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Changes in the concentration, biodegradability, and fluorescent properties of dissolved organic matter during stormflows in coastal temperate watersheds

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[1] Dissolved organic matter (DOM) transport during storms is studied because it is important in the annual watershed export budget for dissolved organic carbon (DOC). We sampled stream water from two watersheds (upland and wetland-dominated) and three subcatchments (bog, forested wetland, and mineral forest) located within the wetland-dominated watershed during a fall and summer storm to investigate changes in the magnitude and chemical quality of DOM during stormflows. Stormflow export of DOC ranged from 2.3 kg C ha^{-1} in the upland watershed to 13.9 kg C ha^{-1} in the bog subcatchment. Biodegradable DOC (BDOC) export for these same storms ranged from 0.6 kg C ha^{-1} in the upland watershed to 4.2 kg C ha^{-1} in the bog subcatchment. The percent BDOC decreased during both storms in the upland watershed, while percent BDOC increased in the three wetland streams. Parallel factor analysis (PARAFAC) modeling of fluorescence excitation-emission matrices further showed that as stream water DOM concentrations increased during stormflows in the upland watershed, the contribution of protein-like fluorescence decreased and humic-like fluorescence increased. However, the contribution of protein-like fluorescence increased and humic-like fluorescence decreased slightly in the three wetland streams. These results indicate that shifts in the biodegradability and chemical quality of DOM are different for upland and wetland watersheds. Taken together, our findings suggest stormflows are responsible for substantial export of BDOC from coastal temperate watersheds. Moreover, we found that PARAFAC modeling of fluorescent DOM is an effective tool for elucidating shifts in the quality of stream water DOM during storms.

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1. Introduction

[2] Dissolved organic matter (DOM) is an important control on biological, chemical and physical processes in aquatic ecosystems. As a result, stream water yields of DOM during high flows have been studied in a wide variety of ecosystems including: subarctic [*Petrone et al.*, 2006], hardwood forest [*Inamdar et al.*, 2006], peatland [*Worrall et al.*, 2002], and arid [*Jones et al.*, 1996]. Because concentrations of DOM typically increase with increasing discharge, stormflows commonly account for a substantial portion of seasonal and annual watershed DOM yields [*Jones et al.*, 1996; *Hinton et al.*, 1997]. Previous research demonstrated that a single 2–3 day storm during the fall accounted for 31% of the autumn dissolved organic carbon (DOC) flux in an Ontario headwater stream [*Hinton et al.*, 1997]. Since DOM export during stormflows is an important link in the watershed carbon cycle, knowledge of how different landcover types (e.g., wetlands and upland forest) influence the concentration and chemical quality of DOM exported during stormflows is essential for elucidating the cycling of DOM in watersheds.

[3] Hydrologic flowpaths are an important control on surface water DOM concentrations during high flows [*Welsch et al.*, 2001; *Zhang et al.*, 2007]. Stream water DOM concentrations in well-drained soils typical of forested watersheds increase sharply with discharge because of inputs of DOM-rich water from riparian areas [*Hinton et al.*, 1998; *McGlynn and McDonnell*, 2003] and DOM transported via near-surface soil flowpaths [*Hornberger et al.*, 1994; *Boyer et al.*, 1997; *Schiff et al.*, 1997], both of which are diluted later in the storm by low DOM hillslope water that enters the stream through deeper flowpaths. Storm runoff generation in wetlands is dissimilar to forested watersheds in that runoff occurs primarily as shallow throughflow at the acrotelm/catotelm interface [*Worrall et*

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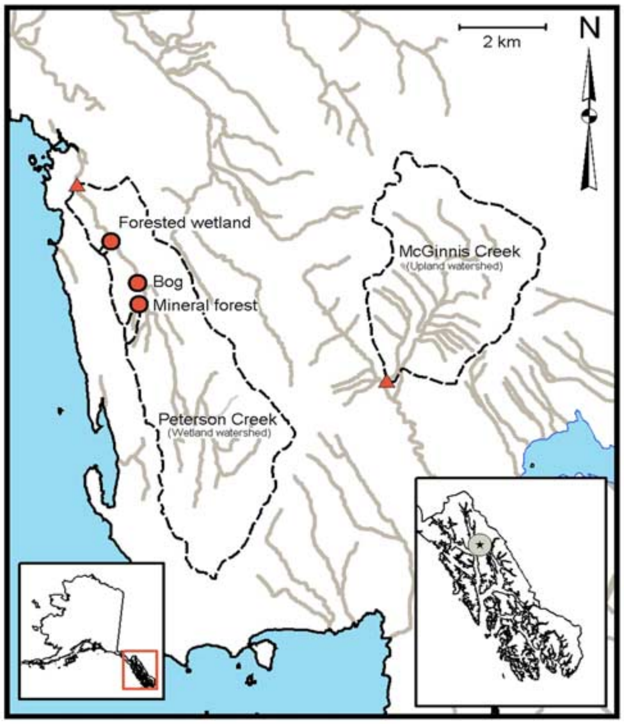

Figure 1. Location of watershed (triangles) and subcatchment (circles) study sites near Juneau, Alaska.

al., 2002, 2003]. The relationship between DOC concentration and discharge in wetland dominated watersheds is generally poor and can even be negative because of dilution effects [*Hinton et al.*, 1997; *Worrall et al.*, 2002]. Thus, the frequency or period of time since the last storm [*Hinton et al.*, 1997], the storm duration and intensity [*Worrall et al.*, 2002] and the extent of wetland coverage within a watershed [*Gergel et al.*, 1999] are important controls on watershed DOM yields during storms.

[4] The increase in stream water DOM associated with high-flow events is typically coupled with a change in the quality of DOM [*Gremm and Kaplan*, 1998; *Hood et al.*, 2006; *Zhang et al.*, 2007]. This shift in the chemical quality of DOM can occur because terrestrial DOM source pools mobilized during high flows differ from those leached during base flows. For example, the specific UV absorbance ($SUVA_{254}$) of DOC, which is an indicator of aromatic C content [*Weishaar et al.*, 2003], increased during stormflows in Pacific coastal watersheds [*Hood et al.*, 2006]. However, in a small forested stream in Pennsylvania, carbohydrate concentrations were enriched during stormflow relative to base flow [*Gremm and Kaplan*, 1998]. These findings suggest that stream metabolic activity may be influenced by changes in DOM character associated with stormflows because aquatic microbial heterotrophs are dependent on the fraction of DOC that is biodegradable [*Volk et al.*, 1997]. However, few studies have examined how the biodegradable fraction of DOC (BDOC) changes during stormflows. In a small Pennsylvania stream, BDOC concentrations increased threefold during a stormflow [*Kaplan and Newbold*, 1995]. Moreover, BDOC concentrations increased during stormflows in a forested Appalachian stream, although the fraction of BDOC was not significantly different relative to base flow [*Buffam et al.*, 2001]. The results from both studies indicate that BDOC yields increase during storms, although the magnitude of this increase has not been quantified.

[5] Efforts to quantify stormflow BDOC yields are hampered by the difficulties associated with combining BDOC incubations with the high-resolution sampling required to characterize storm events. Several recent watershed-scale studies have used rapid spectroscopic analyses, such as fluorescence excitation-emission matrices (EEMs) and $SUVA_{254}$, to trace changes in the chemical quality of stream water DOM [*Hood et al.*, 2006; *Vidon and Soyeux*, 2008]. Fluorescence excitation-emission matrices can also be analyzed using the multivariate modeling technique parallel factor analysis (PARAFAC), a three-way decomposition method similar to principal component analysis [*Cory and McKnight*, 2005; *Stedmon and Markager*, 2005a]. PARAFAC has been used to trace changes in DOM production and consumption over short time periods during laboratory photodegradation experiments [*Stedmon and Markager*, 2005b]. Thus, PARAFAC analysis of fluorescence EEMs has the potential to provide detailed information about how the chemical quality of stream water DOM shifts during storms.

[6] Most watershed-scale studies of the production and export of DOM have focused on measuring bulk concentrations and fluxes of DOM. Bulk measurements of DOM; however, provide little information about how the chemical quality of DOM in dominant catchment source pools changes during storms. We combined high-resolution measurements of DOC concentrations, PARAFAC modeling of fluorescence EEMs and BDOC incubations to trace changes in the concentration and chemical quality of DOM during two storms from two forested watersheds and three small subcatchments of varying landcover and soil type. In particular, we wanted to evaluate the importance of storms for facilitating the loss of labile DOM from these watersheds. Our hypotheses are (1) that during storms, soil surface horizons and streams will become tightly linked, which will result in an increase in stream water DOC and BDOC yields, and (2) that shifts in the fraction of BDOC would be dependent on the extent and type of wetland present within a watershed or subcatchment.

