Agricultural Practices and Hydrologic Conditions Shape the Temporal Pattern of Soil and Stream Water Dissolved Organic Matter

Guillaume Humbert, Thomas Parr, Laurent Jeanneau, Rémi Dupas, Patrice Petitjean, Nouraya Akkal-Corfini, Valérie Viaud, Anne-Catherine Pierson-Wickmann, Marie Denis, Shreeram Inamdar, et al.

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

Short title:

Spatiotemporal controls of soil and stream water DOM

Authors:

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

* **Corresponding author** (Present address)

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

g.humbert86@gmail.com

Affiliations

[a] AGROCAMPUS OUEST, INRA, SAS, F-35000 Rennes, France

[b] University of Delaware, Department of Plant and Soil Science, Newark, DE, 19716, United States

[c] Univ Rennes, CNRS, Géosciences Rennes, F-35000 Rennes, France

Author contributions

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

Abstract

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

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

Highlights

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

Introduction

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

Agricultural land use and management affect the quantity and composition of soil and stream water DOM. These influences can be conceptualized as the combined effects of short- and long-term positive and negative feedbacks (Chantigny 2003). Liming, animal manure, and fertilizer application are examples of practices with short-term effects on DOM quantity and quality. Shifts in vegetative cover type and quantity of plant litter returned to the soil are examples of practices driving long-term effects. In soils, forested and arable lands typically differ in DOM quantity and composition. The net effect of this is that forest soils typically contain a larger proportion of high molecular weight DOM that is less microbially decomposed, whereas cropland or pasture commonly contain a greater proportion of low molecular weight DOM that is more highly decomposed or microbially derived (Chantigny 2003). However, the degree of difference between 'natural' and agricultural land covers depends on landscape context, spatial scale, and temporal scale (Stanley and others 2012). Therefore, understanding the differences in DOM composition between arable soils and non-cultivated soils, such as in tree or grass buffers may provide a useful tool in assessing degree of impact agriculture has on surface water and the effectiveness of best management practices in reducing that impact.

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

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

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

To address the critical knowledge gap regarding the effect that land management has on aquatic DOM, we investigated how different watershed sources, cultivated soils receiving manure applications and non-cultivated riparian grassland and forest, contribute to stream water DOM. We hypothesized that seasonal interactions between hydrology and agricultural practices would impact the composition of DOM in stream water and groundwater. We tested this hypothesis by characterizing DOM quantity and composition in the stream and its primary DOM sources of an intensively farmed watershed (i.e. groundwater in the riparian grasslands, riparian woodlands and upland croplands; livestock-impacted runoff) during different hydrologic conditions (i.e. seasonal and storm) over the course of a year. Our specific objectives were (i) to differentiate stream water DOM sources using their fluorescent dissolved organic matter (FDOM) composition; (ii) to describe the dynamics in DOM composition of groundwater over the year; and (iii) to assess the contribution of various sources to stream DOM across seasonal and event-driven hydrologic conditions. By providing a mechanistic understanding of source contributions to the stream DOM quantity and composition, this study furthers efforts to assess the impact that agricultural practices may have on the environment.

Materials and methods

Study watershed

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

Ninety percent of the total watershed area is used for agriculture (Figure 1b, Table S1). These areas are fertilized in the spring with both organic (predominantly swine slurry) and mineral fertilizers. The cropping systems used in this watershed and the area allocated to each crop type have changed little over the past 20 years (Viaud and others 2018). See detailed land use and management summary in Text S1 and Table S1. Soils are silty loams, classified as Luvisols (IUSS Working Group and others 2006), well-drained in the upland domain and waterlogged in valley bottoms (Figure 1a). Approximately 20% of the watershed topsoil (< 0.4 m depth), mostly around the stream network, is seasonally waterlogged and can be hydrologically connected to the stream (Figure 1a). On average, these seasonally waterlogged soils are covered by cropland (55%), permanent grassland (29%, i.e. permanent grassland and fallow lands), and woodland (7%). While tile drains were installed > 40 years ago, they have not been maintained. Therefore, it is unlikely that significant quantities of runoff from upland croplands bypasses riparian areas via tile drains.

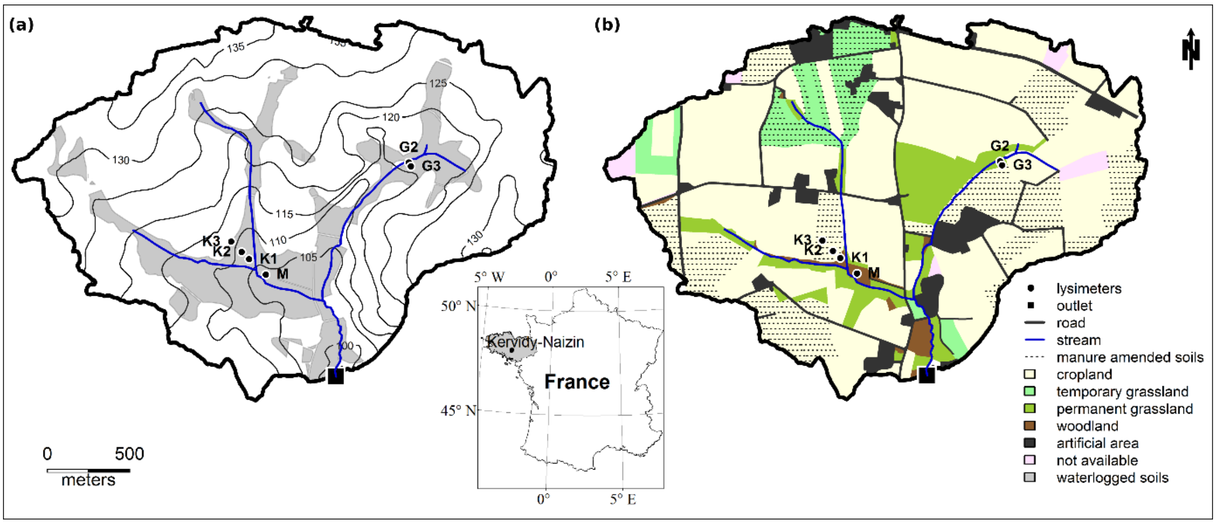

Figure 1. Location and maps of the study-site. **(a)** Elevation map of the KN watershed and periodically waterlogged soils with redoximorphic features above 0.4 m deep (grey area). **(b)** Land use map and location of parcels amended with swine slurry before or during the water year 2013-2014. Artificial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

Identification of DOM sources

Previous studies established that stream water DOM in the KN watershed was primarily allochthonous and derived from the upper layers of riparian wetland and hillslope soils (Texts S2 and S3; Morel and others 2009; Lambert and others 2013). Accordingly, groundwater (or soil pore water) was sampled in six sites from soil horizons at depths ranging from 0.1 to 1 m (two to four horizons per site). The six sites were selected in the seasonally waterlogged zone representing three different land covers at different distances from the stream (i.e. riparian grassland and riparian woodland closer to the stream, and upland cropland further from the stream) (Figure 1 and Table 1). Management at the cropland sites was consistent with the other cropping systems in place in the KN watershed (Tables 1 and S1); with maize-cereals-vegetables rotation covering 35% of the total watershed area and 47% of the seasonally waterlogged area. In addition to groundwater DOM sources, livestock-impacted DOM can be transported to the stream through the surface and subsurface runoff from farmyards, manure amended soils, and septic tanks (Baker 2002; Old and others 2012). Swine-slurry-impacted runoff previously characterized by Jaffrezic and others (2011) was used as the end member for DOM from this source in this study (Text S4).

