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**<sup>14</sup>C characteristics of dissolved lignin along a forest soil profile**

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21 **Abstract**

22 Lignin is a key component of soil dissolved organic carbon (DOC) and is recently  
23 suggested to track  $^{14}\text{C}$ -young DOC components. However, direct evidence is still lacking to  
24 prove this hypothesis in the soil. Here, utilizing molecular radiocarbon dating, we present the  
25 first  $^{14}\text{C}$  dataset on dissolved lignin through a Podzol soil profile. Dissolved lignin and hydroxy  
26 phenols had similar  $^{14}\text{C}$  content as soil organic carbon (SOC) and DOC in the surface organic  
27 layer. However, in contrast to SOC, both DOC and dissolved lignin phenols exhibited  
28 consistent and higher  $\Delta^{14}\text{C}$  values in the mineral soils. Coupled with lignin phenol  
29 concentration data, our results suggest that dissolved lignin comprises a key DOC component  
30 throughout this Podzol profile and is mainly supplied by surface leachates with young  $^{14}\text{C}$  ages.

31

32 **Keywords:** Soil organic carbon, dissolved organic carbon, lignin phenols, hydroxy phenols,  
33 compound-specific radiocarbon analysis.

34

35 Dissolved organic carbon (DOC) is the most bioavailable and reactive fraction of soil  
36 organic carbon (SOC; Kalbitz et al., 2000), whose source and age are related to DOC dynamics  
37 and the potential stability of SOC (Moore et al., 2013). As such, dissolved organic matter from  
38 fresh litter, root exudates and pre-aged roots with decadal turnover times supplies  $^{14}\text{C}$ -enriched  
39 DOC to the soil (Hansson et al., 2010; Wu et al., 2014), albeit with minimal influences on the  
40 leaching of slow-cycling SOC (Tu et al., 2011). By contrast, dissolved organic matter released  
41 from old soil organic matter (SOM) introduces relatively  $^{14}\text{C}$ -depleted DOC (Hagedorn et al.,  
42 2004; Lee et al., 2018), representing a critical pathway for the loss of relatively stable SOC  
43 (Moore et al., 2013). Hence, delineating the above source and age variations of soil DOC is  
44 essential for accurately assessing DOC dynamics and its impact on SOC stability. As bulk  
45 DOC consists of complex components with varied sources and ages (Kaiser et al., 2004), it is

46 difficult to fully understand patterns and drivers for its age variation. It is also challenging to  
47 routinely analyze DOC-<sup>14</sup>C, especially for low-DOC samples. Therefore, there has been an  
48 interest in seeking a potential indicator of young (and vice versa, old) DOC components in the  
49 soil to track their relative variations with changing environment (Benk et al., 2018).

50 Plant-derived lignin moieties are an important component of forest soil DOC (Kalbitz et  
51 al., 2006). Litter accumulating on the forest floor is considered to be the primary source of  
52 DOC and dissolved lignin (Wu et al., 2014), conferring both a young age in surface soils  
53 (Trumbore et al., 1992). With increasing depths, lignin-derived compounds may be selectively  
54 retained by sorption to reactive iron minerals and become less abundant in deeper soils relative  
55 to microbial-derived products (Kalbitz et al., 2003a). In mineral soils, desorption and/or SOM  
56 degradation may also introduce old (non-lignin) components into DOC (Hagedorn et al., 2004;  
57 Jia et al., 2017; Lee et al., 2018), thereby increasing age offsets between dissolved lignin and  
58 DOC with depth. Somewhat in line with this postulation, lignin phenols have been shown to  
59 trace relatively young surface carbon pools in the arctic watersheds by molecular radiocarbon  
60 dating (Feng et al., 2013; 2017). Moreover, using ultra-high resolution mass spectrometry,  
61 Benk et al. (2018) found that lignin-derived phenolic compounds (especially dimers) were key  
62 molecular species associated with young <sup>14</sup>C age in terrestrial dissolved organic matter in the  
63 critical zone. However, radiocarbon dating of lignin phenols, first used in marine and riverine  
64 systems (Feng et al., 2013; 2017), has not been conducted in soils so far to provide direct  
65 evidence for this emerging hypothesis. Filling the gap will help to verify dissolved lignin  
66 phenols as a tracer for young DOC in terrestrial environments and to improve our  
67 understanding of soil DOC dynamics.

