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Effects of land use and riparian flowpath on delivery of dissolved organic carbon to streams

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Abstract

A set of near-stream flowpaths in pasture, native forest and exotic pine plantations in New Zealand was sampled to describe differences in dissolved organic carbon (DOC). The quantity and bioavailability of DOC varied among flowpaths in different land uses, with higher concentrations of DOC in near-stream flow paths than the parent groundwater emerging from the hillslope. Tiles incubated in these waters did not consistently yield higher bacterial growth rates than tiles incubated in groundwaters. DOC composition, measured as fluorescence and absorbance properties and extracellular enzyme fingerprints, differed significantly among land uses and position along flowpath.

Differences in riparian vegetation can indirectly affect DOC by altering exposure to ultraviolet radiation. A 2-h exposure of water from subsurface flowpaths to full sunlight caused marked changes in fluorescence characteristics of water from the pasture catchment but only small changes in water from the native forest catchment. There were up to fivefold differences in extracellular enzyme activities on tiles incubated in light-exposed water for the native forest site, but not for the pasture site. Bacterial growth and respiration were higher on tiles incubated in native forest water exposed to sunlight, but there was no light effect on growth for tiles incubated in water from the pasture flowpath. These results indicate that riparian flowpaths will affect the quantity and character of DOC delivered to streams and ultraviolet exposure may, at least in some cases, alter DOC bioavailability.

One of the most obvious environmental changes caused by human activity is conversion of land use/landcover, commonly reducing forest cover due to expanding areas of agriculture and residential land use (Turner et al. 1994; Quinn et al. 2000). This development inevitably affects both water quality and quantity in associated surface and subsurface waters. For example, changes in landcover in the Hudson River drainage basin have led to major changes in sediment, carbon, and nitrogen loadings to the river (Howarth et al. 1996). In New Zealand, expansion of agriculture has resulted in loss of ~70% of native vegetation with major effects on stream biota, water chemistry, and channel morphology (Quinn and Hickey 1990; Quinn et al. 1997). Stream ecologists have studied consequences of land-use change for some time because stream water chemistry and biota are useful indicators and integrators of land-use change within the catchment (Roth et al. 1996). Land-use effects on stream biota can be long lived, for instance Harding et al. (1998) found that stream insect and fish biodiversity were most strongly related to the proportion of agriculture in the catchment 50 yr previously. Also, certain land uses are known to be particularly harmful to stream biota due to excess nutrient loading and sedimentation (Allan et al. 1997). In addition to these fairly direct consequences of changes in catchment land use and riparian habitats, there are potential indirect effects including changes in stream temperatures and exposure to solar radiation.

It is now obvious that microbial communities in streams play a role in some components of stream food webs (Hall and Meyer 1998) and are responsible for many important nutrient transformations (Holmes et al. 1996; Jones et al. 1995). Microbial responses to shifts in catchment vegetation have not been widely studied, although recent results from a manipulation of litter input to streams suggest strong effects on both the abundance and decomposition activity of the microbial community (Wallace et al. 1997; Tank et al. 1998).

Dissolved organic carbon is a significant source of carbon and energy in many stream ecosystems, and its contribution

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to higher trophic levels is largely mediated by heterotrophic bacteria (Findlay et al. 1993; Jones 1995). DOC in stream ecosystems is almost always the largest pool of organic carbon, and fluctuations in quantity and composition of DOC can influence microbial metabolism (Bott et al. 1984). A wide variety of sources in the stream channel contribute DOC, including leaf litter, benthic algae, and macrophytes. Several sources outside the stream channel also supply DOC, and these include wetlands (Mulholland 1997; Dillon and Molot 1997) and shallow soil flowpaths (Boyer et al. 1997; Hinton et al. 1998). Forest and agricultural soils differ in water-soluble carbon concentrations and microbial metabolism of that carbon (Boyer and Groffman 1996), so DOC export from these land uses may affect delivery of available carbon to groundwaters and streams. Precipitation contains appreciable quantities of DOC (Willey et al. 2000), and although direct interception by stream channels is probably small, precipitation may represent a significant term in whole-catchment carbon budgets.

Removal of DOC from streamwater is also a complex process involving microbial metabolism in surface sediments (Kaplan and Newbold 1993) and along subsurface flowpaths (Findlay et al. 1993). Additionally, there are cases where adsorption of dissolved materials to surfaces acts to retain soluble compounds within a stream reach, allowing subsequent microbial metabolism (Freeman and Lock 1995; Fiebig 1997). Sorption to metal hydroxides can reduce DOC concentrations and influence the chemical characteristics of DOC in transport (McKnight et al. 1992).

We examined land-use effects on the quantity, composition, and bioavailability of DOC entering small streams in pasture, native forest, and exotic pine catchments in New Zealand. The direct effects of land use may be related to carbon release by vegetation and litter or differences in near-stream flowpaths. Effects of differential stream shading and exposure to ultraviolet (UV) radiation were examined to document possible photolytic effects on DOC composition and bioavailability.

Methods

Site description—All streams in this study are within 3.5 km of each other at the Whatawhata Research Centre and the adjacent native (podocarp-hardwood) forest reserve west of Hamilton (175°15′E; 37°47′S) on the North Island of New Zealand. The area is dominated by steep (>30°) to hilly topography, with parent rocks of sedimentary sandstones and siltstones (greywacke and argillite) laid down in the Mesozoic upon which has developed yellow brown earth soils (Kaawa hill soil, an Ochreptic Hapludult, and the Waingaro steepland soil, an Umbric Dystrochrept). Patches of overlying volcanic ash remain in less steep parts of the catchments, and these have formed yellow brown loam soils (Dunmore silt loam, a Typic Hapludand). The pasture area was converted from native forest approximately 75 years ago and is intensively farmed, stocked with sheep and cattle, and vegetated with clover and pasture grasses. The pine catchments were also converted from native forest to pasture approximately 75 years ago and then were planted with *Pinus radiata* 28 years ago. Phosphorus fertilizer application to pasture occurs at a rate of 22 kg P ha^{-1} yr^{-1}, predominantly as reactive rock phosphate. No artificial N fertilizer is applied but symbiotic N fixation by forage legumes is expected to be up to 55–85 kg N ha^{-1} yr^{-1} for pasture receiving a higher P fertilization (55 kg P ha^{-1} yr^{-1}) at the study area (Ledgard et al. 1987). The pine plantation has not received any fertilizer for at least the last 20 yr and probably not since pines were planted 28 years ago.

