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Insights into bulk stable isotope alteration during sediment redistribution to edge-of-field: impact on sediment source apportionment

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Abstract Organic tracers (bulk δ^{13}C and δ^{15}N) are being increasingly used in sediment/particulate organic carbon source apportionment studies at the catchment scale to support sustainable land management decisions. Here, the use of these isotopic tracers in sediment fingerprinting depends on the critical assumption that δ^{13}C and δ^{15}N values remain conservative during the sediment delivery continuum. Such assumption, however, requires critical evaluation, especially since standard tracer conservation tests applied in conjunction with catchment scale studies are prone to masking potential issues at smaller spatial scales including the field scale. Against this background, our study evaluated the subtle isotopic shift associated with sediment redistribution to edge-of-field and assessed the impact on sediment source apportionment. In a C_3-grass dominated study field, δ^{13}C and δ^{15}N values exhibited differences (i.e., Δ^{13}C = 1.4 ± 0.7‰ and Δ^{15}N = 0.4 ± 0.4‰) between soil depths of 0–5 cm and 5–10 cm. Sampled sediments at the edge-of-field flume had higher δ^{13}C values than the 0–5 cm soil layer; i.e., Δ^{13}C values were 0.3 ± 0.4‰ and 0.8 ± 0.4‰ for suspended and deposited (materials deposited in a basket downstream of a flume) sediment, respectively. In contrast, δ^{15}N values increased in suspended (Δ^{15}N = 0. 8 ± 0.6‰) but decreased (Δ^{15}N = − 0.4 ± 0.5‰) in deposited sediment, compared to the 0–5 cm soil layer, suggesting that the N isotopes can respond differently in edge-of-field sediment types. Although current fingerprinting work tends to not take explicit account of organic tracer alteration during transport or after deposition, our results demonstrate that correcting sediment δ^{13}C and δ^{15}N values for tracer alteration in a Bayesian un-mixing model generated robust and reliable estimates of source contributions to both target sediment types. We therefore recommend taking account of the subtle but consistently altered δ^{13}C and δ^{15}N values along the sediment cascade in un-mixing modelling to help better discriminate sources and to improve un-mixing model estimates at the catchment scale.

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Introduction

The dynamics of stable carbon (C) and nitrogen (N) isotope signatures in the plant–soil–sediment continuum have been used to provide information for tracing nutrient and sediment sources, and for understanding biogeochemical processes and energy flows at the catchment scale (Fox and Papanicolaou 2007; Jensen et al. 2018; Nagel et al. 2009). In sediment source fingerprinting studies, bulk stable isotopes of C (δ^{13}C) and N (δ^{15}N) have been used to differentiate land use activities which can drive soil erosion and which are responsible for generating high sediment loads within river systems (Collins et al. 2019; Guan et al. 2017; Mahoney et al. 2019). As the δ^{13}C and δ^{15}N values of sediment can provide insights into both biogeochemical processes and the relative contributions from catchment sources (Ohkouchi et al. 2015), and are simple and inexpensive to analyse, the use of these tracers in combination with others (e.g., optical, geochemical) for sediment source apportionment purposes has expanded greatly (Collins et al. 2017).

Increasing numbers of studies have reported the use of bulk δ^{13}C and δ^{15}N values as tracers for sediment source apportionment at the catchment scale (Collins et al. 2013; Fox and Martin 2015; Fox and Papanicolaou 2007; Gomes et al. 2019; Laceby et al. 2015; Mahoney et al. 2019). The use of bulk δ^{13}C and δ^{15}N values for sediment source fingerprinting in fluvial systems relies heavily on the critical assumption that these tracers remain conservative during sediment redistribution. However, there is a need to revisit this assumption associated with the consistently conservative behaviour of tracers across scales (Collins et al. 2014; Ford et al. 2020; McCarney-Castle et al. 2017; Sherriff et al. 2015; Upadhayay et al. 2018b). The isotopic signatures of bulk sediment samples integrate the ^{13}C and ^{15}N compositions of both organic and inorganic material modified by any secondary isotopic alteration that occurs during sediment transport and redistribution. Tracer transformation weakens the specificity of tracer signatures for individual sources (Bianchi and Canuel 2011) and can increase uncertainty in sediment source appointment estimates (Collins et al. 2017; Cooper et al. 2014).

