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Changes in the character of stream water dissolved organic carbon during flushing in three small watersheds, Oregon

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[1] The hydrologic and biogeochemical responses of forested watersheds to inputs of rainfall and snowmelt can be an indicator of internal watershed function. In this study, we assess how the quantity and quality, both chemical and spectroscopic, of stream water DOC changes in response to a 6-day storm event during the wet season of 2003 in three small (<1 km^2) basins in the H. J. Andrews Experimental Forest, Oregon. The watersheds included one old-growth watershed (WS02) and two previously logged watersheds (WS01 and WS10). Prestorm concentrations of DOC ranged from 1.5 to 2.2 mg C L^{-1} in the three watersheds and increased approximately threefold on the ascending limb of the storm hydrograph. Concentrations of DOC were both highest in the unharvested, old-growth watershed. The specific UV absorbance (SUVA, 254 nm) of DOC in the three watersheds increased by 9 to 36% during the storm, suggesting that DOC mobilized from catchment soils during storms is more aromatic than DOC entering the stream during baseflow. The increase in SUVA was most pronounced in the previously harvested catchments. Chromatographic fractionation of DOC showed that the percentage of DOC composed of non-humic material decreasing by 9 to 22% during the storm. Shifts in the fluorescence properties of DOC suggest that there was not a pronounced change in the relative proportion of stream water DOC derived from allochthonous versus autochthonous precursor material. Taken together, these results suggest that spectroscopic and chemical characterization of DOC can be used as tools to investigate changing sources of DOC and water within forested watersheds.

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1. Introduction

[2] During precipitation events, solute concentrations often exhibit a flushing response, peaking prior to the hydrograph peak. This characteristic flushing response has previously been observed for both dissolved organic carbon (DOC) [*Boyer et al.*, 1997] and dissolved organic nitrogen (DON) [*Vanderbilt et al.*, 2003]. Recent research on watershed responses of stream dissolved organic matter concentrations suggests that there are distinct source areas of DOC within a watershed that are mobilized during storms. In particular, runoff and DOC during the rising limb of the storm hydrograph are dominated by inputs from riparian areas, while later in the storm there is an increase in the contribution of water and solutes from catchment hillslopes [*McGlynn and McDonnell*, 2003]. This finding suggests that the DOC dynamics observed at the outlet of a watershed are controlled by the hydrologic connectivity of different landscape units or source pools within the watershed.

[3] Within a catchment, riparian zones, soil water, interflow or overflow, and deeper groundwaters may all act as sources of stream water and DOC. Previous studies of stream DOC patterns with respect to hydrologic response have focused on concentrations of bulk DOC [*Hornberger et al.*, 1994; *Boyer et al.*, 1997, 2000]. However, the spectroscopic and chemical characterization of DOC can provide information about how the quality as well as the amount of DOC in stream water changes during hydrologic events. For example, spectroscopic analyses such as specific UV absorbance and fluorescence have the potential to provide information about shifts in the chemical character [*Weishaar et al.*, 2003] and precursor material [*McKnight et al.*, 2001] of aquatic DOC. Previous research has shown that stream water DOC derived from different source pools and along different flowpaths within a catchment can have unique chemical and spectroscopic characteristics [*McKnight et al.*, 1997; *Hood et al.*, 2003]. Thus shifts in the character of stream water DOC during storm events have the potential to provide information about which source pools of DOC are hydrologically connected to the stream, and/or transformations of DOC along flowpaths to catchment outlets. As a result, we propose that the charac-

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Table 1. Physical Characteristics and Land Use History for Watersheds 1, 2, and 10 in the H. J. Andrews Experimental Forest

Watershed	Area, ha	Elevation, m	Average Basin Slope, %	Aspect	Land Use
1	96	442–1013	63	WNW	100% clear-cut 1962–1966
2	60	526–1067	61	NW	450-year-old forest
10	10.2	425–700	70	SW	100% clear-cut 1975

terization of stream DOC has the potential to be a useful hydrologic tracer, just as multiple cation and isotopic species can be useful cotracers [e.g., *Rice and Hornberger*, 1998; *Kendall et al.*, 2001].

[4] The purpose of this study was to evaluate and compare the flushing of cations and stream water DOC in small watersheds during a multiday storm event. We provide a descriptive characterization of DOC export by using spectroscopic and chemical analyses to identify how the quality of DOC changes during the storm. These techniques should allow us to discern whether the type, and therefore source and potentially the flowpath of DOC are changing through the course of the storm event. Additionally, these measures of DOC quality provide insight into the variability in the chemical character of DOC among different sources of DOC within the catchments.

