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Atmospheric Measurement Techniques Discussions

Interactive comment on "CO_2, CO and CH_4 measurements from the NOAA Earth System Research Laboratory's Tall Tower Greenhouse Gas Observing Network: instrumentation, uncertainty analysis and recommendations for future high-accuracy greenhouse gas monitoring efforts" *by* A. E. Andrews et al.

Anonymous Referee #1

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The paper by Andrews et al. presents the technical setup of the NOAA network of 8 tall tower sites to measure atmospheric CO_2 and CO (and partly CH_4) concentrations. The authors comprehensively describe the evolution of the instrumentation, its automation, and its evaluation from the 1990s to the current state to achieve the WMO comparability goals. The applied CO_2 analyzers are also compared to the most

recent laser based technology. The subject of the paper perfectly matches the scope of AMT; the methods need clarification on a few points mentioned below. However, the text needs considerable work to reduce lengths, avoid repetitions, and get a clearer structure before being published in AMT.

Main scientific concerns:

(1) Consistent negative bias of in situ CO_2 measurement:

The flask - in situ comparison shows a dominating positive bias (Table 5). In turn the in situ measurement might be too low. Another indication for a low bias in the in situ CO_2 is given by the tank air experiment provide to the inlet (p1506/L2). I guess, that is due to the Nafion setup. The counter-flow of the Nafion dryer is operated with reduced pressure; thus, giving a pressure difference leading to diffusion. CO_2 permeation is preferred to other gases, resulting in a CO_2 depletion. As the calibration gases also flow through the Nafion dryer, this bias is partly compensated. However, a membrane with few water allows less CO_2 diffusion than a wet membrane; therefore, the sample air is depleted more than the dry calibration gases (even if the air at the Nafion outlet has same humidity, the water concentration changes at the Nafion inlet). This hypothesis is further strengthened by other arguments: Stephens et al. (2011) use a Nafion setup with almost no pressure drop in the counter-flow, and they see not a loss of CO_2 (p1509/L5)! Moreover, there is also a slight positive offset of the Licor to the lab-calibrated Picarro (Rella et. al.,2012) (p1510/L11). Finally, the target tanks get an increased low bias, when measured independent from other dry air, i.e. a wetter membrane (p1503/L28). An open question is why Picarro and Licor show comparable results at BAO on the long term (p1511/L4ff). I suppose, both analyzer share the calibration gases lines (judging on p1512/L14f)? May you go through your experiment in section 6.2.1 again to clarify this?

(2) Statistical background of the uncertainty calculations:

To sum up different uncertainty terms to one error number (p1496/L14) is restricted to statistically independent error sources. However, the 7 components described here

are often not independent (e.g. u_p and u_b), or no random numbers with a normal distribution. Some are even biases that should be corrected for (u_stdeq, u_smpeq, u_wv). The ideas presented here are valuable indicators when remotely assessing the analyzers deficiencies, but they should not be used in models for carbon flux estimates, which often strictly rely on a Gaussian error distribution.

Comments on presentation style:
Please, substantially shorten the text to do a favor to reader and reviewers. To cut the length of more than a half seems reasonable, even without losing valuable information. Only the most eye-catching examples are pointed out in the specific comments below (repetitions, unnecessary information). I prefer a more precise/scientific than narrative style. The manuscript often illustrates the full story behind the development with all its drawbacks. Even though science works like that, in my eyes, that does not match the AMT journal style. I recommend clear statements about the final setup, with some short reasoning, why the materials/methods were chosen by either citing own experiences (instead of the full story) or other references (currently done very rarely). When rewriting the text, a clearer structure can be achieved by a clear division between the setup description and its evaluation. Now, it is often confusing when technical solutions from different points in time and sites are mixed and even mixed up with future suggestions, which sometimes even leave open whether they have been already applied. I would recommend a restructuring of the manuscript, e.g.: *A Introduction* (chapter 1) *B Instrumentation/Hardware* (instrumentation chapter 2.1-2.10, incl. leak checks, lab validations 6.2) *C Automation* (calibration 4 + 5.1, alerts 3.1, data uncertainty 5.2) *D Results* (Data evaluation (target, Picarro): 6.1, 6.3.1, 2.11+6.3.2+6.3.3, 6.3.4; add time series) *E Conclusions* (incl. short list of future recommendations (chapter 3.2, 7, 8)) Even though the discussion of data results is out of scope of the paper and the journal, I would personally prefer a figure with the time series of e.g. CO_2 from all stations. It would easily visualize Table 1 and would easily illustrate what kind of signal can be seen from the data to prove the introductory words