In sediment source fingerprinting studies, researchers typically use the so-called bracket or range test to determine the alteration of a tracer signature (Foster and Lees 2000; Wilkinson et al. 2013). This simple mathematical test, however, has some important limitations. Firstly, it does not confirm the absence of tracer alteration, but instead, is more indicative of the lack of any major alteration to tracer concentrations (Collins et al. 2013, 2014). It therefore lacks sensitivity. Secondly, since most source fingerprinting studies are undertaken at the catchment scale, application of the bracket test for screening conservative tracers remains a black-box approach which fails to elucidate mechanisms driving changes in tracer content (Koiter et al. 2013). It therefore lacks specificity. Thirdly, the mechanisms of sediment transfer and their controlling factors are scale-dependent (Collins et al. 2020) suggesting that the catchment scale integrates across many smaller spatial scales, meaning that information is lost. A successful range test result at the catchment scale may therefore mask non-conservative behaviour at smaller scales. Since investigation of these issues with a view to refining procedural steps for source fingerprinting is potentially resource demanding, the international research community continues to acknowledge the shortcomings of applying the conventional bracket test at the catchment scale only, as one limitation common to source fingerprinting studies. This clearly points to the need to investigate tracer conservation at smaller spatial scales representative of the sediment delivery cascade including to edge-of-field in agricultural landscapes where excessive sediment loss is frequently reported as an issue in conjunction with nutrients and pollutants. A recent global review of sediment source tracing has underscored the need for such detailed work (Collins et al. 2020).

To the best of our knowledge, no studies have systematically assessed how the δ^{13}C and δ^{15}N of source soils associated with sediment transfer can be altered between the point of mobilisation and edge-of-field which can be taken as the first meaningful spatial boundary in agricultural landscapes. This current knowledge gap is important since decomposition of soil organic matter may alter the δ^{13}C and δ^{15}N values of target sediment samples collected at different

spatial and temporal scales (Cui et al. 2016; Hu et al. 2016; Kirkels et al. 2014). Despite this risk of tracer alteration, sediment source apportionment studies do not account for any fractionations when using isotope un-mixing models to estimate source proportions. Although Bayesian tracer un-mixing models (e.g., MixSIAR) have the functionality to include isotopic fractionation effects, the international sediment fingerprinting community assumes that the isotopic alteration factor is zero due to the lack of data for the ^{13}C and ^{15}N transformation factor during sediment redistribution. MixSIAR is highly sensitive to the isotope fractionation factors used in model formulation (Bond and Diamond 2011; Stock and Semmens 2016).

Here, we hypothesise that incorporating shifts in the $\delta^{13}C$ and $\delta^{15}N$ of sediment organic matter during transport to and upon deposition at the edge-of-field, into the input parameters of an un-mixing model, will result in realistic changes in the model estimation of source contributions. We test this hypothesis by assessing the proportions of two sources (i.e., surface vs subsurface) of edge-of-field sediments using paired values of $\delta^{13}C$ and $\delta^{15}N$ in a hydrologically-isolated field scale catchment. For clarification, since this study is at the field scale, it neither explores the potential impacts of landscape geomorphological features nor does it estimate processes-specific isotope transformation factors. Instead, we explore explicitly the impact of measured $\delta^{13}C$ and $\delta^{15}N$ alteration in a widely used Bayesian un-mixing model with regards the robustness of the sediment source apportionment estimates generated.

Methodology

Site description

This study was conducted on a hydrologically-isolated field scale catchment of the North Wyke Farm Platform (NWFP; 50°46′10″N, 3°54′05″W), Rothamsted Research, located in SW England (Fig. 1a). The 6.7 ha catchment is bounded by a 800 mm deep French drain (Orr et al. 2016). Water collected in the French drain is channelled downslope towards a concrete sampling pit and flume where the monitoring of discharge and various physio-chemical parameters is undertaken.

The study catchment is part of the 'Permanent Pasture' treatment of the NWFP; namely, the maintenance of the current sward by grazing, cutting, and business-as-usual fertilizer applications. Within the study field, perennial ryegrass (*Lolium perenne* L.) and creeping bent grass (*Agrostis stolonifera* L.) are the dominant species with a mixture of other 'weed' species such as yorkshire fog (*Holcus lanatus* L.), marsh foxtail (*Alopecurus geniculatus* L.), and rough meadow grass (*Poa trivalis* L.). The pasture is managed by low density grazing (cattle and sheep) and by cutting silage for winter feed. The sward is sustained through the application of farm yard manure between silage cuts and inorganic N:P:K fertilizers which are applied at recommended rates on the basis of routine soil analyses (DEFRA 2010). The soils of the study catchment have been classified as a stagnivertic cambisol (Harrod and Hogan 2008) with an acidic soil pH of 5.8 ± 0.1 during the period spanning July 2018 to March 2019 (https://nwfp.rothamsted.ac.uk/). The study field lacks depressions and significantly trampled areas.

