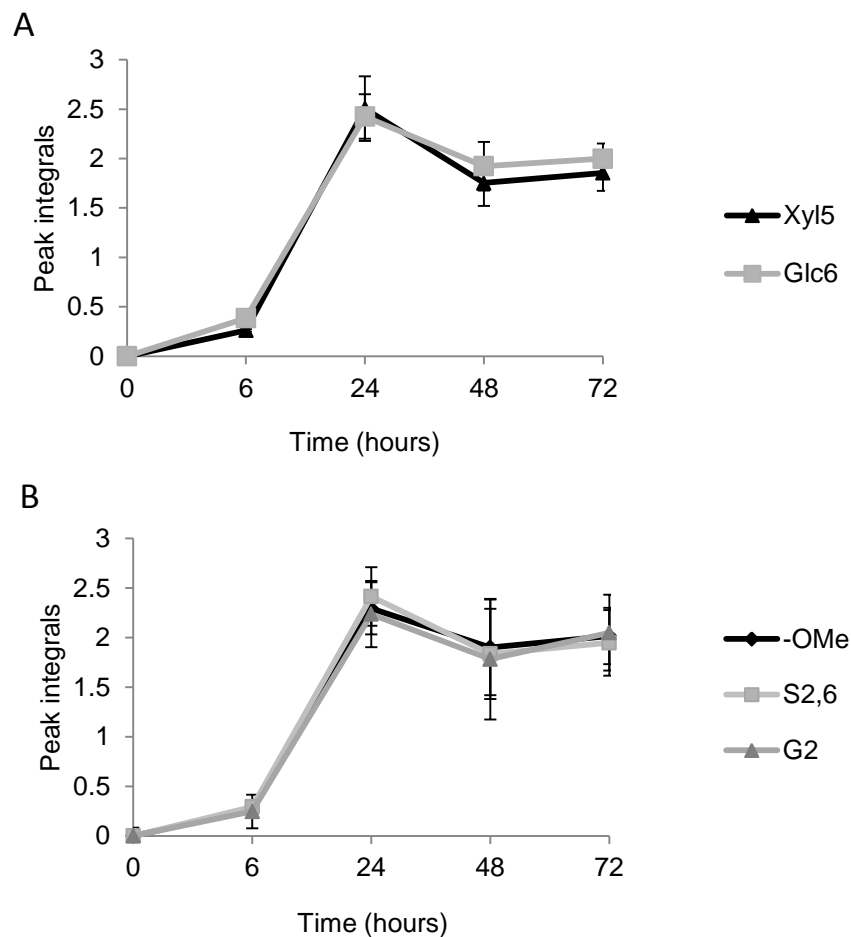
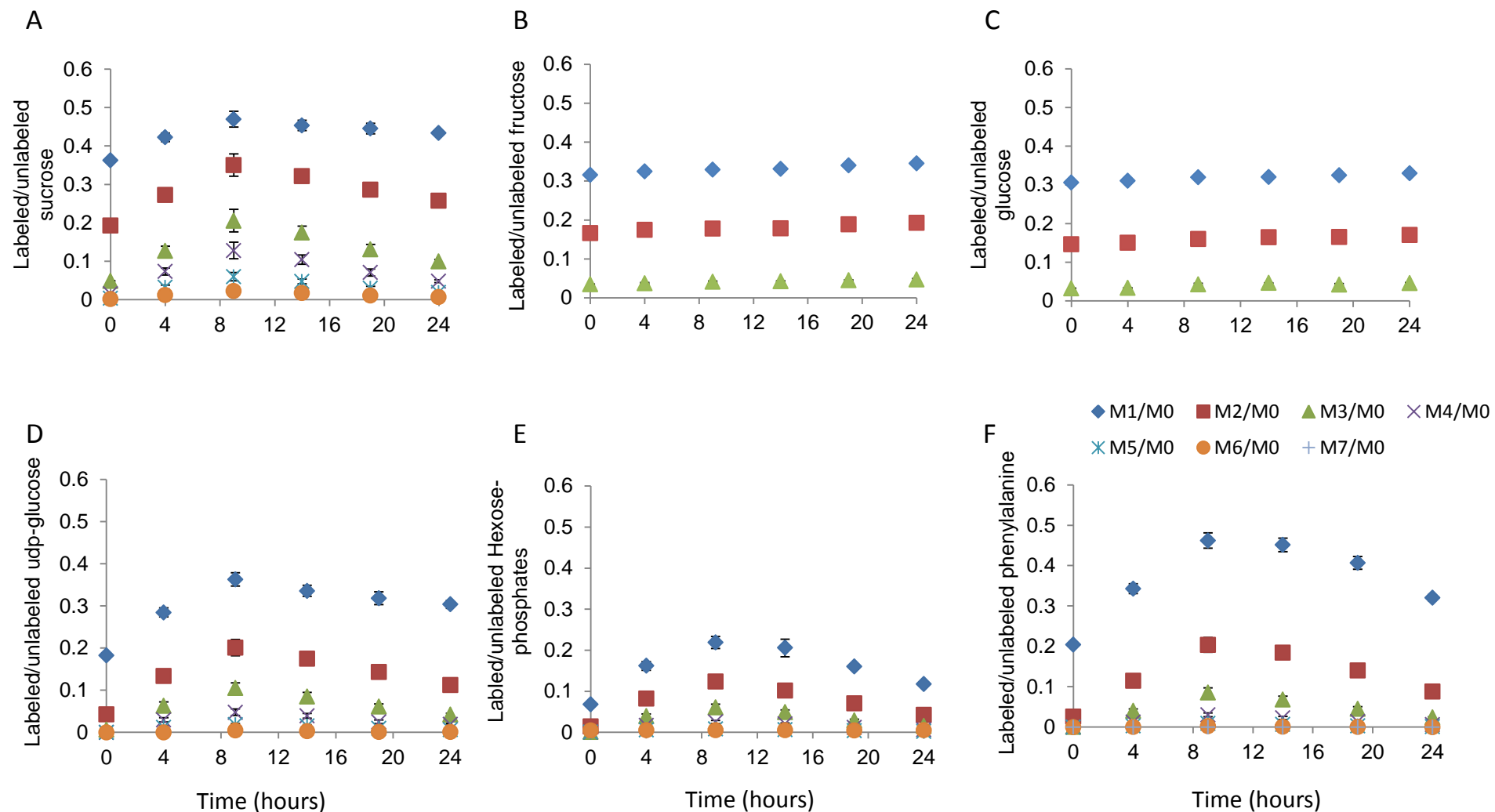