2. Methods

2.1. Site Descriptions

[7] Stream water was collected from two coastal forested watersheds, one of which has a high wetland coverage, and three subcatchment outlet streams draining a bog, forested wetland and mineral forest in the Tongass National Forest, southeast Alaska (Figure 1). The study sites were located near Juneau, Alaska, with mean monthly temperature ranging from $-2°C$ to $14°C$ and a mean annual precipitation of 1400 mm, much of which falls (~600–800 mm) during the autumn. After the spring snowmelt, increased evapotranspiration and low precipitation result in a brief period (June–mid-July) of soil water table drawdown. Therefore, streamflow in the region typically reaches a minimum in late winter or during the early summer drawdown period and peaks during the autumn rainy season.

Table 1. Characteristics for the Two Watersheds and Three Subcatchments Included in This Study

	Wetland Extent (%)	Dominant Vegetation	Area (ha)	Average Basin Slope (%)	Range of Average Daily Q
Wetland watershed	53	*Tsuga heterophylla, Vaccinium* spp.	2300	14	1.0–10 m^3 s^{-1}
Upland watershed	<5	*Alnus* spp., *T. heterophylla*, *P. sitchensis*	2000	24	1.0–15 m^3 s^{-1}
Bog[a]	>90	*Sphagnum* spp., ericaceous shrubs	1	3–5	0.1–10 L s^{-1}
Forested wetland[a]	>75	*Sphagnum* spp., *Lysichiton americanum,*	6	5–10	0.1–35 L s^{-1}
Mineral forest[a]	<10	*T. heterophylla*, *Vaccinium* spp.	23	10–15	1.0–60 L s^{-1}

[a]Subcatchment located within the wetland watershed.

[8] The two study watersheds (upland and wetland) represent different combinations of wetland coverage, glacial recession, dominant vegetation and valley morphology (Table 1). The upland watershed (McGinnis Creek) is a young landscape with many early successional attributes typical of recently deglaciated terrain. In the upper part of the watershed, soils are thin with sparse vegetation dominated by *Alnus* spp., and in the lower reaches of the watershed, the landscape is older consisting of an uplifted marine terrace. As a result, allochthonous contributions of DOM remain low throughout the year. The wetland-dominated watershed (Peterson Creek) in contrast is slightly larger and 53% of the watershed area is covered with wetlands, resulting in stream water DOC concentrations that remain >5 mg C L^{-1} throughout the year [*Hood et al.*, 2007]. The wetland watershed has gradual relief consisting of a landscape mosaic of peatlands mixed with coniferous forest. Uplifted marine terraces with some colluvial and alluvial sediments dominate the lower reaches of the wetland watershed.

[9] The three subcatchments (bog, forested wetland and mineral forest) are located within the Peterson Creek watershed and represent the dominant landscape types within the watershed. The bog subcatchment is typical of the slope bog [*National Wetlands Working Group* (*NWWG*), 1988] wetland type and is composed of deep, moderately decomposed organic material (dysic, Typic Cryohemist, Kina series) with peat accumulations >2 m. Water and nutrient supply to the bog are dominated by atmospheric inputs although groundwater and surface runoff can be important along the perimeter. The forested wetland subcatchment is typical of the raised peatland swamp [*NWWG*, 1988] with 0.4 m of well-decomposed peat overlaying glacial till (Terric Cryosaprist, Maybeso series). The forested wetland site has formed on the same deposits as the bog, but has a steeper slope leading to greater water and nutrient contributions from groundwater and surface flow. The mineral forest subcatchment is predominantly spodosol (Typic Humiccryod) with wet, organic-rich patches found within the site. The soils are moderately deep and moderately well drained because of the steep slope of the catchment. The soils are colluvial material derived from bedrock dominated by igneous intrusive material.

2.2. Field Methods

[10] Automated water samplers (ISCO model 3700) were used to sample stream water from the five sites over the course of two storms: (1) 6–9 September 2006 and (2) 9–14 July 2007. The two storms were selected because they are typical of the storms observed during the fall wet season and the summer drawdown period (Figure 2). Therefore, the two storms capture the seasonal changes that occur in streamflow and antecedent soil moisture conditions in the region. One liter samples were collected every 2 h on the ascending limb of the hydrograph and every 4–8 h on the descending limb. Water samples were removed from the ISCO daily, filtered through precombusted, Gelman A/E glass fiber filters (0.7 μm pore size) and stored in the

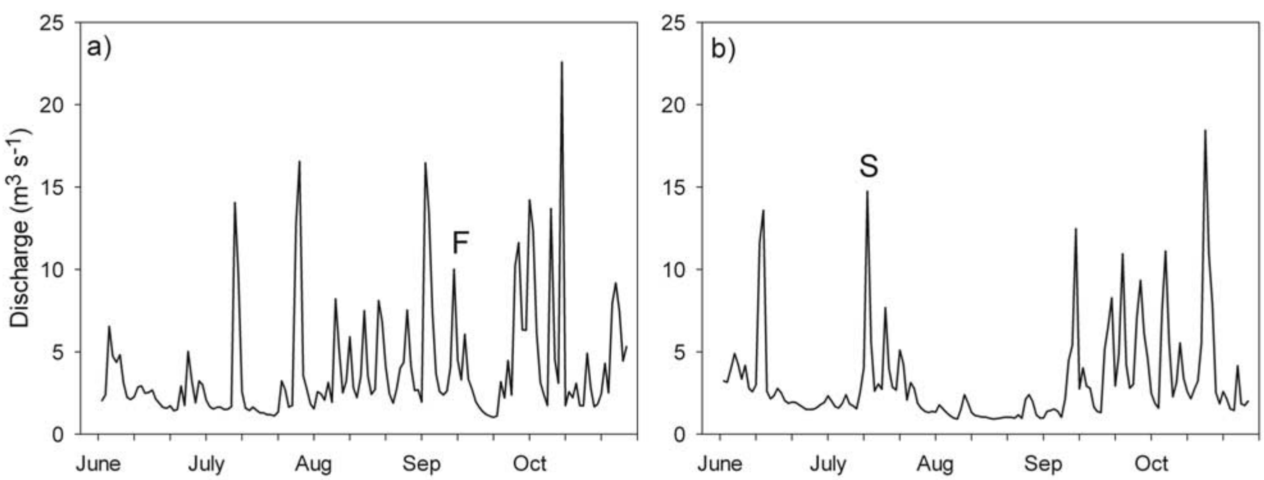

Figure 2. Discharge for the upland watershed (McGinnis Creek) during (a) 2006 and (b) 2007. Capital letters F (6–9 September storm) and S (9–14 July storm) indicate the two storms sampled.

refrigerator until analysis. DOC concentrations were analyzed within 48 h and spectroscopic analyses were completed within one week of collection. In addition, soil water was collected from three, 25 cm deep soil piezometers located within each subcatchment to identify soil DOM precursor material. Soil water was collected once before, twice during and once after the storm.

[11] Streamflow was measured continuously for both watershed outlet streams using a stilling well equipped with a pressure transducer and a rating curve was built using the stage-discharge relationship. Stream discharge at the three subcatchment outlet streams was measured continuously using V notch weirs equipped with pressure transducers. Precipitation was measured using tipping bucket gages at each of the subcatchment outlet streams. Storm yields of DOC and BDOC were calculated for the period between the initial increase in discharge and when streamflow returns to near-prestorm levels using the sample-discharge interpolation method described by *Hinton et al.* [1997].

2.3. DOC Analysis and BDOC Incubations

[12] Stream water DOC concentrations were determined by high-temperature combustion using a Shimadzu TOC-V Organic Carbon with a lower detection limit of 0.4 mg C L^{-1}. Analytic precision for DOC ranged from 0.02 to 0.04 mg C L^{-1} (mean standard deviation for identical samples reanalyzed during analytical runs) for DOC concentrations less than 5 mg C L^{-1} and 0.2–0.3 mg C L^{-1} for samples greater than 5 mg C L^{-1}. Biodegradable DOC (BDOC) was calculated as the difference in DOC before and after a 30 day laboratory incubation following the methods of *Fellman et al.* [2008a]. Briefly, water initially filtered through a 0.2 μm filter, a bacterial inoculum was added and samples were incubated at 25°C for 30 days in the dark. After 30 days, the solution was refiltered through a 0.2 μm filter, DOC was remeasured and BDOC was calculated as the difference in sample DOC before and after the 30 day incubation. If necessary, samples were diluted to approximately 15 mg C L^{-1} to prevent excessive microbial growth. The bacterial inoculum was prepared by leaching soil collected from the riparian zone at each one of the sites, diluted 1:1 with deionized water and incubated at 25°C for 24 h before addition to the sample solution.

[13] Specific UV absorbance ($SUVA_{254}$) was measured using a 1.0 cm quartz cell on water samples allowed to warm to room temperature following the procedures of *Weishaar et al.* [2003]. Three dimensional fluorescence excitation-emission matrices (EEMs) of DOM were created by measuring fluorescence intensity across a range of excitation and emission wavelengths [*Hood et al.*, 2007]. Water samples were diluted to avoid inner filter effects according to *Green and Blough* [1994] and EEMs were corrected for instrument bias and Raman normalized using the area under the water Raman peak at excitation 350 nm.