Table 1. Selected characteristics of sampling sites.

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

Hydrological monitoring and water sampling

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

A variable sampling frequency approach was used to capture the effects of land management on stream water and groundwater DOM over time, and seasonal and pulsed change in water flow paths (Figure 2b). Stream water and groundwater were sampled during regularly scheduled 'baseflow' sampling campaigns for DOC concentration and DOM composition every 7 or 14 days from October 2013 to May 2014 (20 sampling campaigns total). The effects of land management (i.e. land cover and practices) on stream water and groundwater DOM over time were investigated with these samples collected whatever the discharge and groundwater levels. Although baseflow sampling occasionally occurred on rising or falling limbs of the hydrograph, the composition and dynamics reported here indicate that scheduled sampling predominantly reflects baseflow DOM composition. Hereafter we refer to these as baseflow samples. Sampling frequency decreased to every 14 days after the transition from the rewetting to the wetting period (i.e. from January 2014) due to less temporal variation in hydrology and DOM composition. Drying prevented stream water sampling prior to October 28, 2013, and groundwater sampling from June through October 2014. In addition, stream water was sampled manually on a daily basis at the watershed outlet for dissolved organic carbon concentration ([DOC]). This allowed us to assess the validity of weekly sampling for capturing the stream DOM dynamics (Figure 2b). Finally, the changes in stream water DOM with management practices over pulsed changes in water flow paths were investigated for seven storm events spanning 3 hydrologic seasons (1 rewetting season, 4 wetting season, 2 drying season) and maximum discharges ranging from 49-794 $l\ s^{-1}$. We collected samples for DOM quantity and composition at 30-minute intervals using a refrigerated (4°C) ISCO sampler.

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

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

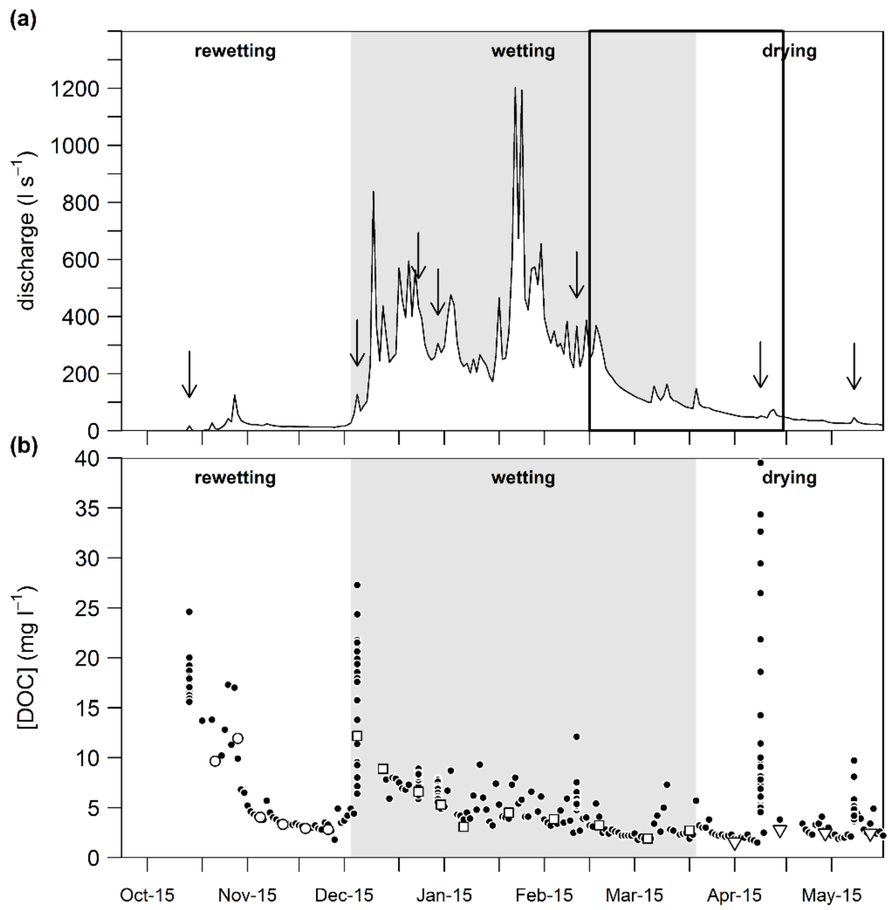

Figure 2. Hydrochemical monitoring from October 2013 to May 2014. **(a)** Mean daily discharge. The rectangle with solid thick lines indicates the time period when more than 70% of organic amendment applications occurred. Arrows indicate the sampled events. **(b)** Stream water dissolved organic carbon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

DOM characterization

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

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

Data handling and statistical analysis

Parallel factor analysis (PARAFAC) was used to identify statistically independent classes of fluorescent molecules (Stedmon and Rasmus 2008). The analysis was performed from 715 groundwater and stream water sampled during the study period. Prior to conducting PARAFAC, a DI blank was subtracted from all EEMS and their fluorescence intensities were normalized by the area under the Raman peak at ex. 350 nm. The PARAFAC modeling was performed in Matlab R2008b using the drEEM v.0.2.0 toolbox as described by Murphy and others (2013). Due to noise at low ex. and high em. wavelengths, we only modeled the EEM region within ex. 250-420 nm and em. 250-524 nm. To save computation time, we modeled em. at 2 nm intervals. The final model was validated by split-half validation. The EEMs previously obtained from DOM in swine-slurry-impacted runoffs were not used in modeling, rather they were fit to our validated model to estimate the PARAFAC scores of livestock-impacted DOM sources (R^2 ranging from 0.85 to 0.95, n= 6; Jaffrezic and others 2011). For each component, we report PARAFAC results as absolute scores (F_{max} values; Raman Units (RU)) as well as percent abundance (%; individual component score divided by the sum of absolute scores for all identified components in a sample x 100). We compared the PARAFAC components modeled from our data set to previous studies, using a modified Tucker's Congruence Coefficient (mTCC), with values ≥ 0.95 indicative of a close match (Parr and others 2014).

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

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

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

Results

Spatial variations in quantity and composition of groundwater DOM

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

The quantity and composition of DOM varied with land cover. Groundwater [DOC] varied significantly ($p < 0.05$) among riparian grassland (22.4 ± 13.7 mg l^{-1}; mean ± standard deviation) > riparian woodland (17.2 ± 9.9 mg l^{-1}) > upland cropland (6.4 ± 5.6 mg l^{-1}) (Figure S3a). The relative abundance of microbially processed and protein-like DOM in groundwater decreased in the order upland cropland > riparian grassland > riparian woodland ($p < 0.05$); with averaged FI (1.66 > 1.46 > 1.43), β:α ratio (0.57 > 0.47 > 0.43), %KN4 (20 > 14 > 12) and %KN5 (4 > 3 > 2) (Figures S3d-e, and S3i-j). Conversely, mean %KN2 increased ($p < 0.05$) among the three different land covers with cropland (22) < grassland (28) < woodland (30) (Figure S3g). The DOM composition was more aromatic in riparian grassland and woodland than in upland cropland; with higher average values ($p < 0.05$) for $SUVA_{254}$ (3.64-3.77 > 2.86; Figure S3b), HIX (0.97 > 0.95; Figure S3c) and for %KN3 (19-20 > 16; Figure S3h). The %KN1 was higher in average in the upland cropland than in the riparian lands (39 > 36; Figure S3f).

