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1 Pyrogenic carbon content and dynamics in top and subsoil of French forests

2

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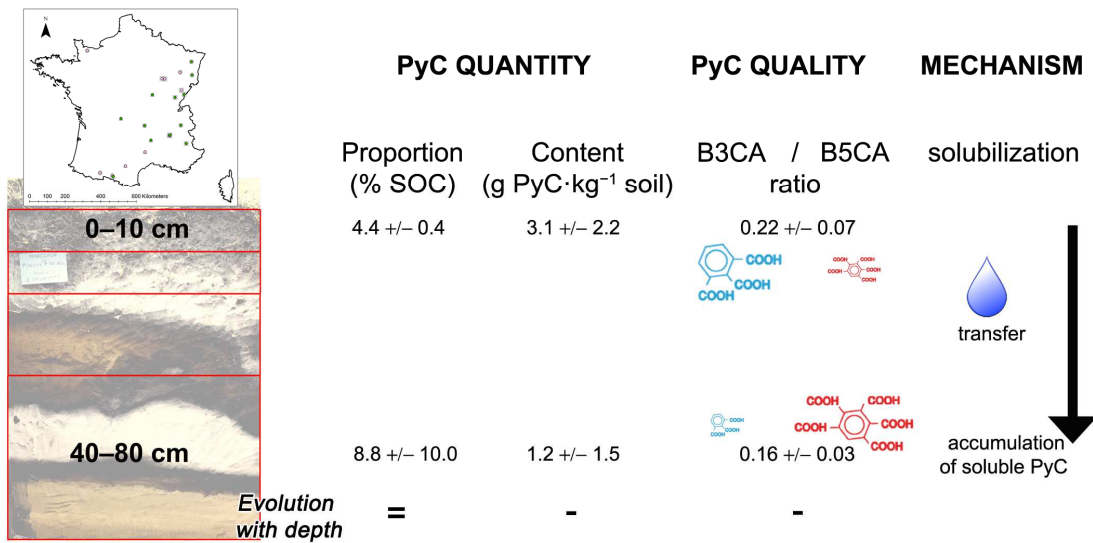
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17 **Graphical Abstract**



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19

20 **Abstract**

21 Pyrogenic carbon (PyC) may leave the soil surface where it is deposited, either through
 22 degradation, lateral transport or transfer within the profile. However, PyC has been
 23 seldom measured in the subsoil. We estimated the quantity and molecular composition of
 24 PyC in the topsoil and subsoil of 22 French forests with diverse soil types and vegetation
 25 cover. While the absolute PyC content decreased with depth, its proportion to the soil
 26 organic carbon remained constant or tended to increase. The benzene polycarboxylic
 27 acids pattern indicated that more condensed structures were found in the subsoil. Our
 28 results show that PyC transfers through the soil profile, probably as soluble fraction, and
 29 tends to accumulate in the subsoil, specifically in podzolic soils.

30

31 **Keywords:** pyrogenic carbon; benzene polycarboxylic acids; soil type; solubilization;
 32 subsoil; forest soils;

33 Soil pyrogenic carbon (PyC) represents about 10–15% of total soil organic carbon
34 (SOC) worldwide (Forbes et al., 2006; Preston and Schmidt, 2006; Bird et al., 2015;
35 Reisser et al., 2016 and references therein) and can locally reach up to 35–45% (Schmidt
36 et al., 1999; Skjemstad et al., 2002).

37 Deep (> 30 cm) SOC accounts for a significant amount of total SOC (Jobbágy and
38 Jackson, 2000), and is older and more stable than surface SOC (Rumpel and Kögel-
39 Knabner, 2010; Balesdent et al., 2018). This raises the question of how much PyC
40 contributes to deep SOC stocks. However, to date, studies on PyC have mostly focused
41 on surface soils, where the PyC is deposited after a fire. Only a few studies report PyC in
42 deeper soil horizons (e.g., Rodionov et al. 2006; Guggenberger et al., 2008; Rodionov et
43 al. 2010; Vasilyeva et al., 2011; Abney et al., 2017) and out of the 55 studies considered
44 in the meta-analysis of Reisser et al. (2016), only 4 considered a complete soil profile.
45 Since PyC has to be transferred from the surface to reach deeper soil layers, its quality
46 may be prone to changes with depth that have not been studied yet.

