



HAL
open science

Spectral characteristics of soil dissolved organic matter: Long-term effects of exogenous organic matter on soil organic matter and spatial-temporal changes

N.Y. Musadji, L. Lemée, L. Caner, G. Porel, P. Poinot, C. Geffroy-Rodier

► To cite this version:

N.Y. Musadji, L. Lemée, L. Caner, G. Porel, P. Poinot, et al.. Spectral characteristics of soil dissolved organic matter: Long-term effects of exogenous organic matter on soil organic matter and spatial-temporal changes. *Chemosphere*, 2019, pp.124808. 10.1016/j.chemosphere.2019.124808 . hal-02284823

HAL Id: hal-02284823

<https://hal.science/hal-02284823>

Submitted on 21 Dec 2021

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution - NonCommercial 4.0 International License

1 **Spectral characteristics of soil dissolved organic matter: long-term effects of exogenous**
2 **organic matter on soil organic matter and spatial-temporal changes**

3

4 N.Y Musadji^{1,2}, L. Lemée¹, L. Caner¹, G. Porel¹, P. Poinot¹, C. Geffroy-Rodier^{1,*}

5 1 Institut de Chimie des Milieux et Matériaux de Poitiers (IC2MP), CNRS, Université de
6 Poitiers, France

7 2 Institut National Supérieur d'Agronomie et de Biotechnologies (INSAB), Université des
8 Sciences et Techniques de Masuku (USTM), Gabon

9

10 *Corresponding author



11

12

13 **Abstract**

14

15 The aim of this study was to evaluate the long-term effect of urban and green waste compost
16 exogenous organic matter (EOM) on soil dissolved organic matter (DOM). A luvisol
17 was amended 7 years before the study. DOM was investigated along a soil profile down to
18 one meter depth regarding seasonal variations (autumn and spring). DOM sampled by suction
19 cups was characterized using dissolved organic carbon (DOC) content and excitation
20 emission matrix (EEM) fluorescence. The variability of DOM concentrations was pronounced
21 but no major change in composition was determined. The results obtained, reinforced by
22 statistical analysis, showed that the DOM quality was mainly influenced by soil management
23 (organic matter amendment) whereas the quantity mainly depended on the season (heavy
24 precipitation event). DOM humic characteristics were strongly dependent on amendment and
25 changed with depth but was not affected by the season. Long term effect of compost organic
26 matter was highlighted after a 7-years amendment.

27 **Keywords:** DOM, Exogenous organic matter, Field experiments, Seasonal changes,
28 Fluorescent proxies

29

30

31 **1. Introduction**

32 Soil dissolved organic matter (DOM), which represents a small portion of soil organic matter
33 (SOM < 2%), is the most dynamic and reactive fraction in terrestrial ecosystems (Haynes,
34 2005; Marschner and Kalbitz, 2003). DOM plays a key role in bioavailability and transport of
35 organic and inorganic compounds among which contaminants resulting from anthropogenic
36 activity (Akkanen et al., 2004; Bolan et al., 2011). DOM's response to environmental
37 changes is rapid (Borisover et al., 2012; Chantigny, 2003; Chen et al., 2016; Fließbach et al.,
38 2007; Gregorich et al., 1994; Haynes, 2000; Sharma et al., 2017). Its characterization is an
39 important issue for soil environmental studies as DOM is a useful indicator for SOM quality
40 (Filep et al., 2015; Haynes, 2005; Jones et al., 2014) and soil management impact (Haynes,
41 2005; Seifert et al., 2016a; Sharma et al., 2017; Sun et al., 2017). Although quantifying DOM
42 amount (commonly by measuring Dissolved Organic Carbon concentration) is necessary, it is
43 also important to characterize DOM composition, because its reactivity and properties are
44 driven by its components.

45

46 Many analytical methods have been used to characterize the heterogeneous molecular
47 composition of DOM. Optical techniques such as UV-Vis and fluorescence spectroscopies
48 have been the most widely applied to assess DOM composition, to retrace its sources and to
49 improve its characterization (Korak et al., 2014; Leenheer and Croué, 2003). Excitation
50 emission matrix (EEM) fluorescence is widely used to describe fluorescent DOM (Borisover
51 et al., 2012; Chen et al., 2003; Coble, 1996; Gonçalves-Araujo et al., 2016; Ohno et al., 2007;
52 Pan et al., 2017). The EEM fluorescence spectra highlight three major fluorophores
53 characterizing humic/fulvic- and protein-like components (Baker and Lamont-Black, 2001;
54 Chen et al., 2003). Dissolved organic matter is also constituted by low molecular weight
55 substances such as organic acids and amino acids.

56

57 DOM dynamics has been extensively studied in numerous laboratory experiments using
58 disturbed soil samples, but few studies have been conducted in field conditions (Chantigny,
59 2003; Embacher et al., 2007). The extraction methods and conditions to recover water
60 extractable organic matter, vary greatly among different studies and their effects on DOM
61 components are poorly documented (Xie et al., 2017). Experiments at field scales are needed
62 to characterize undisturbed samples(Deb and Shukla, 2011).

63 In order to obtain deeper insights into its mid- and long-term dynamics, soil DOM from a
64 research site was monitored up to 7 years after an exogenous organic matter amendment. The
65 availability of soils in adjacent plots with the same soil formation offers an opportunity to
66 evaluate amendment effects on SOM and DOM. The main objectives of our study were (i) to
67 quantify the temporal variability (seasonality) from the top soil to 1 meter depth and (ii) to
68 quantify the influence of organic fertilization on DOM on long term. These characterizations
69 were performed by bulk analyses and EEM fluorescence.

70 **2. Materials and methods**

71 **2.1 Experimental site**

72 The study was conducted in the Hydrogeological Experimental Site which is a part of the
73 Network of National Hydrogeological Sites (SNO H+) and of the French network of Critical
74 Zone Observatories: Research and Applications (OZCAR) of the University of Poitiers
75 located in the Regional Observatory of Deffend (OR, Mignaloux-Beauvoir, France). The soil
76 is a luvic cambisol fully characterized (Celerier et al., 2009).The studied area, currently under
77 grassland, was previously divided into 3 control plots and 3 amended plots. Each plot had a
78 total area of 3 x 3 m². The plots were separated in all direction by a border space of 2 m. The

79 compost was produced at the platform of La Villedieu du Clain (France) in open air windows
80 from 80% green waste and 20% biowaste obtained from district selective collection.

81 The molecular characterization of this compost has been published in (Som et al., 2009). A
82 unique amendment was performed in March 2006. Urban green waste compost was amended
83 on 3 plots (T, 150 t.ha⁻¹) closed to 3 control plots (C, grassland without amendment), all
84 equipped with suction cups.

85

86 **2.2 Water samples and bulk analyses**

87 Each plot was equipped with 12 ceramic suction cups (31 mm, SDEC, France) to collect soil
88 solutions disposed in triplicates at 15, 30, 60 or 100 cm depth. The installation of triplicates
89 suction cups in 6 plots at 4 depths was cost and time consuming but allowed the sampling of
90 soil solution directly in the field without any disturbance of the soil nor extraction of the
91 organic matter. For this study, sampling was performed in autumn 2012 and spring 2013.
92 Samples were then filtered through 0.45 µm filters (Polycap 75 TF, Whatman) and the pH
93 was measured. Samples were then stored in glass bottles at 4°C prior to analysis.

94 DOC measurements were performed with a Shimadzu Total Organic Carbon Analyzer (TOC-
95 V CPN, Japan). The instrument was run in Non Purgeable Organic Carbon mode (NPOC).
96 Samples for DOC analyses were acidified with 2 N HCl and sparged with high purity air to
97 remove inorganic carbon. For each sample, the result was the mean of a least three injections
98 (standard deviation <0.1 and variation coefficient < 2 %).