The podocarp-hardwood native forest is dominated by tawa (*Beilschmiedia tawa*), rewarewa (*Knightia excelsa*), and rimu (*Dacrydium cupressinum*), with tanekaha (*Phyllocladus trichomanoides*) and kahikatea (*Dacrycarpus dacrydioides*) also common canopy trees. Average annual rainfall is 1,600 mm, mean air temperature 13.7°C, and mean solar radiation 11.2 MJ m^{-2} d^{-1} (NIWA unpubl. data).

In each of the land-use categories (pasture, native forest, pine forest) we located three groundwater seeps and excavated where necessary to sample water as it emerged from bedrock outcrops or from conductive gravelly layers within the soil profile. In the pastures there were two flowpaths leading from the seeps to the stream: one across the surface of the soil and thus in contact with vegetation and the atmosphere, the second along the contact between the underlying bedrock and the lower soil boundary and thus in contact with deeper soils. For catchments with native forest vegetation we sampled at points where subsurface flowpaths discharged to the stream but could not locate triplicate surface flowpaths of a length comparable to those in the pasture catchment (c. 20 m). In the pine catchment we sampled surface flow after groundwater had emerged and traveled for distances comparable to those in the pasture catchment but could not extract samples from subsurface flowpaths. Thus, we have triplicate groundwater seeps in each of three land uses (pasture, pine, native) and near stream surface and subsurface flows for two of the three land uses (surface flows in pasture and pine, subsurface flows in pasture and native). The distance from groundwater seeps to the stream channel ranged from 20 to 40 m.

Previous and subsequent studies in these catchments have confirmed differences in soil characteristics among land uses. Nguyen and Downes (1999) found higher organic matter content and moisture and lower bulk density in pasture riparian soils than in soils at comparable locations in native forest or pine catchments. A tracer study confirms relatively slow movement of water through subsurface flowpaths (~1 cm d^{-1} at 50 cm depth) in pasture riparian soils with faster flows (~300 cm d^{-1} near the surface) under wet conditions (D. Burns, United States geological survey pers. comm.). We do not have volumetric estimates of surface versus subsurface discharge to the stream for the different sampling locations. Field observations suggested subsurface flow was predominant in the native forested sites at the time of our sampling, surface flow predominated in the pine catchment, and both surface and subsurface water movement were evident in the pasture catchment. The steep sideslope topography and incised stream channel make it very unlikely that there was significant return flow from the stream channel to riparian soils, at least under the flow conditions at the time of our sampling.

Water samples from seeps and surface flows were collected during late February 1998 directly into acid-washed (20% HCl, 6 rinses) containers occasionally requiring small funnels or tubes to minimize contact with surrounding sediment. Subsurface flow was sampled by driving perforated PVC tubes (20 mm ID) horizontally into the stream bank to intercept water 20–40 cm before it emerged as trickles along the bank. Dissolved oxygen (DO) and temperature were measured (YSI model 55) immediately on unfiltered samples in the field. Samples were held on ice until return to the laboratory where they were filtered (prerinsed Whatman GF/C) prior to measurement of conductivity, DOC, inorganic nutrients, and fluorescence and absorbance characteristics.

Experimental procedures—To examine microbial response to potential differences in DOC derived from the various land uses and flowpaths, we collected several liters of water from each flowpath (pasture : groundwater [GW], subsurface [sub], and surface [surf]; native : GW, sub; pine : GW, surf) and incubated small (20 × 20 × 6 mm) unglazed precombusted ceramic tiles in the different types of water for 10 d. Eight tiles were stacked on edge in small tubes with 90 ml of appropriate source water. All tiles and tubes were soaked in several changes of deionized water before the experiment to remove any potential contaminants. One tube was prepared for each of three GW seeps in each of three land-use categories (i.e., $n = 9$), six sub flowpaths (three pasture, three native) and six surf flowpaths (three pasture, three pine) for a total of 21 tubes. To provide a consistent inoculum for all treatments, we combined 1 ml of water from each of the 21 sample bottles then redistributed 1 ml to each of the 21 tubes. Tubes were placed upright on a shaker table (~50 rpm) in the dark at 20°C. For the first 48 h water was not exchanged to allow colonization of the tiles, then water was changed daily to avoid any possible depletion of either inorganic nutrients or DOC. After 10 d of incubation in each water treatment, oxygen uptake was measured for each tube and then tiles were allocated to measures of bacterial production, a suite of extracellular enzyme activities, and quantity of biofilm developed.

To examine indirect effects of riparian shading, specifically the potential for photolysis of DOC, we collected water from a single subsurface flowpath in both a pasture and a native forest catchment. We did not use either streamwater or surface flowpath water for our photolysis experiment because we would not know its prior exposure to sunlight. Also, subsurface water had higher absorbance in the photoreactive portion (300 nm) of the spectrum. Water (~2 liters) from each of the two subsurface flowpaths was split into two portions in shallow pans, one of which was exposed to full sun for 2 h centered on solar noon on a cloudless summer day [26 February 1998; UVA (315–400 nm) = 70 W m^{-2}, UVB (290–315 nm) = 2.2 W m^{-2}; UV calculated from relationships of McKenzie et al. 1996]. The other pan was kept covered with black plastic. After exposure, four tubes of tiles were filled with water from one of the four combinations (pasture, light or dark; native, light or dark) resulting in four replicates of each treatment. Tubes were incubated for 9 d, water changed, and tiles allocated for the various analyses as described above.

Tile blanks were prepared just as for experimental tiles by incubating tiles in deionized water following the same schedule for water changes and biofilm assays. Rates of thymidine incorporation and oxygen consumption on tile blanks were only 14% and <10%, respectively, of rates on tiles incubated in natural waters indicating minimal contamination by DOC released from tiles or containers.

Analyses—DOC was measured on filtered water samples using a Shimadzu 5000A TOC analyzer, which employs high-temperature combustion and IR detection of CO_2. Inorganic nutrients (dissolved reactive phosphorus [DRP], NO_3-N, NH_4-N) were analyzed by simultaneous autoanalysis; phosphorus by automated molybdenum blue/ascorbic acid colorimetry, cadmium column reduction of NO_3 to NO_2, then diazotization with sulphanilamide and NEDDE and NO_2-N subtracted from NO_3-N, and automated phenol/hypochlorite colorimetry, respectively (APHA 1989). Absorbance characteristics of different water samples were measured at several wavelengths in a 4 cm cell on a Shimadzu UV-160A Spectrophotometer. Fluorescence characteristics were measured on a Perkin Elmer LS50B Spectrofluorometer using an excitation of 370 nm (slit width = 2.5) and measuring fluorescence at 450 and 500 nm (slit width = 5), as well as integrated fluorescence over 450–500 nm.

