

Land use and hydrologic flowpaths interact to affect dissolved organic matter and nitrate dynamics

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Abstract The transport and transformation of dissolved organic matter (DOM) and dissolved inorganic nitrogen (DIN) through the soil profile impact down-gradient ecosystems and are increasingly recognized as important factors affecting the balance between accumulation and mineralization of subsoil organic matter. Using zero tension and tension lysimeters at three soil depths (20, 40, 60 cm) in paired forest and maize/soybean land uses, we compared dissolved organic C (DOC), dissolved organic N (DON) and DIN concentrations as well as DOM properties including hydrophilic-C (HPI-C), UV absorption ($SUVA_{254}$), humification index and C/N ratio. Soil moisture data collected at lysimeter locations suggest zero tension lysimeters sampled relatively rapid hydrologic flowpaths that included downward saturated flow through the soil matrix and/or rapid macropore flow that is not in equilibrium with bulk soil solution whereas tension lysimeters sampled relatively immobile soil matrix solution during

unsaturated conditions. The effect of land use on DOC and DON concentrations was largely limited to the most shallow (20 cm) sampling depth where DOC concentrations were greater in the forest (only zero tension lysimeters) and DON concentrations were greater in the cropland (both lysimeter types). In contrast to DOC and DON *concentrations*, the effect of land use on DOM *properties* persisted to the deepest sampling depth (60 cm), suggesting that DOM in the cropland was more decomposed regardless of lysimeter type. DOC concentrations and DOM properties differed between lysimeter types only in the forest at 20 cm where soil solutions collected with zero tension lysimeters had greater DOC concentrations, greater $SUVA_{254}$, greater humification index and lower HPI-C. Our data highlight the importance of considering DOM quality in addition to DOC quantity, and indicate long-term cultivation reduced the delivery of relatively less decomposed DOM to all soil depths.

Keywords Dissolved organic C (DOC) · Dissolved organic N (DON) · Land-use · Soil depth · Subsoil · Cultivation

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Introduction

Dissolved organic matter (DOM) and dissolved inorganic nitrogen (DIN) are key components of many biogeochemical processes. At the soil pedon scale

DOM is a highly dynamic pool of OM that links the processes of soil organic matter (SOM) formation and decomposition (Sollins et al. 1996). At the ecosystem scale DOM represents a major flux of C and nutrients from terrestrial to aquatic systems (Raymond and Bauer 2001; Wilson and Xenopoulos 2009). Recent research has highlighted important links among DOM, ecosystem nutrient losses, and ecosystem C balances. Leaching of DOM can account for a significant proportion of N loss from forested and agricultural systems, contributing to the maintenance of ecosystem N limitation (Perakis and Hedin 2007; van Kessel et al. 2009). The C and N stoichiometry of DOM can affect DIN loss from soils to aquatic ecosystems by controlling microbial N demand and nitrate immobilization (Taylor and Townsend 2010). Moreover, there is significant uncertainty about the role of DOM in ecosystem C balances: DOM can contribute to subsoil organic matter storage or promote subsoil organic matter decomposition (Fontaine et al. 2007; Marin-Spiotta et al. 2011).

Despite these uncertainties, there are common patterns in DOM dynamics across ecosystems. With increasing soil depth, concentrations of dissolved organic C (DOC), dissolved organic nitrogen (DON), and DIN typically decrease and DOM becomes further decomposed (e.g. Qualls et al. 2002; Dittman et al. 2007; Sanderman et al. 2008). However, within a given environment, changes in ecosystem structure can affect these patterns. For example, vegetation and soil management directly affect DOM/DIN dynamics by controlling the quantity and biochemistry of net primary productivity (e.g. Chantigny 2003). Vegetation and soil management can also indirectly affect DOM/DIN dynamics by impacting soil hydrology (Castellano and Kaye 2009).

Hydrologic flowpaths and flow rates are well known to affect DOM/DIN transport and transformation from surface to subsoils. Hydrological flow rate can interact with the rates of microbial immobilization and chemical adsorption processes to affect the transfer of DOM/DIN to insoluble SOM (Kaiser and Guggenberger 2005; Maggi et al. 2008; Castellano et al. 2013). Cultivation can disrupt rapid preferential hydrologic flowpaths, thereby altering hydrologic flow rate (Jarvis 2007).

How changes in land use affect DOM components (C and N) and properties across soil depths, particularly with regard to different hydrologic flowpaths,

remains largely unknown. This knowledge gap hampers predictions of the growing influence of agricultural intensification on net soil C and N balances as well as the properties of DOM exported from agricultural watersheds. Indeed, a lack of data comparing DOM associated with fast versus slow hydrologic flowpaths has impeded the development of models that estimate the contribution of DOM to various biogeochemical processes across different soils (Neff and Asner 2001).

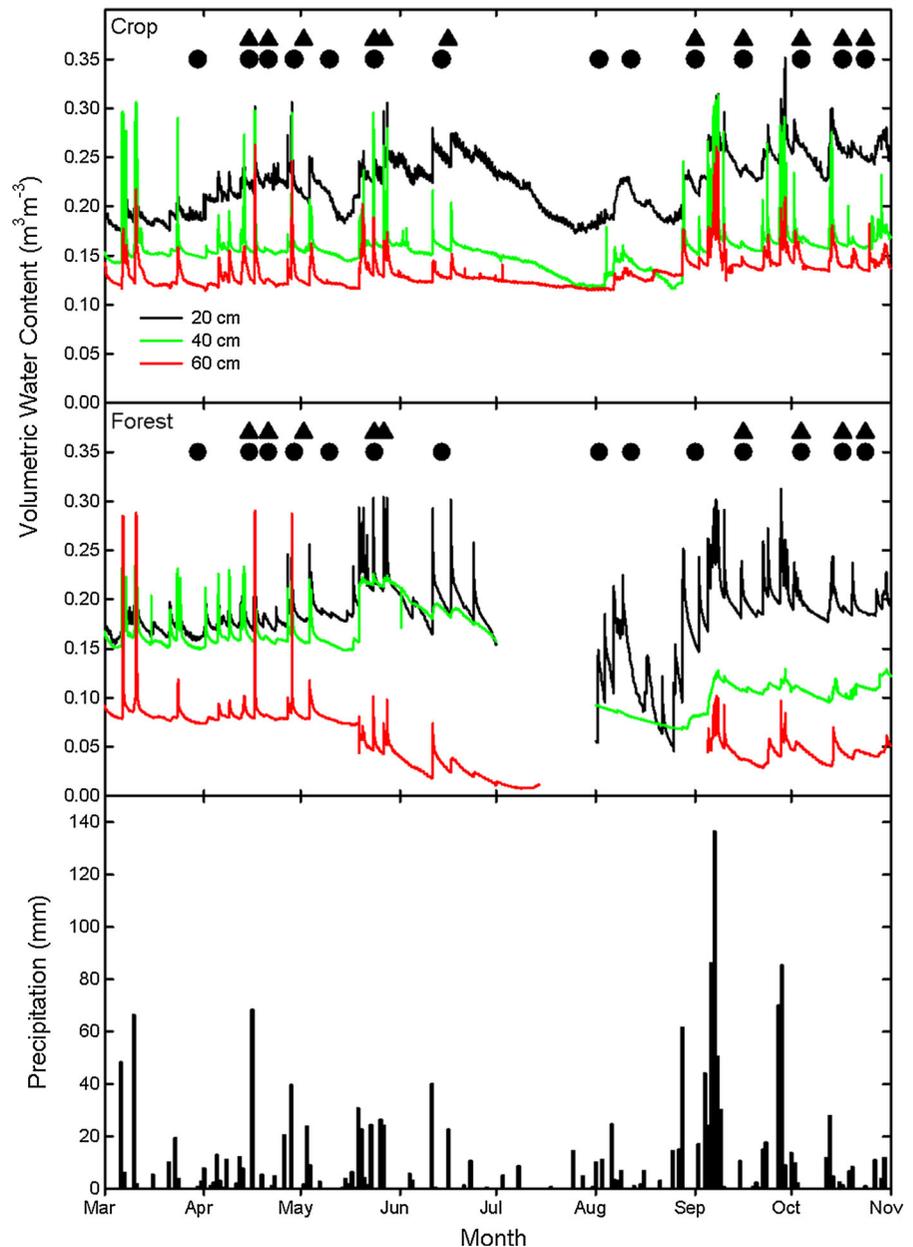
In Pennsylvania, USA, we installed replicated sets of soil moisture sensors, tension lysimeters, and zero-tension lysimeters at 20, 40 and 60 cm soil depths in paired forest and annual crop land uses. Data suggests tension and zero-tension lysimeters can be used to sample soil solution associated with relatively slow and fast hydrologic flow paths, respectively (Fares et al. 2009). Accordingly, we hypothesized that soil solution sampled with zero tension lysimeters would have less decomposed DOM with greater DOC, DON, and DIN concentrations than tension lysimeters (e.g. Kaiser and Guggenberger 2005; Castellano et al. 2013), but the differences between lysimeter types would be greater in forest soils due to a lack of soil disturbances (e.g., cultivation) that disrupt rapid macropore hydrologic flowpaths (Jarvis 2007). Further, we hypothesized that frequent disturbance (cultivation) and relatively high decomposition of DOM in the cropland leads to relatively limited vertical changes in DOC, DON, and DIN concentrations and DOM properties.