99 For a given plot, triplicates having the same DOC and pH values were mixed for further
100 studies. 78 samples were then taken into account for this study.

101

2.3 Spectroscopic analyses

102
103 All samples were diluted to obtain a concentration of 5 mgL⁻¹. Fluorescence spectra were
104 recorded with a Spex Fluoromax-2 ISA spectrofluorometer (Jobin Yvon, Edison, USA)
105 equipped with a 450 W Xe lamp. Samples were placed in a 1 cm quartz cuvette thermostated
106 at 20°C. 41 individual emission scans (300-550 nm, at 5 nm intervals) at 5 nm excitation
107 wavelength intervals between 200 nm and 400 nm were recorded. Data were all normalized to
108 the Raman peak of the Milli-Q water. EEM plots were assembled by combining the individual
109 emission spectra using SigmaPlot 11 (Systat Software, Inc., San Jose, CA, USA). The fulvic
110 acids from the control soil were used as reference. Based on the corrected absorbance and
111 EEM fluorescence data, general features and three optical indices were used to further
112 describe the compositional characteristics of soil DOM: (1) A₂₅₄, UV absorbance at 254 nm to
113 estimate aromaticity of DOM; (2) Fluorescence index (FI), the ratio of the emission intensity
114 at 450 nm to 500 nm at an excitation of 370 nm, used to reflect the relative microbial
115 contribution (>1.9) or terrestrial plant one (<1.4) (Coble, 1996; McKnight et al., 2001); (3)
116 Humification index (HIX), the ratio of the peak integrated area under the emission spectra
117 435–480 nm and under the sum of the emission spectra 300–345 nm and 435–480 nm at an
118 excitation of 254 nm to reflect important complexity and condensation (H/C ratios) of
119 terrigenous contribution (>10) (Birdwell and Engel, 2010; Ohno, 2002); (4) Biological index
120 (BIX) is an indicator of the relative contribution of the recently microbially produced DOM,
121 calculated as the ratio of emission intensity at 380 nm to 430 nm at excitation 310 nm
122 (Huguet et al., 2009).

123

124

125 **2.4 Statistical analysis**

126 Descriptive statistics of DOC, pH and fluorescence indexes according to season, depth and
127 plot management were presented in box and whiskers plots. One-way ANOVA was used to
128 assess the difference between median and mean values. Principal component analysis (PCA)
129 was used to identify possible spatial-temporal trends. PCA was done using all sampling points
130 ($n = 78$) covering the study period. Five quantitative variables were analyzed: DOC, pH and
131 fluorescence indexes (HIX, FI and BIX). All statistical tests were conducted by R Core Team
132 (2019). Pearson's product moment correlation was used to determine the correlation of the
133 different components to physical, biological and chemical environmental variables. The
134 means for each of sampling periods were used in the correlation analysis against the five
135 quantitative parameters. Pearson's product moment correlation coefficients were analyzed
136 using Sigma Stat version 3.5 (Systat Software).

137 **3. Results and discussion**

138 **3.1 Seasonal and spatial variations of pH and DOC**

139 Bulk analyses were performed on 78 samples collected from 15 to 100 cm depth in autumn
140 and spring. The 3 control triplicates and the 3 amended soils exhibited the same tendencies.

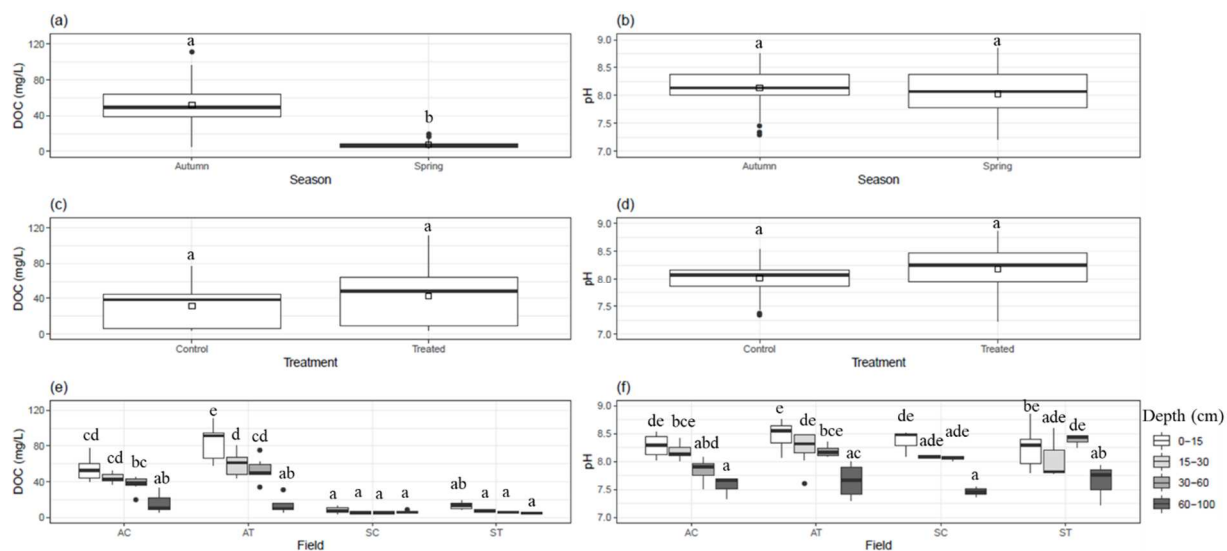
141 The seasonal and spatial variations of pH and DOC concentrations are shown in Fig. 1 and
142 summarized in Table 1. No seasonality variation was observed in pH values (Fig.1b) with
143 mean values of 8.1 (7.3-8.7) for autumn and 8.0 (7.2-8.8) for spring samples but a decrease
144 was observed with increasing depth (Fig.1f).

145
146 A significant difference ($p < 0.05$) between autumn and spring DOC was observed (Fig.1a).
147 Mean DOC values (5th and 95th percentiles) were 51.8 (ranging from 5.9 to 110.9) mg.L⁻¹ and
148 7.7 (3.7-19.2) mg.L⁻¹ in autumn and spring, respectively. Mean DOC rain value for the period
149 was about 6.6 mg.L⁻¹ close to DOM spring values. Previous studies have reported that the

150 amount of water extractable OM depends on leachate volumes (Mertens et al., 2007; Tipping
 151 et al., 1999). In controlled conditions intensive and repeated leaching was shown to reduce
 152 DOC concentration (Christ and David, 1996). The low spring DOC values closed to the
 153 rainfall DOC value were thus attributed to the rainy spring event.

154
 155 For both soil treatments (Fig.1.e), DOC concentrations decreased with increasing soil depth
 156 which was consistent with previous studies for different soil types and under various
 157 vegetation systems (Seifert et al., 2016b; Sharma et al., 2017; Xi et al., 2018).

158
 159 Fig. 1c-d pointed out the long-term effect of amendment. After 7-years, the control and
 160 amended plots showed the same basic pH values but still exhibited different DOC contents.
 161 DOC mean values were 31.1 (3.7-77.1) mg.L⁻¹ for non-amended soil referenced as control
 162 and 42.5 (4.2-110.9) mg.L⁻¹ for the amended soil. Higher DOC concentrations in amended
 163 plots were relevant with the abundance of plant residues and their degradation products
 164 contained in compost (Musadji, 2013). The higher contents found in amended plot on the top
 165 soil (down to 60 cm) confirmed the previous studies devoted to short-term effect of OM
 166 amendment on water-extractable organic matter (Erich et al., 2012; Federici et al., 2017;
 167 Mouloubou et al., 2016; Turrión et al., 2012).

