Atmos. Meas. Tech. Discuss., 1, S264–S273, 2009
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Atmospheric Measurement Techniques Discussions



# *Interactive comment on* "Methodology and calibration for continuous measurements of biogeochemical trace gas and $O_2$ concentrations from a 300-m tall tower in central Siberia" *by* E. A. Kozlova et al.

**E. A. Kozlova et al.**

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We would like to thank both reviewers for their positive evaluations of our work and useful comments which helped to improve this manuscript.

Reply to Reviewer #2:

On page 284 isotopic measurements from flasks are mentioned. Is 14C-CO2 indeed analysed from flasks?

We apologise for erroneously mentioning the 14C-CO2 flask analyses in the text. Up to date, air samples have been analysed for only 13C-CO2 and 18O-CO2. We would



Full Screen / Esc
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Interactive Discussion
Discussion Paper

have liked to add 14C analyses as well (in fact, we were planning to do so in the beginning), however, larger flasks are needed for such analyses which would create many additional logistical problems.

I assume that the authors have tested all parts of the equipment. They report repeatability of the Target Tank measurements (page 303/304), however I urge them to provide any additional information they have that shows that 40um filters, nylon unions and rotameters do not influence the measurements. (Page 286)

The reviewer raises a very important point that the Target Tank (or any cylinder) alone is not an adequate measure of system repeatability. For that reason, we also reported repeatability from the ambient air measurements themselves (Table 2), and based on these good results, we gain confidence that all other components (such as filters, nylon unions and rotameters) do not influence the measurements.

In addition, we did test all important parts of our system particularly where the wetted materials could potentially interfere and change the composition of air. Particular care was taken to select materials less prone to oxidation (like stainless steel) and with the least permeability to O2 (being the most difficult gas species to measure of the ones presented in the paper). All filters are composed entirely of stainless steel, and we have now mentioned this in the text. Each line has only one nylon union (at the entrance of the measurement laboratory; needed for lightning protection), which is negligible in comparison to the total length of the Synflex tubing needed to sample from the 300 m tower. The Synflex tubing itself is made of two layers of plastics with an intermediate layer of aluminium but we can confidently say that these materials do not affect the air composition in the sample lines with high flowrate and low residence time. There does remain an outstanding question if slower flowrates and high residence times with Synflex tubing may create artefacts, as we have discussed in Section 4.1. If present, however, our data show that these effects are minor (for O2) and negligible for all other species. Another crucial concept of our measurement system is the constant purging of the sampling lines (even when not in use) that allows us to establish pressure



**AMTD**

1, S264–S273, 2009

Interactive Comment



equilibrium in the whole measurement system.

On page 289, the authors state that changes in ambient pressure only change the bypass flow, but not the flow through the analyser. I am a bit doubtful about this; I think that both flows would be affected.

There may be very small fluctuations in flow through the analyser caused by changes in ambient or upstream pressure, as the reviewer suggests. However, we have found these to be below the level of detection of our flowmeters, even given quite significant changes in upstream pressure (much greater for example, than any possible changes in ambient pressure). We have observed that despite the relatively large changes in the bypass flow, which can happen for example when using several cylinders during calibration (owing to slight differences in the regulators' settings), the analysers' flowrate has been quite stable. However, we cannot state that there are absolutely no fluctuations in the analyser's flowrate owing to changes in the upstream pressure, this would have to be tested using much more precise equipment than ours, but we found that the flowrate stability that we achieve is sufficient for the precision goals of the O2 measurements. To minimise the mentioned fluctuations in the upstream pressure we always set the outlet pressure of all cylinders to be approximately the same with the air pressure from airlines.

Page 295: The long term stability of WSS tanks is assessed by analysis of long term secondary standards 3-4 times a year. Please provide information that regulators are well purged and seasoned before analysis so that no old gas sitting in the regulators will be analysed. Also, are 3-4 analysis per year enough to provide sufficient calibration points?

The reviewer raises an important point, which should always be considered when a calibration cylinder is only used periodically. Our LabView program allows for longer purging times prior to analyses of LSS cylinders (in comparison with the more frequently used WSS cylinders). We have added this clarification to the text.



**AMTD**

1, S264–S273, 2009

Interactive Comment



The S2 scale correction based on trends observed from periodic analyses of LSS cylinders can only be applied when a sufficient amount of data (usually over several years) has been collected. We wrote that unfortunately LSS cylinders were not available at ZOTTO for most of the period of measurements. Our suggested frequency of LSS analyses of 3-4 times per year is based on the experience obtained from Ralph Keeling's laboratory and his long-term record of S2 level stability.