47 Drivers explaining PyC stocks in soil have been often related to fire properties. However,
48 in a recent global study, Reisser et al. (2016) showed that soil properties like pH or clay
49 content had a stronger impact on the PyC concentration than fire characteristics, land use
50 or climate. It is yet unclear if this global picture still holds at a landscape or regional
51 scale.

52 In this study, we took advantage of a large network of forest sites and an established PyC
53 characterization and quantification method to address the following research questions:

- 54 • Does PyC contribute significantly to total SOC in the subsoil?
- 55 • Does PyC quality evolve with depth?

56 We explored the effects of depth and of two potential drivers (soil class and vegetation
57 type) on PyC quantity and quality using a balanced design.

58

59 We analysed soil samples collected from sites of the French national network for the
60 long term monitoring of forest ecosystems (“RENECOFOR”). This network consists of
61 102 sites in managed forests, with even-aged stands. Mineral soil samples of the network
62 were collected by layers up to 1-m depth to ensure comparability among sites and
63 facilitate subsequent sampling to monitor SOC evolutions. Here, we chose to focus on
64 samples collected at two depths: 0–10 cm, hereafter topsoil and 40–80 cm, hereafter
65 subsoil. Details related to sample collection are available in Soucémarianadin et al.
66 (2018a). We selected 22 sites, out of the entire network, to cover a diversity of soil
67 classes and vegetation types. Soil classes were the following: (i) entic Podzols, (ii) eutric
68 Cambisols and (iii) dystric Cambisols (IUSS Working Group, 2015). Forest vegetation
69 was separated into two types with stands dominated by either (i) coniferous [silver fir
70 (*Abies alba* Mill.) or Norway spruce (*Picea abies* (L.) H. Karst.)] or (ii) deciduous [beech
71 (*Fagus sylvatica* L.)] trees. Study plots were mainly found in midslope or upslope
72 positions (Table S1).

73 Bulk < 2 mm-sieved soil samples were ground and carbon concentrations were
74 determined by dry combustion. Samples with carbonates were first decarbonated (Harris
75 et al., 2001).

76 PyC was measured using the benzene polycarboxylic acids (BPCA) molecular marker
77 method, which consists of extracting organic molecular markers specific from PyC
78 (Glaser et al., 1998; Brodowski et al., 2005). We followed the protocol described in

79 Wiedemeier et al. (2013). We used a conversion factor of 2.27 (Glaser et al., 1998) to
80 calculate PyC proportion (% SOC) and content ($\text{g PyC}\cdot\text{kg}^{-1}$ soil). While this ratio has
81 been criticized in the literature (e.g., Schneider et al., 2010), we used it to compare our
82 values with previous reports of PyC quantitative estimates (Reisser et al., 2016). We also
83 used the distribution patterns of BPCA markers as a quality indicator of the PyC. High
84 proportion of B5CA and B6CA were indicative of more condensed and aromatic material
85 (Wiedemeier et al., 2015), while B3CA and B4CA were the product of small condensed
86 units of 3 aromatic rings minimum (Ziolkowski et al., 2011).

87 We used paired t-test and multivariate models (see Soucémarianadin et al. (2018b) for
88 details) to assess the effects of the three factors (depth, soil class and vegetation type) on
89 the quantity and quality of PyC using R software (R Core Team, 2016). A generalized
90 least squares function (Pinheiro et al., 2016) was used for the linear mixed models, with
91 forest site as a random effect. Model selection was implemented with a top-down
92 strategy.