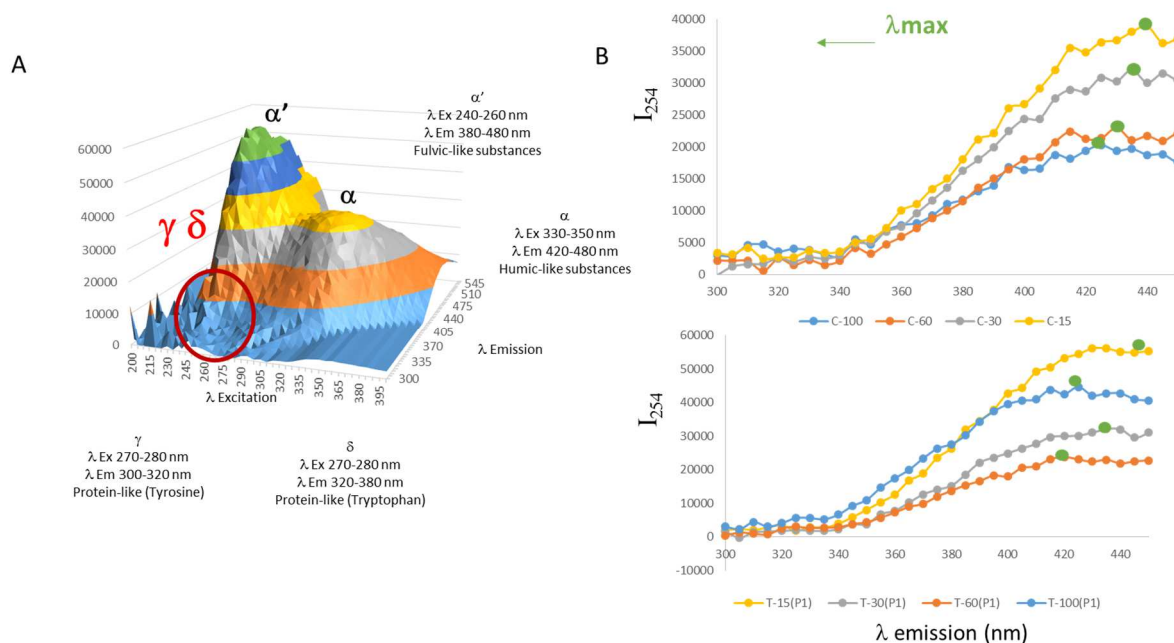


169 Fig. 1: DOC (mg.L⁻¹) and pH mean values according to two Seasons Autumn (A) and Spring (S) a, b); two
 170 soils: compost treatment (T) compared to control (C) c, d), and four depths (15, 30, 60 and 100 cm). Boxes
 171 plots indicate 25th and 75th percentiles, solid lines within boxes refer to median values, in-box points
 172 represent the mean value and the close circles represent the outliers values. The subscripts letters after the
 173 data indicate the similarity and the differences. The same letter indicates that the mean values are similar
 174 within a group and between groups. Different subscripts represent significant difference between compared
 175 groups at p-value < 0.05

176 3.2 DOM spectroscopic characteristics

177 3.2.1 General spectral features

178 Excitation emission matrix fluorescence measurements were performed to discriminate DOM
 179 inputs and amendment effect. All the samples exhibited humic-like fluorophores highlighting
 180 the presence of terrestrial biomaterials such as lignin and protein-like one. This kind of
 181 fluorophoric compounds allows the selective and sensitive distinction of relative contribution
 182 of natural materials in DOM (Chen et al., 2003; Coble, 1996; Hudson et al., 2007), reflecting
 183 different origins (Huguet et al., 2009; McKnight et al., 2001).

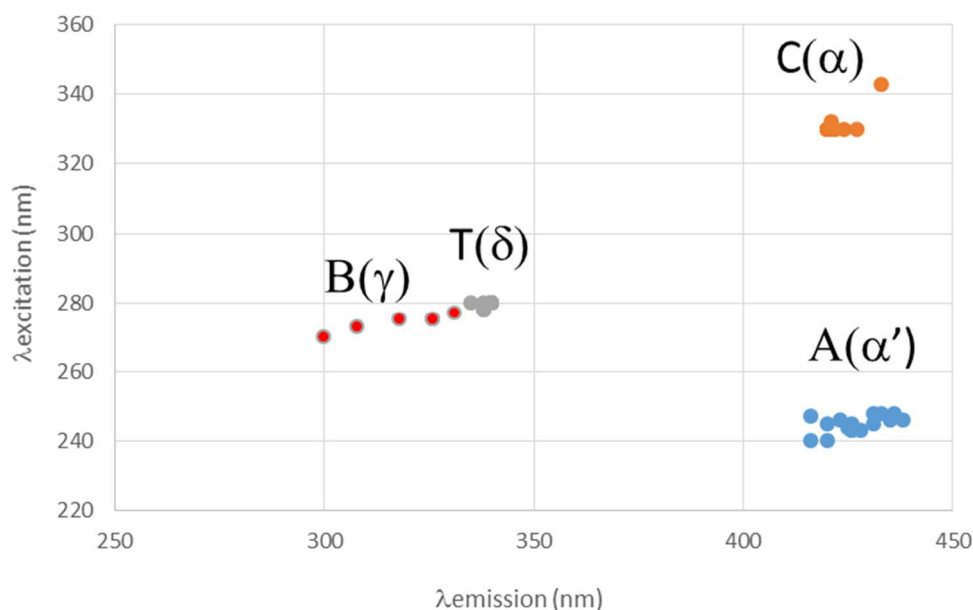


184

185 Fig. 2: A]. Representative excitation emission matrix fluorescence (EEMF) spectrum. Colors show the relative
 186 fluorescence intensity of DOM. The identified components contained humic-like substances (C/α) and recent
 187 materials / fulvic acid-like substances (A/α') located at $\lambda_{ex}/\lambda_{em}$ 330-350/420-440 nm and 240-260/420-480 nm
 188 respectively. Protein-like substances (δ/T , γ/B) were detected at $\lambda_{ex}/\lambda_{em}$ 270-280/300-340 nm. B]. Fluorescence
 189 spectral loadings at 254 nm depending on depths (15, 30, 60 and 100 cm) and treatments (control and treated
 190 plots) in autumn.

191 Representative excitation emission matrix fluorescence spectra of DOM with three major
192 peaks identified and labelled according to Coble (1996) and Parlanti et al. (2000) are
193 presented in Fig. 2. EEMF data corrected to DOC contents were higher for spring samples
194 than for autumn samples (Musadji et al, 2019). Whatever the season and treatments, maxima
195 band α' shifted to lower wavelengths with increasing depth (Musadji et al, 2019). This trend
196 could be due to the decrease in high molecular weight compounds (HMW) and the decrease
197 in aromatic components (Coble, 1996; Corvasce et al., 2006; Hassouna et al., 2010; Sharma et
198 al., 2017; Sierra et al., 2005). This assumption was in accordance for both soils with the shift
199 in emission wavelengths of maximal intensity at 254 nm also decreasing with depth (Fig.2).
200 In addition, down to 60 cm depth, fluorescence intensities were higher for treated plots than
201 for control. After 7 years, exogenous compounds from the compost were then significantly
202 present in DOM. Moreover, a high amount of aromatic compounds was measured in the
203 deepest samples (Fig. 2b) of the amended plots suggesting that at the long term the compost
204 influence is not restricted to the upper horizons of soil.

