

Supporting Information for:
Fractionation of organic matter due to reaction with ferrihydrite:
coprecipitation versus adsorption

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Figure SI-1: Turbidity (absorbance at 860 nm) during coprecipitation experiments.

Figure SI-2: Particle-associated C (adsorbed and coprecipitated) versus C concentration of the equilibrium solution for experiments with the forest-floor extract and lignin. Data of adsorption experiments are fitted with a Langmuir-type isotherm.

Figures SI-3 and SI-4: ¹³C CPMAS NMR spectra of supernatants from adsorption and coprecipitation experiments performed with both the forest-floor extract and lignin.

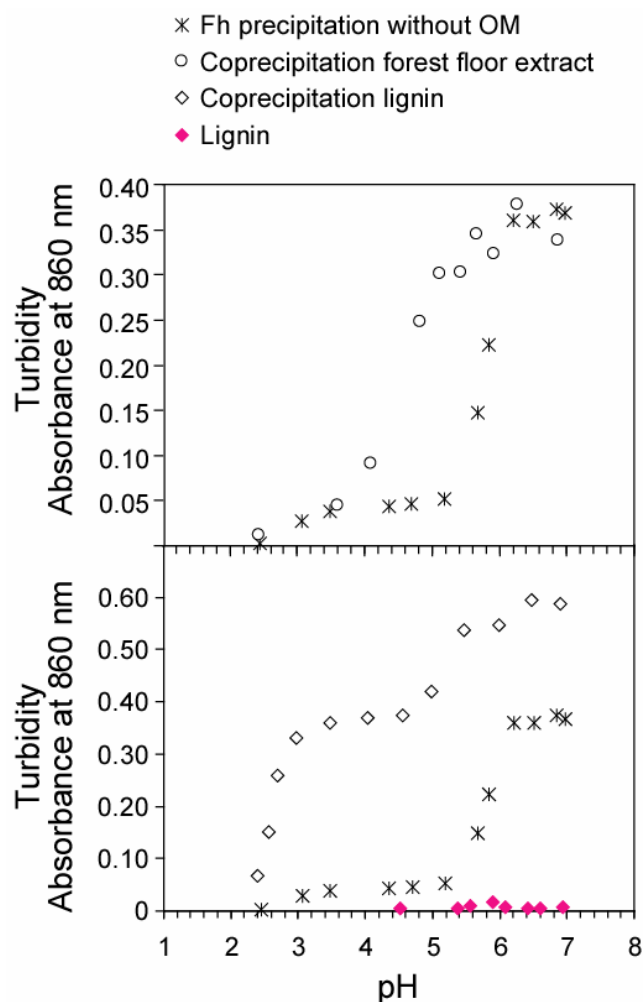
Table SI-1: Peak assignment of FTIR-absorption bands for the forest-floor extract. Band positions of the forest-floor extract are determined from minima of the 2nd derivative.

Figures SI-5 and SI-6: All FTIR spectra of products from adsorption and coprecipitation experiments performed with both the forest-floor extract and lignin.

Figure SI-7: Relation between total sugar and total organic C (a) and arabinose and total sugar (b) concentrations of supernatants from adsorption and coprecipitation experiments with the forest floor extract. Figure 7c shows the relation of galactose + mannose (GM) vs. arabinose + xylose (AX).

References with regard to the peak assignments in Table SI-1

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Figure SI-1: Turbidity during coprecipitation experiments was measured as the absorbance at 860 nm (Cary 50 Conc UV-Visible Spectrophotometer, Varian, Darmstadt) and is interpreted as a measure of the amount of suspended particles in solution. These data show that ferrihydrite precipitation in OM-free solutions rapidly starts at pH 5.8, whereas coprecipitation with the forest-floor extract begins at pH 4.5. During coprecipitation with lignin, we observed a first increase in turbidity immediately after KOH addition and a second one at pH 5. We assume that the first turbidity increase is related to the formation of Fe-OM complexes, while the one at pH 5 is caused by ferrihydrite coprecipitation. In a pure lignin solution, we did not observe any colloid formation.