93

94 The mean PyC content in these French forest topsoils was $3.1 \text{ g PyC}\cdot\text{kg}^{-1}$ soil,
95 representing 4.4% of total SOC (Table 1). This proportion was comparable to topsoils in
96 Switzerland (0.6–4.7% of total SOC; Reisser, 2018) and in the “Centre” region of France
97 (mean PyC = 5.3% of total SOC; Paroissien et al., 2012). However, our average PyC
98 proportion to SOC was relatively low when compared to global values that average
99 13.7% of total SOC (Reisser et al., 2016). This could be linked to the ongoing fire
100 suppression over Europe that started in the 18th century (Pyne, 1997). The mean
101 distribution of total BPCA among the four markers (Fig. 1; Table S2) was quite similar to

102 what have been measured in Swiss forest topsoils (Reisser, 2018). In these topsoils,
103 B5CA represented a proportion of total BPCA (23–51%; Reisser, 2018) similar to the one
104 we observed in French forest soils. We also observed similar B6CA proportions to those
105 reported in topsoils of alpine Leptosols (about 25%; Eckmeier et al., 2013). However, a
106 few samples had very different proportions of B5CA and B6CA (Fig. S1). Specifically,
107 the PyC in HET09 topsoil had a very low B5CA proportion (6%; Fig. S1), while PyC in
108 HET21 and SP25 subsoils displayed relatively low B6CA (5% and 1%, respectively) and
109 high B5CA proportions (52% and 55%, respectively; Fig. S1). Moreover, given the
110 relative proportion of B6CA, around 30% (Fig. 1; Table S2), we assumed that soot
111 contribution to total PyC had been minimal (e.g., Li et al., 2015) and that the PyC present
112 in these forest soils originated mostly from biomass burning through forest fire.
113 Historical records showed that charcoal had been produced on-site in some of these
114 forests (Table S1). However, no trace of kilns was observed on the sampling plots and
115 although anthropogenic charcoal production might have constituted a source of PyC in
116 some of our study plots, it is thus unlikely to be significant.

117

118 Although absolute PyC content decreased significantly with depth, PyC proportion
119 tended to increase with depth (Fig. 2; Table 1). This increase was however not significant
120 (Table 2). These results suggest a preferential transfer of PyC to the subsoil compared to
121 other SOC moieties. Studies including samples from both topsoil and subsoil (> 30-cm
122 depth) are not common, as shown by the meta-analysis of Reisser et al. (2016), but some
123 previous observations agreed with our results. In Longleaf pine forests of the southern
124 USA, despite PyC content decreasing significantly with depth in most sites, PyC

125 proportion (5–7% of SOC) was independent of depth (Butnor et al., 2017). A tendency
126 for PyC proportion to increase with depth was observed in Russian Chernozems (from
127 7% to 10% SOC in 0–10 cm and 30–50 cm, respectively), in a mixed-grass savanna in
128 Texas (5–9% BPCA-C at 0–10 cm vs. 7–13% BPCA-C at 10–20 cm) and in black soils
129 of the Southern Alps (Dai et al., 2005; Hammes et al., 2008; Eckmeier et al., 2010).
130 However, non-linear evolutions of PyC proportion with depth have been reported
131 (Rodionov et al., 2006; Hammes et al., 2008; Soucémariadin et al., 2014) and
132 distribution of PyC proportion in the complete soil profile cannot thus be inferred from
133 our results.

134 Downwards transfer of PyC by leaching, either through particulate or soluble forms, has
135 been evidenced in various field conditions (Hockaday et al., 2006; Leifeld et al., 2007;
136 Major et al., 2010; Santos et al., 2016). Although PyC quality did not change drastically
137 between the top and deep soil layers (Fig. 1), we observed a significant decrease in B3CA
138 and a concomitant significant increase in more condensed B5CA (Table S2). Abiven et
139 al. (2011) observed that, over time, B5CA tended to preferentially solubilize, contrary to
140 B3CA. These quality changes were also observed when comparing dissolved organic
141 matter and particulate organic matter in rivers (Wagner et al., 2015). Our results therefore
142 suggest a significant contribution of soluble PyC to the deeper soil horizons. Meanwhile,
143 we did not observe any significant change in the B4CA/B6CA or B5CA/B6CA ratios
144 with depth (Table S2). As these ratios are mainly affected by PyC decomposition in soils,
145 this result suggests that no major PyC degradation occurred in our soil profiles (Singh et
146 al., 2014; Guggenberger et al., 2008).