right in the conclusions. Moreover, a small map showing all sites in the US would nicely illustrate the network.

Specific comments (page/line):
1463/22ff: It is sometimes difficult to follow the introduction, because it sometimes does not follow a clear argumentation line. The order of arguments in the paragraph starting on page 1464/22 might be put in a better way, to understand the idea to use a tall tower for atmospheric measurements. At the moment the whole work is not well motivated. I would also put paragraph 1466/12ff in front of p1465/21, as it first describes the networks, than it more and more focusses to the presented network. The last paragraph also fits better on p.1466/12. You mention already many important facts, but I miss a clear argumentation that culminates in a clear statement about the novelty/importance of your work for the science community.

1464/9: leave out this sentence here, no connection.

1464/28: This footprint was calculated for a tracer without diurnal cycle, for CO_2 the far distance signal is diluted much faster.

1465/23: since when it expanded? 2007?

1465/26: why > 300 m, why is it representative for the planetary boundary layer?

1466/17ff: What other models exist apart from Carbon Tracker? Why this model is introduced and emphasized here so comprehensively?

1467/21 and Table 1: Please mention full name of the station at the first time you mention it, later you may use the 3-letter-abbreviation.

1467/26ff: Why so much advertisement of the system at this position, when it is not even presented yet?

1468/5f: What kind of measurement technique is the Licor? please mention it before presenting all alternatives

1468/10: "core of the tall tower system". If it is also your system remains unclear.

1468/11f: Please provide the exact type number and company name.

1468/16: in section 6.3.1 nothing about the Licor calibration frequency is written

1468/16: insensitivity to environment > minimize calibration gas? This is not necessarily directly linked; an internally erratic sensor also needs many calibrations.

1469/6: please give the type and company in an unambiguous way throughout the whole paper, e.g. (type: xyz, full Manufacturer name, country), see also 1469/16, 1470/5, 1470/8, 1470/10 etc.

1469/19: What happens, if the flow does not return?

1469/24: Is the pressure drop of 44 hPa realistic? It is probably a correct theoretical number on a straight tube, but I would expect a much larger pressure drop in practice. Did you ever but a pressure sensor upstream the first pump to validate this number?

1470/22: Which box? Only clear when reading the paper the second time.

1471/2: Where is the transducer in the figures? It is not so easy to follow without an overview figure.

1471/4: Why Viton?

1471/4: Is quick-connect fittings a general term? You mention the producer only later.

1471/25: poorly motivated, why drying of H_2O is necessary (only in chapter 7.3) **1472/7**: What is the final dew point? **1472/13**: I see!

1473/6: What laboratory and field tests? Why you write here the type of the Picarro?

1473/8ff: Write this description in the beginning of the paragraph, describe Fig.2b, than you can present the performance.

1473/14: Improved drying, yes, but also improved CO_2 diffusion!

1474/22: Did you ever estimate the maximal tolerable leak rate of this valves? This gets even more important for more stable analyzer in the future, as the calibration gas sits longer time and gives room for CO_2 diffusion. The Parker 9-series gives 10E-7 cc/sc/atm, the 99-series would have 10E-8. Standard valves have several orders of magnitude larger leaks rates. The Valco multi-position valve has 10E-10 cc/sc/atm, you may keep in mind for the future.

