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Transport and humification of dissolved organic matter within a semi-arid floodplain

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ABSTRACT

In order to understand the transport and humification processes of dissolved organic matter (DOM) within sediments of a semi-arid floodplain at Rifle, Colorado, fluorescence excitation–emission matrix (EEM) spectroscopy, humification index (HIX) and specific UV absorbance (SUVA) at 254 nm were applied for characterizing depth and seasonal variations of DOM composition. Results revealed that late spring snowmelt leached relatively fresh DOM from plant residue and soil organic matter down into the deeper vadose zone (VZ). More humified DOM is preferentially adsorbed by upper VZ sediments, while non- or less-humified DOM was transported into the deeper VZ. Interestingly, DOM at all depths undergoes rapid biological humification process evidenced by the products of microbial by-product-like (i.e., tyrosine-like and tryptophan-like) matter in late spring and early summer, particularly in the deeper VZ, resulting in more humified DOM (e.g., fulvic-acid-like and humic-acid-like substances) at the end of year. This indicates that DOM transport is dominated by spring snowmelt, and DOM humification is controlled by microbial degradation, with seasonal variations. It is expected that these relatively simple spectroscopic measurements (e.g., EEM spectroscopy, HIX and SUVA) applied to depth- and temporally-distributed pore-water samples can provide useful insights into transport and humification of DOM in other subsurface environments as well.

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Introduction

Dissolved organic matter (DOM) represents the most mobile organic carbon pool in terrestrial and aquatic ecosystems (Kalbitz et al., 2000b; Leenheer and Croue, 2003; Mopper et al., 2007; Tfaily et al., 2013). Transport and microbiological humification of DOM play key roles in the cycling and distribution of global carbon and nutrients within and between water, soil, vegetation and atmosphere (Kalbitz et al., 2000b; Leenheer and Croue, 2003; Mopper et al., 2007; Xu and Saiers, 2010). DOM in soil solutions originates from plant litter, soil humus, microbial biomass, and root exudates (Kalbitz et al., 2000b). It serves as a

carbon and energy source for microbial activity, and affects various biogeochemical processes such as nutrient cycling and metal speciation and transport (Dong et al., 2010; Kalbitz et al., 2000b; Nebbioso and Piccolo, 2013; Schnitzer and Khan, 1972; Tfaily et al., 2013). DOM is a complex and poorly understood mixture of natural organic matters (NOMs), and generally composed of heterogeneous aromatic and aliphatic components containing various functional groups (e.g., carboxyl, phenol, enol, alcohol, carbonyl, amine, and thiol) (Chen et al., 2003; Kalbitz et al., 2000b; Schnitzer and Khan, 1972). DOM in soil solutions is estimated to be composed of 50% hydrophobic (fulvic and humic) acids and 30% hydrophilic acids, with the remainder of identifiable molecular compounds such as

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carbohydrates, carboxylic acids, amino acids and hydrocarbons (Herbert and Bertsch, 1995; Tipping, 2002). Such complicated structures make it a challenge to precisely characterize changes in chemical composition during transport through the subsurface.

While DOM has been extensively studied in temperate soils, forest and aquatic ecosystems (Kalbitz et al., 2000b; Mopper et al., 2007; Qualls and Haines, 1992; Tfaily et al., 2013), relatively little is known about DOM dynamics in the semi-arid ecosystems (Klemmedson, 1989; Sherman et al., 2012; Vidal-Abarca et al., 2001). Semi-arid ecosystems have been recognized recently as an increasingly important component of the global carbon cycle (Ahlstrom et al., 2015; Poulter et al., 2014), with capacity to slow the rate of atmospheric CO₂ concentration increase. Ahlstrom et al. (2015) studied contributions of regional ecosystems in CO₂ uptake, and concluded that the global trend and inter-annual variability of the CO₂ sink are dominated by semi-arid ecosystems. Poulter et al. (2014) investigated the global carbon balance over the past 30 years and identified an anomaly driven by growth of semi-arid vegetation in the southern hemisphere, with 60% of carbon uptake attributed to Australian ecosystems. These studies suggest that semi-arid ecosystems play important role in global carbon cycling and CO₂ sequestration. Moreover, the soils in the arid and semi-arid have the potential for large carbon storage (Lal, 2004; Lal et al., 2007; Thomey et al., 2014) given that arid and semi-arid regions cover 45% of the earth's land surface (Schimel, 2010). Therefore, understanding the dynamics of carbon pools (e.g., DOM) in semi-arid ecosystems is essential for predicting their responses and feedbacks to global changes in climate and hydrobiogeochemical cycles.