147 While PyC solubilization seems to be consistent with the BPCA distribution patterns,
148 alternative transfer processes may have occurred. For example, mesofauna could
149 contribute to PyC transfer through bioturbation, but this was probably limited in our
150 coniferous sites and in our acidic soils, which tend to have few earthworms. Particle
151 movement in the soil macro-porosity after PyC fragmentation could have also played an
152 important role in plots where charcoal pieces have been observed (Table S1). Erosion
153 could impact horizontal transfer of PyC in sloping landscapes (e.g., Rumpel et al., 2006;
154 Abney et al., 2017). Further burial of PyC in depositional landforms could affect its
155 vertical distribution (Abney and Berhe, 2018). However this vertical transfer process was
156 unlikely to dominate in our study plots given their geomorphologic position (Table S1)
157 and the absence of colluvial soils in our data set.

158

159 Multivariate models showed that PyC quantity (content) and quality (relative proportion
160 of B3CA) were influenced by soil class, while vegetation type was only marginally
161 influential in B6CA distribution (Table 2). PyC proportion was higher in Podzols subsoils
162 than in both Cambisols subsoils (Fig. 2). This could be due to an increased solubilization
163 in Podzols caused by the podzolization process itself, during which transfer of organic
164 matter and sesquioxides takes place (Lundström et al., 2000; Buurman and Jongmans,
165 2005). High dissolved PyC concentrations were indeed measured in the E horizon of
166 Podzols from sites that experienced severe burning around 100 years prior to sampling
167 (Santos et al., 2017). Similar to OC, PyC was shown to be retained and to accumulate in
168 podzolic B horizons (Soucémariadin et al., 2014; Santos et al., 2017). In these horizons,
169 PyC was associated with the fine fraction and PyC content was correlated with

170 sesquioxide content (Soucémariadin et al., 2014). PyC accumulation was also observed
171 in other soil types rich in Fe and Al oxides (Major et al., 2010; Cusack et al., 2012;
172 Rumpel et al., 2012). These previous observations suggest that dissolved PyC is likely to
173 be stabilized in the subsoil of podzolic soils either through organo-mineral or organo-
174 metallic complexes.

175 The marginal effect of vegetation type on PyC content, proportion and quality compared
176 with soil class may be linked to the time frame that needs to be considered for PyC
177 evolutions. In these managed forests, trees were planted and current species may not
178 reflect species composition over the last centuries, which is the time frame related to PyC
179 turnover. Conversely, soil class encompassed long temporal scale (millennium) matching
180 PyC longer turnover and infrequent inputs into the soil, resulting in patterns over longer
181 timescale.

182

183 A few conclusions could be drawn from the observations we made in the soil profiles of
184 these twenty-two French forest sites. First, PyC transferred to and accumulated in the
185 subsoil in all soil types. Second, PyC appeared to transfer downwards preferably through
186 solubilization, specifically in podzolic soils. Third, the accumulation of PyC in the
187 subsoil was soil class dependent, but not related to present vegetation. Yet, our
188 investigation presents certain limitations and more studies on PyC in the complete soil
189 profile should be carried on in diverse soil types to further improve our understanding of
190 PyC transfer and accumulation in mineral soils.

191

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200

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350

351 **Tables and figures captions**

352 **Table 1.** Range (mean, minimum, maximum) of PyC proportion (percentage of total
353 SOC) and content (g PyC/kg soil), ratio of B3CA/B5CA markers, SOC content (g OC/kg
354 soil), pH in water and texture for topsoil and subsoil layers in the 22 study plots.

355

356 **Table 2.** Details of models and their significant terms selected to explain variations in
357 PyC quantity and quality in the 22 soil profiles. All models used a gls function (see
358 details in the *Statistical analyses* section). NS (non significant): $p > 0.1$; T (trend) $p < 0.1$;
359 * $p < 0.05$; ** $p < 0.01$ and *** $p < 0.001$.