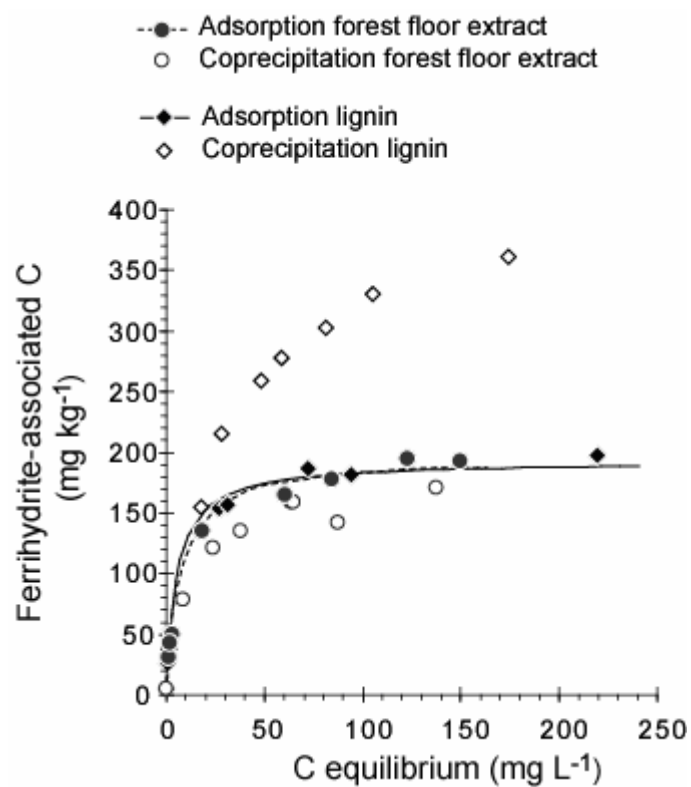


Figure SI-2: Ferrihydrite-associated C (adsorbed and coprecipitated) versus C concentration of the equilibrium solution for experiments with the forest-floor extract and lignin. Data of adsorption experiments are fitted with Langmuir isotherms