Materials and methods

Study site

The study was conducted within a long-term research watershed operated by the USDA Agricultural Research Service (Bryant et al. 2011). The watershed falls within the Ridge and Valley Physiographic Province of east-central Pennsylvania and has a humid temperate climate with mean annual precipitation of 1,060 mm (1968–2002). Mean monthly temperatures in the watershed range from -4°C in January to 21°C in July (Fig. 1). The watershed is underlain by deeply folded acidic shales and fine sandstones of the Trimmers Rock Formation and is overlain by soils of colluvial and residual origin.

Fig. 1 Soil volumetric water content at 20 min intervals and three depths in the cropland (*top panel*) and forest (*middle panel*). Symbols indicate tension lysimeter (*triangles*) and zero tension lysimeter (*circles*) sampling dates. Daily precipitation is displayed in the *lowest panel*



Within the larger watershed, we sampled an adjacent forest and cropland on a well-drained residual soil (loamy-skeletal, mixed, active, mesic Typic Dystrudept) that had slopes of $<1^\circ$. The forest was dominated by oak (*Quercus* spp.) and hickory (*Carya* spp.) and had not been harvested in at least 50 years. The cropland was maintained in a maize–maize–soybean rotation. The rotation was in maize in 2009 and 2010. We sampled in the soybean year in 2011. In maize years of the crop rotation, the soil was tilled

with a chisel plow every spring to depth of 25.4 cm. In the soybean year there was no tillage. Synthetic N fertilizer applications to maize were 34 kg N ha^{-1} applied as urea–ammonium–nitrate. This was supplemented with dairy cow manure N to achieve an approximate total N application of 146 kg N ha^{-1} to maize. All P fertilization was applied through manure. No nutrient inputs (manure or otherwise) were made in the soybean phase of the crop rotation. We sampled during the soybean phase to minimize large,

immediate effects of DOM additions through manure applications to corn phases of the rotation. Although N inputs to maize and soybean differ, total dissolved N leaching does not typically differ between maize and soybean phases of the maize–soybean crop rotation (Randall et al. 1997; Lawlor et al. 2008). Daily precipitation was measured from March 1 to October 31, 2011 with a manual rain gauge at a location that was ~3 km from the experiment.

Soil solution sampling and soil moisture measurement

In 2009, we established three replicate lysimeter nests each in the forest and cropland. Each nest was ~16 m² and contained three sub-replicate tension and three sub-replicate zero-tension lysimeters at 20, 40, and 60 depths. The 20 cm depth corresponded to bottom of the A soil horizon while the 40 and 60 cm depths were in the B horizon which extended to >80 cm. In total, 54 individual tension and 54 individual zero tension lysimeters were installed. After installation in November 2009, lysimeters were allowed a 17 month equilibration period during which they were sampled every 2–4 weeks. These samples were discarded. After soil thawing in March 2011, we began to collect samples for analysis.

Tension lysimeters (PrenartTM, Denmark) were fabricated from a porous (2 µm) quartz material. A –70 kPa vacuum was placed on the lysimeter for ~18 h during which a sample was collected. Vacuums on tension lysimeters were set after collection of zero tension lysimeter soil solution (see below) and solution was collected after 24 h. In the forest, tension lysimeters did not yield samples from May to September due to dry soil conditions. Zero tension lysimeters were fabricated from polyvinylchloride pipe (30.0 × 9.6 cm) that was cut in half lengthwise and inserted laterally into the soil profile at a ~15° angle. The downward end of the pipe was capped and fitted with a 5 × 1.9 cm pipe nipple that was packed with glass wool and drained through low-density polyethylene tubing to a 2.5 L opaque high-density polyethylene collection bottle. The collection bottles were stored at 1 m soil depth in plywood housing (~40 × 40 × 100 cm) that was covered with lid level with the soil surface. In contrast to tension lysimeters, zero tension lysimeters passively ‘catch’ water that is advectively transported into the collection

area. Soil moisture data presented herein suggest this advective transport of soil water was limited to periods of intense or extended rainfall. Samples were collected from zero tension lysimeters after rain events. Upon collection, all soil solutions were kept on ice in a cooler for <4 h. The samples were stored in the freezer (–4 °C) until start of analyses. Before analyses, the samples were thawed and filtered (0.45 µm Millipore) and analyzed for ammonium–N (NH₄–N), nitrate–N (NO₃–N), DOC and total N concentrations. The large number of lysimeters in this study (108) precluded the collection and filtration of samples on the same day. The delay in filtration could have promoted reactions between OM > 0.45 µm, DIN, and DOM. It is unclear how such reactions may have impacted our results. However, we expect the amount of OM > 0.45 µm was minimized by the glass wool filter in zero tension lysimeters and the 2 µm pore size of tension lysimeters.

With each nest of tension and zero tension lysimeters in the forests and cropland, we installed one Decagon EC-5 volumetric water content (VWC) sensor at each soil depth (N = 3 soil moisture sensors per land use per depth). Sensors were installed with lysimeters in 2009. The sensors determined VWC every 20 min by measuring the dielectric constant of the soil. Sensors were calibrated in re-packed soil columns in the laboratory. In the forest, 20 and 40 cm sensors failed during July and 60 cm sensors failed from July 1 to September 4. Our observations from work with these sensors in other experiments suggest drying soils led to a loss of contact between the sensor and soil.

Chemical and spectroscopic analyses

Carbon and N concentrations of DOM samples were measured after acidification with a TOC analyzer (Shimadzu TOC/TN-L_{CPN}, Tokyo, Japan) using the high temperature catalytic oxidation method. Inorganic N forms (NH₄⁺ + NO₃[–]) were determined on a microplate spectrophotometer with a detection limit of 0.1 mg N L^{–1} (Sime et al. 1995; Hood-Nowotny et al. 2010). DON was calculated as the difference between the concentrations of total and inorganic N.

