focus was on CO2 it would have been mandatory to compare such measurements with the well established non-dispersive infrared gas analyzers (e.g. LICOR, Inc.), which are the state-of-the-art for trace gas flux monitoring applications and networks. The work presented here does not address this important point and, therefore, unfortunately it looks like a comparison of what the authors had available and not what has to be evaluated to address a given problem or application. In its present form the manuscript is too ambitious and a title like "a case study" or "a user perspective" would be much more appropriate. As a member of the Atmospheric Monitoring Techniques editorial board I felt obliged to comment on this manuscript.

[1] Werle, P.: Accuracy and precision of laser spectrometers for trace gas sensing in the

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presence of optical fringes and atmospheric turbulence, Appl. Physics B102, 313-329, 2011.

[2] Werle, P.: Time domain characterization of micrometeorological data based on a two sample variance, Agric. Forest Meteorol. 150, 832-840, 2010.

[3] Werle, P., Mazzinghi, P., D′Amato, F., De Rosa, M., Maurer, K., Slemr, F.: Signal processing and calibration procedures for in-situ diode-laser absorption spectroscopy, Spectrochimica Acta A 60, 1685-1705, 2004

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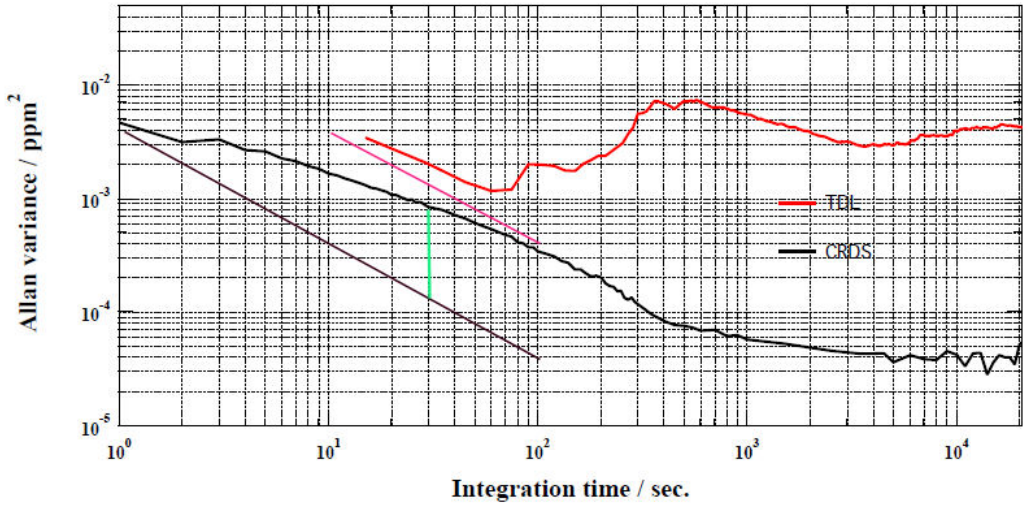

Fig. 1. Allan variance for TDL and CRDS with expected decrease proportional to 1/T for unaffected accuracy. The vertical green line indicates the deviation at 30 s time scale used for the intercomparison

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