68 Here we utilize a well-monitored site in a Norway spruce forest at the Long-term Forest  
69 Ecosystem Research (LWF) station of Beatenberg, Switzerland (46°43'N, 07°46'E; Schaub et  
70 al., 2011), where soil DOC is regularly sampled and easily accessible along an organic-rich

71 profile. We employ the recently developed method of radiocarbon dating dissolved lignin  
72 (Feng et al., 2017), and present a benchmark study to analyze the  $^{14}\text{C}$  content of dissolved  
73 lignin relative to bulk DOC and SOC along an 80-cm soil profile. By comparing  $^{14}\text{C}$  offsets  
74 among these components, we attempt to examine source variations (from fresh litter, pre-aged  
75  $^{14}\text{C}$ -enriched roots with decadal turnover times and old SOM) in DOC and dissolved lignin  
76 with depth. We also demonstrate the use of compound-specific  $^{14}\text{C}$  analysis in testing dissolved  
77 lignin as a potential tracer for young DOC components in soils (Benk et al., 2018).

78 Soils at the study site are classified as Podzols with a sandy texture and have a thick  
79 organic layer (20 cm; van der Voort et al., 2017). Bulk soils were collected using a soil corer  
80 from four depths in November 2012: 20 cm above the mineral soil surface ('surface sample';  
81 denoted depth of -20 cm) and at -5, 30 and 60 cm (all referred to as 'subsurface samples';  
82 Graf Pannatier et al., 2011; 2012). The first two depths were in the organic soil layer. Soil  
83 solutions were sampled periodically from July 2011 to October 2012 at the same depths using  
84 the established facilities including zero-tension lysimeters (for the surface sample) and  
85 ceramic suction cups (for the subsurface samples; Graf Pannatier et al., 2011; 2012). In total,  
86 23 solution samples were collected, including 11 samples with ample quantities for lignin  
87 phenol quantifications. Samples collected in May 2012 from the depths of -20, 30 and 60 cm  
88 were further used for  $^{14}\text{C}$  analysis of individual phenols.

89 Soil solutions were filtered through pre-washed 0.45- $\mu\text{m}$  filters, stored in plastic bottles  
90 and kept in the fridge in the dark at 4°C before analysis. The filtrates and bulk soil samples  
91 were acidified with hydrochloric acid to remove inorganic carbon. A subset of the filtrate was  
92 kept frozen before DOC measurement on a Shimadzu TOC-V organic carbon analyzer.  
93 Another subset (~5–8 mL) was freeze-dried using an oil-free vacuum-pump powered freeze  
94 dryer (Christ, Alpha 1-4 LO plus). The freeze-dried filtrates and bulk soil samples were then  
95 measured on the Mini radioCARbon DAting System (MICADAS) accelerator mass

96 spectrometry (AMS) system coupled to an elemental analyzer (Wacker et al., 2010) for  $^{14}\text{C}$   
97 contents of DOC and SOC, respectively. All  $^{14}\text{C}$  data were reported as  $\Delta^{14}\text{C}$  (‰). Lignin and  
98 hydroxy phenols were released using alkaline copper oxide oxidation (Feng et al., 2015) with  
99 individual phenols isolated by high-performance liquid chromatography (Feng et al., 2017)  
100 and measured as  $\text{CO}_2$  for  $^{14}\text{C}$  content on the Mini radioCarbon Dating System (MICADAS;  
101 Wacker et al., 2013). Radiocarbon contents were corrected against procedural blanks as  
102 described in Feng et al. (2017). Further details on analytical methods and blank assessment  
103 can be found in the Supplementary Information (SI) and Fig. S1.

104 Along the soil profile, DOC concentrations decreased with depth whereas lignin and  
105 hydroxy phenols exhibited large variability in abundance (Table 1). Dissolved lignin and  
106 hydroxy phenols showed positive correlations with DOC concentrations in the subsurface ( $P$   
107  $< 0.05$ ) but not surface samples (Fig. 1), suggesting that lignin is a key component of DOC in  
108 the mineral soils. Our results contrast with the down-profile decrease of lignin phenols relative  
109 to carbohydrates in the DOC of two forest soils (Kaiser et al., 2004). These differences may  
110 be attributed to (i) the strong leaching process and low content of reactive minerals (i.e., clay,  
111 iron and aluminum oxides) in the examined Podzols (van der Voort et al., 2017), preventing  
112 strong sorption and retention of lignin in the upper soils (Kalbitz and Kaiser, 2008), and/or (ii)  
113 preferential biodegradation of non-phenolic DOC components (such as carbohydrates and  
114 proteins) during transport to depth (Kalbitz et al., 2003b), leading to relatively consistent  
115 contribution of lignin to bulk DOC.