2. Methods

2.1. Site Description

[5] This study was conducted in three small basins in the H. J. Andrews Experimental Forest, west central Oregon (longitude 122°15′; latitude 44°12′). The basins were similar in elevation range and slope ranged in size from 10.2 to 96 ha (Table 1). The climate in the lower elevations of the western Cascade Mountains is xeric with warm, dry summers and cool to cold wet winters. Mean annual precipitation is 2200 mm, 80% of which occurs between November and April. Forest and riparian soils are formed from highly weathered volcanics with silt textures, high rock fragment content and moderate organic horizons [*Dyrness*, 1969]. Because of the steep topography in these basins, shallow soils with little profile development predominate [*Rothacher et al.*, 1967; *Dyrness*, 1969]. Most of the soil types have moderately high field capacities. Stream channels are steep and confined with a mixed substrata ranging from exposed bedrock to unsorted sediments comprised of boulders to silt. Large wood is present in the channels in some locations. Each basin has a stream gauging station with digital stage recorders and well-established rating curves of stage-discharge relationships (http://www.fsl.orst.edu/lter/data.cfm; Hydrology database HF004).

[6] Native vegetation in the three basins is Douglas fir (*Pseudotsuga menziesii*) dominated 450-year-old forests. Watershed 2 (WS02) continues to be an unharvested, undisturbed basin. Watershed 1 (WS01) was 100% clear-cut between 1962 and 1966; no roads were constructed and large trees, including those in the riparian zone, were removed using cable logging methods. Logging slash was broadcast burned and hillslopes were replanted [*Dyrness*, 1973]. Herbs and shrubs recovered quickly on hillslopes in WS01, and conifer trees became the dominant cover by the 1990s [*Halpern and Franklin*, 1990]. Presently the downstream section of stream channel in WS01 has complete canopy closure dominated by red alder (*Alnus rubrus*) [*Johnson and Jones*, 2000]. In watershed 10 (WS10), clear-cutting occurred during 1975, using a running skyline system which carried logs >20 cm in diameter or >2.4 m in length uphill and out of the basin. The watershed was not broadcast burned but was replanted. Several debris flows occurred during 1986 and 1996 storms, scouring much of the downstream channel (∼350 m length) to bedrock [*Swanson et al.*, 1998]. The removal of large wood and substrata by these debris flows eliminated much of the hyporheic zone. Nutrient dynamics were intensively studied before and after forest harvest in WS10 [*Triska et al.*, 1984; *Sollins et al.*, 1980] and concentrations of dissolved organic carbon (DOC) during storms presently are similar to those following harvest [*Dahm*, 1980].

2.2. Sample Collection and Chemical Analyses

[7] Stream water samples were collected at the gauging station in each of the three basins as 1L grab samples approximately twice daily during a storm spanning 14–21 November 2003. Samples were filtered through ashed Whatman GFF filters within 12 hours of collection. Samples were refrigerated immediately after collection and remained refrigerated during shipping and until analysis for DOC and DOC characteristics, which occurred within 4 days of collection. DOC was analyzed by high-temperature combustion on a Shimadzu TOC-V Organic Carbon Analyzer in Juneau, Alaska. Additional stream samples at the basin gauging stations were collected with Sigma autosamplers programmed to collect 1 L every 2 hours during the initial portion of the storm and then every 4 hours during the hydrograph recession. These samples were filtered through ashed Whatman GFF within 48 hours of collection and frozen until analysis for major cations (Na^+, K^+, Mg^{2+}, and Ca^{2+}). Cation analyses were performed in Juneau, Alaska, on a Dionex DX500 Ion Chromatograph.

2.3. Dissolved Organic Carbon Characterization

[8] Stream water DOM was analyzed for UV-visible absorbance following the procedure of *Weishaar et al.* [2003]. UV measurements were made on a Genesys 5 UV-Vis spectrophotometer (Thermo Electron Corporation) using distilled water as a blank. A quartz cell with a 1.0-cm path length was used. Refrigerated samples were warmed to room temperature before analysis and duplicate analyses were performed approximately every 10 samples to ensure instrument stability. Specific UV absorbance (SUVA) was calculated by dividing the UV absorbance at 254 nm, measured in inverse meters (m^{-1}), by the DOC concentration and is reported in units of L $mg\text{-}C^{-1}$ m^{-1}.

[9] The fluorescence properties of DOC in stream water samples were measured using a Fluoromax-3 multiwavelength fluorescence spectrophotometer with a xenon lamp. Emission intensities were measured at 450 nm and 500 nm using an excitation of 370 nm to calculate the fluorescence index (FI) following the procedure of *McKnight et al.*