Understanding how DOM varies spatially and seasonally is important for elucidating its transport and humification, which requires characterization of the molecular composition and reactivity. Many advanced analytical techniques have greatly enhanced our ability to detect and characterize the molecular composition of DOM, including Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS), advanced nuclear magnetic resonance (NMR), Fourier transform infrared spectrometry (FT-IR), and fluorescence excitation–emission matrix (EEM) spectroscopy (Leenheer and Croue, 2003; Mopper et al., 2007). Among these, optical analyses are cost effective methods for analyzing DOM with minimal alteration of its physicochemical environment. EEM spectroscopy has become a popular technique for characterizing DOM because of its high sensitivity, use of small sample volume and simple sample preparation (Kalbitz et al., 2000a; Ohno, 2002). The collection of excitation and emission pairs contained in EEMs that can be interpreted as fingerprints to identify the types of fluorescent components of DOM based on the positions of excitation/emission maxima (Chen et al., 2003; Coble, 1996, 2007; Coble et al., 1990). This characteristic is useful for the detection of DOM sources (Chen et al., 2003; Coble, 1996), oxidation state (Cory and McKnight, 2005; Klapper et al., 2002), metal binding (Ohno et al., 2008), decomposition (Tfaily et al., 2013), and transport processes (Ohno and Bro, 2006; Xu and Saiers, 2010) in a variety of environments. Another simple optical method, the specific UV absorbance (SUVA), defined as the UV absorbance at a specific wavelength (typically 254 nm) normalized for dissolved organic carbon (DOC) concentration, is a useful parameter for

estimating the dissolved aromatic carbon content (%) in water samples (Weishaar et al., 2003). The measurements of EEMs and SUVA can be easily incorporated as a characterization tool in studies of the chemical composition and transport of DOM (Chen et al., 2003; Coble, 2007; Weishaar et al., 2003; Xu and Saiers, 2010).

In this study, we hypothesized that the infiltrating water leaches decay by-products of plant residues and soil organic matter (SOM) from top soil, down into the deeper vadose zone (VZ), and where it undergoes further decomposition throughout the humification process. In order to understand the transport and humification of DOM, we apply the optical techniques (SUVA and fluorescence spectroscopy) for tracking the spatial (depth) and seasonal variations of DOM concentrations and composition at field scale from the VZ to groundwater within the semi-arid floodplain at Rifle, Colorado.

1. Materials and methods

1.1. Site description

The Rifle Site (Fig. 1a) is located on a floodplain along the Colorado River, in semi-arid western Colorado. This 8.8 ha site was intermittently used for vanadium and uranium mining and milling from 1926 to 1958 (DOE, 1999). The mill tailings and underlying contaminated sediments were removed in 1994 and 1995, replaced with locally derived, uncontaminated, floodplain soils (loam, with variable amounts of gravel and cobbles), and vegetated with drought-tolerant perennial grasses by 1996 (Arora et al., 2016; DOE, 1999; Tokunaga et al., 2016). Roots are abundant in the upper 1.0 m, and absent below 1.5 m. The loam soil (1.5 to 2 m thick) is underlain by Colorado River floodplain alluvium containing sands, gravels and cobbles (Fig. 1b) (Shroba and Scott, 1997), interspersed with finer textured and locally organic-rich sediments (Campbell et al., 2012; Yabusaki et al., 2011). This coarse alluvium generally extends to depths of 6 to 7 m, and includes the upper aquifer, with depths to the water table typically ranging from 3 to 4 m (Fang et al., 2009; Tokunaga et al., 2016; Yabusaki et al., 2011). The relatively low permeability Tertiary Wasatch Formation siltstone provides the lower boundary of the unconfined upper aquifer.