205 Qualitatively, humic fluorophores are the most abundant in all samples whatever the season,
206 treatment or depth considered. This result is in accordance with many studies (Leenheer and
207 Croué, 2003; Sierra et al., 2005).



208

209 Fig. 3: Mean wavelength values characteristics of fluorescent components A, B, C and T for the all seasons,
 210 depths and treatments where x-axis and y-axis represent respectively the scan range of emission and excitation
 211 wavelengths. Red and grey colors are respectively for autumn and spring samples (see Table 1).

212 No major difference was observed for humic-like components (Fig. 3). Proteins-like
 213 fluorophores, being good markers of soil ecosystem evolution (Singleton et al., 2003) and
 214 diagnostic for bacterial community behavior (Malik and Gleixner, 2013; Tipping et al., 1999)
 215 were also identified. EEMF plot contours of spring DOM were dominated by fluorescent
 216 amino acids, especially in control samples (Fig. 3). Spring samples were already described as
 217 rich in carbohydrates and amino sugars (Kaiser et al., 2001). In autumn, the peaks attributed
 218 to fluorescent amino acids tyrosine (γ) were found as main amino acid fluorescent
 219 components except for deep horizons waters samples. In spring, δ peak was much more
 220 pronounced with higher BIX values in control samples.

221

222

223 3.2.2 Fluorescence proxies

224 Fluorescence proxies were used to point out DOM differences (Table 1). The highest FI and
 225 BIX values are correlated with the highest relative contribution of microbial derived organic

226 matter to the DOM. FI and BIX values of reference soil fulvic acids were respectively 1.0 and
227 0.5. HIX for reference soil fulvic acids was 15.8 confirming that high values (between 10 and
228 16) are characteristic of strongly humified organic material, mainly of terrestrial origin.

229 Mean FI DOM values (1.4 for autumn and 1.5 for spring) reflected a mixture of plant derived
230 and microbial input. The mean BIX ranged from 0.7 for autumn to 0.8 for spring, confirmed
231 with a significant difference ($p < 0.05$) a higher input of microbial material in spring samples.
232 The mean HIX values ranged from 11.0 for autumn to 8.3 for spring. HIX mean values
233 decreased with increasing depth (Table 1 and Fig. 4 g, h and i). The mean values ranged from
234 13.3 at 0-15 cm to 3.9 at 60-100 cm for control and from 17.0 at 0-15 cm to 5.7 at 60-100 cm
235 for amended plots in autumn. The fluorescence proxies showed that DOM in topsoil (0-15
236 cm) was strongly humified with important terrigenous contribution (highest HIX and lowest
237 FI and BIX values), whereas the deeper was marked by autochthonous components. During
238 spring, the values were lower but with a similar trend. Contrary to DOC contents, no
239 significant seasonal difference in fluorescence proxies was observed. The fluorescent DOM is
240 thus similar whatever the season considered. The drastic loss of DOM content, observed
241 during the spring, is thus more due to dilution rather than a change in DOM molecular
242 composition. This phenomenon was then related to precipitation and subsequent infiltration,
243 as already inferred.

244 The organic matter of the compost was still present in DOM. Amended samples exhibited
245 higher HIX values, with a significant difference ($p < 0.05$), compared to control ones (Fig.4d).
246 Mean HIX values ranged from 8.0 for control plots to 12.0 for amended soil solutions.
247 According to HIX scales, control plots presented an important recent autochthonous input (6
248 $< \text{HIX} < 10$), whereas amended plots were distinguished by a strong humic character with an
249 important terrigenous contribution ($\text{HIX} > 10$) (Birdwell and Engel, 2010). Amended plots
250 were characterized by more humified pools, represented by complex aromatic substances that

251 derive from lignocellulosic polymers, exhibiting a strong recalcitrance towards
252 biodegradation (Marinari et al., 2010). Conversely, control samples exhibited higher FI and
253 BIX values. The humic character of DOM for amended soil induced a lower bacterial
254 reworking in spring, particularly in the deeper horizon (60-100 cm).

255

256 **3.3 Statistical treatment using principal component analysis (PCA)**

257

258 PCA (Fig. 5) and Pearson's correlation (Musadji et al, 2019) were conducted to further
259 investigate the association among DOM characteristics and abiotic factors. Due to their
260 definition, FI and BIX presented opposite trend to HIX. Table 2 in Musadji et al, (2019)
261 shows a strong and positive correlation ($r = 0.96$) between FI and BIX, whereas a close and
262 negative correlation was observed for HIX with FI ($r = - 0.95$) and BIX ($r = - 0.97$). In Fig. 5,
263 two PCA components, accounting for 94.60 % of the total variance, were extracted. The
264 quantitative active variables show a strong contribution ($|r| > 0.89$; $p < 0.002$) to the 1st factor
265 (PCA 1) which explains 89.04 % of the total variance. This latter was positively associated
266 with DOC, HIX and pH, whereas BIX and FI were negatively correlated. The 2nd component
267 (PCA 2), which is responsible of only 5.56% of the total variance, does not allow to
268 discriminate the OM, which thus induces that PCA 1 is associated to quality of DOM.

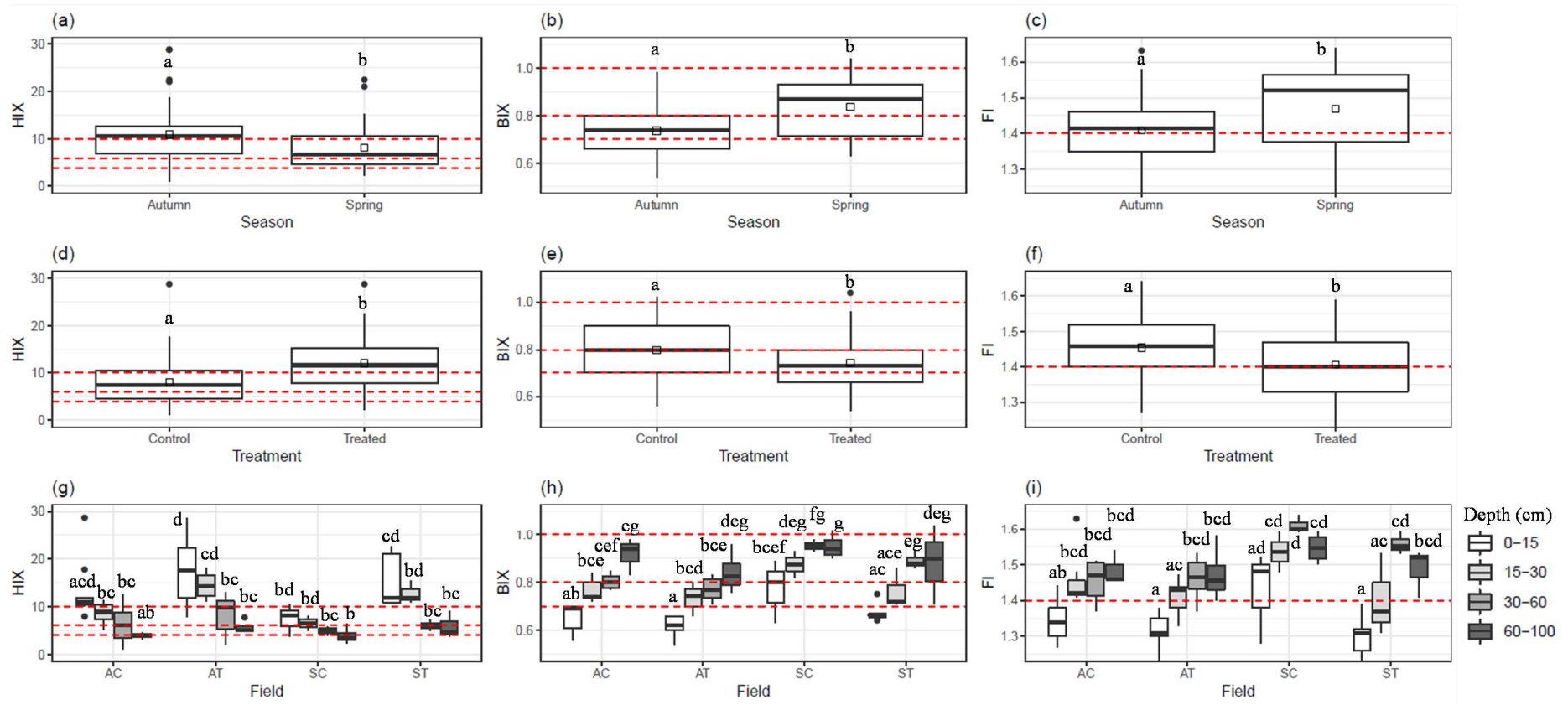
269 The individuals plot of abiotic factors associated to PCA is presented in the Fig.5. The
270 proximity of the points on the factorial planes was interpreted in terms of similarity between
271 the variables. PCA was consistent with the above-mentioned results showing the
272 discrimination between seasonal, depth and treatment parameters. Parameters, such as HIX,
273 DOC and pH, were positively correlated with autumn and treatment, whereas FI and BIX
274 were associated to spring. Strong terrigenous character was higher in topsoil (0-30 cm),
275 whereas microbial compounds were more important in the deeper horizon. The intermediate