In addition to dissolved C and N concentrations, we also analyzed DOM properties. These included the following measures: The DAX-8 resin fractionation procedure was used for DOM characterization by determining the proportion of hydrophilic DOM (Leenheer 1981). Briefly, 15 mL of aliquots of acidified

(pH <2) extracts were injected with a peristaltic pump into a DAX-8 packed glass column (200 × 10 mm) at rate of 180 mL h⁻¹. The initial 3 mL of leachate was decanted and the remainder of the leachate was re-circulated through the column. After each sample, the column was rinsed with 15 mL 0.05 M HCl (180 mL h⁻¹). The collected solutions were pooled and classified as the hydrophilic OM (HPI-OM) fraction. After each run, the columns were rinsed with successive cycles of two 30 mL solutions 0.1 M HCl and two 30 mL solutions of 0.1 M NaOH at 450 mL h⁻¹ (1st run) and 100 mL h⁻¹ (2nd run). Finally, the column was rinsed with 0.01 M HCl until the pH and UV₂₅₄ absorbance was stable. The C and N concentrations of the HPI-OM were determined as above.

We assessed the UV absorption of DOM samples, a property that has been shown to reflect the proportion of aromatic compounds (Weishaar et al. 2003). The UV absorption of the samples was measured with a Perkin Elmer 552 spectrophotometer at 254 nm using a 1-cm quartz cell. The specific UV absorption (SUVA₂₅₄) was calculated as:

$$SUVA_{254} = 100 * UV_{abs}/b * DOC \quad (1)$$

where SUVA is the specific ultraviolet absorption (l mg⁻¹-C m⁻¹); UV_{abs} is ultra-violet light absorption at 254 nm; *b* is the path length of the UV (cm); DOC = DOC concentration in the samples (mg-C L⁻¹).

We used the fluorescence emission property of DOM to determine the humification index (HI). The excitation–emission fluorescence spectra were recorded using an excitation wavelength of 254 nm and emission range of 300–470 nm at 5 nm slits with a Jobin–Yvon Horiba Fluoromax fluorimeter. The HI concept is based on the observation that the emission spectra of fluorescing molecules of more decomposed OM shift toward longer wavelengths as a result of a decrease in the H:C ratio of fluorescing compounds. Accordingly, the proportion of the fluorescence region at longer to shorter wavelengths can be used to quantify the relative degree of humification. The HI was calculated as (Ohno 2002):

$$HI = \left(\sum I_{435-480} \right) / \left(\sum I_{300-345} + \sum I_{435-480} \right) \quad (2)$$

where *I* is the fluorescence intensity at the given wavelengths. The HI varies from 0 to 1 and serves as a highly sensitive property to compare DOM samples

with a range of C concentrations and properties. Higher HI values suggest a larger proportion of humified compounds or further humified OM.

Statistical analyses

All statistical analyses were carried out using SAS 9.2. The effect of soil depth, land-use, and lysimeter type (between-subject variables) on DOM components and properties were analyzed by split plot analysis of variance (ANOVA) with repeated measures over time (within-subject factor). Land-use was considered as the main plot variable and lysimeter type and soil depth as split plot variables. The interactions between land-use and soil depth were further examined with post hoc contrast tests. Data in figures are mean ± standard error. To understand the mechanisms affecting soil solution NO₃⁻ concentrations, we used regression analyses to explore across-soil depth relationships between NO₃⁻ and DOC, DON, and DOM properties.

For each of the two continuous VWC sampling periods that were separated by a period of sensor failure (July), mean VWC was analyzed by split plot ANOVA. Land-use was considered as the main plot variable and soil depth as the split plot variable. Spatial and temporal variability in mean VWC was also analyzed using the coefficient of variation (CV). Spatial CVs were determined from the mean and standard deviation of coincident VWC measurements from each set of three replicate sensors within each land use at each depth (calculated every 20 min). Subsequently the individual CVs were averaged over time within depth and land use for the two continuous sampling periods (March–June and August–October). We note that spatial variation in mean VWC was calculated across the three replicate lysimeter nests, not within nests, thus precluding formal statistical analysis with ANOVA. Temporal CVs were calculated within each replicate lysimeter nest from the mean and standard deviation of each individual sensor during each of the two continuous sampling periods. Accordingly, temporal CVs were analyzed with the same ANOVA model as mean VWC data. The 60 cm soil depth was not included in analyses of the August–October sampling period due to sensor failure through 4 September.

Table 1 Soil properties

Soil depth (cm)	Sand (%)	Silt (%)	Clay (%)	SOC (g kg ⁻¹)	TN (g kg ⁻¹)	C/N	pH	EC (mS cm ⁻¹)
Forest								
0–20	36.7	45.3	18.0	91.9	4.8	19.1	4.7	0.8
20–40	36.3	49.3	14.3	10.8	0.7	15.5	4.8	0.4
40–60	43.3	45.3	11.3	2.6	0.3	10.5	4.7	0.2
Cropland								
0–20	39.0	49.3	11.7	20.2	1.6	12.8	6.6	0.4
20–40	40.9	42.7	16.4	6.8	0.6	10.9	6.3	0.2
40–60	45.5	41.3	13.1	3.3	0.3	10.2	5.7	0.2

SOC soil organic carbon, TN total nitrogen, CN carbon-to-nitrogen ratio, EC electrical conductivity

Results

Soil texture was similar among land uses. However, total soil organic C (SOC), total soil N and C/N ratios were higher in the forest than the cropland at 0–20 and 20–40 cm depths. The forest had lower pH at all soil depths and higher electrical conductivity at 0–20 cm (Table 1).

During the March–June period of VWC measurements (prior to period of VWC sensor failure), mean VWC decreased with soil depth ($P = 0.01$), but was not affected by land use or the interaction between land use and soil depth (Table 2; Fig. 1). During the same measurement period there were no effects of land use, soil depth or their interaction on the temporal CV of mean VWC. During the August–October VWC measurement period (after VWC sensor function was restored), mean VWC was greater in the cropland ($P < 0.01$) while the temporal CV of VWC was greater in the forest ($P < 0.01$) and increased with soil depth ($P < 0.01$). Within each depth, the spatial CV of VWC was consistently greater in the forest than cropland (Table 2). Similar to the March–June measurement period, mean VWC decreased with soil depth in both land uses ($P < 0.01$). At each soil depth, VWC measurements with individual sensors were dynamic over time and lacked sustained maxima over periods greater than 20 min (one VWC measurement; Fig. 1). Coupled with a regional groundwater depth of ~60 m (Bryant et al. 2011) and lysimeter locations on well-drained residual soils, these VWC data indicate that zero tension lysimeters sampled hydrologic flow traveling downward from the soil surface rather than upward from a rising water table.

Across lysimeter types and land uses, DOC concentration was greater in the forest than cropland ($P = 0.03$, Table 3). This was primarily due to higher DOC concentrations at 20 cm in the forest versus cropland (averaged 20.8 ± 1.1 vs. 9.6 ± 0.3 mg C L⁻¹ for zero-tension and 11.2 ± 1.2 vs. 9.3 ± 0.5 mg C L⁻¹ for tension lysimeters; Table 3; Fig. 4). For zero tension lysimeter samples mean DOC concentrations at 40 and 60 cm were also greater in the forest than cropland (10.5 ± 0.5 vs. 8.9 ± 0.4 mg C L⁻¹ for 40 cm and 9.7 ± 0.4 vs. 8.3 ± 0.5 mg C L⁻¹ for 60 cm). However, for tension lysimeters, DOC concentrations were only higher in the forest at 20 cm while mean DOC concentrations were similar between land-uses at 40 cm (9.9 ± 1.2 vs. 8.8 ± 0.3 mg C L⁻¹) and 60 cm (6.4 ± 0.4 vs. 6.8 ± 0.2 mg-C L⁻¹; Table 3; Fig. 4).