1475/9f: Why is the temperature control relative to the room temperature? Why you do not use a simple, but absolute controller? With this setup the performance relies on a good air conditioning, which is much more difficult to achieve.

1476/5: Where is this pressure controller located in Fig. 1 or 2? I though you are using a MKS pressure controller (p 1475/L18)? The whole section would benefit from a better figure and/or clearer structure.

1476/22: I guess, the motivation to include a filter in the setup to avoid introduction of debris is clear if you mention it once in you manuscript but not every time you mention a filter.

1476/23: Why you scrub CO from air, even though you want to measure it? You explain it one sentence later. Please turn the arguments to make reading easier. That is valid for the whole section: Your argumentation line: CO measurement principle > pump removed > cell pressure sample flow > sensors removed > zero removed > external gas > ...; why not using: CO measurement principle > cell pressure sample flow > external gas > zero removed > pump removed > sensors removed > ... . It is arduous reading right now.

1477/4ff: Almost no valuable information. Shorten it.

1477/15: Repetition to 1475/11. Cut once.

1477/15ff: Merge it to: Maximum operating temperature for both analyzers are 45 degC.

1477/25f: "RTD(). We performed ..." > cut it to: ", which is optimally placed in the center of the enclosure." Of course, there were tests done etc., but a paper cannot be a log of all lab experiments.

1478/10: The whole paragraph gives few valuable information. That the temperature control relative to ambient air can cause trouble is obvious (see my comment on p. 1475). I would summarize the full paragraph to one sentence: We use a doubled calibration frequency at the WGC site, because of a higher variability in room temperatures.

1479/10ff: Shorter or completely cut.

1479/19ff: Shorter, as it is really no novel innovation (e.g. The PC and data logger is synchronized to a time server to limit the time drift below ... sec.) Why you are not using GPS sensors to permanently getting current time stamps? Or use a clock card for the PC to provide constant time even without internet? To synchronize with an internet time server, each operating system already has an internal routine provided.

1479/26ff: The paragraph is quite narrative and can be shortened.

1480/15: Why you start a paragraph with pointing to another one? Please restructure.

1480/16: Did you test this pressure regulator for diffusion effects on CO_2 and CO? How much flushing is required? Is this type still available, as I cannot find it in the online product cataloque?

1481/2: It is confusing to read the metric units for the OD, since it is ordered in inch only.

1481/11: The WGC installation... > The installation at WGC site? For the reader all site names are not necessarily common.

1481/21f: The sentence reads like an advertising booklet from the manufacturer. The sentence before already implies that the control is done by the instrument.

1481/26f: There are a lot of other sensors not included in the Picarro. This information is not necessary for the understanding of the system (might be enough to show it in an overview plot and a table of all sensors (with unique names) in the supplement).

1481/28f: Exhaust is described in 2.4, and in Fig. 2b. Data acquisition is described in 2.9. It is somewhat redundant information that disturbs a fluent reading.

1482/21f: Of course the alerts developed over time. It is not worth to mention in a scientific paper.

1483/2: Why not discussing all cases at one place?

1484/6ff: Very narrative paragraph. I am interested in the final solution, with a short note that certain valves should be avoided.

1485/6: This kind of leak check is also not too novel. Did you estimate a maximum tolerable leak rate for this pressure test?

1485/7ff: Very narrative and often in contrast to high-accuracy measurements.

1485/24ff: Repetition to 2.8

1486/7: A 24 h cycle is always bad for a calibration cycle as it mimics other influences e.g. from temperature diurnal cycle. You mention this shortcoming later, but this is experience from other research groups as well.

1486/18: Why you show and discuss Fig. 5 at this place? You did not even mention the calibration, but already show the data.

1487/11ff: Your thoughts are correct but everybody can do them, when setting up a different system. You should justify your choice when you mention the 5-minute-sampling the first time.

1487/21f: You considered it, but what happened? Why you decided against it? You may put it into the future recommendations.