Bacterial production on tiles was determined by incubating three tiles in 10 ml of the appropriate treatment water with 40 μCi of 20 μCi nmole^{-1} ^{3}H-TdR for 5 h in the dark. Incubation was terminated by addition of 0.5 ml of 5% formaldehyde; tiles were gently washed two times with 5% formaldehyde and then frozen until extraction of ^{3}H-DNA as described in Findlay et al. (1984). Zero-time controls were incubated in parallel to live samples.

Enzyme activity in tile biofilms was assayed at room temperature on suspensions of biofilm obtained by scrubbing four tiles in 5 ml of deionized water. Aliquots (100 μl) were dispensed into 96 well microplates with 100 μl Methylumbelliferone (MUF)-labeled substrates (Enzyme: substrate: abbreviation; esterase: 4-MUF-acetate: ACE; phosphatase: 4-MUF-phosphate: PHOS; leucine aminopeptidase: l-leucine 7-amido-4-methyl-coumarin: LEU-AP; β-glucosidase: 4-MUF-β-D glucoside: BETA; α-glucosidase: 4-MUF-α-D glucoside: ALPHA; β-xylosidase: 4-MUF-β xyloside: XYL; β-N-acetylglucosaminidase: 4-MUF-N-acetyl-β-glucosaminide: NAG) to yield a final substrate concentration of 400 μM. Fluorescence was measured at approximately hourly intervals for 6 h. Substrate blanks (MUF-substrate plus buffer) and sample blanks (biofilm suspensions plus buffer) were run each time. All types of blanks had rates of enzyme activity less than 10% of fluorescence observed in tiles incubated with treatment waters. Potential quenching due to color differences among biofilm suspensions was determined by adding known quantities of free MUF to microplate wells containing the different biofilm suspensions. Differences among treatment types in quenching were less than 5% of the grand mean.

Biofilm respiration was measured by capping the tubes containing tiles for approximately 24 h before tiles were removed for other analyses. Fresh treatment water of known air-saturated DO was added to tubes immediately before they

were sealed by a plastic lid adhered with silicone grease. Dissolved oxygen before and after the incubation was measured with a YSI Model 50B DO meter with stirring BOD probe (Model 5905). The meter was calibrated in moist air and checked in air-saturated water regularly during measurements. Blanks were run with clean tubes filled with distilled deionized water. We assumed respiration on tube walls was the same as on tiles to calculate oxygen consumption per cm^2 of total surface area inside the tube. Quantities of epilithic biofilm were estimated by scrubbing tiles in deionized water, diluting fivefold, then analyzing the biofilm suspensions for total organic carbon on a Shimadzu 5000A TOC analyzer.

Total dissolved amino acids in the water samples were measured with o-phthaldialdehyde derivative technique of Mopper and Lindroth (1982) using an excitation wavelength of 330 nm and an emission wavelength of 450 nm. Glycine (Sigma) was used as a calibration standard and the total dissolved amino acid concentrations were expressed in μM glycine units.

Land-use and flowpath effects on bacterial growth, respiration, and enzyme activity were examined with ANOVA using log-transformed data. Because of our unbalanced design (no surface waters in the native catchment, no subsurface in pine) we had to combine across land uses or examine each land use separately to conduct a posteriori tests for significant differences. Principal components analyses were used to simplify the multivariate enzyme data, and enzyme activities were standardized (mean = 0, SD = 1) before analysis. All statistical analyses were run with Statistica®.

Results

Flowpath water characteristics—Water from the various flowpaths exhibited large differences in inorganic chemistry, DOC concentration, absorbance, and fluorescence characteristics. Spot measurements of DO concentrations in the water during sampling showed that the groundwaters in all land uses, surface flow from the pine, and subsurface flow in the native forest wetlands were relatively well aerated (DO $>$ 5 mg L^{-1}). In contrast, both surface and subsurface flows from the pasture wetlands had $<$2 mg L^{-1} DO. Conductivities varied within a fairly narrow range (Table 1) except for the pasture subsurface flowpath that had 2–3 times higher conductivity than any other sample. Groundwater collected in pasture or pine catchments was greatly enriched with nitrate relative to groundwater from the native forest catchment (Table 1). Nitrate concentrations in both pasture and pine surface flowpath samples were much lower than in groundwater (Table 1), and nitrate concentrations had been reduced to near zero in the pasture subsurface flowpath. In contrast to nitrate, ground water DRP concentrations did not vary as dramatically among land use but averaged 55% lower in surface and subsurface than groundwaters (two-way ANOVA, $p = 0.03$, $F = 5.3$). Ammonium concentrations were very low except in the pasture surface and subsurface flowpaths where they were both high and variable.

All groundwaters had consistently low concentrations of DOC with means less than 1 mg C L^{-1}, whereas surface and subsurface flows from different land uses differed significantly in DOC concentration (two-way ANOVA, $p = 0.0005$, $F = 7.4$; Fig. 1A). Surface and subsurface waters were always enriched in DOC relative to the source groundwater with differences in means ranging from twofold in native sites to tenfold in pine sites. Fluorescence characteristics also differed among flowpath location (Fig. 1B) with both the fluorescence ratio and fluorescence per unit carbon (data not shown) significantly different among flowpath locations (ANOVA $p = 0.025$, $F = 4.43$; $p = 0.055$, $F = 3.3$, respectively). Water from pasture subsurface flowpaths had fluorescence ratios significantly lower than pasture groundwater surface flows, and pine surface water was significantly lower than groundwater from pine catchments. Absorbances vary predictably given the differences among sources in bulk DOC concentrations with, for example, almost fivefold higher absorbance at 270 nm for pasture subsurface water relative to any of the groundwaters (data not shown).

Table 1. Chemical characteristics of water from groundwater seeps, surface and subsurface flowpaths in the three different land uses. Values for conductivity, nitrate, ammonium and dissolved reactive phosphorous were measured for the separate containers used as source waters for experimental treatments and are reported as means (±SE). ND = no data.

