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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Atmospheric oxygen and carbon dioxide observations from two European coastal stations 2000–2005: continental influence, trend changes and APO climatology" *by* C. Sirignano et al.

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This is an interesting manuscript, presenting and analysing a new dataset of atmospheric O_2 and CO_2 concentrations from 2 European stations, and presenting some interesting discussion, for example regarding use of the APO tracer at stations with non-trivial anthropogenic influences. Thus the manuscript provides a valuable addition to the field, and should be published.

Having said that, I think that the paper requires a large number of improvements before it will be of a quality acceptable for publishing. The majority of these improvements are of a minor nature, but unfortunately they are very numerous. The long time involved for me to put these suggestions together is such that I was not able to separate out the more important problems from the minor problems – my apologies, both

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Interactive Discussion

Discussion Paper

to the editors and authors. Thus, apart from a few general points listed immediately below, I have made my comments – both major and minor – page by page.

General:

1. The English, while good, is possibly not of high enough standard for a journal publication. This is a decision that the editors should make. I think that none of the authors are native English speakers, thus they may consider enlisting the services of a professional proof-reading company in order to improve the English of the manuscript. I have given a few English-related corrections below, but I have not been comprehensive.
2. The methods section requires much more detail regarding the laboratory analyses. For example, with the mass spectrometer, no information is given regarding how the sample and reference gases are introduced to the mass spec, how their pressures are balanced and equilibrated, if they are further dried, and so on – is their technique exactly the same as discussed in Bender *et al.*, GBC, 2005?, in which case they can cite this paper (but would need to clarify which methodology, since more than one is described in Bender *et al.*), or are there differences?, in which case they must be described. A more explicit distinction between reference and standard gases should be given. Is the reference gas derived from a high pressure cylinder? Regarding the GC analyses, rather than a personal communication to Worthy, the authors should cite the Worthy *et al.* 2003 paper in "Canadian Baseline Program: Summary of Progress to 2002". In addition, many more details should be given, since these authors do not have exactly the same techniques as in Worthy *et al.* (e.g. for CO analysis, pre- and main columns are reversed). No mention is given of carrier gases, carrier gas flows, run-times, purification techniques used, sample loop volumes, etc. These must all be given, or else appropriate literature cited.
3. The authors alternate between using the words "concentration", "mixing ratio" and "mole fraction" – please be consistent throughout the paper, and only use an alternative if there is a strong reason for doing so. This issue is further confused by discussing both "mixing ratios" and "O_2/N_2 ratios" sometimes in the same sentence, and then going on to mention "oxygen mixing ratios" (e.g. Abstract). This is extremely confusing. Thus I would suggest to consistently employ the word "concentration", and to make clear that atmospheric O_2/N_2 ratios are used as a proxy for O_2 concentration.
4. It is awkward to use the unit "micro-mol*(mol dry air)^-1" throughout the manuscript. The authors state that sample air and calibration gases are either dry or dried prior to being analysed, and this is sufficient to justify removing "dry air" from the unit. The authors might consider further to simply replace the unit they use with "ppm", which although having a subtlely different meaning, is an

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accepted unit within the carbon cycle community – the authors even claim themselves that the 2 units are identical (p. 20122).

5. There are numerous problems with the references, with many missing from the reference list, and others in the list, but I think never cited. Please pay careful attention to fixing these errors – I have not spent the time to note them below, other than to state when I think that inappropriate references have been used.
6. There are several examples where the authors have used the word "anthropogenic" incorrectly. Typically, the authors actually mean fossil fuel (and cement manufacture), yet by definition, "anthropogenic" could also refer to land use change influences. (e.g. pp. 20115, 20129).
7. The authors seem to randomly swap between "O_2" and "oxygen". I suggest to write "oxygen (O_2)" in the first example in the paper, and thereafter to consistently use the shortened form. To a lesser extent, the same problem occurs with "carbon dioxide" and "oxygen-nitrogen ratio".