1488/9ff: To find optimal calibration times, the trial and error method can be successful, but it does not necessarily is. Why you don't use more sophisticated methods like Allan variance to determine the calibration time?

1488/22ff: The experiences with the prototype system can be shortened.

1489/13: Difficult to follow: You doubt the linearity of the fifth-order polynomial results, and you want to check it with 4 tanks only?

1489/25: How do you guarantee the 0 ppb CO in the scrubbed air?

1490/3f: You start here to discuss the measurement technique again (see sect. 2.6)

1490/16ff: Some repetitions, and some ideas can be moved to future recommendations.

1491/13: Why you mention it here? The analyzer used is out of context here and confuses the reader.

1491/28ff: What does this sentence mean?

1492/5f: Reference for this statement? Why you still do it, it seems not necessary?

1492/17ff: Redundancies to earlier descriptions.

1493/12f: The baseline is added to the raw differential CO_2 data? Not subtracted, right?

1493/20ff: merge it with information of chapter 2.8

1494/14f: Why you don't use one long calibration every 3 days? Would save calibration gas and equilibration time.

1494/21: Repetition.

1495/7ff: This discussion fits into the introduction to motivate the paper, not here when describing the methods.

1495/23: Many studies... Give references!

1495/25: Repetition.

1496/1ff: The given information of the paragraph has no value at this place. You may mention the magnitude of the calibration scale differences that contribute to your absolute uncertainty in one sentence. The rest is either redundant or not related to your work.

1496/14: You missed the "square root" of the quadrature sum of the seven terms? The condition for this is statistical independency of all terms, but they aren't (see scientific concern (2)).

1497/15: Standard deviation from 3 values is hardly statistics.

1497/17f: How does this function look like? As a first estimate, it is probably linear to the distance from the baseline measurement. But shouldn't it be $\sigma/2$ in the middle? The whole idea might be better handled more serious from a statistic point of view (e.g. use Allan variances). At the moment the green line in Fig. 6 already includes parts of the instrumental noise u_p.

1498/3f: The statement here confuses. How the target tanks are distributed is written somewhere else, and a different pattern is suggested here. Why you did not use it from the beginning?

1498/10f: Up to which CO_2 concentration this estimates is valid?

1498/22f: Why do you use the prediction interval instead of the confidence interval? From my understanding, the prediction interval is used to predict an unknown statistical distribution, but here you know the measurement data already and should use the confidence interval. Am I wrong here? Maybe you can give a short reasoning/references here.

1499/10: The difference isn't an uncertainty estimate. It is a bias that can/should be

corrected for, e.g by using an exponential fit. Best would be to exclude it by sufficient flushing and/or an optimized setup (dead volume, diffusion).

1499/10: This difference isn't an uncertainty estimate neither (not like a standard deviation). Did you try to extrapolate the function in Fig. 9 to estimate the equilibrium value? The decay time of the exponential fit should be related to the mixing time of your cell/setup (mixing time = volume / flow).

1500/10: Please use SI units here and replace 10E6 by 1, than the formula is valid for any unit. Otherwise the H_2O should also be divided by 100.

1500/25: What is the relative importance of each of your 7 terms for the final time series? It would be nice to see it exemplarily on some part of a time series (similar to Fig. 11).

1501/19: Repetition.

1502/5: at WKT only?

1502/9: If you use the Licor water corrected output, than you don't need the dilution error term. If still used, it becomes more complicated. Did you evaluate the influence of the wrong H_2O measurement on your final result? Maybe the internal algorithm gives overcorrected data for negative H_2O readings.

1502/11ff: Shift it to Sect. 3.2

1503/10f: The target tanks indeed provide an independent measure of analytical uncertainty. Why it is not used in chapter 5.2, it is a better statistical measure.

1503/12: Did you ever check the influence of the pumps separately? Why you use the pumps upstream the analyzer and not downstream like the Picarro?