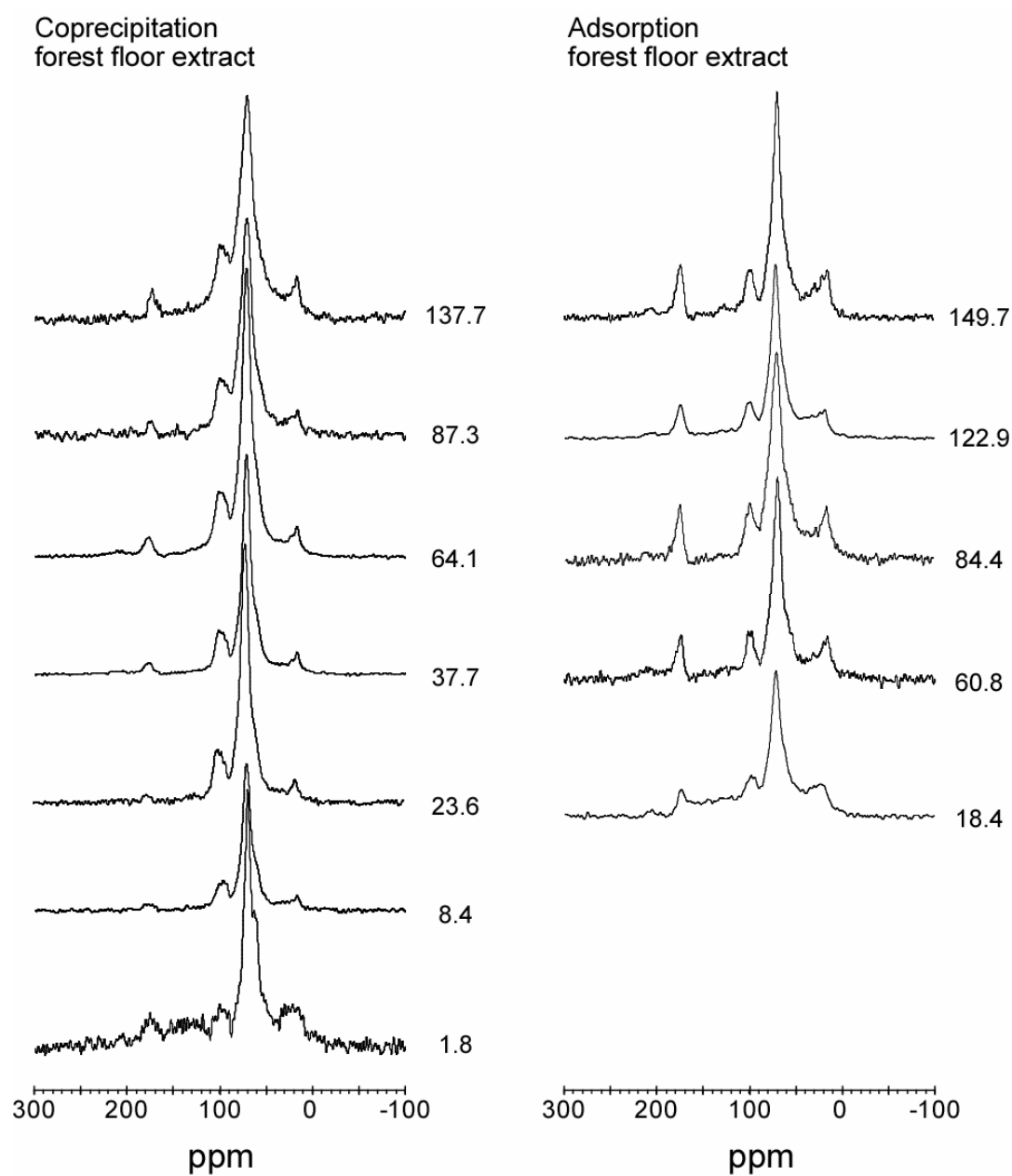


Figure SI-3: ^{13}C CP MAS NMR spectra of the supernatants from coprecipitation (left) and adsorption (right) experiments with the forest-floor extract. Numbers to the right of each spectrum give the C concentration of the equilibrium solution in mg L^{-1} . The corresponding spectrum of the original forest-floor extract is given in Figure 2.