Page Specific:

p. 20114:

1. change "land biota" to "land biotic"
2. what is "O_2 fraction"?

p. 20115:

1. the ratio of carbon uptake between the land biosphere and oceans is not stable even now, so it is not quite appropriate to consider "how stable the ratio will be in future" – I suggest to reword this sentence.
2. "production statistics" is ambiguous, and "anthropogenic" used incorrectly (see above).
3. "decennial" is incorrect here, meaning lasting for or recurring every 10 years. The authors should use "decadal" which means a time period of 10 years.
4. "directly reconstruct" – remove "directly"

p. 20116:

1. "annual oxygen concentration changes" and "annual fluxes", should each say "seasonal. . . ". It may also be worth clarifying at this point that seasonal amplitudes vary with latitude.

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p. 20117:

1. Friedrich *et al.* citation – I'm not sure if it's appropriate to cite an internal project report such as this. Perhaps a better citation could be Gurney *et al.*, JGR (2005), or citations to the 'Vulcan' project.
2. first use of CIO, expand in full.
3. inappropriate citation to 2x Tans *et al.* papers – these papers did NOT discuss O_2 measurements.
4. paragraph starting "We present. . . " I think better belongs in the last paragraph of the Introduction, where the authors discuss the 2 stations presented in the paper.

p. 20118:

1. Remove "and atmospheric CO_2 concentration observations" from first sentence.
2. delete sentence beginning: "After all, atmospheric O_2. . . "
3. When mentioning the previous atmospheric O_2 observation studies, I suggest to add a citation to Tohjima *et al.*, Tellus, 2008.
4. line 13-14 – unclear what is the "measured data" and "model results".
5. first use of APO, need to write in full.
6. sentence beginning "For clean air stations" – this is only correct on short time scales, and is incorrect, for example, on interannual timescales. Please correct.

p. 20119:

1. discussion on winds observed at Lutjewad is confusing. First the authors discuss northerly winds as being continental. Later in the same paragraph they discuss south-westerly and westerly winds as coming from the continent. In fact, westerly winds would be coming from the North Sea, and I'm confused how the northerly winds fit into the picture. Please clarify. It may also aid the reader to give approximate percentages when the wind is coming from the dominant directions for a typical year.
2. delete sentence starting "Air flask samples. . . " - this belongs in the Methods.
3. I do not think that the goal was to examine O_2/CO_2 ratios, but rather O_2 and CO_2 data. Please clarify.
4. "testcase" should be 2 words

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Interactive Comment

p. 20120:

1. Start a new paragraph at: “Air is collected. . . ”
2. air is not “carried” to the laboratory. I presume a pump is used. This should be clarified, and, because of the importance of sampling pumps to atmospheric measurements, make and model of the pump should be given, together with evidence that the pump is suitable for atmospheric O_2 and CO_2 measurements and does not introduce artefacts (either cite previous literature if available, or mention internal laboratory tests). This also applies to the pump mentioned at Mace Head station.
3. to what pressure are the flask samples filled?
4. “cryogenic drying” is too vague – please state to what dewpoint the samples are dried.
5. delete sentence on “restricted baseline conditions”, as it was stated on the previous page.
6. start sentence beginning “The regular laboratory. . . ” as a new paragraph, and make clear now discussing samples from both stations.

p. 20121:

1. equation 1. does NOT give delta in units of per meg, as stated, but rather per mil, since the factor of 1,000 is used, not 1,000,000.
2. I assume that the “idle time” refers to the lag after switching. Why is this so long? Other mass spectrometer systems have a lag of about 1 second, compared to 120 sec here.
3. delete the phrase “as for the GC measurements”, since the GC has not yet been introduced.
4. Were CH_4 and CO data actually used in the calculation of APO, as apparently stated here? If so, this is inconsistent with the earlier discussion of APO in the Introduction, so the Introduction needs to be modified, clearly stating how CH_4 and CO are used.
5. Hewlett Packard should be Agilent
6. Worthy and Huang (2005) and Miller (2006) refs are missing from the reference list.

p. 20122:

1. it is not clear if the sample actually passes through the membrane pump. Please clarify. If it does, then the pump is crucial, so please state make and model, and if it has been tested to not produce any artefacts.

