

## ***Interactive comment on “Continuous measurements of atmospheric oxygen and carbon dioxide on a North Sea gas platform” by I. T. Lujikx et al.***

**A. Manning (Referee)**

a.manning@uea.ac.uk

Received and published: 21 October 2009

Lujikx et al. present a methodology for high precision atmospheric O<sub>2</sub> and CO<sub>2</sub> measurements at a remote location, in their case from an oil and gas platform in the North Sea. The paper is interesting, fairly concise, and well-written. The methodology presented is similar to that which has been published by others, but with several notable novel features which make this paper publish-worthy. Novel features include: integration of CarboCap CO<sub>2</sub> analysers with an Oxzilla O<sub>2</sub> analyser, chiller switching mechanism, lower reference gas flowrate in comparison to sample gas flowrate, and of course the very unique sampling station itself. The main deficiency of the paper is the ab-

C622

sence of information, discussion, and perhaps pertinent experimental tests on a few key points which I describe below.

I recommend publication, with the following suggested revisions, partitioned into more or less significant revisions:

Significant:

P. 1696, L.10-11, and elsewhere: All NDIR CO<sub>2</sub> analysers are known to have non-linear responses, even those that attempt to apply internal linearity corrections. But only 2 calibration cylinders have been used to routinely establish the Carbocap CO<sub>2</sub> response function. Please can you comment if you have done non-linearity tests in the laboratory? And comment on your estimate of additional imprecision added to your measurements because of only using 2 calibration cylinders (perhaps the non-linearity response is relatively constant over time, and thus if this response is calibrated in the laboratory, 2 cylinders could then be enough at the remote site?). This could (should?) be an additional topic to add to your future improvements section on P. 1709.

P. 1697: 5-minute ref/sample switching with an Oxzilla is much slower than that used by others (and as already published in several papers). I imagine this slower switching has been forced upon you because of the slow sweepout time of the CarboCap analysers downstream, and also because of the slow (compared to other workers) reference gas flowrate of 40 mL/min. Please comment further on this switching time, and also describe in greater detail the Allen variance test done to determine the optimal number of data points for averaging. It would also be worth explicitly citing the other papers and stating that this time is slower than they used – one objective of a new paper such as this is to highlight differences from previous work, discussing their advantages/disadvantages. (Similarly, please also describe in further detail the Allen variance optimisation for the CarboCaps (P.1702).

P. 1697-1698: why have you not used an aspirated air inlet? (see Blaine et al., ACP, 2006). It has been well documented that at low flowrates such as used here, there are

C623

likely to be O<sub>2</sub> fractionation problems at the air intake, unless an aspirated inlet is used. Have you carried out tests to prove that your own inlet design does not cause such fractionation problems? (which appear to be related to ambient temperature changes, and the existence or absence of direct sunlight on the intake).

P.1698: As with Reviewer #1, I am concerned regarding use of a Nafion dryer. The authors cite Neubert et al. (2004) for more details, however, the only details I found in that paper were: "Since the composition of this dry air is almost identical to that of the inlet air (the dry air is actually the inlet air from a short time before), the risk of influencing the sample air composition due to eventual diffusion processes through the membrane is minimized."

- In other words, it appears that there has been no testing, and reliance only on a theory. This is not acceptable in the world of high precision O<sub>2</sub> measurement. I am aware of some brief, unpublished Nafion O<sub>2</sub> tests by B. Stephens, but I am not sure of the results, only that Stephens concluded \*not\* to use these dryers in his work. The Ph.D. thesis of R. Langenfelds (2002) discusses Nafion tests for O<sub>2</sub>, apparently with encouraging results, but for flask sample collection, not for continuous measurement. Ideally, the authors should carry out their own tests – if they have not already, I strongly encourage them to do so, and in this paper, either discuss the results obtained, or add these tests to the future improvements section of the paper.

P. 1698: has the KNF pump used being tested for O<sub>2</sub> and CO<sub>2</sub> measurement? If so, please state, and/or cite appropriate literature. State also the wetted materials of the pump.

P. 1698: the reference gas flowrate of 40 mL/min, being lower than the sample flowrate is a significant departure from 'typical' usage of an Oxzilla system, and thus should be discussed in greater detail. First state the motivation, which I assume is to increase the lifetime of reference gas cylinders. Second, state what tests, if any, were done to demonstrate no (or little) loss of precision by employing different flowrates, and also the

C624

length of time needed to wait to reestablish equilibrium after switching the changeover valve. Again, I am aware of unpublished tests by B. Stephens attempting to do this, and again, I believe his conclusion was not to go ahead with such a design with ref/sample flow differences.

