Supplemental material

'Carbon isotope anomaly in the major plant C_1 pool and its global biogeochemical implications'

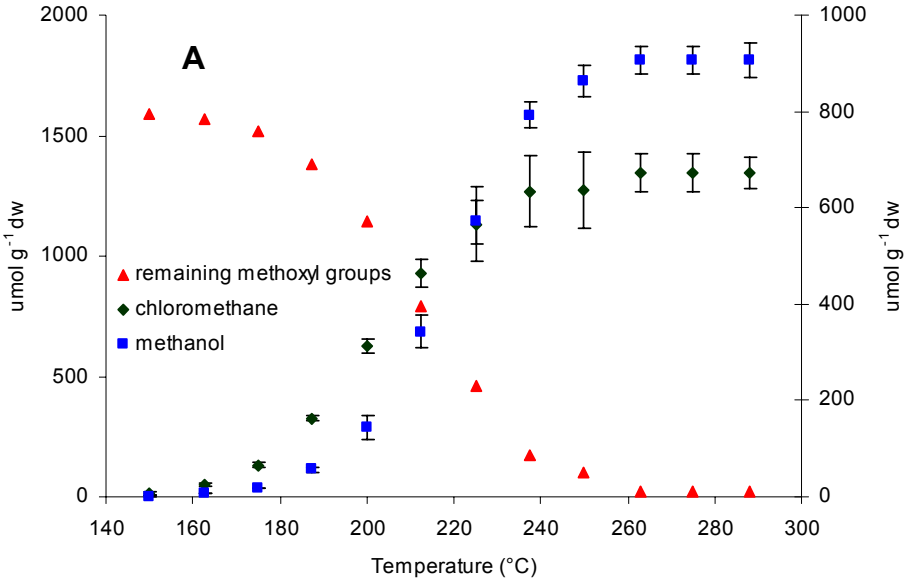
Table S1. $\delta^{13}C$ values[1] of chloromethane produced on heating dried leaf tissue at 40, 50 and 60ºC.

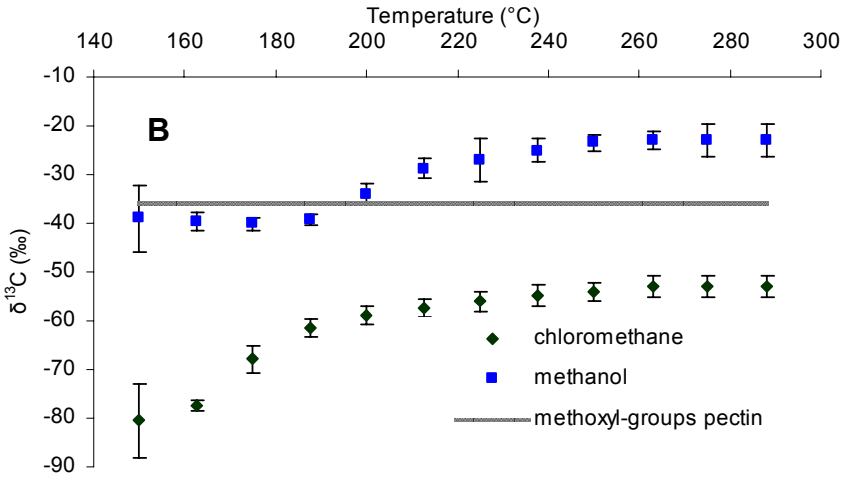
Plant common name (*species*)	**Chloromethane (CM)** ($\delta^{13}C$)	**Biomass (B)** ($\delta^{13}C$)	**Pectin methoxyl (PM)** ($\delta^{13}C$)	**$\Delta^{13}C$ (CM-PM)** ($\delta^{13}C_{PM}$-$\delta^{13}C_B$)
C_3-leaf tissue[2]				
European ash (*Fraxinus excelsior*)		-27.9 ± 0.2	-73.7 ± 1.0	
40°C	-147.0			-73.3
50°C	-142.6			-68.9
60°C	-129.0			-55.3
Wych elm (*Ulmus glabra*)		-30.8 ± 0.1	-69.2 ± 0.3	
40°C	-138.9			69.7
50°C	-130.4			-61.2
60°C	-126.9			-57.7
Cocksfoot (*Dactylis glomerata*)		-29.3 ± 0.2	-50.7 ±0.2	
40°C	-119.2			-68.5
50°C	-113.5			-62.8
60°C	-110.3			-59.6

[1]All values in ‰, analytical measurements see Methods. [2]Leaves were collected at Crossgar, N. Ireland in July 2003.

Sample preparation: Freeze-dried milled leaf samples (5g) placed in glass vial (44ml) and sealed with Mininert® valves were heated for 8h at 30°C, then temperature was progressively increased from 40 °C to 60 °C in 10 °C increments. Each temperature step was held for 8h. $\delta^{13}C$ of chloromethane was measured by GC-MS-IRMS at the end of each temperature step. Carbon isotope signatures for chloromethane at 30°C could not be measured because amounts were below the detection limit of the analytical method.