Over the past decade, the Rifle floodplain was used as an integrated Field Research Challenge site by the U.S. Department of Energy (DOE), for understanding and predicting subsurface environmental controls on movement of contaminants at the field scale (Fang et al., 2009; Janot et al., 2016; Williams et al., 2011). To date, the dynamics of DOM have not been the focus of studies at this site, although elevated concentrations of NOM have been observed in its subsurface, especially within the naturally reduced zones (NRZs) adjacent to the Colorado River (Arora et al., 2016; Campbell et al., 2012; Janot et al., 2016; Yabusaki et al., 2011). More generally, it is expected that seasonal variations in precipitation (rain and snow) and evapotranspiration exert important influences on dynamics of the DOM pool in the subsurface of this semi-arid floodplain. In particular, late spring (April and May) snowmelt and rainfall could leach fresh DOM from plant residue and

Fig. 1 – (a) Rifle floodplain, along the Colorado River, showing groundwater flow direction (blue), and location of monitoring sites. (b) Cross-section through three monitoring sites along the groundwater flow path shown in Panel a. Also shown are the depths of finer-texture fill soil, coarse alluvium, and low permeability shale.

SOM, and supply bioavailable DOM to the deeper VZ and aquifer.

1.2. Pore-water sampling and analyses

Within the floodplain, three locations (TT01, TT02 and TT03) were selected along a groundwater flow transect (Fig. 1a), with TT01 located furthest north (up-gradient), TT02 within the central floodplain, and TT03 further down-gradient and adjacent to naturally reducing zones (NRZs) (Campbell et al., 2012; Janot et al., 2016). In March 2013, these sites were instrumented with vertically stratified pore-water samplers (Soilmoisture Equipment Corp. 1900 series soil water samplers; and Solinst CMT, 3-Channel System). These installations provided vertically- and temporally-resolved pore-water samples from the VZ and aquifer (Fig. 1b). Samples were filtered in the field using 0.45 μm Millipore filters and collected in ultra-clean glass vials without headspace. All samples were transported to the laboratory on ice and stored at 3°C prior to analysis. DOC was analyzed as non-purgeable organic carbon (NPOC) and dissolved inorganic carbon (DIC) concentrations were determined using a Shimadzu TOC-VCPH analyzer (Japan). Dissolved cation and anions were analyzed using inductively coupled plasma mass spectrometry (ICP-MS) (Elan DRC II, PerkinElmerSCIEX, USA) and ion chromatography (IC) (Dionex ICS-2100, Thermo Scientific, USA), respectively. The pH values of pore-water samples were measured in the range of 7.4–7.8.

Pore-water samples were collected from April 18 to December 20, 2013 for various analyses. A heavy snow event

on April 17, 2013 was followed by rapid snowmelt (Appendix A Fig. SI-1). We selected May 3, 2013 for the depth profile samples because pore waters were recovered from most of sampling depths after snowmelt. The depths above –1.5 m represent the rooted upper VZ, and the depths from –1.5 to –3.36 m for TT01, and –1.5 to –3.14 m for TT03 represent the deeper VZ. The depth at –3.97 m for TT01 and depth at –4.58 m for TT03 represent the groundwater (GW) samples. Two depths were selected for each location for tracking the seasonal variations of DOM, i.e., in the upper VZ at –0.5 m, and in deeper VZ at –3.36 m for TT01 and –3.0 m for TT03. Here we only present results from TT01 and TT03 since the TT02 data varied in similar manner as TT03.

1.3. Spectroscopic analyses

Fluorescence EEM spectra were measured at room temperature with a clear quartz cuvette (10 mm path length) using a HORIBA Jobin Yvon Fluorolog-3 spectrometer with a xenon lamp light source. Excitation wavelengths were scanned from 245 to 400 nm in 5 nm intervals and emissions were measured at each excitation wavelength from 300 to 550 at 2 nm increments. The data acquisition was carried out in signal/reference mode using a 5 nm band pass on both excitation and emission monochromators. Prior to measurement of samples, the excitation and emission correction was conducted routinely for instrumental bias (Cory et al., 2010; Lawaetz and Stedmon, 2009). Blank EEMs were collected routinely using deionized water. Sample fluorescence intensities were adjusted by subtracting the intensity of the deionized water. Highly concentrated DOM samples were diluted to an UV absorbance <0.2 at 254 nm to prevent inner-filter effects (Ohno, 2002). Deionized water Raman spectra were also recorded routinely with emission wavelength from 300 to 500 nm at an excitation wavelength 350 nm (Appendix A Fig. SI-2). The integrated area, A_{rp} , under the Raman peak of deionized water has been used for normalization of fluorescence intensities to Raman unit (R.U.) (Lawaetz and Stedmon, 2009). The fluorescence intensities for the Rayleigh and Raman scatter bands were deleted and set to zero. The emission spectroscopy (300–480 nm) for each sample at a specific excitation wavelength of 254 nm was measured for HIX calculation. SUVA was measured by taking the UV absorbance of a DOM sample at 254 nm and dividing it by the DOC concentration (Weishaar et al., 2003). The potential interference from co-existing inorganic ions (e.g., Fe(II/III), nitrate, sulfate, and bicarbonate) was tested and to be negligible in samples.

