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Atmospheric Measurement Techniques Discussions
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Interactive comment on "Development and field testing of a rapid and ultra-stable atmospheric carbon dioxide spectrometer" *by* B. Xiang et al.

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We sincerely thank both reviewers for their efforts and also valuable comments to our work presented in the paper. Below are our responses to each of the comments and the changes we've made in the revised paper (author comment, AC). The original reviewer comments (RC) are also listed for reference.

Anonymous Referee #1

Overview

[RC] This manuscript describes field testing of a second generation spectrometer designed for measurement of atmospheric CO2. Improvements over the first generation instrument are presented, along with data from an 8-month deployment at a typical field site. The performance of the instrument in its current form is impressive. While the authors suggest that this instrument could be operated as an "absolute device", the use of minimal calibration gas seems like a relatively easy way to improve the performance and provide quality control.

General Comments

[RC] Overall, the manuscript is well-written and should be of general interest. Publication is recommended with minor corrections.

Specific Comments

[RC] P8102, L3: Suggest to use the SI unit "μmol/mol" on first use of "ppm". Also applies to p8013, L20.

[AC] "ppm" at these two locations have been changed to "μmol/mol (ppm)".

[RC] P8102, L14: delete "another". "Field measurements agree well with those of a commercially available ...."

[AC] Done.

[RC] P8103, L9: Suggest re-phrasing as " . . . deployed in situ, and variations in the composition of gas delivered to the sensors may limit the accuracy of the measurement."

[AC] Done.

[RC] P8103, L29: While the performance of the ABC is certainly impressive, it may be comparable to that of an un-calibrated Picarro (see fig 12a in Andrews et al., 2014, Atmos. Meas. Tech., 7, 647–687, 2014).

[AC] We have added references on the performances of long-term in-situ Picarro measurements (e.g., Andrews et al., 2014 and Richardson et al., 2012) to our later discus-

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sion on instrument comparisons. This sentence has also been changed to “This performance puts the ABC instrument among the best CO_2 instruments currently available”.

[RC] P8104, L19: check McManus et al citations. McManus et al (2010) not found in reference list.

[AC] The correct citation has been added to the reference list.

[RC] P8105, L21: What is the isotopic composition of the 4% CO_2 in the reference cell. Does this matter?

[AC] We did not measure the CO_2 isotopic composition in the quartz reference cell. Because ABC measures the major CO_2 isotopologue (i.e., $^{12}C^{16}O_2$) and it was initially calibrated using NOAA WMO gas standards with natural composition of CO_2, the reported total CO_2 values from ABC ambient air measurements is not dependent on the reference cell CO_2 isotopic composition.

[RC] P8107, L27: Possibly mention the set-point for temperature control here. From Fig. 3 it appears to be 298K, but could also mention in text.

[AC] The set point of the chiller was varied by the control program actively according to the ambient temperature variation, as can be seen from Fig. 3. As a result, the optic temperature (e.g., sample cell in Fig. 3) was maintained at a fairly constant value. This has been discussed in the next paragraph. P8108, L16-17 has been added with this constant value of cell temperature: “…such that the sample cell temperature stayed constant to within about 30mK around 298.15 K over 7K changes in the ambient temperature…”.

[RC] P8111, L6. It is not explicitly stated if the air samples analyzed by ABC were dried. I assume they were with reference to Xiang et al 2013, but a statement specifying the drying procedure should be added.

[AC] This sentence has been changed to “ABC currently measures Nafion (Perma Pure PD-200T-48) dried air samples but does have the potential for water measurement and

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correction.”

[RC] P8112, L11: Check spelling of “Scot-Marrin”.

[AC] The spelling has been corrected to “Scott-Marrin”.

[RC] P8112, L26: I object to the term “tank science”. Knowledge and experience related to the stability of trace gases in cylinders is no different to that related to any other critical component or experimental design. We, as scientists, must simply discover what works best. In that sense is “tank science”, really any different from “pressure transducer science”, “optics science” (e.g. fringes), etc.? Confirmation of the benefits of aluminum over steel is worth mentioning. Why not leave it at that?