Across lysimeter types, the proportion of hydrophilic DOC (HPI-C) varied significantly with time in both land-uses but there was no clear temporal pattern across land uses, depths and lysimeter ($P < 0.01$; Table 3; Figs. 2, 3). The proportion of HPI-C was greater in the cropland than forest ($P = 0.03$; Table 2) due to greater proportions of HPI-C in zero-tension lysimeters (Table 3; Fig. 4). The proportion of HPI-C in zero-tension lysimeters at 20 cm in the cropland was greater than the forest (24.7 ± 0.5 vs. 16.4 ± 0.5 %), but the difference between the land-uses decreased with depth (25.4 ± 0.6 vs. 22.1 ± 0.6 % at 40 cm and 26.3 ± 0.7 vs. 23.6 ± 0.7 % at 60 cm).

Consistent with a lower proportion of HPI-C in the cropland, mean SUVA and HI values for DOM sampled with zero tension lysimeters were greater in the forest than the cropland at 20 cm (SUVA: 4.3 ± 0.1 vs. 3.7 ± 0.2 L mg C cm⁻¹ and HI:

Table 2 Soil water content every 20 min for two discrete sample periods that were separated by instrument failure (see “Materials and methods” section)

Soil depth (cm)	Soil volumetric water content (VWC)					
	Mean VWC (m ³ m ⁻³)		Spatial CV (%)		Temporal CV (%)	
	Cropland	Forest	Cropland	Forest	Cropland	Forest
March 1, 2011–June 30, 2011						
20	21.9	18.7	7.4	17.0	14.0	14.2
40	15.9	17.4	25.6	55.6	14.2	25.8
60	12.9	6.7	65.9	71.4	16.8	37.1
August 1, 2011–October 31, 2011						
20	23.5	17.0	10.2	20.9	13.2	20.7
40	15.8	10.0	22.0	55.2	21.4	47.1
60	14.1	–	41.0	–	16.8	–

There were significant main effects of land use and soil depth on volumetric water content (VWC) and the temporal coefficient of variation in VWC during the August–October sampling period (see “Results”)

Table 3 Probability values ($P > F$) from repeated measures ANOVA for the main effects of land-use (cropland vs. forest), soil depth, lysimeter type (zero-tension vs. tension) and sampling date on DOC, DON and nitrate concentrations and DOM properties and nitrate concentration

Explanatory variable	DOC	DON	NO ₃ ^{-N}	C/N ratio	HPI-C	SUVA	HI
Sampling date	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Land-use	0.03	0.04	0.01	0.01	0.03	0.12	0.03
Soil depth	<0.01	0.02	0.03	0.01	<0.01	<0.01	<0.01
Lysimeter type	0.015	0.60	0.11	0.38	0.26	0.96	0.41

For interactions see Tables 4 and 5

HPI-C hydrophilic carbon, *SUVA* specific UV absorption, *HI* humification index

0.96 ± 0.01 vs. 0.97 ± 0.00 ; Fig. 4). However, in contrast to 20 cm, mean HI at 40 and 60 cm for both lysimeters were significantly lower in the forest than cropland ($P < 0.01$; Table 4). Similarly, mean SUVA values of DOM sampled with tension lysimeters were lower in the forest than the cropland (2.6 ± 0.1 vs. 3.4 ± 0.1 L mg C cm⁻¹ for 40 cm and 2.2 ± 0.06 vs. 2.8 ± 0.07 L mg C cm⁻¹ for 60 cm).

The C/N ratio of DOM varied significantly with time ($P < 0.01$; Table 3; Figs. 2, 3). Interestingly, the C/N ratio of forest soil solution sampled with tension lysimeters was greatest in the spring whereas the C/N ratio of forest soil solution sampled with zero tension lysimeters was greatest in the fall. Across lysimeter types and depths, the C/N ratio of DOM was greater for the forest than cropland ($P = 0.01$; Table 3; Fig. 4).

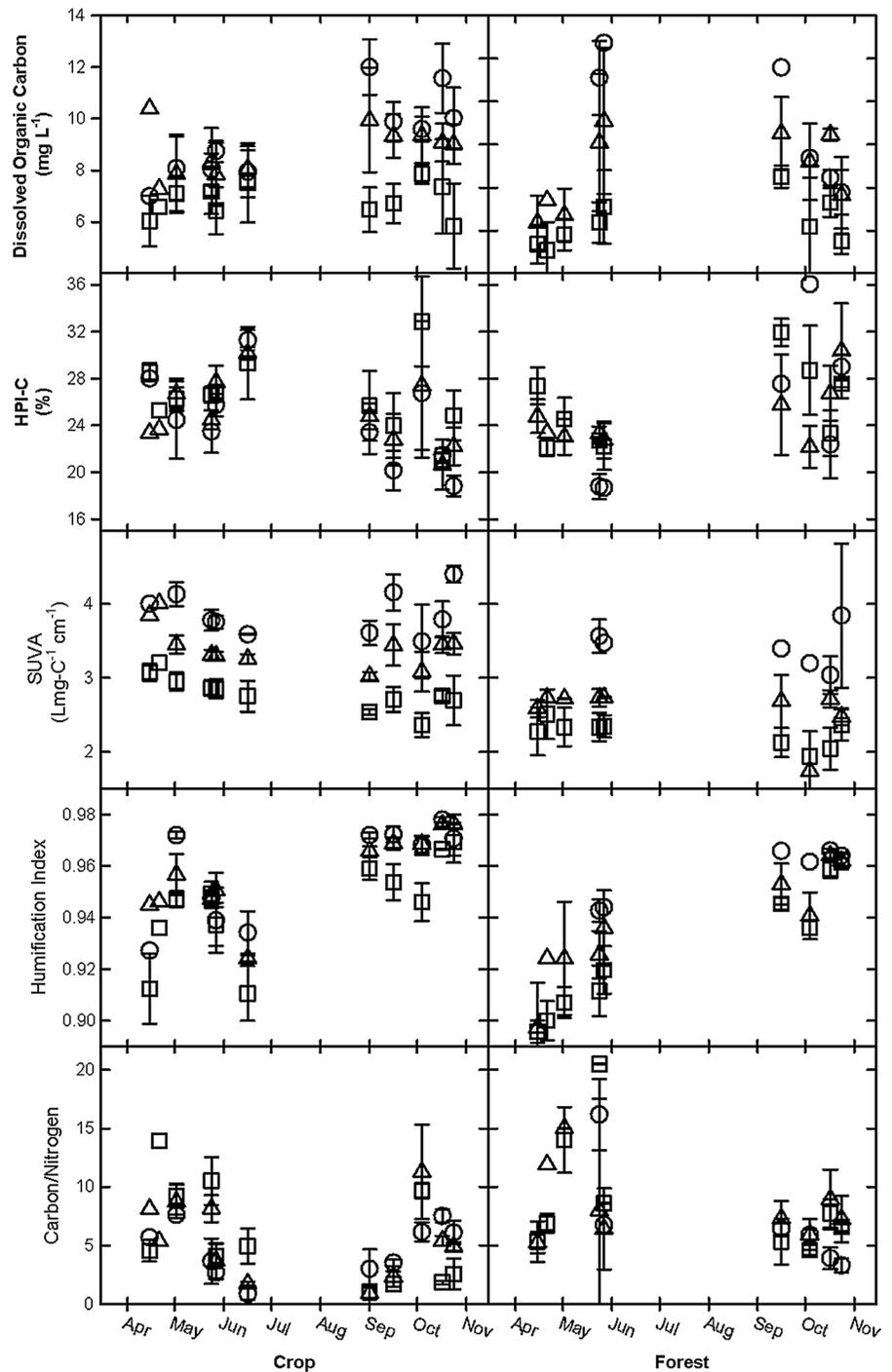
Dissolved ammonium was undetectable (<0.1 mg NH₄-N L⁻¹). However, nitrate and DON varied significantly during the sampling period ($P < 0.01$,

Table 3; Fig. 5) with maximum concentrations in late summer and early fall (August–October). Across lysimeter types, concentrations of DON and NO₃⁻ were higher in the cropland than forest ($P = 0.04$ and $P < 0.01$, respectively; Table 3; Fig. 4). The overall concentration of NO₃⁻ was 1.7–4.0 times greater than DON in the forest and 2.3–5.1 times greater than DON in the cropland.

