

Reply to the two remaining comments of editor

Our reply is given in black font and the newly added paragraphs to the new version of the manuscript in italics, whereas the comments of the editor are marked in red.

Associate Editor Decision: Publish subject to minor revisions (review by editor) (11 Oct 2019) by Christof Janssen

Comments to the Author:

Dear Authors,

Thank you again for your mail pointing out that the review process is too slow. I hope to be as clear as possible so that any further unnecessary step can be avoided.

Generally speaking, I strongly approve your work and the article. It should certainly be published. However, the current version is inaccurate or erroneous in describing the link between mixing ratios and delta values. This needs to be clarified before publication. There are two points:

1. *A simple calculation using a dry three component model atmosphere of O₂, N₂ and others x = (Ar +) with relative abundances of 0.2094, 0.7809 and .0997 (TOHJIMA et al, Geophys Res Lett 30, 1653 (2003)) shows that the O₂ mole fraction mf should change with a change dR in the R=O₂/N₂ ratio as $d(mf) = (1+x)/(1 + R + x)^2 * d(R)$ (assuming that all change in O₂/N₂ comes from O₂ and not from N₂). The slope in the $\delta = d(R)/R$ over $d(mf)$ diagram is thus given by $R (1 + R + x)^2 (R(1+x))^{-1}$. Plugging in numbers yields 6.04, which is close but different (why ?) from your value of 5.78 per meg per 1 ppm. The number of 4.8 per meg per 1 ppm on the first page of the manuscript is just wrong. Please correct the introduction and explain the origin of the factor 5.78 or 6.04 per meg per 1 ppm that readers can understand. You should provide details in an appendix. The section that you have added during the last revision refers to the wrong number of 4.8 per meg ppm⁻¹ and is superfluous at this section in the manuscript. Note that the examples that you have provided in the proposed appendix to manuscript version 7 did not include changes of O₂ and contained an error. Your examples were concerned with the addition/dilution of the O₂ mixing ratio by gases other than O₂ and N₂. It is correctly stated that this does not change the O₂/N₂ ratio, but changes O₂ and N₂ mole fractions. However in the ongoing calculation you then assume that the mole fraction of N₂ remains constant while the mole fraction of O₂ gets diluted. This certainly impacts the ratio, but the approach is self-contradictory and leads to the calculation of a meaningless number. Note that dilution cannot be used to determine a delta over $d(mf)$ slope. When you calculate the change of the O₂ mole fraction as a function of the dilution dx analogously to the above approach, you get $d(mf) = 1/(1 + R + x)^2 * d(x)$. However, since R does not depend on x, $dR/dx=0$. So the line traced by dilution by gases other than O₂ or N₂ should be horizontal (slope of 0 per meg per 1 ppm).*

2. *The paper lacks a dedicated statement on uncertainties related to the measurement of delta. All of the uncertainty discussion is concerned with mole fraction measurements, but since results need to be reported as delta values, the uncertainty of delta cannot be omitted. Using the above derived transfer coefficient from O₂ mole fraction to delta, one can convert a mole fraction uncertainty of 5 ppm into*

an equivalent value for delta. However, there are additional factors that impact delta (and don't have an effect on the O2 mole fraction), i.e. variability and lack of knowledge of the mole fraction of non-characterized atmospheric compounds. This is why the discussion needs to be extended. Please Mention these additional error sources and give a rough estimate of their contribution so that the reader can judge the degree of agreement with other measurement methods.

Once these two issues are clarified, the paper can be published. Note that these issues have been raised in previous editor remarks, but have not been addressed. I am sorry that they have not been raised at or before the expert review stage, but only came up later in the review process.

Please take the time to carefully address the two above points so that any further revision becomes unnecessary. If the points are not addressed satisfactorily, I will send the revised version to one or more referees, whom I will ask to give a rapid and independent expert opinion on the issue.

With kind regards,

Christof Janssen

Dear Christof Janssen

We believe that the publication you are referring to in your comments is the publication of Tohjima et al. 2000 (JGR, Vol. 105, 2000) and not Tohjima et al. Geophys Res Lett 30, 1653 (2003), as the latter publication does not cover the points mentioned in your comments.

Equation 1 given in Tohjima et al. 2000 describes the total derivative of oxygen mole fraction. This is equivalent to what we have tried to describe in the proposed appendix to manuscript version 7, except that we obviously have missed to clearly state that we kept the nitrogen mole fraction constant since the Picarro analyzer is unable to measure N₂, Ar or CO₂. This of course, as you correctly mentioned, will lead to additional uncertainty due to the dilution effect of such changes. We have clarified these points in the following statements.

Following your view which is based on Thojima et al., 2000, it is correct that the per meg to ppm conversion has a slope of 6.04 if we consider only the changes in oxygen. It changes slightly to 6.11 per meg per ppm, when we talk about nitrogen changes only, and also as correctly stated in your statement above the slope is zero (horizontal line) when talking about any other changes of air components. The fact that our supplementary plot shows slopes of 5.78 (for the first five standards) or 6.08 (for all standards except ST-7) is due to a mixed influence from pure O₂, pure N₂ and other air component dilution effects. The lower slope of 5.78 documents particularly the influence of the CO₂ dilution effect.