[14] PARAFAC modeling of fluorescence EEMs was conducted with MATLAB using the PLS_toolbox version 3.7 (Eigenvector Research, unpublished data, 2006) following the procedures of *Stedmon et al.* [2003]. Our PARAFAC model identified a total of nine unique components within the fluorescence EEMs for stream water DOM and the model was validated using core consistency diagnostics [*Ohno and Bro*, 2006] followed by a split-half validation [*Stedmon et al.*, 2003]. Of the nine components identified by the PARAFAC model, we focus our analyses on the following four components: humic-like (ex = 240 nm/em = 450–460 nm), fulvic-like (ex = 340 nm/em = 410 nm), tryptophan-like (ex = 280 nm/em = 336 nm) and tyrosine-like (ex = 275 nm/em = 304 nm). These four components were selected because they explained a large amount of the variability in the data set and have been previously identified in other studies [*Baker*, 2001; *Cory and McKnight*, 2005; *Stedmon and Markager*, 2005a]. Here we refer to fluorescence components as "humic-like, fulvic-like or protein-like" since these components are likely a mixture of similar fluorophores rather than pure fluorophores [*Stedmon et al.*, 2003]. The percent contribution of each of the components was determined by quantifying the relative abundance of each component in comparison to the total fluorescence of all the modeled PARAFAC components.

3. Results

3.1. Hydrology

[15] During 6–9 September and 9–14 July, approximately 48 mm and 72 mm of precipitation fell in the study watersheds, respectively. Prestorm specific discharge for the upland and wetland watersheds taken together averaged 0.41 mm h^{-1} for the fall storm (wet season) and 0.23 mm h^{-1} for the summer storm (drawdown period). Specific discharge in the two watersheds increased an average of 170% during the fall storm and over 500% during the summer storm. For the three subcatchments, prestorm specific discharge averaged 0.14 mm h^{-1} and 0.03 mm h^{-1} for the fall and summer storms, respectively. Specific discharge in the three subcatchments increased by greater than 900% for both fall and summer storms.

3.2. Stream Water DOC and BDOC Concentrations

[16] Stream water DOC concentrations increased significantly during the fall and summer storms for all five sites ($p < 0.001$; t-test (Table 2)). Main stem DOC concentrations during the fall storm increased 69% in the upland watershed and 26% in the wetland watershed (Figures 3a and 3b). However, the increase in DOC concentration was greater during the summer storm than for the fall storm as concentrations increased 400% and 365% for the upland and wetland watersheds, respectively (Figures 3c and 3d). Concentrations of DOC during both storms were significantly greater in the wetland watershed compared to the upland watershed ($p < 0.001$; t-test). The prestorm DOC concentrations in the three subcatchment streams ranged from 4 to 22.5 mg C L^{-1} and were higher before the fall storm (Figures 4a, 4b, and 4c) than for the summer storm (Figures 4d, 4e, and 4f). The bog subcatchment showed the smallest increase in DOC concentration during both storms with an average increase of 45%, whereas concentrations in the mineral forest stream increased an average of 217%.

[17] Stream water BDOC concentrations were significantly greater during stormflows relative to base flow for all five sites ($p < 0.001$; t-test (Table 2)), although there was a slight decrease in BDOC concentration during the fall storm for the upland watershed. Similar to DOC, concentrations of BDOC were significantly greater in the wetland watershed

Table 2. Mean and Standard Error of DOC and BDOC Concentrations for the 6–9 September and 9–14 July Storms[a]

	6–9 Sep Base Flow		6–9 Sep Stormflow		9–14 Jul Base Flow		9–14 Jul Stormflow	
	DOC (SE)	BDOC (SE)	DOC (SE)	BDOC (SE)	DOC (SE)	BDOC (SE)	DOC (SE)	BDOC (SE)
Upland watershed	3.2 (0.04)	1.4 (0.01)	4.6 (0.10)	1.3 (0.03)	1.3 (0.02)	0.5 (0.01)	2.4 (0.13)	0.7 (0.05)
Wetland watershed	11.8 (0.05)	2.2 (0.08)	13.2 (0.2)	2.8 (0.1)	4.0 (0.17)	0.3 (0.01)	8.8 (0.40)	1.7 (0.31)
Bog[b]	19.0 (0.11)	3.4 (0.12)	22.9 (0.33)	4.7 (0.21)	16.6 (0.10)	1.8 (0.21)	19.3 (0.40)	3.5 (0.49)
Forested wetland[b]	22.3 (0.22)	3.7 (0.17)	27.7 (0.53)	5.5 (0.26)	14.6 (0.25)	0.9 (0.04)	21.9 (0.87)	3.8 (0.60)
Mineral forest[b]	10.1 (0.02)	1.7 (0.01)	12.3 (0.58)	2.1 (0.16)	5.3 (0.38)	0.9 (0.12)	10.3 (0.71)	2.4 (0.41)

[a]Base flow means were calculated from three measurements before each storm, and stormflow means were calculated from samples collected for the period between the initial increase in discharge and when streamflow returns to near-prestorm levels. Standard error is ±1, and BDOC concentrations are in mg C L^{-1}.

[b]Subcatchment located within the wetland watershed.

compared to the upland watershed ($p < 0.001$; t-test). Percent BDOC in the upland watershed was high before both storms (35–45%) and decreased on the ascending limb of the hydrograph (Figure 5). This drop in the percent BDOC corresponded to a decrease in BDOC concentration from 1.5 (prestorm) to a minimum of 1.1 mg C L^{-1} during the fall storm and an increase (0.5 to a maximum of 1.1 mg C L^{-1}) during the summer storm because the increase in DOC concentration more than offset the decrease in percent BDOC. Percent BDOC in the wetland watershed increased on the ascending limb of the hydrograph for both storms and peaked at 25% for the fall storm and 33% (Figure 5). In addition, stream water in the wetland watershed showed a sharp peak in BDOC (up to 30%) early on the fall storm hydrograph that was rapidly diluted as streamflow increased. The lower reach of the wetland watershed hosts large anadromous salmon runs in late July and August and this pulse in BDOC was attributed to labile DOM flushed from salmon carcasses in the riparian zone back into the stream [*Fellman et al.*, 2008b].

[18] Concentrations of BDOC for all three subcatchments increased during both storms and ranged from a presummer storm low of 0.8 mg C L^{-1} in the forested wetland to a high of 8.5 mg C L^{-1} in the bog during peak streamflow in the summer storm (Figure 4). Percent BDOC in the three subcatchments increased sharply with discharge during both storms, peaked between 25 and 27% during the fall storm and 30–35% during the summer storm and decreased to

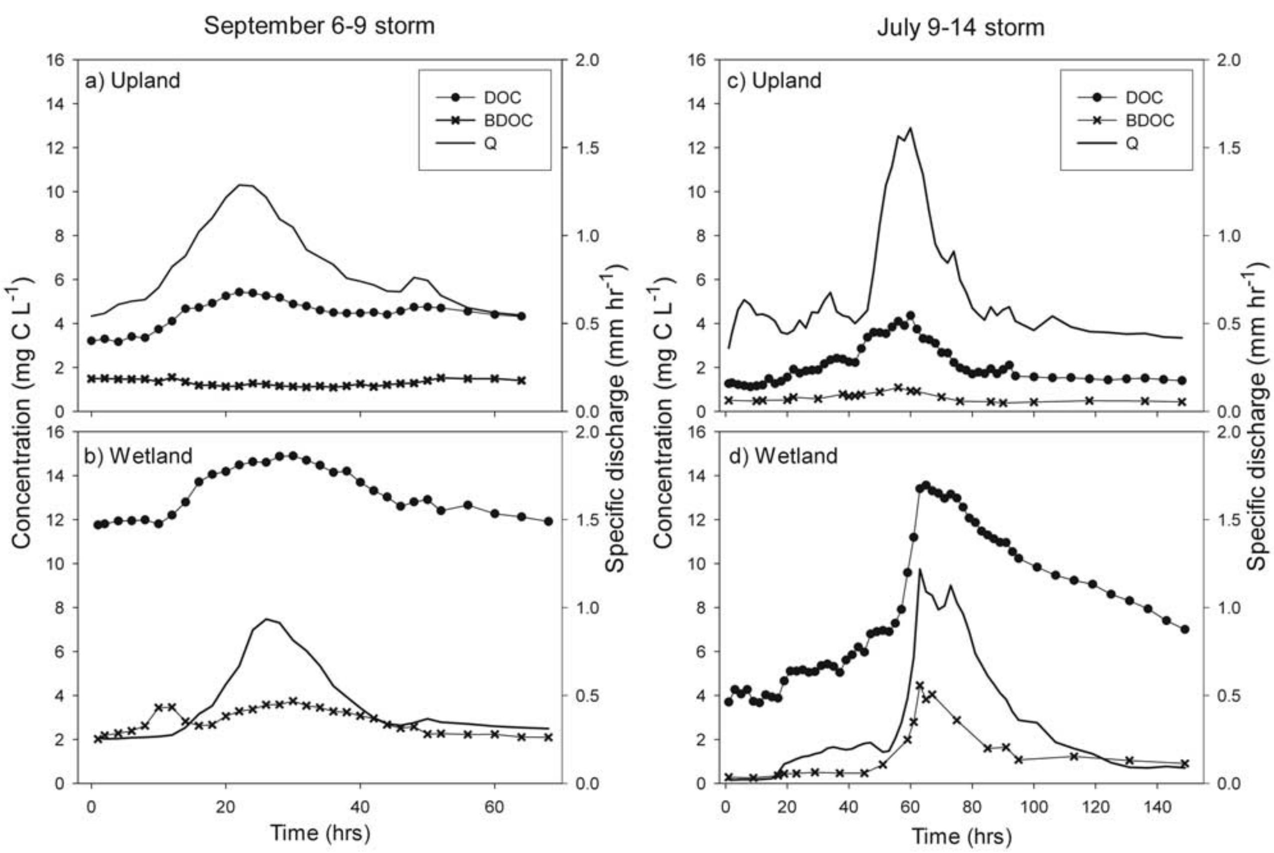

Figure 3. Relationship between stream water DOC and BDOC concentrations and specific discharge (Q) for the 6–9 September and 9–14 July storms in the upland and wetland watersheds.

