The origin and function of dissolved organic matter in agro-urban coastal streams

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[1] Streams draining urban and agriculture catchments are often a source of inorganic nutrients to downstream aquatic ecosystems, but little is known about how changes in land use influence the quality and biodegradability of dissolved organic matter (DOM). We used parallel factor analysis of excitation-emission fluorescence spectroscopy and biodegradation incubations to examine how DOM composition influences bioavailable dissolved organic carbon (DOC) in surface waters of urban and agricultural catchments during summer (low flow), winter (high flow) and spring (flow recession). Percent bioavailable DOC was variable for all catchments (2–57%) and negatively related to percent humic-like fluorescence, but positively related to percent protein-like fluorescence and simple fluorescence metrics of DOM precursor material (fluorescence index and β:α values). Conversely, highly variable DOC concentrations (2–140 mg L^{-1}) were negatively related to protein-like fluorescence and positively related to humic-like fluorescence. Elevated concentrations of DOC (>30 mg L^{-1}) in agro-urban streams revealed fluorescence indices (<1.3) typical of wetland and forest-dominated ecosystems, suggesting that enriched stream DOM is either derived from the destabilization of legacy soil carbon or currently produced from remnant wetlands and patches of native vegetation. Overall, we demonstrate that fluorescence characteristics can be used to predict bioavailable DOC in human-dominated catchments to better understand the flow of carbon and nutrients in aquatic food webs for improved monitoring and management of coastal ecosystems.

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1. Introduction

[2] The imprint of human activities on biogeochemical cycling is evident in coastal regions where high population density, and associated carbon and nutrient loading contribute to the eutrophication of coastal ecosystems [*Valiela et al.*, 1992]. In Australia, continental population density is low, but coastal regions are especially vulnerable because more than 85% of the population lives within 50km of the coast, mainly concentrated in capital cities. For example, the Swan-Canning estuary that bisects Perth in Western Australia has experienced an increase in algal blooms and hypoxia in recent decades due largely to increased anthropogenic contributions of nitrogen and phosphorus [*Robson and Hamilton*, 2003]. While the impact of anthropogenic contributions of inorganic N and P to estuarine algal production is widely studied, little is known about the ecological role of terrigenous dissolved organic matter (DOM), which is often the major source of fixed carbon to coastal waters [*Hedges et al.*, 1997].

[3] The export of land-derived DOM provides a linkage between terrestrial and aquatic ecosystems, and a carbon [*Wetzel*, 1992] and nutrient [*Keil and Kirchman*, 1991] substrate to aquatic heterotrophs. Microbial oxidation of DOM to CO_2 in fluvial networks is an important component of the global carbon budget [*Battin et al.*, 2008] and in some cases high levels of DOM can contribute to anoxia in estuarine waters [*Rixen et al.*, 2008]. The quantity and quality of terrestrial DOM entering aquatic ecosystems depends largely on precursor organic material and hydrologic flowpaths. For instance, stream water concentrations of dissolved organic carbon (DOC) and nitrogen (DON) often increase during storms due to hydrologic mobilization of soil organic matter [*Petrone et al.*, 2006], and concurrent biochemical changes may also change the relative percentage of DOM that is degraded in aquatic ecosystems [*Fellman et al.*, 2009; *Hood et al.*, 2006; *Vidon et al.*, 2008]. Moreover, broad-scale changes in land use, such as conversion of forests and

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wetlands to agriculture can alter the chemical complexity of DOM [*Wilson and Xenopoulos*, 2009], and anthropogenic pollution may increase the bioavailability of DOM in agricultural [*Williams et al.*, 2010] or urban streams [*Wiegner and Seitzinger*, 2001]. However, few studies have shown a connection between the biochemical composition of DOM and its lability in mixed land use coastal catchments.

[4] The characterization of DOM by fluorescence excitation-emission matrix (EEM) spectroscopy combined with parallel factor analysis (PARAFAC [*Stedmon et al.*, 2003]) has proliferated in the last several years to trace DOM dynamics in freshwater and marine ecosystems. In particular, PARAFAC analysis of EEMs has been used to characterize changes in DOM associated with soil type [*Fellman et al.*, 2008], land use [*Williams et al.*, 2010; *Wilson and Xenopoulos*, 2009], geology [*Yamashita et al.*, 2010], and streamflow [*Fellman et al.*, 2009], as well as to quantify riverine inputs to coastal waters [*Kowalczuk et al.*, 2010]. For instance, *Wilson and Xenopoulos* [2009] used fluorescence DOM characterization to show an increase in the contribution of recently produced DOM along a land use gradient of increasing cropland coverage and decreasing wetland coverage. Moreover, simple fluorescence metrics, such as the fluorescence index (FI) and the freshness index (β:α) were used to show that this recently produced DOM was less structurally complex than wetland DOM.

[5] In the Swan-Canning catchments of Western Australia, recent studies have shown that C and N loads to the estuary are dominated by DOC and DON with relatively minor contributions from particulate C and N [*Petrone*, 2010]. Perennial urban drains and streams contribute the greatest DOC and DON loads per unit area and are the main source of terrestrial carbon and nutrients during the dry summer months. In ephemeral agricultural streams, DOM inputs are greatest during the wet winter months and DOC and DON concentrations increase dramatically with flow. Therefore, a greater understanding of the timing, biochemical composition, and biodegradability of DOM exported from agro-urban catchments may be particularly important for evaluating potential impacts on downstream aquatic ecosystems.

[6] Our objective in this study was to examine the relationship between DOM concentration, fluorescence characteristics and bioavailability in mixed land use catchments where rainfall and flow are strongly seasonal. We sampled streams during autumn low flow (April), winter high flow (August), and flow recession in spring (November), and focused on agricultural and urban catchments that are a priority for rehabilitation due to high DOM loading. We sought to answer one major research question: Can ecological function (e.g., DOM bioavailability) be quantitatively linked with the origin of DOM using fluorescence characteristics to assess if this cost effective and simple technique can be incorporated into monitoring programs for improved management of coastal streams and estuaries?

2. Study Site

[7] The Swan-Canning estuary bisects the city of Perth in southern Western Australia, and encompasses numerous subcatchments, which vary widely in drainage area, land use, soil type, and underlying geology. The climate is Mediterranean with two-thirds of the annual rainfall (850–1200 mm) occurring during the winter months of June through September. All four study catchments lie on the Swan Coastal Plain and are underlain by highly weathered quaternary alluvial and aeolian deposits known as Bassendean Sands, which are siliceous with little clay or silt content and have little capacity to adsorb DOM [*He et al.*, 1998].

