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Guillaume Humbert, Thomas Parr, Laurent Jeanneau, Rémi Dupas, Patrice Petitjean, et al.. Agricultural Practices and Hydrologic Conditions Shape the Temporal Pattern of Soil and Stream Water Dissolved Organic Matter. *Ecosystems*, 2020, 23 (7), pp.1325-1343. <10.1007/s10021-019-00471-w>. <insu-02417211>

HAL Id: insu-02417211

<https://insu.hal.science/insu-02417211v1>

Submitted on 20 Dec 2019

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HAL Authorization

1 **Agricultural practices and hydrologic conditions shape the temporal**
2 **pattern of soil and stream water dissolved organic matter**

3 **Short title:**

4 **Spatiotemporal controls of soil and stream water DOM**

5 Authors:

6 Guillaume Humbert*^a, Thomas B. Parr^b, Laurent Jeanneau^c, Rémi Dupas^a, Patrice Petitjean^c, Nouraya Akkal-Corfini^a, Valérie
7 Viaud^a, Anne-Catherine Pierson-Wickmann^c, Marie Denis^c, Shreeram Inamdar^b, Gérard Gruau^c, Patrick Durand^a, Anne
8 Jaffrézic^a

9 *** Corresponding author** (Present address)

10 Sorbonne Université, UPEC, CNRS, IRD, INRA, IEES, F-75005 Paris, France

11 g.humbert86@gmail.com

12 **Affiliations**

13 ^a AGROCAMPUS OUEST, INRA, SAS, F-35000 Rennes, France

14 ^b University of Delaware, Department of Plant and Soil Science, Newark, DE, 19716, United States

15 ^c Univ Rennes, CNRS, Géosciences Rennes, F-35000 Rennes, France

16 **Author contributions**

17 GH, LJ, PP, ACPW, GG, and AJ designed the experiment, GH, LJ, RD, PP, MD collected the hydro-
18 chemical data. NAC and VV collected and analyzed the agricultural land and management data, GH
19 and TBP analyzed the data, all authors contributed to writing the paper.

20 **Abstract**

21 This study investigates the combined effects of land management, and hydrology on the temporal
22 dynamics of dissolved organic matter (DOM) quantity and composition in stream water and
23 groundwaters in an agricultural watershed. We assessed dissolved organic carbon (DOC)
24 concentrations, DOM UV-Vis absorbance, and DOM fluorescence in groundwater under cultivated
25 upland, riparian grassland, and riparian woodland land covers, as well as in the stream water at the
26 watershed outlet and livestock-impacted runoff. During one year, stream water and groundwater
27 were monitored weekly to biweekly, complemented by sub-hourly stream sampling during 7 storm
28 events. Results showed that: i) Groundwater DOC concentration was lower in cultivated upland
29 ($6.4 \pm 5.6 \text{ mg l}^{-1}$) than in riparian grassland and woodland ($22.4 \pm 13.7 \text{ mg l}^{-1}$ and $17.2 \pm 9.9 \text{ mg l}^{-1}$,
30 respectively). ii) The proportion of microbially-processed compounds decreased in the order upland
31 cropland > riparian grassland > riparian woodland. iii) Principal component analysis (PCA) of
32 groundwater DOM revealed a change in composition indicating that low aromaticity microbially-
33 processed compounds were preferentially exported to the stream. iv) PCA of stream DOM indicated
34 that seasonal increases in groundwater elevation expanded the contributing source areas, thereby
35 increasing the connectivity between upland croplands and the stream, which amplified the effects of
36 cultivation on fluvial DOM during the winter. v) Storm events occurring after manure application in
37 spring produced hot moments of manure-derived protein-like DOM transport to streams. Together,
38 these results suggest that cultivated uplands in agricultural lands using animal manure as fertilizer
39 may leach more DOM than vegetative buffers.

40 **Key words:** DOM fluorescence, groundwater, agricultural watershed, riparian soils, buffer strip,
41 animal manure

42 **Highlights**

- 43 - Cultivation increased microbially processed DOM in groundwater
- 44 - Groundwater elevation increase amplified the effects of cultivation on fluvial DOM
- 45 - Manure-derived DOM can be transported to the stream during storm events

46 **Introduction**

47 Cropland and pasture account for nearly 40% of Earth's land surface (Foley and others 2005).
48 The production and management practices (e.g. tillage, engineered drainage, and organic and
49 inorganic fertilizer application) used on these lands are biogeochemically reactive with direct and
50 indirect effects on the carbon cycle. Frequently overlapping temporally and spatially, the net effect of
51 these practices on carbon sequestration in terrestrial soils (Han and others 2016), transport to, and
52 processing in fluvial networks (Stanley and others 2012) varies with environmental context. Much of
53 the carbon export from terrestrial soils occurs as dissolved organic matter (DOM) (Stanley and others
54 2012) and during high discharge periods (Humbert and others 2015). The quantity and composition
55 of this terrestrially derived DOM affects aquatic ecosystem functions and derived ecosystem services
56 (Wallace and others 2008). However, a better understanding of the linkages between management
57 actions and ground and surface water DOM dynamics is needed to enhance science-based
58 management and restoration solutions (i.e. practices to maintain 'natural' DOM regimes; Stanley and
59 others 2012).

60 Agricultural land use and management affect the quantity and composition of soil and
61 stream water DOM. These influences can be conceptualized as the combined effects of short- and
62 long-term positive and negative feedbacks (Chantigny 2003). Liming, animal manure, and fertilizer
63 application are examples of practices with short-term effects on DOM quantity and quality. Shifts in
64 vegetative cover type and quantity of plant litter returned to the soil are examples of practices
65 driving long-term effects. In soils, forested and arable lands typically differ in DOM quantity and
66 composition. The net effect of this is that forest soils typically contain a larger proportion of high
67 molecular weight DOM that is less microbially decomposed, whereas cropland or pasture commonly
68 contain a greater proportion of low molecular weight DOM that is more highly decomposed or
69 microbially derived (Chantigny 2003). However, the degree of difference between 'natural' and
70 agricultural land covers depends on landscape context, spatial scale, and temporal scale (Stanley and
71 others 2012). Therefore, understanding the differences in DOM composition between arable soils

72 and non-cultivated soils, such as in tree or grass buffers may provide a useful tool in assessing degree
73 of impact agriculture has on surface water and the effectiveness of best management practices in
74 reducing that impact.

75 While these agriculturally driven changes to soil DOM quantity and composition do not
76 necessarily change the quantity of DOM exported from watersheds to surface waters, they do alter
77 the composition frequently towards more microbially-processed sources (Wilson and Xenopoulos
78 2009; Williams and others 2010; Graeber and others 2015). This may occur through several different
79 hydrologic and microbial processes. Subsurface drainage can transport microbially processed DOM to
80 streams from deep, organic-poor soil horizons (Dalzell and others 2011). In streams with sufficient
81 light, nutrient enrichment may enhance in-stream algal productivity and release of exudates (Stanley
82 and others 2012). Finally, terrestrial DOM altered by agricultural practices can be transported to the
83 stream from arable soils through seasonal and event-driven changes in water flow paths (Fuß and
84 others 2017; Fasching and others 2019). The dynamics of this process, while better understood at the
85 storm event scale (Naden and others 2010; Singh and others 2014) are understudied at the seasonal
86 scale (Shang and others 2018). However, the latter approach can contribute to better understand the
87 environmental and ecological controls that drive contradictory stream DOM responses to agricultural
88 management of lands (increasing the proportion of DOM compounds with high molecular weight;
89 Graeber and others 2012; Shang and others 2018).

90 Seasonal changes in groundwater elevation regulate the hydrologic connectivity between a
91 stream and its watershed resulting in variable source areas contributing to streamflow. Under the
92 assumption of conservative transport, each source area contributes a unique quantity and
93 composition of stream DOM (Laudon and others 2011). For example, Lambert and others (2013)
94 showed that a strong change in the isotopic composition of stream DOM toward the one of upland
95 sources was related to the rise of the upland groundwater. These drivers of stream DOM dynamics
96 are periodic mechanisms with greater seasonal than inter-annual variability (Humbert and others
97 2015). Agriculture impacts the spatial distribution and timing of OM inputs within a watershed and

98 seasonal and event-driven hydrology regulate the spatial extent of the contributing area, however,
99 their combined effects are seldom considered.

100 Riparian wetlands are typically a dominant source of DOM export during stormflow in the
101 headwater watersheds (Morel and others 2009), however in agricultural watersheds, management
102 practices can introduce novel sources of DOM which may come to dominate exports during
103 stormflows (Naden and others 2010; Singh and others 2014). During a brief period (<1 month)
104 following surficial manure application, storm events can cause the 'pulsed' transport of manure-
105 derived DOM to stream ecosystems. During these pulses, the flux of manure-derived DOM is small
106 (0.004-0.016%) relative to the total mass of manure applied (Naden and others 2010; Singh and
107 others 2014). However, strong changes in DOM optical properties indicated that its contribution to
108 stream water DOM exceeded those from other terrestrial sources. This leaves a large pool of
109 manure-derived organic matter that can feed medium to longer-term biogeochemical reactive
110 processes and transports. This longer-term potential of the flux and its DOM signature have not been
111 investigated, but may be important as seasonal variations in groundwater hydrology enhance the
112 connectivity of agricultural lands with surface waters.

