Biogeosciences Discussions, 1, S330–S332, 2004
www.biogeosciences.net/bgd/1/S330/

Biogeosciences Discussions

Interactive comment on "Carbon isotope anomaly in the major plant C_1 pool and its global biogeochemical implications" *by* F. Keppler et al.

Anonymous Referee #4

Received and published: 3 November 2004

The paper provide new information on the 13C of C1 group that should help explain some of the observed signal in plant emitted compounds. Although supportive information in nature (and "elucidating the C cycle is a bit ambitious here), this paper should provide insights to, and better understanding of the evolution of 13C signals. The paper is therefore of interest to isotope biogeochemist and to chemist in general. The paper, however, suffer from serious flaws in the presentation, interpretations and discussion of the data and need major revisions. It is not obvious that all the points raised below can be addressed only by revisions of the exiting, presented, dataset.

Main points:

1. Presenting the data as cumulative amount and the isotopic composition of the cumulative samples is not a good idea. Data is available to calculate the mass balance for the material added at each temperature step, but it is difficult for the reader to do it based on the figures. For the concentrations, it is just confusing. For the isotopes this way of presentation misses the point. The authors measure d13C of the products

methanol and methyl chloride as a function of temperature and compare it to pectin, which was measured in a different way. In other words, they do not see the potential change in isotopic composition of the pectin methyl groups as it is being consumed in the reaction. Drawing the pectin as a line of constant composition might be misleading (It seems quite clear from the data that the pectin 13C should not be constant, as the 2 products have compensating fractionation, but this is not discussed). Furthermore, there is enrichment with temp in the cumulative MeOH and MeCl. That implies that when produced at higher temperature these compounds become more enriched. Is that due to smaller fractionation at higher temperatures (this is kinetic effect that might not very temp-sensitive, but the temp range is very large), or is this due to enrichment of the reactant (the pectin) as it is being consumed. Might be both, but from the way the data is presented it is difficult to judge. There is no discussion of these issues.

2. There is no discussion or suggestion of what is the carbon source for methyl chloride. As far as I understand, what is known about MeCl production is that it is mediated by s-adenosyl methionine but not sure the C source is well known. This paper suggests that it may be the plant methoxy pool in pectin and lignin, but the data are not really sufficient to claim that. It was observed recently that methyl halides are very depleted (including Ref. from the same group), but this might very well be a fractionation in the synthesis. It is not convincing, based only on the data presented that MeCl, which is emitted from plants, is produced from pectin. Only showing that pectin has 13C depleted methyl groups does not necessarily provide the evidence for that. Detailed description of the control experiments is missing and could help in this respect.

3. The conditions of the experiment do not mimick emission from plants, or fungi that feed on wood. It might be an attempt to mimic MeCl emission in biomass burning but temperature is not the whole story in this case, and 150 to 300C is not really fire temperatures. In other words explanation is missing for what is the logic behind the experimental strategy. Actually it seems more reasonable temperature measurements may exist, but for some reason this is put them in the supplemental material.

BGD

1, S330–S332, 2004

Interactive Comment

4. The criticism made above is valid also for suggesting lignin as a carbon source for methanogens. Having depleted 13C does not mean that it is the source of all other depleted compounds, and this is all the data show about lignin. To my knowledge there is no indications for methanogens using lignin, and that when they use CO_2 they would produce depleted methane due to fractionation not due to depleted CO_2. So the interpretations are not convincing, or the data is not sufficient to support it.

Minor comments:

Is the term fractionation used in the right way (p. 397) when comparing pectin to biomass. Although fractionation can be defined as the difference between 2 compounds even if there is no process relating them, it is awkward and certainly miss some comments.

The authors refer to methoxy (or methoxyl, it is the same) groups in the abstract and in the methods but to methyl groups of esters in the results (p. 397). Lignin has methoxy groups so that is OK. Pectin has ester groups but no methoxy groups.

Last paragraph: methyl transferase enzymes fractionate to the same extent as Rubisco. Explanation is needed this is obtained from the data or an appropriate reference is needed.

There are no MeCl data and it is indicated there was no detectable emission, except for the halophytes. The CAM plant Batis maritima is a known methyl halide emitter (I guess this is one of the halophytes). It would be interesting to see the MeCl data for this plant.

Interactive comment on Biogeosciences Discussions, 1, 393, 2004.