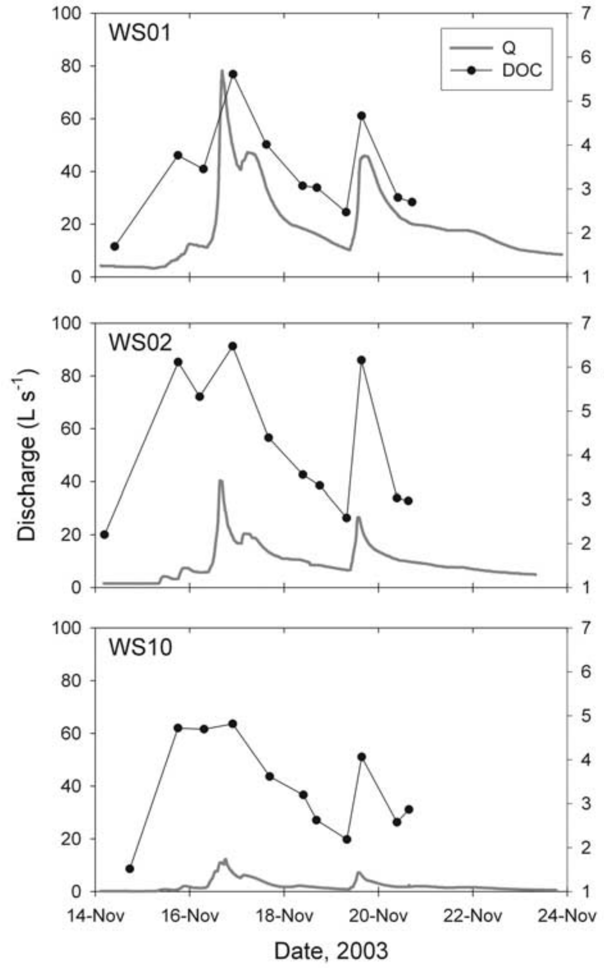

Figure 1. Relationship between concentrations of stream water DOC and discharge in the three study catchments.

[2001]. The intensity values for both the 450 nm and 500 nm scans were adjusted by subtracting the intensity of the blank. The FI was calculated as the ratio of the emission intensity at 450 nm to that at 500 nm produced with excitation at 370 nm. The standard deviation of samples analyzed in triplicate was typically less than 0.01. Fluorescence properties of DOC are related to the presence or absence of lignin in precursor materials and can therefore serve as a simple tool to distinguish the extent to which DOC is derived from aquatic autochthonous material that lacks lignin (high FI value ~1.8) versus detrital or allochthonous material that contains lignin (low FI value ~1.3) [*McKnight et al.*, 2001].

[10] For each of the three watersheds, a selection of 1L grab samples from prestorm (14 November), peak storm (16 November) and post storm (22 November) periods were analyzed for chemical properties of DOC. A 250-mL subsample of each 1L grab sample was fractionated into operationally defined humic and nonhumic fractions using XAD-8 Amberlite resins [*Hood et al.*, 2003]. This technique reproducibly isolates compositionally distinct fractions of DOM from the molecular continuum observed in natural waters [*Aiken et al.*, 1992]. In headwater streams, the humic fraction, which adsorbs to the XAD-8 resin, is composed primarily (>90%) of fulvic acids with a small proportion of humic acids [*Thurman*, 1985]. What we refer to as the nonhumic fraction is a heterogeneous class of substances that passes through the XAD-8 resin including carbohydrates, carboxylic acids and amino acids [*Qualls and Haines*, 1991; *Thurman*, 1985]. Mass balance analyses show that DOC recovery was almost complete, with the sum of the DOC measured in the humic and non-humic fractions between 95 and 105% of DOC in the original sample.

3. Results

3.1. DOC and Major Ion Hysteresis

[11] Pre-storm concentrations of DOC were 1–2 mg-C L^{-1} with the highest concentration in the old growth watershed (Figure 1). During the 15–16 November storm event, DOC concentrations increased by approximately 200% in all three watersheds peaking at 5–7 mg-C L^{-1}. DOC concentrations increased again during the second storm event on 19 November, although peak concentrations were somewhat lower, possibly because DOC pools had been flushed in the earlier storm event. In all three watersheds, concentrations of DOC showed a clockwise hysteresis with higher concentrations on the ascending limb of the hydrograph compared to the descending limb (Figure 2), similar to C2 plots (clockwise hysteresis loop, in which initially there is a sharp increase in solute concentration, as discharge increases), as defined by *Evans and Davies* [1998]. These results indicate that the water entering the stream during the early part of the storm had higher concentrations of DOC compared to water entering the stream late in the storm.

[12] We also analyzed samples for major cations to compare flushing dynamics of inorganic solutes with DOC flushing dynamics. In WS01, all major ions show an initial depression of concentration (dilution effect) as discharge increases, and then substantial increase in concentration with discharge (Figure 3). Similar to DOC, all WS01 major ion hysteresis loops are generally clockwise, except for each of the nested loops which have some degree of anticlockwise behavior corresponding to the second rise in the hydrograph. In WS02, initial concentrations of major ions are diluted by increased discharge, but subsequent shape or characterization cannot be determined in any case except that of K^+, which demonstrates an initial clockwise loop followed by an anticlockwise loop (Figure 3). In WS10, Na^+, Mg^{2+}, and Ca^{2+} hysteresis loops indicate dilution of concentrations with increasing discharge (similar to *Evans and Davies'* [1998] C3 loop (a clockwise hysteresis loop decreasing in solute concentration as discharge peaks), but the K^+ loop demonstrates an initial rise in concentration with discharge, similar to *Evans and Davies'* [1998] C2 loop (Figure 3). In the cases of WS01 and WS10, DOC hysteresis loops are most similar to corresponding K^+ hysteresis loops.