Plant, soil and sediment sample collection and processing

The study was conducted from October 2018 to March 2019, which typically represents the wettest period of the year (Fig. 1c). Grass and soil samples were collected from the study field using a georeferenced 25 m square sampling design (Fig. 1a). At each sample location, grass and a single soil core was collected using a 10.5 cm diameter soil corer to a depth of 10 cm. The soil core was then divided into two sections i.e., 0–5 and 5–10 cm. Tree leaf litter and cattle dung samples were also collected from four locations in the field scale catchment (Fig. 1a). Tree leaf litter and dung samples were collected randomly in each area and composited per site. All the samples were stored in a fridge at 4 °C prior to further processing.

The grass, soil, dung and tree litter samples were oven-dried for 96 h at 60 °C. Roots were removed from the soil cores by hand and kept in 50 mL containers and rhizosphere soil was removed by shaking for 3 min at 180 rmp in 35 mL of autoclaved, phosphate buffer solution (6.33 g L^{-1} NaH_2PO_4, 8.5 g L^{-1} Na_2HPO_4 anhydrous, pH 6.5, 200 µl L^{-1} surfactant) (McPherson et al. 2018). The roots were

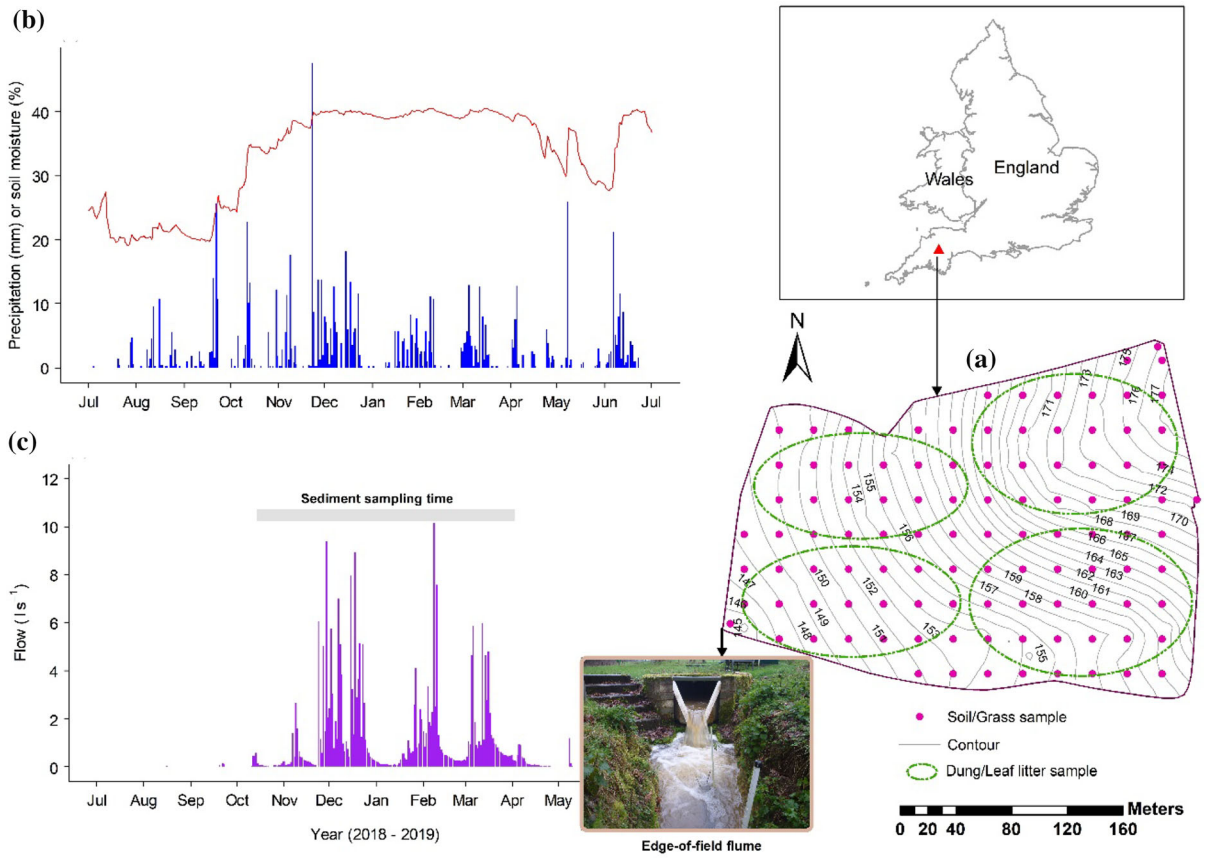

Fig. 1 Study field topography with sampling locations (**a**); study period with hydro-meteorological conditions—daily precipitation (vertical blue bar) and soil moisture (horizontal red line) (**b**), and; water flow in the edge-of-field flume over the duration of sediment sampling (grey bar) (**c**). (Color figure online)

further washed in distilled water 3–4 times to remove the excess phosphate buffer and soil. Roots samples were frozen at – 20 °C and then freeze-dried.

Suspended sediment samples were collected from the edge-of-field flume located at the low point of the study field (Fig. 1a) using two time-integrated mass-flux samplers (also known as Phillips tubes; Phillips et al. 2000). Additionally, a basket (L: 60 cm × B: 40 × H: 28.5 cm) filled with gravel (> 4 mm Ø, rinsed with 0.05 M H_2SO_4 followed by several rinses with distilled water) was inserted just downstream of the flume to collect additional sediment samples (hereafter referred to as 'deposited sediment') which mimic natural sediment deposition in streams and rivers (Acornley and Sear 1999; Schindler Wildhaber et al. 