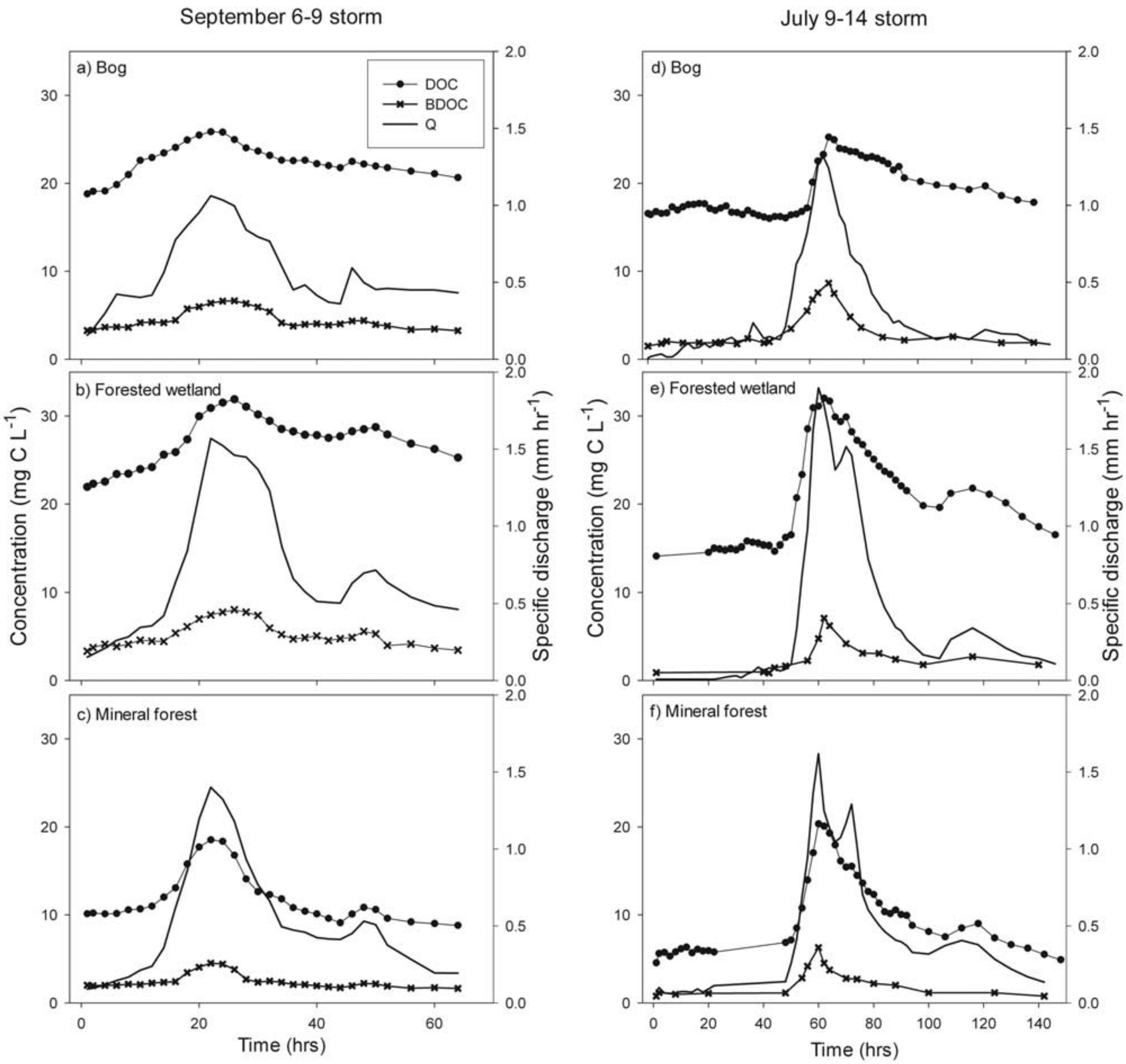

Figure 4. Relationship between stream water DOC and BDOC concentrations and specific discharge (Q) for the 6–9 September and 9–14 July storms in the three subcatchment streams.

near-prestorm levels on the descending limb of the storm hydrograph (Figure 6). The relative percent increase in BDOC was smallest in the mineral forest subcatchment during both storms.

3.3. Spectroscopic Properties and PARAFAC Modeling

[19] The response in optical properties of DOM in the five sites was similar for both storms, but more pronounced during the summer storm than the fall storm. The shift in optical properties of DOM was most pronounced in the upland watershed during the summer storm where $SUVA_{254}$ and the relative contribution of the humic-like component (determined from PARAFAC modeling) increased by more than 100% (Figures 7a and 7c). However, the wetland watershed showed a slight decrease in $SUVA_{254}$ and humic-like fluorescence during both storms (Figures 7b and 7d). Evaluating the three subcatchment streams showed that $SUVA_{254}$ and the contribution of the humic-like component decreased slightly in the bog and forested wetland during both storms (Figure 8). However, both measures increased in the mineral forest subcatchment during the two storms (Figure 8). The contribution of the fulvic-like component decreased at all sample sites during both storms, but the relative decrease was greater in the upland watershed and the mineral forest subcatchment compared to the wetland sites. Additionally, humic-like fluorescence was a strong predictor of $SUVA_{254}$ for all five sites taken together ($r^2 = 0.67$; $p < 0.001$ (Figure 9a)).

[20] The relative contribution of protein-like fluorescence (sum of tyrosine- and tryptophan-like components) was

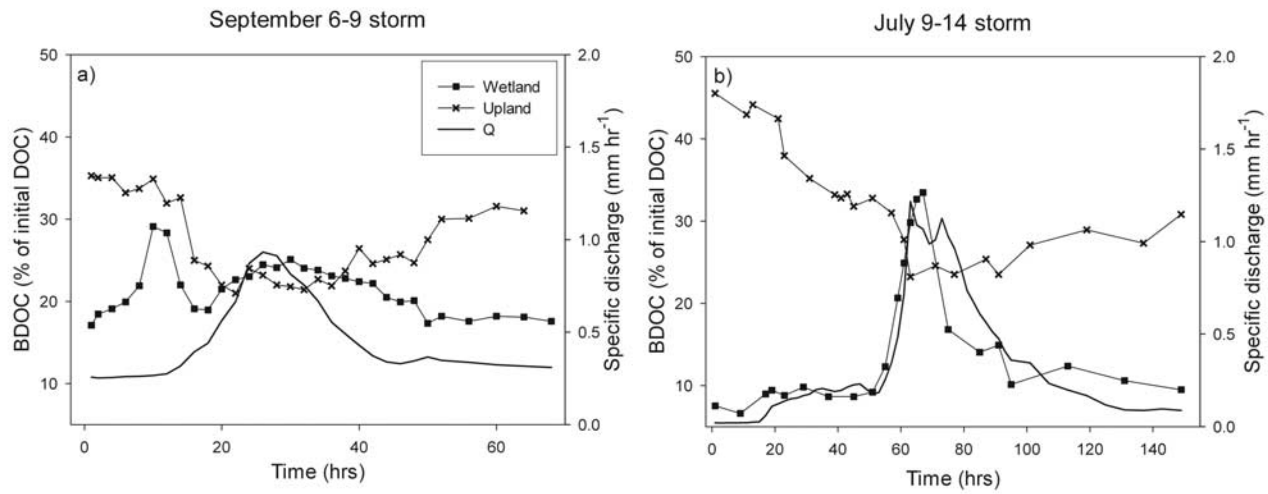

Figure 5. Relationship between percent BDOC and specific discharge (Q) for the 6–9 September and 9–14 July storms in the upland and wetland watersheds. Specific discharge from the wetland watershed is shown for timing.

significantly correlated with BDOC for all five sites taken together ($r^2 = 0.74$; $p < 0.001$ (Figure 9b)). The contribution of the tryptophan-like component increased with stormflow in all five sites during both storms, although the tyrosine-like component increased in four of the sites and decreased in the upland watershed (Figure 10). The contribution of the tryptophan-like component ranged from 0 to 9% and typically peaked on the ascending limb of the storm hydrograph, whereas the tyrosine-like component ranged from 0 to 34% and peaked coincident with maximum DOC concentrations in the wetland sites. Similar to percent BDOC, stream water in the wetland watershed showed a peak in tyrosine-like fluorescence on the ascending limb of the fall storm hydrograph that was attributed to protein-rich DOM flushed from salmon carcasses in the riparian zone back into the stream (Figure 10a).