Soil depth

Across lysimeter types and land uses, DOC concentration decreased with soil depth ($P < 0.01$; Table 3). However, the decrease was largest for forest zero-tension lysimeters from 20 to 40 cm depths (20.8 ± 1.2 to 10.5 ± 0.5 mg C L⁻¹) (Table 4; Fig. 4). There was relatively little change in DOC concentrations from 40 to 60 cm (Fig. 4) although mean DOC concentrations were higher at 40 than 60 cm for

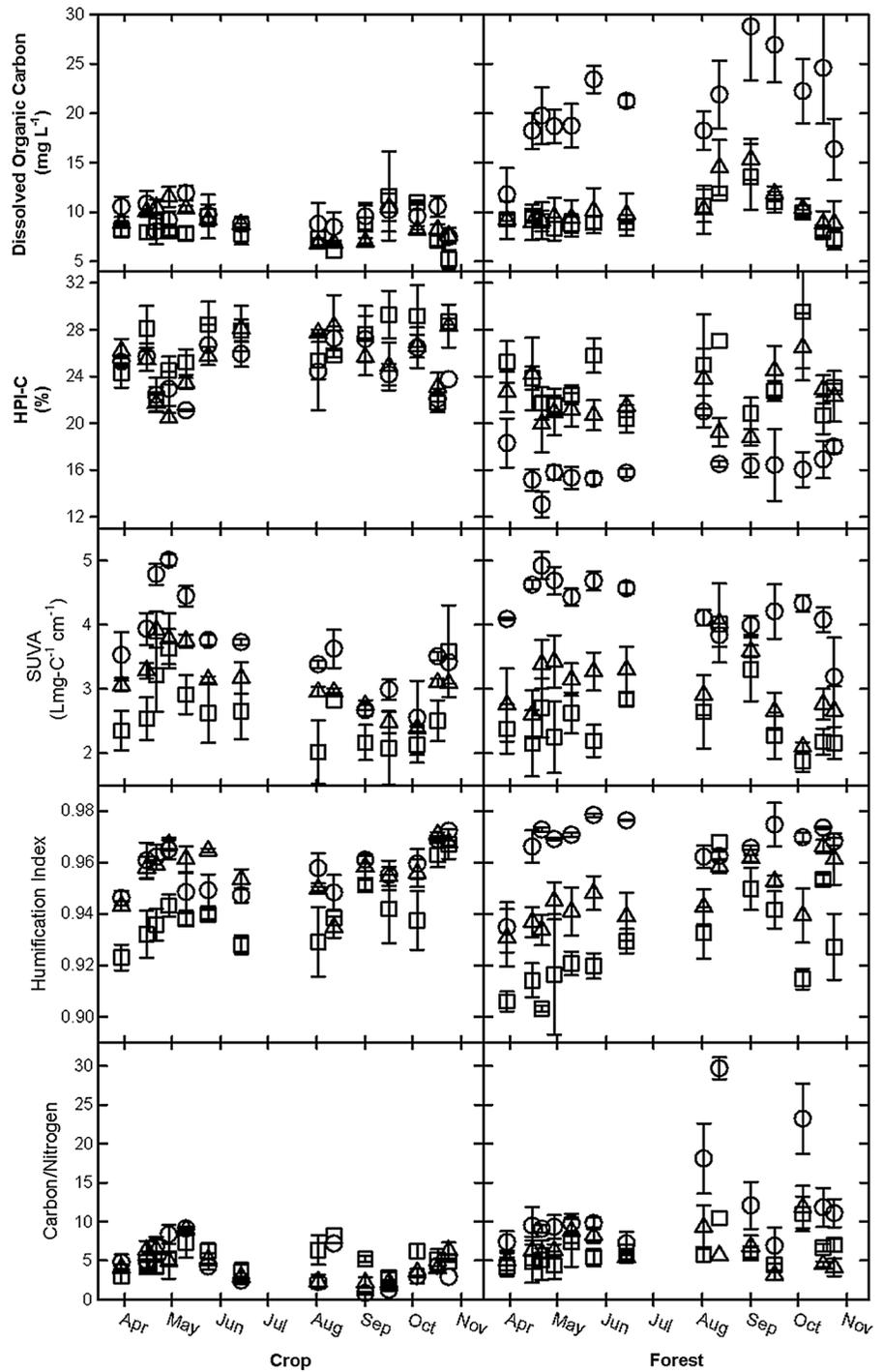
Fig. 2 Tension lysimeter dissolved organic carbon concentrations and dissolved organic matter properties for each sampling event at each depth: circles 20 cm, triangles 40 cm, squares 60 cm



zero-tension lysimeters (cropland: 9.0 ± 0.4 vs. 8.2 ± 0.4 mg C L⁻¹; forest: 10.4 ± 0.5 vs. 9.6 ± 0.4 mg C L⁻¹) and tension lysimeters (cropland: 8.8 ± 0.3 vs. 6.8 ± 0.2 mg C L⁻¹ and forest: 8.9 ± 0.6 vs. 6.4 ± 0.4 mg C L⁻¹).

Consistent with a decrease in DOC concentration with depth, the proportion of HPI-C generally increased with depth (Table 3; Fig. 4). This was largely the result of a significant ($P < 0.01$; Table 3) increase in the proportion of HPI-C from 20 to 40 cm

Fig. 3 Zero tension lysimeter dissolved organic carbon concentrations and dissolved organic matter properties for each sampling event at each depth: *circles* 20 cm, *triangles* 40 cm, *squares* 60 cm



in forest zero-tension lysimeters (16.4 ± 0.1 to 22.1 ± 0.6 %), with little change in HPI-C proportion from 40 to 60 cm for either of the land-uses (Table 4; Fig. 4).

The HI and SUVA properties of DOM also changed with soil depth ($P < 0.01$; Table 3; Fig. 4). The SUVA values for both lysimeters decreased ($P \leq 0.05$) from 20 to 40 cm (average decrease of

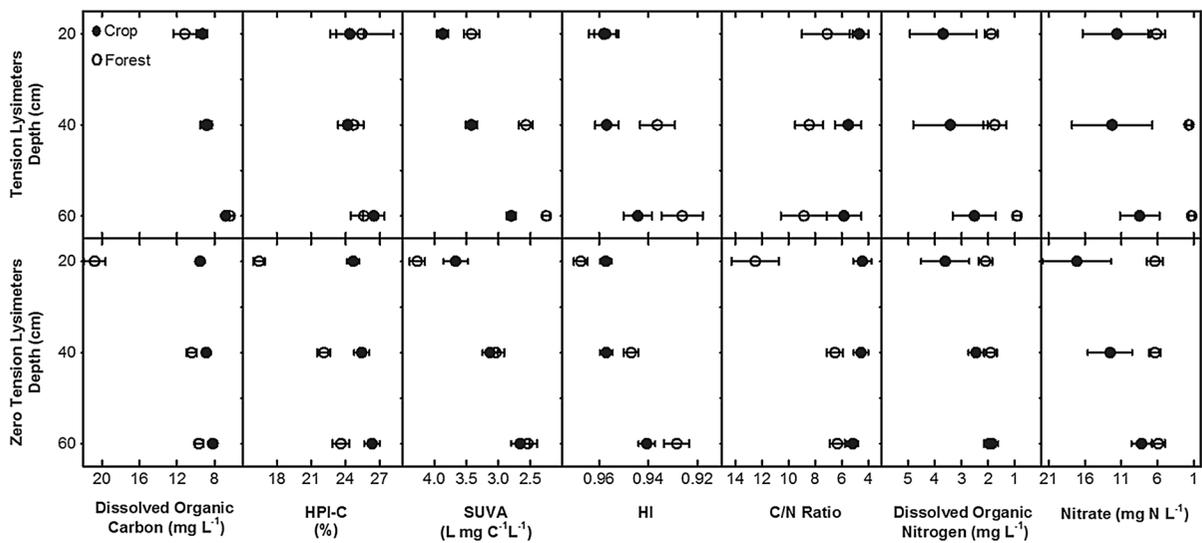


Fig. 4 Mean soil solution properties within land uses, lysimeter types and depths for the complete sampling period