1.4. Humification index (HIX)

HIX values were computed as the ratio of the area of the emission spectrum at 435–480 nm to the emission area at 300–345 nm at an excitation wavelength of 254 nm. This calculation proposed by Zsolnay and co-workers (Cox et al., 2000; Zsolnay et al., 1999) was selected in this work because it uses the integrated area of fluorescence intensity at a range of wavelength values rather than use of the intensity of arbitrarily selected wavelengths for the index (Ohno, 2002). HIX values can be applied to evaluate spatial (depth) and temporal trends and extent of DOM humification. Increasing

HIX values are indicative of more humic, structurally complex DOM.

2. Results and discussion

2.1. Spatial and seasonal variations of DOC and SUVA

DOC concentrations varied with depth and seasons in the VZ (Figs. 2 and 3). The depth profile of DOC for TT01 shows higher concentrations at the deeper VZ (soil, –2.43 and –3.36 m) than the upper VZ (–0.5 and –0.95 m), unlike for the TT03 depth profile where higher concentrations of DOC were observed in the upper VZ (–0.5 m) than the deeper VZ (–1.5, –2.5, and –3.14 m) (Fig. 1a). The differing depth profiles of DOC concentrations between the two monitored profiles likely reflects hydrological influences associated with TT01 being near the base of a hillslope with intermittent discharge from saline seeps, and TT03 being representative of the main body of the floodplain.

Seasonal variations of DOC concentrations generally increase in late spring to summer, reach highest in late summer and fall, and then begin to decrease in early winter. This seasonal change is consistent with previous studies (Kalbitz et al., 2000b). Increase in DOC concentrations can be linked to high evapotranspiration due to elevated temperature as well as higher microbial and plant activity (Brooks and Lemon, 2007; Kalbitz et al., 2000b; Liechty et al., 1995). Pore-water samples from the upper VZ (–0.5 m) were not available for TT01 after June 3, 2013, and for TT03 during late summer and fall because of drier conditions. In addition, DOC concentrations started to decrease in November, particularly for TT03–0.5 m samples, as shown in Fig. 3b. Monthly precipitation (rain and snow) exceeds potential evapotranspiration from November through March at the Rifle floodplain (Tokunaga et al., 2016), resulting to the increases in

shallow vadose zone water storage, and dilution of DOC concentrations. Even with seasonal dilution, it is apparent that DOC concentrations in VZ samples are significantly greater than in GW samples (Fig. 2a).

The SUVA at 254 nm is strongly correlated with the dissolved aromatic carbon fraction in water samples (Weishaar et al., 2003). The depth profiles of SUVA (Fig. 2b) indicate that the aromatic carbon fractions are higher in the upper VZ and GW samples than in the deeper VZ samples. This result is consistent with other reported observations (Corvasce et al., 2006; Qualls and Haines, 1992; Tfaily et al., 2013). The seasonal variations of SUVA (Fig. 3) suggest that the aromatic carbon fraction increases rapidly from late spring to early summer, and then slowly reach maxima from late summer through fall to early winter for the selected depths. However, for the TT03–3.0 m samples (Fig. 3d), SUVA increases more rapidly from May to September.