[21] Changes in the fluorescence characteristics of stream water DOM for the 9–14 July storm were reflected in soil water, collected from piezometers located in subcatchment soils. In soil water, prestorm protein-like fluorescence was greater than 13% for the bog and forested wetland and indicates a pool of labile DOM in soil solution that was potentially available to flush to streams (Figure 11). The contribution of protein-like fluorescence in soil water decreased greater than 61% during the storm for the three subcatchments, whereas stream water protein-like fluorescence showed an initial increase followed by a gradual decrease during the remainder of the storm. As streamflow returned to prestorm levels, soil pools of protein-rich DOM were depleted and soil surface horizons and subcatchment outlet streams become poorly linked as protein-like fluorescence in stream water returned to near-prestorm levels of less than 2%.

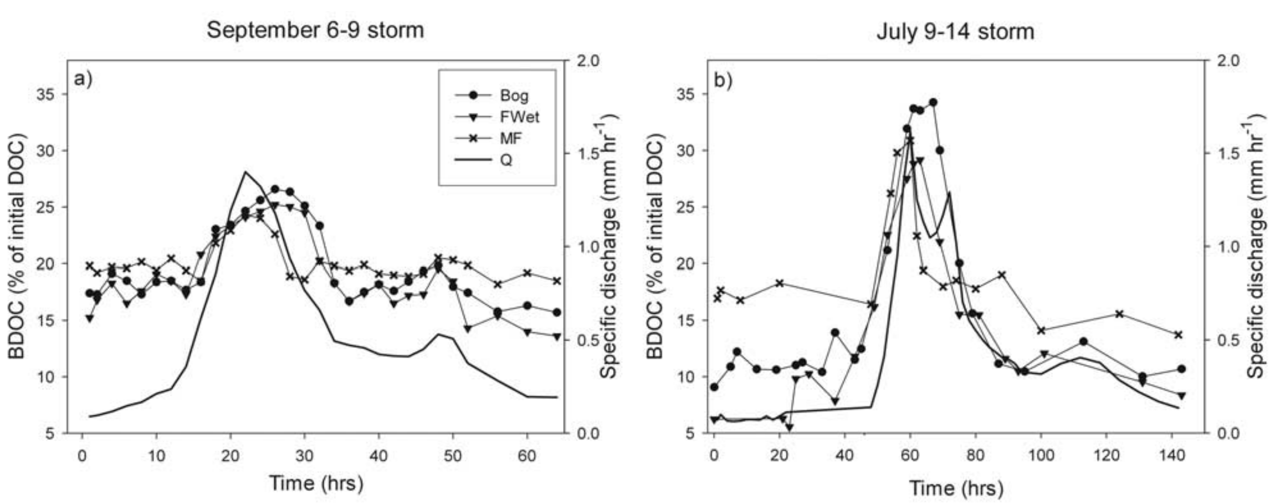

Figure 6. Relationship between percent BDOC and specific discharge (Q) for the 6–9 September and 9–14 July storms in the bog, forested wetland (FWet), and mineral forest (MF) subcatchments. Specific discharge from the mineral forest is shown for timing.

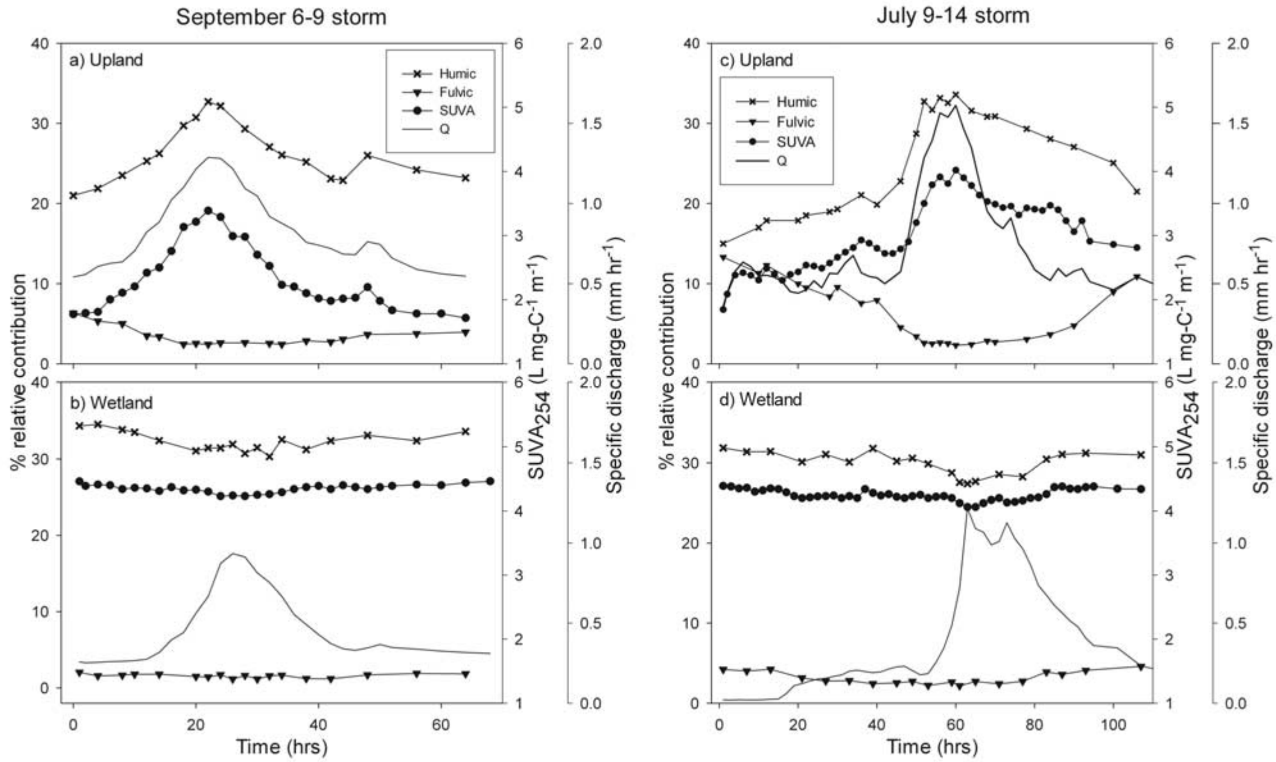

Figure 7. Relationship between specific discharge (Q), $SUVA_{254}$, and the relative contribution of the humic- and fulvic-like PARAFAC components for the 6–9 September and 9–14 July storms in the upland and wetland watersheds.

3.4. Export of DOC and BDOC

[22] Area-weighted DOC export was greatest for the forested wetland and bog subcatchments exceeding 10 kg C ha^{-1} for both storms (Table 3). Specific DOC flux (areal DOC flux corrected for the specific discharge for the entire storm) ranged from 0.01 to 0.11 kg C ha^{-1} mm^{-1} and was greatest for the forested wetland and bog subcatchments for both storms. Areal DOC flux for all five streams was significantly greater for the summer storm compared to the fall storm (t-test; $p = 0.002$), whereas specific DOC flux was not significantly different between the two storms (t-test; $p > 0.5$). Similar to DOC, areal BDOC flux and specific BDOC flux were greatest in the bog subcatchment for both storms (Table 3). Areal BDOC flux and specific BDOC flux were significantly greater (t-test, $p < 0.005$) for the summer storm compared to the fall storm for all five streams. BDOC export for all sites accounted for an average of 25% and 31% of DOC export for the fall and summer storms, respectively and BDOC contributed the greatest to DOC flux in the mineral forest subcatchment.

4. Discussion

4.1. Stream Water DOC and BDOC Concentrations

[23] Storms increased stream water DOC concentrations in all five sites, which is consistent with findings in other forested [*Hinton et al.*, 1998; *Buffam et al.*, 2001; *Inamdar et al.*, 2004] and wetland watersheds [*Worrall et al.*, 2002; *Inamdar and Mitchell*, 2007]. Our results support the idea that DOC source pools and hydrologic flow paths are different between base flow and stormflow [*Worrall et al.*, 2002; *McGlynn and McDonnell*, 2003]. Stream water DOC concentrations were significantly higher in the wetland compared to the upland watershed, which is consistent with the idea that DOC concentrations are related to soil organic carbon content [*Aitkenhead-Peterson et al.*, 2005]. However, the relative percentage increase in stream water DOC from base flow to stormflow was greater in the upland watershed and mineral forest subcatchment in comparison to the three wetland sites. This is because base flow DOC in streams draining forested watersheds is low in comparison to streams draining wetlands. We therefore suggest stormflow export of DOC is a more substantial proportion of annual DOC export in upland forest compared to wetland-dominated watersheds.