3.2. Spectroscopic Properties of DOC

[13] The specific UV absorbance of DOC increased during the storm events in all three watersheds (Figure 4). The shift in SUVA of DOC was most pronounced in WS01

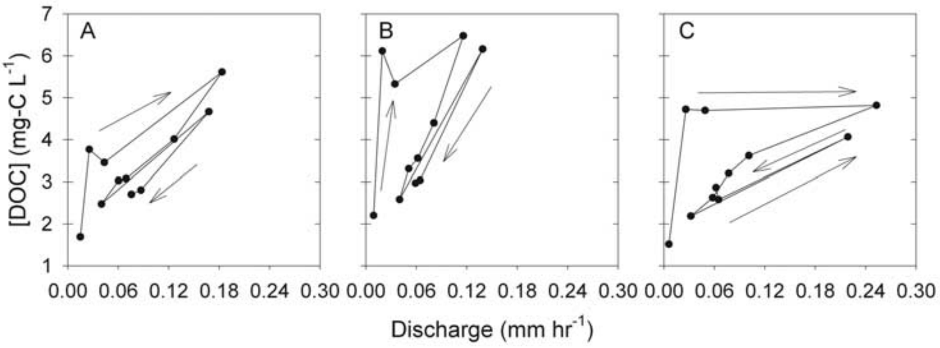

Figure 2. Concentration/discharge plots for DOC in (a) watershed 1, (b) watershed 2, and (c) watershed 10. All plots showed a clockwise hysteresis during storm events, generally a C2 shape with higher DOC concentrations on the ascending limb of the hydrograph compared to the descending limb. Discharge is normalized to watershed area.

and WS10. These previously harvested watersheds both showed an increase in SUVA of approximately 35% during the storm. In contrast, in WS02, the old growth watershed, there was only a small (<10%) increase in SUVA during the storm. Similar to concentrations of DOC, SUVA showed a clockwise hysteresis with higher values on the ascending limb of the hydrograph (data not shown).

[14] The fluorescence properties of DOC varied between catchments. In WS01, the FI of DOC decreased by approximately 0.1 during the storm, which suggests there was a change in the source of DOC during the storm event in this watershed [*McKnight et al.*, 2001]. In addition, the FI was inversely correlated with DOC concentration ($r^2 = 0.74$, $p < 0.01$; Figure 5) in WS01. The FI in WS10 also decreased during the storm, while in WS02 the FI increased slightly. However, the magnitude of the shift in the FI in these two watersheds was quite small (~0.04; Figure 5). During the entire sampling period, the FI values for DOC in the old growth watershed (WS02) were significantly lower than the FI values for DOC in the two harvested watersheds, WS01 ($p < 0.001$) and WS10 ($p < 0.001$).

3.3. Chemical Properties of DOC

[15] The chemical character of DOC shifted toward more humic material during the storm in all three study watersheds. The humic content of stream water DOC was lowest during prestorm base flow (54–60% of DOC) on 14 November (Figure 6). As discharge and DOC concentrations increased during the storm, the humic content of DOC increased between 9 and 22% in the study watersheds, with no distinction among the three watersheds. The humic content of DOC decreased in the post storm samples but remained elevated compared to the prestorm samples.

4. Discussion

[16] The dynamics of bulk DOC observed during storm flow in this study were similar to those observed in other forested headwater catchments [*Hinton et al.*, 1998; *Buffam et al.*, 2001; *McGlynn and McDonnell*, 2003]. Concentrations of stream water DOC were closely related to discharge and showed a clockwise hysteresis with higher concentrations on the rising limb compared to the falling limb of the hydrograph. The fact that DOC concentrations responded rapidly and increased by ~200% in the three watersheds suggests that there is a near-stream source of DOC contributing to stream concentrations during the early response to storm events. Furthermore, in each of the DOC hysteresis plots, after the initial flushing of DOC (after the first four points of each plot in Figure 2), there is an approximately linear response between DOC concentration and discharge, with approximate slopes of 17.2, 36.4, and 9.5 for WS01, WS02, and WS10, respectively. Assuming that the first few points are indicative of near-stream dynamics and the later data are representative of the larger watershed response, this suggests that there is more DOC yield, per unit area, from the old-growth forest than from the two logged watersheds.