- on further investigation, I could not find anywhere mention of the sample gas flowrate. What is this? Please state. Perhaps the above is incorrect, and you also have an equivalent slow sample gas flowrate??

P. 1698, L26-28: this sentence is incorrect. Have a look at any vacuum extraction system employing glass traps immersed in liquid N<sub>2</sub> (I believe you have many in Groningen), and you will see that all the water vapour freezes at the liquid N<sub>2</sub> interface, not deeper in the traps, and the presence of glass beads will not improve the water trapping efficiency (the reason hypothesised is that any remaining water is in the presence of ice crystals, which will not stick to either the walls or glass beads, but will be swept out of the trap). The main reason most of us use glass beads in such cryogenic traps is to reduce the volume of the trap, thus reducing the residence time and reducing the time to re-establish the O<sub>2</sub>/N<sub>2</sub> gradient within the trap after any flow/pressure disturbance (e.g. switching any valve upstream or downstream).

How long is the 1/4" Synflex tubing from the air intake to the measurement system? What is the residence time of the sample air in this tubing? What is the total residence time from the air inlet to the analysers? I think Reviewer #1 may have asked these questions also.

P. 1699: I am not sure of the typical lifetime of Valco 2-position valves, and I imagine that this is heavily dependent on the rotor material chosen. The valve upstream of the Oxzilla, switching every 5 minutes, will switch over 100,000 times in one year – is the valve rated for this? Please state the rotor material used, the manufacturer's stated lifetime of the valve+rotor, and planned routine maintenance checks to ensure no cross-port leakage – this is a subtle, but influential problem, which can easily go

C625

unnoticed.

Equation 5 is incorrect and should be deleted. The correct relationship between ppm and per meg is 6.04 per meg / ppm, and this can be seen from the author's following Equation 6, setting  $\Delta_{CO2}$  to zero. Unfortunately, the original Keeling et al. (1998) publication giving the 4.77 value has been repeatedly misunderstood by many in the O<sub>2</sub> community. Keeling et al. (1998) are not wrong – they have simply been misunderstood. Please read (and cite) Kozlova et al., GBC (2008), paragraph 17, for the first published clarification of this common error.

- Note: on P.1707, 4.77 is the correct factor to use to determine the O<sub>2</sub>/CO<sub>2</sub> ratio (since here a comparison is being made to CO<sub>2</sub>), but it is incorrect to write 'converted to ppm'. To avoid confusion, I suggest to delete this sentence entirely, and add units to the ratio value of -1.31, namely 'moles of O<sub>2</sub> per mole of CO<sub>2</sub>'.

P.1705: a better design would be to measure the Target cylinder at least twice as often as the routine calibrations – in this case, at least every ~11 hr. One reason is that if it is always measured the same length of time after a calibration, possible aliasing effects will not be noticed. Two Target measurements within each calibration cycle would provide much more robust data quality checking.

P.1706: 'This compares well to...' – it would assist the reader and be more scientific if you gave some quantities here – what were the seasonal cycles of these other stations? If there were differences, it might be interesting to discuss possible reasons. You could possibly also compare to the O<sub>2</sub> and CO<sub>2</sub> amplitudes found at two other stations at approximately the same latitude: Shetland Islands and Zotino Tall Tower, as given in Kozlova et al., GBC (2008). One fact I find immediately interesting is that the F3 CO<sub>2</sub> amplitude (16 ppm) is almost identical to Shetlands (15.4 ppm), but the F3 O<sub>2</sub> amplitude (110 per meg) is significantly smaller (SIS = 163 per meg).

P.1708-9: regarding the large negative excursions in O<sub>2</sub>: Manning (Ch. 4.4, 2001) also observed a very similar feature, in that case of about 100 per meg – possibly,

C626

you might like to cite this work. Similarly, at first glance, CO<sub>2</sub> appeared to be constant in Manning's observations, but upon closer examination, CO<sub>2</sub> was found to increase, albeit by a very small amount in comparison to the very large O<sub>2</sub> change – this finding is consistent with suspected upwelling waters, which could be expected to have anti-correlated effects on O<sub>2</sub> and CO<sub>2</sub>, but with the CO<sub>2</sub> effect significantly dampened. Can you look for a similar CO<sub>2</sub> effect in your results? Possibly the imprecision of the CarboCaps might preclude such an analysis?

- I am not sure what is meant by supported by wave period measurements – please explain (I note that Reviewer #1 has asked for more details here too).

- please state the wind direction, and importantly, the wind speed during the period of observations. This has a significant impact on the following hypothesis that the observed atmospheric O<sub>2</sub> changes were due to a marine O<sub>2</sub> sink.