276 horizon (30-60 cm) was characterized by a mixture of fresh organic matter and microbial
277 biomarkers. As DOM participates to the vectorization of inorganic compounds resulting from
278 anthropogenic activity (Akkanen et al., 2004; Bolan et al., 2011), its dynamics is a major
279 environmental issue. According to PCA, treated and control DOM samples are significantly
280 different in terms of concentration and humification. The PCA results demonstrated that
281 DOM characteristics in autumn and spring could be discriminated due to their different DOC
282 values. The presence of organic matter of compost was still significant after 7 years thus
283 demonstrating the long-term effect of an organic amendment.

284 Table1: Mean values of DOM characteristics (n = 78).

Samples & seasons	Depth (cm)	n	DOC (mg.L ⁻¹) ± sd	pH ± sd	HIX ± sd	FI ± sd	BIX ± sd
Fulvic acid	0-30	1	-	-	15.8	1.0	0.5
Seasonal variation							
Autumn	0-100	52	51.79 ± 23.55 ^a	8.1 ± 0.3 ^a	11.0 ± 6.1 ^a	1.4 ± 0.1 ^a	0.7 ± 0.0 ^a
Spring	0-100	26	7.73 ± 3.88 ^b	8.0 ± 0.4 ^a	8.3 ± 5.2 ^a	1.5 ± 0.1 ^b	0.8 ± 0.1 ^b
Treatment							
Control	0-100	37	31.31 ± 21.48 ^a	8.0 ± 0.3 ^a	8.0 ± 5.0 ^a	1.5 ± 0.1 ^a	0.8 ± 0.1 ^a
Treated	0-100	41	42.50 ± 32.85 ^a	8.1 ± 0.4 ^a	12.0 ± 6.0 ^b	1.4 ± 0.1 ^b	0.7 ± 0.1 ^b
Samples							
AC	0-15	9	54.73 ± 11.57 ^{cd}	8.3 ± 0.2 ^{de}	13.3 ± 6.4 ^{acd}	1.3 ± 0.1 ^{ab}	0.7 ± 0.1 ^{ab}
	15-30	7	44.35 ± 5.68 ^{cd}	8.2 ± 0.1 ^{bce}	8.6 ± 2.2 ^{bc}	1.5 ± 0.1 ^{bcd}	0.8 ± 0.0 ^{bce}
	30-60	6	37.03 ± 9.32 ^{bc}	7.8 ± 0.2 ^{abd}	6.4 ± 4.3 ^{bc}	1.5 ± 0.1 ^{bcd}	0.8 ± 0.0 ^{cef}
	60-100	3	16.68 ± 14.52 ^{ab}	7.5 ± 0.2 ^a	4.0 ± 0.8 ^{ab}	1.5 ± 0.0 ^{bcd}	0.9 ± 0.1 ^{eg}
	0-100	25	43.01 ± 15.36^b	8.0 ± 0.2^a	9.2 ± 5.5^{ab}	1.4 ± 0.1^a	0.8 ± 0.1^a
AT	0-15	9	83.74 ± 17.86 ^e	8.4 ± 0.2 ^e	17.0 ± 6.7 ^d	1.3 ± 0.0 ^a	0.6 ± 0.0 ^a
	15-30	8	60.85 ± 13.55 ^d	8.2 ± 0.3 ^{de}	14.4 ± 2.6 ^{cd}	1.4 ± 0.1 ^{ac}	0.7 ± 0.0 ^{bcd}
	30-60	6	53.37 ± 14.21 ^{cd}	8.2 ± 0.1 ^{bce}	8.3 ± 4.4 ^{bc}	1.5 ± 0.1 ^{bcd}	0.8 ± 0.0 ^{bce}
	60-100	4	14.33 ± 11.32 ^{ab}	7.6 ± 0.3 ^{ac}	5.7 ± 1.3 ^{bc}	1.5 ± 0.1 ^{bcd}	0.8 ± 0.8 ^{deg}
	0-100	27	59.92 ± 26.97^c	8.2 ± 0.3^a	12.6 ± 6.2^b	1.4 ± 0.1^a	0.7 ± 0.1^a
SC	0-15	3	8.27 ± 4.84 ^a	8.4 ± 0.2 ^{de}	7.4 ± 3.4 ^{bd}	1.4 ± 0.1 ^{ad}	0.8 ± 0.1 ^{bcef}
	15-30	2	5.01 ± 0.45 ^a	8.1 ± 0.0 ^{ade}	6.5 ± 2.2 ^{bd}	1.5 ± 0.1 ^{cd}	0.9 ± 0.1 ^{deg}
	30-60	3	5.53 ± 0.08 ^a	8.0 ± 0.0 ^{ade}	4.9 ± 1.0 ^{bc}	1.6 ± 0.0 ^d	1.0 ± 0.0 ^{fg}
	60-100	4	6.27 ± 1.90 ^a	7.5 ± 0.1 ^a	4.0 ± 1.8 ^b	1.5 ± 0.0 ^{cd}	1.0 ± 0.1 ^g
	0-100	12	6.38 ± 2.60^a	7.9 ± 0.4^a	5.5 ± 2.4^a	1.5 ± 0.1^b	0.9 ± 0.1^b
ST	0-15	5	13.58 ± 4.28 ^{ab}	8.3 ± 0.4 ^{bc}	15.4 ± 5.9 ^{cd}	1.3 ± 0.1 ^a	0.7 ± 0.0 ^{ac}
	15-30	3	7.90 ± 0.67 ^a	8.1 ± 0.0 ^{ade}	12.7 ± 2.4 ^{bd}	1.4 ± 0.1 ^{ac}	0.8 ± 0.1 ^{ace}
	30-60	3	5.90 ± 0.48 ^a	8.4 ± 0.1 ^{de}	6.0 ± 1.1 ^{bc}	1.6 ± 0.0 ^{cd}	0.9 ± 0.0 ^{eg}
	60-100	3	5.06 ± 1.06 ^a	7.6 ± 0.4 ^{ab}	5.8 ± 2.8 ^{bc}	1.5 ± 0.1 ^{bcd}	0.9 ± 0.2 ^{deg}
	0-100	14	8.89 ± 4.48^a	8.1 ± 0.4^a	10.7 ± 5.7^{ab}	1.4 ± 0.1^a	0.8 ± 0.1^a