[17] Concentrations of major cations showed a similar clockwise hysteresis response with discharge. In comparing the cation hysteresis among basins, it is surprising to find that there is so little interpretation possible in the old-growth watershed (WS02). This may suggest a more complicated set of flowpaths and responses to storms than previous studies have assumed with two or three end-member mixing analyses [e.g., *Evans and Davies*, 1998]. The inconsistent hysteresis patterns support the findings of *Chanat et al.* [2002], who state that variability in hydrologic flowpaths may easily confound interpretation of concentration-discharge relationships at catchment outlets. The similarity of the Na^+, Mg^{2+}, and Ca^{2+} hysteresis loops in WS01 and WS10 are also intriguing in that they suggest that within these harvested watersheds, all three ions have similar sources and fluxes to the stream throughout these storms. It is also interesting to note that the K^+ hysteresis is similar to the DOC hysteresis in WS01 and WS10, but not in WS02. This would suggest that K^+ has a similar set of sources and flowpaths to the stream as DOC in the harvested watersheds. Given that both of these watersheds have forests less than 50 years old, such a response may be indicative of the difference in vegetation influences, compared to the old-growth watershed.

[18] Stream K^+ and Na^+ responses are likely to have some contribution from precipitation, while Ca^{2+} and Mg^{2+} are more likely to have solely weathering contributions. Thus comparing the three watershed responses, there is an increased contribution of Ca^{2+} and Mg^{2+} concentrations in the harvested watersheds (WS01 and WS10) than the old-

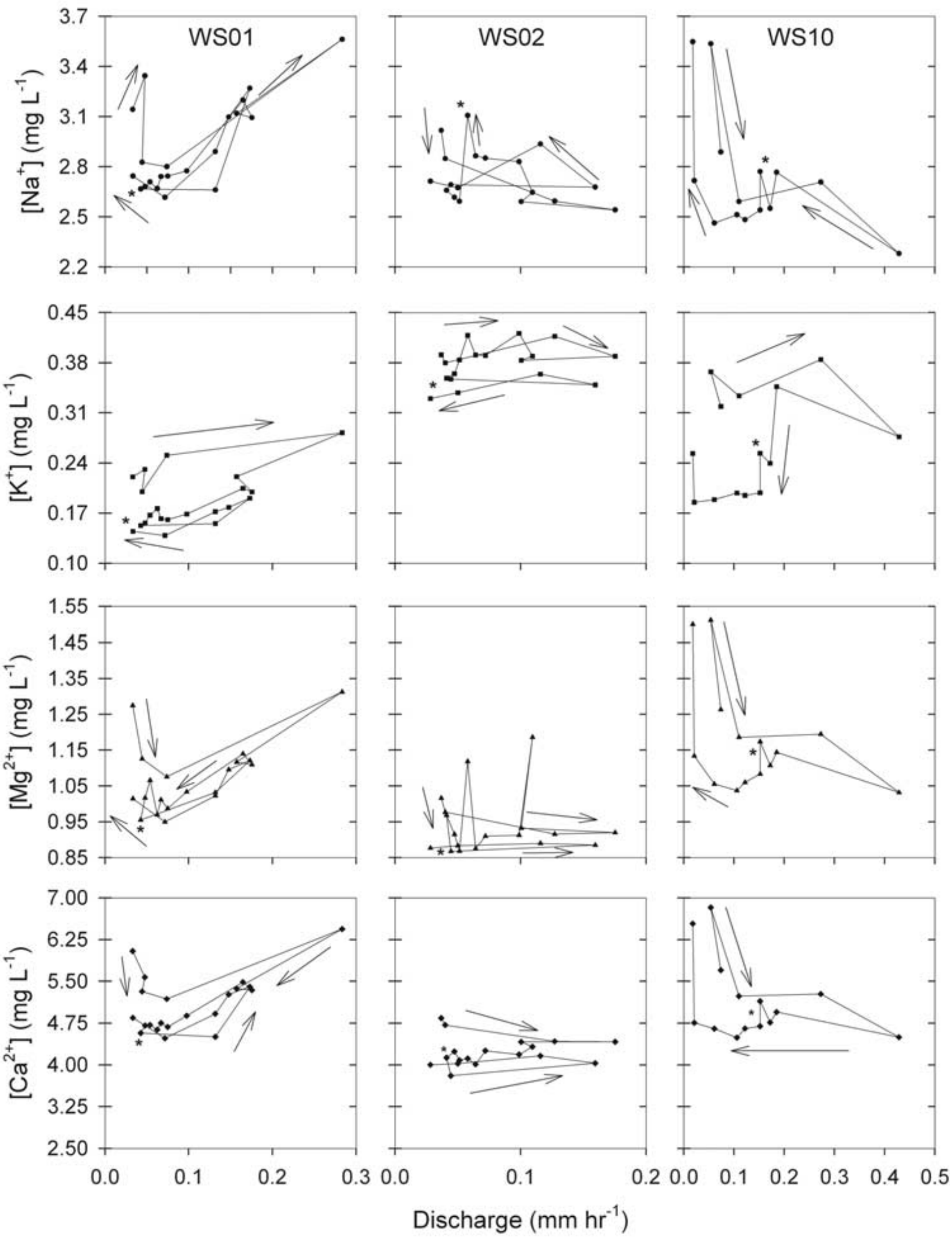

Figure 3. Concentration/discharge plots for major ions in watersheds 1, 2, and 10 for November 2003 storm. The beginning of the second rainfall event and increase in discharge is denoted by an asterisk on each plot. Discharge is normalized to watershed area.