- are satellite SST data available for this time and location? This might also support (or not) the upwelling hypothesis.

- Reviewer #1 has suggested a slightly different approach to the marine O<sub>2</sub> uptake examination. As a further extension, I would suggest to calculate the (ballpark) expected change in ocean O<sub>2</sub> in mL/L corresponding with the observed atmospheric change. Then see if any data exist from the North Sea showing such observed changes in North Sea dissolved O<sub>2</sub>. This may perhaps be easier to grasp than the present discussion of 10 % saturation and 3500 per meg. I will email the first author such a calculation I did (unpublished) as an extension to the event mentioned above and discussed in Manning (Ch. 4.4, 2001).

- these events are perhaps the most 'exciting' to come out of the work. As such, it may be worth adding a sentence about them in the Abstract.

P. 1709: you could perhaps compare your APO seasonal amplitude with that of the other stations discussed on P. 1706. I think you should clarify that any correction for

C627

fossil fuel influences is likely to be relatively small.

Fig. 1 (and corresponding text): I would strongly suggest to move the needle valves and flowmeters which are immediately upstream of the Oxzilla, to be immediately upstream of the 4-way changeover valve. Especially the needle valves, which represent a flow restriction. Making this change will result in faster sweepout times for the Oxzilla and CarboCap cells, allow for more data points to be averaged, or conversely faster switching of the valve. If the authors are in agreement with this suggestion, they could add it to the further improvements section.

Fig. 4: There is a notable drop and then recovery in O<sub>2</sub>/N<sub>2</sub> between 18-21 Jun – do you have an explanation for this? If you do, it would be good to discuss it in your text, because it adds insight into what the Oxzilla analyser is sensitive to.

Less significant:

It is confusing to refer to 'mixing ratios' in this paper, considering that O<sub>2</sub> 'mixing ratios' are reported as O<sub>2</sub>/N<sub>2</sub> ratios, but these are different ratios. It might be correct to refer to 'O<sub>2</sub>/N<sub>2</sub> ratio mixing ratios', but this would confuse everyone. I suggest to write 'O<sub>2</sub> concentrations', together with 'O<sub>2</sub>/N<sub>2</sub> ratios' where appropriate. For consistency, I also recommend to use 'CO<sub>2</sub> concentrations'.

Abstract and P.1707: The lack of night-time inversions is certainly a contributing factor to the low observed day to day variability in comparison to continental stations, but I suspect that the remoteness from large local sources and sinks to be a more dominant factor.

The word 'data' is plural. See, e.g. Abstract: 'data is' should be 'data are'.

P. 1694, L. 8: delete 'to our knowledge' Also P. 1695, L.29

P. 1694, L.10: delete 'additional'

Abstract, last sentence: this sentence (large excursions) appears to contradict the one

C628

just above it (low day-to-day variability). I understand what is meant, however, I suggest a re-wording.

P. 1695, L.1-3: sentence is vague and unclear.

P. 1695, L.4: add 'absolute' to 'The absolute variations of O<sub>2</sub>...'

P. 1695, L.11: 'decennia' should be 'decade'

P. 1695, L.14: need to add the GC technique for O<sub>2</sub>/N<sub>2</sub> measurement, that is: Tohjima, Y., Method for measuring changes in the atmospheric O<sub>2</sub>/N<sub>2</sub> ratio by a gas chromatograph equipped with a thermal conductivity detector, Journal of Geophysical Research-Atmospheres, 105 (D11), 14575-14584, 2000.

P. 1695, L.20: for continuous O<sub>2</sub> measurement, suggest to add the first and longest-running example of these: Manning, A. C., Temporal variability of atmospheric oxygen from both continuous measurements and a flask sampling network: Tools for studying the global carbon cycle, Ph.D. thesis, University of California, San Diego, La Jolla, California, U.S.A., 2001.

P. 1695, L.27: local effects are not 'avoided', rather there are simply not many of them at the chosen location. Suggest to reword.

P. 1696, L. 23: give company name of the Max-250 (Maxtec Inc.). Also, there are different Max-250 models, suggest to give more explicit model number (probably 250B?).

P. 1697, L.12: for this ref/sample switching, please cite Stephens et al., JAOT, 2007. (the first person to setup such testing with an Oxzilla).

P.1698, L.9: I am not familiar with any KNF pump model number starting with 'PM', and could not find such a pump on their web pages. Are you sure about this model number?

