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Apportioning sources of organic matter in streambed sediments: An integrated molecular and compound-specific stable isotope approach

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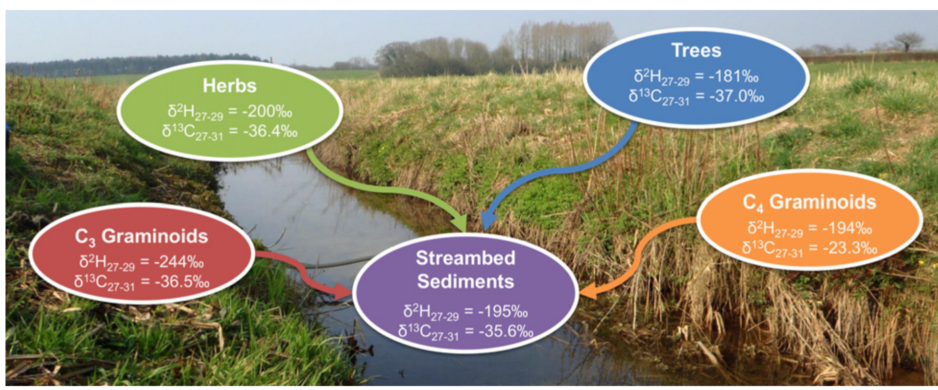
HIGHLIGHTS

- Organic contributions from trees, herbs and C_3/C_4 graminoids are apportioned.
- δ^2H provides strong discrimination between plant functional types.
- $\delta^{13}C$ provides strong contrasts between C_3 and C_4 plants.
- δ^2H and $\delta^{13}C$ values could not differentiate aquatic and terrestrial species.
- *n*-Alkane ratios compliment isotopic discrimination.

GRAPHICAL ABSTRACT



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ABSTRACT

We present a novel application for quantitatively apportioning sources of organic matter in streambed sediments via a coupled molecular and compound-specific isotope analysis (CSIA) of long-chain leaf wax *n*-alkane biomarkers using a Bayesian mixing model. Leaf wax extracts of 13 plant species were collected from across two environments (aquatic and terrestrial) and four plant functional types (trees, herbaceous perennials, and C_3 and C_4 graminoids) from the agricultural River Wensum catchment, UK. Seven isotopic ($\delta^{13}C_{27}$, $\delta^{13}C_{29}$, $\delta^{13}C_{31}$, $\delta^{13}C_{27-31}$, δ^2H_{27}, δ^2H_{29}, and δ^2H_{27-29}) and two *n*-alkane ratio (average chain length (ACL), carbon preference index (CPI)) fingerprints were derived, which successfully differentiated 93% of individual plant specimens by plant functional type. The δ^2H values were the strongest discriminators of plants originating from different functional groups, with trees ($\delta^2H_{27-29} = -208‰$ to $-164‰$) and C_3 graminoids ($\delta^2H_{27-29} = -259‰$ to $-221‰$) providing the largest contrasts. The $\delta^{13}C$ values provided strong discrimination between C_3 ($\delta^{13}C_{27-31} = -37.5‰$ to $-33.8‰$) and C_4 ($\delta^{13}C_{27-31} = -23.5‰$ to $-23.1‰$) plants, but neither $\delta^{13}C$ nor δ^2H values could uniquely differentiate aquatic and terrestrial species, emphasizing a stronger plant physiological/biochemical rather than environmental control over isotopic differences. ACL and CPI complemented isotopic discrimination, with significantly longer chain lengths recorded for trees and terrestrial plants compared with herbaceous perennials and aquatic species, respectively. Application of a comprehensive Bayesian mixing model for 18 streambed sediments collected between September 2013 and March 2014 revealed considerable temporal variability in the

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apportionment of organic matter sources. Median organic matter contributions ranged from 22% to 52% for trees, 29% to 50% for herbaceous perennials, 17% to 34% for C_3 graminoids and 3% to 7% for C_4 graminoids. The results presented here clearly demonstrate the effectiveness of an integrated molecular and stable isotope analysis for quantitatively apportioning, with uncertainty, plant-specific organic matter contributions to streambed sediments via a Bayesian mixing model approach.

1. Introduction

Sediment fingerprinting has become a popular technique for apportioning the sources of deposited and suspended sediments across a range of aquatic environments via a mixing model approach (Mukundan et al., 2012; Guzmán et al., 2013; Walling, 2013). As the number and type of source apportionment studies have increased over recent years, there has been a shift in research focus towards re-evaluating and advancing existing fingerprinting procedures (e.g. Koiter et al., 2013; Cooper et al., 2014a; Smith and Blake, 2014; Laceby and Olley, 2014; Pulley et al., 2015). Because the majority of existing fingerprinting studies have focused solely on inorganic sediment provenance (e.g. Collins et al., 2013; Thompson et al., 2013; Wilkinson et al., 2013), the apportionment of organic matter in fluvial sediments in agricultural settings remains largely undeveloped. Understanding the origins of fluvial organic matter is important because organic material can constitute a significant percentage of the total sediment volume (e.g. Cooper et al., 2015). Furthermore, elevated organic matter concentrations are associated with enhanced transport of nutrients and heightened biological oxygen demand, thus leading to a degradation of water quality (Hilton et al., 2006; Withers and Jarvie, 2008). Whilst an understanding of the amount of organic material transported in fluvial systems can be achieved by monitoring the fluxes of dissolved (DOC) and particulate organic carbon (POC) at the catchment outlet (Alvarez-Cobelas et al., 2012; Némery et al., 2013), such measurements are unable to yield quantitative information on the specific sources of this organic load.

Addressing this matter, compound-specific isotope analysis (CSIA) has the potential to facilitate the identification of organic matter contributions to riverine sediments by exploiting differences in the stable isotopic composition amongst different plants at either the species or plant functional type level (Marshall et al., 2007). Of particular interest in this study are the carbon ($\delta^{13}C$) and hydrogen (δ^2H) stable isotopic compositions of plant *n*-alkanes. Although *n*-alkanes represent only a small fraction of total organic matter, these compounds have unique biological origins which allow them to be used as plant-specific biomarkers of organic matter contributions (Meyers, 1997). Compared with other plant biochemical components, such as carbohydrates, amino acids and lignin, long-chain *n*-alkanes also persist in the environment due to a high resistance to degradation (Bourbonniere and Meyers, 1996), thus making them suitable conservative fingerprints for sediment source apportionment. Variability in the carbon and hydrogen isotopic compositions of plant *n*-alkanes is driven by a complex combination of differences in plant physiology/biochemistry and a range of environmental factors, including temperature, humidity, light availability, salinity and the isotopic composition of water and CO_2 (O'Leary, 1988; Farquhar et al., 1989; Sessions et al., 1999; Hou et al., 2007; Sachse et al., 2012). Importantly, this means that the degree of isotopic fractionation is theoretically unique for each individual plant, thereby allowing distinct *n*-alkane isotopic signatures to develop that can be used to differentiate between different plant types.

A number of studies have previously been successful in using the $\delta^{13}C$ isotopic signatures of soils and sediments to identify fluvial sediment contributions derived from allochthonous and autochthonous sources (e.g. McConnachie and Petticrew, 2006; Schindler Wildhaber et al., 2012; Fu et al., 2014; Wang et al., 2015), or from different land-use types based on the dominant vegetation cover (e.g. Fox and Papanicolaou, 2007; Gibbs, 2008; Blake et al., 2012; Hancock and Revill, 2013; Laceby et al., 2014). Similarly, previous studies have used molecular ratios such as the average chain length (ACL) and carbon preference index (CPI) to differentiate organic material of higher plant origin from algal or microbial contributions, or to identify petrogenic hydrocarbon inputs (e.g. Pancost and Boot, 2004; Jeng, 2006). However, to our knowledge, the usefulness of integrating both molecular ratios and compound-specific δ^2H and $\delta^{13}C$ values of individual organic compounds for quantifying organic matter source apportionment in stream sediments via a Bayesian mixing model approach has never been assessed. Therefore, the main objectives of this study were as follows:

(i) to assess the effectiveness of δ^2H and $\delta^{13}C$ values of long-chain *n*-alkanes (C_{27}, C_{29}, and C_{31}) in differentiating (a) plants derived from different functional types and (b) plants growing in aquatic and terrestrial environments;
(ii) to determine whether *n*-alkane ratios (ACL and CPI) can enhance discrimination between plant groups when used in combination with isotopic values;
(iii) to use these isotopic values and molecular ratios as fingerprints within a Bayesian mixing model to quantitatively apportion, with uncertainty, plant-specific organic matter contributions to streambed sediments.

We applied this novel CSIA fingerprinting technique to streambed sediments collected over a 7-month period between September 2013 and March 2014 from an agricultural headwater catchment of the River Wensum, Norfolk, UK.

2. Methods

2.1. Study location

The River Wensum is a nutrient enriched, lowland calcareous river system, which drains an area of 593 km^2 in Norfolk, UK. The Wensum catchment is divided into 20 sub-catchments, one of which, the 20 km^2 Blackwater sub-catchment, represents the area intensively monitored as part of the River Wensum Demonstration Test Catchment (DTC) project (Outram et al., 2014). For observational purposes, the Blackwater sub-catchment is divided into six 'mini-catchments' A to F, each of which has a bankside monitoring kiosk at the outlet. The 5.4 km^2 mini-catchment A provided the focus for this research (Fig. 1). Situated ~40 m above sea level with gentle slopes that rarely exceed 0.5°, intensively farmed arable land constitutes 92% of this headwater catchment. A 7-course crop rotation is practiced with autumn and spring sown wheat and barley, sugar beet, oilseed rape and spring beans. A small and variable amount of land is also lain down to maize for game bird cover. The remainder of mini-catchment A is covered by 3% improved grassland, 2% semi-natural grassland, 1.5% deciduous woodland, 0.5% coniferous woodland and 1% rural settlements. From May to September, emergent macrophytes dominate stream primary productivity, with this vegetation being cleared at the end of the growing season (mid-October) to improve catchment drainage and prevent winter flooding of the surrounding arable land. A weather station at the outlet to mini-catchment A recorded average precipitation totals of 808 mm $year^{-1}$ and a mean average annual temperature of 9.2 °C during April 2012–March 2014.