113 To address the critical knowledge gap regarding the effect that land management has on
114 aquatic DOM, we investigated how different watershed sources, cultivated soils receiving manure
115 applications and non-cultivated riparian grassland and forest, contribute to stream water DOM. We
116 hypothesized that seasonal interactions between hydrology and agricultural practices would impact
117 the composition of DOM in stream water and groundwater. We tested this hypothesis by
118 characterizing DOM quantity and composition in the stream and its primary DOM sources of an
119 intensively farmed watershed (i.e. groundwater in the riparian grasslands, riparian woodlands and
120 upland croplands; livestock-impacted runoff) during different hydrologic conditions (i.e. seasonal and
121 storm) over the course of a year. Our specific objectives were (i) to differentiate stream water DOM
122 sources using their fluorescent dissolved organic matter (FDOM) composition; (ii) to describe the
123 dynamics in DOM composition of groundwater over the year; and (iii) to assess the contribution of

124 various sources to stream DOM across seasonal and event-driven hydrologic conditions. By providing
125 a mechanistic understanding of source contributions to the stream DOM quantity and composition,
126 this study furthers efforts to assess the impact that agricultural practices may have on the
127 environment.

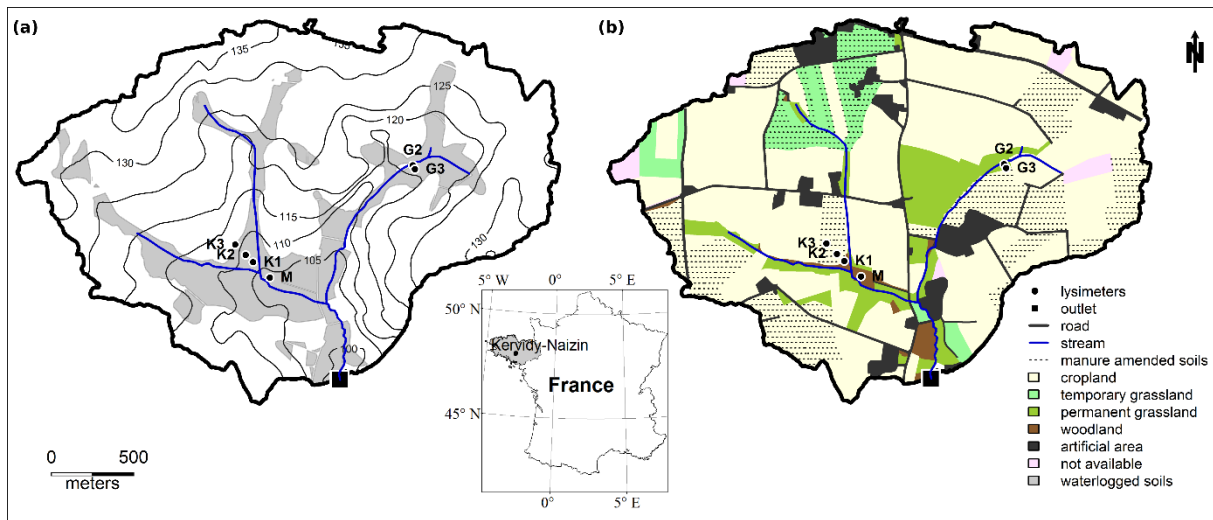
128 **Materials and methods**

129 **Study watershed**

130 The Kervidy-Naizin watershed (KN) is a 5 km² agricultural watershed that is part of the Agrhys
131 environmental research observatory in Brittany, France (Figure 1). The watershed is drained by an
132 intermittent 2nd order stream. The riparian zone is close-canopied with little light reaching the stream
133 channel. The climate is temperate oceanic, with average annual (2000-2014) rainfall of 845 mm,
134 specific discharge of 341 mm, and temperature of 11.2 °C. Elevation ranges from 93-135 m above sea
135 level, with gentle slopes < 5% (Figure 1a). Previous research on groundwater fluctuations and soil
136 moisture deficit assessments in this watershed have defined three hydrologic periods or
137 “hydroseasons” (Figure S1; see details in Humbert and others 2015): (i) riparian rewetting (hereafter
138 ‘rewetting’; October-December 2013), characterized by increasing riparian wetland soil moisture; (ii)
139 rise of upland groundwater (hereafter ‘wetting’; December 2013-March 2014), characterized by high
140 groundwater elevation in the upland domain, prolonged waterlogging of wetland soils, and lateral
141 water flows to the stream from wetland soils; and (iii) drying of watershed soils (hereafter ‘drying’;
142 April-May 2014), as groundwater draws down.

143 Ninety percent of the total watershed area is used for agriculture (Figure 1b, Table S1). These
144 areas are fertilized in the spring with both organic (predominantly swine slurry) and mineral
145 fertilizers. The cropping systems used in this watershed and the area allocated to each crop type
146 have changed little over the past 20 years (Viaud and others 2018). See detailed land use and
147 management summary in Text S1 and Table S1. Soils are silty loams, classified as Luvisols (IUSS
148 Working Group and others 2006), well-drained in the upland domain and waterlogged in valley
149 bottoms (Figure 1a). Approximately 20% of the watershed topsoil (< 0.4 m depth), mostly around the

150 stream network, is seasonally waterlogged and can be hydrologically connected to the stream (Figure
 151 1a). On average, these seasonally waterlogged soils are covered by cropland (55%), permanent
 152 grassland (29%, i.e. permanent grassland and fallow lands), and woodland (7%). While tile drains
 153 were installed > 40 years ago, they have not been maintained. Therefore, it is unlikely that significant
 154 quantities of runoff from upland croplands bypasses riparian areas via tile drains.



155
 156 **Figure 1.** Location and maps of the study-site. **(a)** Elevation map of the KN watershed and periodically waterlogged soils
 157 with redoximorphic features above 0.4 m deep (grey area). **(b)** Land use map and location of parcels amended with swine
 158 slurry before or during the water year 2013-2014. Artificial area gathers housing and livestock buildings. Not available areas
 159 are agricultural parcels where agricultural practices applied were unknown.

160 Identification of DOM sources

161 Previous studies established that stream water DOM in the KN watershed was primarily
 162 allochthonous and derived from the upper layers of riparian wetland and hillslope soils (Texts S2 and
 163 S3; Morel and others 2009; Lambert and others 2013). Accordingly, groundwater (or soil pore water)
 164 was sampled in six sites from soil horizons at depths ranging from 0.1 to 1 m (two to four horizons
 165 per site). The six sites were selected in the seasonally waterlogged zone representing three different
 166 land covers at different distances from the stream (i.e. riparian grassland and riparian woodland
 167 closer to the stream, and upland cropland further from the stream) (Figure 1 and Table 1).

168 Management at the cropland sites was consistent with the other cropping systems in place in the KN
 169 watershed (Tables 1 and S1); with maize-cereals-vegetables rotation covering 35% of the total

170 watershed area and 47% of the seasonally waterlogged area. In addition to groundwater DOM
 171 sources, livestock-impacted DOM can be transported to the stream through the surface and
 172 subsurface runoff from farmyards, manure amended soils, and septic tanks (Baker 2002; Old and
 173 others 2012). Swine-slurry-impacted runoff previously characterized by Jaffrezic and others (2011)
 174 was used as the end member for DOM from this source in this study (Text S4).

175 **Table 1.** Selected characteristics of sampling sites.

Land use	Vegetation	Adjacent field	Organic fertilization of field/adjacent field
<i>Upland cropland K2 - K3</i>			
cropland	maize (<i>Zea mays</i>)	-	400 kg C ha ⁻¹ of swine slurry applied on May 2, 2014 (after maize sowing)
<i>Riparian woodland K1</i>			
woodland buffer strip 50 m wide	shrubs and trees (<i>Populus negro</i> , <i>Salix coprea</i> , <i>Betula alba</i>)	maize residues (<i>Zea mays</i>)	400 kg C ha ⁻¹ of swine slurry applied on May 2, 2014
<i>Riparian grassland G2 and G3</i>			
grassland buffer strip 50 m wide	unfertilized herbaceous species (<i>Dactylis glomerata</i> , <i>Agrostis canina</i>)	winter barley (<i>Hordeum vulgare</i>)	400 kg C ha ⁻¹ of swine slurry applied on April 9, 2014
<i>Riparian woodland M</i>			
woodland buffer strip 60 m wide	shrubs and trees (<i>Populus negro</i> , <i>Salix coprea</i> , <i>Betula alba</i>)	maize residues (<i>Zea mays</i>)	n.a.

176 Hydrological monitoring and water sampling

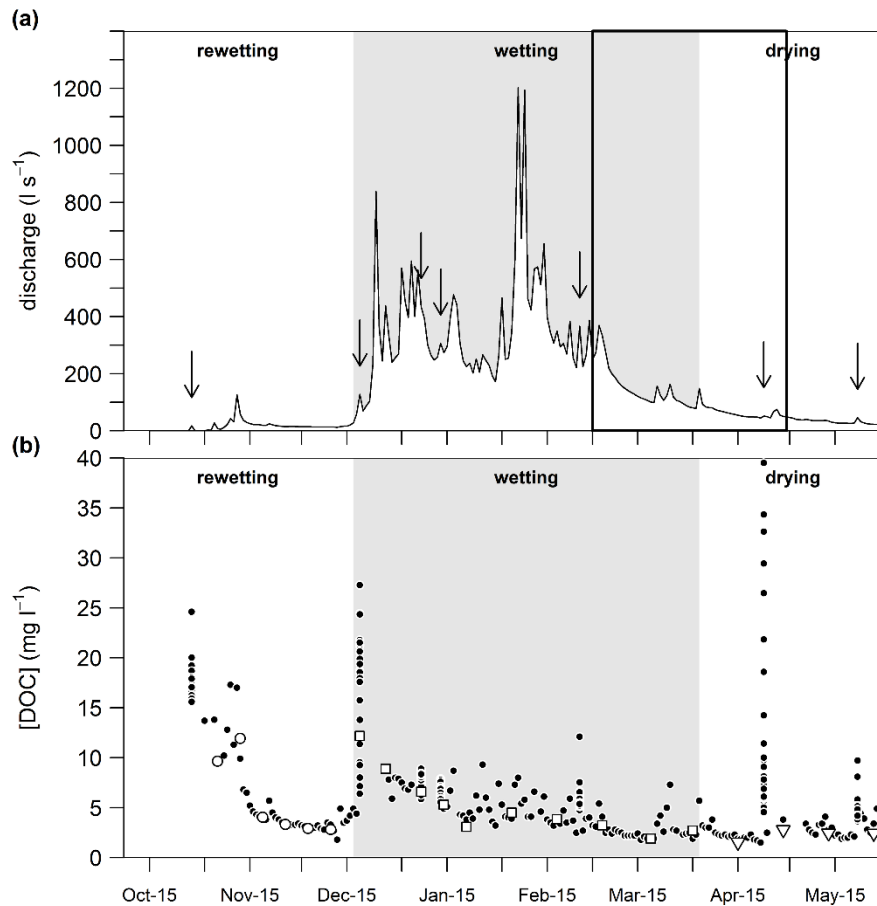
177 Stream discharge (l s⁻¹) was calculated from the stream stage (m) recorded at one minute
 178 intervals using a float-operated sensor (Thalimèdes OTT, ±2 mm) and a stage-discharge relationship
 179 (Figure 2a). Groundwater depth was recorded at 15-minute intervals using pressure sensors
 180 (Orpheus Mini OTT, ±2 mm) along two transects of 2-10 m deep piezometers (G2-3 and K1-3, Figures
 181 1 and S1).