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2. It is dangerous to screen data based on the criteria of high concentration values alone. CO and CH_4 cut-offs of 300 and 2000 ppb respectively will most likely remove real ambient data, especially at the LUT site.
3. Please state what percentage of data were removed based on the various rejection criterias applied (also in the fitting procedure described on following page). This information can be relegated to Figure caption, if desired.
4. Please clarify if the fitting routine results in constant or varying seasonal amplitude and phasing.

p. 20123:

1. the discussion about "longer and flatter winter [passages]" is only true for CO_2, not O_2 – please clarify and fix the following text accordingly.

p. 20124:

1. the authors' text regarding the contrasting response rates in the atmosphere from marine versus land biotic processes is correct, however, two additional considerations have been omitted from their discussion: 1) they have discussed time lags (or the lack of them) for the impact of marine/land processes to be seen in the atmosphere, but they have not discussed possible time offsets in the marine versus land processes themselves; 2) there are definitely some land processes with significant lags, for example, soil respiration processes occur on many different time scales.
2. What does "RBC" mean?
3. Sentence beginning "The Mace Head record. . . " is confusing: discusses phase lags, but actually the winter peak exhibits a phase *lead* whereas the summer peak is a lag. Even more confusing because previous sentence was about LUT *O_2*, whereas now the discussion suddenly switched to CO_2 – I suggest to discuss one species at a time, and clarify if leads or lags.

p. 20125:

1. are the authors implying that the MHD record is not mitigated by the Gulf Stream?
2. I agree that LUT is sampling air masses of much more local origins, but the Gulf Stream is not 'local'.
3. Table 1 gives an O_2 amplitude for MHD of 113 per meg, NOT the values of 102 per meg reported here!
4. Please give a citation for the "rectifier effect"

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Interactive Comment

5. I think it is inappropriate to compare the seasonal amplitudes at MHD and LUT with those found at Puy de Dome and Griffin, since these measurements were at altitude in an aircraft, and clearly seasonal amplitudes attentuate with altitude. Furthermore, it is incorrect to refer to Griffin (in Scotland) as a "continental station".

p. 20126:

1. suggest to replace Prentice *et al.*. (2001) with Bender *et al.*, GBC (2005).
2. I am not sure why the authors have chosen to compare to the period 1990-2000 from Manning and Keeling (2006). That paper also presents data from 1993-2003, a time period closer to the author's study, and which is also a more robust estimate by Manning and Keeling. I suggest to change.

p. 20127:

1. "peculiar" is a subjective and non-scientific term, delete.
2. "following paragraph" should say "following section"
3. I do not understand how the MHD or LUT atmospheric observations can be used to derived fossil fuel combustion data??? As the authors later state themselves, these come from inventory statistics such as Marland *et al.* or BP, so I have no understanding what has been done in this paragraph. Please clarify.

p. 20128:

1. (and previous page) discussion surrounding Randerson *et al.* and Ciais *et al.* papers: while both of these papers suggest processes that would result in oxidative ratios smaller than 1.1, the ratios are still significantly above zero. Thus, a rapid change in the O_2 trend as seen in the MHD and LUT records, if caused by terrestrial processes, must also be seen in the CO_2 record – the authors need to state this. I do see a little observational evidence for this in the Fig 3 CO_2 loess fits – it would be easier to observe if the authors zoomed in on the y-axis scale for CO_2.
2. Can the authors also comment on the fact that the observed O_2 trends at both MHD and LUT were *increasing* for the early part of the record, which is very unexpected behaviour.
3. The authors cite the Jungfraujoch dataset from Valentino *et al.*, then go on to say that this dataset provides further evidence for their hypothesis of land processes playing a greater role. However, Valentino *et al.*'s conclusion was the exact opposite, that oceanic processes were the reason behind their observations, and that they could not be explained by land processes. If the authors