[AC] This sentence has been removed.

[RC] P8113, L11: Comment on accuracy: To be used as an absolute device (i.e without calibration), a traceability chain would need to be established. I can see that, in principal, the ABC could do this, but it would require periodic re-calibration of the quartz reference cell, and temperature and pressure sensors to establish traceability to national standards, or periodic comparison to a “reference ABC”. The expense and work required to do this would not be trivial.

[AC] We agree with the reviewer that procedures to ensure ABC’s long-term stability (in another word, absolute accuracy) are not trivial. Our initial goal of developing ABC is to replace compressed gas cylinders with small quartz cells contained CO2 samples, in order to relieve the expensiveness and intensiveness of tank operations (which we understand has already been established over the past decades and commonly considered reliable). To further reduce the operational cost of ABC, we will continue to investigate and improve the accuracy and stability of our instrument parts, such as T and P sensors.

[RC] P8113, L18: Overall I agree that this system has the potential to offer very stable CO2 measurements, but I would change “without costly reference gas transport and

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consumption” to “with minimal reference gas consumption”.

[AC] This has been changed accordingly.

[RC] Fig 4a: Results of the high and low surveillance tanks (moving in opposite directions) suggests a linearity change during the period. For practical deployment, the use of reference gases, even sparingly, would likely improve the results.

[AC] We also noticed these changes of the surveillance tanks. However, given only three sampling time points for each tank, we are not sure whether these changes are systematic or random, and whether instrumental or tank related. Meanwhile the performance of the continuous measurements of working tanks (as shown in Fig. 4 for the same period as surveillance tanks and in Fig. 4b for individual tank sampling during a week) is more representative and indicates that the instrument is quite stable within 0.1 ppm and showing no drift trends. In general, we agree with the reviewer that periodic reference tank measurements are needed for ABC quality assurance.

[RC] Fig.6: Since steel tanks are known to be poor choices as reference materials for long term CO2 measurement, does including them in Fig. 6 add any information? It just seems to complicate the issue. Either the steel tanks were not properly calibrated in the first place, or out-gassing of water vapor o

[AC] We prefer not to throw away steel tank surveillance measurements in our discussion or in Fig. 6, because they provide valuable information to our field stability and accuracy experiments (as long as we could understand the causes behind their variations). First, the steel tanks cover a wider CO2 range (332 - 496 ppm) than the aluminum ones (347 - 457 ppm), which nicely expand the ABC’s linear response (i.e., working range of CO2). Second, the in-situ sampling period of steel tanks (Jun 2013 - Feb 2014) was longer than that of aluminum tanks (Sep 2013 – Feb 2014), better showing ABC’s stability over longer period.

[AC] In our field experiments, surface reactions and gas impurities are likely the causes for the temperature effect on steel tanks. However, we feel that the advantages of aluminum over steel tanks are not well known within the science community. Limited literature and documents can be found or referenced until recently (Leuenberger et al., "Gas adsorption and desorption effects on cylinders and their importance for long-term gas records", Atmos. Chem. Phys. Discuss., 14, 19293-19314, 2014). We think it is worth discussing our on-site observations to raise awareness on this issue.

Anonymous Referee #2

General Comments

[RC] This paper is a follow-up to a previous paper by the same author about essentially the same instrument, which measures CO2 with very little drift over time. This manuscript describes technical improvements that have been made and it describes the instrument stability over a long-term deployment in the field. Although the results seem only an incremental step in novelty over what was already described in the previous paper, they still should be published, because they show the performance of the analyzer in the field, which is what most will interest future users. The main finding is that the analyzer is remarkably stable over a long period of time. I recommend publication, although I did have a few more questions about analyzer performance that were not answered in the manuscript as it is currently written.