	Conductivity (μS cm^{-1})	NO_3-N (μg L^{-1})	NH_4-N (μg L^{-1})	DRP (μg L^{-1})	Amino acids (μM)
Pasture					
GW	96 (13)	835 (156)	0 (0)	54 (28)	4.2 (0.6)
Sub	284 (21)	3(1)	138 (77)	24 (17)	9.6 (2)
Surf	128 (38)	156 (126)	20 (20)	34 (25)	6.4 (3.7)
Pine					
GW	112 (3)	1,007 (338)	2 (1)	81 (15)	3.4 (2)
Sub	ND	ND	ND	ND	ND
Surf	114 (1)	411 (125)	10 (7)	25 (13)	2.6 (0.7)
Native					
GW	118 (15)	6 (5)	2 (1)	41 (15)	3.5 (1.0)
Sub	97 (21)	6 (5)	2 (2)	16 (8)	2.8 (0.5)
Surf	ND	ND	ND	ND	ND

Concentrations of free amino acids did not differ among groundwaters (Table 1), and concentrations in groundwater were not significantly lower than pasture or pine surface waters or native forest subsurface water. Pasture subsurface waters had a significantly higher concentration of amino acids than any of the groundwaters. These concentrations are such that amino acids constitute 17% of groundwater DOC, 9% of pasture surface DOC, 5% of pasture subsurface DOC, and only 1.5% of pine surface DOC.

Biofilm response—The absolute rates of enzyme activities varied significantly among flowpath locations (Table 2). Four of the seven enzymes assayed (ACE, ALPHA, BETA, and PHOS) differed significantly ($p < 0.05$) by flowpath location when data were combined across land use. For example, β-glucosidase activity (averaged across land uses) was twofold higher on tiles incubated in subsurface water than in groundwater. Xylosidase activity was also on average 1.6 and threefold higher in surface and subsurface flowpaths than ground-

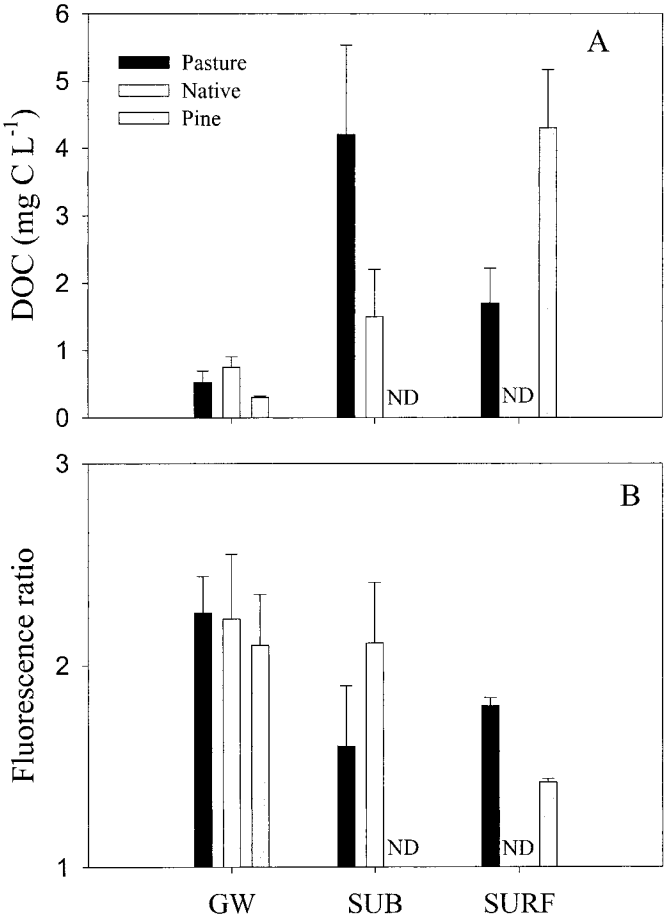

Fig. 1. (A) Dissolved organic carbon concentration and (B) fluorescence ratios by land use and flowpath position. Each value is the mean of three separate source water collection points (±1 SE). ND = no data.

waters, but these differences were only statistically significant for the pine catchment. In contrast to the marked effects of flowpath on enzyme activity, we found no significant differences in enzyme activity among land uses when comparing similar flowpath positions across pasture, pine, and native catchments. For instance, BETA activity only ranged from 0.2 to 0.3 nmol MUF tile^{-1} h^{-1} among groundwaters from the three land uses.

Given the relatively large number of response variables (seven different enzymes) that are often intercorrelated, the best way to examine differences among enzymes across sampling locations is to combine the variables in a principal components analysis, thus simplifying the comparison to 2–3 composite variables. The first two principal components account for 70% of the total variability, allowing two-dimensional plots of different treatments to describe most of the information in the data set. The resulting plot of mean sample scores (Fig. 2) shows the enzyme patterns for all three types of groundwater are quite similar, whereas other flowpath and land-use combinations spread out along the two axes. As we would have predicted from the fluorescence characteristics, the pasture subsurface and pine surface waters are most distinct from their parent groundwaters, with mean PCA axis 1 scores significantly (ANOVA, $p = 0.006$, $F = 6.8$) different from groundwater. The native forest subsurface water is also separated from the groundwaters but did not differ significantly in PCA axis 1 score from these, and the pasture surface waters plot very close to the groundwater cluster (Fig. 2).

Bacterial production differs significantly ($p = 0.006$, $F = 6.7$) among flowpath locations when data are combined across land uses (Fig. 3A). Examining differences along flowpaths within each land-use category reveals that surface waters support twofold higher bacterial production than groundwaters. Groundwater DOC supports bacterial production as high as that supported by subsurface waters despite the higher concentration of DOC in subsurface water (Fig. 1A). Epilithon respiration increased slightly but not significantly along each individual flowpath in pine and native land uses but showed no pattern among the different flowpaths in the pasture sites (Fig. 3B).