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wish to cite this paper here, they need to make clear that they are contradicting the conclusions of Valentino *et al.*

4. Sentence "As final remark. . . " – I am not sure what is being discussed here. At LUT, for example, I see a decrease in the trend in both O_2 and CO_2 at the end of the record, opposite to that stated here.

p. 20129:

1. suggest to cite Keeling and Shertz, 1992, not Keeling *et al.*, 1996.
2. ". . . due to anthropogenic changes. . . " – this is not correct, because land use change is also anthropogenic, with a ratio of approx. 1.1, not 1.4. Later in same paragraph 'anthropogenic' is again used incorrectly – state fossil fuel (and cement).
3. as written in Equations 2 and 3, 'B' and 'O' are carbon sources, not sinks. This is very unusual terminology, and thus must be clarified. Better would be to rewrite the equations with B and O as carbon sinks as typically done in the literature. Line 22 on the same page incorrectly refers to these terms as carbon sinks, further confusing the issue. Subsequent equations in the paper propagate the same confusion.
4. oxidative ratio, phi, also includes cement manufacture.
5. write "w.r.t." in full

p. 20130:

1. the calculation methodology used to derive the global carbon sinks is outdated and no longer used. I suggest to calculate first the oceanic sink using APO data, then calculate the land biospheric sink using CO_2 data. This methodogy, together with its several advantages, has been explained in detail in Manning and Keeling, Tellus (2006), and was also used in Battle *et al.*., Science (2000), Bender *et al.*, GBC (2005), and Tohjima *et al.*, Tellus (2008).
2. (also previous page) should be clarified that phi and beta are *molar* ratios, and that they represent moles of O_2 consumed per mole of CO_2 produced (or vice versa). Otherwise, the values should be negative (which would also impact the equations).
3. Marland *et al.* fossil fuel data are available through to the end of year 2005, in other words, for the full time period shown in this paper, thus there is no need to estimate emissions for years 2002-2005. I suggest to redo these calculations with the consistent fossil fuel dataset.
4. The Raupauch *et al.* reference does not need to be used here at all. All relevant data are in the much more comprehensive and authoritative Marland *et al.*

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p. 20131:

1. as above, please compare to the more recent 1993-2003 results from Manning and Keeling.

p. 20132:

1. the discussion about APO is confusing. First, some of it is being repeated from that given already in the Introduction. Second, the authors main focus is on APO seasonality, but this is not only what APO can be used for, hence this sentence is wrong: “Therefore it is applied to describe the seasonal variation. . . .”. Next, having focussed on seasonal aspects, Equation 6 appears out of the blue, which is for the global budget, making for very confusing reading. I recommend that the authors:

   (a) define APO

   (b) discuss APO in a seasonal context

   (c) discuss APO from a long-term trends / global budget context

making clear distinctions between these 3 aspects.

1. Equation 6 is inconsistent with the given APO definition (and text on p. 20133) where CH_4 and CO should be included. This inconsistency is propagated through the paper, for example in Equation 7.
2. The term (phi – beta) x delta-F is NOT “residual of the terrestrial processes”, on the contrary, it is the residual of fossil fuel combustion processes.
3. I would not say “. . . this assumption can not be used. . . ”, but rather “. . . does not apply as well. . . ”

p. 20133:

1. “high methane consumption” is a bit confusing. I assume the authors mean high natural gas usage, so why not say this? Methane consumption could get confused with natural processes (e.g. wetlands, ruminants).
2. The fertiliser effect on the oxidative ratio (lower than the assumed value of 1.1) is opposite to the effect from methane (higher than the assumed value of 1.1), so I do not see how both of these effects can “add an extra, not accounted for, negative trend to the APO series” – please clarify.