[RC] There were two questions I was left with after reading the manuscript. 1) Is the sample dried prior to measurement, or is the measurement corrected for the influence of water vapor? If it is dried, how is that accomplished in this experiment? Page 8111 Line 6 mentions that it could correct for water vapor, but drying is not mentioned anywhere.

[AC] This sentence has been changed to "ABC currently measures Nafion (Perma Pure PD-200T-48) dried air samples but does have the potential for water measurement and correction."

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Interactive Comment

[RC] 2) I would have liked to see some mention of how the analyzer responds to motion/vibration, i.e. if on a vehicle or aircraft. The lack of calibration need would be ideal for such applications where calibration gases are even more problematic than at a stationary site with plenty of space. Perhaps if this has not been examined, it could be part of future efforts to field test the instrument and could be mentioned as such.

[AC] As mentioned in the draft, ABC was developed for the purpose of long-term remote site measurements, so it has not been specifically designed to survive extreme vibrational conditions. This could be part of our goal for future ABC development.

[RC] Other questions: 3) What inlet pressure range can be used? No plumbing diagram is given, but it seems clear that the analyzer has its own pump to pull ambient-pressure air through. Does the flow rate vary based on inlet pressure – or can it be varied by the user for different applications?

[AC] The plumbing diagram is described elsewhere (Wehr et al., 2013). ABC currently uses its own pump (peak pumping speed 110 L/m, Variance SH110). The cell pressure is controlled by a flow controller (500 sccm range, MKS 0248A-00500SV) in response to possible inlet pressure change or pumping speed change. The sample flow rate can be varied by user for different applications. However, the user needs to make sure that the pressure in the sample cell and the quartz reference cell pressure is balanced (5 Torr) by choosing appropriate pumps.

[RC] 4) What are the size/weight and power requirements?

[AC] A typical Aerodyne Dual (laser) system (the same platform that ABC was built on) has dimensions of 530 mm x 660 mm x 710 mm (W x D x H), weight of 72 kg, and draws electrical power of 500 W, 120/240 V, 50/60 Hz.

[RC] 5) What is the response time of the analyzer to a quick change in mole fraction? (i.e. What kind of response does the instrument have when switching over to a tank measurement – this comes up in the figures for the tank measurements – how much

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data needs to be cut out at the beginning?)

[AC] At the current field sampling system setting (e.g., inlet tube length, sample cell flow, etc), the time constant for ABC to respond to a tank change and to reach 1 – 1/e (∼ 63.2%) of the tank value is ∼ 3 seconds, while the wait time for ABC to stabilize (i.e., within 0.1 ppm of the measurement leveling off) is ∼ 30 seconds. Our sampling duration for each tank was 2 minutes and we always took the last 30 seconds period data for consistency and accuracy.

[RC] Clearly the stability that the field deployment shows is impressive and the authors seem to recommend that it can be deployed with no calibration in the field beyond occasional replacement of the quartz reference cell. But although the authors compare with the manufacturer specs of the Picarro CRDS unit, they do not compare with literature about the stability of those analyzers (Scott J. Richardson, Natasha L. Miles, Kenneth J. Davis, Eric R. Crosson, Chris W. Rella, and Arlyn E. Andrews, 2012: Field Testing of Cavity Ring-Down Spectroscopy Analyzers Measuring Carbon Dioxide and Water Vapor. J. Atmos. Oceanic Technol., 29, 397–406. doi: http://dx.doi.org/10.1175/JTECHD-11-00063.1 or Karion, A., Sweeney, C., Wolter, S., Newberger, T., Chen, H., Andrews, A., Kofler, J., Neff, D., and Tans, P.: Long-term greenhouse gas measurements from aircraft, Atmos. Meas. Tech., 6, 511-526, doi:10.5194/amt-6-511-2013, 2013.). Do the authors have any idea how the stability of different individual units will vary, i.e. is this good performance the norm for this type of analyzer?