Page 300 and 301: The authors suggest possible reasons for the poor performance of ND21972, possible a leak. A large leak should show up in the pressure measurements of tanks, does it?

The reviewer raises a good point; however, the size of a leak we are referring to would not significantly influence the pressure depletion rate measurements of this cylinder, and we have added this clarification to the text. The precision of the cylinder pressure measurements does not allow for detection of such small pressure changes, and the leak would have to be at least 'snoop-detectable' to be somewhat seen in the overall cylinder pressure changes.

The authors speculate that the stabilisation of the FID and ECD detectors took $>$2 months. Were these brand new, off the shelf detectors? I find it otherwise hard to imagine that it took so long for them to settle down.

The detectors were relatively new, however, we did observe a very long stabilisation period in the performance of both the methaniser and the ECD, and this result was strongly backed up in an analysis of variations in our calibration parameters over time. With respect to the ECD our experience has also been confirmed by other colleagues (e.g. A. Jordan, pers. comm.).

P 319, Figure 3: Any explanation for the strong baseline shift of the O2 measurements, shown in Figure 3?

The strong O2 baseline drift is mainly caused by temperature variations (this has been



**AMTD**

1, S264–S273, 2009

added to the text). The Pink Box's temperature is kept very stable (+/-0.006°C), however, even such a degree of stability does not completely eliminate the baseline variability. Nevertheless, the baseline drift itself does not adversely affect the reproducibility of our O2 measurements since the reference gas (referred to as WT) measurement brackets every air measurement allowing corrections for short-term baseline variations. In addition, it is important to note that the magnitude of the observed baseline drift has to be evaluated relative to the measurement precision and the abundance of O2 in the atmosphere. For example, the magnitude of the O2 sensor baseline drift shown in the figure corresponds to a change of only 0.006% in the atmospheric O2 concentration.

Technical corrections: P 283, L 23: order of citations 1995, 1997, 1998

Done.

P 296, L 20: Is the height or the area used? What determines when which is used?

The peak heights are used for all species. The reproducibility of the same chromatograms calculated both with height and area was compared, and the parameter which provided us with the better result was selected for the routine calculations. This clarification has been added to the text.

P302, L 9: Can you give a % value for these tolerances?

We agree with the reviewer that quantifying these tolerances would be helpful. However, since our installation was in the preliminary stages of operation, we were still adjusting and optimising these values during the time period of measurement. Thus, we would prefer not to quote values in the text, since the optimal values were still being fine-tuned over the period of measurement.

P 305, L 10/11: not clear what is meant by this

This has been re-phrased for clarity.

P 305, L 18-20: please can you rephrase this sentence, it is not clear.



**AMTD**

1, S264–S273, 2009

Done.

P 305, L 17: Comma behind ’is’

Done.

P 307, L 22: Comma after ’tubing’

Done.

P 314, L 17-21: I can’t find the Zhou et al. reference in the text.

Neither can we. The reference was removed from the text.

P 316, Table 2: A suggested change for the headers of the table, "Repeatability achieved", "from Target Tanks", "from airlines".

Partially changed.

P 317, Fig 1: Diagram is very detailed, could it be simplified? In the figure caption could you replace "in actuality" by "in reality"?

Our diagram is indeed quite detailed. However, every piece of equipment shown in the diagram is discussed in the text. We think it is necessary to provide such a detailed schematic owing to the focus of our paper being on the development of an integrated and automated system.

’In actuality’ is replaced by ’in reality’.

P 320, Figure 4: Could you please add a zero line in the top diagram "CO2 difference"

Done.

Reply to Reviewer #3.

This paper is generally well written and informative, highlighting the standard of atmospheric monitoring station that can be achieved by a big research group with a big budget. The main complaint with the written text is that the Concluding Discussion



**AMTD**

1, S264–S273, 2009



section falls between two stools. If it is a conclusion it is far too long; if it is discussion then it is very repetitive of preceding section. This would benefit from including only the major highlights without providing details of precisions and sampling heights again. Suggestions for further improvements or development work, currently buried in S207 this section, could also be highlighted here.

We respectfully disagree with the reviewer about the structure of our Concluding Discussion. The concept behind the contents of this section is both to summarise the text from the previous sections and to add some points (which we consider to be important), which have not been discussed earlier and would otherwise be buried in the text. For these reasons this section in our opinion should have something from both 'conclusions' and 'discussion', which also facilitates the reading of the manuscript for those less interested in all technical details presented in other sections.