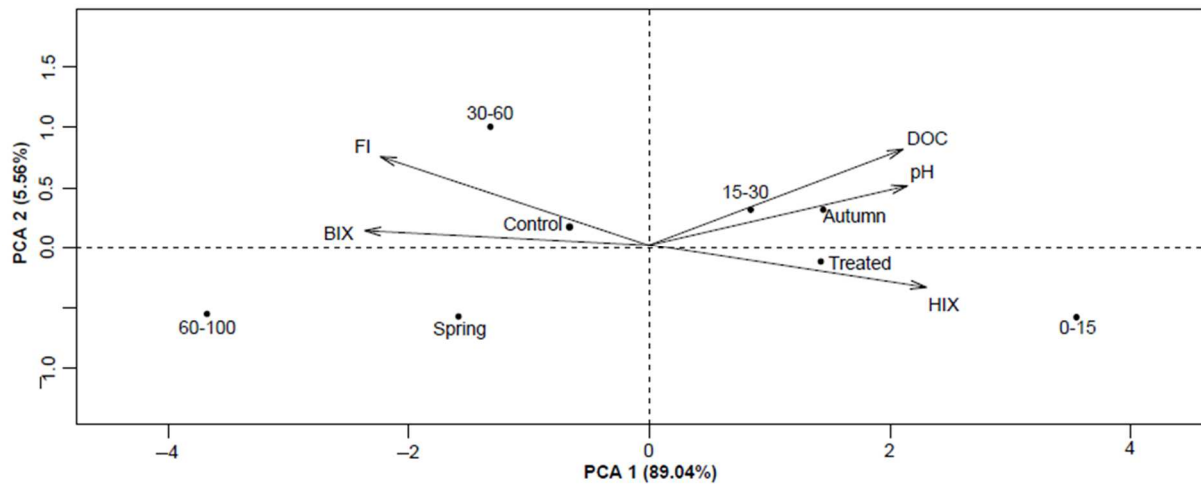
285 Notes: AC- control plot at autumn, AT- treated field at autumn, SC- control field at spring, ST- treated field at spring. The subscripts letters after the data indicate the
 286 similarity and the differences. The same alphabet indicates that the compared group are similar. Different subscripts represent significant difference between compared groups
 287 at p-value < 0.05. Control soil fulvic acids were used as reference for fluorescence proxy.



288

289

290 Fig. 4: Treatment (field), temporal (season) and spatial (depth) variations of HIX, FI and BIX. Boxes plots indicate 25th and 75th percentiles, solid lines within boxes refer to
 291 median values, in-box points represent the mean value and the close circles represent the outliers values. The subscripts letters after the data indicate the similarity and the
 292 differences. The same alphabet indicates that the compared group are similar. Different subscripts represent significant difference between compared groups at P-value < 0.05.
 293 AC- control field at autumn, AT- treated field at autumn, SC- control field at spring, ST- treated field at spring. The red dotted lines represent the different fluorescent
 294 proxies' scales (see Section 2.3).



295

296 Fig. 5: Biplot Principal Correspondence Analysis (PCA) of quantitative variables (HIX, FI and BIX) of DOM in
 297 percolating waters for control and treated soils.

298 **Conclusion**

299 The present study provides a new insight in soil quality measurement by DOM monitoring in
 300 response to soil treatments or environmental changes. Suction cups soil solutions analysis
 301 enables the DOM characterization at several depths in term of structure and origin without
 302 any pretreatment nor disturbance. As expected a strong rainfall period strongly affects DOC
 303 content. The results demonstrate that the combined use of 3D fluorescence and DOC
 304 measurement is necessary to understand the OM evolution as a drop in DOC value is not
 305 always associated with a change in OM quality. The spectroscopic fluorescence indices,
 306 effective indicators of the DOM properties, show in addition that a long term improvement in
 307 SOM can be achieved by organic amendment with an increase in amount of OM that has
 308 influenced the bacterial activity.

309

310

311

312

313 **References**

- 314 Akkanen, J., Vogt, R.D., Kukkonen, J.V.K., 2004. Essential characteristics of natural
315 dissolved organic matter affecting the sorption of hydrophobic organic contaminants.
316 *Aquat. Sci. - Res. Boundaries* 66, 171–177. <https://doi.org/10.1007/s00027-004-0705->
317 [x](https://doi.org/10.1007/s00027-004-0705-x)
- 318 Baker, A., Lamont-Black, J., 2001. Fluorescence of Dissolved Organic Matter as a Natural
319 Tracer of Ground Water. *Ground Water* 39, 745–750. <https://doi.org/10.1111/j.1745->
320 [6584.2001.tb02365.x](https://doi.org/10.1111/j.1745-6584.2001.tb02365.x)
- 321 Birdwell, J.E., Engel, A.S., 2010. Characterization of dissolved organic matter in cave and
322 spring waters using UV–Vis absorbance and fluorescence spectroscopy. *Org.*
323 *Geochem.* 41, 270–280. <https://doi.org/10.1016/j.orggeochem.2009.11.002>
- 324 Bolan, N.S., Adriano, D.C., Kunhikrishnan, A., James, T., McDowell, R., Senesi, N., 2011.
325 Dissolved Organic Matter, in: *Advances in Agronomy*. Elsevier, pp. 1–75.
326 <https://doi.org/10.1016/B978-0-12-385531-2.00001-3>
- 327 Borisover, M., Lordian, A., Levy, G.J., 2012. Water-extractable soil organic matter
328 characterization by chromophoric indicators: Effects of soil type and irrigation water
329 quality. *Geoderma* 179–180, 28–37. <https://doi.org/10.1016/j.geoderma.2012.02.019>
- 330 Celerier, J., Rodier, C., Favetta, P., Lemee, L., Ambles, A., 2009. Depth-related variations in
331 organic matter at the molecular level in a loamy soil: reference data for a long-term
332 experiment devoted to the carbon sequestration research field. *Eur. J. Soil Sci.* 60, 33–
333 43. <https://doi.org/10.1111/j.1365-2389.2008.01085.x>
- 334 Chantigny, M.H., 2003. Dissolved and water-extractable organic matter in soils: a review on
335 the influence of land use and management practices. *Geoderma* 113, 357–380.
336 [https://doi.org/10.1016/S0016-7061\(02\)00370-1](https://doi.org/10.1016/S0016-7061(02)00370-1)

337 Chen, M., He, W., Choi, I., Hur, J., 2016. Tracking the monthly changes of dissolved organic
338 matter composition in a newly constructed reservoir and its tributaries during the
339 initial impounding period. *Environ. Sci. Pollut. Res.* 23, 1274–1283.
340 <https://doi.org/10.1007/s11356-015-5350-5>

341 Chen, W., Westerhoff, P., Leenheer, J.A., Booksh, K., 2003. Fluorescence
342 Excitation–Emission Matrix Regional Integration to Quantify Spectra for Dissolved
343 Organic Matter. *Environ. Sci. Technol.* 37, 5701–5710.
344 <https://doi.org/10.1021/es034354c>

345 Christ, M.J., David, M.B., 1996. Temperature and moisture effects on the production of
346 dissolved organic carbon in a Spodosol. *Soil Biol. Biochem.* 28, 1191–1199.
347 [https://doi.org/10.1016/0038-0717\(96\)00120-4](https://doi.org/10.1016/0038-0717(96)00120-4)