Photolytic effects—There was no significant difference in total DOC concentration following the 2-h light exposure for either type of subsurface water (DOC = 3.7 ± 0.01 and 5.6 ± 0.27 mgC L^{-1} in pasture and native source waters), so our dose was not sufficient to cause measurable direct photooxidation. Exposure of subsurface water to sunlight for 2 h caused a 37% reduction in fluorescence yield in water from the pasture but no significant change in fluorescence for water from the native catchment. The decline in fluorescence is consistent with changes in photochemistry following exposure of humic materials to direct sunlight (Moran and Zepp 1997). There was no significant difference in absorbance in the UV range (270 or 340 nm) for either type of water following exposure to sunlight, but water from the native flowpath had greater absorbances (1.2 ± 0.09 vs. 0.5 ± 0.05) at these wavelengths initially. Nitrate and ammonium N concentrations were very low in the native and pasture subsurface waters (3 ± 1 and 12 ± 5 μg L^{-1}, respectively) and were unaffected by light exposure. Light exposure did not influence DRP of the native flowpath water (mean 18 μg L^{-1}), but there was an unexplained decline in pasture flowpath DRP from 53 to 9 μg L^{-1} after UV exposure.

The response of the extracellular enzymes on tiles incubated in water previously exposed to sunlight is counter to what we would have predicted from the magnitude of the change in fluorescence characteristics for the two types of water. There were no significant differences between enzymes for the pasture light versus dark treatments, whereas water from the native catchment showed six of the seven enzymes (all but esterase) were significantly increased twofold to sixfold following light exposure (Table 2). For the pasture subsurface water, exposure to sunlight had a negligible effect on the relative enzyme activities (Fig. 4) despite the decline in fluorescence yield. For the native catchment subsurface water there was a marked effect with a large separation in the scores of enzyme activities from biofilms incubated in dark versus light waters (Fig. 4). Parallel with the results of enzyme activities, there were large and significant differences in bacterial production supported by light versus dark native subsurface water but no significant effect of sun-

Table 2. Field Sites—Table of mean enzyme activities (nmol MUF tile^{-1} h^{-1}) for the different source waters and flowpath positions. Specific statistical comparisons are presented in the text. Each value is the average activity (SE = 1 Std. Error) for tiles incubated in water collected from three separate locations. Abbreviations for enzymes are given in the text. ND = No data. Photolysis Experiment—Table of mean enzyme activities (nmol MUF tile^{-1} h^{-1}) for tiles incubated in sunlight-exposed or control water from pasture or native forest subsurface flowpath. None of the enzyme activities differed significantly between light and dark treatments in pasture water, all enzymes except Ace showed significant light/dark differences in native forest water. Each value is the average activity for tiles from four separate incubation containers.

	Alpha		Beta		Nag		Xylo		Phos		Leu		Ace	
	Mean	SE	Mean	SE	Mean	SE	Mean	SE	Mean	SE	Mean	SE	Mean	SE
Field sites														
Pasture														
GW	0.20	0.12	0.20	0.08	0.07	0.03	0.05	0.02	0.29	0.06	0.24	0.06	0.06	0.03
Sub	0.63	0.39	0.43	0.17	0.12	0.03	0.33	0.22	0.98	0.15	0.73	0.16	0.91	0.24
Surf	0.16	0.04	0.19	0.06	0.08	0.04	0.08	0.03	0.59	0.31	0.32	0.08	0.17	0.08
Pine														
GW	0.14	0.04	0.29	0.06	0.05	0.01	0.06	0.01	0.23	0.05	0.26	0.03	0.16	0.05
Sub	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Surf	0.22	0.06	0.35	0.07	0.20	0.07	0.16	0.02	0.38	0.10	0.49	0.07	0.05	0.01
Native														
GW	0.15	0.04	0.31	0.08	0.06	0.01	0.10	0.03	0.23	0.06	0.29	0.13	0.08	0.06
Sub	0.32	0.10	0.73	0.10	0.09	0.05	0.11	0.06	0.32	0.05	0.32	0.22	0.39	0.33
Surf	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Photolysis experiment														
Pasture														
Dark	0.13	0.03	0.25	0.07	0.04	0.00	0.09	0.02	0.81	0.09	0.38	0.03	1.20	0.32
Light	0.09	0.01	0.12	0.02	0.05	0.00	0.06	0.01	0.85	0.20	0.48	0.05	1.18	0.22
Native														
Dark	0.05	0.01	0.11	0.02	0.05	0.00	0.04	0.01	0.13	0.01	0.31	0.02	0.44	0.04
Light	0.32	0.03	0.56	0.04	0.29	0.03	0.30	0.04	0.24	0.05	0.97	0.11	0.51	0.21

light exposure on the ability of pasture subsurface water to support bacterial growth (Fig. 5A). Similarly, bacterial respiration was increased approximately twofold following exposure of native subsurface water to sunlight, but there was no effect for pasture subsurface water (Fig. 5B). The quantity of epilithic biofilm recovered from tiles followed treatment effects on bacterial growth, with a statistically significant ($p = 0.03$) 50% increase in biofilm from tiles incubated in native subsurface water following sunlight exposure but no difference for pasture subsurface water (data not shown).

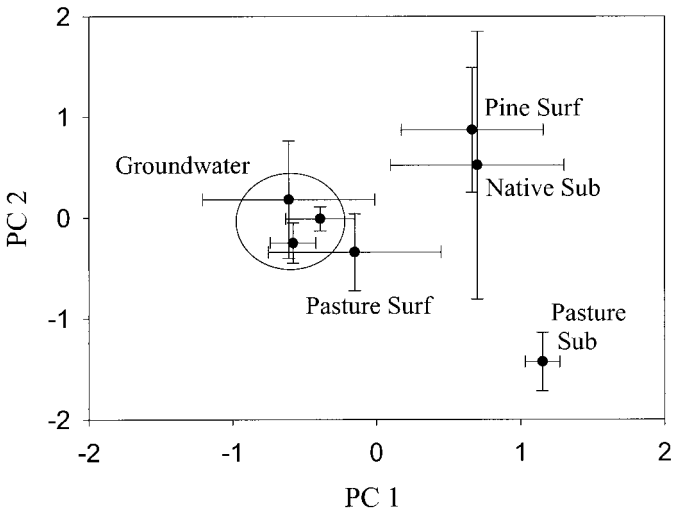

Fig. 2. Plot of sample scores on first two principal components, which together account for about 70% of the total variance in the data set. Principal components are linear combinations of the seven enzyme activities. Each point is the mean PCA score derived from tiles incubated in the source waters described above (±1 SE). Values within the circle are all groundwater locations.

