

Interactive comment on “Carbon isotope anomaly in the major plant C₁ pool and its global biogeochemical implications” by F. Keppler et al.

F. Keppler et al.

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We note the comments of referee 4 but consider them to be superficial and ill-conceived. The comments give us the impression that he/she believes the manuscript deals with the origin of chloromethane in biological material. However, the central issue in our paper is the high ¹³C depletion of the plant methoxyl pool which we believe could be used as a tool to trace the origin of several atmospheric gases.

We cannot accept the referee's view that our paper suffers from serious flaws in its presentation, interpretation or discussion of the data. However, in light of comments by this referee we have incorporated the supplementary material into the main body of the paper for clarity.

We would like to comment on the main points raised by the referee in what appears to us to be a logical order:

Referee comment 2

We find the referee's arguments in this section very difficult to follow. We can only

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assume that he/she is not au fait with the current literature in this subject area. Our group clearly demonstrated that pectin is a major source of chloromethane released to the atmosphere by leaf material (Hamilton et al, Science, 301, 206-209, 2003.). In this paper we suggested that this source could be responsible for up to 80% of the global chloromethane budget. Furthermore we demonstrated that the process involved in chloromethane production was non-enzymic and was solely an abiotic process involving thermal denaturation of pectin. The referee appears not to be aware of these observations. In this paper we now provide unequivocal evidence based on isotope studies that the methoxyl groups of pectin are the source of methyl groups of both the chloromethane and methanol produced during its thermal denaturation. Therefore we are at a loss to understand the referee's comments '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 ^{13}C depleted methyl groups necessarily provide the evidence for that'.

Referee comment 1

It serves no useful purpose as regards the central thesis of this paper to present the data for amounts of chloromethane or methanol or their isotopic composition for individual temperatures as suggested by the referee. We are not attempting to investigate the mechanisms by which chloromethane or methanol are formed. We are interested in demonstrating the overall mass balance between pectin methoxyl pool, chloromethane and methanol during thermal degradation in order to define their interrelationship.

Referee comment 3

In our investigations (Figure 1) we did not attempt to mimic either chloromethane formation from plants or fungi or chloromethane emission by biomass burning as the referee seems to think. We will insert on page 397 the rationale for heating experiments and move the supplementary material to the paper as suggested.

Referee comment 4

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We do not suggest lignin as a carbon source for methanogens. However, it is clear from the literature and as stated in our manuscript that C1 compounds such as methanol and methyl halides can act as substrates for methylotrophic methanogenic bacteria forming CH₄ (Whiticar, 1999; Cicerone and Oremland, 1988). It is also known that in soils, under aerobic conditions, demethylation of pectin and lignin, both enzymically (e.g. Fall and Benson, 1996; Ander and Eriksson, 1985) and abiotically (e.g. Dec et al., 2001, Keppler et al., 2000) is very probably an important source of several C1 VOCs. If, however in the upper horizon of wetlands, peat bogs and rice paddies, methanogens are utilizing methanol and other C1 substrate from the plant methoxyl pool with ¹³C values averaging -50 per mil, the production of CH₄ more highly depleted than previously envisaged might be expected.

Referees minor comments:

1. For purposes of clarity we will change 'fractionation' to 'signature' on p. 397.
2. Throughout the script we will make the appropriate changes from 'methyl' to 'methoxyl' as suggested.
3. Insert 'Based on our data' and remove 'In conclusion'.
4. Yes interesting but this paper was not dealing with this subject. We will be submitting information for publication in this area in the near future.

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