2012). Sediment samples were retrieved from the Phillips tubes and basket at the same time approximately every 2 months from October 2018 to March 2019. Suspended sediment retrieved from the two Phillips tubes was kept separately in 25 L containers. Deposited sediment collected in the gravel filled basket was collected by emptying the pebbles into a plastic sack and repeatedly washing them, with the resultant washing solutions combined and collected in 25 L containers. Bulk sediment samples in the 25L containers were stored at 4 °C for a week to permit settling, whereupon the overlying water was decanted. Dewatered sediment samples were frozen at − 20 °C and subsequently freeze-dried.

Sample analysis

Sediment particle size was measured using a bench top LISST 100x (Sequoia Scientific, Inc.) to establish the size distributions of the particulate material being transported to the edge-of-field. Primary particle size

distributions showed that > 97% of the sampled sediment was < 106 µm (Fig. S1). Accordingly, all soil samples were sieved based on this sediment particle size information. Additionally, soil and sediment samples (each four), were selected randomly and further sieved into particle size subfractions (i.e., < 32 µm, 32–63 µm, 63–106 µm) to examine any potential differences within the < 106 um particle size range. The dried grass, root and litter samples were milled and sieved to < 500 µm. Milled and sieved soil, sediment and plant materials were then weighed into tin capsules and analysed using a Carlo Erba NA2000 elemental analyser (CE Instruments, Wigan, UK) interfaced with a PDZ Europa 20-22 isotope ratio mass spectromer (SerCon Ltd., Crewe, UK). The elemental and isotopic reference standard was IA-R001 (wheat flour from Iso-Analytical, calibrated against IAEA-N-1 and IAEA-CH6: %N = 1.791%; %C = 40.46%; δ^{15}N = 2.51‰; δ^{13}C = − 25.99‰). Average standard deviations for elemental and isotopic reference standards were 0.42% and 0.2‰ for carbon and 0.03% and 0.2‰ for nitrogen, respectively. The isotopic results were expressed as natural abundance (δ) in parts per mil (‰) compared to international standards. Here, TC and its isotopic composition of samples are presumed to represent organic carbon while TN and its isotopic composition reflect both organic and bound (soil or sediment) inorganic nitrogen.