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

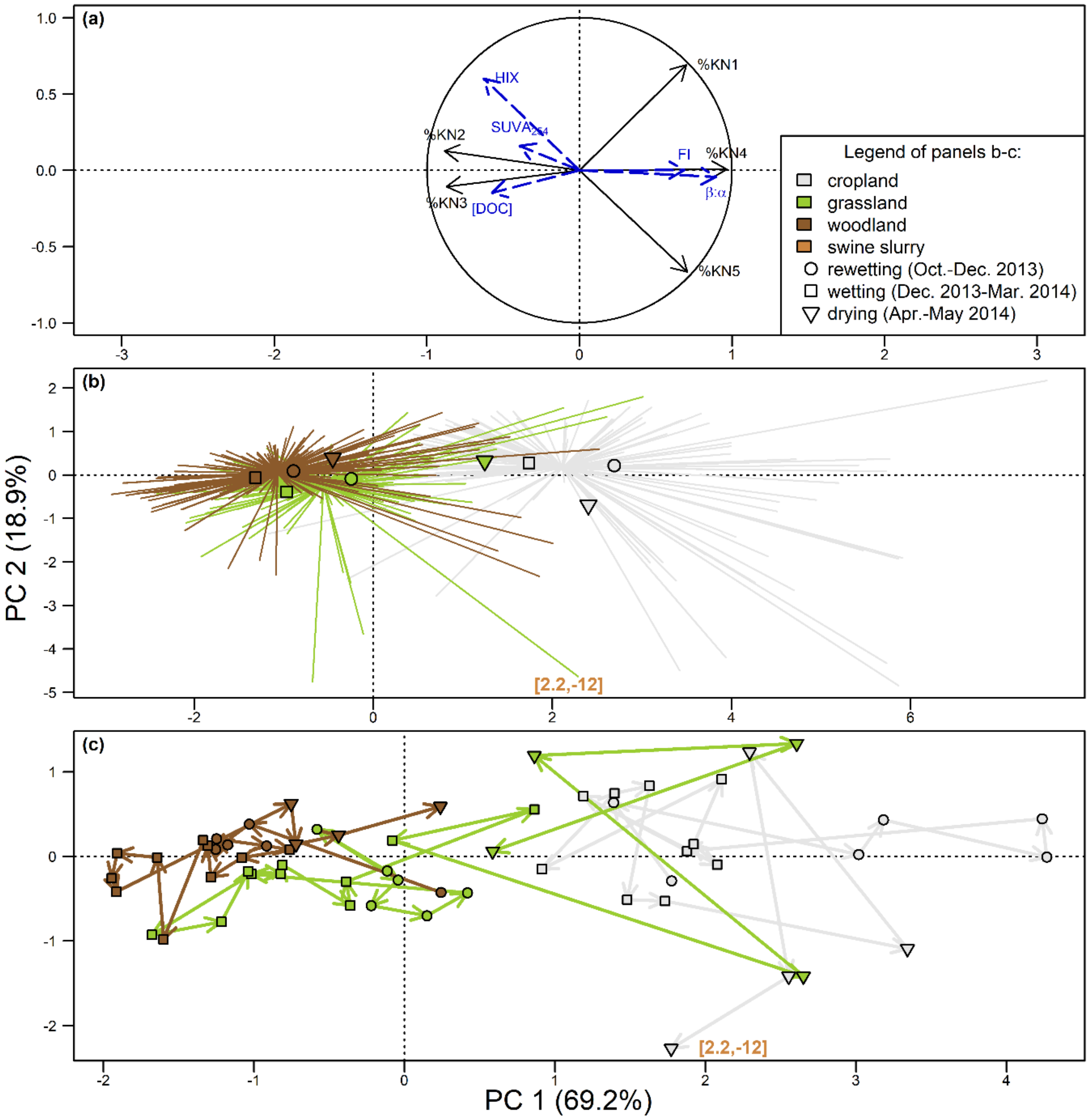

Figure 3. Principal component analysis (PCA) of groundwater fluorescent dissolved organic matter (FDOM) composition. The first two axes explain 88% of the variance in percent abundance PARAFAC components for the soil solutions of different land covers. **(a)** Loading plot showing the contribution of percent abundance of PARAFAC components to the computing of the first two principal components (PC). Blue dashed arrows indicate supplementary variables ([DOC], $SUVA_{254}$, FI, HIX, β:α) not used in the calculation of the PARAFAC component PCA, but do facilitate its interpretation. **(b)** Scores plot showing annual and seasonal centroids aggregated by land cover. Annual centroids were built from 126, 119 and 187 samples for cropland, grassland, and woodland, respectively. Centroids of rewetting, wetting and drying periods were built from 34-70, 73-98 and 11-19 samples, respectively. **(c)** Close-up view of scores plot showing temporal dynamics of centroids aggregated by land cover. Centroids were built from 2-12, 1-12 and 4-15 samples for cropland, grassland, and woodland, respectively. The FDOM composition determined for the swine-slurry-impacted runoff is presented as supplementary individual in figures b and c. Its location on the score plot is indicated with brackets [PC1, PC2].

Temporal variation in quantity and composition of groundwater DOM

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

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

Median groundwater [DOC] decreased during the wetting period (i.e. from December to 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 grassland, and from 16.4 to 10.8 mg l^{-1} in riparian woodland. The decrease in %KN5 and increase in %KN3 were the common dynamics observed for groundwater DOM composition of all land covers (Figures 3c, S7, and S9). Contrasted dynamics were observed among the land covers for others fluorescence components; with low decrease in median %KN2, and low increase in median %KN4 of both upland cropland and riparian grassland groundwater, while these components remained rather stable in riparian woodland groundwater (Figures 3c, S6, and S8).

Increasing median groundwater [DOC] was monitored in all land covers from March to May 2014 (Figure S4). This trend was rather progressive in riparian grassland and woodland, while occurring mainly during the transition from wetting to drying period in upland cropland (increasing from 2.8 to 6.4 mg l^{-1} on average). Concurrently, median %KN5 more than doubled for groundwater DOM composition of all land covers (Figures 3c, S7, and S9). The protein-like signature of livestock-impacted DOM sources was detected in cropland groundwater throughout the drying period, with the May samples, collected after manure was applied to the fields having at least a 60% higher abundance of protein-like compounds compared to pre manure application April samples. A similar signature was detected in the DOM groundwater of riparian grassland, but only on April 15 (first green triangle in Figure 3c), though its composition was more microbially processed than the other samples between February and May.