Our view is consistent but follows another path, namely that the CRDS analyzer measures an O₂ concentration which requires to be converted to an O₂/N₂ ratio. Since no information about N₂ is available one assumes a constant value, i.e. N₂ of the standard. Therefore, eq. 1 in the manuscript reduces to $(O_{2,SA}/O_{2,ST}-1)*10^6$ or $\Delta O_2/O_{2,ST}*10^6$. The value obtained is an estimated $\delta O_2/N_{2,est}$ ratio, which indeed slightly different to the true $\delta O_2/N_{2,true}$. The effect of water dilution (amount of water vapor is measured by the CRDS analyzer) is taken into account as described in the manuscript. Yet any other dilution effect is not considered except if additional information is available, e.g. CO₂ concentration measurements. Indeed this dilution effects can be significant and are displayed in the following table.

Change in ppm		ΔO_2 apparent (change + dilution effect)	$\delta O_2/N_{2,true}$ (per meg) ($\delta O_2/N_{2,true}/\Delta O_2$ in per meg/ppm)	$\delta O_2/N_{2,est}$ (per meg) ($\delta O_2/N_{2,est}/\Delta O_2$ in per meg/ppm)	Difference in $\delta O_2/N_2$ (true – est) in per meg
ΔCO_2 only	10	-2.0946	0 (0)	-10 (4.77)	10
ΔAr only	10	-2.0946	0 (0)	-10 (4.77)	10
ΔO_2 only	10	7.9054	47.74 (6.04)	37.74 (4.77)	10
ΔN_2 only	10	-2.0946	-12.81 (6.11)	-10 (4.77)	-2.81

$\delta O_2/N_{2,true}$: for instance measured by mass spectrometry; $\delta O_2/N_{2,est}$: for instance measured by Picarro.

Incorrectly assumed N_2 , Ar, CO_2 or any additional gas component lead to changes in the estimated $\delta O_2/N_{2,est}$ values as stated in the table. For example a 10 ppm increase in CO_2 lead to an incorrect value of -10 per meg in $\delta O_2/N_{2,est}$ compared to the true $\delta O_2/N_{2,true}$ value. This is simply the dilution effect that the increased CO_2 concentration has on the correspondingly measured O_2 concentration (dilution in oxygen corresponds to the percentage-wise assignment of the excess CO_2 in ppm to oxygen, i.e. -10 ppm x oxygen mole fraction = 2.0946, if O_2 mole fraction corresponds to 0.20946). As you can see an addition of 10 ppm of N_2 leads to a reduced and opposite effect for the difference in $\delta O_2/N_2$ (true – est) because the dilution effect on O_2 is unable to compensate the change from the increase in nitrogen, therefore it scales with -10 ppm x (oxygen mole fraction/nitrogen mole fraction). This also tells us that the difference in the Delta values (true – est) scales with the O_2/N_2 ratio present in the sample. Therefore, best results are obtained when the calibration gases for which the gas composition is known equals closely the sample gas composition. In our case this is given – but can certainly be improved – since we are comparing air composition to air standard compositions. Yet, determinations of the standards that has been used in this study have a range in N_2 concentrations of -110 to +110 ppm for the ST-1 to ST-5, whereas ST-6 (+700 ppm) and ST-8 (-6200 ppm) are significantly off. Therefore, special attention is required for the precise determination of standard gas composition and to control the air sample composition by means of flask measurements in order to detect potential fractionation effects during air intake.

The following text will be included in the Appendix:

Appendix: Uncertainty consideration during conversion of ppm to per meg

Generally, the Delta notation ($\delta(O_2/N_2)$), as given in equation 1 of this publication (also shown below), is used in order to circumvent the influences of dilution by other gas components when determining oxygen mole fractions. Yet, several instruments are measuring the oxygen mole fraction such as the paramagnetic cell, the UV-cell as well as the instrument by CRDS analyzer presented here. Therefore, a thorough consideration of the conversion from ppm (mole fraction) to per meg ($\delta(O_2/N_2)$ notation) is necessary which is explained in this appendix.

Following equation 1 in Thojima et al., 2000, the per meg to ppm conversion has a slope of 6.04 if only a change in oxygen is applied as seen in table A1. It changes slightly to 6.11 per meg per ppm, when we talk about nitrogen changes only, or to a slope zero (horizontal line) when talking about any other changes of air components excluding oxygen and nitrogen. The fact that our supplementary plot shows slopes of 5.78 (for the first five standards) or 6.08 (for all standards except ST-7) is due to a mixed influence dilution effects. The lower slope of 5.78 documents particularly the influence of the CO_2 dilution effect.

$$\delta \left(\frac{O_2}{N_2} \right) (\text{per meg}) = \left(\frac{O_2}{N_2} \right)_{\text{sample}} - 1 \cdot 10^6 \quad (1)$$

Note that under the assumption the atmospheric N_2 content is constant (i.e. $N_{2\text{sample}}$ equals $N_{2\text{reference}}$), we convert relative changes in oxygen given in per meg following equation 1 to oxygen changes in parts per million (equivalent to micromol/mol) by multiplying by the O_2 mole fraction ($O_{2\text{reference}}$) expressed as 209500 ppm (the O_2 mole fraction of atmospheric air) (Machta and Hughes, 1970). Hence 1 ppm corresponds approximately to 4.8 per meg, or 1 per meg to 1/4.8 (209500/106) ppm.