182 A variable sampling frequency approach was used to capture the effects of land management
 183 on stream water and groundwater DOM over time, and seasonal and pulsed change in water flow
 184 paths (Figure 2b). Stream water and groundwater were sampled during regularly scheduled
 185 'baseflow' sampling campaigns for DOC concentration and DOM composition every 7 or 14 days from
 186 October 2013 to May 2014 (20 sampling campaigns total). The effects of land management (i.e. land
 187 cover and practices) on stream water and groundwater DOM over time were investigated with these
 188 samples collected whatever the discharge and groundwater levels. Although baseflow sampling

189 occasionally occurred on rising or falling limbs of the hydrograph, the composition and dynamics
190 reported here indicate that scheduled sampling predominantly reflects baseflow DOM composition.
191 Hereafter we refer to these as baseflow samples. Sampling frequency decreased to every 14 days
192 after the transition from the rewetting to the wetting period (i.e. from January 2014) due to less
193 temporal variation in hydrology and DOM composition. Drying prevented stream water sampling
194 prior to October 28, 2013, and groundwater sampling from June through October 2014. In addition,
195 stream water was sampled manually on a daily basis at the watershed outlet for dissolved organic
196 carbon concentration ([DOC]). This allowed us to assess the validity of weekly sampling for capturing
197 the stream DOM dynamics (Figure 2b). Finally, the changes in stream water DOM with management
198 practices over pulsed changes in water flow paths were investigated for seven storm events spanning
199 3 hydrologic seasons (1 rewetting season, 4 wetting season, 2 drying season) and maximum
200 discharges ranging from 49-794 l s⁻¹. We collected samples for DOM quantity and composition at
201 30-minute intervals using a refrigerated (4°C) ISCO sampler.

202 Groundwater samples were collected with zero-tension lysimeters installed close to
203 piezometers. Three months prior to the start of our study, lysimeters were installed at 6 sites in
204 triplicate (spaced ca. 1 m apart) in 13 soil layers for a total of 39 lysimeters. The lysimeters collected
205 free-draining soil solution while maintaining in situ-anoxic conditions.

206 All samples were stored in polypropylene bottles in the dark at 4°C until filtration and
207 analysis. All manually collected samples were filtered within 24 hours, while automated ISCO samples
208 were typically filtered within 1 week. All filtration was performed with cellulose acetate membrane
209 filters (0.22 µm, Sartorius) prewashed with 500 ml of deionized water and then rinsed with sample.



210

211 **Figure 2.** Hydrochemical monitoring from October 2013 to May 2014. **(a)** Mean daily discharge. The rectangle with solid
 212 thick lines indicates the time period when more than 70% of organic amendment applications occurred. Arrows indicate the
 213 sampled events. **(b)** Stream water dissolved organic carbon concentration ([DOC]) from daily grab samples, storm events
 214 (both in black dots), and regularly scheduled samples (open dots, squares, and triangles for the rewetting, wetting, and
 215 drying periods, respectively).

216 DOM characterization

217 Filtered samples were analyzed for DOC concentration and DOM composition. The
 218 concentration of DOC was analyzed using the high-temperature catalytic oxidation method as TC-IC
 219 (Shimadzu TOC-V_{CSH}, ±5%). Dissolved organic matter composition was characterized using ultra-violet
 220 and visible light (UV-Vis) absorbance and excitation-emission matrix (EEM) fluorescence. The UV-Vis
 221 absorbance measures the light-absorbing DOM (colored DOM or CDOM) and fluorescence measures
 222 the part of CDOM that, after absorbing light, reemits it (FDOM; Coble 2007). The UV-Vis absorbance
 223 of DOM was measured in a 10 mm quartz cell on a spectrophotometer (Perkin-Elmer Lambda 20) at

224 0.5 nm intervals from 200 to 600 nm. Specific ultraviolet absorbance at 254 nm (SUVA₂₅₄;
225 l·mg C⁻¹·m⁻¹) was calculated as the UV-Vis absorbance at 254 nm per meter (m⁻¹) divided by the DOC
226 concentration (mg C·l⁻¹). Samples with higher values of SUVA₂₅₄ are typically more aromatic
227 (Weishaar and others 2003). Fluorescence analysis was performed using a Perkin-Elmer LS 55
228 scanning spectrofluorometer. The EEMs were collected by scanning fluorescence emissions (em.)
229 between 250 nm to 600 nm in 0.5 nm increments at a scan speed of 1500 nm min⁻¹ at each of the
230 excitation (ex.) wavelengths from 200-420 nm in 5 nm increments. All EEMs were then corrected for
231 instrumental bias following the manufacturer's method, inner-filter effects (Ohno 2002), and dilution
232 (where necessary). If the prior UV-Vis measurements indicated that the absorbance at 254 nm was
233 greater than 0.3, samples were diluted to <0.2 so the inner-filter correction procedure would be
234 valid (Ohno 2002).

235 **Data handling and statistical analysis**

236 Parallel factor analysis (PARAFAC) was used to identify statistically independent classes of
237 fluorescent molecules (Stedmon and Rasmus 2008). The analysis was performed from 715
238 groundwater and stream water sampled during the study period. Prior to conducting PARAFAC, a DI
239 blank was subtracted from all EEMS and their fluorescence intensities were normalized by the area
240 under the Raman peak at ex. 350 nm. The PARAFAC modeling was performed in Matlab R2008b
241 using the drEEM v.0.2.0 toolbox as described by Murphy and others (2013). Due to noise at low ex.
242 and high em. wavelengths, we only modeled the EEM region within ex. 250-420 nm and em. 250-524
243 nm. To save computation time, we modeled em. at 2 nm intervals. The final model was validated by
244 split-half validation. The EEMs previously obtained from DOM in swine-slurry-impacted runoffs were
245 not used in modeling, rather they were fit to our validated model to estimate the PARAFAC scores of
246 livestock-impacted DOM sources (R² ranging from 0.85 to 0.95, n= 6; Jaffrezic and others 2011). For
247 each component, we report PARAFAC results as absolute scores (F_{max} values; Raman Units (RU)) as
248 well as percent abundance (%; individual component score divided by the sum of absolute scores for
249 all identified components in a sample x 100). We compared the PARAFAC components modeled from

250 our data set to previous studies, using a modified Tucker's Congruence Coefficient (mTCC), with
251 values ≥ 0.95 indicative of a close match (Parr and others 2014).

252 In addition to PARAFAC components, we calculated three fluorescence indices. The
253 fluorescence index (FI) describes the relative dominance of microbially vs. terrestrially derived
254 organic matter in a sample; higher values (greater than 1.4) indicate a preponderance of microbial
255 DOM and lower values (less than 1.4) indicate predominantly terrestrial sources (Cory and others
256 2010). The humification index (HIX) describes the condensation of DOM (Ohno 2002); values range
257 from 0 to 1 and higher values indicate more condensed DOM (i.e. with higher aromaticity and
258 molecular weight). The $\beta:\alpha$ ratio, or freshness index, ranges from 0 to 1; relatively higher values
259 indicate more recently derived DOM (Wilson and Xenopoulos 2009).

260 All statistical analyses were performed in [R] (R Core Team, 2014). We estimated the
261 correlations between variables with Spearman's rank-order correlations (r_s ; *cor.test*). We used
262 principal components analysis (PCA) to understand the responses of DOM composition as measured
263 by PARAFAC fluorescence components in stream water and groundwater to different land uses and
264 land management practices through time (FactoMineR R package; Husson and others 2013).
265 Specifically, we constructed three separate PCA analyses to assess the DOM sources diversity and the
266 contribution of these sources to stream DOM across seasonal and event-driven hydrologic conditions
267 using the percent abundance of fluorescence components. These PCAs analyzed: 1) changes in
268 composition of groundwater DOM with land cover, season and time (432 groundwater samples); 2)
269 changes in composition of stream water DOM with seasonal and pulsed changes in water flow paths
270 (93 stream water samples); 3) changes in stream DOM with management practices (31 stream water
271 samples). In all PCA analyses five supplementary variables ([DOC], $SUVA_{254}$, FI, HIX, $\beta:\alpha$) were
272 displayed to facilitate interpretation of the PARAFAC PCA results. Supplementary variables or
273 individuals are not used in the initial PCA computation, rather their coordinates are calculated based
274 on their correlations with the variables used in the PCA (Text S5).