Statistical analysis and tracer un-mixing model formulation

Arithmetic means and standard deviations of TC%, TN%, δ^{13}C and δ^{15}N values were calculated for grass leaves, roots, soil, sediment, dung and tree leaf litter samples. Similarly, TC:TN % ratios (hereafter referred to as 'C/N ratios') were calculated for all samples. A student's t-test was used to compare the isotope data to confirm statistical differences between the means of the groups (e.g., surface soil and target sediments, target sediment types) after data normality (Shapiro–Wilk test) and homoscedasticity (Levene test) checks. Additionally, statistical differences in isotope values within plant and soil and target sediment samples were determined using analysis of variances. When the analysis of variance detected a statistical significance ($\alpha = 0.05$), the Tukey's pairwise multiple comparison test was performed to identify which compartments were significantly different.

The alterations of δ^{13}C and δ^{15}N values (also known as discrimination factors) during sediment redistribution from surface source soils to the edge-of-field flume were estimated according to the following Eqs. (1) and (2):

$$\Delta^{13}C = \delta^{13}C_{soil(0-5\text{cm})} - \delta^{13}C_{sediment} \quad (1)$$

$$\Delta^{15}N = \delta^{15}N_{soil(0-5\text{cm})} - \delta^{15}N_{sediment} \quad (2)$$

Note that the bulk stable isotope values of surface soil samples were used to calculate the isotopic shift based on the study field characteristics i.e., a permanent pasture field with a 32 m difference in elevation (Fig. 1a), impermeable soil and geology, and flashy hydrological responses to effective rainfall leading to large volumes of surface runoff. In general, a strong correlation between the enrichment factor from the Rayleigh model and the slope of the regression line (hereafter referred to as 'β') of $\delta_{\text{substrate}}$ vs ln (concentration of substrate) has been reported in the international literature (Acton et al. 2013; Garten et al. 2007; Mobius 2013; Wang et al. 2018; Wynn et al. 2006). Therefore, regression was used to assess the relationship between δ^{13}C and TC% as well as between δ^{15}N and TN% using the source soil and target sediment samples.

Biplots were used to assess source contributions qualitatively to both types of target sediment (i.e., suspended and deposited) samples. The concentration-dependent Bayesian tracer un-mixing model i.e., MixSIAR was used to estimate the contributions of the 0–5 cm and 5–10 cm soil layers to the suspended and deposited sediment. The inclusion of concentration-dependence provided a means of addressing the nonlinear mixing of isotopes in sediments (Upadhayay et al. 2018a). The MixSIAR framework was formulated using different scenarios: i.e., (i) uninformative prior + no adjusted discrimination factor; (ii) informative prior + no adjusted discrimination factor; (iii) uninformative prior + adjusted discrimination factor, and; (iv) informative prior + adjusted discrimination factor. This provided a basis for assessing how an adjusted discrimination factor might improve the source apportionment results.

Our field observations showed that rainfall produces flashy hydrological responses leading to large

volumes of surface runoff. On this basis, we formulated prior information that most of the sediments (> 95%) delivered to the edge-of-field flume are derived from surface soil erosion. The discrimination factor in MixSIAR was adjusted by incorporating tracer values associated with sediment redistribution to edge-of-field obtained from Eqs. 1 and 2. The Markov Chain Monte Carlo (MCMC) parameters in MixSIAR were set as extreme. Convergence of model runs was checked via Gelman-Rubin and Geweke diagnostic statistics. The best model fit was determined by leave-one-out cross-validation (LOO) and Akaike weights which provide probability information that each model will make the best prediction using the new data (McElreath 2016; Stock et al. 2018). Means and corresponding 95% Bayesian credible intervals (CI) were reported from the posterior distributions to describe predicted sediment source contributions and corresponding uncertainties. All statistical analysis and un-mixing modelling were conducted using R software version 3.5.1 (R Core Team 2018) with the multcomp (Hothorn et al. 2008) and MixSIAR (Stock et al. 2018) packages. Figures were plotted using the ggplot2 package (Wickham 2009).

Results

Carbon and nitrogen contents and their isotopic composition

Plant samples

The mean %TC and %TN contents of the grass leaves were 39.4 ± 3.2% and 3.1 ± 0.4%, respectively (Fig. 1a, b and Table S1). The TC and TN contents of the roots were 34.6 ± 4.9% and 0.9 ± 0.1% for the 0–5 cm surface soil and 33.4 ± 5.6% and 0.9 ± 0.1% for the 5–10 cm subsurface soil samples. The TC and TN contents of roots at two depths were not significantly different; however, the TC and TN contents of the grass leaves were significantly higher than the corresponding values measured in all root samples. The C/N ratio of the grass leaves was 12.9 ± 2.3, compared with 38.2 ± 5.7 and 37.9 ± 6.3 for the 0–5 cm and 5–10 cm root samples, respectively. The C/N ratio was significantly ($p < 0.001$) higher in the root samples compared to the leaf material irrespective of root depth.