The increased aromatic carbon fraction with seasons is likely due to the biological humification process, resulting in DOM with high aromaticity and more recalcitrance to mineralization processes (Kalbitz et al., 2000b). The higher aromatic carbon fraction at upper VZ in the spring (Fig. 2b) suggests that aromatic compounds are preferentially adsorbed within the upper VZ (McKnight et al., 1992), leaving less aromatic compounds available to transport into the deeper VZ. The lower DOC concentrations and the reverse trend of SUVA values with depth for GW samples (Fig. 2) likely reflect the different sources of DOC from the deeper VZ samples. The evapotranspiration from late spring through early fall limits net water recharge from the VZ into the GW, with an estimated annual velocities ranging from 0 to at most about 0.1 m/year and an average of only about 0.03 m/year (Tokunaga et al., 2016). The flux of GW is from upper floodplain ranges from 0.1 m to 0.8 m/day, generally south-southwest to the adjacent Colorado River (Anderson et al., 2003; Williams et al., 2011). The DOC in the GW is expected to have been humidified to higher aromatic compounds during its long time transport.

2.2. Fluorescence EEM

Selected fluorescence EEM spectra (contour maps) for TT03 pore-water samples are presented as a depth profile (Fig. 4a) and as a seasonal trend (Fig. 4b). There are four distinct types of fluorescent peaks identified in EEMs as shown in Fig. 4. Each peak characterizes a maxima excitation/emission wavelength pair. Based on reported summaries by Coble (2007) and Chen et al. (2003), these four peaks can be grouped to specific fluorophore components (A, M, B and T) as shown in Fig. 4. Specifically, A with a strongest peak at Ex 250–260 nm/Em 400–460 nm typically represents autochthonous fulvic acid-like (FA-like) or humic acid-like (HA-like) components, M with a moderate peak at Ex 290–310 nm/Em 380–410 nm represents the HA-like component, B with a peak at Ex 275 nm/Em 305 nm and T with a peak at Ex 275 nm/Em 340 nm generally are assigned to the protein-like material, i.e., tyrosine-like and tryptophan-like matter, respectively. The peaks of B and T have been found to strongly correlate with bioavailable DOM and biological processes (Coble, 2007; Inamdar et al., 2012), and thus tyrosine-like and tryptophan-like matter are generally considered as the microbial by-product-like matter (Chen et al., 2003; Hosen et al., 2014; Osburn et al., 2012). Based on the EEM

Fig. 2 – Depth profiles of dissolved organic carbon (DOC) and specific UV absorbance (SUVA) (254 nm) at TT01 and TT03 locations. The data obtained from the samples collected on May 3, 2013.

Fig. 3 – Seasonal variations of DOC and SUVA (254 nm) at TT01 and TT03 locations.

spectra in Fig. 4, the FA-like (A) and HA-like (M) substances are identified to be the major fluorescent components of DOM with various amounts of microbial by-product-like matter (B and T) in pore-water samples. For comparison, a GW sample from TT03 –4.58 m and a reference Suwannee River NOM sample from International Humic Substance Society (IHSS) were analyzed and presented in Appendix A Fig. SI-3. It is apparent that only two peaks (A and M) are observed for these two samples, i. e., FA-like and HA-like substances.

The depth profile of EEM spectra (Fig. 4a) shows much higher concentration of FA-like (A) and HA-like (M) substances in upper VZ (–0.5 m, with a dilution factor (DF) = 5) than in deeper VZ (–1.5, –2.5 and –3.14 m), which is consistent with the trend of DOC concentration in Fig. 2a. Distinct peaks of tyrosine-like (B) or tryptophan-like (T) matter were obtained in all VZ samples, with much stronger signals in deeper VZ, especially at around depths –2.5 m (Fig. 4a) and –3.0 m (Fig. 4b), suggesting strong microbial activity in the deeper VZ (Inamdar et al., 2012; Tokunaga et al., 2016).

Seasonal variation of EEM spectra at depth –3.0 m (Fig. 4b) shows a rapid increase of FA-like (A) and HA-like (M) substances from late spring (Apr 26, May 15) to summer (Jul 16, with DF = 2 for Jul 16 and Dec 19), reaching maxima in late summer and fall, and decreasing in early winter (other similar EEM spectra not shown for brevity). This trend is consistent with SUVA results with aromatic carbon mainly from FA-like and HA-like substances. Interestingly, the peak of the tyrosine-like (B) decreased rapidly from late spring to early summer, suggesting that rapid microbial humification of DOM occurred in the VZ, particularly at late spring and early summer.