275 Univariate and multivariate statistics were used in addition to the PCAs to assess our

276 hypotheses. Significant differences among land covers were assessed for each variable by applying a
277 paired Monte Carlo permutation test stratified by sampling date to account for potential temporal
278 variations (*oneway_test*, coin R package, 9999 iterations; Hothorn and others 2008). In complement
279 to the first of the three PCAs, the significance of land cover control on the composition of
280 groundwater DOM was tested using global and pairwise permutative multivariate analyses of
281 variance based on the percent abundance of fluorescence (PERMANOVA; *adonis*, vegan R package,
282 999 iterations; Oksanen and others 2006). Finally, we tested for the presence of dispersion effects in
283 the PERMANOVA (*betadisp*, vegan R package, 999 iterations; Oksanen and others 2006), to ensure
284 that the differences resulted from different mean values of groups and not from differences in
285 within-group variance (Anderson 2001).

286 **Results**

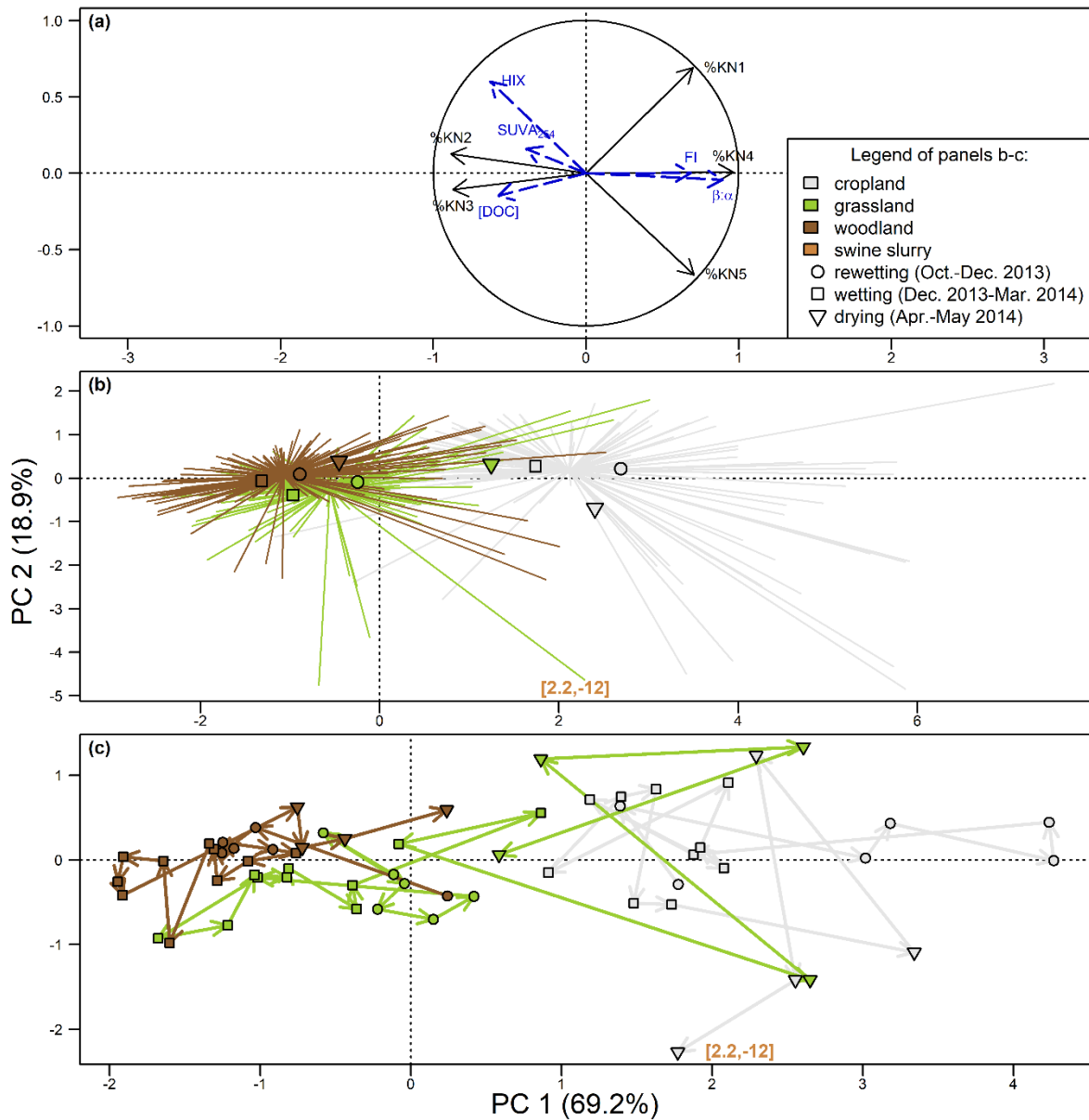
287 **Spatial variations in quantity and composition of groundwater DOM**

288 PARAFAC modeling resolved a five-component model ('Kervidy-Naizin model'; abbreviated
289 KN1-5; Figure S2), with components similar in shape and location to those observed in previous
290 studies (Table S3). Across samples, components KN1 and KN4 comprised $37.1 \pm 2\%$ and $14.8 \pm 3.6\%$
291 of total fluorescence, respectively. Both of these components have been associated with plant-
292 derived and microbial-derived materials (McGarry and Baker 2000; Cory and McKnight 2005). The
293 KN2 fluorophore accounted for $26.8 \pm 3.9\%$ of total fluorescence and it resembled fluorescence
294 associated with plant-derived aromatic compounds in previous studies (McGarry and Baker 2000;
295 Fellman and others 2009). The KN3 component ($17.9 \pm 3.5\%$) resembled components highly
296 associated with forested land covers (Stedmon and Markager 2005; Lapierre and Frenette 2009).
297 Component KN5 ($3.4 \pm 2.8\%$) resembled protein-like fluorescence frequently associated with
298 microbially-derived DOM (Cory and McKnight 2005; Fellman and others 2009; Singh and others
299 2013).

300 The quantity and composition of DOM varied with land cover. Groundwater [DOC] varied
301 significantly ($p < 0.05$) among riparian grassland ($22.4 \pm 13.7 \text{ mg l}^{-1}$; mean \pm standard

302 deviation) > riparian woodland ($17.2 \pm 9.9 \text{ mg l}^{-1}$) > upland cropland ($6.4 \pm 5.6 \text{ mg l}^{-1}$) (Figure S3a). The
303 relative abundance of microbially processed and protein-like DOM in groundwater decreased in the
304 order upland cropland > riparian grassland > riparian woodland ($p < 0.05$); with averaged FI
305 ($1.66 > 1.46 > 1.43$), $\beta:\alpha$ ratio ($0.57 > 0.47 > 0.43$), %KN4 ($20 > 14 > 12$) and %KN5 ($4 > 3 > 2$) (Figures
306 S3d-e, and S3i-j). Conversely, mean %KN2 increased ($p < 0.05$) among the three different land covers
307 with cropland (22) < grassland (28) < woodland (30) (Figure S3g). The DOM composition was more
308 aromatic in riparian grassland and woodland than in upland cropland; with higher average values
309 ($p < 0.05$) for SUVA₂₅₄ ($3.64\text{-}3.77 > 2.86$; Figure S3b), HIX ($0.97 > 0.95$; Figure S3c) and for %KN3
310 ($19\text{-}20 > 16$; Figure S3h). The %KN1 was higher in average in the upland cropland than in the riparian
311 lands ($39 > 36$; Figure S3f).

312 This difference in groundwater DOM composition among the land covers was depicted by a
313 PCA presented in Figure 3. The principal component axis (PC) 1 distinguished the origin of DOM
314 (plant-derived vs. microbially processed) and PC 2 distinguished its character (protein-like vs.
315 aromatic) (Figure 3a). Although the PCA (Figures 3b) shows distinct locations of land cover centroids,
316 the analysis of group dispersions heterogeneity suggests that dispersion effects are also present. This
317 means that PERMANOVA results cannot be conclusively interpreted to provide significant evidence
318 that land cover influenced the DOM composition (Table S4). Although being close to each other in
319 the PCA analysis, grassland and woodland DOM differed significantly from each other ($F = 23.1$,
320 $p < 0.01$), as revealed by the pairwise comparisons (Table S4). While the centroid of cropland DOM
321 was distinct from grassland and woodland ($p < 0.01$), it also had higher dispersion ($p < 0.001$), likely
322 due to the higher range of groundwater sampling depth and short-term effects of agricultural
323 practices.



324

325 **Figure 3.** Principal component analysis (PCA) of groundwater fluorescent dissolved organic matter (FDOM) composition.

326 The first two axes explain 88% of the variance in percent abundance PARAFAC components for the soil solutions of different

327 land covers. **(a)** Loading plot showing the contribution of percent abundance of PARAFAC components to the computing of

328 the first two principal components (PC). Blue dashed arrows indicate supplementary variables ([DOC], SUVA₂₅₄, FI, HIX, β:α)

329 not used in the calculation of the PARAFAC component PCA, but do facilitate its interpretation. **(b)** Scores plot showing

330 annual and seasonal centroids aggregated by land cover. Annual centroids were built from 126, 119 and 187 samples for

331 cropland, grassland, and woodland, respectively. Centroids of rewetting, wetting and drying periods were built from 34-70,

332 73-98 and 11-19 samples, respectively. **(c)** Close-up view of scores plot showing temporal dynamics of centroids aggregated

333 by land cover. Centroids were built from 2-12, 1-12 and 4-15 samples for cropland, grassland, and woodland, respectively.