This is used in our approach since the Picarro instrument measures the O_2 concentration which requires to be converted to an O_2/N_2 ratio. Since no information about N_2 is available one assumes a constant value, i.e. N_2 of the standard. Therefore, eq. 1 in the manuscript reduces to $(O_{2,SA}/O_{2,ST}-1) \times 10^6$ or $\Delta O_2/O_{2,ST} \times 10^6$. The value obtained is an estimated $\delta O_2/N_{2,est}$ ratio, which indeed is slightly different from the true $\delta O_2/N_{2,true}$. The effect of water dilution (amount of water vapor is measured by the CRDS instrument) is taken into account as described in the manuscript. Yet any other dilution effect is not considered except if additional information is available, e.g. CO_2 concentration measurements. Indeed this dilution effects can be significant and are displayed in the following table A1.

Table A1: ppm to per meg conversion calculations for air-like compositions

Change in ppm		ΔO_2 apparent (change + dilution effect)	$\delta O_2/N_{2,true}$ (per meg) ($\delta O_2/N_{2,true}/\Delta O_2$ in per meg/ppm)	$\delta O_2/N_{2,est}$ (per meg) ($\delta O_2/O_{2,est}/\Delta O_2$ in per meg/ppm)	Difference in $\delta O_2/N_2$ (true – est) in per meg
DCO ₂ only	10	-2.0946	0 (0)	-10 (4.77)	10
DAr only	10	-2.0946	0 (0)	-10 (4.77)	10
DO ₂ only	10	7.9054	47.74 (6.04)	37.74 (4.77)	10
DO ₂ only	10	-2.0946	-12.81 (6.11)	-10 (4.77)	-2.81

$\delta O_2/N_{2,true}$: for instance measured by mass spectrometry; $\delta O_2/N_{2,est}$: for instance measured by Picarro G-2207.

Incorrectly assumed N_2 , Ar, CO_2 or any additional gas component can lead to changes in the estimated $\delta O_2/N_{2,est}$ values as stated in the table A1. For example a 10 ppm increase in CO_2 lead to an incorrect value of -10 per meg in $\delta O_2/N_{2,est}$ compared to the true $\delta O_2/N_{2,true}$ value. This is simply the dilution effect that the increased CO_2 concentration has on the corresponding O_2 concentration measurements (dilution in oxygen corresponds to the percentage-wise assignment of the excess CO_2 in ppm to oxygen, i.e. -10 ppm x oxygen mole fraction = 2.0946, if O_2 mole fraction corresponds to 0.20946). As you can see from table A1 an addition of N_2 of 10 ppm leads to a reduced and opposite effect for the difference in $\delta O_2/N_2$ (true – est) because the dilution effect on O_2 cannot compensate the change from the increase in nitrogen, therefore it scales with -10 ppm x (oxygen mole fraction/nitrogen mole fraction). This also shows that the difference in the Delta values (true – est) scales with the $\delta O_2/N_2$ ratio present in the sample. Therefore, best results are obtained when the calibration gases for which the gas composition is known equals closely the sample gas composition. In our case this is given – but can certainly be improved – since we are comparing air composition to air standard compositions. Yet, determinations of the standards that has been used in this study have a range in N_2 concentrations of -110 to +110 ppm for the ST-1 to ST-5, whereas ST-6 (+700 ppm) and ST-8 (-6200 ppm) are significantly off compared to our primary standard used for mass spectrometric determination. Therefore, special attention is required for the precise determination of standard gas

composition and the control of the air sample composition by means of flask measurements in order to detect potential fractionation effects during air intake.

Furthermore, we changed the text in the introduction section referring to equation 1 which was written as:

“ Note that under the assumption the atmospheric N₂ content is constant (i.e. N₂sample equals N₂reference), we convert relative changes in oxygen given in per meg following equation 1 to oxygen changes in parts per million (equivalent to micromol/mol) by multiplying by the O₂ mole fraction (O₂reference) expressed as 209500 ppm. (the O₂ mole fraction of atmospheric air) (Machta and Hughes, 1970). Hence 1 ppm corresponds approximately to 4.8 per meg, or 1 per meg to 1/4.8 (209500/106) ppm.”

New text in manuscript after eq. 1

Equation 1 is used to convert oxygen mole fraction changes expressed in ppm (as measured by several techniques such as paramagnetic cell, UV-cell as well as the by the CRDS analyzer presented here) into changes in $\delta O_2/N_2$. This is associated with the influence of dilution effects on the mole fractions but not necessarily on the ratios. These conversion difficulties and their expressions in uncertainties are discussed in the Appendix.