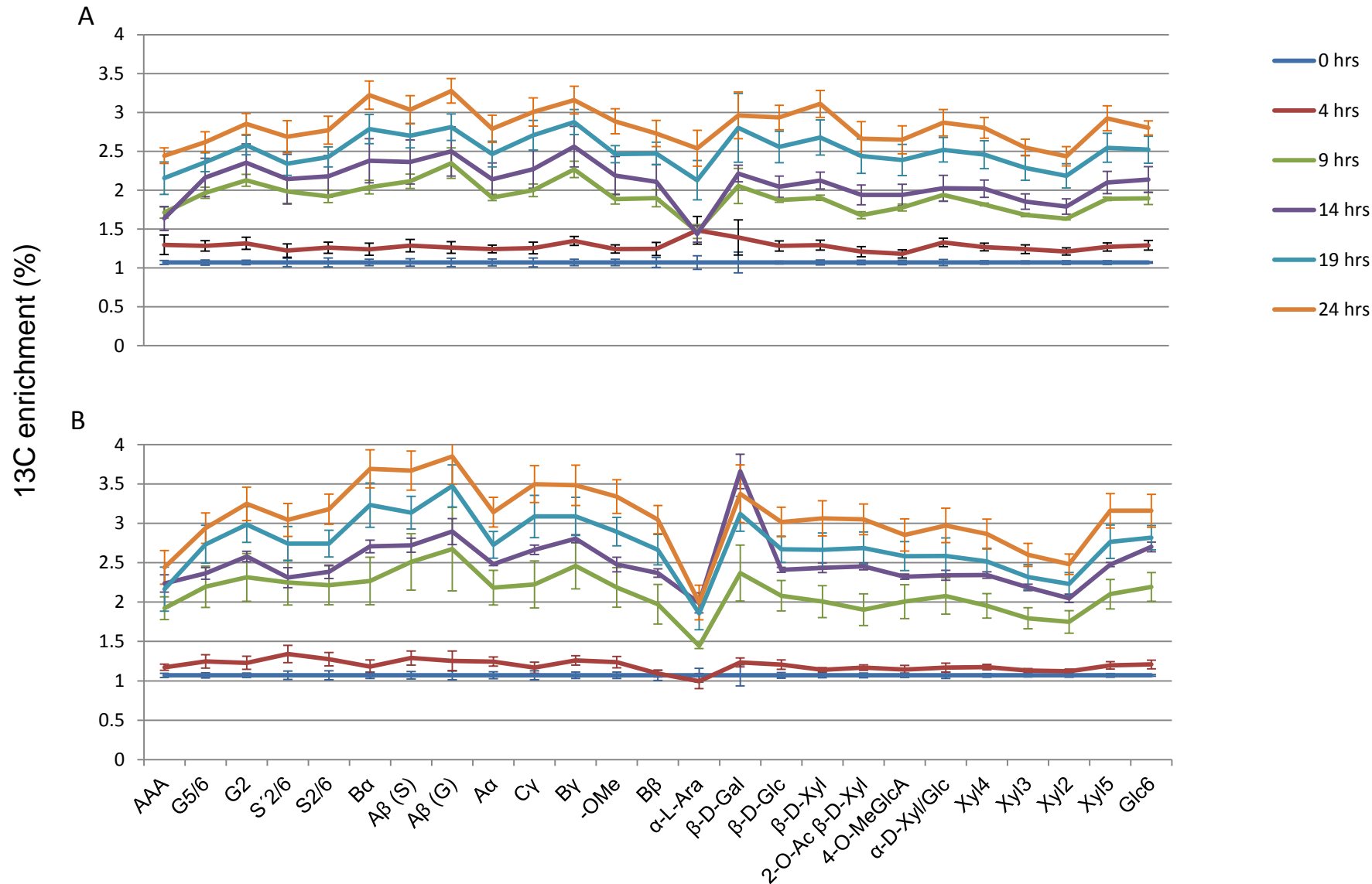
**Figure S1.** Assembly of the labelling experiment. Two month old wild type hybrid aspen trees were placed in a transparent chamber and labelled with  $^{13}\text{CO}_2$  under controlled environment. The temperature and humidity were kept constant using an climate control unit (A).  $\text{CO}_2$  level was monitored by a  $\text{CO}_2$  detector (PP SYSTEMS) (B).  $^{13}\text{CO}_2$  injection was performed using a 1 L syringe (Hamilton) (C).