[24] The percentage and absolute concentration of BDOC shifted in all study streams and provides evidence that the lability of DOM changes during stormflows. During storms, DOM source areas will change and differing flow paths will entrain DOM with different chemical properties. More specifically, the combination of flowpath analysis and ^{14}C content of DOC in streams draining forested watersheds suggests that during stormflows, stream water DOM is of recent origin and originates from the litter or upper A horizons [*Schiff et al.*, 1997; *Palmer et al.*, 2001] or from near-stream riparian sources [*McGlynn and McDonnell*, 2003]. This DOM is relatively labile because shorter soil residence times decrease the opportunity for biodegradation in the soil. Similar to forested watersheds, DOM leached from wetlands during stormflows occurs primarily through

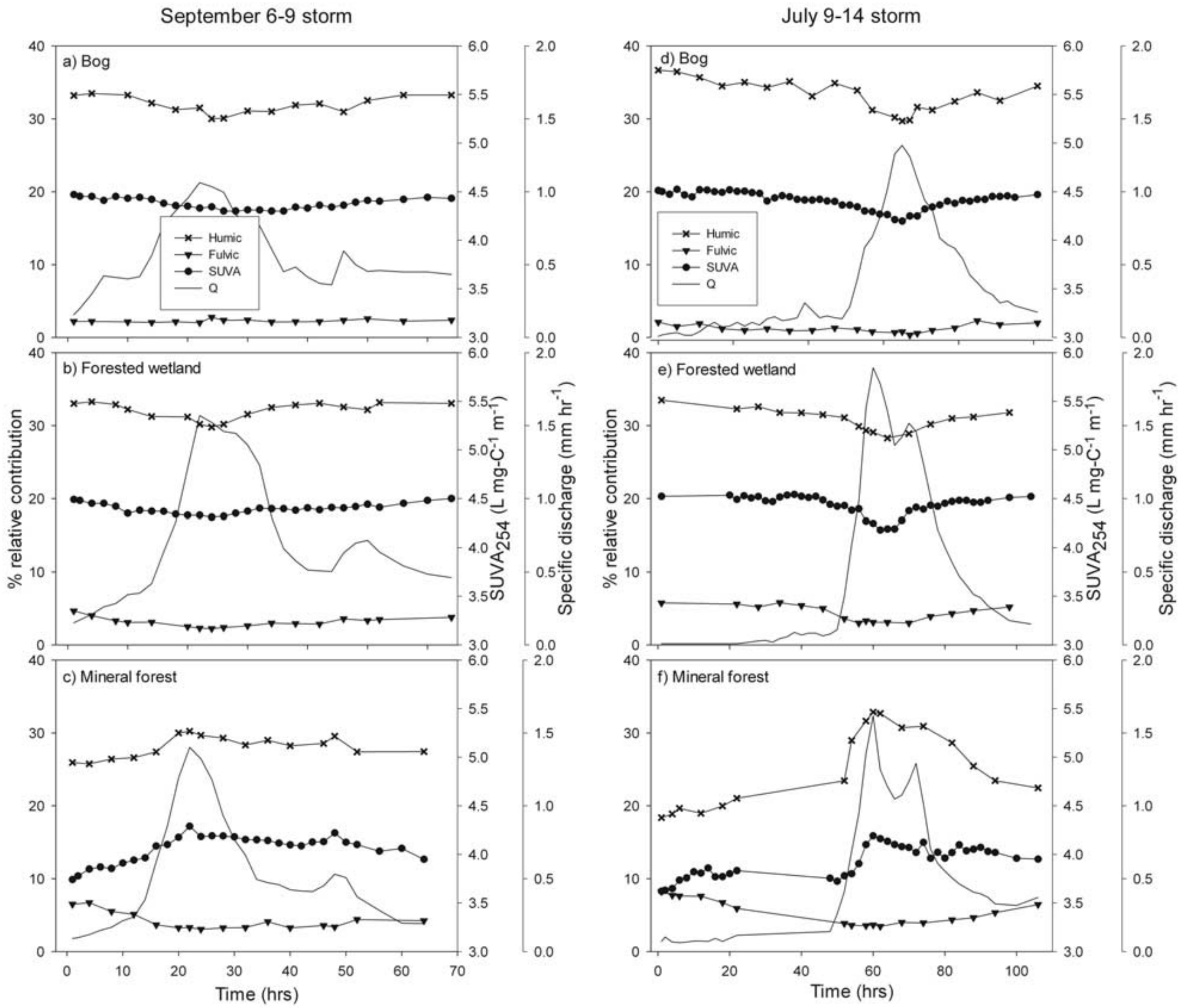

Figure 8. Relationship between specific discharge (Q), $SUVA_{254}$, and the relative contribution of the humic- and fulvic-like PARAFAC components for the 6–9 September and 9–14 July storms in the three subcatchment streams.

shallow flowpaths [*Worrall et al.*, 2003] resulting in the delivery of labile DOM of recent origin to streams [*Schiff et al.*, 1997; *Fraser et al.*, 2001].

[25] Previous estimates of BDOC in aquatic ecosystems have shown that 1–75% of DOM in natural systems is biodegradable, thus the BDOC values (6–45%) reported in this study fall within the range of previously reported values [*Sun et al.*, 1997, and references therein]. The observed increase in BDOC during stormflows relative to base flow in the three wetland sites and the mineral forest subcatchment is similar to results in White Creek, Pennsylvania, where the fraction of BDOC was greater during stormflows than base flow [*Gremm and Kaplan*, 1998]. In contrast, the decrease in percent BDOC during stormflows in the upland watershed is consistent with research in a forested Appalachian stream [*Buffam et al.*, 2001] and from small tributaries draining into the Ogeechee River [*Leff and Meyer*, 1991]. These findings indicate that flushing of soils during storms contributes both labile and recalcitrant forms of DOM to streams. Thus, watersheds contain spatially distinct source pools, such as different landscape/soil types, that contribute contemporaneously to the pool of BDOC in stream water.

[26] Concentrations of BDOC were significantly greater for the wetland compared to the upland watershed, although percent BDOC in the upland stream was generally greater than in the wetland stream. The greater DOC concentrations in the wetland watershed led to the higher concentrations of BDOC, which exceed total DOC concentrations in many temperate streams [*Kaplan et al.*, 2006]. This suggests stormflows are an important mechanism for the transfer of labile DOM from wetlands to downstream aquatic ecosystems. Our finding that the relative percent increase in BDOC was greater in wetland sites is because base flow percent BDOC in the upland and mineral forest streams was higher compared to the wetland streams. This is likely due to a combination of autochthonous production of labile DOM and from adsorption of recalcitrant forms of DOM with passage through the mineral soil horizons [*Qualls and*

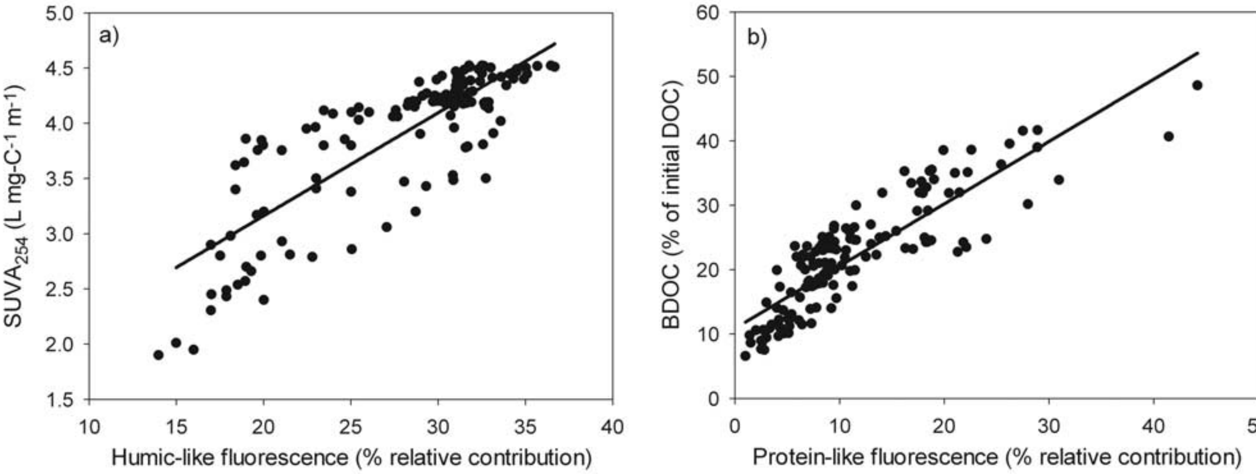

Figure 9. Regression models describing the relationship between (a) the contribution of humic-like fluorescence and $SUVA_{254}$ and (b) the contribution of protein-like fluorescence (sum of tyrosine- and tryptophan-like PARAFAC components) and percent BDOC for the 6–9 September and 9–14 July storms.

