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Comparing molecular composition of dissolved organic matter in soil and stream water: Influence of land use and chemical characteristics

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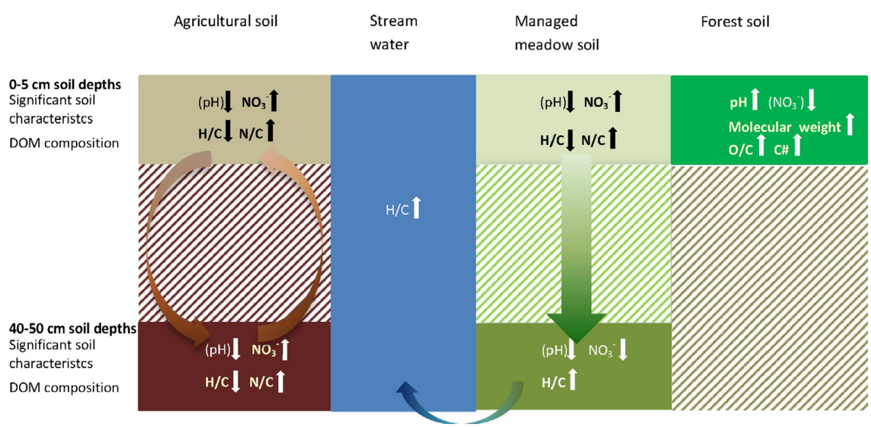
HIGHLIGHTS

- Environmental parameters as pH and nitrate significantly affect chemical composition of DOM
- DOM molecular composition variation was apparent in the vertical stratification of undisturbed soils
- DOM became less aromatic with depth inundisturbed soils
- Stream DOM is mainly of allochthonous origin and predominantly derived from alongside stream subsoil/groundwater

GRAPHICAL ABSTRACT



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ABSTRACT

Electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry (ESI-FT-ICR-MS) was used to examine the molecular composition of dissolved organic matter (DOM) from soils under different land use regimes and how the DOM composition in the catchment is reflected in adjacent streams. The study was carried out in a small area of the Schwingbach catchment, an anthropogenic-influenced landscape in central Germany. We investigated 30 different soil water samples from 4 sites and different depths (managed meadow (0–5 cm, 40–50 cm), deciduous forest (0–5 cm), mixed-coniferous forest (0–5 cm) and agricultural land (0–5 cm, 40–50 cm)) and 8 stream samples. 6194 molecular formulae and their magnitude-weighted parameters ($(O/C)_w$, $(H/C)_w$, $(N/C)_w$, $(AI\text{-}mod)_w$, $(DBE/C)_w$, $(DBE/O)_w$, $(DBE\text{-}O)_w$, $(C\#)_w$, $(MW)_w$) were used to describe the molecular composition of the samples.
The samples can be roughly divided in three groups. Group 1 contains samples from managed meadow 40–50 cm and stream water, which are characterized by high saturation compared to samples from group 2 including

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Carbon cycle
Soil carbon
Catchment

agricultural samples and samples from the surface meadow (0–5 cm), which held more nitrogen containing and aromatic compounds. Samples from both forested sites (group 3) are characterized by higher molecular weight and O/C ratio. Environmental parameters vary between sites and among these parameters pH and nitrate significantly affect chemical composition of DOM. Results indicate that most DOM in streams is of terrestrial origin. However, 120 molecular formulae were detected only in streams and not in any of the soil samples. These compounds share molecular formulae with peptides, unsaturated aliphatics and saturated FA-CHO/FA-CHOX. Compounds only found in soil samples are much more aromatic, have more double bonds and a much lower H/C ratio but higher oxygen content, which indicates the availability of fresh plant material and less microbial processed material compared to stream samples.

1. Introduction

Dissolved organic matter (DOM) is an important constituent of terrestrial and aquatic ecosystems. In most eco-regions worldwide, DOM is produced during decomposition and solubilization of either recent plant biomass or from soil organic matter (SOM) and serves as a link between terrestrial and aquatic systems. Since streams are net heterotrophic, they consume more energy than they create, a large proportion of DOM in river ecosystems is derived from terrestrial sources (Rasilo et al., 2015; Houser et al., 2005). Consequently, processes controlling DOM composition and concentration in fluvial systems are largely determined by conditions in the catchment area (Houser et al., 2005; Strayer et al., 2003; Huryn et al., 2002).

DOM pools in terrestrial ecosystems are small compared to pools of soil organic matter (SOM) but they are considered to be a key indicator of soil quality (Jones et al., 2014) due to their rapid response to land use and vegetation change. Previous studies showed that land use and vegetation can affect DOM composition e.g. DOM leachates from humified organic soils often are dominated by highly aromatic high-molecular-weight compounds (Wickland et al., 2007). Land use changes and vegetation also affect soil properties such as pH, moisture, temperature and nutrient availability (Cohen et al., 2008). DOM is the primary energy source for microorganisms and affects their activity and abundance in soils. Both soil properties and microbial activity interact with DOM composition. Components of DOM differ in decomposability. For example, hydrophobic acids, rich in aromatic structures, are difficult to decompose for microorganisms, whereas leachates from living vegetation and fresh litter have a high contribution of low-molecular-weight carbohydrates, which are easy to decompose (Marschner and Kalbitz, 2003). However, fresh plant organic carbon is only available in the upper soil horizons and lost in the upper 20 cm. DOM at greater depths of mineral soils is mainly a product of SOM and only to a minor extent derived from fresh plant organic carbon (Malik and Gleixner, 2013; Steinbeiss et al., 2008; Fröberg et al., 2007). This might be of importance, when the quality of DOM transported to inland waters is considered, because different carbon pools are activated during base- and overland-/interflow. DOM derived from fresh plant material which is restricted to the upper part of the soil is transported to inland waters mainly during overland-/interflow caused by heavy precipitation events, whereas mainly old and highly processed deep DOM are transported to the aquatic systems during baseflow (Fellman et al., 2009; Sanderman et al., 2009). This will result in low concentrations of highly altered DOM in stream water (Sanderman et al., 2009) which reaches streams during most times of the year and thus, is the dominant pool for DOM in streams (Fiebig, 1995). Stream DOM concentration and chemistry reflect the combined influences of terrestrial biogeochemical cycling of organic matter and the discharge regime of the catchment, which is influenced by abiotic factors such as hydrology, precipitation and temperature. Low-order-streams are the first important link in the transporting route of DOM from their soil sources to their sinks, because they integrate chemical compounds from groundwater, surrounding landscape and in-stream processes, whereas the molecular formulae diversity decreases with stream order (Mosher et al., 2015). Spatial and seasonal patterns which affect soil biogeochemical cycling are supposed to determine the concentration and composition of DOM found in streams and rivers.

The objective of this study was to examine the composition of terrestrial DOM and its influence on stream water DOM in immediate vicinity. We compared DOM composition from different vegetation sites and two different depths within a small area of the catchment and at two nearby points in the streams. DOM was characterized using Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR-MS). Analytical techniques such as FT-ICR-MS provide information about the molecular composition of DOM. Due to the high mass accuracy, molecular formulae can be assigned to individual detected masses within the complex DOM mixture (Koch et al., 2005; Kujawinski et al., 2004). Characteristic fingerprints, consisting of many thousand molecular formulae, allow the distinction of DOM of different origins (Koch et al., 2005) and to identify unique molecular formulae for different ecosystems including rivers (Roth et al., 2014).

2. Materials and methods

2.1. Study site and sampling

The study site is a small area inside the 23.4 km^2 Schwingbach catchment. Samples were taken close to the junction of the Vollnkirchner Bach and the Schwingbach (SI-Figure). The Schwingbach and its tributary the Vollnkirchner Bach are low-mountainous creeks located in Hüttenberg (50°30′0″ N, 8°37′0″ E, Hesse, Germany). The Schwingbach is 10.9 km long, with an altitude range from 233 to 415 m a.s.l. The Vollnkirchner Bach is 4.7 km long and drains a 3.7 km^2 subcatchment. Both creeks are part of the "Study landscape Schwingbachtal" of the Justus Liebig University Giessen (Orlowski et al., 2014; Lauer et al., 2013). Land use is dominated by forested sites (36.9%) and arable land (39%), whereas grassland sites (10.5%) are mainly distributed along the stream. Soils are forested Cambisols as well as agricultural Stagnosols with thick loess layers (Stagnic Luvisols). Gleysols can be found predominantly under grassland sites along the streams.

Meteorological data were recorded at a climate station at the catchment outlet of the Vollnkirchner Bach including air temperature and precipitation. The climate station is equipped with an automated weather station (Campbell Scientific Inc., AQ5, UK) including a CR1000 data logger. Soil moisture and temperature were measured in 10 cm depth and 40 cm depth in grassland, 20 cm depth and 40 cm depth in agriculture soils and in 5 cm depth in deciduous forest soils (only soil moisture). Soil moisture and temperature was measured with permanently installed EC-5 sensors at forested and 10 cm grassland sites and 5TM-sensors at agriculture and 40 cm grassland sites equipped with EM50 data logger. The climate is classified as temperate with a mean annual temperature of 10.5 °C and annual precipitation sum of 588 mm for the hydrological year 01.11.2013–31.10.2014 (fb09-pasig.umwelt.uni-giessen.de:8081). Data are shown in Fig. 1.

Soil samples were taken twice a month in February, April, June, August and October from a managed meadow (0–5 cm, 40–50 cm), deciduous forest (0–5 cm), mixed-coniferous forest (0–5 cm) and