[AC] We have added references on the performances of long-term stationary Picarro measurements to our discussion on instrument comparisons: "Its (ABC) stability of < 0.3 ppm peak-to-peak over 8 months surpasses or competes with that of any major brand CO2 spectrometer (Picarro G2301 Specification Sheet, http://www.picarro.com/assets/docs/CO2_CH4_H2O_in_Air.pdf; Andrews et al., 2014; Richardson et al., 2012)." We expect the same stability and accuracy performances from potential future ABC instruments.

Specific Comments

[RC] P8107 L7: It was not clear how a flow controller was used to control cell pressure more accurately than the pressure sensors that were tested. What was the flow rate?

[AC] The flow rate of ABC sample cell varied slightly around 400 sccm by a flow controller, in order to keep the cell pressure within 10 mTorr of the set point (5 Torr). It is not necessary to maintain the cell pressure within 1 mTorr, but more importantly, the measurement of the pressure should be accurate within 1 mTorr for accurate spectral simulation and mixing ratio calculation. This is why we made efforts to test three pressure sensors on their zero- and span- drifts.

[RC] P8109 L15: What are the repercussions after such a power or pump failure? What maintenance or recovery procedure is required after such a disruption? (This is an important piece of information for instruments running at remote locations).

[AC] In general, the restored performance of ABC was not affected by power or pump failure. (1) In terms of power failure, a universal power supply (UPS) was used to protect ABC from a short-term power outage. For a long power break out, the instrument computer was equipped with remote connection and the ability and settings to restart itself, so either the user or the computer can restore the instrument back to full function. (2) In terms of pump failure, the inlet flow controller will stop the sample flow in response to the pressure built up in the cell assuring a safe shutdown. Of course, the user would need to be physically present to replace the pump.

[RC] P8110, L4: Is this typical over any given week? (the authors should mention this, to make clear that this particular week was not chosen because of the good stability - perhaps it was chosen as typical or because it showed a large temperature range?).

[AC] This example week was chosen because of a large environment temperature swing. This has been clarified in the text.

[RC] P8110, L12: Some Picarro analyzers have demonstrated much better stability than this spec, which is quite conservative. Would all ABC analyzers be able to achieve this high stability as the one shown here?

[AC] We have added references on Picarro long-term measurement performances both from manufacture specification and from field experiments. This sentence has been changed to “Its stability of < 0.3 ppm peak-to-peak over 8 months surpasses or competes with that of major brand CO2 spectrometer (Picarro G2301 Specification Sheet, http://www.picarro.com/assets/docs/CO2_CH4_H2O_in_Air.pdf; Andrews et al., 2014; Richardson et al., 2012)”. We expect the same stability and accuracy performances from potential future ABC instruments as the current one demonstrated in this work.

[RC] P8111 L4: Is this the manufacturer (Picarro) spec or the precision of the actual analyzer at the site? Picarro’s web site claims 1-sigma precision of < 70 ppb at 5 seconds (half what is stated here) – again, some literature claims better precision than this, but presumably the manufacturer spec is conservative.

[AC] The precision of 0.15 ppm every 5 sec is from Picarro G2301 manufacture spec sheet (http://www.picarro.com/assets/docs/CO2_CH4_H2O_in_Air.pdf). The report time interval for Picarro varies upon instrument and measurement conditions. In this sentence we meant to highlight the ABC’s measurement capability at high frequency and with high precision, a potential feature for eddy covariance measurements.

[RC] P8111 L5: Is this typical, or were the measurements only existing for this one week?

[AC] The agreement between Picarro and ABC CO2 measurements during the week shown here is typical. Measurements of both instruments overlap more than seven months at Harvard Forest.

[RC] P8111 L6: If it is not applied for this test, how are the measurements accounting for water vapor? Is the sample dried?

[AC] The ABC sample inlet is dried using a Nafion dryer, reducing the water content to lower than 200 ppm at all times according to another in-line Aerodyne QCLS water measurement.

[RC] Table 1: Looking at the last column with the tank measurements: these are very small differences, but the slope of the linear fit is changing with time. Some tanks are going up, some down. Seems like a user would not get to the 0.1ppm level reproducibility without working tanks (or with?).