1503/19ff: Very narrative again.

1504/12: 0.2 ppm are quite a high bias, in case the data is used for carbon flux esti-

mates.

1504/15ff: This section is again written like an anecdote. It is not clear why you give all this information to the reader, but without conclusions from it.

1505/3: May this difference be due to surface effects? When switching from wet to dry air the H_2O molecules in the tubing and valves give place to the less adherent CO_2. At the outlet one would see the remaining water and less CO_2. The whole experiment depends a lot on time scales and materials used. In combination with my scientific concern (1), this experiment can give central answers to the observed biased, thus may need to get more attention. Please, double-check the sign of the differences (it is written the opposite way from the explanation in brackets p1505/L3f)

1505/11ff: The paragraph could be more precise. The described test is quite limited to stable conditions. The inlet tubes may bias the air for highly variable conditions the most.

1506/5ff: First paragraph rather fits into introduction.

1506/14ff: Did you do a storage test for the flasks? Are Teflon O-rings ideal? How long do flasks wait until analysis? Please mention the drying (it can be only seen from the supplement).

1507/27ff: No valuable information in this paragraph except the last sentence.

1509/12: Why the bias should systematically should increase with time?

1509/24: Please work on it, and include it in the paper. A bias should be excluded from every measurement system.

1511/12ff: This is the central sentence of the section. The rest can be condensed.

1511/17f: Why you describe both setups here? Why you mention a firmware update?

1513/12ff: By far too much information. That can be written in the log file of the data, if

somebody is interested in data during a certain time. It cannot be part of a publication to list every failure individually.

1514/22ff: Repetitions...

1515/19: Why four tanks? An absolute and linear instrument might even live with one single tank to track the drift. These recommendations may hold true for your system, but are not necessarily true for other setups. For that reason, the manuscript cannot compete with a full review paper here.

1515/25ff: Many repetition follow and by far too many sentences. Yes, you should have a cycle not equal to 24 h. That is the only recommendation here.

1516/13 - 1519/11: Many repetitions. This part can be strongly reduced.

1519/12: Where do these ideas come from? Why it should be in this paper?

1520/6: The conclusions are insufficient. Please summarize, what you achieved, what accuracy you can reach, what validations have been done. Then give a more specific outlook what experiments or improvements can be done in the near future. Please also cover CO and CH_4 measurements. CO seems to be the most difficult species to reach WMO specifications.

1520/11: Don't argue what you would need for hypothetical further work, but summarize the work you have done, e.g. show a resulting time series. An outlook may include some hints for further hypothetical work in the end.

1520/21: So the whole setup is insufficient for the purpose it was built for?

1520/21f: "Several research groups..." and what have you done?

Table 4: why you give medians here? The standard deviation is the only valid measure that can be used for adding up independent error estimates.

Fig. 1: Confusing picture, as it is hard to follow the air stream. Additionally, the reader

is sometimes lost in the text, which component is exactly meant. A clear flow diagram with unique notations would help.

Fig. 9: The unit of XCO_2Difference is probably not ppm? The legend suggests unitless, as it is normalized. Why the data starts negative? It should result in a drift from the positive side, as it is normalized to the difference to the previous interval?

Supplement Fig. 4: How do the inlets look like? Are they ice shielded? Do you have any lightning protection?

Minor corrections (page/line):
1467/15f: (Jeong, et al. 2012) and (Deeter et al., 2012) are missing in the reference list.

1493/18: stored in an array. Why array? Just "stored." is enough.

1498/12: Start a new paragraph before "The range ..."

1514/2: "fantastic resource" sounds funny in a scientific publication.

Fig. 7: Legend: Please, be consistent with the text: use u_ex instead of u_ext.

Fig. 8: b) CO unit is not ppm, but ppb?

Fig. 11: The name of the vertical axis might be changed, as standard deviations are also shown.

Fig. 14: Legend: Description is mixed up: a) is Picarro, b) is Licor not vice versa.

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