P. 1698, L.12: 'multivalve' to 'multiposition valve'

C629

P. 1698, L.13 – same problem as mentioned by Reviewer #1 on P.1697, L8.

P. 1698, L.17: is 'Bronckhorst' the Dutch-variant spelling for this company? If so, no worries. I am only familiar with the German 'Bronkhurst', but the Germans are known to have messed up Dutch spelling :-)

P. 1698, L.25: do you have 2 Neslab CC-100's? It is not quite clear to me how you warm up one system while the other remains cold – I can only imagine that you have 2 Neslab's? Please clarify.

P. 1699, L.6: actually, the pressures in the sample/ref lines could be different from each other. What is most important is that these pressures be kept very stable. In applications such as these, it is easiest to simply keep them identical to each other, but it is not a requirement.

P. 1699, L.10: MKS precision of 0.3% F.S. – why so bad? Seems to me that you have a control problem, since these controllers usually control at much better than this. This could likely be a partial explanation for problems with the O2 precision obtained.

P. 1699, L.14: since a few years, Dekabon changed their name to 'Synflex'. Please also state which kind of Synflex tubing – 1300, perhaps?

P. 1700, L.12: state that the '% O2' values are those reported directly from the Oxzilla.

P. 1701, L.9-15: I found this section unclear. Try to reword. In particular, I do not understand 'consisting of several weeks', since you have already stated that you do a calibration every 23 hours. It sounds like you are averaging the results from all these calibrations, which can't possibly be true?!

P. 1701: Keeling et al. (1998) has been cited for Equation 6, however, that paper did not present a CO2 dilution correction (as stated in that paper, their equation was given on a CO2-free basis). Stephens et al. (2003) have a similar equation, with CO2 correction, but have an additional term specific to their VUV analyser which confuses matters for the application discussed in this paper. Therefore I suggest citing Kozlova et al., GBC,

C630

(2008) for this equation.

P. 1701: In Eq. 6, there is also a potential for confusing the constant term 'XO2' with the term 'delta\_XO2'. I suggest to use a different label, e.g. 'S\_O2' (or something similar) as used in Kozlova et al. (2008).

P.1701, L.18: 'Further explanation is given in Sect. 3.4' – I didn't find this?

P.1702, L.5: 'in ppm' – I assume that these are the values reported directly from the CarboCaps? If so, please state. While the CarboCap may well report in 'ppm' units, the way you employ your calibration cylinders, you do not actually treat them as real 'ppm'. If so, it might be less confusing to simply state 'Carbocap units', rather than ppm.

P.1702, L.13: delete sentence 'There is no need for...' – I think you mean relative to the so-called O2/N2 mole fraction to per meg conversion, but this is just confusing, and best to delete – since you \*do\* actually convert the raw CarboCap ppm values to 'real' ppm values, via your calibration data.

P.1702, L.21-29: some of this is repetitive and the rest of it belongs in the Introduction. Please delete/move as appropriate.

P.1704, L.4: change 'fills air flasks' to 'fills flasks with air'

P.1704, L.5: write 'CIO' (in full) in front of 'lab'

P.1705, L.5: what does 'satisfactory' mean?

P.1706, L.23-24: change 'seasonal cycle of delta\_O2/N2' to 'seasonal cycles' since refers to CO2 also.

P.1707, L20: suggest to add the  $r^2$  value for what I assume is a linear least squares fit line?

P. 1709: Is delta\_CO2 in Equation 7 really the same as in equation 6? On the Scripps O2/N2 scale, it is not, since an arbitrary factor of 350 ppm is subtracted in the APO

C631

equation, compared to 363.29 ppm in the O<sub>2</sub>/N<sub>2</sub> equation. I realise, however, that these data are not on the Scripps scale, so I ask only for clarification.

P.1709, Discussion: this text is better suited for the 'outlook' section. I suggest to move the text, and delete the 'discussion' section entirely.

P.1709: Please state the motivation for wanting to make the suggested changes. Why would, or might, these changes lead to better results?

WMO reference: year should be 2009, not 2008.

Fig 3: the human brain is wired to think of blue as oceans, not land mass! – can you change the colour scheme? (I've had this problem in a couple of your presentations too – perhaps it's because I'm not a European and so less familiar with the map outline of Europe!).

Fig. 4: I'm not sure if the insets bring any added value to the figure?

Figs 4+5: x-axes could be improved, e.g. I can not see tick marks. Also Figs 8 and 9.

Fig. 5: sigma values should be '±' values – this also applies in the corresponding text.

Fig. 6: again, I am not sure if the insets bring any added value to the figure, and I would suggest possibly deleting.

Fig. 7: suggest to add the value for the O<sub>2</sub>/CO<sub>2</sub> ratio in the caption (repeating from the text).

---

Interactive comment on Atmos. Meas. Tech. Discuss., 2, 1693, 2009.