[AC] We also noticed these up and down changes in the aluminum surveillance tanks. However, given only three sampling time points for each tank, we are not sure whether these changes are systematic or random, and whether instrumental or tank related. Meanwhile the performance of the continuous measurements of the working tanks (as shown in Fig. 4 for the same period as surveillance tanks and in Fig. 4b for individual tank sampling during a week) is more representative and indicates that the instrument is quite stable within 0.1 ppm and showing no drift trends.

[RC] Figure 4 a. This is a very nice figure showing really terrific stability. However. . . The aluminum tank values (or differences) don't seem to correspond with the table 1 values. Looking at Tank 4, there should be a 0.35 ppm difference between the first and last measurements according to the table but in the figure it is less than 0.2 ppm? Or perhaps I am misunderstanding the table or figure – if so, they should be clarified.

[AC] We apologize for our mistake sourcing the measurement results when making this figure. We have made sure that values presented in Table 1 are the correct raw tank measurements and we have updated Fig.4a accordingly in the revised draft.

[RC] Figure 4b caption: Is this an average of the last 30 seconds of a 2-minute measurement? (at 1 Hz)?

[AC] Yes, this has been clarified in the caption.

[RC] Figure 6: Including the residuals for the steel tanks, which were shown to have issues unrelated to the analyzer, magnifies the axis on the lower plot so that it is not easy to determine the residuals for the aluminum tanks. I would recommend only showing the aluminum tanks here.

[AC] We prefer not to throw away steel tank surveillance measurements in our discussion or in Fig. 6, because they provide valuable information to our field stability and accuracy experiments (as long as we could understand the causes behind their variations) and raise the awareness of the tank material issue.

[AC] First, the steel tanks cover a wider CO2 range (332 - 496 ppm) than the aluminum ones (347 - 457 ppm), which nicely expand the ABC's linear response (i.e., working range of CO2). Second, the in-situ sampling period of steel tanks (Jun 2013 - Feb 2014) was longer than that of aluminum tanks (Sep 2013 – Feb 2014), better showing ABC's stability over longer period. Third, we feel that the advantages of aluminum over steel tanks are not well known within the science community. Limited literature and documents can be found or referenced until recently (Leuenberger et al., "Gas adsorption and desorption effects on cylinders and their importance for long-term gas records", Atmos. Chem. Phys. Discuss., 14, 19293-19314, 2014). We think it is worth discussing our on-site observations to raise awareness on this issue.

Technical Corrections

[RC] P8107 L25. "was developed" – should this be "became commercially available"? (otherwise it implies that it was developed by the authors for this specific project?).

[AC] Aerodyne is not yet offering ABC as a commercial product. We are continuing to improve the instrument with respect to compactness, robustness, multi-species, broad applications, etc.

[RC] P8110 L 25: Should perhaps read: "using the same Picarro CO2 instrument". (the mentioning of the Licor is confusing here).

[AC] This has been changed to "Both the Picarro calibration tanks and the ABC reference tanks were calibrated against WMO standards at Harvard University, but using

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different instruments (Picarro and Licor, respectively)".

[RC] P8111 L13: "Majorly" should be reworded.

[AC] "Majorly" has been changed to "primarily"

[RC] P8111 L25: 3%, not per mil.

[AC] A slope of 0.997 is 3 ‰ different from unity.

[RC] P8112 L8: "tank" should be "tanks"

[AC] This has been changed.

[RC] P8112 L13: Kept going up after the temperature stabilized? Unclear wording.

[AC] We have changed the sentence to "During this hour, ABC measurements from the steel tank went up by 0.7 ppm; . . .".

[RC] P8112 L26: Not clear what "tank science" means, or why it is in quotes?

[AC] We have deleted this sentence to avoid confusion.

Interactive comment on Atmos. Meas. Tech. Discuss., 7, 8101, 2014.