[8] Once extensive lakes and wetlands on the coastal plain have been mostly drained for urban development and agriculture, but remnant permanent and ephemeral wetlands dominated by the Myrtaceae, Proteaceae and Restionaceae are underlain with humic podzols. Native vegetation dominated by a mix of sclerophyllous trees and shrubs (including *Eucalyptus, Melaeluca, Bansksia* and *Allocasuarina*) are found throughout all catchments on well drained soils. Mills St Drain and Bannister Creek have been largely cleared for industrial, commercial and residential use and now have significant impervious surfaces that are underlain by Bassandean sands with shallow groundwater (<3 m below the surface). Bannister Creek is a mixture of natural stream reaches and incised drains whereas Mill St Drain is an incised urban drain network that facilitates movement of shallow groundwater to the Swan-Canning estuary. Southern River and Ellen Brook are mainly natural waterways with fewer modified drain tributaries. Both catchments contain remnant native bushland but were largely cleared for agriculture, and a shift from agriculture to urban land use is now taking place with ongoing development. Additionally, Southern River and Ellen Brook receive base flow discharge from large and deeper groundwater systems, and seasonally perched wetlands develop in both catchments during winter. Please see *Petrone* [2010] for further details on catchment characteristics and seasonal hydrology.

3. Methods

3.1. Catchment Land Use, Discharge, and Sample Collection

[9] We sampled stream water from two urban catchments (Bannister Creek, 23 km^2 and Mills St Drain, 10 km^2) and two predominately agricultural catchments (Southern River, 149 km^2 and Ellen Brook, 664 km^2; Figure 1) during 2009. The larger agricultural catchments were located on the urban fringe, and the smaller urban catchments closer to the city center. Full details of catchment land cover characteristics, seasonal streamflow and water chemistry are covered elsewhere [*Petrone*, 2010].

[10] Surface water was collected during autumn low flow (28 April), winter high flow (4 August), and flow recession in spring (10 November) from all four catchments. We sampled three tributaries of the main stem and the catchment outlet in Bannister Creek, Mills St Drain and Southern River. In the larger Ellen Brook catchment, we sampled at least six tributaries, three sites of the main stem approximately 10 km apart, including the catchment outlet. Our intent for this sampling design was to capture spatial variability within the four catchments and to evaluate how seasonal changes in flow affect the composition and lability of DOM in catchments of varying land use. However, the ephemeral agricultural catchments were only sampled in winter and spring owing to negligible flows in the autumn while the perennial urban catchments were sampled for all three periods. Some tributaries of Ellen Brook were also dry

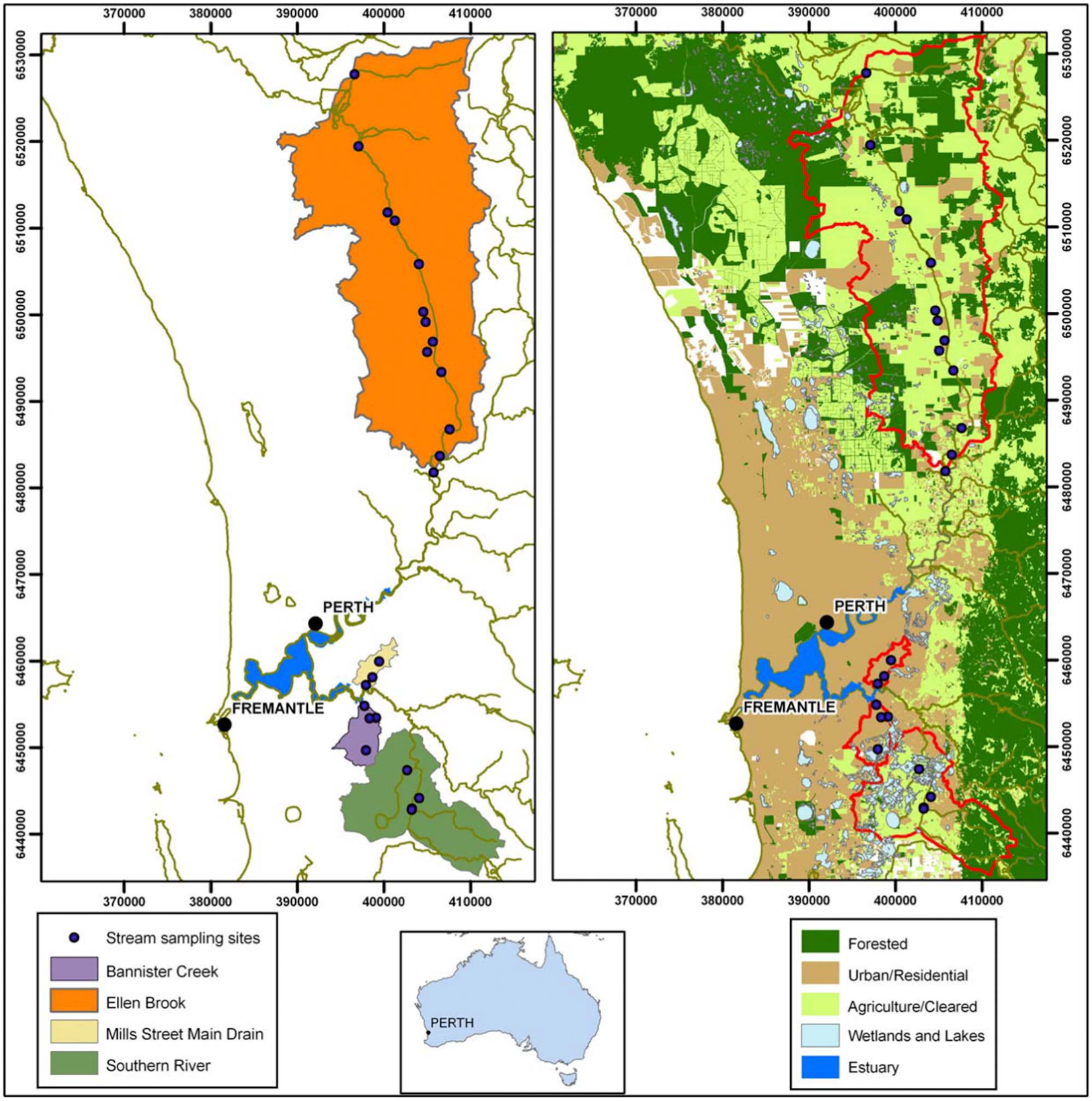

Figure 1. Map of study catchments with sampling sites, including (left) major stream and river networks, and (right) major land use with catchment area in red outline.

in November (see Table 2 for sample numbers during the sampling periods).

[11] Approximately 1 L of water was collected from each stream in acid-washed plastic bottles. Stream water was filtered through precombusted glass fiber filters (Whatman GF/F 0.7 nominal pore size) within 24 h. Samples were stored on ice during transport to the laboratory and were refrigerated at 4°C for up to one week prior to chemical analysis or DOM bioavailability incubations. Samples for bioavailability incubations were further filtered in the laboratory through 0.2 μm polyvinylidene Millipore filters to remove the majority of microbes.

[12] We used the Perth airport (Bureau of Meteorology, 009021; http://www.bom.gov.au/) as a measure of daily precipitation. Stream discharge is continuously monitored by the Western Australia Department of Water (http://www.water.wa.gov.au/) on an hourly basis. Weirs are established at all sites and stage height is converted to discharge with established rating curves.