Haines, 1992]. The observed decrease in stormflow BDOC in the upland watershed could result from the dilution of labile DOM derived from in-stream production that occurs during periods of constant discharge [*Kaplan and Bott*, 1982]. Thus, even though the DOM entering the upland stream during stormflows is a mixture of both labile and recalcitrant forms of DOM, the overall response is a decrease in the fraction of BDOC present in stream water.

[27] Overall, we found DOM entering the stream during stormflows to be more biodegradable in four out of the five sites and thus, these labile DOM inputs are potentially an important source of nutrients and energy for aquatic heterotrophs. Previous research during storms in a forested Appalachian stream found bacterial abundance in the water column to increase approximately fivefold relative to base flow [*Buffam et al.*, 2001]. However, the extent of DOM utilization during storms is likely dependent on the extent to which microbial communities in the stream are disrupted by the increased discharge and the scouring of the streambed that accompanies stormflows [*Gremm and Kaplan*, 1998].

4.2. Spectroscopic Properties of DOM

[28] The $SUVA_{254}$ of DOC and PARAFAC analysis of fluorescent DOM proved to be useful indicators of changes in the chemical quality of DOM during storms. The fluorescent properties of DOM shifted toward more humic-like in the upland watershed and mineral forest subcatchment stream. This provides evidence that near-surface soil horizons are being flushed and that these soil horizons are a primary contributor of DOM to streams during storms [*Hornberger et al.*, 1994; *Boyer et al.*, 1997; *Zhang et al.*, 2007]. The contribution of humic-like fluorescence was significantly correlated with $SUVA_{254}$, which suggests that the humic-like component can be used as an indicator of aromatic C content. Previous research has shown that the humic fraction of DOM has a greater aromatic C content than the nonhumic DOC fraction [*Hood et al.*, 2005]. Thus, the shift in aromaticity is consistent with the observed shift in the fluorescent properties of DOM toward a greater percentage of humic DOM during stormflows.

[29] The increase in humic-like fluorescence during the summer storm was most pronounced in the upland watershed as the ratio of the humic-like component to the fulvic-like component increased from 1.1 to 14.6. These results suggest that during base flow in forested watersheds, fulvic DOM inputs from groundwater contribute greatly to the stream water pool of DOM. As the water table rises into the surface organic horizons, humic DOM is flushed to the stream, increasing the ratio of humic- to fulvic-like fluorescence in the stream. This finding corroborates previous research in a northern hardwood forest showing that extractable humic acids dominate the surface organic horizons and decrease with depth in the soil profile until the more mobile fulvic acids eventually became the dominant fraction in the B horizons [*Ussiri and Johnson*, 2003]. The three wetland sites showed a larger decrease in $SUVA_{254}$ and humic-like fluorescence during the summer storm, which could result from the very low discharge and high $SUVA_{254}$ values present before the summer storm. The DOC draining peatlands during low-flow conditions can be very biologically degraded [*Fraser et al.*, 2001]. Therefore, the flushing of freshly leached DOM from the previously aerobic surface horizons would be less aromatic and likely responsible for the observed decrease in $SUVA_{254}$ and humic-like fluorescence observed in the wetland streams.

[30] The observed increase in protein-like fluorescence in four of the five study streams is consistent with other studies that have found stormflow DOM to be enriched in carbohydrates [*McDowell and Likens*, 1988; *Gremm and Kaplan*, 1998] and dissolved amino acids [*Lytle and Perdue*, 1981] relative to base flow. Previous results from a freshwater marsh along the Williamson River, Oregon showed that >96% of the dissolved amino acids in soil solution are associated with aquatic humus and proposed that flushing of soil humic substances from the adjacent landscape transports amino acids into the stream during spates [*Lytle and*

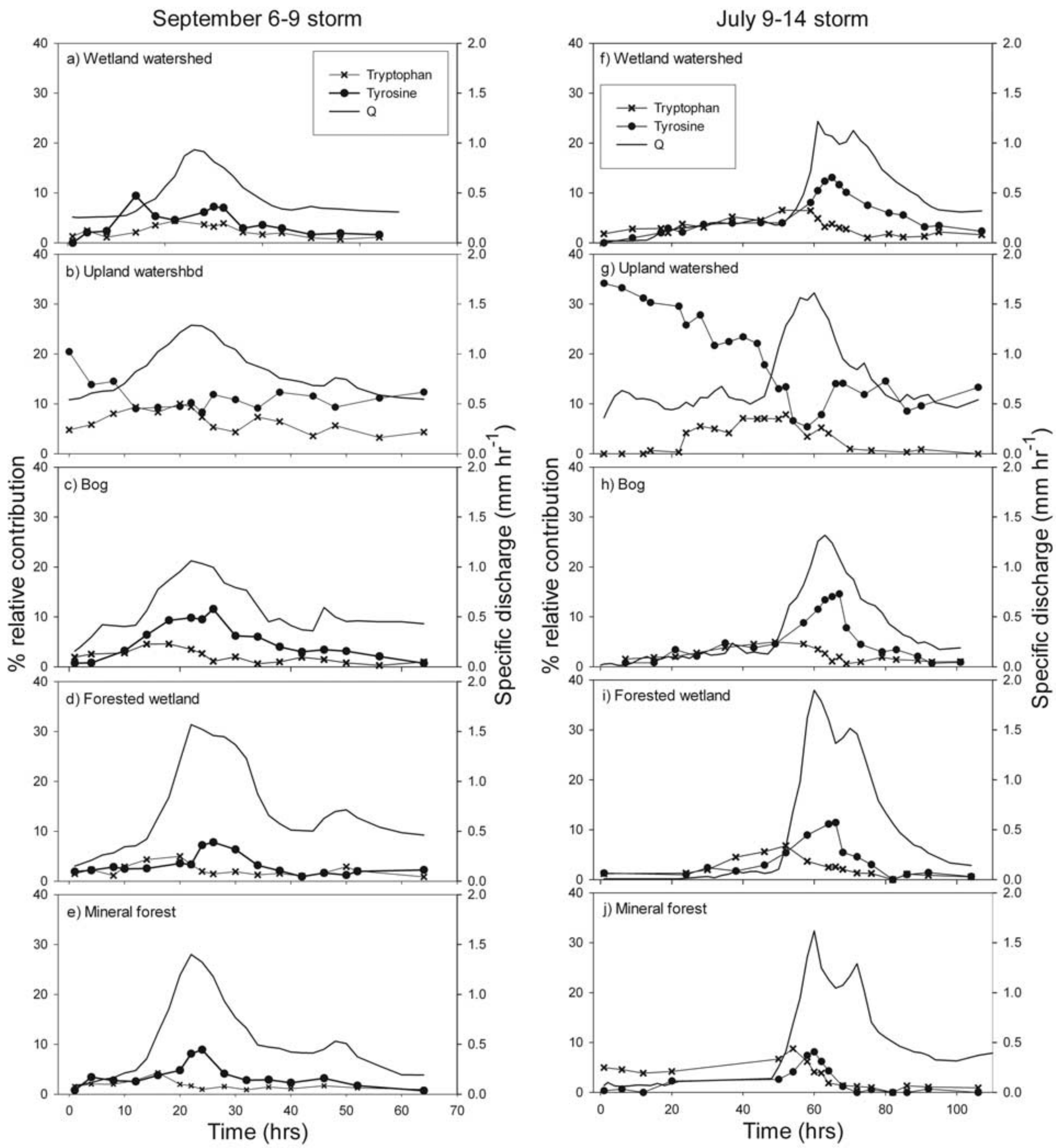

Figure 10. Relationship between specific discharge (Q) and the relative contribution of tyrosine- and tryptophan-like components for the 6–9 September and 9–14 July storms in the two study watersheds and three subcatchments.

Perdue, 1981]. The decrease in total protein-like fluorescence for the upland watershed during both storms could result from the dilution of high autochthonous production of amino acids by terrestrial DOM inputs. Fluorescence analysis of benthic algal leachate taken from the upland watershed stream showed a high contribution of protein-like fluorescence (45–50%), which is consistent with the prestorm fluorescent properties of DOM in the stream. Even though the flushing of soils contributes DOM enriched in amino acids, the overall response in the stream water pool of DOM is a decrease in protein-like fluorescence in the upland watershed. These findings demonstrate that DOM delivered to upland streams during storms is rich in humic-like material, aromatic C and generally lower in protein content. However, wetland DOM inputs to streams during stormflows are slightly less aromatic and enriched in proteinaceous DOM relative to base flow.