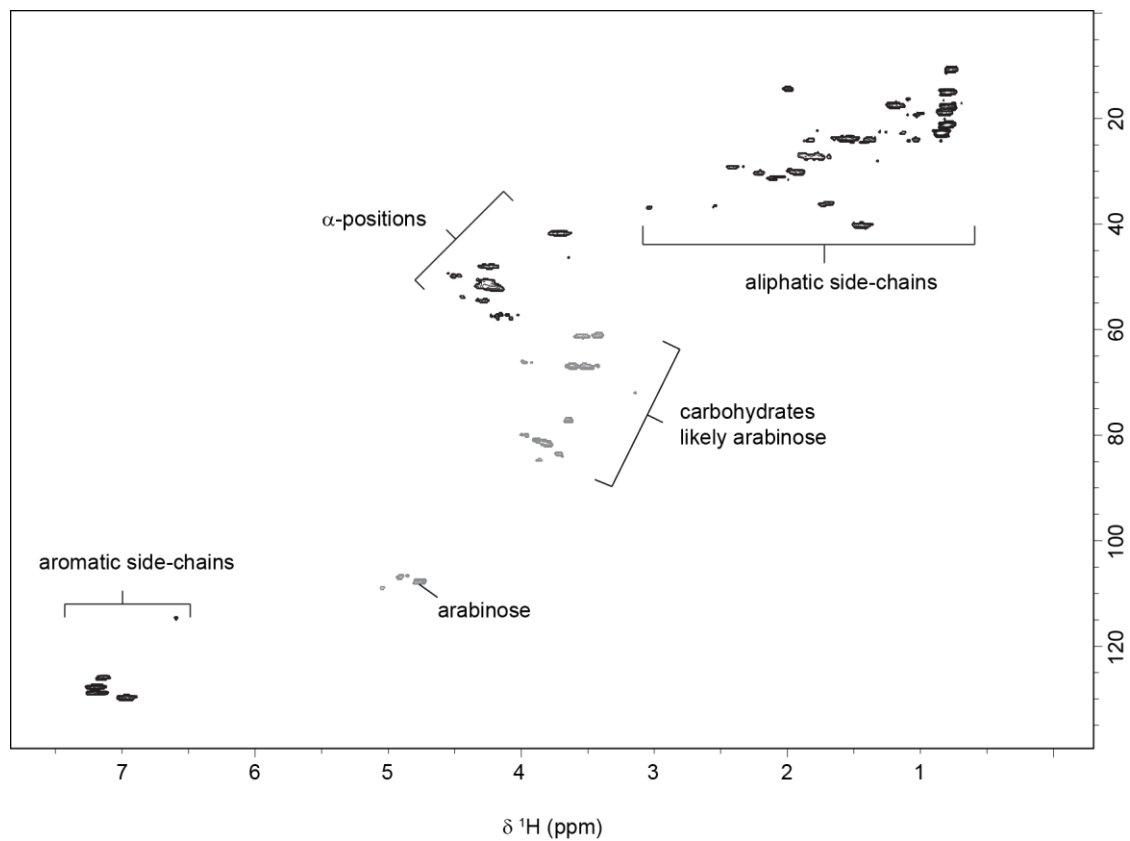
**Figure S2.** Incorporation of  $^{13}\text{C}$  in the cell wall polymers of developing wood in two-month old hybrid aspen. Trees were supplied with  $^{13}\text{CO}_2$  for 4 hours and samples were collected at 0, 6, 24, 48 and 72 hours from the start of the experiment.  $^{13}\text{C}$  incorporation was determined by 2D-NMR. Data is shown for signature peaks of cellulose, xylan and lignin. (A)  $^{13}\text{C}$  peak integrals shown for xylan (Xyl5) and cellulose (Glc6). (B)  $^{13}\text{C}$  peak integrals shown for S-lignin (S2,6) and G-lignin (G2) and methoxy groups (-OMe). Error bars represent the standard error of mean (SEM) of three biological replicates.