growth watershed (WS02). This suggests that as a greater proportion of each watershed is flushed from the storm, there is perhaps a larger reservoir of old water influenced by mineral weathering in WS01 and WS10 than in WS02. The enhanced concentrations of weathering products in WS10 are consistent with the more recent logging in this catchment, compared to WS01, and the fact that it is a smaller catchment. WS01 and WS10 differ in their Na^+ and K^+ responses in that WS10 appears to be flushed of K^+ in the first storm, with no substantial increases in stream concentration until return to low discharge, and the WS10 Na^+ response is a general dilution through the first storm, with stream concentrations returning to near background at the end of the storm. In WS01, on the other hand, both Na^+ and K^+ respond up and down a roughly linear relationship between solute concentration and discharge after the first few points, similar to DOC dynamics discussed above.

[19] Further comparison of the DOC to cation hysteresis responses among basins shows that there is a difference in the response to the second storm (that of 19 November). WS01 and WS02 DOC loops are clockwise for both storms, but the WS10 DOC response is different, with the second being slightly anticlockwise. The WS01 K^+ demonstrates a clockwise loop for the first storm, and an anticlockwise loop for the second storm, and all of the WS10 cation loops are clockwise (Figure 3). We have no catchment end-member

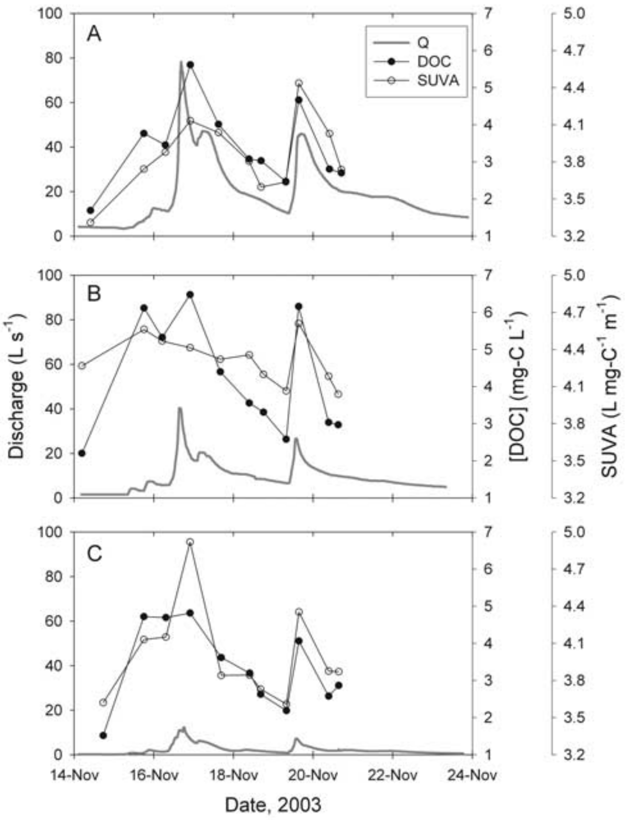

Figure 4. Time series of specific UV absorbance (SUVA, 254 nm) of DOC, DOC concentration, and discharge in (a) watershed 1, (b) watershed 2, and (c) watershed 10. SUVA increases with the increase in discharge and DOC concentration in all three watersheds.

concentration data for DOC or any of the cations, though these results suggest that there are differences, even at short timescales, in the hydrologic response of these watersheds to storm events.

[20] We propose that DOC is a useful hydrologic tracer, in the watershed context, because, unlike major ions or isotopes, we can characterize quality or character of DOC, not just the amount. Particularly within the context of ecohydrologic investigations, the character of DOC may prove a useful tracer, which could help to determine not only which pools of DOC contribute to streamflow, but also the chemical characteristics of each source. *Weishaar et al.* [2003] have previously demonstrated that, across a wide range of eco-regions, there is a strong relationship between SUVA and percent aromaticity of DOC as determined by ^{13}C-NMR. Thus the change in SUVA evident in all three watersheds indicates that the increase in DOC concentrations during the storm was associated with a shift in the chemical character of DOC. Using our SUVA measurements with the model of *Weishaar et al.* [2003], we calculate that the aromatic carbon content of DOC in our study watersheds increased from 25–29% during base flow to 32–35% near the storm peak. Previous research has shown that the humic fraction of DOC is more aromatic than the non-humic fraction [*Aiken et al.*, 1996; *Hood et al.*, 2005]. Thus the increase in the aromaticity of DOC during the storm is also consistent with the observed shift in the chemical fractions of DOC toward a higher percentage of humic DOC during peak storm flow.