Discussion

The largest and most consistent differences we observed in DOC composition and ability to support bacterial growth were related to locations along the pasture flowpaths. Water from the pasture surface flowpath differed more than twofold from pasture groundwater in its ability to support bacterial productivity. The shift in relative enzyme activities scores for tiles incubated in pasture subsurface water compared to the parent groundwaters suggests differences in the composition of these DOC pools. Therefore, water traversing these near-stream flowpaths in a pasture catchment results in a very different quantitative and qualitative contribution of DOC to the stream than if that groundwater had been delivered from seeps directly to the stream channel. Surface flows in pine catchments also caused large changes in DOC fluorescence, enzyme fingerprints, and bacterial production, so this land use will also have particularly strong effects on DOC delivered to the stream channel. Subsurface flowpaths in the native forest catchment did not have a large effect on either DOC composition or bacterial growth. This suggests the presence/absence of these riparian wetland flowpaths in native forest has less net effect on DOC delivered to the stream channel.

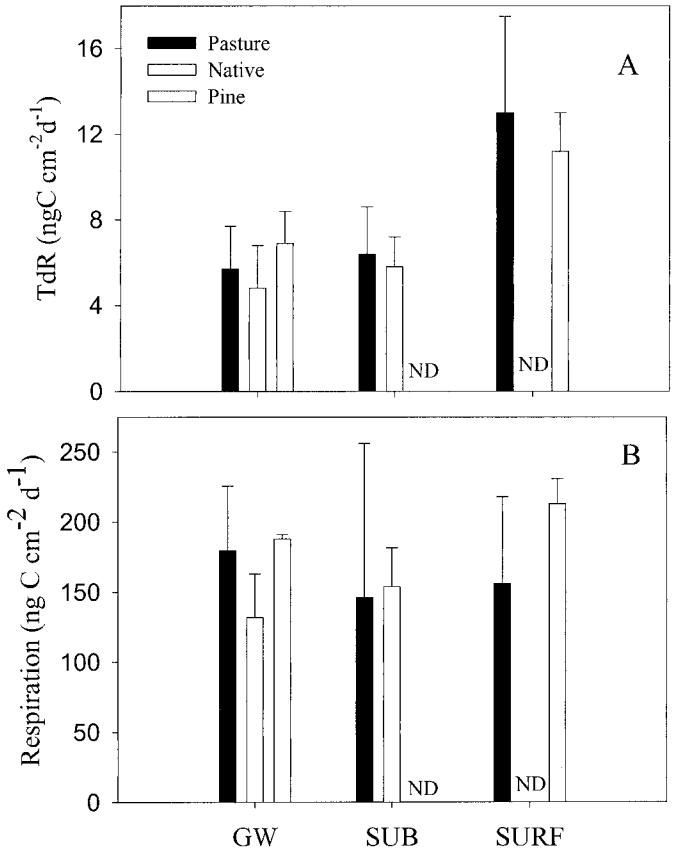

Fig. 3. (A)Thymidine incorporation into DNA for tiles incubated in water from the three land uses and flowpath positions. Each point is the mean of tiles from triplicate incubation containers ±1 SE. ND = no data. (B) Respiration rates for incubation containers containing tiles incubated with the various treatment waters. Values are means of three replicate tubes (±1 SE) for a given water source, each containing eight tiles.

In contrast to the near-stream flowpath differences we have documented for two of the three land uses, there was no difference in DOC concentrations or extracellular enzyme signatures produced by microbes exposed to groundwaters from these land uses. Apparently, in this geological system, any land-use–induced change in DOC occurring as water moved from precipitation through surface soils into the groundwater pool has disappeared (or never occurred) by the time groundwater reemerges near the stream bank. Shifts in land use will therefore affect the quantity and nature of DOC delivered to the stream due to changes occurring within the near-stream flowpaths rather than during groundwater recharge within the hillslope system.

Although the quantity and composition of DOC in groundwater from the three land uses was similar, there were large differences in groundwater nitrate-N between the native forest and the pine and pasture catchments. Differential effects of land use, i.e., similarity in groundwater DOC among catchments contrasted with large differences in nitrate, demonstrate that different solutes are influenced at different points along the soil water–groundwater–riparian flowpath.

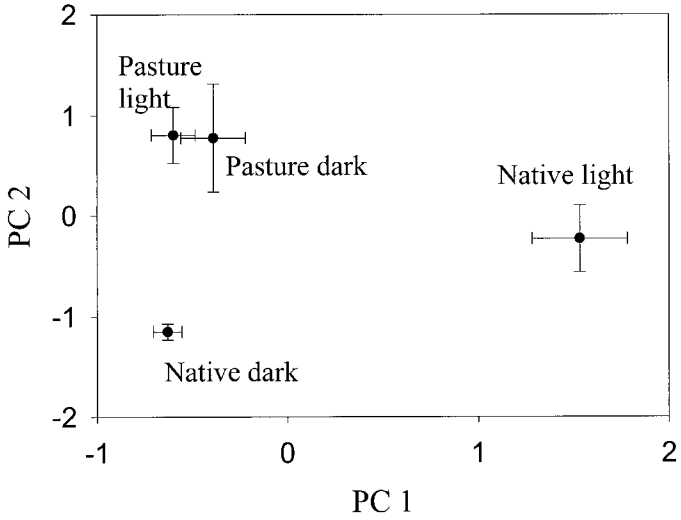

Fig. 4. Mean sample scores for enzyme activities on tiles incubated in the light and dark treatments of native and pasture subsurface water. The first two principal components together account for 90% of the total variance. Each point is the mean of tiles from four replicate tubes incubated with water from one of the source/light treatments (±1 SE).