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

Temporal variation in quantity and composition of stream water DOM

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

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

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

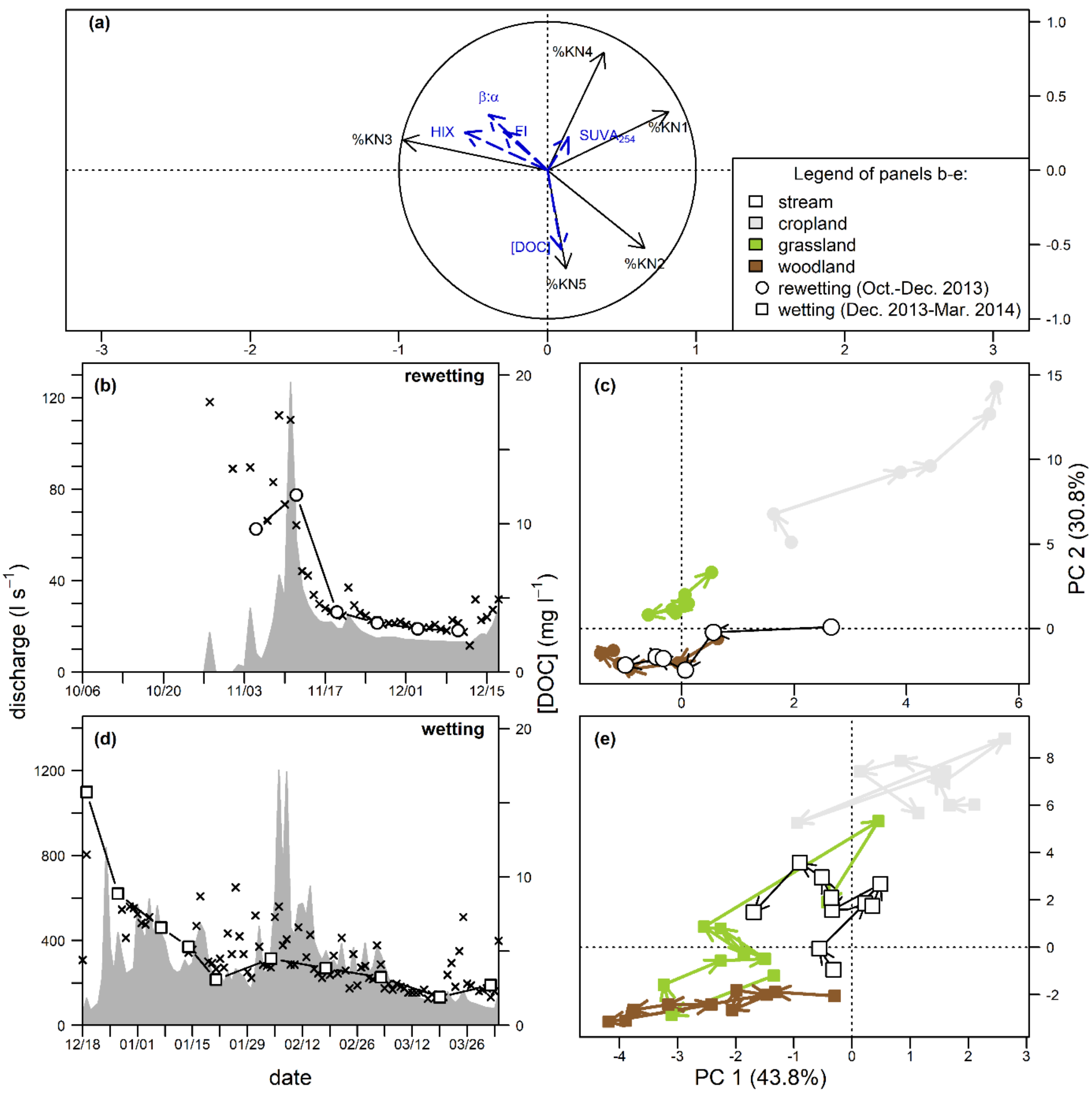

Figure 4. Baseflow dynamics of fluorescent dissolved organic matter (FDOM) composition in stream water during the rewetting and wetting periods. **(a)** In the PCA plots, the first two principal components (PC) explain 75% of the variance in percent abundance of PARAFAC components for the stream water samples of rewetting and wetting periods (baseflow and stormflow samples). Loading plot showing the contribution of percent abundance of PARAFAC components to the computing of the first two PCs. Blue dashed arrows indicate supplementary variables ([DOC], $SUVA_{254}$, FI, HIX, β:α) not used in the calculation of the PARAFAC component PCA, but do facilitate its interpretation. **(b and d)** Mean daily discharge (grey area) and [DOC] for the daily samples (black cross) and the samples collected manually weekly or fortnightly (white symbols) over the rewetting and wetting periods. Note the changes in axis scales for discharge. **(c and e)** Score plots showing the temporal dynamics of the stream water FDOM composition over the rewetting and wetting periods. The temporal dynamics of centroids aggregated by land cover as depicted in Fig. 3c are presented. Centroids were built from 2-