3.2. Bioavailability Incubations

[13] The bioavailability of DOC (BDOC) was quantified by measuring changes in DOC concentration over a one month laboratory incubation. Water from each stream was placed into three replicate 40 mL plastic vials following a modified procedure from *Fellman et al.* [2009] and *Petrone et al.* [2009]. Prior to the incubation, water samples were warmed to room temperature (25°C) and 2 mL of inoculum

Table 1. Description of the Eight Different Fluorescence Components Identified by PARAFAC in This Study

Component	Excitation and Emission Maxima (nm)	Component Name[a]	Description
1	excitation 240, emission 430–470	A (1), 1 (2), 2 (3), 1 (4), 1 (5)	Widespread humic-like, but is most common in wetlands and forest streams
2	excitation 290–300, emission 500–516	2 (2), 5 (3), 6 (4), 2 (5)	Humic-like, correlated with aromatic C content
3	excitation 240, emission 410–420	3 (2)	Widespread humic-like component
4	excitation 275–280, emission 336–356	T (1), 7 (2), 8 (3), 5 (4), 5 (5)	Tryptophan-like, fluorescence resembles free tryptophan
5	excitation 320–340, emission 416–450	C (1), 4 (2), 1 (3)	Humic-like, high molecular weight and aromatic
6	excitation 240, emission 376–390	12 (3)	Humic-like, correlated with aliphatic C content
7	excitation 290–295, emission 410–420	M (1), 5 (2), 3 (3), 2 (4)	Marine humic-like, but can be found in wastewater, wetland and forest streams
8	excitation 260–275, emission 304–308	B (1), 8 (2), 13 (3)	Tyrosine-like, fluorescence resembles free tyrosine

[a]References are shown in parentheses: 1, *Coble* [1996]; 2, *Stedmon and Markager* [2005]; 3, *Cory and McKnight* [2005]; 4, *Williams et al.* [2010]; 5, *Yamashita et al.* [2010].

was added to 30 mL of sample water (1:15 inoculum to water). In all samples, we used a common bacteria inoculum from an upper estuary site that receives water from the subcatchments to evaluate how estuarine microbial communities respond to seasonal changes in DOM composition from subcatchments. The microbial inoculum was prepared 1 day prior to the start of the incubation using a sediment slurry (1:3 sediment to water) collected from the upper estuary site. All vials were incubated in the dark at 25°C in a constant temperature room for one month. Experimental results are reported as mg C L^{-1} consumed over the course of the experiment or as percent DOC consumed of the initial DOC concentration.

3.3. Fluorescence Characterization of DOM and PARAFAC Modeling

[14] Fluorescence excitation-emission matrices (EEMs) of DOM were measured on a Varian Cary Eclipse fluorometer with a 1 cm quartz cuvette by measuring fluorescence intensity across excitation wavelengths ranging from 240 to 450 nm (5 nm increments) and emission wavelengths ranging from 300 to 600 nm (2 nm increments). All water samples were warmed to room temperature before fluorescence analysis. All samples were diluted to an optical density of 0.02 at 300 nm to minimize inner filter effects [*Green and Blough*, 1994]. An EEM of Milli-Q water run on the same day was subtracted from each sample EEM and all EEMs were corrected for instrument bias using correction files provided by Varian. Sample EEMs were Raman normalized using the area under the water Raman peak at excitation wavelength 350 nm.

[15] Parallel factor analysis (PARAFAC), a multivariate modeling technique that decomposes the fluorescence signature of DOM into individual fluorescence components, was used to analyze EEMs [*Cory and McKnight*, 2005; *Stedmon et al.*, 2003]. PARAFAC was conducted using the PLS_toolbox version 3.7 in MATLAB [*Eigenvector*, 2006] following the procedures of *Stedmon et al.* [2003]. A triangle of zeros was inserted into the area of missing data to remove Raman and Rayleigh scatter. To incorporate environmental variability and assist in DOM source discrimination, the PARAFAC model included 60 water samples collected from urban and agricultural streams in Swan-Canning catchments and 60 estuarine water samples (data array consisted of 120 EEMs with 151 emission and 43 excitation wavelengths). Our PARAFAC model identified a total of eight fluorescence components within the EEMs (Table 1), and model results are described in more detail elsewhere [*Fellman et al.*, 2011]. Split-half validation was used to determine the appropriate number of components [*Stedmon et al.*, 2003]. In addition, we calculated the fluorescence index (FI) at excitation 370 nm as the ratio of emission intensities at 450 and 500 nm [*McKnight et al.*, 2001] and the freshness index (β/α) values according to *Parlanti et al.* [2000] and *Wilson and Xenopoulos* [2009] to help identify DOM source material and to asses the relative contribution of recently produced DOM.

3.4. Analytical Chemistry and Data Analysis

[16] An autoanalyzer was used to measure NH_4-N by the phenol hypochlorite method and NO_3-N by cadmium reduction. DOC was measured by nonpurgeable organic carbon combustion catalytic oxidation/NDIR and total dissolved nitrogen (TDN) by chemiluminescence on a Shimadzu TOC-VCPH with a TNM-1 module. DON was calculated as the difference between TDN and dissolved inorganic N (DIN = NO_3^- + NH_4^+). Soluble reactive phosphorus (SRP) was measured by the molybdate-antimony technique on a spectrophotometer [*Murphy and Riley*, 1962].

[17] We used linear regression to assess the relationship between BDOC (as percent of intitial DOC concentration) and DOC:DON and fluorescence PARAFAC components. Logarithimic regressions were used to compare DOC:DON and fluorescence PARAFAC components with DOC concentration [*Sigmastat*, 2009].

4. Results

4.1. Stream Discharge and C, N, and P Concentrations

[18] Rainfall was below average for Perth in 2009 with 616 mm recorded at the Perth airport compared to the 65 yearlong-term average of 783 mm. Nearly 90% of annual rainfall was in the winter months from May to September. The highest monthly rainfall was in July (145 mm), and the highest daily rainfall of 27 mm occurred on 19 July (Figure 2). Major peaks in flow were observed in late May for Mills St Drain and Southern River in response to three consecutive days of rain, and in the latter part of July and mid-August for all catchments. Flow recession began in late-September and low flows (<100 ML d L^{-1}) were again observed from October through December (Figure 2).