116 The  $\Delta^{14}\text{C}$  values of bulk SOC showed clear evidence for the presence of ‘bomb  $^{14}\text{C}$ ’  
117 (Trumbore, 2009), peaking at the bottom of the organic layer ( $\sim 167\text{‰}$  at  $-5$  cm) and decreasing  
118 to  $-173\text{‰}$  at 60 cm (Fig. 2a), reflecting rapid accumulation of organic carbon at this site (van  
119 der Voort et al., 2018). In contrast to SOC, DOC displayed relatively constant  $\Delta^{14}\text{C}$  values  
120 throughout the profile during the sampling period ( $74\sim 108\text{‰}$ ; Fig. 2a and Table S1). These

121 DOC- $\Delta^{14}\text{C}$  values, similar to those reported for DOC collected at the same site during May-  
122 September 2015 (van der Voort et al., 2017), are close to that of surface SOC ( $\sim 82\%$ ). Our  
123 observations are similar to those reported for soils from an old Norway spruce forest where  
124 surface soil DOC was more  $^{14}\text{C}$ -enriched than the atmosphere (Karlton et al., 2005). Given  
125 that atmospheric  $\text{CO}_2$  had a  $\Delta^{14}\text{C}$  value of  $\sim 38\%$  during our sampling years (Levin et al., 2013),  
126 DOC emanating from recently synthesized litter and root exudates was unlikely to make a  
127 large contribution to soil DOC at our study site. By the same token, degradation products of  
128 old SOM in the mineral soils are likely minor contributors to DOC at depth. Instead, leachates  
129 from the surface organic layers appeared to be the main source of DOC throughout the examined  
130 profile.

131 Similar to bulk DOC, individual lignin phenols showed similar and positive  $\Delta^{14}\text{C}$  values  
132 ( $78\text{--}180\%$ ) throughout the profile (Fig. 2b and Table S2). For the surface sample, hydroxy  
133 phenols potentially derived from proteins, tannin-like compounds and/or demethylation of  
134 lignin (Goñi et al., 2000) exhibited higher  $\Delta^{14}\text{C}$  values ( $108\text{--}180\%$ ) than that of DOC ( $96\%$ ),  
135 indicating that non-phenolic DOC components with somewhat lower  $^{14}\text{C}$  contents (likely from  
136 newly synthesized organic matter) comprise a larger proportion of DOC in the organic layer.  
137 This interpretation is consistent with the contrasting relationships between DOC and dissolved  
138 phenol concentrations in the subsurface versus surface samples (Fig. 1). For subsurface  
139 samples, dissolved lignin phenols exhibited higher  $\Delta^{14}\text{C}$  than bulk SOC or solvent-extractable  
140 lipids isolated from the same depth (van der Voort et al., 2017), suggesting minor contribution  
141 from SOM decomposition.

142 Overall, we conclude that lignin is a key DOC component in the Podzol subsurface soil  
143 and remains relatively young throughout the examined profile, providing first direct evidence  
144 for the recent postulation that dissolved lignin phenols may trace  $^{14}\text{C}$ -young DOC in terrestrial  
145 (soil) settings (Feng et al., 2017; Benk et al., 2018). Leachates from the surface serve as the

146 main source of DOC and dissolved lignin in the deeper soil while contributions from pre-aged  
147 roots and SOM decomposition are minimal at our site. However, these patterns need to be  
148 further confirmed using dissolved lignin  $^{14}\text{C}$  analysis in deeper soil horizons that were not  
149 available at this study site and for soils without thick organic layers and/or contain more  
150 reactive minerals to interact with lignin and/or experience less intensive leaching. We postulate  
151 that larger  $^{14}\text{C}$  offsets may be found between (young) dissolved lignin and (old) bulk DOC in  
152 the latter soils due to higher inputs from aged non-lignin components (such as microbial  
153 carbon or black carbon) to bulk DOC at depth. If this is the case, quantification of dissolved  
154 lignin phenols may open an analytical window for assessing the relative variation of young  
155 terrestrial DOC in complex systems when the expensive and sensitive  $^{14}\text{C}$  analysis is not  
156 allowed. Coupled with bulk DOC measurement, this advance will also facilitate the evaluation  
157 of old DOC release from terrestrial settings (such as the arctic rivers) and improve our  
158 understanding of DOC dynamics.

159

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**Table 1.** Concentrations of dissolved organic carbon (DOC), lignin and hydroxy phenols in the Podzol soil profile at three sampling times.

