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Characterizing dissolved organic matter in eroded sediments from a loess hilly catchment using fluorescence EEM-PARAFAC and UV–Visible absorption: Insights from source identification and carbon cycling

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ABSTRACT

The chemical characteristics of dissolved organic matter (DOM) in soils that experience erosion and deposition are key to the biogeochemical cycle of carbon on the earth's surface. However, data related to the transport and fate of DOM from soils that experience erosion and different management practices are scarce, particularly at catchment scales. In this study, soil samples (uppermost 10 cm) were collected from uplands representing four land use types (cropland, fallow, grassland, and forests) as well as gullies, and sediment samples (100 cm sampled at 10 depths) were collected from sediments retained by a check dam. Chemical characteristics of DOM in soils and sediments, as well as subsequent source identification, were inferred from UV–Visible absorption and fluorescence excitation emission matrix (EEM)-parallel factor analysis (PARAFAC) as well as principal component analysis (PCA). The results indicated higher aromaticity, hydrophobic fraction, and molecular size in DOM from forest soils than those from other land use types and gullies. These factors were also higher in soils at the eroding sites than in sediments. EEM-PARAFAC analysis demonstrated that more protein-like components (tyrosine-like and tryptophan-like combined, accounting for > 42.77%) were present in sediments compared to soils with terrestrial humic-like substances. PCA results revealed that approximately 72% of the variance in the DOM characteristics was explained by the first two principal components and that the DOM in upland and gully soils had a negligible contribution to DOM in sediments. Combined our results indicate that, despite the large amount of sediment-associated carbon that is transported by erosion and trapped in check dams, DOM is likely mineralized during soil transport. Furthermore, biological production of new organic compounds (autochthonous sources) are likely the major source of sediment DOM in depositional settings.

1. Introduction

Dissolved organic matter (DOM) in soils is the most dynamic and bioavailable fraction of soil organic matter (SOM). DOM in natural environments is typically defined as OM that passes through a filter of 0.45 μm pore size and plays an important role in the biogeochemical cycles of carbon and other elements (in particular nitrogen) (Lal, 2003; McDowell, 2003; Battin et al., 2009). DOM can become part of the mineral-associated SOC pool by bonding to fine soil particles (Kaiser and Kalbitz, 2012). DOM is also responsible for stimulating soil microbial activity to promote the decomposition of organic matter (Kuzyakov and Cheng, 2001). Studies have shown that DOM is a heterogeneous mixture of aliphatic and aromatic polymers and its composition varies in time and space depending on proximity to sources and exposure to degradation processes (Kalbitz et al., 2003; Stedmon et al., 2003; Zsolnay, 2003; Wickland et al., 2007). DOM in inland watersheds can originate from allochthonous (e.g., plant litter and soil organic matter), autochthonous (e.g., dead bacteria, plankton, animal bodies, and macrophytes) and anthropogenic sources (e.g., effluent organic matter and manure) (Zsolnay, 2003; Lozovik et al., 2007; Derrien et al., 2017). Studies had previously suggested that source of DOM can determine its chemical properties and persistence in soils and

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sediments (Lal, 2003; Liu et al., 2018b). Moreover, lateral movement of sediment and water in the soil system transports some of the terrestrial DOM to rivers or reservoirs via runoff, leaching, and subsurface flow processes (McDowell, 2003). When stream water with high concentration of DOM (esp. nitrogen and phosphorus components) enters streams it can cause ecological problems, i.e., eutrophication and non-point source pollution; or be an indicator for changes in flux of C in the earth system ex. due to climate change or other environmental perturbations (Lal, 2004; Santos et al., 2016), including land degradation (Ma et al., 2014). Furthermore, improved understanding of the variables that regulate flux and dynamics of DOM between aquatic and terrestrial ecosystems is essential to determine the fate of laterally transported DOM on wide-ranging processes on the surface of the Earth (Stedmon et al., 2003; McCorkle et al., 2016).

Soil erosion, especially water erosion, connects the biogeochemical cycles of carbon in the terrestrial biosphere and the hydrosphere (Berhe et al., 2007; Assouline et al., 2017; Nie et al., 2018). Soil erosion laterally redistributes up to 5 Pg C annually in both dissolved and particulate forms of C associated with different sized mineral particles (Berhe et al., 2007; Ma et al., 2014; Wang et al., 2014). There is currently no consensus as to how much of the terrestrial carbon mobilized by soil erosion is mineralized during or after transport (Berhe et al., 2018). Some studies suggest that as low as 0 to 20% of eroded C can be mineralized during transport (Berhe et al., 2018) while others suggest that 80 to 100 % of eroded C, which is approximately 1.14 Pg C yr^{-1}, can be emitted to the atmosphere from mineralization of eroded C (Lal, 1995; Durrieu et al., 2000). Regardless of the actual amount of carbon mineralization during transport of eroded C, most of the mineralizable carbon in eroded material is expected to be associated with free particulate carbon or DOC (Lal, 2003; Ma et al., 2014). To date, although the effect of soil erosion on C dynamics (Berhe and Kleber, 2013; Li et al., 2017; Liu et al., 2018a, 2018b) and associated release of greenhouse gas are widely recognized (Lal, 2004), data related to the transport and fate of DOC in eroding systems is unavailable, particularly at catchment scale.