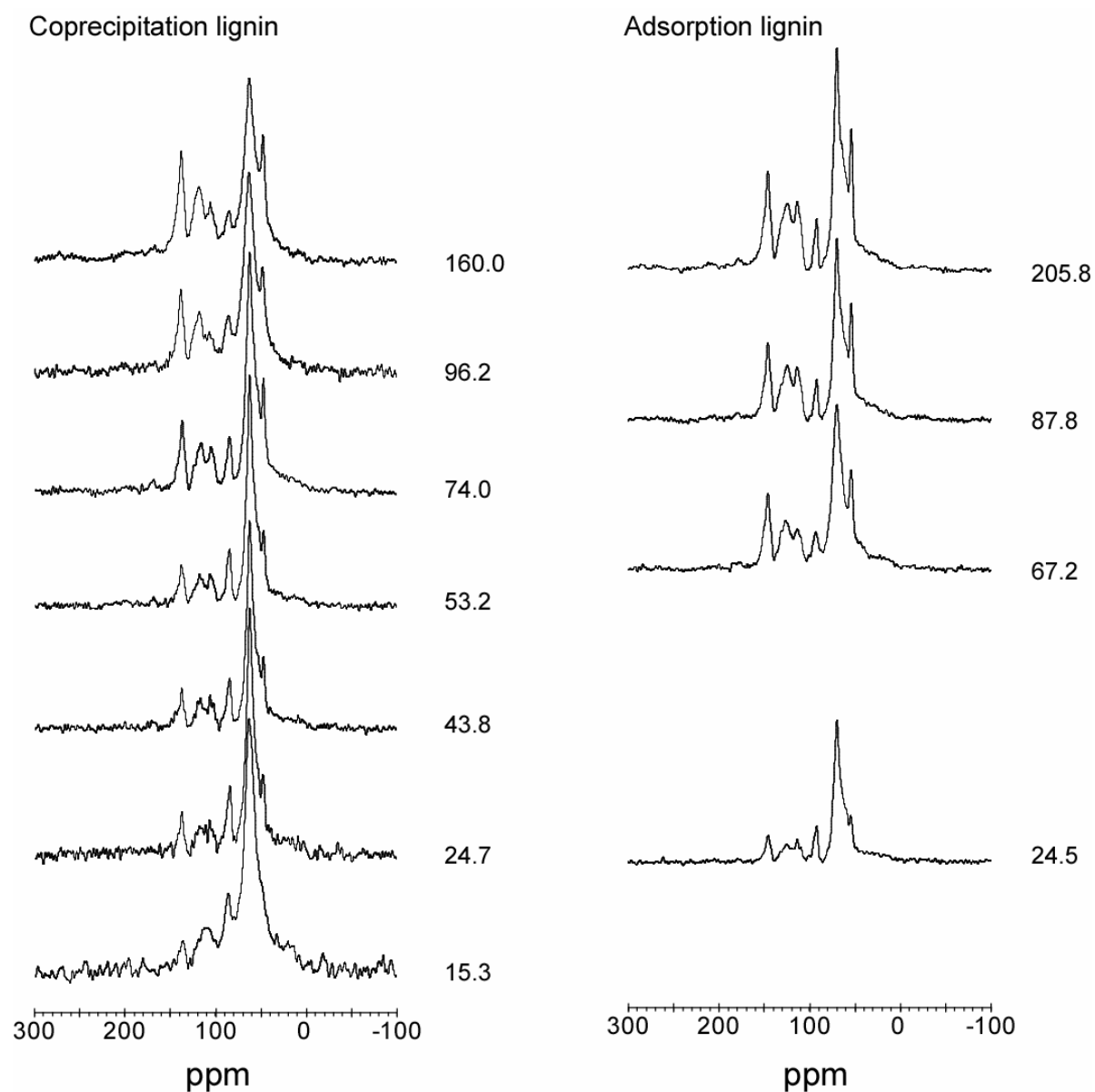


Figure SI-4: ^{13}C CP MAS NMR spectra of the supernatants from coprecipitation (left) and adsorption (right) experiments with lignin. Numbers to the right of each spectrum give the C concentration of the equilibrium solution in mg L^{-1} . The corresponding spectrum of the original lignin is given in Figure 2.

69 Table SI-1: Peak assignment of FTIR-absorption bands for the forest-floor extract. Band positions of
70 the forest-floor extract are determined from minima of the 2nd derivative.
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Peak position reference (cm ⁻¹)	Peak position forest floor extract (cm ⁻¹)	Peak assignment	Reference
1780-1760	1783	C=O stretch of γ - lactones	(1)
1725-1710	1726	C=O stretch of COOH or COOR	(2, 3, 4, 1)
1650-1600	1631	asym. C-O stretching in COO ⁻ , aromatic C=C stretching; H ₂ O; C=O in amide I	(2, 3, 5, 4, 1)
1550-1542	1548	N-H in plane deformation and C-N stretching of amide II	(3, 6, 7, 8, 1)
1525-1512	1517	aromatic C=C stretching	(2, 3, 5, 6, 1)
1460-1440	1462	C-H ₂ , C-H ₃ deformation (scissoring) in polysaccharides	(9, 3, 7, 2, 1)
1425-1400	1409	sym. stretch of COO ⁻ , C-OH def. of COOH	(3, 5, 7, 1)
1420-1200	1377	O-H in plane def. coupled with C-H def. in polysaccharide	(9)
1280-1180	1266	C-O stretch of phenolic OH or aryl ethers; asym. C-O stretch of ester and COOH	(2, 8, 4)
	1232		
	1205		
1160-1150	1148	C-O-C stretch of glucosidic link. in polysacch., coupled with C-OH stretch and OH def.	(6, 9, 8)
1079-1060	1077	C-O stretch coupled with C-C stretch and O-H def. in polysaccharides	(10, 9, 8)
1056-1033	1032	C-O stretch coupled with C-C stretch and O-H def. in polysaccharides	(10, 9, 8)
953-807	885	C1-H deformation of polysaccharides	(10, 9)
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765	777	ring breathing of polysaccharides	(9)