[31] The relative contribution of tryptophan-like fluorescence peaked on the ascending limb of the hydrograph for all sites and suggests a near stream, riparian origin. In

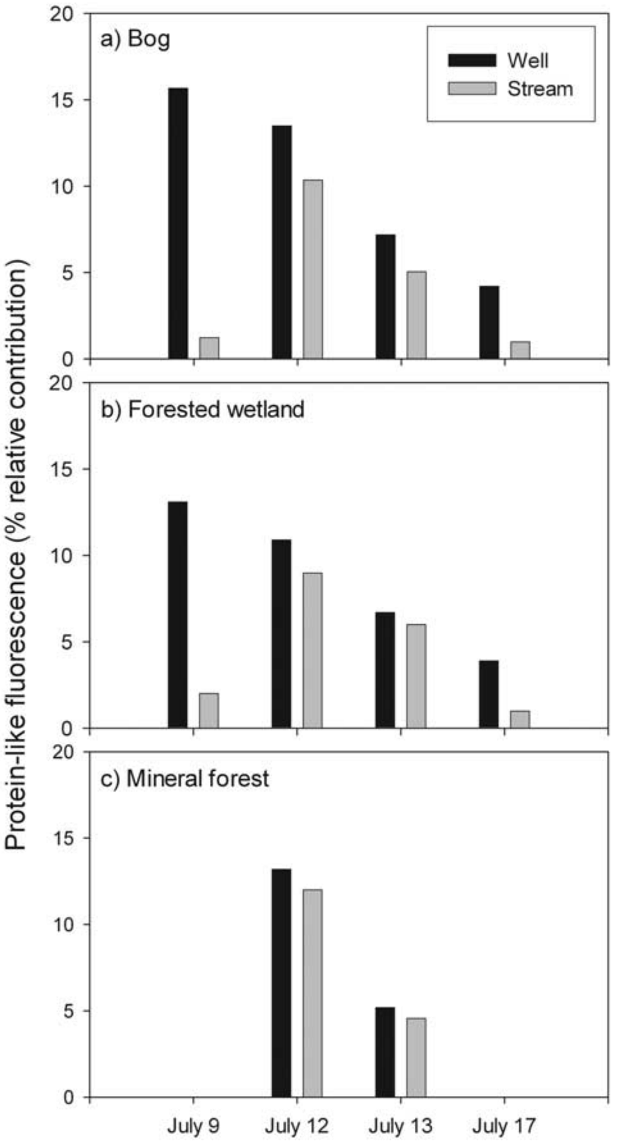

Figure 11. The contribution of protein-like fluorescence (sum of tyrosine- and tryptophan-like PARAFAC components) for the 9–14 July storm in the three subcatchment streams and soil pore water collected from 25 cm piezometers located within each subcatchment.

contrast, the contribution of tyrosine-like fluorescence generally peaked coincident with maximum DOC concentrations. Tyrosine fluoresces well in its monomer form and indicates the presence of more degraded peptide material. DOM with a greater contribution of tryptophan-like fluorescence has been associated with the presence of intact proteins or less degraded peptide material [*Mayer et al.*, 1999; *Yamashita and Tanoue*, 2004]. The behavior in protein-like fluorescence in our study suggests that fresh DOM, perhaps from throughfall in the riparian forest or the flushing of riparian soils could be responsible for the peak in tryptophan-like fluorescence early in the storm hydrograph. However, the peak in tyrosine-like fluorescence could indicate partially degraded organic material that has been recently solubilized during the flushing of soil surface horizons. This result suggests that DOM entering streams during storms is derived from multiple, spatially distinct sources within the watershed and streamflow integrates the watershed flushing response, as proposed by *Boyer et al.* [1997].

[32] The contribution of protein-like fluorescence was strongly correlated with BDOC for all sites taken together and suggests PARAFAC analysis of DOM fluorescence can be used as an indicator of labile DOM in natural environments [see *Fellman et al.*, 2008a]. PARAFAC modeling of DOM fluorescence has also shown that during BDOC incubations with soil pore water collected from boreal forests, there is a selective degradation of protein-like fluorophores while other compounds remain or increase in relative abundance [*Wickland et al.*, 2007]. These results indicate that during our BDOC incubations, protein-like fluorophores are a readily available source of C, energy, and N for heterotrophic microbes. Thus, the lability of organic forms of N could strongly influence nutrient limitation and overall stream production at our sites, particularly during low-streamflow conditions when DOM is low in protein-like fluorescence.

[33] The observed changes in protein-like fluorescence in both soil water and subcatchment outlet streams confirm the utility of using PARAFAC modeling of fluorescence EEMs to elucidate the coupling of terrestrial and aquatic ecosystems during storms. Differences in protein-like fluorescence between soils and streams also demonstrated that terrestrial DOM source pools are poorly linked with streams during base flow conditions. However, as hydrologic flowpaths change to near surface soil horizons, soil DOM source pools become linked with streams as the chemical quality of DOM in stream water is very similar to that in soil solution.

4.3. DOC and BDOC Export

[34] Our finding that the specific DOC flux was not significantly different between the fall and summer storms suggests stream water DOC concentrations are controlled primarily by changes in stream discharge, which is similar to other studies of peat-covered catchments [*Worrall et al.*, 2008]. However, the significant difference in specific BDOC flux between the fall and summer storms suggests that stormflow BDOC yields are controlled by multiple factors including changes in stream discharge, antecedent hydrologic conditions and seasonal changes in BDOC production. Additionally, BDOC export for all sites averaged 25% and 31% of DOC export for the fall and summer storms and suggests that stormflows are responsible for a substantial flux of labile DOM from terrestrial to aquatic ecosystems.

[35] Few studies report DOC fluxes from peatland catchments for individual storms, although our calculated export from the two upland forest streams (2.3–3.4 kg C ha^{-1}) falls within the range of other studies of forested watersheds [*McGlynn and McDonnell*, 2003; *Inamdar et al.*, 2006]. Modeled annual DOC export from coastal temperate watersheds of southeast Alaska ranges from approximately 40–99 kg C ha^{-1} in forested watersheds and 130–190 kg C ha^{-1} from watersheds with high wetland coverage (R. T. Edwards, unpublished data, 2007). Therefore, the average export we report for the upland (3 kg C ha^{-1}) and wetland (9.5 kg C ha^{-1}) watersheds suggests DOC export during

Table 3. Summary of DOC and BDOC Fluxes for the 6–9 September and 9–14 July Storms

	Specific Q^a (mm)	DOC Flux (kg ha^{-1})	DOC Flux[b] (kg ha^{-1} mm^{-1})	BDOC Flux (kg ha^{-1})	BDOC Flux[b] (kg ha^{-1} mm^{-1})	DOC (%)
			September 2006			
Wetland watershed	30	3.2	0.10	0.7	0.02	22
Upland watershed	46	2.3	0.05	0.6	0.01	27
Bog[c]	35	12.6	0.36	3.2	0.09	25
Forested wetland[c]	39	10.8	0.28	2.5	0.06	24
Mineral forest[c]	40	2.9	0.07	0.8	0.02	28
			July 2007			
Wetland watershed	37	4.1	0.11	1.3	0.04	31
Upland watershed	67	3.4	0.05	1.0	0.02	28
Bog[c]	38	13.9	0.37	4.2	0.11	30
Forested wetland[c]	44	12.1	0.27	3.3	0.07	27
Mineral forest[c]	47	3.4	0.07	1.2	0.03	37

[a]Specific discharge (Q) is the total amount of discharge for the entire storm.
[b]Area-weighted DOC and BDOC flux per specific discharge for the entire storm.
[c]Subcatchment located with the wetland watershed.

midsummer and fall storms could account for a large portion of annual watershed DOC export. Our findings reinforce the importance of individual storms for DOM export from forested and wetland watersheds in coastal temperate watersheds.

5. Conclusions

[36] The results of this study support previous observations in other streams of changes in the concentration and chemical quality of DOM during stormflows. Thus, our results highlight the importance of individual storms for the export of DOC and BDOC from watersheds. Our finding that specific BDOC flux was significantly different between the fall and summer storm indicates that the frequency and duration of storms, season, and watershed wetland coverage can impact BDOC export from coastal temperate watersheds. Stormflow BDOC concentrations were significantly greater in the wetland compared to the upland watershed, suggesting that wetlands could be an important source of labile DOM to southeast Alaskan streams. Because many of the watersheds in southeastern Alaska drain directly into nearshore marine ecosystems, these findings have important implications for productivity in coastal food webs that depend on terrestrial carbon as a source of energy and nutrients.

[37] The observed changes in protein-like fluorescence during stormflows suggest a strong linkage developed between terrestrial and aquatic ecosystems that is responsible for the delivery of labile DOM from soil source pools to streams. These findings indicate PARAFAC modeling of fluorescence EEMs is an effective tool for elucidating shifts in the quality of stream water DOM during storms. Moreover, DOM delivered to upland streams during storms is rich in humic-like material, aromatic C and generally lower in protein-like DOM. However, wetland DOM inputs to streams during stormflows are slightly less aromatic and enriched in proteinaceous DOM relative to base flow. Taken together, the importance of individual storms for watershed DOM export combined with the variation in the concentration and chemical quality of DOM exported from the different landscape types makes it difficult to predict the effects of climate change on DOM export from watersheds.

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