348 Coble, P.G., 1996. Characterization of marine and terrestrial DOM in seawater using
349 excitation-emission matrix spectroscopy. *Mar. Chem.* 51, 325–346.
350 [https://doi.org/10.1016/0304-4203\(95\)00062-3](https://doi.org/10.1016/0304-4203(95)00062-3)

351 Corvasce, M., Zsolnay, A., D’Orazio, V., Lopez, R., Miano, T.M., 2006. Characterization of
352 water extractable organic matter in a deep soil profile. *Chemosphere* 62, 1583–1590.
353 <https://doi.org/10.1016/j.chemosphere.2005.07.065>

354 Deb, S.K., Shukla, M.K., 2011. A Review of Dissolved Organic Matter Transport Processes
355 Affecting Soil and Environmental Quality. *J. Environ. Anal. Toxicol.* 01.
356 <https://doi.org/10.4172/2161-0525.1000106>

357 Embacher, A., Zsolnay, A., Gattinger, A., Munch, J.C., 2007. The dynamics of water
358 extractable organic matter (WEOM) in common arable topsoils: I. Quantity, quality
359 and function over a three year period. *Geoderma* 139, 11–22.
360 <https://doi.org/10.1016/j.geoderma.2006.12.002>

361 Erich, M.S., Plante, A.F., Fernández, J.M., Mallory, E.B., Ohno, T., 2012. Effects of Profile
362 Depth and Management on the Composition of Labile and Total Soil Organic Matter.
363 Soil Sci. Soc. Am. J. 76, 408. <https://doi.org/10.2136/sssaj2011.0273>

364 Federici, E., Massaccesi, L., Pezzolla, D., Fidati, L., Montalbani, E., Proietti, P., Nasini, L.,
365 Regni, L., Scargetta, S., Gigliotti, G., 2017. Short-term modifications of soil microbial
366 community structure and soluble organic matter chemical composition following
367 amendment with different solid olive mill waste and their derived composts. Appl.
368 Soil Ecol. 119, 234–241. <https://doi.org/10.1016/j.apsoil.2017.06.014>

369 Filep, T., Draskovits, E., Szabó, J., Koós, S., László, P., Szalai, Z., 2015. The dissolved
370 organic matter as a potential soil quality indicator in arable soils of Hungary. Environ.
371 Monit. Assess. 187. <https://doi.org/10.1007/s10661-015-4700-6>

372 Fließbach, A., Oberholzer, H.-R., Gunst, L., Mäder, P., 2007. Soil organic matter and
373 biological soil quality indicators after 21 years of organic and conventional farming.
374 Agric. Ecosyst. Environ. 118, 273–284. <https://doi.org/10.1016/j.agee.2006.05.022>

375 Gonçalves-Araujo, R., Granskog, M.A., Bracher, A., Azetsu-Scott, K., Dodd, P.A., Stedmon,
376 C.A., 2016. Using fluorescent dissolved organic matter to trace and distinguish the
377 origin of Arctic surface waters. Sci. Rep. 6, 33978.

378 Gregorich, E.G., Monreal, C.M., Carter, M.R., Angers, D.A., Ellert, B.H., 1994. Towards a
379 minimum data set to assess soil organic matter quality in agricultural soils. Can. J. Soil
380 Sci. 74, 367–385. <https://doi.org/10.4141/cjss94-051>

381 Hassouna, M., Massiani, C., Dudal, Y., Pech, N., Theraulaz, F., 2010. Changes in water
382 extractable organic matter (WEOM) in a calcareous soil under field conditions with
383 time and soil depth. Geoderma 155, 75–85.
384 <https://doi.org/10.1016/j.geoderma.2009.11.026>

385 Haynes, R., 2000. Labile organic matter as an indicator of organic matter quality in arable and
386 pastoral soils in New Zealand. *Soil Biol. Biochem.* 32, 211–219.
387 [https://doi.org/10.1016/S0038-0717\(99\)00148-0](https://doi.org/10.1016/S0038-0717(99)00148-0)

388 Haynes, R.J., 2005. Labile Organic Matter Fractions as Central Components of the Quality of
389 Agricultural Soils: An Overview, in: *Advances in Agronomy*. Academic Press, pp.
390 221–268.

391 Hudson, N., Baker, A., Reynolds, D., 2007. Fluorescence analysis of dissolved organic matter
392 in natural, waste and polluted waters—a review. *River Res. Appl.* 23, 631–649.
393 <https://doi.org/10.1002/rra.1005>

394 Huguet, A., Vacher, L., Relexans, S., Saubusse, S., Froidefond, J.M., Parlanti, E., 2009.
395 Properties of fluorescent dissolved organic matter in the Gironde Estuary. *Org.*
396 *Geochem.* 40, 706–719. <https://doi.org/10.1016/j.orggeochem.2009.03.002>

397 Jones, D.L., Simfukwe, P., Hill, P.W., Mills, R.T.E., Emmett, B.A., 2014. Evaluation of
398 Dissolved Organic Carbon as a Soil Quality Indicator in National Monitoring
399 Schemes. *PLoS ONE* 9, e90882. <https://doi.org/10.1371/journal.pone.0090882>

400 Kaiser, K., Guggenberger, G., Haumaier, L., Zech, W., 2001. Seasonal variations in the
401 chemical composition of dissolved organic matter in organic forest floor layer
402 leachates of old-growth Scots pine (*Pinus sylvestris* L.) and European beech (*Fagus*
403 *sylvatica* L.) stands in northeastern Bavaria, Germany. *Biogeochemistry* 55, 103–143.
404 <https://doi.org/10.1023/A:1010694032121>

405 Korak, J.A., Dotson, A.D., Summers, R.S., Rosario-Ortiz, F.L., 2014. Critical analysis of
406 commonly used fluorescence metrics to characterize dissolved organic matter. *Water*
407 *Res.* 49, 327–338. <https://doi.org/10.1016/j.watres.2013.11.025>

408 Leenheer, J.A., Croué, J.-P., 2003. Peer Reviewed: Characterizing Aquatic Dissolved Organic
409 Matter. *Environ. Sci. Technol.* 37, 18A-26A. <https://doi.org/10.1021/es032333c>

410 Malik, A., Gleixner, G., 2013. Importance of microbial soil organic matter processing in
411 dissolved organic carbon production. *FEMS Microbiol. Ecol.* 86, 139–148.
412 <https://doi.org/10.1111/1574-6941.12182>

413 Marinari, S., Dell'Abate, M.T., Brunetti, G., Dazzi, C., 2010. Differences of stabilized
414 organic carbon fractions and microbiological activity along Mediterranean Vertisols
415 and Alfisols profiles. *Geoderma* 156, 379–388.
416 <https://doi.org/10.1016/j.geoderma.2010.03.007>

417 Marschner, B., Kalbitz, K., 2003. Controls of bioavailability and biodegradability of dissolved
418 organic matter in soils. *Geoderma* 113, 211–235. [https://doi.org/10.1016/S0016-](https://doi.org/10.1016/S0016-7061(02)00362-2)
419 [7061\(02\)00362-2](https://doi.org/10.1016/S0016-7061(02)00362-2)

420 McKnight, D.M., Boyer, E.W., Westerhoff, P.K., Doran, P.T., Kulbe, T., Andersen, D.T.,
421 2001. Spectrofluorometric characterization of dissolved organic matter for indication
422 of precursor organic material and aromaticity. *Limnol. Oceanogr.* 46, 38–48.
423 <https://doi.org/10.4319/lo.2001.46.1.0038>