334 The FDOM composition determined for the swine-slurry-impacted runoff is presented as supplementary individual in

335 figures b and c. Its location on the score plot is indicated with brackets [PC1, PC2].

336 **Temporal variation in quantity and composition of groundwater DOM**

337 The composition and quantity of DOM were highly variable over time. However,
338 groundwater [DOC] presented similar patterns among the three different land covers (Figure S4).
339 Associated with these [DOC] dynamics, Figures S5 to S9 show for each land cover the temporal
340 variations in the groundwater % abundance of fluorescence components. Figures 3b and c map these
341 changes in the first two axes of the PCA performed from groundwater FDOM composition.

342 From the third sampling date of the rewetting period, groundwater median [DOC] decreased
343 from 10.5 to 2.5 mg l⁻¹ in cultivated upland and from 26.5 to 6.3 mg l⁻¹ in riparian grassland (Figure
344 S4). Main changes were observed for fluorescence components %KN4 and %KN5, with medians
345 increasing by factors ranging from 1.3 to 2.2 (Figures 3c, S5-9). Groundwater median [DOC] remained
346 rather stable over this period in riparian woodlands (ranging from 13.9 to 16.4 mg l⁻¹), with a DOM
347 composition mainly characterized by a progressive decrease in median %KN5 from 1.73 to 1.17.
348 These changes occurred during a dry period (18 days without precipitation) within the 72-day long
349 rewetting period (216 mm of total rainfall; Figure S1). Lower groundwater elevations were monitored
350 in riparian grassland and cultivated upland than in riparian woodland.

351 Median groundwater [DOC] decreased during the wetting period (i.e. from December to
352 February; Figure S4); from 8.2 to 2.8 mg l⁻¹ in cultivated upland, from 30.5 to 10.2 mg l⁻¹ in riparian
353 grassland, and from 16.4 to 10.8 mg l⁻¹ in riparian woodland. The decrease in %KN5 and increase in
354 %KN3 were the common dynamics observed for groundwater DOM composition of all land covers
355 (Figures 3c, S7, and S9). Contrasted dynamics were observed among the land covers for others
356 fluorescence components; with low decrease in median %KN2, and low increase in median %KN4 of
357 both upland cropland and riparian grassland groundwater, while these components remained rather
358 stable in riparian woodland groundwater (Figures 3c, S6, and S8).

359 Increasing median groundwater [DOC] was monitored in all land covers from March to May
360 2014 (Figure S4). This trend was rather progressive in riparian grassland and woodland, while
361 occurring mainly during the transition from wetting to drying period in upland cropland (increasing

362 from 2.8 to 6.4 mg l⁻¹ on average). Concurrently, median %KN5 more than doubled for groundwater
363 DOM composition of all land covers (Figures 3c, S7, and S9). The protein-like signature of livestock-
364 impacted DOM sources was detected in cropland groundwater throughout the drying period, with
365 the May samples, collected after manure was applied to the fields having at least a 60% higher
366 abundance of protein-like compounds compared to pre manure application April samples. A similar
367 signature was detected in the DOM groundwater of riparian grassland, but only on April 15 (first
368 green triangle in Figure 3c), though its composition was more microbially processed than the other
369 samples between February and May.

370 Superimposed on these patterns, pulsed [DOC] were observed in the groundwater of all land
371 covers subsequently to rain events responsible for increased groundwater levels during the transition
372 from rewetting to wetting period and on February 4 (Figures S1 and S4). Concurrently, the median
373 %KN5 doubled at the transition period in the riparian woodland groundwater and %KN5 increased by
374 factors ranging from 1.1 to 1.5 in groundwater DOM of all land covers on February 4 (Figures 3c and
375 S9).

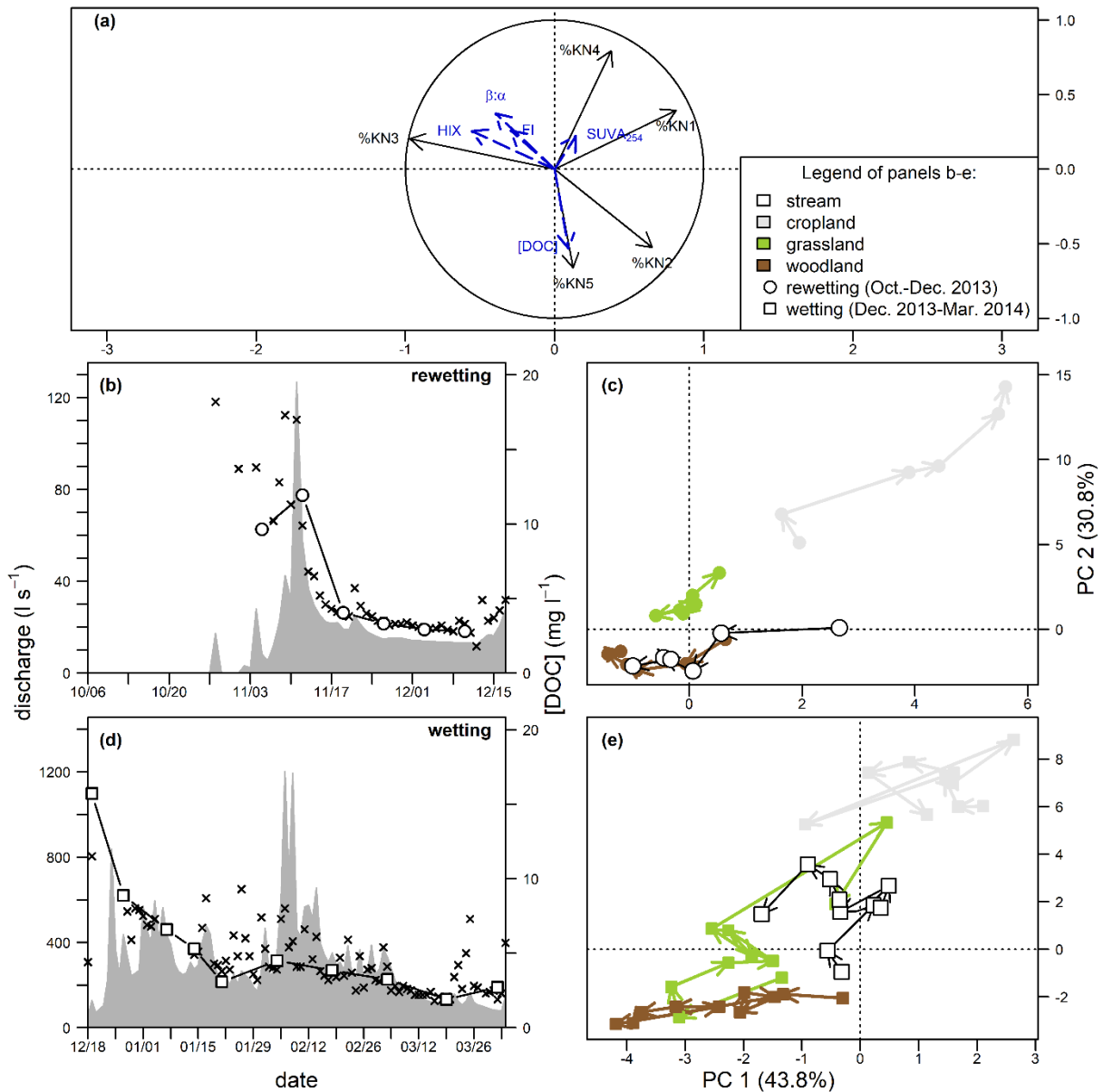
376 **Temporal variation in quantity and composition of stream water DOM**

377 The quantity and composition of groundwater DOM from the three land covers constrained
378 the ones observed in stream water over time (Figure S3). Stream water [DOC] (5.3 ± 4 mg l⁻¹) was
379 consistently lower ($p < 0.05$) than [DOC] in riparian grassland and woodland groundwaters, but was
380 not significantly different from [DOC] in upland croplands groundwaters (Figure S3a). Daily stream
381 [DOC] decreased from approximately 12 to 3 mg l⁻¹ over the course of the water year (Figure 2b),
382 with a more pronounced decrease when the water year began. Pulsed increases in concentration
383 were observed during the storm events and the rises in groundwater elevation, but were
384 progressively damped over the water year (Figures 2b, 4 and 6), as evidenced by the lack of marked
385 increase in [DOC] in February, whereas high discharge was monitored. Contrasting with this general
386 pattern, high [DOC] (i.e. >30 mg l⁻¹) was monitored during stormflow on April 23 (Figures 2b and 6d).

387 Associated with these concentration dynamics, temporal variations in the DOM composition

388 of the stream water are detailed in figure S10 and depicted in the PCA presented in Figures 4 and 5. It
389 was conducted with the % abundance of fluorophores obtained from both baseflow and stormflow
390 samples of the rewetting and wetting periods. The PC axes 1 and 2 distinguished the stream DOM
391 sources; with PC1 negatively related to the DOM composition of riparian woodland groundwater,
392 and PC2 positively related to the DOM composition of cultivated upland groundwater (Figure 4a).