2.3. Humification index (HIX)

Spatial and seasonal variations in TT03 fluorescence emission spectra at a fixed excitation (254 nm) are presented in Fig. 5. The fluorescence intensities have been normalized to Raman units (R.U.), and divided by sample DOC concentration (mmol/L). All spectra show a similar shape and broadband with a maximum of fluorescence intensity at 440 nm, except the samples from TT03 deeper VZ (–2.5 and –3.0 m) in spring, where a secondary broad band maximum occurred at 300–325 nm. The depth profile of Fig. 5a shows the red-shifting of the emission spectra in the sequence; deeper VZ (–1.5, –2.5 and –3.14 m) → upper VZ (–0.5 m) → GW (–4.58 m). The red-shifting of seasonal emission spectra with a time trend of spring (Apr 26, May 15) → summer (Jul 16) → fall (Sep 04) → winter (Dec 19) is clearly observed (Fig. 5b). A similar trend was also observed for TT01 samples. The red-shifting of the emission spectra toward longer wavelength indicates the formation of more humified DOM (Cox et al., 2000; Ohno, 2002; Ohno and Bro, 2006).

The depth profile and seasonal variations of HIX values are presented in Figs. 6 and 7, respectively. The greater HIX value indicates the greater humification extent of DOM by formation of more complex and condensed (aromatic) structure (Cox et al., 2000; Ohno, 2002; Zsolnay et al., 1999).

Ohno (2002) determined the HIX values of three representatives of DOM, and observed that the initially non- or less-humified DOM from plant residue have HIX of 1.33 ± 0.03 , soil water-soluble DOM have HIX of 5.18 ± 0.22 , and soil FA have HIX of 15.9 ± 5.9 . Compared with Ohno's data, our depth profiles of HIX values from samples collected May 3 (Fig. 6)

Fig. 4 – Fluorescence excitation–emission matrix (EEM) spectra of pore-water samples from TT03 (fluorescence intensities are normalized to Raman units). (a) depth profile for samples collected May 3, 2013 (left), and (b) seasonal variations in deeper vadose zone (–3.0 m depth). Note: A, M, B and T represent the fulvic acid-like (FA-like), humic acid-like (HA-like), tyrosine-like and tryptophan-like matter, respectively.

suggest that DOM in TT03 deeper VZ (–1.5, –2.5 and –3.14 m) were from plant residue or microbial origins with HIX values of 1.37–3.11. DOM in TT01 whole VZ (–0.5 m to –3.36 m) were from SOM with HIX values of 5.42–8.31. DOM in TT03 upper VZ (–0.5 m) with a HIX value of 13.01 and DOM in GW samples with HIX values of 16.70 for TT01 (–3.97 m) and 10.50 for TT03 (–4.58 m) are indicative of soil FA-like and HA-like substances. HIX value for the IHSS Suwannee River NOM was analyzed to be 24.6 with a sample UV absorbance = 0.210, which is comparable with the value of 28.5 for the fulvic acid (FA) Ohno extracted from a soil with a UV absorbance = 0.480. It should be noted that the fluorescence intensities were not corrected to R.U. in Ohno's spectra. However, it is expected that the HIX values obtained by Ohno and in this work are similar with

respect to the HIX values calculated from the ratios of the emission intensities in the same two ranges of wavelengths.

Our seasonal trends in HIX values shown in Fig. 7 suggest that all DOM undergoes further humification through the end of year with the most rapid humification occurring in late spring and early summer, leaving relative stable end-products of more FA-like and HA-like substances. The seasonal variations of HIX values exhibited different patterns for TT01 and TT03 (Fig. 7). In the upper VZ (Fig. 7a and c), DOM was less humified in TT01 with HIX values of 4.79–8.88, relative to HIX values of 5.26–13.82 at TT03. HIX was not measured after June 3 for TT01–0.5 m because evapotranspiration left surface soils too dry to allow collection of pore-water samples. In contrast, the deeper VZ DOM in TT01 was more

Fig. 5 – Spatial and seasonal variations of fluorescence emission spectra at an excitation wavelength 254 nm for TT03 pore water samples. Note: all spectra are normalized to Raman units (R.U.) and unit DOC concentration ((mmol/L)⁻¹).

humified (HIX values of 8.02–17.74) than in TT03 (HIX values of 1.09–10.2) (Fig. 7b and d). This difference may reflect the different redox conditions. Microbial activity in the upper VZ (Fig. 7a and c) may be higher at TT03 than at TT01, resulting in rapid transformation of less humified DOM (HIX = 5.3) to more recalcitrant DOM (HIX > 13.0) in the late spring. In contrast,

Fig. 6 – Depth profiles of HIX values at TT01 and TT03 locations. The data obtained from the samples collected on May 3, 2013.