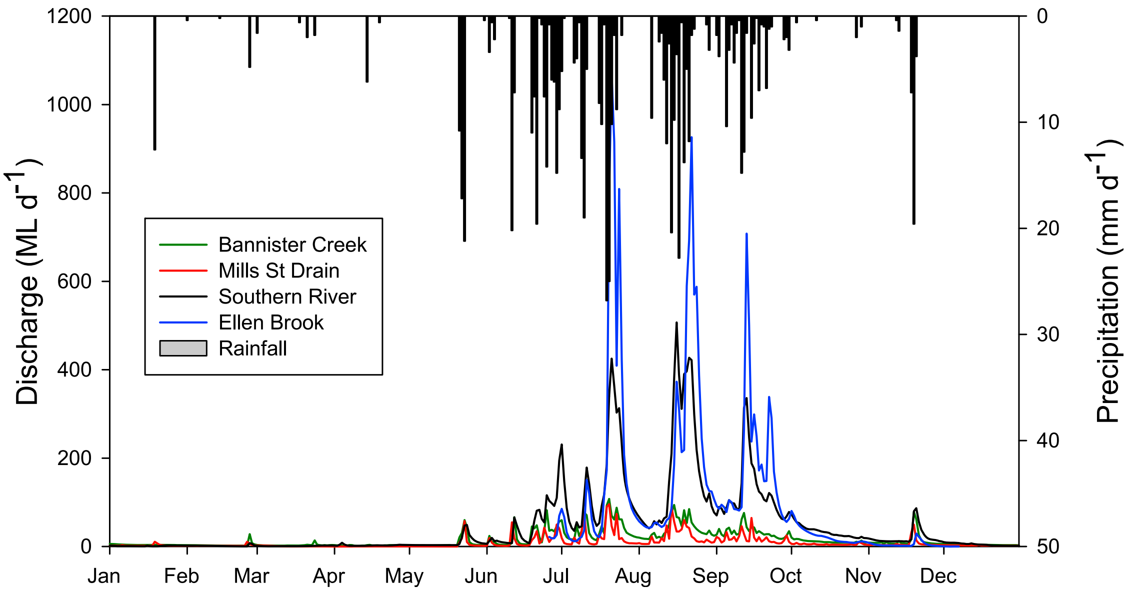

Figure 2. Hydrograph for Mills St Drain, Bannister Creek, Southern River and Ellen Brook and precipitation at the Perth International Airport during 2009.

[19] Mean concentrations of DOC and DON were variable (DOC from 3.7 to 55.1 mg L^{-1}; DON from 0.34 to 2.38 mg L^{-1}) across catchments and sampling seasons (Table 2). DOC and DON were especially high in the Ellen Brook catchment during winter (DOC > 50 mg L^{-1}; DON > 2.0 mg L^{-1}). For the remaining catchments, the greatest overall DOC and DON concentrations were observed in spring, and lower concentrations were observed for the urban catchments and some Southern River sites during high flow in winter. Concentrations of DOC and DON were highly correlated across catchments ($r^2 = 0.93$, $p < 0.0001$), but DOC was not related to inorganic N or P. Concentrations of DIN were typically lower than DON across catchments and season, and the highest concentrations of both DIN and SRP were found in the agricultural catchments (Table 2).

4.2. DOM Characteristics

[20] The spectral characteristics of the eight fluorescence PARAFAC components are outlined in detail elsewhere [*Fellman et al.*, 2011], and are similar to those published in freshwater [*Balcarczyk et al.*, 2009; *Yamashita et al.*, 2010] and marine environments [*Coble et al.*, 1998; *Stedmon and Markager*, 2005]. Humic-like components C1–3 and C5 all have emission maxima at wavelengths greater than 420 nm, and are considered aromatic and derived primarily from terrestrial higher plant material. Since these four components were highly correlated and behave similarly in the study catchments, we focus our discussion on humic-like C1. Components 6 and 7 have emission maxima at short wavelengths (<415 nm) and are considered less aromatic than the other four humic-like components. Component 6

Table 2. Flow and Mean (±SE) Stream C, N and P for the Urban and Agricultural Catchments During the Autumn, Winter and Spring Sampling[a]

Catchment	Dominant Land Use	Flow (ML d^{-1})	n	DOC Mean (mg/L)	DOC SE	DON Mean (mg/L)	DON SE	NO_3 Mean (mg/L)	NO_3 SE	NH_4 Mean (mg/L)	NH_4 SE	PO_4 Mean (mg/L)	PO_4 SE	DOC:DON Mean	DOC:DON SE
Autumn (April)															
Bannister Creek	Urban	2.8	4	26.4	1.6	1.00	0.05	0.104	0.069	0.086	0.034	0.033	0.010	26.5	1.6
Mills St Drain	Urban	0.2	4	13.0	0.5	0.67	0.02	0.115	0.040	0.108	0.041	0.028	0.006	19.5	0.8
Winter (August)															
Bannister Creek	Urban	17.3	4	11.5	3.1	0.36	0.10	0.273	0.059	0.107	0.026	0.038	0.006	32.4	1.7
Mills St Drain	Urban	5.9	4	3.7	0.1	0.34	0.07	0.159	0.006	0.096	0.028	0.044	0.004	11.2	2.3
Southern River	Agriculture	45.5	4	13.4	8.6	0.56	0.40	0.639	0.317	0.042	0.011	0.150	0.109	23.8	2.7
Ellen Brook	Agriculture	44.0	13	55.1	9.8	2.38	0.39	0.208	0.105	0.071	0.014	1.030	0.392	23.1	0.7
Spring (November)															
Bannister Creek	Urban	6.5	4	38.5	3.4	1.00	0.09	0.220	0.071	0.267	0.182	0.091	0.041	38.4	0.9
Mills St Drain	Urban	3.3	4	29.4	1.2	0.74	0.05	0.100	0.048	0.102	0.034	0.086	0.020	40.0	1.6
Southern River	Agriculture	12.3	4	22.5	10.9	0.94	0.36	0.126	0.051	0.038	0.020	0.102	0.046	23.8	2.3
Ellen Brook	Agriculture	2.7	10	41.9	5.1	1.49	0.18	0.186	0.151	0.028	0.015	0.447	0.076	28.1	2.2

[a]The number of stream sampling sites within each watershed ranged from 4 to 13, and all reported values are the average of all of the sites sampled.

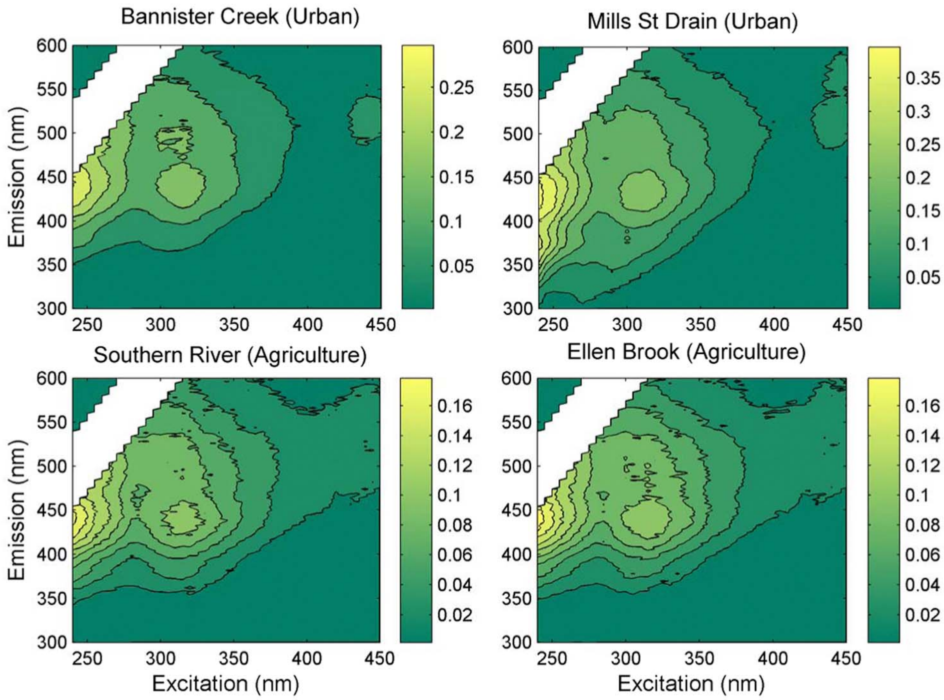

Figure 3. Excitation-emission matrices of stream water collected in winter (August) at the outlet of each subcatchment.

has previously been correlated with percent aliphatic C content [*Cory and McKnight*, 2005]. Protein-like C4 and C8 have fluorescence characteristics similar to tryptophan and tyrosine and can be an indicator of DOM lability and bacterial production [*Hudson et al.*, 2007]. Here we refer to the sum of the C4 and C8 components as “protein-like” fluorescence.

[21] Visual analysis of EEMs from streams at the four catchment outlets in August reveal a primary humic-like fluorescence peak at 240 nm excitation and 430–450 nm emission identified as C1 (Figure. 3). An additional humic-like peak at 240 nm and 384 nm emission was prominent in the Mill Street Drain EEM, but was less well developed for the other catchments. Protein-like peaks attributed to tyrosine-like and tryptophan-like fluorescence were visible in the urban Mills Street Drain EEM at 270–280 nm excitation and <350 nm excitation. However, these peaks were difficult to visually detect in EEMs where high humic-like fluorescence is observed (e.g., Southern River), although they were quantified in the PARAFAC model.

4.3. DOM Bioavailability and Fluorescence Characteristics

[22] For the urban catchments, BDOC values expressed as mass loss (mg L^{-1}) and as the percentage of initial DOC degraded (%) were low and least variable in autumn (Figure 4). Percent BDOC increased in winter for Mills St Drain, but was greatest for Bannister Creek in spring. Although greater percent BDOC was observed in winter for Mills St Drain, total BDOC changed little from autumn since DOC concentration was low. The greatest total BDOC was observed for Mills St Drain and Bannister Creek in spring when percent BDOC was moderate (~30%) and DOC concentrations were high. For the agricultural catchments, BDOC percent and mass loss followed similar patterns for each catchment between winter and spring. For example, Southern River percent BDOC was moderate (~25%) and BDOC mass loss was low on both dates while Ellen Brook with elevated DOC concentrations showed low percent BDOC yet high mass loss on both dates.

[23] Despite high within-catchment variability, there were consistent patterns in fluorescence components for individual catchments across sample dates. For example, Mills St Drain had the highest mean COMP 6%, protein-like %, FI and β:α, but the lowest humic-like C1% contribution across all catchments for autumn, winter and spring (Figure 4). Conversely, Ellen Brook had the lowest mean contribution of COMP 6 and protein-like fluorescence and FI and β:α values, but the highest contribution of humic-like fluorescence in winter and spring. In general, the range of FI (1.23–1.30) and β:α (0.45–0.50) for Bannister Creek, Southern River and Ellen Brook was indicative of terrestrial plant-derived DOM. Ranges of FI (1.33–1.42) and β:α (0.56–0.62) were consistently higher in Mills St Drain, and suggests a contribution from anthropogenic or autochthonous DOM. Ratios of DOC:DON ranged from 11.2 to 40.0 and were variable across catchments and between sampling periods (Table 2). For instance, Mills St Drain had the lowest average DOC:DON ratio in August (11.2), but was the greatest in spring (40.0). The DOC:DON range was smaller in Southern River and Ellen Brook (23.1 and 28.1) compared to Bannister Creek (27.1 to 38.4; Figure 4). Overall, we found a significant positive relationship between concentrations of BDOC and DOC ($R^2 = 0.51$, $p < 0.0001$).

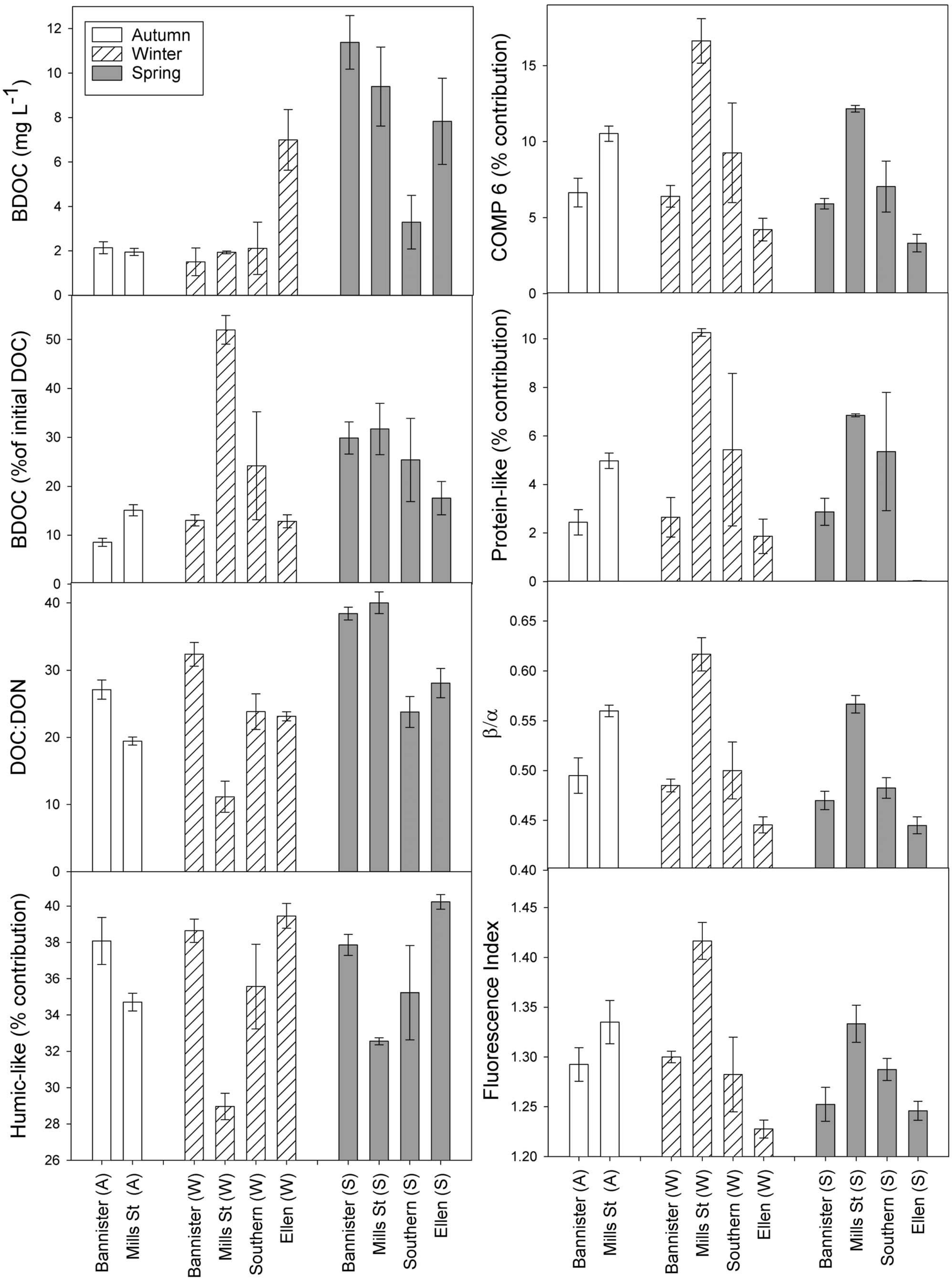

Figure 4. BDOC (as percent change and mg L^{-1}), DOC:DON, and fluorescence components/indices for catchments during the autumn, winter and spring sampling seasons.

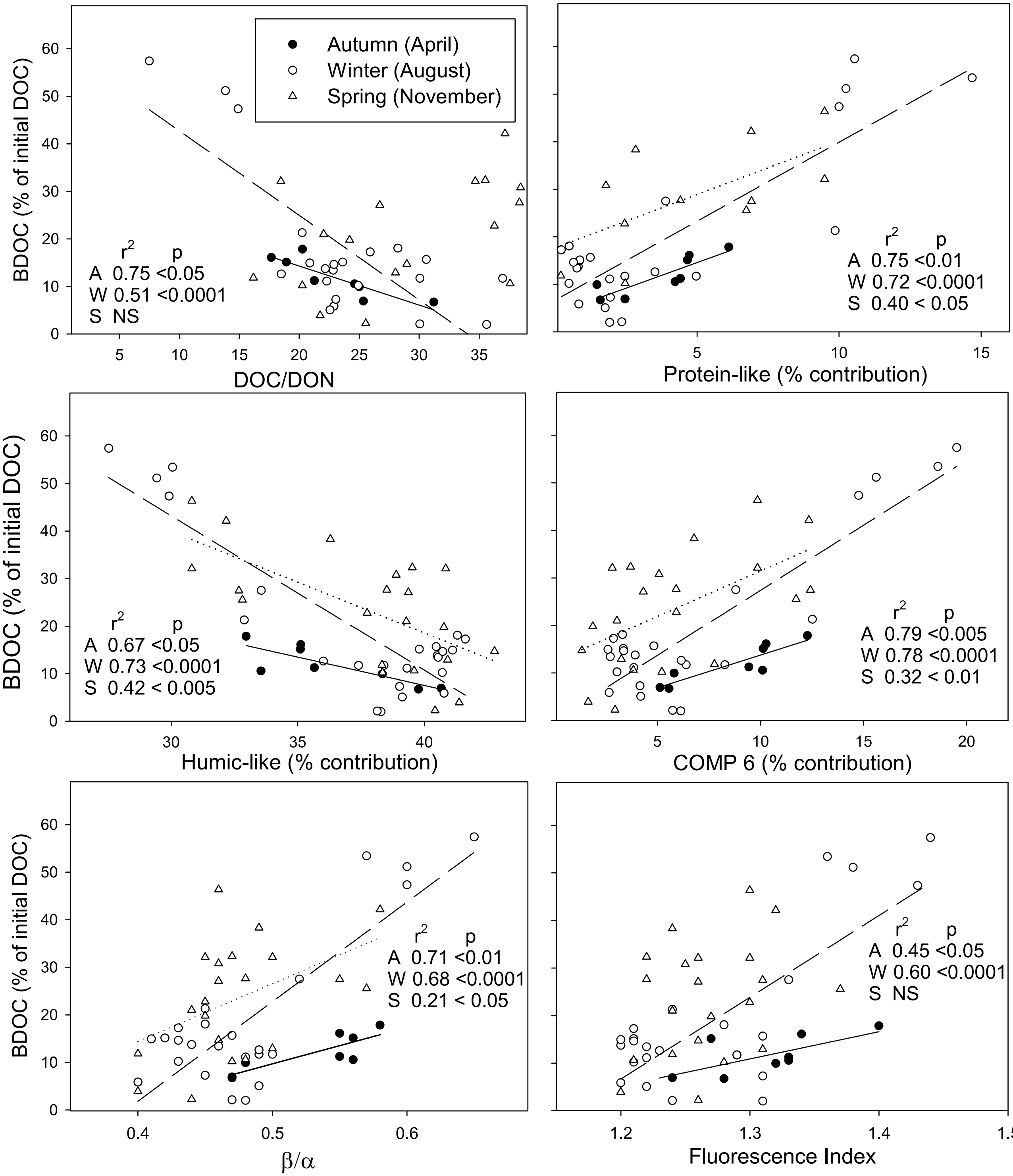

Figure 5. Linear regressions between BDOC and DOC:DON, DOM fluorescence components and indices for the autumn, winter and spring sampling seasons. NS denotes linear regressions that were not significant at $p < 0.05$.

4.4. Prediction of DOC Bioavailability

[24] Seasonal relationships between percent BDOC and biochemical composition were significant for DOC:DON ratios and all fluorescence comparisons, except in November when DOC:DON and FI values were not significant (Figure 5). Overall, significant relationships between percent BDOC and DOM composition were consistently negative for DOC:DON and humic-like C1%, but positive for COMP 6%, protein-like %, FI and β:α. Linear regression of DOM chemical characteristics explained the greatest variation in