The $\delta^{13}C$ of grass leaves was − 31.0 to ± 0.8‰, while that of the root material was − 30.9 ± 0.4‰ for the 0–5 cm layer and − 30.9 ± 0.5‰ for the 5–10 cm layer (Fig. 1c). The $\delta^{15}N$ of grass leaves was 3.5 ± 1.3‰, and that of the root material was 3.8 ± 1.4‰ for the 0–5 cm layer and 2.8 ± 1.0‰ for the 5–10 cm layer (Fig. 2d). While there was no significant difference in $\delta^{13}C$ for any of the different grass fractions (Fig. 2c), the $\delta^{15}N$ value of the 5–10 cm roots were significantly lower than the 0–5 cm roots and the grass leaves ($p < 0.001$) (Fig. 2d). The tree leaf litter $\delta^{13}C$ and $\delta^{15}N$ values were − 29.9 ± 0.5‰ and − 0.1 ± 0.6‰, respectively, while the corresponding respective values for the dung samples were − 30.9 ± 0.4‰ and 6.2 ± 0.7‰ (Table S1).

Soil samples

The soil %TC was 6.6 ± 0.6% in the 0–5 cm samples which was higher ($p < 0.001$) than the TC in the 5–10 cm samples which was 4.4 ± 0.5% (Fig. 3a). The %TN of the soil was also higher ($p < 0.001$) in the 0–5 cm layer compared to the 5–10 cm layer, with a mean of 0.7 ± 0.1% compared to 0.5 ± 0.1% (Fig. 3b). The C/N ratio was also significantly higher ($p < 0.001$) in the 0–5 cm soil (9.6 ± 0.3) compared to 5–10 cm soil (8.8 ± 0.2). In the regression plot of TC vs TN (Fig. S2a), there is an intercept of 0.15% and 0.11% TN and 0%TC for the 0–5 cm and 5–10 cm soil layers, respectively, suggesting that there is a considerable amount of inorganic nitrogen in the soil layers. The $\delta^{13}C$ value of the 0–5 cm layer soil was − 30.3 ± 0.3‰ which was lower ($p < 0.001$), than the 5–10 cm soil (− 28.9 ± 0.7‰; Fig. 3c). In contrast, the $\delta^{15}N$ value of the two soil depths were similar with values of 6.0 ± 0.4‰ and 6.5 ± 0.5‰, respectively (Fig. 3d).

Sediment samples

The mean %TC and %TN content of the target suspended sediment samples was 5.6 ± 0.9%, and 0.6 ± 0.1%, respectively, which was higher ($p < 0.001$) than the corresponding values measured in deposited sediment which were 3.4 ± 0.2% and 0.35 ± 0.03% (Fig. 3a and b). A regression plot (TC vs TN) (Fig. S2b) showed that there is a significant fraction of inorganic nitrogen in the suspended