[21] The shift in the chemical character of DOC during storm flow in H. J. Andrews appears to be similar to changes in DOC during snowmelt in seasonally snow covered headwater catchments. Previous research has shown that the percentage of humic DOC in stream water humic can increase 30–40% [*Easthouse et al.*, 1992; *Kaushal and Lewis*, 2003; *Hood et al.*, 2003] and SUVA can increase by >2 L mg-C^{-1} m^{-1} [*Hood et al.*, 2005] during the early stages of snowmelt before decreasing back to presnowmelt levels on the descending limb of the snowmelt hydrograph. The shifts in the humic content of DOC (approximately 10–20%) and SUVA (0.8–1.4 L mg-C^{-1} m^{-1}) that we observed during storm flow were smaller but showed a similar relationship to discharge. From a biogeochemical standpoint, the fact that the aromaticity and chemical character of DOC changed during the storm indicates that the DOC entering the stream as storm flow is derived from more than one source pool within the catchment, and that the increase in DOC during the storm does not simply represent the mobilization of additional DOC from the source pool that supplies DOC during base flow.

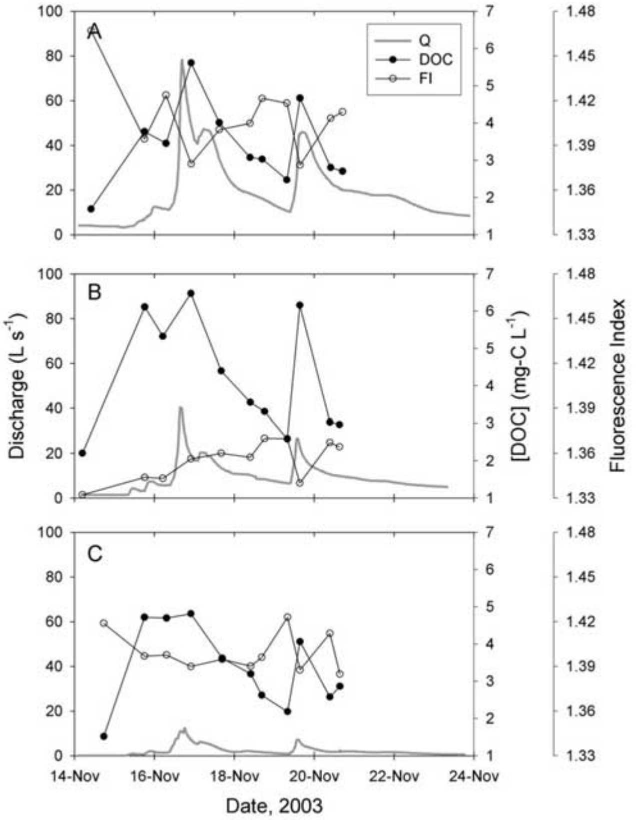

Figure 5. Time series of fluorescence index (FI), DOC concentrations, and discharge in (a) watershed 1, (b) watershed 2, and (c) watershed 10. DOC concentrations and FI tend to be inversely related in watersheds 1 and 10; as DOC concentrations increase, FI decreases.

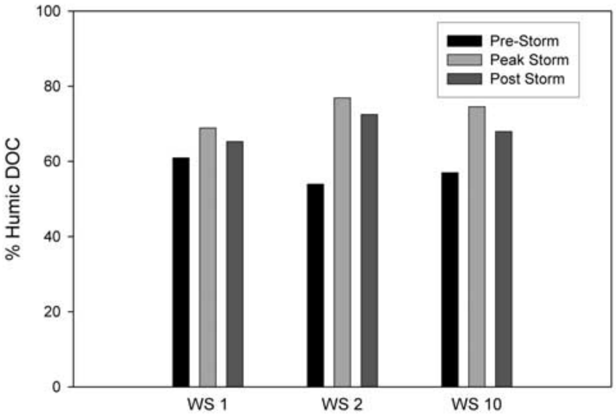

Figure 6. Humic content of DOC from WS01, WS02, and WS10 at three points on the storm hydrograph.

[22] For DOC to be used as a hydrologic tracer, changes in DOC character must be linked with sources of stream water within the catchment. *McGlynn and McDonnell* [2003] have previously suggested that catchment DOC dynamics during storm events are controlled by the mixing of spatially distinct streamflow source waters at the catchment outlet. Following the model of *McGlynn and McDonnell* [2003], our results are consistent with the idea that early in the storm DOC is derived from riparian zones and shallow organic soils which have high concentrations of aromatic DOC. The decrease in DOC concentration and aromaticity later in the storm is associated with water from deeper mineral soil on hillslopes that enters the stream after hillslope soil moisture deficits have been satisfied.