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

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

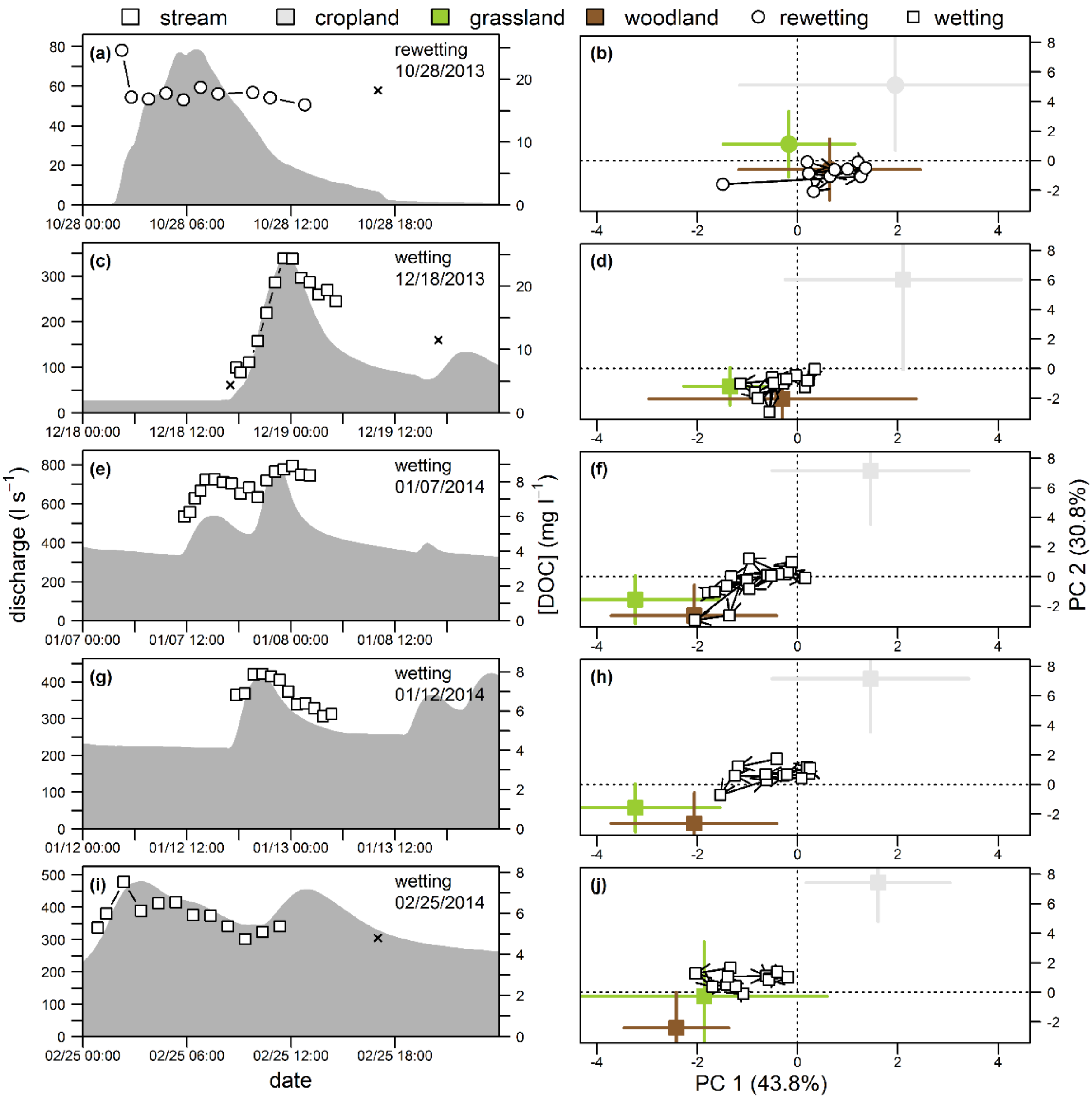

Figure 5. Storm flow dynamics of fluorescent dissolved organic matter (FDOM) composition in stream water during rewetting and wetting periods. **(a, c, e, g, i)** Discharge (grey area) and [DOC] for storm events (white symbols) and daily samples (black cross). Note the changes in axis scales for discharge and concentration. **(b, d, f, h, j)** Score plots showing the change in stream water FDOM composition during storm events. Mean and standard deviation of FDOM composition aggregated by land cover type are presented for soil solutions sampled before or after (rewetting, figure b) the storm event. Note that each white symbol resulted from the DOC concentration or the FDOM composition of a unique sample collected at the watershed outlet.

Livestock-impacted DOM sources affected stream water DOM only during drying period storm events occurring shortly after the swine slurry was applied to the soils. The PCA presented in Figure 6 was conducted with the % abundance of fluorophores obtained from both baseflow and stormflow of the drying period. The first and second PC axes (PC1, PC2) distinguish stream DOM sources. The PC1 represented a gradient of DOM derived from livestock-impacted source to DOM derived primarily from riparian woodland groundwater. The PC2 represented a gradient of increasing contributions from groundwater underlying cultivated uplands (Figure 6a). Although increasing in %KN5 as compared to DOM composition of wetting period baseflow (Figure S10), little variation was observed over the course of the drying period baseflow, the stream DOM composition reflected a mixture of riparian grassland and woodland sources. However, livestock-impacted DOM clearly altered the amount and composition of stream water DOM during the two storm events.

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

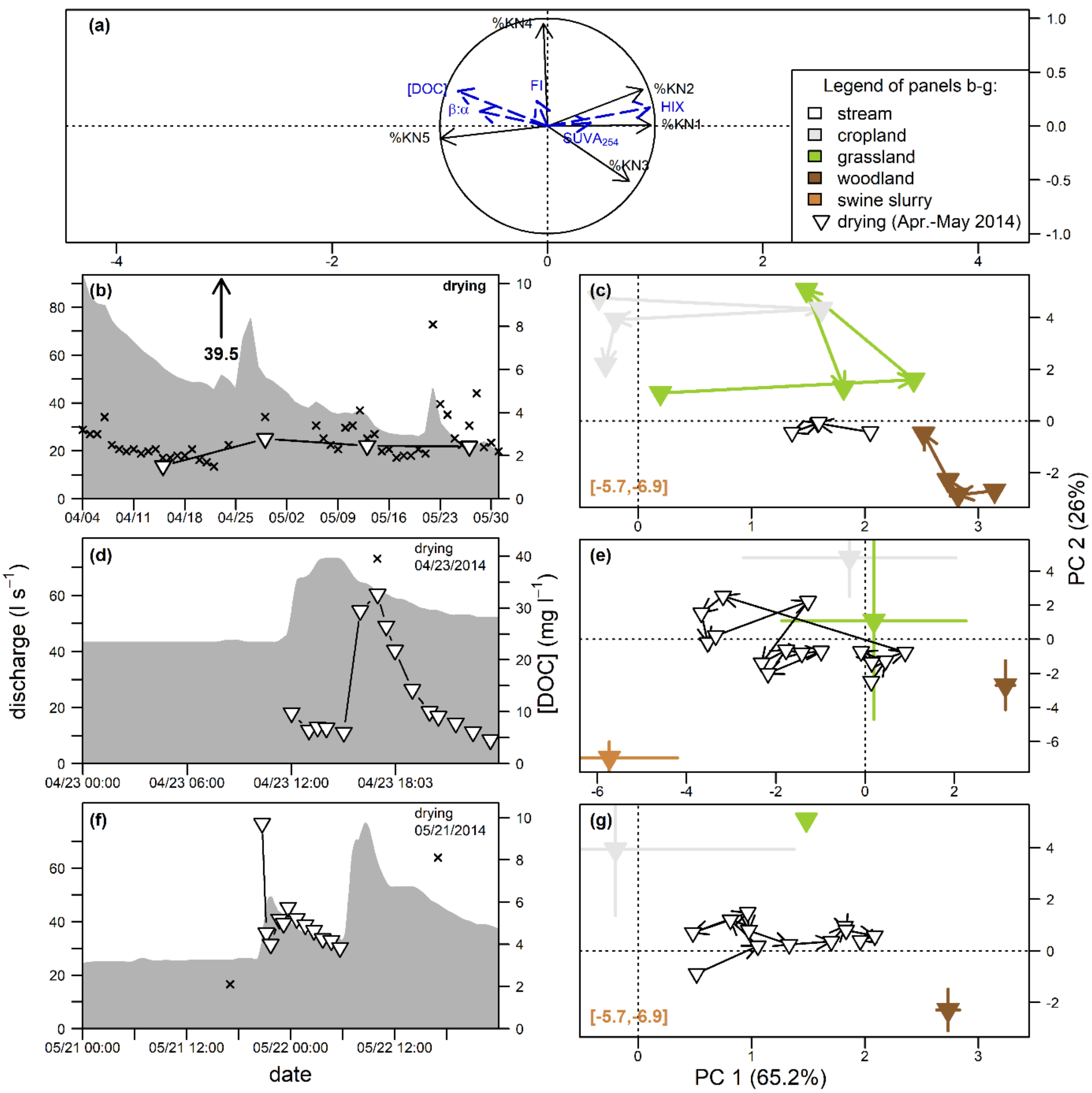

Figure 6. Principal component analysis (PCA) of fluorescent dissolved organic matter (FDOM) composition in stream water of drying period. The first two axes explain 79% of the variance in percent abundance of PARAFAC components for the stream samples (baseflow and storm event samples). **(a)** Loading plot showing the contribution of percent abundance of PARAFAC components to the computing of the first two PCs. Blue dashed arrows indicate supplementary variables ([DOC], $SUVA_{254}$, FI, HIX, β:α) not used in the calculation of the PARAFAC component PCA, but do facilitate its interpretation. **(b, d, and f)** Discharge (averaged daily in b; grey area) and [DOC] for baseflow stream water and storm events (white symbols) and daily samples (black cross). Note the changes in axis scales for discharge and concentration. **(c)** Score plots showing the temporal dynamics of the stream water FDOM composition during the drying period. **(e and g)** Score plots showing the change in stream FDOM composition during storm events of the drying period. Axis scales differed to better map the temporal dynamics during the events. The FDOM composition aggregated by land cover type is presented for soil solutions

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 samples for cropland, grassland, and woodland, respectively. Similarly, the FDOM composition determined for the swine-slurry-impacted runoff is presented as supplementary individual in figures c, e, and g. Its location on the score plot can be indicated with brackets [PC1, PC2]. Note that each white symbol resulted from the DOC concentration or the FDOM composition of a unique sample collected at the watershed outlet.