Table 4 Probability values ($P > F$) from repeated measures ANOVA for the interactions between soil depth and land-use (within the same land-use and between two land-uses)

Soil depth (cm)	DOC	DON	$\text{NO}_3^- \text{N}$	C/N ratio	HPI-C	SUVA	HI
Cropland versus forest							
0–20	<0.01	<0.01	<0.01	<0.01	<0.01	0.53	0.51
20–40	0.31	0.07	<0.01	0.03	0.29	0.04	<0.01
40–60	0.66	0.61	0.13	0.09	0.17	0.08	<0.01
Cropland							
0–20 versus 20–40	0.61	0.11	0.23	0.45	0.51	0.02	0.97
20–40 versus 40–60	0.48	0.07	0.02	0.83	0.34	0.02	<0.01
0–20 versus 40–60	0.23	0.002	0.01	0.33	0.11	<0.01	0.01
Forest							
0–20 versus 20–40	<0.01	0.73	0.64	<0.01	<0.01	<0.01	0.01
20–40 versus 40–60	0.22	0.63	0.90	0.73	0.55	0.05	<0.01
0–20 versus 40–60	<0.01	0.42	0.56	<0.01	0.002	<0.01	<0.01

HPI-C hydrophilic carbon, SUVA specific UV absorption

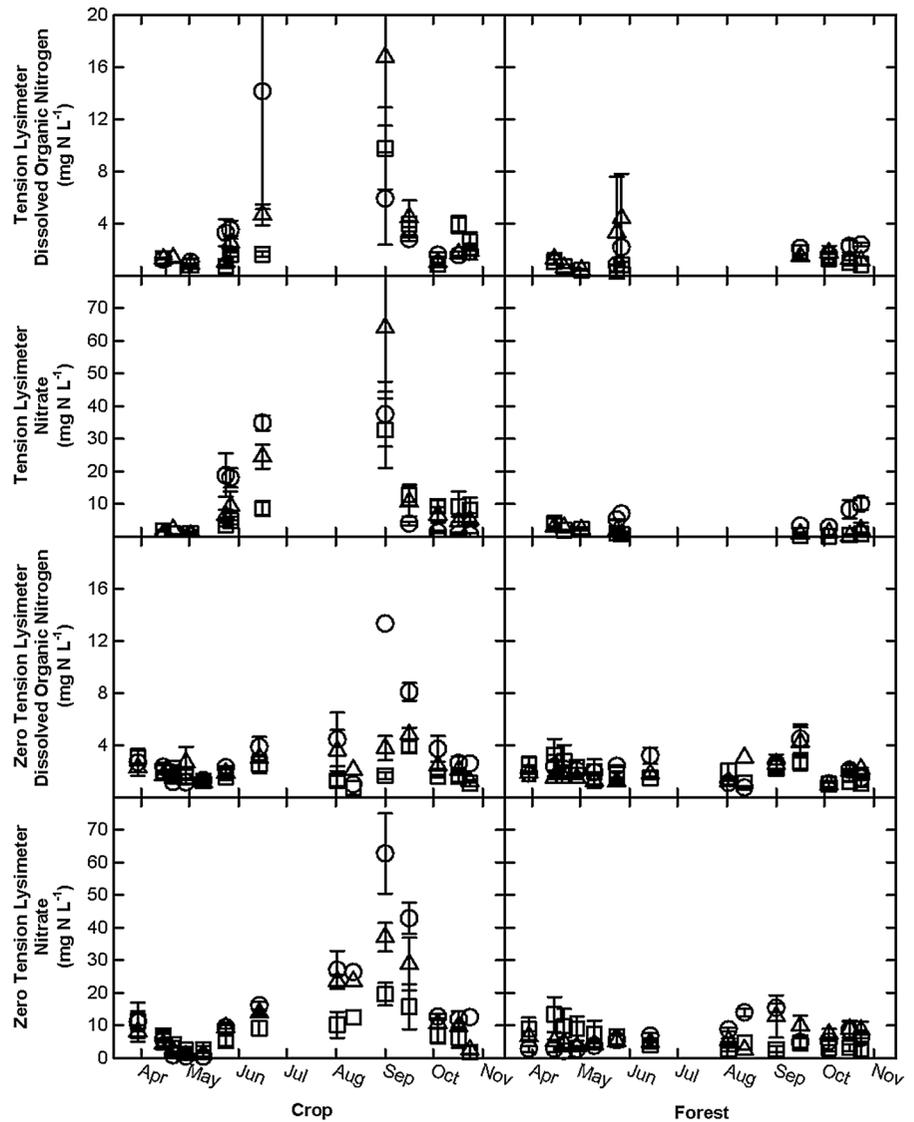
13.1 % for cropland and 26.7 % for forest) and from 40 to 60 cm (average decrease of 16.6 % for cropland and 14.8 % for forest) (Table 4; Fig. 4). The HI declined from 20 to 40 cm only in the forest. However, similar to SUVA, HI values declined ($P < 0.01$) from 40 to 60 cm for both land-uses.

Although there was a main effect of depth on DOM C/N ratio, ($P = 0.01$; Table 2) this was due to a sharp decline in the C/N ratio of DOM in zero-tension lysimeters from 20 to 40 cm in the forest (from 12.5 ± 1.8 to 6.5 ± 0.6 ; Fig. 4). In the forest, the

pattern of change in C/N ratio of DOM from 20 to 40 cm was very different between zero-tension and tension lysimeters (Fig. 4). However, among both lysimeter types, the C/N ratio did not change from 40 to 60 cm in either the cropland or forest.

Across land-uses and lysimeter types, changes in DON and NO_3^- concentrations differed with depth. Across soil depths in the cropland, there were decreases ($P \leq 0.01$; Table 4) in NO_3^- (14.5 ± 3.7 to 8.4 ± 2.0 mg-N L^{-1}) and DON (3.6 ± 0.9 to 2.3 ± 0.4 mg-N L^{-1}). But in the forest, NO_3^- and DON

Fig. 5 Dissolved nitrogen concentrations on each sampling date at each depth: circles 20 cm, triangles 40 cm, squares 60 cm



concentrations decreased with depth only for tension lysimeters (6.1 ± 1.1 to 1.3 ± 0.4 mg-N L⁻¹ for NO₃⁻ and 1.9 ± 0.2 to 0.9 ± 0.1 mg-N L⁻¹ for DON); DON was consistently low in zero tension lysimeters across depths. In zero tension lysimeters, with increasing depth, NO₃⁻ and DON concentrations converged among land uses. However, in zero tension lysimeters, with increasing depth, differences in NO₃⁻ and DON concentrations among land uses were exacerbated (Fig. 4).