424 Mertens, J., Vanderborght, J., Kasteel, R., Pütz, T., Merckx, R., Feyen, J., Smolders, E., 2007.
425 Dissolved Organic Carbon Fluxes under Bare Soil. *J. Environ. Qual.* 36, 597.
426 <https://doi.org/10.2134/jeq2006.0368>

427 Mouloubou, O.R., Prudent, P., Mounier, S., Boudenne, J.-L., Abaker, M.G., Théraulaz, F.,
428 2016. An adapted sequential chemical fractionation coupled with UV and fluorescence
429 spectroscopy for calcareous soil organic matter study after compost amendment.
430 *Microchem. J.* 124, 139–148. <https://doi.org/10.1016/j.microc.2015.08.007>

431 Musadji, N.-Y., 2013. Structure et dynamique du carbone mobile dans le sol. Poitiers.

432 Musadji, N.-Y., Geffroy-Rodier, 2019. Data for dynamics analysis of soil dissolved organic
433 matter. Long term amendment effect. Data in Brief (submitted)

434 Ohno, T., 2002. Fluorescence Inner-Filtering Correction for Determining the Humification
435 Index of Dissolved Organic Matter. *Environ. Sci. Technol.* 36, 742–746.
436 <https://doi.org/10.1021/es0155276>

437 Ohno, T., Chorover, J., Omoike, A., Hunt, J., 2007. Molecular weight and humification index
438 as predictors of adsorption for plant- and manure-derived dissolved organic matter to
439 goethite. *Eur. J. Soil Sci.* 58, 125–132. [https://doi.org/10.1111/j.1365-
440 2389.2006.00817.x](https://doi.org/10.1111/j.1365-2389.2006.00817.x)

441 Pan, H., Yu, H., Song, Y., Zhu, L., Liu, R., Du, E., 2017. Tracking fluorescent components of
442 dissolved organic matter from soils in large-scale irrigated area. *Environ. Sci. Pollut.*
443 *Res.* 24, 6563–6571. <https://doi.org/10.1007/s11356-017-8378-x>

444 Parlanti, E., Wörz, K., Geoffroy, L., Lamotte, M., 2000. Dissolved organic matter
445 fluorescence spectroscopy as a tool to estimate biological activity in a coastal zone
446 submitted to anthropogenic inputs. *Org. Geochem.* 31, 1765–1781.
447 [https://doi.org/10.1016/S0146-6380\(00\)00124-8](https://doi.org/10.1016/S0146-6380(00)00124-8)

448 Seifert, A.-G., Roth, V.-N., Dittmar, T., Gleixner, G., Breuer, L., Houska, T., Marxsen, J.,
449 2016a. Comparing molecular composition of dissolved organic matter in soil and
450 stream water: Influence of land use and chemical characteristics. *Sci. Total Environ.*
451 571, 142–152. <https://doi.org/10.1016/j.scitotenv.2016.07.033>

452 Seifert, A.-G., Roth, V.-N., Dittmar, T., Gleixner, G., Breuer, L., Houska, T., Marxsen, J.,
453 2016b. Comparing molecular composition of dissolved organic matter in soil and
454 stream water: Influence of land use and chemical characteristics. *Sci. Total Environ.*
455 571, 142–152. <https://doi.org/10.1016/j.scitotenv.2016.07.033>

456 Sharma, P., Laor, Y., Raviv, M., Medina, S., Saadi, I., Krasnovsky, A., Vager, M., Levy, G.J.,
457 Bar-Tal, A., Borisover, M., 2017. Compositional characteristics of organic matter and

458 its water-extractable components across a profile of organically managed soil.
459 *Geoderma* 286, 73–82. <https://doi.org/10.1016/j.geoderma.2016.10.014>

460 Sierra, M.M.D., Giovanela, M., Parlanti, E., Soriano-Sierra, E.J., 2005. Fluorescence
461 fingerprint of fulvic and humic acids from varied origins as viewed by single-scan and
462 excitation/emission matrix techniques. *Chemosphere* 58, 715–733.
463 <https://doi.org/10.1016/j.chemosphere.2004.09.038>

464 Singleton, I., Merrington, G., Colvan, S., Delahunty, J.S., 2003. The potential of soil protein-
465 based methods to indicate metal contamination. *Appl. Soil Ecol.* 23, 25–32.
466 [https://doi.org/10.1016/S0929-1393\(03\)00004-0](https://doi.org/10.1016/S0929-1393(03)00004-0)

467 Som, M.-P., Lemée, L., Amblès, A., 2009. Stability and maturity of a green waste and
468 biowaste compost assessed on the basis of a molecular study using spectroscopy,
469 thermal analysis, thermodesorption and thermochemolysis. *Bioresour. Technol.* 100,
470 4404–4416. <https://doi.org/10.1016/j.biortech.2009.04.019>

471 Sun, H.Y., Koal, P., Gerl, G., Schroll, R., Joergensen, R.G., Munch, J.C., 2017. Water-
472 extractable organic matter and its fluorescence fractions in response to minimum
473 tillage and organic farming in a Cambisol. *Chem. Biol. Technol. Agric.* 4.
474 <https://doi.org/10.1186/s40538-017-0097-5>

475 Tipping, E., Woof, C., Rigg, E., Harrison, A., Ineson, P., Taylor, K., Benham, D., Poskitt, J.,
476 Rowland, A., Bol, R., 1999. Climatic influences on the leaching of dissolved organic
477 matter from upland UK moorland soils, investigated by a field manipulation
478 experiment. *Environ. Int.* 25, 83–95. [https://doi.org/10.1016/S0160-4120\(98\)00098-1](https://doi.org/10.1016/S0160-4120(98)00098-1)

479 Turrión, M.B., Lafuente, F., Mulas, R., López, O., Ruipérez, C., Pando, V., 2012. Effects on
480 soil organic matter mineralization and microbiological properties of applying compost
481 to burned and unburned soils. *J. Environ. Manage.* 95, S245–S249.
482 <https://doi.org/10.1016/j.jenvman.2010.10.020>

483 Xi, M., Zi, Y., Wang, Q., Wang, S., Cui, G., Kong, F., 2018. Assessment of the content,
484 structure, and source of soil dissolved organic matter in the coastal wetlands of
485 Jiaozhou Bay, China. *Phys. Chem. Earth Parts ABC, Biogeochemical Processes in the*
486 *Changing Wetland Environment* 103, 35–44.
487 <https://doi.org/10.1016/j.pce.2017.03.004>

488 Xie, W., Zhang, S., Ruan, L., Yang, M., Shi, W., Zhang, H., Li, W., 2017. Evaluating Soil
489 Dissolved Organic Matter Extraction Using Three-Dimensional Excitation-Emission
490 Matrix Fluorescence Spectroscopy. *Pedosphere* 27, 968–973.
491 [https://doi.org/10.1016/S1002-0160\(17\)60466-1](https://doi.org/10.1016/S1002-0160(17)60466-1)

492

493

494 Acknowledgments

495

496 The authors wish to thanks the Europe (FEDER) and Région Nouvelle-Aquitaine Poitou-
497 Charentes (CPER) for funding.

498

499 **CRedit author statement**

500

501 N.Y Musadji: Investigation, Writing- Original draft preparation, L. Lemée Resources, Writing-
502 Reviewing and Editing, L. Caner: Writing- Reviewing and Editing, G. Porel: Resources, P.
503 Pointot Writing- Reviewing and Editing, Formal Analysis, C. Geffroy-Rodier:
504 Conceptualization, Visualisation, Writing- Original draft preparation.

505

506