Discussion

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

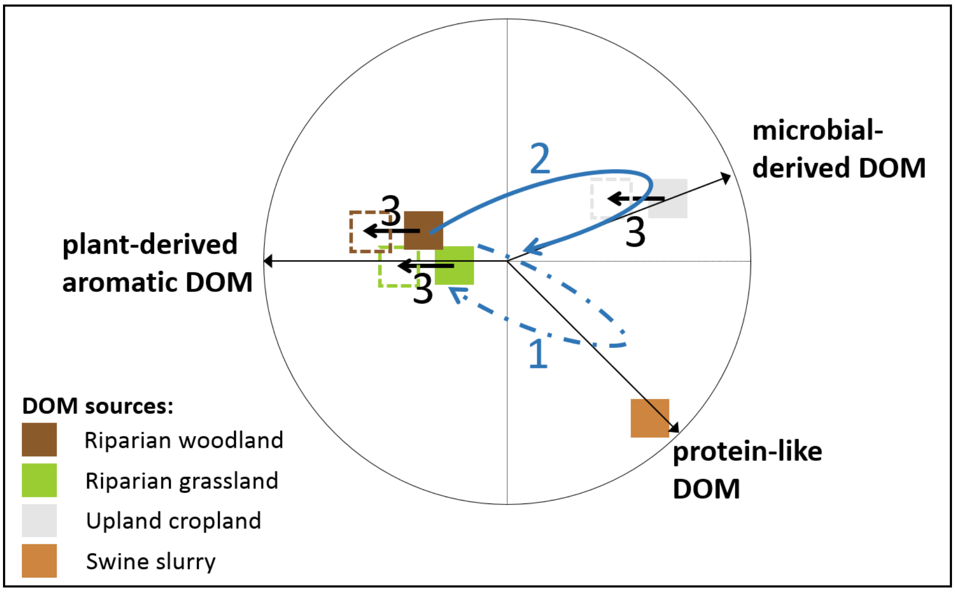

Figure 7. Sketch diagram summarizing the temporal dynamics of DOM composition in stream water and groundwater under the combined impacts of land use, management, and hydrology. It summarizes the results of the principal component analysis conducted in this study. The numbers '1' to '3' refer to the changes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

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

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

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

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

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

Management practices controlling vegetative biomass and the organic amendments directly influence both DOM quantity and composition. Biomass removal during crop harvest combined with herbicide suppression of weed growth decreases the C inputs to soil and subsequently may decrease the C_{org} content of soil and concentration of DOC in groundwater under cropland (Chantigny 2003). The lower C_{org} content observed in cultivated upland compared to riparian grassland and woodland in this study were consistent with these mechanisms (Table S2). In addition to this, Ohno and Bro (2006) reported between- and within-groups variations in the fluorescence signatures of DOM extracted from plants (crops and wetland plants), manures and tree leaves, with the highest variations observed within the manures group. Persistent effects of these materials on groundwater DOM can be hypothesized through repetitive throughfall and/or biomass incorporation in soils combined with adsorption processes to soil particles (Kalbitz and others 2000). An additional indirect mechanism that would involve interactions between the initial quality of the inputs and the decomposer community can also be inferred (Wickings and others 2012). The significance of differences in composition of groundwater DOM observed here between riparian grassland and woodland, where no management practice occurs seems consistent with these hypotheses.

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

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

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

Preferential leaching loss of protein-like DOM from waterlogged soils

Due to its richness in microbially processed compounds with low aromaticity, the cropland DOM pool would be more readily depleted than other watershed DOM pools. Protein-like, microbially-processed DOM was preferentially and progressively leached from waterlogged soils during the rewetting and wetting periods. Continuous waterlogging of all sampled soil profiles in the riparian woodland during the rewetting period and in all land covers during the wetting period altered the DOM that remained in groundwater towards a more aromatic and less protein-like composition (process 3 in Figure 7). In addition, [DOC] decreased in watershed groundwaters during these periods without increasing mineralization of soil organic matter (Figure S4). Buysse and others (2016) reported for KN watershed soils low CO_2 efflux during winter and related this low biological activity to decreasing temperatures and soil waterlogging. The combined lack of chemical moieties necessary to form strong interactions with mineral surfaces and greater water solubility of proteins could explain the preferential elution and transport of hydrophilic or low aromaticity compounds to surface waters (Chassé and others 2015). This preferential leaching and export of low molecular weight protein-like compounds from soils to surface waters is also consistent with the observed decrease in groundwater [DOC] and increase in groundwater DOM aromaticity.

The preferential leaching loss of protein-like DOM from waterlogged soils combined with a seasonal change in production rates of these compounds could explain the seasonal dynamics of stream water [DOC] observed in many headwater watersheds (Mehring and others 2013; Wilson and others 2013). During both the rewetting and wetting periods, the progressive change in DOM composition of watershed groundwater towards higher aromaticity suggests that the remaining DOM moieties are less readily transported from soils to the stream. During these periods, supply limitation of watersheds drives the stream water [DOC] and the pool of readily leachable DOM is not replenished. Consequently, the amount of DOM that can be transported to the stream diminishes and the stream water [DOC] decreases. Conversely during drying periods, transport limitation of watersheds drives the stream water [DOC]. The production rate of readily reachable DOM moieties (i.e. molecules with lower aromaticity) in watershed soils exceeds the rate of DOM export from these soils. In larger rivers and open canopied headwater streams, autochthonous production can significantly contribute to DOM fluxes (Kaplan and Bott 1982). However, in our system where the riparian canopy is closed and little light is transmitted to the stream, we broadly estimate that these fluxes would only have been significant on the last sampling date (on May 27th) where they could have represented <25% of the DOM exported daily (Morel 2009).

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

Since microbially processed DOM has been shown to support high rates of in-stream microbial activity (Williams and others 2010), several environmental issues related to the DOM derived from cultivated and amended soils can be expected (e.g. depressed O_2 levels below those required for aquatic life; increased production potential of greenhouse gas). Given these risks, two management options that have to be tested further can be proposed. (i) The buffer strips enlargement to include all the waterlogged topsoils that can be seasonally connected to the stream network through groundwater fluctuations. (ii) The determination of appropriate periods of animal manure applications based on groundwater fluctuations and the watershed soil moisture rather than calendar (fixed) periods.

Acknowledgments

This work was supported by the French National Research Agency [Project MOSAIC ANR-12-AGRO-0005]; the French Ministry of Scientific Research; the University of Rennes 1; and the French national institute for agricultural research. Long-term monitoring in the Kervidy-Naizin watershed was supported by 'ORE AgrHys' (http://www6.inra.fr/ore_agrhys_eng/). We thank all those who helped with the field and lab work: Armelle Racapé, Gilles Dutin, Yannick Hamon, Nicolas Gilliet and Valentin Lemée.

