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JES JOURNAL OF ENVIRONMENTAL SCIENCES

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

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ARTICLE INFO

Article history:
Received 26 August 2016
Revised 16 November 2016
Accepted 6 December 2016
Available online 29 December 2016

Keywords:
Dissolved organic matter
Transport
Humification
Semi-arid
Fluorescence excitation-emission matrix

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.

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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http://dx.doi.org/10.1016/j.jes.2016.12.011
1001-0742/

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 CO_2 concentration increase. Ahlstrom et al. (2015) studied contributions of regional ecosystems in CO_2 uptake, and concluded that the global trend and inter-annual variability of the CO_2 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 CO_2 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