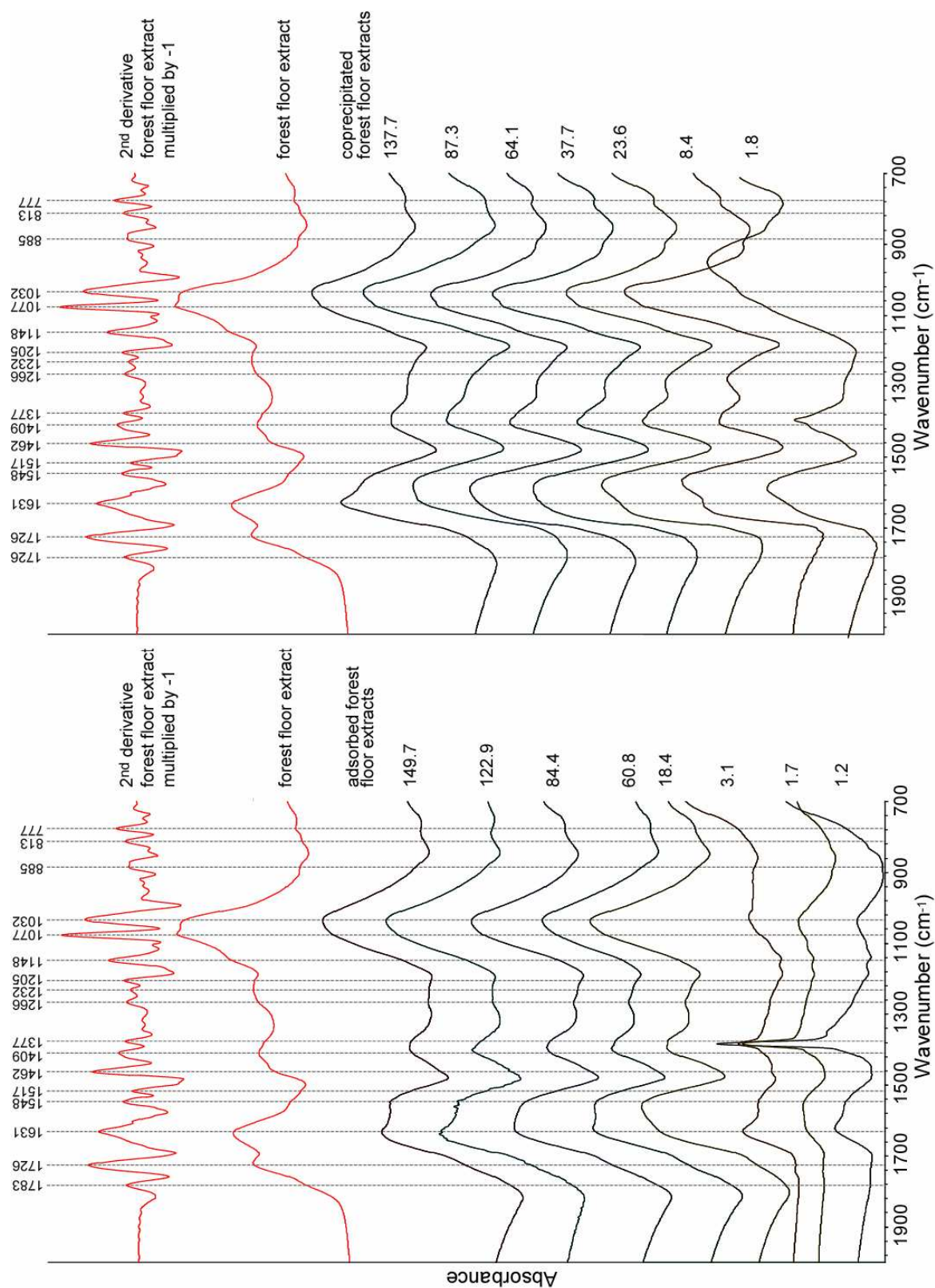


Figure SI-5: All FTIR spectra of adsorbed (left) and coprecipitated (right) forest-floor extracts. Numbers at the right of each spectrum give the C concentration of the equilibrium solution in mg L⁻¹. The spectrum of the original forest-floor extract and its 2nd derivative (multiplied by -1) are given for comparison. Table SI-1 of the supporting information summarizes the peak assignment.