Fig. 7 – Seasonal variations of HIX values at TT01 and TT03 locations.

TT03 commonly has more reducing conditions in its deeper sediments relative to TT01 (Fig. 7b and d), which limits further DOM degradation. The TT03 location is adjacent to a known organic-rich NRZ (Campbell et al., 2012; Janot et al., 2016), and is expected to have a lower redox environment in its deeper sediments.

2.4. Transport and humification of DOM

Plant residue, SOM, and microbial biomass are the sources of DOM in VZ pore-water samples. Plant residue is a major source of carbon-rich, non- or less-humified and highly water-soluble material in soils (Kalbitz et al., 2000b; Ohno, 2002; Ohno and Bro, 2006) and constitutes the initial products of organic matter degradation by microbial activity (Ohno, 2002). In late spring, the snowmelt water leached the plant residue and SOM from top soil with the fresh decay products of microbial origin into deeper VZ sediments. During transport, more aromatic compounds or FA-like and HA-like substances were preferentially adsorbed by the upper VZ sediments, leaving less aromatic DOM or less humified DOM transported into the deeper VZ. This relatively fresh DOM stimulates microbial activity in the deeper VZ, generating CO₂ (Tokunaga et al., 2016), and the microbial by-product-like matter i.e., tyrosine-like and tryptophan-like matter. These processes are supported by the depth profiles of SUVA, EEM spectra, and HIX in Figs. 2b, 4a, 5a and 6.

In spring (e.g., May 3), DOM exhibited a less humified characteristic at all depths, and then exhibited further biodegradation or humification over the year. Rapid humification occurred in late spring and early summer, particularly in the TT03 deeper VZ, resulting in more humified DOM and relatively stable end-products of FA-like and HA-like substances. This humification process was strongly supported by evidence from SUVA, EEM spectra, and HIX measurements in Figs. 3, 4b, 5b and 7. In order to determine whether the interpretations of DOM transport and humification were significantly affected by adsorption-desorption processes (Kalbitz et al., 2000b), we

extracted the sediment samples from TT03 VZ with 10 mmol/L NaHCO₃ solutions for HIX analysis. The extracted DOM showed HIX values ≥ 8.5 in all depths, suggesting that adsorption of “fresh” DOM onto sediments was minor.

Our results show that at the end of year (winter), DOM in all VZ depths have relative higher SUVA and HIX values (Figs. 3 and 7), and less microbial by-product-like matter compared to the late spring (peak B in Fig. 4b). This suggests that the dynamics of DOM undergoes a seasonal variation at this semi-arid site. These processes may suggest an annual cycle despite lack of the data from January to March. As we recently reported, the deeper VZ at this site maintains an environment supportive of year-round microbial respiration, with intermediate water and air saturations, lack of extreme temperatures and salinities, and an annual resupply of organic carbon from recharge (Tokunaga et al., 2016). More generally, the rate and extent of transport and humification of DOM in semi-arid floodplains is dependent on local hydro-biogeochemical and climatic conditions, such as snowmelt/rainfall events, changes of temperature and water table, and redox conditions (Kalbitz et al., 2000b).

3. Conclusion

Although characterization of DOM in semi-arid subsurface is challenging, the combined application of fluorescence EEM spectroscopy, HIX and SUVA on pore-waters was found to be useful for understanding depth and temporal variations of DOM composition at the Rifle floodplain. Our results reveal that the spring snowmelt plays important role in leaching and transport of fresh DOM from top soil into the deeper VZ, where fresh DOM undergoes biological humification over the year. These processes suggest an annual cycle of DOM at this semi-arid floodplain site. These relatively simple spectroscopic measurements (e.g., EEM, HIX and SUVA) applied to spatially- and temporally-resolved pore-water samples can provide useful insights into transport and humification processes of DOM in other environments as well.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.jes.2016.12.011>.

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