393 During the rewetting period, the composition of stream water DOM was closely related to
394 the composition of riparian woodland DOM; in the PCA plot, the ordination spaces occupied by
395 stream water and woodland groundwater FDOM overlapped (Figure 4c). Concurrent with the
396 decrease in stream water [DOC] reported during this period, a progressive increase in aromatic
397 compounds within the composition of stream water DOM can be inferred from the increase in %KN3
398 (from 15.4% to 19.3%). During the wetting period, two patterns are depicted (Figure 4e). First, the
399 composition of stream water DOM became relatively enriched in terrestrial microbially-processed
400 compounds (increases in %KN1 and %KN4, respectively; Figure S10a and d) and resembled the DOM
401 signature of upland croplands (Figure 4e). This does not exclude the contributions to the stream
402 water DOM of riparian woodland and grassland groundwater DOM. However, this riparian
403 groundwater contribution to stream water DOM has decreased during the wetting period as
404 compared to the rewetting period; there is an increasing separation between stream water and
405 riparian groundwater FDOM within the ordination spaces of PCA plot. Noticeably, the greatest
406 change in stream DOM composition occurred approximately two weeks after the rise in groundwater
407 level during the onset of the wetting period (on January 7, 2014). Second, similar to the pattern
408 observed during the rewetting period, %KN3 progressively increased in the composition of stream
409 water DOM over the course of the wetting period (Figures S10b-c). When the wetting period ended
410 (on April 1, 2014), the composition of stream water DOM decreased in %KN1 and %KN4 (by 4.7% and
411 2.6%, respectively), which was more similar to the composition of riparian groundwaters (Figure 4e).



412

413 **Figure 4.** Baseflow dynamics of fluorescent dissolved organic matter (FDOM) composition in stream water during the414 rewetting and wetting periods. **(a)** In the PCA plots, the first two principal components (PC) explain 75% of the variance in

415 percent abundance of PARAFAC components for the stream water samples of rewetting and wetting periods (baseflow and

416 stormflow samples). Loading plot showing the contribution of percent abundance of PARAFAC components to the

417 computing of the first two PCs. Blue dashed arrows indicate supplementary variables ([DOC], SUVA₂₅₄, FI, HIX, $\beta:\alpha$) not used418 in the calculation of the PARAFAC component PCA, but do facilitate its interpretation. **(b and d)** Mean daily discharge (grey

419 area) and [DOC] for the daily samples (black cross) and the samples collected manually weekly or fortnightly (white

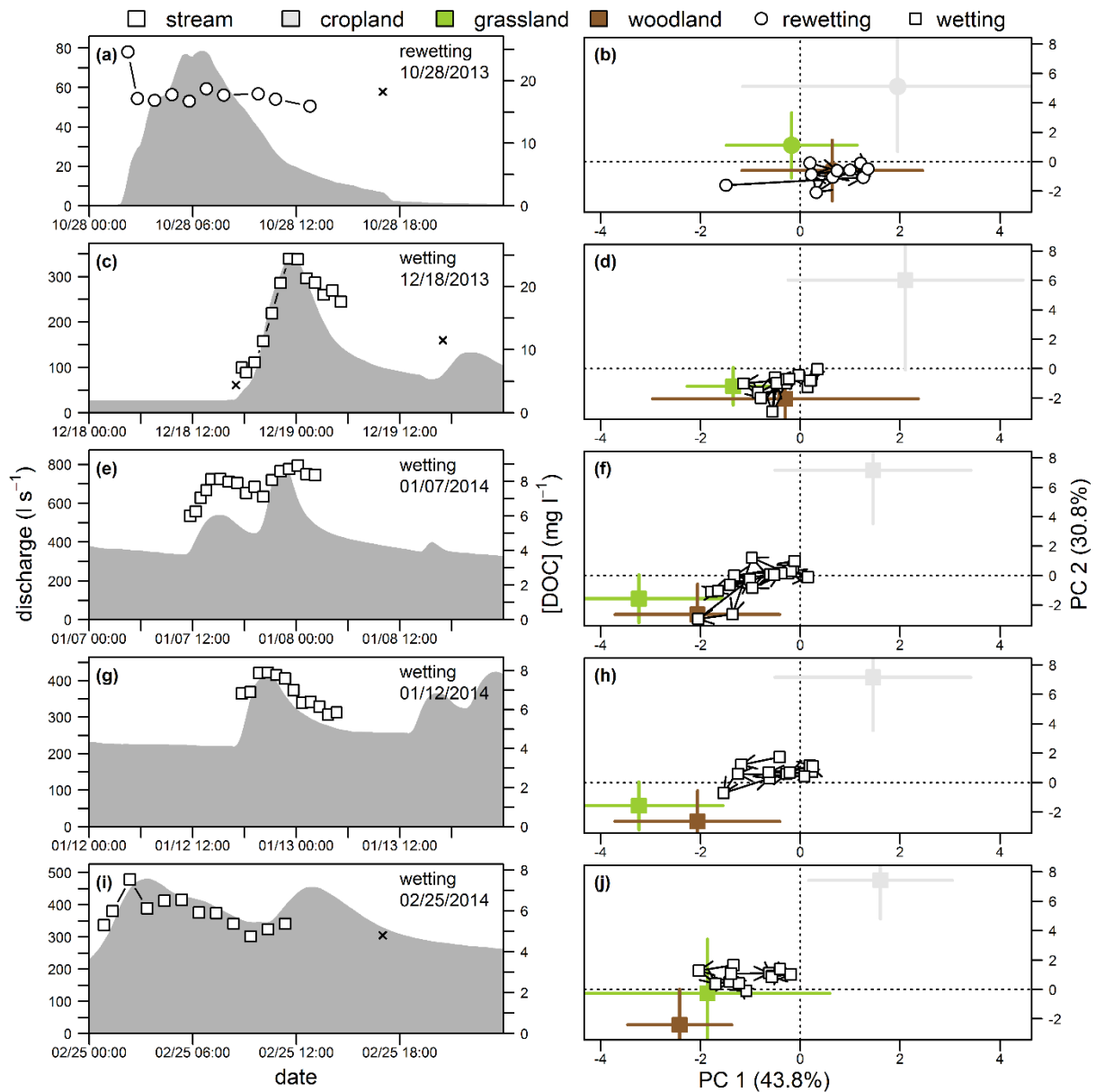
420 symbols) over the rewetting and wetting periods. Note the changes in axis scales for discharge. **(c and e)** Score plots

421 showing the temporal dynamics of the stream water FDOM composition over the rewetting and wetting periods. The

422 temporal dynamics of centroids aggregated by land cover as depicted in Fig. 3c are presented. Centroids were built from 2-

423 12, 1-12 and 4-15 samples for cropland, grassland, and woodland, respectively. Note that each white symbol resulted from
424 the DOC concentration or the FDOM composition of a unique sample collected at the watershed outlet.

425 The composition of stream water DOM differed between the storm events and depended on
426 the hydroseason in which it occurred (Figures 5 and S11). In the rewetting period, during the first
427 storm event, DOM had a fluorescent composition similar to that of riparian woodland groundwater,
428 and exhibited little change in quantity and composition over the course of the event (Figures 5a and
429 b). Relative to the rewetting period, stream water DOM in the first storm event sampled during the
430 wetting period had a slightly more aromatic composition, with an increase in %KN3 from 17.3 ± 0.9 to
431 18.7 ± 0.5 (Figures 5b, 5d, and S11). The DOM signature of stream water was similar to both riparian
432 grassland and woodland sources. As compared to the DOM signature of the first event of the wetting
433 period, the mean %KN5 progressively decreased (from 3.2 ± 0.7 to 2.5 ± 0.3), while the mean %KN4
434 increased (from 13 ± 0.3 to 14.2 ± 0.3). However, the contribution of upland cropland DOM to the
435 stream water DOM was lesser in the stormflow of the wetting period than in baseflow of this period
436 (Figures 5f-5j).



437

438

Figure 5. Storm flow dynamics of fluorescent dissolved organic matter (FDOM) composition in stream water during

439

rewetting and wetting periods. (a, c, e, g, i) Discharge (grey area) and [DOC] for storm events (white symbols) and daily

440

samples (black cross). Note the changes in axis scales for discharge and concentration. (b, d, f, h, j) Score plots showing the

441

change in stream water FDOM composition during storm events. Mean and standard deviation of FDOM composition

442

aggregated by land cover type are presented for soil solutions sampled before or after (rewetting, figure b) the storm

443

event. Note that each white symbol resulted from the DOC concentration or the FDOM composition of a unique sample

444

collected at the watershed outlet.

445

Livestock-impacted DOM sources affected stream water DOM only during drying period