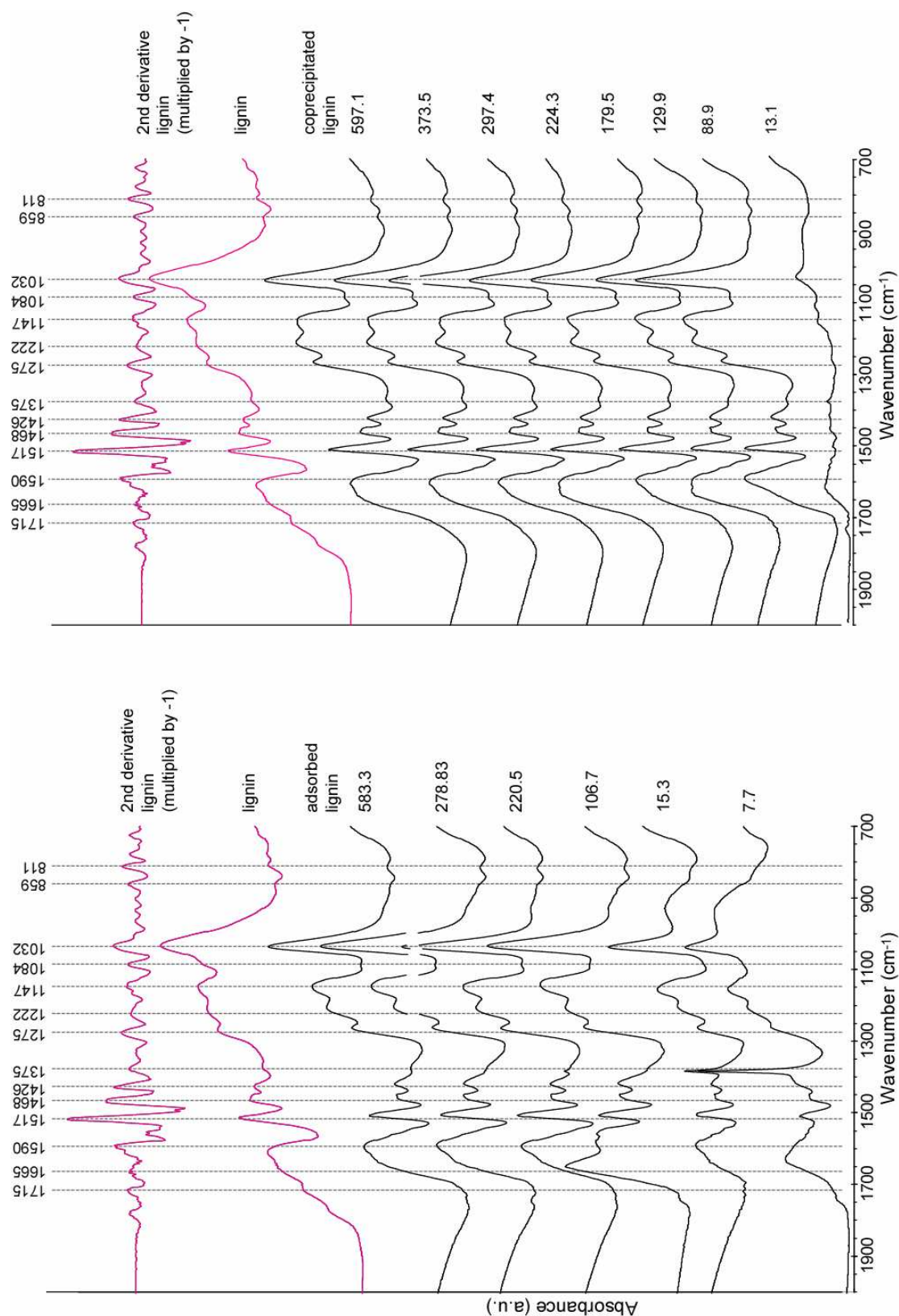


Figure SI-6: All FTIR spectra of the adsorbed (left) and coprecipitated (right) lignin. Numbers at the right of each spectrum give the C concentration of the equilibrium solution in mg L⁻¹. The spectrum of the original lignin and its 2nd derivative (multiplied by -1) are given for comparison.

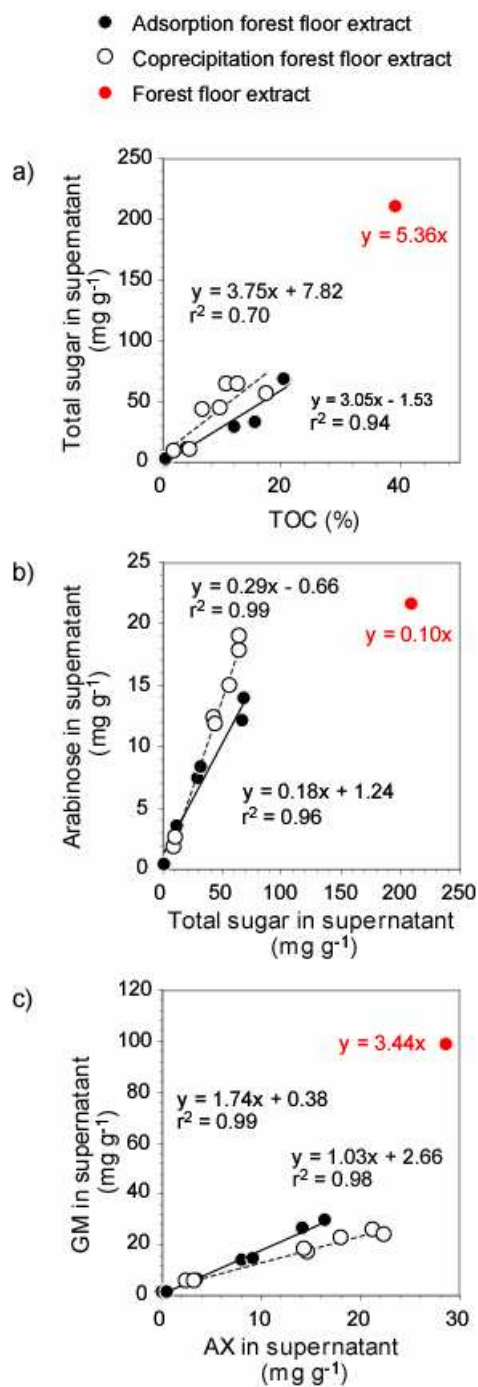


Figure SI-7: Relation between total sugar and total organic C (a) and arabinose and total sugar (b) concentrations of supernatants from adsorption and coprecipitation experiments with the forest-floor extract. Figure 7c shows the relation of galactose + mannose (GM) vs. arabinose + xylose (AX).

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