Depth (cm)	DOC	Lignin phenols <sup>1</sup>		Hydroxy phenols <sup>2</sup>	
	(mg L <sup>-1</sup> )	(µg L <sup>-1</sup> )	(mg g <sup>-1</sup> DOC)	(µg L <sup>-1</sup> )	(mg g <sup>-1</sup> DOC)
2011/07					
-20	64.0	86.7	1.4	53.1	0.8
-5	41.6	219.4	5.3	92.7	2.2
30	28.3	59.0	2.1	29.7	1.1
60	26.4	83.4	3.2	36.3	1.4
2011/10					
-20	52.6	416.8	7.9	85.6	1.6
-5	59.5	235.0	4.0	104.1	1.8
30	37.3	141.0	3.8	47.7	1.3
60	36.6	189.4	5.2	58.3	1.6
2012/05					
-20	38.8	219.4	5.7	41.0	1.1
-5	n.a.	n.a.	n.a.	n.a.	n.a.
30	22.7	68.2	3.0	15.4	0.7
60	26.5	110.7	4.2	19.3	0.7

n.a.: not available.

<sup>1</sup>Lignin phenols include eight monomers: vanillyl, syringyl and cinnamyl phenols.

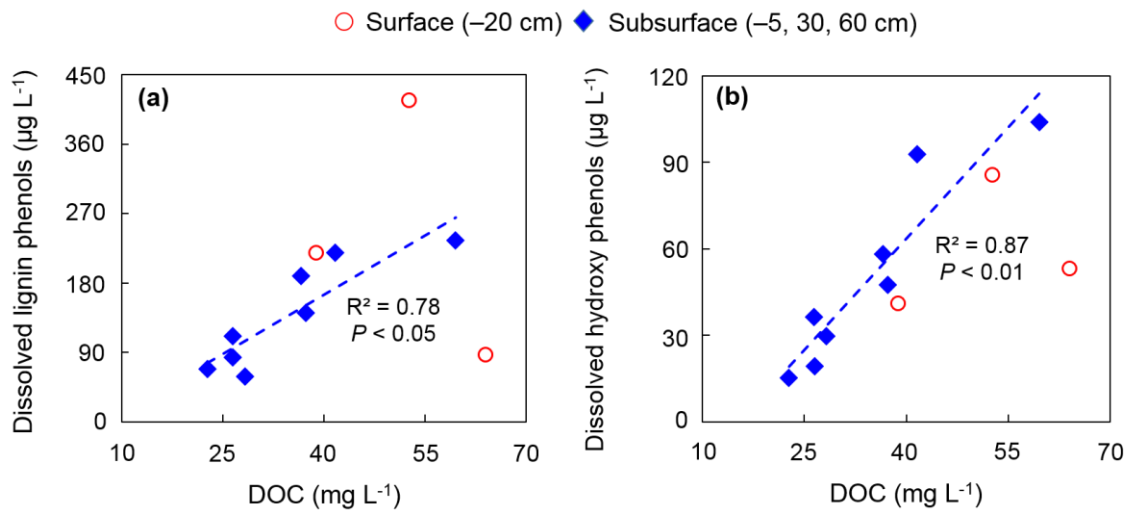
<sup>2</sup>Hydroxy phenols include *p*-hydroxybenzaldehyde, *p*-hydroxyacetophenone, and *p*-hydroxybenzoic acid.

## Figure captions

**Fig. 1.** Correlations of dissolved organic carbon (DOC) with dissolved lignin (a) and hydroxy phenols (b) in the Podzol profile. Blue dashed line shows linear regression for the subsurface samples (n = 8).

**Fig. 2.** The  $\Delta^{14}\text{C}$  values of dissolved organic carbon (DOC; sampled from July 2011 to October 2012 and May-September of 2015; a) and individual phenols isolated from soil solutions in May 2012 (b) in comparison to bulk soil organic carbon (SOC; sampled in September 2012). Black dotted line shows the changing pattern of SOC  $\Delta^{14}\text{C}$  with depth. Errors represent propagated analytical error of  $^{14}\text{C}$  measurement (with procedural blanks considered).  $\dagger\Delta^{14}\text{C}$  values of DOC for May-September of 2015 are obtained from van der Voort et al.(2017);  $\#p$ -hydroxybenzaldehyde and  $p$ -hydroxyacetophenone were combined for  $^{14}\text{C}$  measurement; \*vanillin and acetovanillone were combined for  $^{14}\text{C}$  measurement at 30 cm.

**Figure 1**



**Figure 2**