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3. Following sentence suddenly switches back again to APO climatology, after previous sentence was about APO trends.
4. I am not sure what this means: “the reality by the applied transport models.”?
5. Why has only 1 harmonic been used in the fitting function for APO, after using 3 harmonics for CO_2 and O_2?
6. Suggest to start a new paragraph when start talking about TM3.

p. 20134:

1. OPA is not an “ocean biogeochemical model”. I think that the authors are probably referring to the PISCES model.
2. sentence beginning “The model data...” is confusing, since the previous several sentences just described various model input datasets. Do the authors mean meteorological data?
3. Authors have forgotten to state what land biosphere fluxes were used in their model runs.
4. It appears that the authors have not modelled CH_4 or CO fluxes, thus their model-derived APO is inconsistent with the APO derived from observations. This also casts some doubt about all subsequent model / observations comparisons. I think the simple thing to do would be to remove the CH_4 and CO correction from the APO observations (which I suspect are minor – the authors could comment on the sensitivity of including/excluding these species to the APO values) – this would also fix the existing errors in Equations 6 and 7.

p. 20135/37:

1. for what year are the data in Fig 5 derived from?
2. paragraphs have been forgotten – one paragraph spans almost 4 pages!
3. while I think these pages gives a very interesting discussion about possible problems in the typical assumptions used in the definition of APO, I am confused about one thing: if the oxidative ratio used in the definition of APO is wrong (at the particular location of LUT), then this is equally true for APO calculated from observations as it is for APO calculated from the TM3 model. Therefore, how can one explain the model/observation discrepancies via problems with the oxidative ratio? Did the authors also readjust the observations-calculated APO with the new value for (phi – beta) of 0.64? It appears not, based on Figure 6b, and I think this is in error, and the same APO recalculation needs to be done on the observations.

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4. also in this interesting discussion contrasting model/observations APO results, I think the authors could briefly mention some of the conclusions from previous TM3 APO studies compared to observations, most notably Battle *et al.*, GBC (2006) and to a lesser extent Kozlova *et al.*, GBC (2008). The authors' findings for MHD, for example, are consistent with Battle *et al.*'s findings for Cold Bay, Alasaka, but inconsistent with Kozlova *et al.*'s findings for Shetland Islands. Kozlova *et al.* also conclude, in support of these authors, that APO observations agreement with models at mid-continental sites is much more dependent on the chosen oxidative ratio than at marine sites (although their site in Siberia is clearly very different in characteristic from LUT).
5. I am not convinced by Equation 7: first, as mentioned above, inconsistencies with accounting for CH_4 and CO need to be addressed. Second, there is a term (beta x delta_CO2) which I think is incorrectly treated. This term assumes that all CO_2 changes are due to the land biosphere, which is exactly what the authors state is problematic (and I agree with them). Therefore, I think this term needs to be: ([1-f] x beta x delta_CO2), where 'f' = 'f(t)' as given in Equation 7 – I have changed f slightly, since the entire equation is dependent on time, so it's not necessary to specify this for f only.
6. One might also modify 'phi' in Equation 7 to, for example, phi-subscript 'l', to emphasise that this variable is not the 'standard' global value of 1.4, but should be a locally-derived value which can vary in time and space (as the authors have stated).
7. I am not so convinced by the feature of a double peak in the MHD APO – this is based on a single point only. In any case, the discussion is quite out of place, since the text both before and after this is discussing the issue of the LUT oxidative ratio.

Conclusions section is good.

Figures are all small and hard to read – perhaps will be improved for final publication version? I think some of the symbols are too big, and lines too thick, for example Figs 2 and 4. I would probably remove the minor gridlines from Fig 2. "per meg on Gr. scale" needs to be defined somewhere, probably caption.

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 20113, 2008.