UV–Visible absorption and fluorescence spectroscopy have been widely applied for characterizing the optical properties of dissolved organic matter in a variety of natural environments dominated by solid particles (e.g., soil, sediment, and suspended solids) (Stedmon et al., 2003; Osburn et al., 2012; He et al., 2016), with several valuable indices for differentiating the OM from contrasting sources (Shafiquzzaman et al., 2014; Derrien et al., 2017). For example, He et al. (2016) examined the distribution behavior of sediment organic matter (SOM) between dissolved and particulate phases by comparing the spectroscopic features of pore water OM and alkaline-extractable organic matter of river sediments. Santos et al. (2016) characterized the effect of temperatures on the DOM aromaticity, mean molecular weight, organic C concentration, and major structural components by employing optical spectrophotometry. Furthermore, a series of quality indices are feasible for the sources of DOM, such as the fluorescence index (FI), humification index (HIX), biological index (BIX), and the relative abundance or the ratios of different fluorescent components, which can distinguish autochthonous, allochthonous, and anthropogenic OM (Derrien et al., 2017). Multivariate data analysis methods (e.g., principal component analysis, PCA; parallel factor analysis, PARAFAC) applied to fluorescence EEMs results have also been useful to identify the sources of the DOM in aquatic environments, and enable identification and quantification of fluorescent components in different types of samples, further enhancing the capability of source discrimination (Shafiquzzaman et al., 2014; Yang and Hur, 2014).

The Loess Plateau in the northwestern region of China, characterized by a mountainous and extremely complex topography, is an area of concern due to its high rates of soil erosion and has been intensively studied by the scientific community in recent decades (Wang et al., 2015; Li et al., 2017; Liu et al., 2017a, 2017b). Previous studies estimate that the average rate of soil loss in the Loess Plateau region is 50–100 Mg ha^{-1} $year^{-1}$, with maximum recorded rates of 200–300 Mg ha^{-1} $year^{-1}$ in some regions (Liu and Liu, 2010; Sun et al., 2014). More than 60% of the land area in this region has been subjected to soil erosion that laterally distributes essential nutrients in topsoil (including carbon, nitrogen and phosphorus) (Cai, 2001; Li et al., 2015). Approximately 0.8–1.5 kg of ammonia, 1.5 kg of total phosphorus, and 20 kg of total potassium are lost in each ton of eroded soil as estimated by Cai (2001) and 7.63 Tg C yr^{-1} of soil organic carbon is mobilized by erosion (Zhao et al., 2016). In addition to causing severe ecosystem degradation in the Loess Plateau, the high rates of soil erosion have also endangered the ecological health and security of the middle and lower reaches of the Yellow River due to high sediment load input and water eutrophication (Li et al., 2017). Consequently, the Loess Plateau region has been noted as a region with the most serious poverty and eco-environment fragility in China (Wang et al., 2011).

To control soil and water loss effectively on the Loess Plateau, a series of comprehensive biological and engineering measures were initiated by the Chinese government in 1950s. Vast areas of cropland with a slope gradient that exceeded 25° in mountainous areas were converted to forestland or grassland in the gully and hilly zones and > 90,000 check dams were constructed in gullies and streams (Zhao et al., 2016; Liu et al., 2018a, 2018b). Consequently, the intensity of soil erosion has been greatly mitigated and the sediment export to lower reaches of Yellow river has decreased significantly over the past six decades (sediment loads decreased from 1.34 ± 0.64 Gt yr^{-1} in 1951–1979 to 0.32 ± 0.24 Gt yr^{-1} in 2000–2010) (Miao et al., 2010; Wang et al., 2016). As the most widespread and effective strategy to reduce soil and water loss, check dams not only trap all of the sediments that are derived from upstream soil erosion but also intercept massive amounts of SOM in the alluvial wedges (Lü et al., 2012; Liu et al., 2017a). As estimated by Wang et al. (2011), check dams have trapped a total of 2.1×10^{10} m^3 of sediments and 0.095 Gt of organic carbon on the Loess Plateau. The depth of sediment retained by check dams have already reached several meters or tens of meters, and can be used as an important archive of the history of soil erosion and land use changes in this region (Chen et al., 2016; Liu et al., 2018b). The effect of land use type and check dam construction on SOC stocks and source identification of eroded SOM in sediment cores and during rainfall events have been reported in our previous studies in this region (Liu et al., 2017a, 2017b, 2018a). However, little information is available regarding the characteristic of DOM in the retained sediments, and how DOM characteristics in the check dams vary among land use types, gully soils, and sediments. More importantly, source identification of eroded DOM in sediments retained by check dam using spectral fingerprinting approaches is scarce.

Therefore, in order to fill this knowledge gap and as an extension of our previous studies in this region (Liu et al., 2017b, 2018a, 2018b), the main objectives of this study were: (1) to analyze differences in the structural and chemical characteristics of DOM in soils of various upland land use types and gullies by using UV–Vis absorbance and fluorescence spectroscopy; (2) to determine the characteristics of DOM in eroding and deposition soils by comparing selected spectroscopic indicators and EEM spectra; (3) to identify the primary sources of DOM in sediment cores using parallel factor analysis (PARAFAC) and principal component analysis (PCA) as a systematic approach.

2. Materials and methods

2.1. Study area

The study was conducted at a small sub-catchment (Xijiazhai watershed) (3.10 km^2) within the headstream basin of the Luoyugou watershed near Tianshui City, Gansu Province, China (105° 43′ E, 34° 36′ N), which belongs to the typical loess hilly–gully region of the Loess Plateau (Fig. 1). This region is characterized by seasonal alternations of the East Asian summer and winter monsoons, with a mean annual