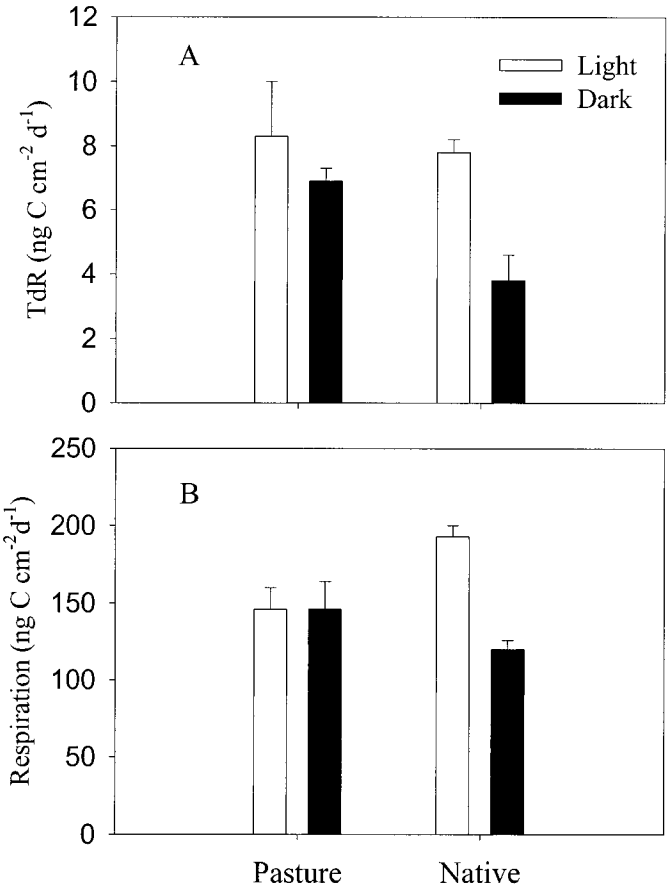

Fig. 5. (A) Thymidine incorporation and (B) respiration for tiles incubated in the light and dark treatments of native and pasture subsurface water. Each point is the mean (±1 SE) of four replicate tubes incubated with water from one of the source/light treatments.

A wide variety of mechanisms might be invoked to explain the differences among flowpaths in DOC quantity and composition. Vegetation, plant litter, or soil organic matter differences among catchments might supply different types of DOC to water moving along flowpaths. Alternatively, differences in residence time (contact time) might explain the changing nature of DOC in the flowpaths. The most obvious physical difference among flowpaths in pasture versus native forest catchments is the high organic fine sediments near the stream bank in the pastures (Davies-Colley 1997; Nguyen and Downes 1999). Organic matter may release DOC and fine sediments will reduce flow velocities, so either or both of these characteristics may contribute to changes in DOC.

In contrast to the pasture flowpath, water traversing native forest soils seems to undergo only slight alteration since resultant bacterial production does not differ among flowpath position. Enzyme fingerprints for groundwater and subsurface water in the native forest catchment are more similar than the groundwater and subsurface water in the pasture catchment. Whether the less dramatic change in the native forest flowpath is due to different microbiological and geochemical reactions, potential nitrogen limitation of microbes in the native flowpath, or simply shorter contact time is not known. The net effect is that there is less alteration of groundwater DOC moving along these flowpaths toward the stream channel.

Surface water in the pine catchment was quite distinct from groundwater both in enzyme fingerprint and ability to support bacterial growth. Surface water leaching of DOC from pine litter may lead to higher concentrations of total DOC as well as significant shifts in composition indicated by changes in fluorescence and enzyme fingerprints. The ratio of fluorescence at 450/500 has been proposed as an indicator of DOC composition (McKnight et al. 2001) with lower ratios associated with greater amounts of aromatic carbon. Differences among catchments and along flowpaths suggest groundwater has low amounts of aromatic material, whereas pine surface water and pasture subsurface waters have a greater contribution from this class of compounds. The surface water from the pine catchment supported high bacterial growth, suggesting that conifer-derived DOC is available to stream microbial communities.

Groundwater DOC from all land uses was capable of supporting bacterial growth at rates not significantly lower than some of the water sources with higher concentrations of DOC. When growth is normalized to bulk DOC and expressed as bacterial production per unit carbon, tiles incubated in pasture groundwater have roughly sixfold higher bacterial growth rates per unit DOC than pasture subsurface water. Although groundwater DOC concentrations are low, their ability to support appreciable bacterial growth suggests either (1) the carbon is directly available for uptake and metabolism and/or (2) the bacteria can acquire groundwater DOC via extracellular enzymes.

One advantage of the enzyme fingerprint approach to characterizing DOC composition is that the loadings of enzymes on the principal components can be used to interpret which biochemical classes of compounds differ across land use or along flowpaths. For instance, the scores for pine surface water are in the upper right-hand portion of the plot (Fig. 2). Mean xylosidase activity on tiles incubated with pine surface water was significantly greater than tiles incubated in pine catchment groundwater ($p = 0.03$, $F = 11.2$). In an earlier study, xylosidase activity on stone biofilms was higher in streams draining pine catchments than activity in biofilms from either pasture or native streams (Findlay et al. 1997), which suggests xylan (hemicellulose) may be a significant proportion of the bioavailable carbon in surface water draining pine catchments.

Leucine aminopeptidase was one of the most powerful enzymes in discriminating among locations. LEU-AP and esterase load positively on PC1 and negatively on PC2, so sites with high activities of these enzymes will plot in the lower right-hand portion of Fig. 2. Enzyme activities from tiles incubated in pasture subsurface water plot in the lower right portion, which suggests peptides are a significant carbon source for these biofilms. High concentrations of amino acids in pasture subsurface water provide independent evidence that protein/peptide degradation is an important component of DOC metabolism at this point in the pasture flowpath.

Interpretation of peptidase activity is complex for at least two reasons; it is an amphibolic enzyme, potentially important in both/either carbon degradation or nitrogen acquisition, and secondly there are land-use-specific differences in apparent control on LEU-AP activity. In the pasture flowpath there is a significant positive relationship between LEU-AP and total amino acids (Fig. 6A), which implies either that increases in amino acid concentrations induce synthesis of this peptidase, or the amino acids are actually accumulating as excess end products of peptidase activity. There was no relationship between LEU-AP and amino acids for the forested catchments (Fig. 6C). In the pasture catchment flowpaths there is a significant negative relationship between LEU-AP and nitrate, which suggests repression of LEU-AP when DIN availability is high (Fig. 6B) or LEU-AP stimulation to acquire nitrogen for growth when nitrate is low.

Dissolved organic nitrogen (DON) is often a major portion of nitrogen export from terrestrial ecosystems (Hedin et al. 1995), and our results show that at least some of the enzymes important in degradation of DON can vary across land uses. In a series of experiments, DON stimulated aminopeptidase activity under N-limiting conditions (Stepanauskas et al. 1999), which supports the idea that the relative amounts of organic and inorganic N will influence degradation of terrestrial DON.