References

Anderson MJ. 2001. A new method for non-parametric multivariate analysis of variance. Austral Ecol 26:32–46. https://doi.org/10.1111/j.1442-9993.2001.01070.pp.x

Baker A. 2002. Fluorescence properties of some farm wastes: implications for water quality monitoring. Water Res 36:189–95. https://doi.org/10.1016/S0043-1354(01)00210-X

Balesdent J, Chenu C, Balabane M. 2000. Relationship of soil organic matter dynamics to physical protection and tillage. Soil Tillage Res 53:215–30. https://doi.org/10.1016/S0167-1987(99)00107-5

Bilal M, Jaffrezic A, Dudal Y, Le Guillou C, Menasseri S, Walter C. 2010. Discrimination of Farm Waste Contamination by Fluorescence Spectroscopy Coupled with Multivariate Analysis during a Biodegradation Study. J Agric Food Chem 58:3093–100. https://doi.org/10.1021/jf903872r

Buysse P, Flechard CR, Hamon Y, Viaud V. 2016. Impacts of water regime and land-use on soil CO2 efflux in a small temperate agricultural catchment. Biogeochemistry 130:267–88. https://doi.org/10.1007/s10533-016-0256-y

Chantigny MH. 2003. Dissolved and water-extractable organic matter in soils: A review on the influence of land use and management practices. Geoderma 113:357–80. https://doi.org/10.1016/S0016-7061(02)00370-1

Chassé AW, Ohno T, Higgins SR, Amirbahman A, Yildirim N, Parr TB. 2015. Chemical Force Spectroscopy Evidence Supporting the Layer-by-Layer Model of Organic Matter Binding to Iron (oxy)Hydroxide Mineral Surfaces. Environ Sci Technol 49:9733–41. https://doi.org/10.1021/acs.est.5b01877

Coble PG. 2007. Marine optical biogeochemistry: The chemistry of ocean color. Chem Rev 107:402–18.

Cory RM, McKnight DM. 2005. Fluorescence spectroscopy reveals ubiquitous presence of oxidized and reduced quinones in dissolved organic matter. Environ Sci {&} Technol 39:8142–9. https://doi.org/10.1021/es0506962

Cory RM, Miller MP, McKnight DM, Guerard JJ, Miller PL. 2010. Effect of instrument-specific response on the analysis of fulvic acid fluorescence spectra. Limnol Oceanogr Methods 8:67–78. https://doi.org/10.4319/lom.2010.8.67

Dalzell BJ, King JY, Mulla DJ, Finlay JC, Sands GR. 2011. Influence of subsurface drainage on quantity and quality of dissolved organic matter export from agricultural landscapes. J Geophys Res Biogeosciences 116:1–13. https://doi.org/10.1029/2010JG001540

European Environment Agency. 2017. Heavy precipitation assessment. Eur Environ Agency. 7fc060b1a7be41adba441f0e844ebeb3

Fasching C, Wilson HF, D'Amario SC, Xenopoulos MA. 2019. Natural Land Cover in Agricultural Catchments Alters Flood Effects on DOM Composition and Decreases Nutrient Levels in Streams. Ecosystems:1–16. http://link.springer.com/10.1007/s10021-019-00354-0

Fellman JB, Miller MP, Cory RM, D'Amore D V., White D. 2009. Characterizing dissolved organic matter using PARAFAC modeling of fluorescence spectroscopy: A comparison of two models. Environ Sci Technol 43:6228–34. https://doi.org/10.1021/es900143g

Foley JA, DeFries R, Asner GP, Barford C, Bonan G, Carpenter SR, Chapin FS, Coe MT, Daily GC, Gibbs HK, Helkowski JH, Holloway T, Howard EA, Kucharik CJ, Monfreda C, Patz JA, Prentice IC, Ramankutty N, Snyder PK. 2005. Global consequences of land use. Science (80-) 309:570–4. https://doi.org/10.1126/science.1111772

Fuß T, Behounek B, Ulseth AJ, Singer GA. 2017. Land use controls stream ecosystem metabolism by shifting dissolved organic matter and nutrient regimes. Freshw Biol. http://doi.wiley.com/10.1111/fwb.12887. Last accessed 16/01/2017

Graeber D, Boëchat IG, Encina-Montoya F, Esse C, Gelbrecht J, Goyenola G, Gücker B, Heinz M, Kronvang B, Meerhoff M, Nimptsch J, Pusch MT, Silva RCS, Von Schiller D, Zwirnmann E. 2015. Global effects of agriculture on fluvial dissolved organic matter. Sci Rep 5:16328. https://doi.org/10.1038/srep16328

Graeber D, Gelbrecht J, Pusch MT, Anlanger C, von Schiller D. 2012. Agriculture has changed the amount and composition of dissolved organic matter in Central European headwater streams. Sci Total Environ 438:435–46. https://doi.org/10.1016/j.scitotenv.2012.08.087

Han P, Zhang W, Wang G, Sun W, Huang Y. 2016. Changes in soil organic carbon in croplands subjected to fertilizer management: A global meta-analysis. Sci Rep 6:27199. https://doi.org/10.1038/srep27199

Haynes RJ, Naidu R. 1998. Influence of lime, fertilizer and manure applications on soil organic matter content and soil physical conditions: A review. Nutr Cycl Agroecosystems 51:123–37. https://doi.org/10.1023/A:1009738307837

Hothorn T, Hornik K, Wiel MA van de, Zeileis A. 2008. Implementing a Class of Permutation Tests: The coin Package. J Stat Softw 28:1–23. https://doi.org/10.18637/jss.v028.i08

Humbert G, Jaffrezic A, Fovet O, Gruau G, Durand P. 2015. Dry-season length and runoff control annual variability in stream DOC dynamics in a small, shallow groundwater-dominated agricultural watershed. Water Resour Res 51:7860–77. https://doi.org/10.1002/2015WR017336

Husson F, Josse J, Le S, Mazet J. 2013. FactoMineR: Multivariate Exploratory Data Analysis and Data Mining with R. http://cran.r-project.org/package=FactoMineR

IUSS Working Group WRB, others. 2006. World reference base for soil resources. World Soil Resour Rep 103.

Jaffrezic A, Jardé E, Pourcher A-M, Gourmelon M, Caprais M-P, Heddadj D, Cottinet P, Bilal M, Derrien M, Marti R, Mieszkin S. 2011. Microbial and Chemical Markers: Runoff Transfer in Animal Manure–Amended Soils. J Environ Qual 40:959. https://doi.org/10.2134/jeq2010.0355

Kaiser K, Kalbitz K. 2012. Cycling downwards - dissolved organic matter in soils. Soil Biol Biochem

52:29–32. https://doi.org/10.1016/j.soilbio.2012.04.002

Kalbitz K, Solinger S, Park JH, Michalzik B, Matzner E. 2000. Controls on the dynamics of dissolved organic matter in soils: A review. Soil Sci 165:277–304.

Kaplan LA, Bott TL. 1982. Diel fluctuations of DOC generated by algae in a piedmont stream1. Limnol Oceanogr 27:1091–100. http://doi.wiley.com/10.4319/lo.1982.27.6.1091

Lambert T, Pierson-Wickmann AC, Gruau G, Jaffrezic A, Petitjean P, Thibault JN, Jeanneau L. 2013. Hydrologically driven seasonal changes in the sources and production mechanisms of dissolved organic carbon in a small lowland catchment. Water Resour Res 49:5792–803. https://doi.org/10.1002/wrcr.20466

Lapierre JF, Frenette JJ. 2009. Effects of macrophytes and terrestrial inputs on fluorescent dissolved organic matter in a large river system. Aquat Sci 71:15–24. https://doi.org/10.1007/s00027-009-9133-2

Laudon H, Berggren M, Ågren A, Buffam I, Bishop K, Grabs T, Jansson M, Köhler S. 2011. Patterns and Dynamics of Dissolved Organic Carbon (DOC) in Boreal Streams: The Role of Processes, Connectivity, and Scaling. Ecosystems 14:880–93. https://doi.org/10.1007/s10021-011-9452-8

McGarry SF, Baker A. 2000. Organic acid fluorescence: Applications to speleothem palaeoenvironmental reconstruction. Quat Sci Rev 19:1087–101. https://doi.org/10.1016/S0277-3791(99)00087-6

Mehring AS, Lowrance RR, Helton AM, Pringle CM, Thompson A, Bosch DD, Vellidis G. 2013. Interannual drought length governs dissolved organic carbon dynamics in blackwater rivers of the western upper Suwannee River basin. J Geophys Res Biogeosciences 118:1636–45. https://doi.org/10.1002/2013JG002415

Morel B. 2009. Transport de Carbone Organique Dissous dans un bassin versant agricole à nappe superficielle.