Figure S1


A
umol g-1 dw
umol g-1 dw
remaining methoxyl groups
chloromethane
methanol
Temperature (°C)


Temperature (°C)
B
δ13C (‰)
chloromethane
methanol
methoxyl-groups pectin

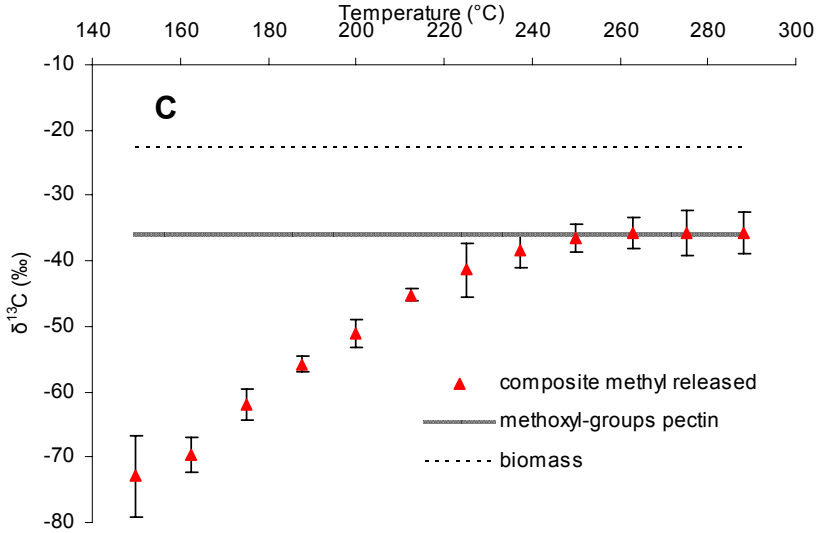

Temperature (°C)
C
δ13C (‰)
composite methyl released
methoxyl-groups pectin
biomass

Figure S1. Amounts and isotopic signatures of chloromethane and methanol formed during progressive heating from 150 to 300°C of pectin and chloride ion. Method: Apple pectin (6 % methoxyl content) was exhaustively dialysed against water, lyopholised and was used to make a pectin solution to which a NaCl solution was added. Upon cooling the gel that formed was lyopholised and finely ground. Chloride content was 0.5 mmol on a dry weight basis. Pectin (100mg) was heated in a glass vessel according to the method of Hamilton et al. (2003) except that temperature programming increments were 12.5 °C instead of 25 °C. (**A**) Cumulative amounts of chloromethane and methanol and residual pectin methoxyl are shown on a molar base. Each point is the mean of three replicate analysis of independent samples (n=3). (**B**) Carbon isotopic composition of accumulated CH_3OH and CH_3Cl at each temperature during progressive heating. For reference the measured initial $\delta^{13}C$ of the pectin methoxyl pool is displayed. Vertical bars show SD for triplicate samples. (**C)** Composite $\delta^{13}C$ values calculated on a molar basis for CH_3OH and CH_3Cl released during heating. For reference the measured initial $\delta^{13}C$ of the pectin methoxyl pool and the original bulk pectin is displayed. Vertical bars show SD for triplicate samples.

Figure S2

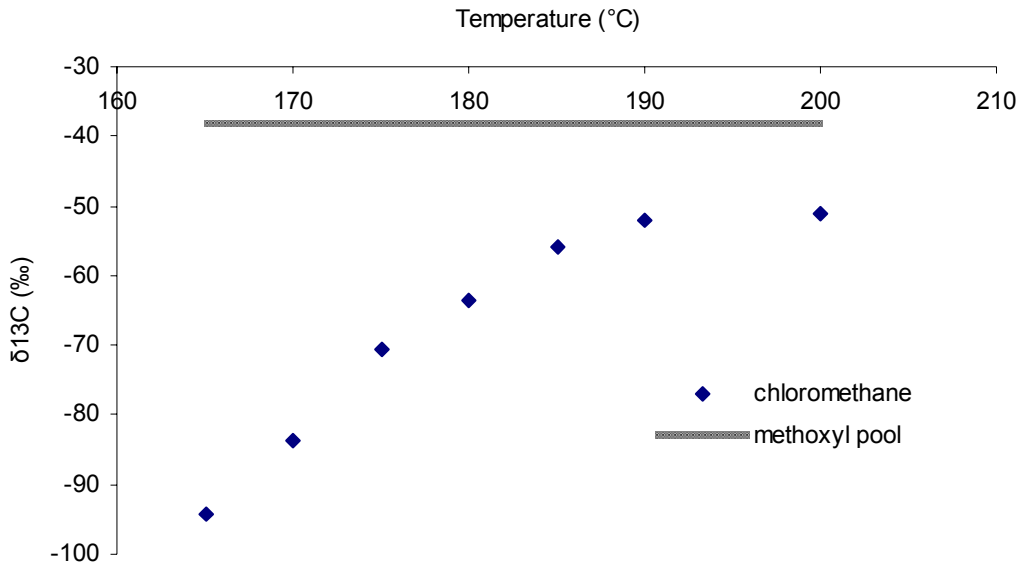


Figure S2 Isotopic signatures of accumulated chloromethane during progressive heating from 160 to 200°C of leucine methyl ester hydrochloride.

Method: Leucine methyl ester hydrochloride (100mg) was heated in a glass vessel according to the method of Hamilton et al. (2003) except that temperature programming increments were 5 °C instead of 25 °C. $\delta^{13}C$ of chloromethane was measured by GC-MS-IRMS at the end of each temperature step. The signature of the methyl ester groups was assessed by measuring the $\delta^{13}C$ of methanol released upon alkaline hydrolysis.