Lysimeter type

There were no differences in soil solution chemistry between lysimeter types in the cropland (Table 4;

Fig. 4). In contrast, DOC concentrations and DOM properties exhibited clear differences between lysimeter types in the forest. These differences were greatest at 20 cm and decreased with soil depth (Fig. 4). Comparisons of soil solutions collected with zero tension and tension lysimeters in the forest demonstrate that zero tension lysimeter solutions had (i) higher DOC concentrations (20.8 ± 1.2 vs. 11.2 ± 1.2 mg C L⁻¹), (ii) wider C/N ratios (12.5 ± 1.8 vs. 7.1 ± 1.9), (iii) higher SUVA (4.3 ± 0.1 vs. 3.4 ± 0.1 L mg-C m⁻¹), (iv) higher HI (0.967 ± 0.00 vs. 0.957 ± 0.01) and, (v) lower proportions of HPI-C (16.4 ± 0.5 vs. 25.4 ± 2.7 %). For forest zero-tension lysimeters, DOC concentration was significantly

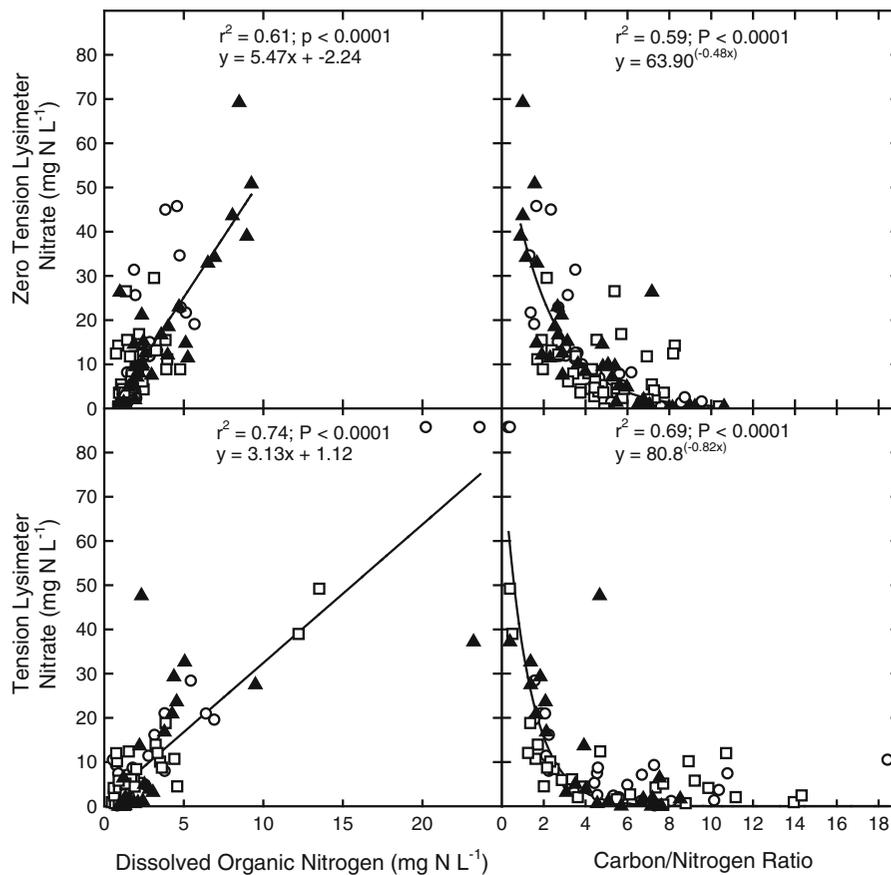


Fig. 6 Relationships between nitrate, dissolved organic nitrogen and the carbon/nitrogen ratio of dissolved organic matter across all depths for the cropland only (there were no

relationships between these variables in the forest). Circles 20 cm, triangles 40 cm, squares 60 cm

($P < 0.01$) correlated with SUVA ($R = +0.79$), HI ($R = +0.73$), and HPI-C ($R = -0.75$).

Dissolved inorganic nitrogen

Across all soil depths, consistent relationships between NO_3^- and DOM occurred only in the cropland. For both tension and zero tension lysimeters, NO_3^- was positively linearly correlated with DON, but negatively exponentially correlated with the C/N ratio of DOM (Fig. 6). Across soil depths within each land use, NO_3^- was not correlated with DOC, SUVA or HI.

Discussion

We could not reject our hypotheses: soil solution chemistry differed between land uses and lysimeter

types. DOM properties indicated that tension lysimeters sampled more decomposed DOM than zero tension lysimeters. However, these differences between lysimeter types were largely limited to the forest. In the cropland, there were no substantial differences in soil solution chemistry between lysimeter types (Table 4; Fig. 4).

Lower spatiotemporal variability in cropland VWC (Table 2) coupled with differences in soil solution chemistry between lysimeter types in the forest, but not the cropland (Fig. 4), are consistent with the concept that the forest contained more relatively rapid preferential hydrologic flowpaths (Flury et al. 1994; Castellano and Kaye 2009; Takagi and Lin 2012) that transported DOM and NO_3^- to subsoils with fewer opportunities for decomposition, immobilization, and physicochemical exchange with the mineral soil (Asano et al. 2006; Maggi et al. 2008; Castellano

Table 5 Probability values ($P > F$) from repeated measures ANOVA for the interaction between lysimeter type (zero tension vs. tension) and land-use (within the same land-use and between two land-uses)

	DOC	DON	NO ₃ ^{-N}	C/N ratio	HPI-C	SUVA	HI
Zero-tension versus tension lysimeter							
Cropland	0.38	0.56	0.11	0.29	0.16	0.04	0.54
Woodland	<0.01	0.96	0.53	0.80	<0.01	0.02	0.05
Cropland							
0–20 cm	0.81	0.46	0.01	0.68	0.16	0.16	0.82
20–40 cm	0.81	0.14	0.94	0.41	0.48	0.18	0.89
40–60 cm	0.29	0.64	0.68	0.45	0.66	0.34	0.47
Forest							
0–20 cm	<0.01	0.92	0.55	<0.01	<0.01	0.03	0.05
20–40 cm	0.89	0.40	0.26	0.13	0.15	0.28	0.11
40–60 cm	0.11	0.40	0.37	0.04	0.28	0.38	0.86

HPI-C hydrophilic C, SUVA specific UV absorption, HI humification index

et al. 2013). In terrestrial and aquatic ecosystems, rapid hydrologic flowpaths typically decrease DOM and DIN turnover rates per unit length transport (Fisher et al. 2004; Lewis et al. 2006). In soils, this may result from decreased contact time with mineral surfaces (Wagener et al. 1998; Asano et al. 2006).

Nevertheless, rapid flowpaths do not always lead to slower turnover rates per unit transport. Extensive transformation of DOM and DIN in rapid flowpaths can occur due to greater substrate supply, diffusivity, and microbial functional diversity than the bulk soil matrix (Bundt et al. 2001). Accordingly, in the cropland, the relative lack of differences in soil solution chemistry between lysimeter types suggests that: (i) both lysimeter types sampled soil solution derived from similar hydrologic flowpaths (i.e., decomposition, immobilization, and chemical exchange kinetics did not differ between lysimeter types) or (ii) decomposition, immobilization, and physicochemical exchange processes proceeded to the point that putative differences in hydrologic flowpaths sampled by the two lysimeter types had a relatively small effect on soil solution (i.e., these biogeochemical transformation processes equalized the chemistry of soil solution transported through different hydrologic flowpaths; e.g., Lajtha et al. 2005).

Agricultural operations associated with the cultivation of annual crops are well known to disrupt preferential hydrologic flowpaths and lower spatio-temporal variability in cropland VWC is consistent with the disruption of preferential flow (Table 2;

Jarvis 2007). However, it is also likely that cropland DOM is generally more decomposed than forest DOM because crop residues from annual plants and their DOM extracts have rapid decomposition kinetics relative to perennial vegetation (Martens 2000; Kalbitz et al. 2003). Moreover, intensive cultivation has been shown to accelerate organic matter decomposition and result in greater proportions of humified DOM in subsoils (Toosi et al. 2012). As a result, the effects of putative differences in hydrologic flowpaths on cropland soil solution chemistry may be difficult to observe because DOM is already highly transformed.

