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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 #3

Received and published: 25 November 2004

I have reviewed the manuscript entitled "Carbon isotope anomaly in the major plant C1 pool and its global biogeochemical implications" by Keppler et al., and find it suitable for publication in Biogeosciences Discussions.

This manuscript presents the stable carbon isotopic analyses of methyl chloride, methanol, acetaldehyde, ethanol, acetone, ester methoxyl and ether methoxyl groups. The results of this study are unique, informative, and of value to those trying to understand the relationships between methoxyl group of pectin and lignin and biogeochemical cycle of atmospheric gases. The manuscript confirms the important finding that the plant methoxyl pool is the predominant source of methyl chloride and methanol.

Moreover, the authors suggest that the carbon isotope composition of methoxyl carbon could help distinguish between biotic and abiotic methyl esters. The research could have implications for distinguishing the signature of ancient life on earth as well as

extraterrestrial life.

The conclusions state that stable carbon isotopes composition of methoxyl pools in plants can be a tool to trace global cycle of C1 atmospheric trace gases. The explanations offered are viable and consistent with what we know from the literature. However, the considerations about CH_4 in the conclusion and in the abstract do not cover the experiments presented in the paper. I recommend publication of the manuscript after consideration of the specific comments listed below.

Specific comments

Page 395 line 17 use stable carbon isotope compositions instead of δ^{13}C values. δ^{13}C is defined later in the paper.

Page 395, Stable carbon isotope measurements: For GC_MS-IRMS, insert the description of the capillary column.

Page 395, line 25: internal precision, 0.2 (permil) specify if it is 1 or 2 sigma and remove the brackets ( ).

Page 395, line 27: An isotope difference is defined between two pools without mentioning that it is the isotopic fractionation. In the other parts of the manuscript the ^{13}C fractionation or KIE are used. It is confusing for non-specialists of isotope chemistry.

Page 396, line 7: remove biomass

Page 396, line 14: compositions instead of signatures

Page 397, line 9: ~ -45.x use everywhere the same number of decimals.

Page 397, line 10: add reference to table 1

Page 397, line 15 place reference Weilacher et al. 1996 at the end of the sentence.

Page 398, lines 5–6: "...showing that pectin methoxyl groups are the major source of both CH3Cl and CH_3OH." Figure 1B does not show that because the δ^{13}C values

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of methoxyl-groups are showed as constant. To have a better idea about the isotope mass balance, the variation of the δ^{13}C of the remaining pectin methoxyl groups should be plotted or δ^{13}C on y axe could be replaced by δ^{13}C*molar fraction. Figure 1 (c) is a better argument.

Page 400, line 23 to page 401, line 6: This part of the conclusion is interesting but the data contained in the paper is not sufficient to support this part of the conclusion. The link between CH_4 and C1 substrate/methanol is not demonstrated by the experiments.

Page 401 line 12: include δ^{13}C values of abiotic methyl esters and ether in order to highlight this point.

Fig. 1 (b) and Fig (d): the line representing the δ^{13}C of methoxl groups pectin pool or the δ^{13}C of biomass is confusing. I would prefer an arrow showing the value on y axe. It would be mathematically more accurate because the δ^{13} value of methoxl groups was not measured at each step of temperature heating.

Fig. 1 (c): Specify that the left y axe refers to pectin methoxyl groups and the right y axe to methanol and chloromethane.

Fig. 2: Tropospheric δ^{13}C values of CH_3Br and CH_3Cl were measured by Bill et al. 2004, Thompson et al. 2002, Rudolph et al. 1997, and by Tsunogai et al. 1999. I recommend modifying the range of the methyl halides box in fig. 2 by using the measurements reported by these authors.

Table 1, caption: to have all the information without checking the text, add “upon isothermal for 20 minutes at 225°C of dried plant”

Table 1, label: “C3-leaf tissue” remove tissue to be consistent with other table labels “C3-leaf”

Table 1 and table 2: Biomass and pectin methoxyl δ^{13}C values of Cocksfoot (Dactylis glomerata), Glasswort (Salicornia sp), Maize (Zea mays), Saltwort (Batis maritima), Scarlet paintbrush (Crassula falcata) are identical in table 1 and in table 2. Are these

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values from the same experiment? Whereas the biomass and pectin methoxyl δ^{13}C values of European ash (Fraxinus excelsior), Wych elm (Ulmus glabra), Hazelnut (Corylus avellana), English oak (Quercus robur), Norway maple (Acer platanoides) are different in table 1 and in table 2. Why didn't you use the average of biomass δ^{13}C?

Additional references

Rudolph, K., D.C. Lowe, R.J. Martin and T.S. Clarkson, A novel method for compound specific determination of d13C in volatile organic compounds at ppt levels in ambient air, Geophysical Research Letters, v. 24, 659–662, 1997.

Tsunogai, U., N. Yoshida and T. Gamo, Carbon isotopic compositions of C2-C5 hydrocarbons and methyl chloride in urban, coastal, and maritime atmospheres over the western North Pacific, Geophysical Research Letters, v. 104, 16033–16039, 1999.

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