Given the effort that has gone into the set-up would it not have been possible to rationalize the analysis intervals and timings so that each species was measured every 15 minutes? This would aid direct correlation of species during short synoptic events and simplify incorporation into global databases.

The three analysers incorporated into this integrated system have very different characteristics from each other. Each was first optimised separately to produce the best possible results for that particular instrument; the second step was to take into account the influence of those optimisation parameters on the other analysers' performances. We finally obtained an optimised situation with an O2 and CO2 measurement every 16 min, and for the GC species every 12 min. In our experience there is no need for any further 'timing optimisations' of these measurements. We do not require high-resolution measurements as would be necessary for example in the case of eddy covariance technique for direct flux estimates. The difference of 4 min in the measurement frequency of different species is not crucial as we do not expect any significant atmospheric changes (which would be of interest to our study) to occur at such short time scales.



**AMTD**

1, S264–S273, 2009



Page 282 - Abstract - Too many sentences starting with 'we'

Changed.

Page 282 - Line 20 - decide whether this sentence should be singular - driver, is, concentration, or plural, drivers, are, concentrations.

Done.

Page 283 - Line 23 - citations should be in date order.

Done.

Page 283 - Line 27 - 'changes in photosynthetic and respiration activities in the local ecosystem' is better

Done.

Page 284 - Line 9 - remove the second 'in Europe'

Done.

Page 287 - Line 12 - How is the level of ethanol in the trap maintained? Is this checked by the on-site scientist?

We have a lid on the top of the chiller to prevent the liquid's evaporation. For this reason, the level of ethanol needs to be checked only very rarely and was usually done during our own visits to the site (twice a year).

Page 292 Lines 12 and 20: How often are the Mol Sieve traps checked and how often do they need replacing?

We did not replace any of the existing Mol Sieve traps during the time the system was in operation. In the presented setup, all GC carrier gases (except Ar-CH4) are supplied by gas generators and therefore require very little further purification and a very rare replacement of the purifying traps.



**AMTD**

1, S264–S273, 2009





Page 301 - Line 5 - Cylinder ND21972 - As the reason for the drift down in O2 ppm Equiv is put down to a 'larger' leak from the cylinder, was it noticed that the pressure in this cylinder was dropping at a faster rate.

Please see the reply to the first reviewer above.

Page 303 - Line 17 - Given that the precision target for CO has not been reached using the methaniser, what where the reasons behind choosing this method for CO analysis instead of a Reduced Species Analyser such as the PP1.

The reason for not reaching the required precision for CO measurements when using the methaniser is not the limitation of the technique itself but the difficult conditions under which we were operating the system (for example, very rare visits to the site, limited time to optimise the system, absence of remote access to the system). This was further confirmed by the fact that the same GC system has been producing very high-precision CO measurements after being moved to a different location (also remote but much more accessible). Other groups also previously reported high-precision CO measurements using the same technique (for example, see the reference to Worthy et al., 2003). In addition, there are two more reasons why we would not have chosen to use a different technique for CO measurements. First, a different measurement technique for CO would require an additional analyser (because we would still need a GC with FID and ECD for CH4 and N2O measurements), which would make our system more complicated and less flexible. Second, the FID response to CO is known to be linear, which is an advantage of this method over the Reduced Species Analysers (which have non-linear responses).

Page 304 - Line 21 - Regarding the lack of explanation for the 300m height data in late 2006, could there be a meteorological explanation. The manuscript has no mention about measurement of meteorological parameters, although temperature measurements from each inlet height should be essential data, particularly if there is the possibility for inversion heights being below the top of the tower at this site.



**AMTD**

1, S264–S273, 2009



Unfortunately, there was no meteorological equipment installed on the tower at the time of our measurements. Our site was still very new and although the installation of the meteorological equipment was always our intention it could not be done until June 2007 for logistical reasons.

Page 308 - Line 12 - Was the influence of tower construction on the 4 and 52m height data for 2005-06 quantified?

Our system was not running during the actual construction of the tower. The tower was built up to 52 m in summer 2005. In September-October 2006 the tower was constructed up to 300 m and we had to halt all measurements for this period.

Figure 2 - Caption requires more explanation. The text explanation refers to only 2 of the graphs.

Additional description was added to the text and the Fig. 2 caption.

Figure 3 - The source of the baseline cycling in raw O2 is not clearly explained in the text.

See the reply to the first reviewer above.

Figure 4 - caption - ppm Equiv - sometimes a space between these, sometimes not -need to stick with the correct protocol.

Done.

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Interactive comment on Atmos. Meas. Tech. Discuss., 1, 281, 2008.