Morel B, Durand P, Jaffrezic A, Gruau G, Molenat J. 2009. Sources of dissolved organic carbon during stormflow in a headwater agricultural catchment. Hydrol Process 23:2888–901.

https://doi.org/10.1002/hyp.7379

Murphy KR, Stedmon CA, Graeber D, Bro R. 2013. Fluorescence spectroscopy and multi-way techniques. PARAFAC. Anal Methods 5:6557–66. https://doi.org/10.1039/c3ay41160e

Naden PS, Old GH, Eliot-Laize C, Granger SJ, Hawkins JMB, Bol R, Haygarth P. 2010. Assessment of natural fluorescence as a tracer of diffuse agricultural pollution from slurry spreading on intensely-farmed grasslands. Water Res 44:1701–12. https://doi.org/10.1016/j.watres.2009.11.038

Ohno T. 2002. Fluorescence inner-filtering correction for determining the humification index of dissolved organic matter. Environ Sci Technol 36:742–6. https://doi.org/10.1021/es0155276

Ohno T, Bro R. 2006. Dissolved Organic Matter Characterization Using Multiway Spectral Decomposition of Fluorescence Landscapes. Soil Sci Soc Am J 70:2028. https://doi.org/10.2136/sssaj2006.0005

Ohno T, He Z, Tazisong IA, Senwo ZN. 2009. Influence of tillage, cropping, and nitrogen source on the chemical characteristics of humic acid, fulvic acid, and water-soluble soil organic matter fractions of a long-term cropping system study. Soil Sci 174:652–60. https://doi.org/10.1097/SS.0b013e3181c30808

Oksanen J, Kindt R, Legendre P. 2006. Vegan: community ecology package. https://cran.r-project.org/package=vegan

Old GH, Naden PS, Granger SJ, Bilotta GS, Brazier RE, Macleod CJA, Krueger T, Bol R, Hawkins JMB, Haygarth P, Freer J. 2012. A novel application of natural fluorescence to understand the sources and transport pathways of pollutants from livestock farming in small headwater catchments. Sci Total Environ 417–418:169–82. https://doi.org/10.1016/j.scitotenv.2011.12.013

Parr TB, Ohno T, Cronan CS, Simon KS. 2014. ComPARAFAC: A library and tools for rapid and quantitative comparison of dissolved organic matter components resolved by parallel factor analysis. Limnol Oceanogr Methods 12:114–25. https://doi.org/10.4319/lom.2014.12.114

Peacock AD, Mullen MD, Ringelberg DB, Tyler DD, Hedrick DB, Gale PM, White DC. 2001. Soil microbial community responses to dairy manure or ammonium nitrate applications. Soil Biol Biochem 33:1011–9. https://doi.org/10.1016/S0038-0717(01)00004-9

R Core Team. 2014. R: A language and environment for statistical computing.

Shang P, Lu YH, Du YX, Jaffé R, Findlay RH, Wynn A. 2018. Climatic and watershed controls of dissolved organic matter variation in streams across a gradient of agricultural land use. Sci Total Environ 612:1442–53. https://www.sciencedirect.com/science/article/pii/S0048969717323409

Singh S, Dutta S, Inamdar S. 2014. Land application of poultry manure and its influence on spectrofluorometric characteristics of dissolved organic matter. Agric Ecosyst Environ 193:25–36. https://doi.org/10.1016/j.agee.2014.04.019

Singh S, Inamdar S, Scott D. 2013. Comparison of Two PARAFAC Models of Dissolved Organic Matter Fluorescence for a Mid-Atlantic Forested Watershed in the USA. J Ecosyst 2013:1–16. https://doi.org/10.1155/2013/532424

Stanley EH, Powers SM, Lottig NR, Buffam I, Crawford JT. 2012. Contemporary changes in dissolved organic carbon (DOC) in human-dominated rivers: Is there a role for DOC management? Freshw Biol 57:26–42. https://doi.org/10.1111/j.1365-2427.2011.02613.x

Stedmon CA, Markager S. 2005. Resolving the variability in dissolved organic matter fluorescence in a temperate estuary and its catchment using PARAFAC analysis. Limnol Oceanogr 50:686–97. https://doi.org/10.4319/lo.2005.50.2.0686

Stedmon CA, Rasmus B. 2008. Characterizing dissolved organic matter fluorescence with parallel factor analysis: a tutorial. Limnol Oceanogr Methods 6:572–9. https://doi.org/10.4319/lom.2008.6.572b

Toosi ER, Castellano MJ, Singer JW, Mitchell DC. 2012. Differences in Soluble Organic Matter After 23 Years of Contrasting Soil Management. Soil Sci Soc Am J 76:628. https://doi.org/10.2136/sssaj2011.0280

Viaud V, Santillàn-Carvantes P, Akkal-Corfini N, Le Guillou C, Prévost-Bouré NC, Ranjard L, Menasseri-Aubry S. 2018. Landscape-scale analysis of cropping system effects on soil quality in a context of crop-livestock farming. Agric Ecosyst Environ 265:166–77. https://doi.org/10.1016/j.agee.2018.06.018

Wallace AJB, Eggert SL, Meyer JL, Webster JR. 2008. Multiple trophic levels of a forest stream linked to terrestrial litter inputs. Science (80-) 277:102–4. https://doi.org/10.1126/science.277.5322.102

Weishaar JL, Aiken GR, Bergamaschi BA, Fram MS, Fujii R, Mopper K. 2003. Evaluation of specific ultraviolet absorbance as an indicator of the chemical composition and reactivity of dissolved organic carbon. Environ Sci Technol 37:4702–8. https://doi.org/10.1021/es030360x

Wickings K, Grandy AS, Reed SC, Cleveland CC. 2012. The origin of litter chemical complexity during decomposition. Ecol Lett 15:1180–8. https://doi.org/10.1111/j.1461-0248.2012.01837.x

Williams CJ, Yamashita Y, Wilson HF, Jaffe R, Xenopoulos MA. 2010. Unraveling the role of land use and microbial activity in shaping dissolved organic matter characteristics in stream ecosystems. Limnol Oceanogr 55:1159–71. https://doi.org/10.4319/lo.2010.55.3.1159

Wilson HF, Saiers JE, Raymond PA, Sobczak W V. 2013. Hydrologic Drivers and Seasonality of Dissolved Organic Carbon Concentration, Nitrogen Content, Bioavailability, and Export in a Forested New England Stream. Ecosystems 16:604–16. https://doi.org/10.1007/s10021-013-9635-6

Wilson HF, Xenopoulos MA. 2009. Effects of agricultural land use on the composition of fluvial dissolved organic matter. Nat Geosci 2:37–41. https://doi.org/10.1038/ngeo391