Atmos. Chem. Phys. Discuss., 8, S10328–S10332, 2009
www.atmos-chem-phys-discuss.net/8/S10328/2009/
© Author(s) 2009. This work is distributed under
the Creative Commons Attribute 3.0 License.

Atmospheric
Chemistry
and Physics
Discussions

Interactive comment on “Oxygen isotopic signature of CO_2 from combustion processes” *by* M. Schumacher et al.

Anonymous Referee #2

Received and published: 9 January 2009

Knowledge of the isotopic composition of the sources and sinks for CO2 is important if we are to gain a complete understanding of the atmospheric CO2 cycle. Given sufficient discrimination between sources and sinks, and provided that the system is not under-determined then it is possible to estimate the magnitude of source and sink fluxes. Burning of fossil fuels and biomass, both anthropogenic and natural, is an important source of atmospheric CO2. However, it is not generally possible to readily discriminate between the different fuels using carbon isotopes alone. If the oxygen isotope composition of the combustion CO2 retains a source signal, or component of the source signal then this may be used to characterise the different contributions. On a global scale, however, given the large water reservoir and the fact that isotope exchange between CO2 and H2O readily occurs, we expect and find that the CO2 oxygen

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

isotope composition tracks that of the local water. Perhaps this is why little attention has been given to measuring the oxygen isotope composition of combustion derived CO2.

In this study Schumacher et al. present the first systematic laboratory study of the controls on the oxygen isotope composition of combustion CO2. They controlled variables such as sample composition, macro and microstructure and combustion conditions (temperature, O2/CO2 ratio etc.). In modelling studies it has always been assumed that fossil fuel and biomass derived CO2 would have an isotopic composition similar to that of atmospheric oxygen. The relatively high temperature of combustion would result in little isotopic fractionation between reactants and products. In contrast Schumacher et al. report widely varying and systematic patterns of isotopic depletion. Whilst it is difficult to interpret the data in terms of a model for combustion it seems clear that diffusion of O2 to the site of oxidation is a key process leading to oxygen isotope depletion in the product CO2.

The oxygen isotope composition of the source material seems to have little effect on the CO2 composition. One assumes that there is isotope equilibration between the microscopically local combustion atmosphere and the CO2. Given this observation, and the rapid equilibration between atmospheric CO2 and H2O it is hard to see how knowledge of the oxygen isotope composition of combustion CO2 can contribute to differentiating the different source fluxes. However, on a local, and at short time scales atmospheric models will surely benefit from the better understanding of combustion CO2 isotope compositions that this paper presents.

Unfortunately, the paper in its present form is not suitable for publication:

i) The text is too long and needs to be condensed and focussed on the experiments at hand. The Introduction contains a reasonably long section on CO2-H2O exchange which is largely irrelevant to the immediate aims and results of this paper. There is scope to shorten both the experimental method detailing (section 2). In this section

CC BY

there is duplication of both equipment and method descriptions relating to the combustion apparatus. The description of the analytical techniques can be shortened. I do not think it necessary to include a full description of the pyrolisis technique used for characterising the source material isotope composition, or the hydrogen and oxygen isotope composition of source water.

ii) The presentation of the results and discussion as a single section (3) is problematic. It is difficult to make an independent assessment of the data. It would help if the results could be presented in table form, giving experiment details including sample type, combustion temperature, combustion efficiency, combustion factor, and isotopic composition. From the way the data is presented I get the impression that each point in the Figures represents the results of a single experiment. It is not clear whether or not these experiments have been replicated. I think that they have not. Given this it is impossible to say anything about internal variability between experiments which may be very high. Without replication the results must be considered to be semi-quantitative.

iii) The text is often difficult to follow and in places I found it to be impenetrable and did not understand what the authors were trying to say. Careful editing and proof reading will dramatically improve the style and flow of the paper. I understand that it is difficult when writing in a language other than your native one, but several of the authors do have wide experience of publishing in english text journals.

I also draw the authors attention to specific technical queries as follows:

a) In places the authors use isotopologues and isotopic composition almost interchangeably. A distinction should be drawn between the meaning of isotopologue and isotopic composition (18995/26 and 18996/23).

b) Does the APCD have a policy regarding using IUPAC recommended definitions? If so then these should be followed in the definition of delta 18-O (eqn. 1)

c) 18999/16-27. The terms emission factor, combustion efficiency and combustion

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

factor are introduced here, yet do not feature as a significant part of the discussion. The authors might consider either shortening the text here (use equations as definitions of these variables) or removing the text altogether.

d) 19000/11 The authors refer to 170 samples and then a sub set of 35 samples. This is confusing. I think they mean 170 experiments and a sub-set of 35 experiments.

e) In section 2, Materials and Methods there is some duplication of material. Consider separating the description of the experimental apparatus from the description of the procedure. On page 19002/4-15 there is a partial description of the method that is repeated on page 19006/8-21.

f) I find the discussion that is based around Figure 2, Figure 3 and 4 and the results very confusing. This is not helped by the difficulty in tracking between the text and Figures and not being able to match the two together. As an example on page 19009/7-23 the authors refer to a series of experiments on needles labelled Iceland and Gifhorn. The first difficulty is there are no samples marked Gifhorn on Figure 3. The second difficulty is that the authors refer to differences between samples on the Figure, and then to differences between samples and the isotopic composition of the starting material which is not on the figure! I found it very difficult to follow the argument that the authors are trying to sustain here.

g) Table 1. The data presented for the starting isotope composition of cellulose and cellulose based material needs qualification. Are the triplicate results simply the data from a triplicate analysis of the same ground and homogenised sample, or do they reflect the true intra sample variability. This is important as the experiments were carried out on whole samples that were not homogenised.

h) Figure 1. This diagram should be presented with all the valve locations. MFC should be converted to Mass Flow Controller.

i) Figure 2. It is difficult to determine what the different arrow styles mean in this diagram and consequently how the different variables might affect combustion and the resultant oxygen isotope composition of CO2. This is an important diagram as it forms the basis of the structure for the discussion of the results. Careful consideration should be given to redrawing this to highlight the important variables that may control the isotope composition.

j) Figure 3. Figure 3 onwards presents a series of different isotope cross-plots. These diagrams are very dense with data from a large number of experiments and it is difficult for the reader to follow all the nuances in the data. First, is it possible to enhance the contrast between the data points? I know the authors intend for the plots to be in colour, but many will use a black and white printed version. Second the authors might consider a careful use of tie lines between similar sample types that link together results from combustion under different experimental conditions. A good example is Figure 4. Here we are invited to consider the effect of combustion temperature on isotope composition. Careful trend lines or tie lines will help to illustrate the trend to more depleted compositions with decreasing temperature.

k) It would help if the isotopic composition of both the starting material and the oxygen (either pure or ambient) were plotted on the diagrams.

In conclusion I find that the paper presents important and new data. The experiments are well conceived and the results provide new insights into the role that combustion conditions play in controlling the oxygen isotope composition of CO2. However the paper does need important editing and rewriting in places to ensure that the results and interpretation are widely accessible.

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 18993, 2008.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper