Fourth reply to the Editor´s comments

We would like to thank the Editor for his comments which we have addressed below. We keep the editor´s comments in red font and our replies in black font.

Dear authors,

Thank you for your corrections. Unfortunately, you haven't taken into account my remarks on the measurement principle and uncertainties.

Please take into account the following minor corrections.

1. Eq 5. Use a consistent notation for the mole fraction of gases, eg f_{O2}, f_{H2O} etc. ….

The functions for the retrieval of mole fractions are different for the different species since they depend on different spectral lines, but we understand the reviewers comment and rewrite eq. 5 as>

$O_{2,dry} = O_{2,raw}/(1-H_2O)$

where H2O is the measured water mole fraction

2. l. 321 It would be easier to understand if you use "multiplied" instead of "normalized".

We have now used the word "multiplied" as requested by the editor

3. The use of units still needs clarification. Since you use delta(O2/N2) in your paper, you should give an estimate of the error that is associated with the conversion from ppm to per meg. It is evident that the assumption of the N2 mole fraction being the same in the sample and reference is overly optimistic (l. 42 of your manuscript. As an aside note that it is not clear what you mean by N2 being constant. Partial pressure or mole fraction of N2 ?). There are natural variations of the partial pressures of CO2, Ar, H2O, etc. that require that if you maintain the same total pressure the mole fraction of N2 in sample and reference must differ at the ppm level, even if the amount of N2 in the atmosphere remains constant. It will be very helpful for the reader if you make the calculation in an appendix.
As I understand it, CRDS can "directly" measure the O2 mole fraction using a calibrated air-like gas mixture (which should not be too dry, otherwise the water correction scheme does not work properly). Conversion into delta(N2/O2) values, however, requires the knowledge of p(N2)/p(air), but from the measurement you know only p(O2)/p(air). Therefore you must make assumptions on Ar, CO2, H2O and all other substances that contribute to air at the ppm level. In this way you can calculate p(N2) = p(air)-p(O2) - p(all contributors at the ppm level).
What is the error of all these assumptions ? Please discuss/mention in the article.

The reviewer is correct that there is an influence of CO2, Ar, H2O or other atmosphere gas component changes on the mole fractions. We are well aware of this fact that has been dealt with in several publications beforehand. An easy way of understanding and estimating this influence can be obtained when noting all gas component of relevance as mole fractions and look at the influence of each when changing one component or several. We are happy to include the following in the Appendix if the editor finds this also helpful.

Addition to Appendix:

Influence of air composition on the measured O_2 and dO_2/N_2 following eq. 1.

The following equation describes exactly this issue:

[N2] + [O2] + [Ar] +[CO2] + [others] = 1 ;   (A1)

where [] denote the mole fractions of the correspondent gas species (e.g. [N2] = 0.780840), all of which sums up to unity. Eq. (A1) can also be multiplied by 10^6 (one million) to express the mole fractions in ppm, e.g. [N2] = 0.780840 that corresponds to 780840 ppm.

If for instance [CO2] is changed to [CO2 + DCO2], DCO2 being a CO2 mole fraction change then eq. A1 changes to

[N2] + [O2] + [Ar] +[CO2+ DCO2] + [others] = 1 + [DCO2];   (A2)

This addition of DCO2 leads to a dilution of all other components correspondent to their mole fractions. Mathematically this is obtained

by dividing eq (A2) by the right-hand side term, e.g. 1 + [DCO2]. This leads to eq (A3)

([N2] + [O2] + [Ar] +[CO2+ DCO2] + [others])/(1 + [DCO2]) = 1;   (A3)

Example 1: CO2 change

From eq (A3) one can see that the ratios of any component with another component (e.g. O2/N2, Ar/N2 etc.) is not changing since the scaling factor (/(1 + [DCO2])) remains the same for the different components. In contrast the mole fractions indeed do change.

In the following we make an example for a DCO2 = 10 ppm

(10 ppm CO2 change) under the assumption that [N2] = 0.780840, [O2] = 0.209460, [Ar] = 0.009340, [CO2] = 0.000400, [others] = 0, The sum of them yields more than 1 and need to be normalized to get [N2] = 0.780809, [O2] = 0.209451, [Ar] = 0.009340, [CO2] = 0.000400, [others] = 0 by the corresponding division.

If now DCO2 = 10 ppm, then the sum of all components is 1.000010 and therefore the following mole fractions are obtained

[N2] = 0.780801, [O2] = 0.209449, [Ar] = 0.009340, [CO2] = 0.000410, [others] = 0

Using eq. 1 to convert it to O2/N2 leads to -10 permeg using [N2] = 0.780809 for both sample and reference as mentioned in the manuscript. DO2 corresponds to 2.1 ppm. This corresponds to 4.77 per meg change in O2/N2 per ppm O2 change.

Example 2: Ar change

In the following we make an example for a DAr = 100 ppm

(100 ppm Ar change) under the assumption that [N2] = 0.780809, [O2] = 0.209451, [Ar] = 0.009340, [CO2] = 0.000400, [others] = 0.

If now DAr = 100 ppm, then the sum of all components is 1.000100 and therefore the following mole fractions are obtained

[N2] = 0.780731, [O2] = 0.209430, [Ar] = 0.009439, [CO2] = 0.000400, [others] = 0

Using eq. 1 to convert it to O2/N2 leads to -100 permeg using [N2] = 0.780809 for both sample and reference. DO2 corresponds to 21 ppm. This corresponds again to 4.77 per meg in O2/N2 per ppm O2 change.

Generally, from these calculations one can see that 1 ppm change of any air component lead to a 4.77 per meg change in dO2/N2 after normalization to unity.

Therefore, it is indeed important to have additional information available for the air composition, in particular about CO2 and Ar mole fractions, otherwise O2 mole fractions or O2/N2 are misinterpreted.

Why do you compare to the standards using delta(O2/N2) instead of f(O2) even if that introduces an additional error ?

We made the comparison using delta(O2/N2) because this is the standard way in the community of expressing O2 variations.