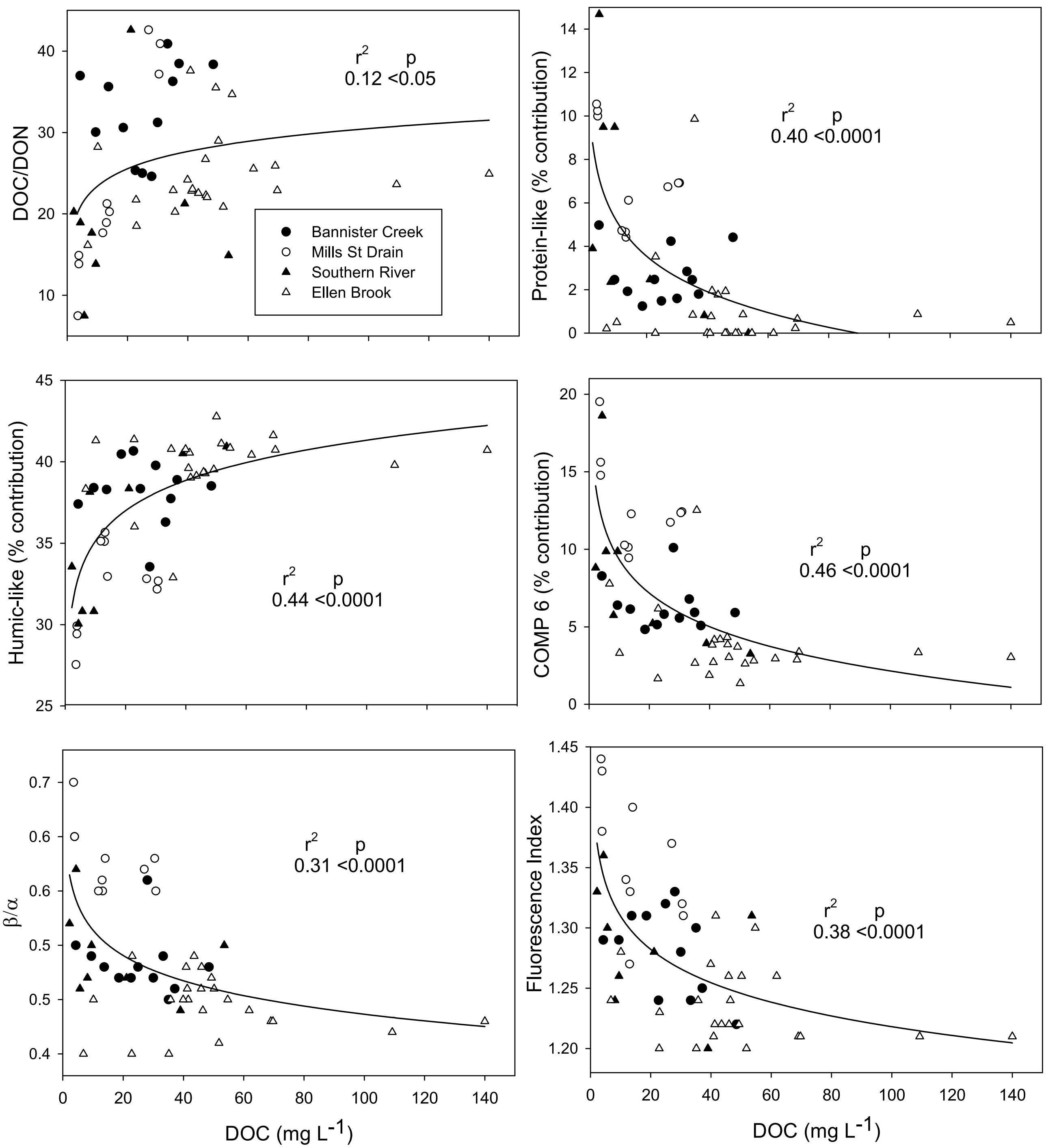

Figure 6. Relationship between DOC:DON, DOM fluorescence components/indices and DOC. The regression lines are in the form of y = y_o + (a*ln(x)), and apply to the entire sample population.

percent BDOC in winter (r^2 from 0.51 to 0.78) compared to autumn (r^2 from 0.32 to 0.67) and spring (r^2 from 0.21 to 0.42).

4.5. DOC Concentration and Fluorescence Characteristics

[25] In general, we observed a significant logarithmic decline in COMP 6%, protein-like %, β:α, and FI with increasing DOC concentration (Figure 6). These patterns were driven mainly by the higher values for COMP 6%, protein-like %, β:α, and FI in the Mills St Drain and Southern River catchments, which tended to have lower concentrations of DOC. In contrast, the higher concentrations of DOC typically found in Bannister Creek and Ellen Brook were associated with lower values in these DOM characterization metrics. The humic-like C1% for stream water DOM increased logarithmically with DOC concentration due mostly to the lower humic-like C1% at the Southern River and Mills St Drain sites and consistently high humic-like C1% in Ellen Brook. There was a weak

relationship between DOC:DON and DOC concentration due to a wide range in DOC:DON at DOC < 40 mg L^{-1}.

5. Discussion

5.1. Fluorescence as an Indicator of DOC Bioavailability

[26] Our findings establish a quantitative connection between BDOC and fluorescence characteristics that has been observed in pristine catchments [*Balcarczyk et al.*, 2009; *Fellman et al.*, 2008, 2009], but has not previously been measured in agro-urban catchments. We observed positive relationships between percent BDOC and both FI and β:α values, indicating that DOM from anthropogenic or autochthonous sources is more readily decomposed in agro-urban streams. Similarly, the strong positive relationship between percent BDOC and percent protein-like fluorescence suggest that N-rich organic compounds may be preferentially utilized to meet microbial energy and nutrient demands. This is consistent with previous studies in Swan-Canning catchments that showed greatest DON consumption at low DOC:DON ratios during laboratory incubations [*Petrone et al.*, 2009].

[27] The wide range of BDOC (2 to 57%) reported in this study reflects a high variability in DOM sources and its composition in agro-urban streams. Overall, the greatest range in BDOC and DOM character was observed in winter when catchment hydrologic connectivity is greatest and the mechanism for streamflow generation differs between catchments. For instance, during winter when high flow in Mills St Drain is dominated by impervious surface pathways from residential and industrial areas [*Petrone*, 2010], DOC and DON concentrations were low but percent BDOC was high. In contrast, consistent DOM character (e.g., high humic-like but low protein-like fluorescence) was observed in Ellen Brook despite a tenfold change in flow from winter to spring. Previous research has shown that the contributing area for flow in this ephemeral stream is from a shallow aquifer in a low-lying alluvial zone that develops with the onset of winter precipitation [*Zammit et al.*, 2005]. Thus, DOC and DON concentrations increase greatly with flow during the winter months as soils become saturated [*Petrone*, 2010], but DOM fluorescence changes little suggesting that DOM sources are similar across the catchment and derived from vascular plant material.

[28] Although we found that percent BDOC was low for streams with elevated DOC, concentrations of total BDOC and DOC were positively related, primarily because increasing concentrations of DOC offset the decrease in the percentage of DOC that is bioavailable. This finding has important implications for aquatic food webs because substantial quantities of BDOC can be delivered to heterotrophic stream communities even when the precursor organic material is relatively recalcitrant. Anoxia occurs seasonally in the upper Swan River [*O'Callaghan et al.*, 2007], and oxygen demand has been mainly attributed to particulate or benthic organic matter stored in sediments [*Hamilton et al.*, 2001]. It is unclear if catchment DOM sources contribute to oxygen demand in the Swan River in a similar manner to what has been previously reported for Indonesian blackwater rivers with high DOC [*Alkhatib et al.*, 2007; *Rixen et al.*, 2008]. In any case, microbial production supported by catchment DOM likely provides an energy source for aquatic foodwebs, and DON mineralization may provide an additional source of N for algal production, particularly during the flow recession in the spring when N is the main limiting nutrient for primary production [*Hamilton et al.*, 2006].