446

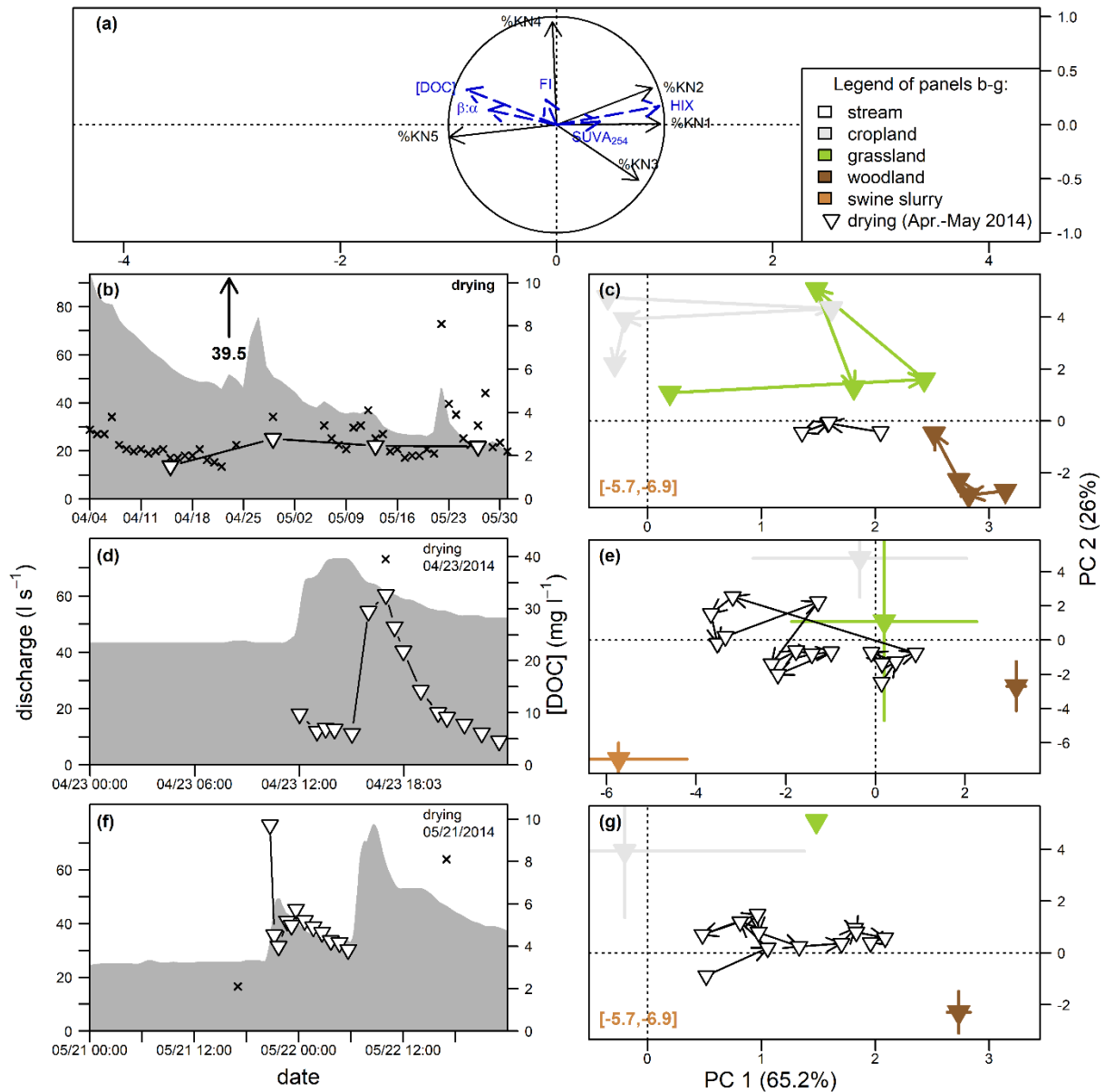
storm events occurring shortly after the swine slurry was applied to the soils. The PCA presented in

447

Figure 6 was conducted with the % abundance of fluorophores obtained from both baseflow and

448 stormflow of the drying period. The first and second PC axes (PC1, PC2) distinguish stream DOM
449 sources. The PC1 represented a gradient of DOM derived from livestock-impacted source to DOM
450 derived primarily from riparian woodland groundwater. The PC2 represented a gradient of increasing
451 contributions from groundwater underlying cultivated uplands (Figure 6a). Although increasing in
452 %KN5 as compared to DOM composition of wetting period baseflow (Figure S10), little variation was
453 observed over the course of the drying period baseflow, the stream DOM composition reflected a
454 mixture of riparian grassland and woodland sources. However, livestock-impacted DOM clearly
455 altered the amount and composition of stream water DOM during the two storm events.

456 The livestock-impacted DOM source used in this study had protein-like component KN5 that
457 was six to twelve times more abundant than terrestrial DOM sources. This is confirmed by the visual
458 inspection of residuals that resulted from KN fluorophores fitting to the swine-slurry-impacted
459 runoff. While the model fits the swine slurry endmember EEMs well, it appears to contain a protein-
460 like component that is not fully explained by the surface and groundwater DOM model. This
461 component may not be transferred to stream water and groundwater due to rapid abiotic (soil
462 interactions) or biotic (microbial degradation) removal. During storms following swine slurry
463 application, increases in protein-like fluorescence (%KN5 ranged from 3.7 to 21) relative to baseflow
464 samples were approximately four times greater than the increases observed during storms occurring
465 before swine slurry application. For example, during the storm event on April 23, the composition of
466 stream water DOM started out similar to riparian grassland and woodland DOM. Over the course of
467 the storm its composition developed characteristics indicating high increases (2-5 fold over baseflow
468 samples) in the contributions from upland cropland and livestock-impacted sources (Figure 6e). The
469 transfer to the stream of swine slurry applied to the soils was quickly mitigated. During the event on
470 22 May, the magnitude of increase in protein-like fluorescence relative to baseflow samples was
471 <1.5. The temporal pattern was reversed, the stormflow DOM was first a mixture of DOM originating
472 from upland cropland treated with swine-slurry and then a mixture of DOM originating from riparian
473 grassland and woodland (Figure 6g).



474

475 **Figure 6.** Principal component analysis (PCA) of fluorescent dissolved organic matter (FDOM) composition in stream water

476 of drying period. The first two axes explain 79% of the variance in percent abundance of PARAFAC components for the

477 stream samples (baseflow and storm event samples). **(a)** Loading plot showing the contribution of percent abundance of

478 PARAFAC components to the computing of the first two PCs. Blue dashed arrows indicate supplementary variables ([DOC],

479 SUVA₂₅₄, FI, HIX, β:α) not used in the calculation of the PARAFAC component PCA, but do facilitate its interpretation. **(b, d,**480 **and f)** Discharge (averaged daily in b; grey area) and [DOC] for baseflow stream water and storm events (white symbols)481 and daily samples (black cross). Note the changes in axis scales for discharge and concentration. **(c)** Score plots showing the482 temporal dynamics of the stream water FDOM composition during the drying period. **(e and g)** Score plots showing the

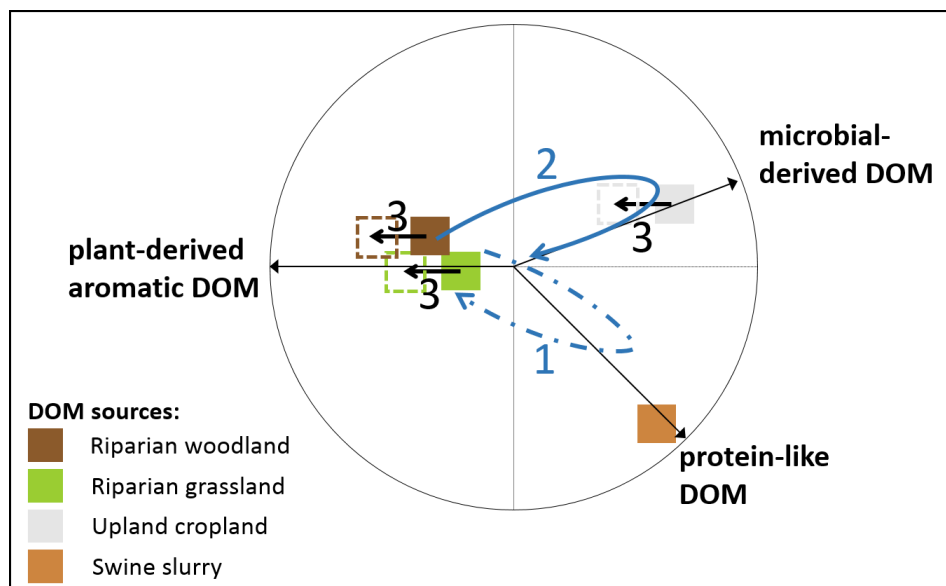
483 change in stream FDOM composition during storm events of the drying period. Axis scales differed to better map the

484 temporal dynamics during the events. The FDOM composition aggregated by land cover type is presented for soil solutions

485 sampled during the drying period (c) and before the storm event (e and g). Centroids were built from 2-12, 1-12 and 4-15
 486 samples for cropland, grassland, and woodland, respectively. Similarly, the FDOM composition determined for the swine-
 487 slurry-impacted runoff is presented as supplementary individual in figures c, e, and g. Its location on the score plot can be
 488 indicated with brackets [PC1, PC2]. Note that each white symbol resulted from the DOC concentration or the FDOM
 489 composition of a unique sample collected at the watershed outlet.

490 Discussion

491 Tillage, cropping and fertilizer application alter the quantity, composition, and timing of DOM
 492 export. These agricultural practices increase the proportion of protein-like compounds likely to be
 493 exported at sub-hourly and annual time-scales (December-May; processes 1 and 2 in Figure 7). More
 494 generally, these practices increased the signature of microbial processing in and reduced the
 495 quantity of groundwater DOM under cultivated uplands compared to grassland and tree buffer
 496 strips. In addition, our results suggested that seasonal waterlogging and hydrological connection to
 497 the stream of soils drives the major changes in their DOM composition by increasing the proportion
 498 of aromatic compounds (October-March; process 3 in Figure 7).



499

500 **Figure 7.** Sketch diagram summarizing the temporal dynamics of DOM composition in stream water and groundwater under
 501 the combined impacts of land use, management, and hydrology. It summarizes the results of the principal component
 502 analysis conducted in this study. The numbers '1' to '3' refer to the changes in DOM composition discussed in the text and
 503 observed in stormflow shortly following application of swine slurry on cultivated uplands, baseflow of the wetting period,
 504 and in groundwater during both the rewetting and wetting periods, respectively.

505 Short-term effects of swine slurry application on stream water and groundwater DOM

506 Climate and biogeochemically reactive management practices interact at different time
507 scales and affect the timing of agriculturally-derived DOM export. Export of swine slurry applied in
508 the uplands was greatest in the spring, when precipitation events occurred during or after
509 application periods, and briefly impacted stream water and groundwater (process 1 in Figure 7).
510 Livestock-impacted DOM was enriched in protein-like compounds (Baker 2002; Naden and others
511 2010) distinguishing it from stream water and groundwater DOM sources. In May, we observed the
512 highest abundance of protein-like compounds in the groundwater of upland croplands – after
513 approximately 400 kg ha⁻¹ of swine slurry was applied. Similarly on April 15th, 6 days after application
514 of swine slurry in the adjacent field, we observed a pulse of protein-like compounds in the grassland
515 buffer strip groundwater. Finally, transport to the stream water of swine slurry applied on cropland
516 was evidenced during a storm event in the main application period, with pronounced increases in
517 stream water [DOC] and abundance of protein-like compounds. Similar vertical and lateral transports
518 of animal wastes were reported elsewhere at plot and watershed scales (Naden and others 2010;
519 Singh and others 2014). With precipitation intensities and durations predicted to increase across
520 Europe, careful planning of the application of organic and inorganic soil amendment will be essential
521 for protecting waterways from agricultural pollutions (European Environment Agency 2017).

522 Long-term effects of agricultural land management on the composition of groundwater DOM

523 The diversity and frequency of operations performed on the cropland (harvest removal,
524 fertilization, liming, tillage and pest management; Table S1) likely mitigate the significance of
525 differences in DOM composition observed between cultivated and non-cultivated lands. For
526 example, the strong short-term effects of swine slurry on DOM composition (see above) obscures
527 longer-term effects that management of land for cropping may have on DOM composition and
528 quantity through direct and indirect mechanisms. These mechanisms could result in lower topsoil
529 [DOC] and more protein-like and less aromatic groundwater DOM in upland cropland than in riparian
530 grassland and woodland (i.e. PARAFAC components KN1, KN4, and KN5; Figure 7).

531 Each agricultural practice can have a persistent effect on groundwater DOM through indirect
532 mechanisms that influence the processing of organic matter in arable soils. For example, previous
533 work showed that animal manure applications could explain persistent differences in DOM
534 composition of cropland groundwater (Ohno and others 2009; Bilal and others 2010). They showed
535 that these signatures were particularly persistent in soils amended with swine slurry which was
536 consistent with the results presented here. Possible explanations for the persistence of the swine-
537 slurry signature in amended soils include: (i) the sorption of manure-derived compounds to binding
538 sites left free due to herbicides and biomass removal (Kaiser and Kalbitz 2012); (ii) the consumption
539 or production alteration of the protein-like DOM either directly or by changing the soil microbial
540 community (Haynes and Naidu 1998; Peacock and others 2001). Tillage of arable soils would also
541 partially explain the change in DOM quantity and composition through soil aggregate disruption and
542 increasing the rate of soil organic matter mineralization (Balesdent and others 2000; Toosi and
543 others 2012).

544 Management practices controlling vegetative biomass and the organic amendments directly
545 influence both DOM quantity and composition. Biomass removal during crop harvest combined with
546 herbicide suppression of weed growth decreases the C inputs to soil and subsequently may decrease
547 the C_{org} content of soil and concentration of DOC in groundwater under cropland (Chantigny 2003).
548 The lower C_{org} content observed in cultivated upland compared to riparian grassland and woodland
549 in this study were consistent with these mechanisms (Table S2). In addition to this, Ohno and Bro
550 (2006) reported between- and within-groups variations in the fluorescence signatures of DOM
551 extracted from plants (crops and wetland plants), manures and tree leaves, with the highest
552 variations observed within the manures group. Persistent effects of these materials on groundwater
553 DOM can be hypothesized through repetitive throughfall and/or biomass incorporation in soils
554 combined with adsorption processes to soil particles (Kalbitz and others 2000). An additional indirect
555 mechanism that would involve interactions between the initial quality of the inputs and the
556 decomposer community can also be inferred (Wickings and others 2012). The significance of

557 differences in composition of groundwater DOM observed here between riparian grassland and
558 woodland, where no management practice occurs seems consistent with these hypotheses.

559 **Seasonal hydrologic control of the impact of agriculture on the composition of stream water DOM**

560 Globally, agriculture frequently increases the abundance of more microbially processed DOM
561 in streams compared to watersheds dominated by 'natural' land cover, but our study suggests that
562 the strength of this effect may be seasonal, weakening when low groundwater levels sustain the
563 stream discharge. In headwater watersheds, the composition of stream water DOM depended on the
564 specific landscape elements connected to the stream (Laudon and others 2011). Although upland
565 croplands are located further from the stream than riparian grasslands and forests, they can
566 significantly affect the composition of stream water DOM during hydrologic wet periods when the
567 rising water table provides a hydrologic pathway to reconnect these soils.

568 The seasonal reconnection of upland croplands to the stream increased the abundance of
569 more microbially processed DOM in streams (process 2 in Figure 7). Similarly, Wilson and Xenopoulos
570 (2009) found that the strength of the correlation between agricultural land use and indicators of
571 aromaticity depended on soil moisture conditions in watersheds of Ontario, Canada; with soil
572 wetness being negatively related to stream DOM aromaticity. In contrast with these results, Graeber
573 and others (2012) observed low seasonal variation in DOM quantity and composition of agriculturally
574 impacted watersheds. The high drainage density reported in the latter study (>76% of agricultural
575 watersheds area) could explain this lack of seasonality in the stream water DOM. Indeed, subsurface
576 drainage lowers the variations of groundwater level and/or of transit time in vadose zone,
577 transporting to the stream whatever the season DOM from deep soil horizons (Dalzell and others
578 2011). However, microbially processed DOM with low rather than high aromaticity is expected to be
579 transported to the stream through subsurface drainage.

580 **Preferential leaching loss of protein-like DOM from waterlogged soils**

581 Due to its richness in microbially processed compounds with low aromaticity, the cropland
582 DOM pool would be more readily depleted than other watershed DOM pools. Protein-like,

583 microbially-processed DOM was preferentially and progressively leached from waterlogged soils
584 during the rewetting and wetting periods. Continuous waterlogging of all sampled soil profiles in the
585 riparian woodland during the rewetting period and in all land covers during the wetting period
586 altered the DOM that remained in groundwater towards a more aromatic and less protein-like
587 composition (process 3 in Figure 7). In addition, [DOC] decreased in watershed groundwaters during
588 these periods without increasing mineralization of soil organic matter (Figure S4). Buysse and others
589 (2016) reported for KN watershed soils low CO₂ efflux during winter and related this low biological
590 activity to decreasing temperatures and soil waterlogging. The combined lack of chemical moieties
591 necessary to form strong interactions with mineral surfaces and greater water solubility of proteins
592 could explain the preferential elution and transport of hydrophilic or low aromaticity compounds to
593 surface waters (Chassé and others 2015). This preferential leaching and export of low molecular
594 weight protein-like compounds from soils to surface waters is also consistent with the observed
595 decrease in groundwater [DOC] and increase in groundwater DOM aromaticity.

596 The preferential leaching loss of protein-like DOM from waterlogged soils combined with a
597 seasonal change in production rates of these compounds could explain the seasonal dynamics of
598 stream water [DOC] observed in many headwater watersheds (Mehring and others 2013; Wilson and
599 others 2013). During both the rewetting and wetting periods, the progressive change in DOM
600 composition of watershed groundwater towards higher aromaticity suggests that the remaining
601 DOM moieties are less readily transported from soils to the stream. During these periods, supply
602 limitation of watersheds drives the stream water [DOC] and the pool of readily leachable DOM is not
603 replenished. Consequently, the amount of DOM that can be transported to the stream diminishes
604 and the stream water [DOC] decreases. Conversely during drying periods, transport limitation of
605 watersheds drives the stream water [DOC]. The production rate of readily reachable DOM moieties
606 (i.e. molecules with lower aromaticity) in watershed soils exceeds the rate of DOM export from these
607 soils. In larger rivers and open canopied headwater streams, autochthonous production can
608 significantly contribute to DOM fluxes (Kaplan and Bott 1982). However, in our system where the

609 riparian canopy is closed and little light is transmitted to the stream, we broadly estimate that these
610 fluxes would only have been significant on the last sampling date (on May 27th) where they could
611 have represented <25% of the DOM exported daily (Morel 2009).

612 In summary, this paper addressed the effects of agriculture on both groundwater and stream
613 water DOM over one water year in a headwater watershed. The PARAFAC analysis of fluorescence
614 EEM data applied in this study allowed a detailed mechanistic understanding of sources and
615 transport mechanisms within an agricultural watershed. Hot moments of manure-derived protein-
616 like compounds transport to the stream water were evidenced during storm events following the
617 initial application of swine slurry on upland croplands. The seasonal rise in upland groundwater
618 drives longer period of alteration of the stream water DOM towards a more microbially processed
619 composition typical of upland croplands amended with swine slurry. These dynamics observed at
620 watershed scale were confirmed by the one observed among DOM pools. Low aromatic protein-like
621 compounds are preferentially leached from waterlogged soils that are hydrologically connected to
622 the stream.

623 Since microbially processed DOM has been shown to support high rates of in-stream
624 microbial activity (Williams and others 2010), several environmental issues related to the DOM
625 derived from cultivated and amended soils can be expected (e.g. depressed O₂ levels below those
626 required for aquatic life; increased production potential of greenhouse gas). Given these risks, two
627 management options that have to be tested further can be proposed. (i) The buffer strips
628 enlargement to include all the waterlogged topsoils that can be seasonally connected to the stream
629 network through groundwater fluctuations. (ii) The determination of appropriate periods of animal
630 manure applications based on groundwater fluctuations and the watershed soil moisture rather than
631 calendar (fixed) periods.

632 **Acknowledgments**

633 This work was supported by the French National Research Agency [Project MOSAIC ANR-12-AGRO-
634 0005]; the French Ministry of Scientific Research; the University of Rennes 1; and the French national

635 institute for agricultural research. Long-term monitoring in the Kervidy-Naizin watershed was
636 supported by 'ORE AgrHys' (http://www6.inra.fr/ore_agrhys_eng/). We thank all those who helped
637 with the field and lab work: Armelle Racapé, Gilles Dutin, Yannick Hamon, Nicolas Gilliet and Valentin
638 Lemée.

639

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