Litter manipulations in forests have shown that the effect of doubling aboveground plant litter on DOM quantity and quality decreases with soil depth (i.e., through flowpaths) until there are little-to-no differences in subsoil DOM quantity or quality (Lajtha et al. 2005). For many variables in our study, we observed a similar pattern: the land use effect diminished with depth particularly in zero tension lysimeters (Table 4; Fig. 4). Consistent with these field observations, the chemistry of DOM extracts differing in initial quality (e.g., C/N ratio, SUVA, HI) converges as decomposition proceeds over time (Kalbitz et al. 2003). Putative differences in hydrologic flowpaths in our study may persist to subsoils, but the results of Kalbitz et al. 2003 and Lajtha et al. 2005 suggest that the effect of differing hydrologic flowpaths on soil solution chemistry will decrease with depth as soil solution transit time increases and biogeochemical transformations accumulate (Kaiser and Kalbitz 2012).

Despite these differences in soil solution, DOM appeared to have experienced significant biodegradation prior to sampling. For example, the C/N ratios of DOM were low compared to plant sources. The relatively decomposed state of DOM could be due to one or a combination of the following factors: (i) large in situ contribution of SOM to DOM, (ii) rapid decomposition of new DOM inputs during the time between lysimeter sampling events, (iii) our delay in sample filtration until after sample collection, freezing, and subsequent thawing, and (iv) rapid chemical exchange of relatively undecomposed DOM with the soil matrix. It is likely that in situ decomposition and chemical exchange of fresh DOM inputs with mineral soil particles prior to our sampling played a significant role because DOM and SOM typically become more decomposed with depth (Kaiser and Kalbitz 2012). It is notable that our most shallow lysimeter location was 20 cm, which is below the deepest sampling depth of many biogeochemical studies. Although it is difficult to speculate how the delay in filtration may have affected our results, we expect the effect to be relatively small due to glass wool filters in the zero tension lysimeters and the small pore size of tension lysimeters (see “Materials and methods” section).

Land use and depth

Changes in DOM properties with depth have been shown for forest ecosystems (e.g. Kaiser et al. 2002; Kaiser and Guggenberger 2005). Our results highlight a similar pattern in cropland although the magnitude of the effect size appears smaller. With increasing depth in both land-uses, DOM generally contained greater proportions of HPI-C and lower proportions of aromatic (SUVA) and humified (HI) components, and lower or unchanged C/N ratios (Table 3; Fig. 4). Changes in DOM properties with soil depth have been related to (i) preferential chemical exchange reactions between DOM and SOM (low vs. high molecular weight compounds) and (ii) biodegradation of fresh DOM inputs that are concentrated in surface soils including aboveground litter and roots (e.g. Kaiser et al. 2002; Kaiser and Guggenberger 2005; Sanderman et al. 2008).

Similarity among forest and cropland DOC concentrations below 20 cm suggests that sorption and decomposition processes maintain consistently low DOC concentrations in the subsoil regardless of land

use (Jardine et al. 1989; Don et al. 2008; Marin-Spiotta et al. 2011). It is, however, important to consider that DOM turnover likely varies between the land-uses because there were large differences in DOM properties (Figs. 4, 5). We did not assess the source of DOM at different soil depths, but it is likely that depending on sampling time, a combination of DOM leaching from topsoil and in situ sources of DOM from SOM and rhizodeposition contributed to subsoil DOM. The relative importance of these sources may be one factor affecting differences in DOM properties between land uses.

Given the similar environmental conditions between land uses, the persistence of land use effects on DOM to 60 cm is consistent with several emerging concepts from our understanding of DOM dynamics. While vegetation affects DOM composition through initial litter quality, cultivation also impacts DOM composition through accelerated decomposition (Tosi et al. 2012). In addition, both vegetation and soil management have been shown to alter the “decomposer community funnel” that affects DOM properties and ultimately SOM storage (Wickings et al. 2012).

Nitrogen dynamics

Although we observed no correlations between DON and NO_3^- in the forest, DON and NO_3^- appeared to be closely linked in the cropland. Across all soil depths, we observed strong correlations between cropland DON, the C/N ratio of DOM, and NO_3^- concentrations (Fig. 6). Mean concentrations of DON were 1.8 times greater at 20 cm and 1.6 times greater at 40 cm in the cropland than forest. Consistent with data from forests and streams (McDowell et al. 2004; Kaushal and Lewis 2005), these data suggest microbial DON production is as an important sink for DIN in the cropland. Together with the strong temporal pattern in cropland NO_3^- concentrations (Fig. 5), these data indicate the microbial community maintains some unsatisfied capacity for N retention despite decades of large N inputs ($\sim 100 \text{ kg N ha}^{-1} \text{ year}^{-1}$). The apparent DON sink for NO_3^- , as well as the higher DON concentrations in the cropland than forest, highlight the need to consider both DON and DIN losses from agricultural systems (van Kessel et al. 2009).

Nitrogen dynamics were consistent with the concepts that zero tension lysimeters sampled more rapid hydrologic flowpaths and more rapid hydrologic

flowpaths limit solute transformation. In the forest, NO_3^- concentrations decreased with depth in tension lysimeters, but not zero tension lysimeters (Fig. 4). In the cropland, the decrease in NO_3^- concentrations with increasing DOM C/N ratios was nearly double for tension than zero-tension lysimeters (Fig. 6) while the slope of the relationship between NO_3^- and DON concentrations was significantly lower for tension lysimeters (i.e., less NO_3^- per DON).

The contrasting results in Fig. 4 (lack of main effect of lysimeter type on cropland soil solution) and Fig. 6 (different slopes between NO_3^- , DON, and C/N ratio among tension and zero tension lysimeters) suggests that flowpaths sampled by cropland tension and zero tension lysimeters do not substantially differ, or the cropland soil solution is sufficiently decomposed such that putative flowpath differences have no detectable effect on soil solution chemistry. Although lower spatiotemporal variability in cropland VWC (Table 2) indicates fewer flowpath differences in the cropland than the forest, it does not indicate differences are non-existent. The contrast between the effects of lysimeter type on cropland N dynamics versus the lack of effect of lysimeter type on cropland soil solution chemistry suggests that differences in hydrologic flowpaths as well as differences in organic matter inputs (i.e., the quality and quantity of net primary productivity) affected the patterns observed in this study. The capacity to model subsoil biogeochemistry will benefit from studies that work to understand the relative importance of hydrological flowpaths versus organic matter input biochemistry on the transport and transformation of soil solution.

Conclusion

In relation to land-use, DOM has been of interest regarding its role as a labile OM pool and its contribution to both net SOM (C and N) storage and loss. Through a paired comparison of forest and cropland, we observed that long-term intensive cultivation of a forest was associated with lower DOC at 20 cm, but higher DON and NO_3^- concentrations from 20 to 60 cm. Based on differences in DOM properties between the forest and cropland, cultivation appeared to enhance DOM decomposition from 20 to 60 cm. DOC concentrations were different between tension and zero tension lysimeters, but this effect was

largely limited to the forest at 20 cm where DOC concentrations were greater in zero tension lysimeters. These data suggest that long-term cultivation has reduced delivery of relatively undecomposed DOM from topsoil to subsoil. Lower spatiotemporal variability in cropland VWC suggests cultivation reduces fast flowpaths which may in turn affect the transport and transformation of soil solution. Nevertheless, stoichiometric DOM-N sinks for NO_3^- appeared to remain in the cropland despite higher NO_3^- concentrations and lower DOM C/N ratios than the forest. The relatively less decomposed DOM in forest zero tension lysimeters may originate from fast flowpaths and contribute to subsoil OM supply that, depending on environmental conditions, can result in an accumulation or loss of subsoil SOM (Kaiser and Guggenberger 2005; Marin-Spiotta et al. 2011).

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