**Figure S3.**  $^{13}\text{C}$  labelling pattern of isotopomers in sucrose derived glucose (A), fructose (B), glucose (C), udp-glucose (D), hexose-phosphates (E) and phenylalanine (F) metabolite pools in developing wood shown as mass to charge ratio of each isotopomer (M1 to M7) to unlabelled isotopomer (M0). Error bars represent the standard error of mean (SEM) of four biological replicates.



**Figure S4.**  $^{13}\text{C}$  labelling patterns of cell wall monomers detected by 2D-NMR. (A) Experiment 1 with dark period between 9 and 14 hours after the start of the  $^{13}\text{CO}_2$  supply. (B) Experiment 2 with dark period between 14 and 19 hours after the start of the  $^{13}\text{CO}_2$  supply. Error bars represent the standard error of mean (SEM) of four biological replicates. Aromatic amino acids (AAA), G-lignin (G5/6, G2), S-lignin (S'2/6, S2/6), Lignin linkage types (Ba, Aβ (S), Aβ (G), Aα, Cγ, Bγ, Bβ), lignin methoxy groups (-OMe), α-L-arabinose (α-L-Ara), β-D-galactose (β-D-Gal), Glucose (β-D-Glc, Glc6, α-D-Xyl/Glc?), Xylose (β-D-Xyl, 2-O-Ac β-D-Xyl, Xyl2, Xyl3, Xyl4, Xyl5, α-D-Xyl/Glc?), Glucuronic acid (4-O-MeGlcA).



**Figure S5.** 2D  $^{13}\text{C}$ - $^1\text{H}$  HSQC NMR spectra of protein derived amino acids with correlating carbohydrate peaks obtained from the  $^{13}\text{C}$  labelled developing wood of hybrid aspen. Correlations above 0.6 (from 0-1 scale) were considered as meaningful. Correlating peaks were identified according to Ohman et al (2014).

# <sup>13</sup>C-incorporation Calculations

for  $i = 0:k$

$$S_i(1:n) = R(1:n) \times \frac{A(i+1)}{R(i)}$$

$$S_i(S_i > A([1:n] + i)) = A([1:n] + i)$$

$$A([1:n] + i) = A([1:n] + i) - S_i(1:n)$$

end

$R$  = <sup>12</sup>C reference MS (mass spectrum)

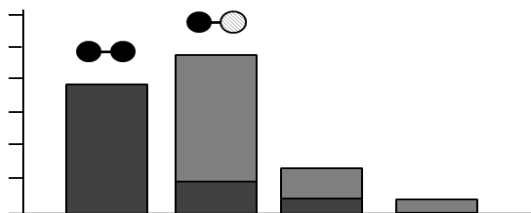
$A$  = <sup>13</sup>C incorporated MS

$S_i$  = estimated MS for each degree ( $k$ )  
of <sup>13</sup>C incorporation

$k$  = number of incorporated <sup>13</sup>C atoms

$n$  = number of isotopes ( $n \leq k + 1$ )

Example 1, Compound A if  $k = 1$



● = <sup>12</sup>C atom

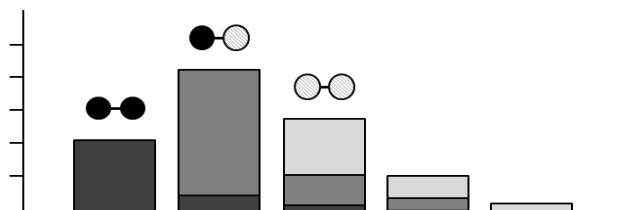
○ = <sup>13</sup>C atom

■  $S_0$  : Isotope distribution from a two carbon compound with zero incorporated <sup>13</sup>C ( $n=3$ ).

■  $S_1$  : Isotope distribution from a two carbon compound with one incorporated <sup>13</sup>C ( $n=3$ ).

■  $S_2$  : Isotope distribution from a two carbon compound with two incorporated <sup>13</sup>C ( $n=3$ ).

Example 2, Compound A if  $k = 2$



**Figure S6.** Example of the <sup>13</sup>C-incorporation calculation by sequential isotope compensation from a reference spectra.