5.2. DOM Concentration and Fluorescence Characteristics

[29] Patterns of DOM concentration and chemical quality observed in this study are unique compared to the global literature. Despite the influence of human-dominated land use, we report some of the highest DOC concentrations in freshwater ecosystems [*Mulholland et al.*, 2003]. Elevated DOC has been associated with mobilization of organic matter in low gradient, blackwater rivers with high wetland or peatland coverage such as in the Ogeechee in southeast USA [*Meyer et al.*, 1997], the Orinoco [*Battin*, 1998] and Amazon [*Richey et al.*, 1990] in South America, and the Siak [*Baum et al.*, 2007] and Dumai [*Alkhatib et al.*, 2007] in Indonesia. The high DOC and DON levels in this study are also consistent with blackwater coastal plain ecosystems with sandy soils that have little capacity to adsorb DOM [*Meyer*, 1990]. Although many wetlands have been removed on the Swan Coastal Plain in the last century due to clearing and drainage for agricultural and urban development, the fluorescence characteristics of elevated DOM in our study streams were consistent with DOM properties of wetland and forest-dominated ecosystems [*Jaffé et al.*, 2008]. For example, sites with DOC greater than 30 mg L^{-1} showed FI and β:α consistently less than 1.3 and 0.5, respectively, typical of wetland/peatland ecosystems [*McKnight et al.*, 2001; *Williams et al.*, 2010].

[30] Overall, the influence of anthropogenic or autochthonous DOM sources was most evident at low DOC concentrations. The highest average FI (1.42), β:α (0.62), and contributions from COMP 6 and protein-like fluorescence were observed for Mills St Drain during high flow in winter when DOC (<4 mg L^{-1}) was low and impervious surfaces from urban and residential development are likely the main contributing area for streamflow [*Petrone*, 2010]. With a greater contribution from groundwater at low flow in autumn and spring, Mills St Drain had lower COMP 6%, protein-like %, β:α, and FI. Nevertheless, these component contributions were still greater than all other catchments, suggesting that base flow in Mills St Drain is also composed of autochthonous or anthropogenic DOM. Protein-like fluorescence has previously been shown to be related to anthropogenic DOM from sewage [*Baker and Spencer*, 2004], and septic systems in Mills St Drain that are known to contribute to stream N and P were only recently converted to the municipal sewer [*Swan River Trust*, 2003].

[31] The fluorescence characteristics of DOM in Bannister Creek largely contrasted with Mills St Drain. Consistently high humic-like fluorescence but low protein-like fluorescence was observed in Bannister Creek across seasons. Much of this catchment was more recently developed in the mid 1990s [*Barron et al.*, 2010], and DOM loss from soils may reflect the historical contribution of native *Eucalyptus* and *Melaleuca* vegetation as well as relic wetlands that have been largely drained for urban development. These findings suggest that current urban land use is superimposed on a

blackwater ecosystem that naturally produces high DOM loading to streams. Thus, we hypothesize that over time as soil and groundwater organic pools become depleted in Bannister Creek, the concentration and composition of DOM may become more similar to Mill St. Drain. In other catchments such as Ellen Brook that were cleared for agriculture post World War II, high DOM loading is somewhat surprising. Recent carbon dating of DOC in rivers of the San Joaquin valley of California has shown that soil organic matter loss can continue decades after clearing for agriculture and urban development [*Sickman et al.*, 2010]. In the same way, losses of soil organic matter from extensive *Melaleuca* wetlands that have been cleared for agriculture may explain the high DOC concentrations presently observed in Ellen Brook.

5.3. DOM Sources and Ecosystem Implications

[32] The dominance of humic-rich DOC during base flow in urban streams and high flow in Ellen Brook suggests that groundwater throughout the Swan Coastal Plain is a major source of humic-rich DOM to streams. *Pabich et al.* [2001] reported that a shallow vadose zone (<1.25 m) contributed to high DOC in groundwater in sandy soil profiles of Cape Code, USA, indicating that the depth of the unsaturated zone is important for DOC attenuation in coastal groundwater systems. Similarly, we hypothesize that shallow vadose zones and near surface groundwater tables in our study act to concentrate groundwater DOM. Groundwater recharge and DOM leaching occurs mainly during winter when precipitation and inundation occurs in wetlands and low lying near-stream zones. With lower precipitation and increasing evaporative demand, soils become drier and the groundwater table declines throughout the summer months [*Zencich et al.*, 2002]. Thus, as the water table declines, DOM and other solutes become concentrated in groundwater systems with low gradients and long residence times. This proposed mechanism is supported by increasing concentrations of Cl^- and DOC in Swan Coastal Plain wetlands over the summer months [*Donn et al.*, 2008], and may partly explain the high concentrations of stream water DOM observed in this study.

[33] The observed change in DOM quality with increasing DOC concentration in this study is consistent with a recent report of DOC characteristics within a tropical river system. For example, *Yamashita et al.* [2010] found a negative relationship between fluorescence index and DOC in Venezuelan tropical rivers that was attributed to an increase in planktonic DOM but a relative decrease in leaf litter DOM at low DOC concentrations. A similar two end-member DOM contribution is also likely in this study, but our results also suggest that a mixture of anthropogenic and autotrophic sources may contribute to protein enriched DOM at lower DOC concentrations. In particular, anthropogenic DOM from surface hydrologic flowpaths is likely the major contributor of labile DOM during high flow in winter in Mills St Drain. Labile DOM during low flow in this catchment may also consist of autotrophic DOM as filamentous algae are frequently observed in urban and agricultural streams.

[34] Future organic matter loading and character in coastal streams and rivers of the Swan Coastal Plain will be primarily influenced by changes in hydrologic flux, land use, and stores of soil organic matter. Recent declines in rainfall and runoff for southwestern Australia [*Petrone et al.*, 2010], if maintained under current climate conditions [*Hope*, 2006], will reduce the freshwater flux to coastal estuaries and oceans. Further, *Robson et al.* [2008] found that the relative contribution of nutrient fluxes from urban drains was greater in low flow years since urban runoff is less affected by reduced rainfall. With these hydrologic changes and a projected doubling of the Perth population (1.6 M in 2010) by 2050, there will likely be a greater contribution of DOM and nutrient fluxes from urban relative to agricultural catchments in the future.

6. Conclusions

[35] Our results provide strong evidence that DOM fluorescence characterization techniques can be used to predict DOM biodegradability in mixed land use catchments over the hydrologic cycle. Humic and protein-like fluorescence were significantly correlated with the percentage of BDOC in stream water across nearly all of the catchments and seasons that we sampled. Further, DOM fluorescence indices (FI and β:α) and humic-like components suggest that high concentrations of DOC and DON in agro-urban streams are derived mainly from vascular plant material. This result is surprising given that most native vegetation has been cleared, and it raises a fundamental question concerning the age and origin of present-day DOM fluxes that may be answered by radiocarbon dating DOC in streams and groundwaters. This may determine whether the bulk of present-day DOC fluxes are derived from the destabilization of soil organic matter due to urbanization and agricultural development [*Sickman et al.*, 2010], or whether stream DOC is contemporary and produced from remnant wetlands and patches of native vegetation in highly modified coastal catchments.

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