Not surprisingly, inorganic nutrients also affect the phosphorus-acquiring enzyme, with a negative correlation between phosphatase activity and DRP when all data were combined ($r = -0.43$, $p = 0.03$). Relatively high concentrations of DRP in groundwater may suppress phosphatase activity, whereas depletion of DRP in ''downstream'' flowpath locations (Table 1) allows increasing levels of phosphatase activity.

Our analysis of DOC composition and bioavailability together with dramatic changes in water chemistry documents the importance of near-stream processing in affecting the material fluxes from terrestrial ecosystems to the stream. Riparian areas and wetlands have long been appreciated as sites of nutrient processing and retention (e.g., Groffman et

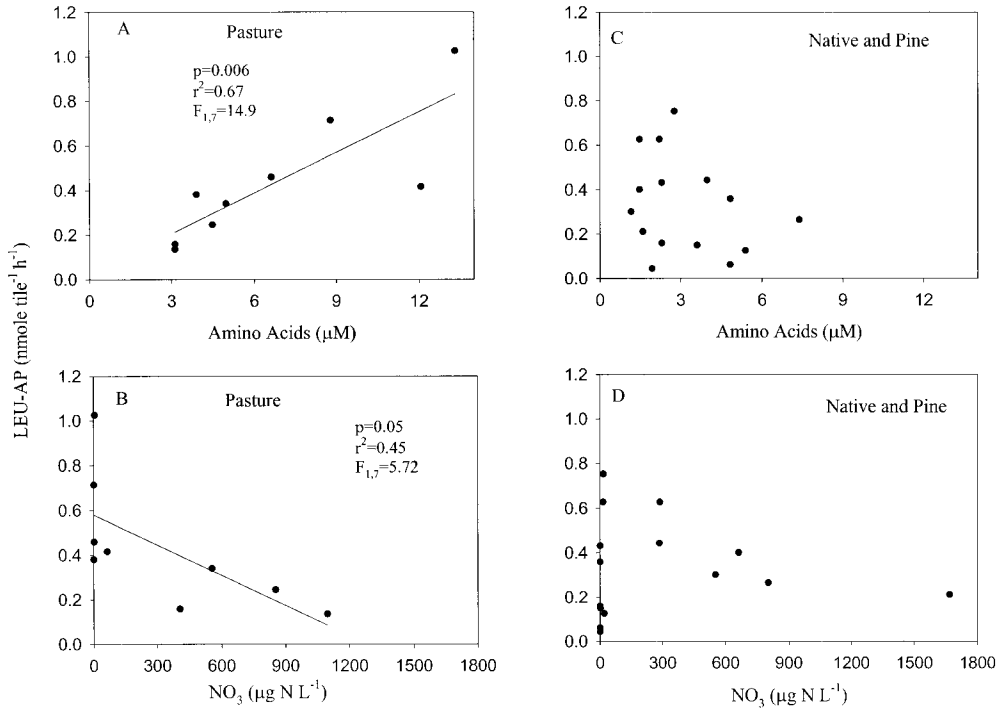

Fig. 6. (A), (C) Relationships between leucine aminopeptidase activity on tiles and total amino acid concentration and (B), (D) nitrate in treatment water for pasture and forested catchments.

al. 1992; Jordan et al. 1997) and are recognized as sources of DOC (e.g., Hinton et al. 1998; Aitkenhead et al. 1999). The physical differences (soil type, organic content, residence time in the flowpath) between the pasture flowpaths and other catchments result in relatively long slow flowpaths in pasture riparian zones, allowing shifts in DOC amount and composition and changes in inorganic nutrient concentrations.

Another obvious indirect effect of vegetational differences among catchments is the exposure of streamwaters to sunlight and potential photolysis. Photolysis is known to result in changes in fluorescence and optical properties of DOC in natural waters (Moran and Zepp 1997) and in many cases also causes increases in apparent bioavailability of carbon (Opsahl and Benner 1998) and nitrogen (Bushaw et al. 1996). Interactions between humic materials, iron, and light can alter redox biogeochemistry of surface waters (Voelker et al. 1997). Photolysis of streamwater DOC has not been examined extensively, although Wiegner and Seitzinger (in press) found land-use–specific effects of photolysis on nitrate generation. Light-exposure of subsurface water from the native catchment caused large shifts in relative enzyme activity and the expected increase in bacterial productivity, respiration, and accumulated biomass of biofilms grown in the presence of that DOC. In contrast, pasture subsurface water showed no displacement of enzyme fingerprints and no stimulation of bacterial growth despite the 35% change in fluorescence yield (Fig. 5). Although there were differences in fluorescence characteristics, we did not see any evidence of photobleaching, and absorbances at 270 and 340 nm were unaffected by our light exposures. Opsahl and Benner (1998) also found significant changes in DOC composition (lignin components) that were not associated with changes in UV absorbances. Apparently the photochemical processes affecting the fluorescent and absorptive properties in these waters can be independent of the photochemical changes, causing shifts in DOC composition (enzyme fingerprints) and bioavailability (bacterial growth). The UV absorbance (270 nm) was higher for the native subsurface than for the pasture water, and perhaps the magnitude of any photolytic effect will be predictable from simply knowing that a water sample is highly absorptive in the UV region. Absorbance at 440 nm was a good predictor of the magnitude of the photolytic stimulation of bacterial cell accumulation in a series of samples from a humic lake (Reche et al. 1998). Absorbance at 365 was significantly correlated with enhancement of bacterial yield in a range of water samples representing groundwaters, streams, and lakes (Bertilsson 1999). It has been proposed that UV exposure will have negative effects in systems with relatively high amounts of labile DOC and stimulatory effects in cases where DOC is fairly refractory (Obernosterer et al. 1999). In aggregate, photolytic effects can be biologically significant, but we do not have simple predictors of when light exposure might lead to changes in DOC metabolism.

Overall our results show that land use can affect the quantity and quality of dissolved organic matter moving from terrestrial ecosystems into streams. These effects seem to be as much a function of the physical nature of the riparian flowpaths as the vegetational differences, although the presence/absence of trees indirectly affects slumping of hillslope soils into the near-stream area and has direct effects on local light conditions. Whatever the mechanism, different flowpath locations embedded in different land uses generate sub-

stantial variability in DOC concentration, composition, and bioavailability. Photolysis alters the nature of some types of DOC but effects seem to be separated from measured changes in fluorescence or photobleaching. As humans continue to alter land use and land cover, these changes will spread in subtle yet important ways to influence carbon export and metabolism in streams and other aquatic ecosystems.

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