360

361 **Fig. 1.** Mean (\pm standard deviation) relative distribution of total BPCA among the four
362 BPCA markers in the topsoil and subsoil.

363

364 **Fig. 2.** Comparison of PyC proportion (% of total SOC) in topsoil (0–10 cm) and subsoil
365 (40–80 cm) samples for the 22 forest plots. For each site, a symbol and color represent
366 the corresponding vegetation type and soil class, respectively. Podzols are above (or on)
367 the 1:1 line, whereas the two other soil classes tend to be below the line.

BPCA markers relative contribution (%)

0 20 40 60 80 100

mean topsoil



mean subsoil



■ B3CA ■ B4CA ■ B5CA ■ B6CA

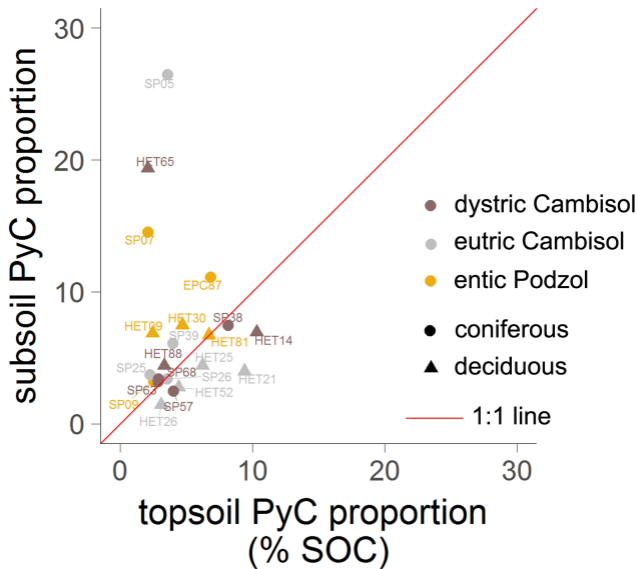


Table 1. Range (mean, minimum, maximum) of PyC proportion (percentage of total SOC) and content (g PyC/kg soil), ratio of B3CA/B5CA markers, SOC content (g OC/kg soil), pH in water and texture for topsoil and subsoil layers in the 22 study plots.

Factor	classes	PyC proportion (% SOC)			PyC content (g BPCA-C/kg soil)			B3CA/B5CA ratio			SOC content (g/kg soil)			pH _{water}			clay content (%)*			sand content (%)*			
		n	mean	min.	max.	mean	min.	max.	mean	min.	max.	mean	min.	max.	mean	min.	max.	mean	min.	max.	mean	min.	max.
DEPTH																							
	topsoil	22	4,4	1,9	10,3	3,1	0,8	10,4	0,22	0,12	0,41	72,4	22,3	147,1	5,0	4,1	7,5	27	6	45	32	1	83
	subsoil	22	8,8	1,4	44,3	1,2	0,1	6,1	0,16	0,09	0,2	13,4	3,3	42,4	5,9	4,6	8,7	20	5	53	42	6	85
	All	44	6,6	1,4	44,3	2,2	0,1	10,4	0,19	0,09	0,41	42,9	3,3	147,1	5,5	4,1	8,7	23	5	53	37	1	85

* data from Ponette et al. (1997).

Table 2. Details of models and their significant terms selected to explain variations in PyC quantity and quality in the 22 soil profiles. All models used a gls function (see details in the *Statistical analyses* section). NS (non significant): $p > 0.1$; T (trend) $p < 0.1$; * $p < 0.05$; ** $p < 0.01$ and *** $p < 0.001$.

Response variable	Transformation	Predictors in final model and level of significance	n ^a
PyC proportion	1/	depth ^{NS} + soil ^{NS} + depth × soil ^T	44
PyC content	1/sqrt	depth*** + soil**	44
B3CA	1/	depth** + soil ^T	44
B5CA	1/	depth**	43
B6CA	no	veg ^T + soil ^{NS} + veg × soil ^T	42
B4CA	1/	no significant factor	44

^a outliers were identified with Cook's distance.