[23] In forest soils, DOC concentrations commonly decrease with increasing soil depth owing primarily to sorption in mineral soils [e.g., *Hinton et al.*, 1998; *Kaiser and Zech*, 2000; *Yano et al.*, 2005]. In our study, both concentrations of DOC and SUVA of DOC were lowest before and after the storm when streamflow is largely sustained by groundwater flow through mineral soil horizons. Previous research at H. J. Andrews Experimental Forest has shown that the majority of the decrease in DOC concentrations between 0–10 cm and 70 cm depth in the soil profile of old growth Douglas-fir forest was due to losses in the aromatic strong hydrophobic acid fraction of DOC, while less aromatic DOC fractions such as bases increased with soil depth [*Yano et al.*, 2004]. Similarly, batch isotherm experiments have shown that sorption with mineral phases preferentially removes the larger, more aromatic components of DOC from the solution phases which results in reduction in molar absorptivity at 280 nm [*Meier et al.*, 2004]. These findings are consistent with our hypothesis that the sharp increase in SUVA early in the storm is associated with storm flow DOC derived from riparian zones and shallow organic horizons that has had little contact with mineral soils. Later in the storm, storm flow from hillslopes enters the stream via deeper flowpaths and transports DOC that has a lower specific UV absorbance. These results suggest that shifts in SUVA for stream water DOC can provide information about shifts in catchment flowpaths between organic and mineral horizons.

[24] There were not dramatic differences in DOC dynamics between the previously harvested watersheds (WS01 and WS10) and the old growth watershed (WS02), however WS02 did have higher concentrations of DOC and higher SUVA of DOC, particular during base flow. In H. J. Andrews, *Yano et al.* [2005] have previously shown that changes to litter inputs such as doubling of wood or litter do not appreciably change the chemical composition of leachate from the O-horizon into the soil profile. However, our results would suggest that a higher proportion of water in the old growth watershed enters the stream via organic horizon flowpaths, most likely in the riparian zone.

[25] The temporal patterns of FI with discharge and DOC were more variable between watersheds than the patterns in SUVA. Results from WS01 show that as concentrations of DOC increase, the FI decreases suggesting that the source of the stream DOC is more “terrestrial,” from lignin-containing precursor material [*McKnight et al.*, 2001]. This pattern is less evident in WS02 and WS10. The FI values of DOC in the two harvested watersheds, WS01 and WS10, were significantly higher than the FI values of DOC in the old growth watershed (WS02) suggesting that a larger percentage of DOC in the harvested watersheds is derived from microbial precursor material. The common element among all of these catchments is that they have up to several km of first to second order stream. These sections of stream, particularly in the harvested watersheds that have higher light availability in the stream channel, may be the source of microbially derived DOC from algal and microbial material associated with stream sediments or hyporheic locations.

[26] During the storm, the FI decreased to more “terrestrial” values in both harvested watersheds, while in the old growth watershed the FI increased slightly but remained at a low, “terrestrial” value. These results are consistent with the fact that, in forested watersheds, stream water DOC is derived almost exclusively from allochthonous, terrestrial sources during the storm events [e.g., *Hinton et al.*, 1998; *McGlynn and McDonnell*, 2003]. The FI appears to be less useful as a hydrologic tracer because it is not possible to discriminate DOC derived from distinct terrestrial hydrologic pools using the FI. However, the FI does provide information about stream water sources of DOC and may be useful in catchments where there is a substantial shift in the balance of allochthonous and autochthonous microbial material during storm flow or in open basins where there is higher algal productivity. The use of more advanced fluorometric characterization techniques for DOC such as three-dimensional excitation-emission matrices (EEMs [*Klapper et al.*, 2002]) may prove useful for fingerprinting DOC from discrete terrestrial catchment source pools such as organic versus mineral soil horizons. This, in turn, would improve the potential for using the fluorescence characteristics of DOC as a hydrologic tracer.

[27] Overall, our results support previous findings suggesting that stream water DOC dynamics during storm events are controlled by the mixing of spatially distinct streamflow source waters at the catchment outlet. Measurements of the specific UV absorbance of DOC proved to be a simple way to trace changes in the chemical character of DOC during storm flow. Our results suggest that SUVA has the potential to be a useful hydrologic tracer because it can provide information about shifts in the proportion of storm

flow entering the stream via flowpaths through mineral soil horizons. The fluorescence index was an indicator of the relative contributions of terrestrial allochthonous versus microbial autochthonous DOC, however the FI appears to have less direct application as a hydrologic tracer at the watershed scale. Overall, our results suggest that the use of DOC as a watershed tracer would be improved by (1) a more complete assessment of DOC pools and the characteristics of the DOC in each pool, and (2) a careful assessment of possible changes to DOC character and quality along specific watershed flowpaths.

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