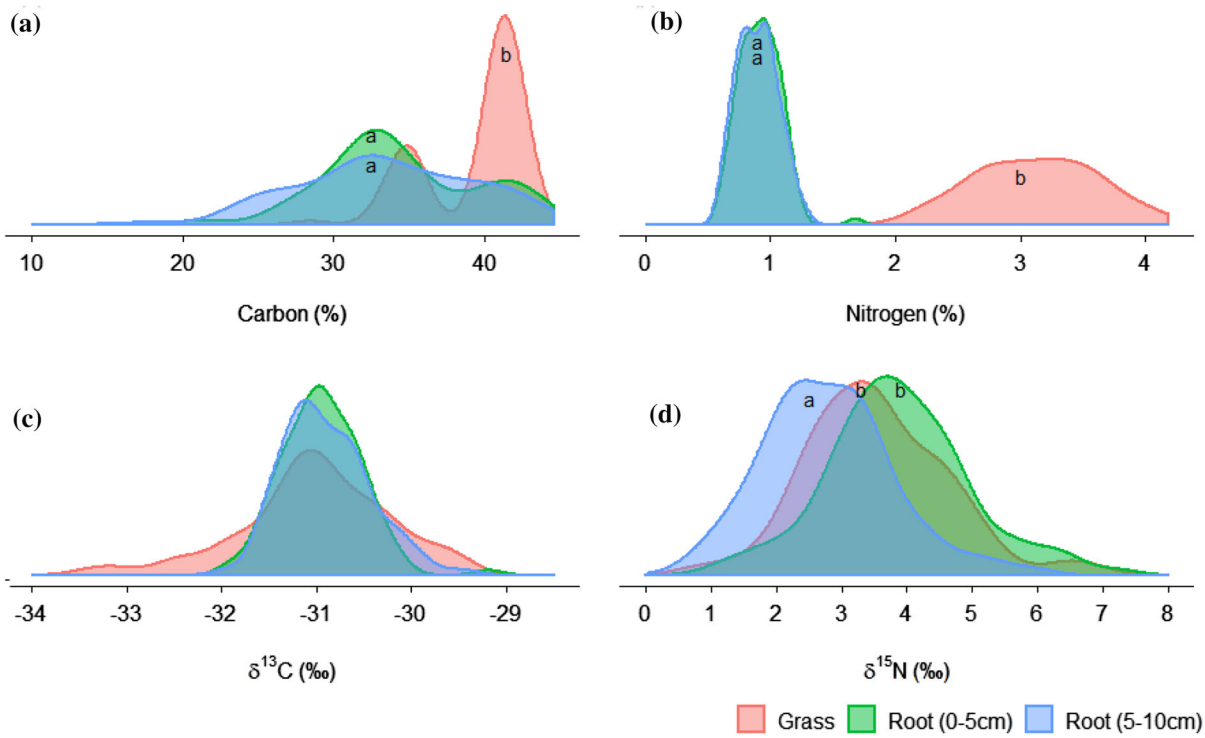

Fig. 2 Density plots and statistical significance tests for **a** %TC, **b** %TN, **c** δ^{13}C, and **d** δ^{15}N, for the grass and root samples. Only statistically significant differences are differentiated by letters

sediment samples (0.28% TN at 0%TC) compared to deposited samples (negative intercept). The δ^{13}C of both suspended and deposited sediment samples were similar i.e. − 30.0 ± 0.2‰ and − 29.5 ± 0.2‰, respectively (Fig. 3c). However, the δ^{15}N of the deposited sediments (5.7‰ ± 0.3) was significantly lower ($p < 0.001$) than in the suspended sediment samples (6.8 ± 0.4‰) (Fig. 3d). The C/N ratio of the suspended (9.4 ± 0.9) and deposited (9.4 ± 0.3) sediment samples was not significantly different.

Alteration of C and N isotopic composition in the plant–soil–sediment continuum

The 0–5 cm soil layer had significantly higher ($p < 0.001$) δ^{13}C and δ^{15}N values compared to grass roots at the same depth and the same can be said for the soil and roots in the 5–10 cm layer, although the difference was not significant (Table S1). The Δ^{13}C and Δ^{15}N values in the 0–5 cm and 5–10 cm soil layers showed high variability with values ranging from − 2.5 to − 0.2‰ (− 1.4 ± 0.7‰) and − 1.6 to 0.5 (− 0.4 ± 0.4‰), respectively. The slopes of the regression lines fitted between δ^{13}C and ln (C%) and δ^{15}N and ln (N%) were − 2.96 and − 0.75, respectively, across the soil depths (Fig. S3).

The %TC and %TN content of both deposited and suspended sediment samples was found to be significantly ($p < 0.001$) different to both source soil depths. In both cases, the deposited sediment had a significantly lower %TC and %TN than either of the soil depths, while the suspended sediment had %TC and %TN contents that was significantly different to, but in between, those measured in the 0–5 cm and 5–10 cm layer soil samples (Fig. 3a, b). The C/N ratio in surface soil (9.6 ± 0.3) was similar to that of the deposited and suspended sediment samples (9.4 ± 0.3 and 9.4 ± 0.9, respectively).

In contrast to the %TC and %TN data, which exhibited a consistent pattern in both suspended and deposited sediment, differences were observed in the δ^{13}C and δ^{15}N values. Although there was no difference between the δ^{13}C values of the suspended and deposited sediment samples, both had δ^{13}C values that were directly in between those of the 0–5 cm and 5–10 cm layer soils. The suspended sediment samples

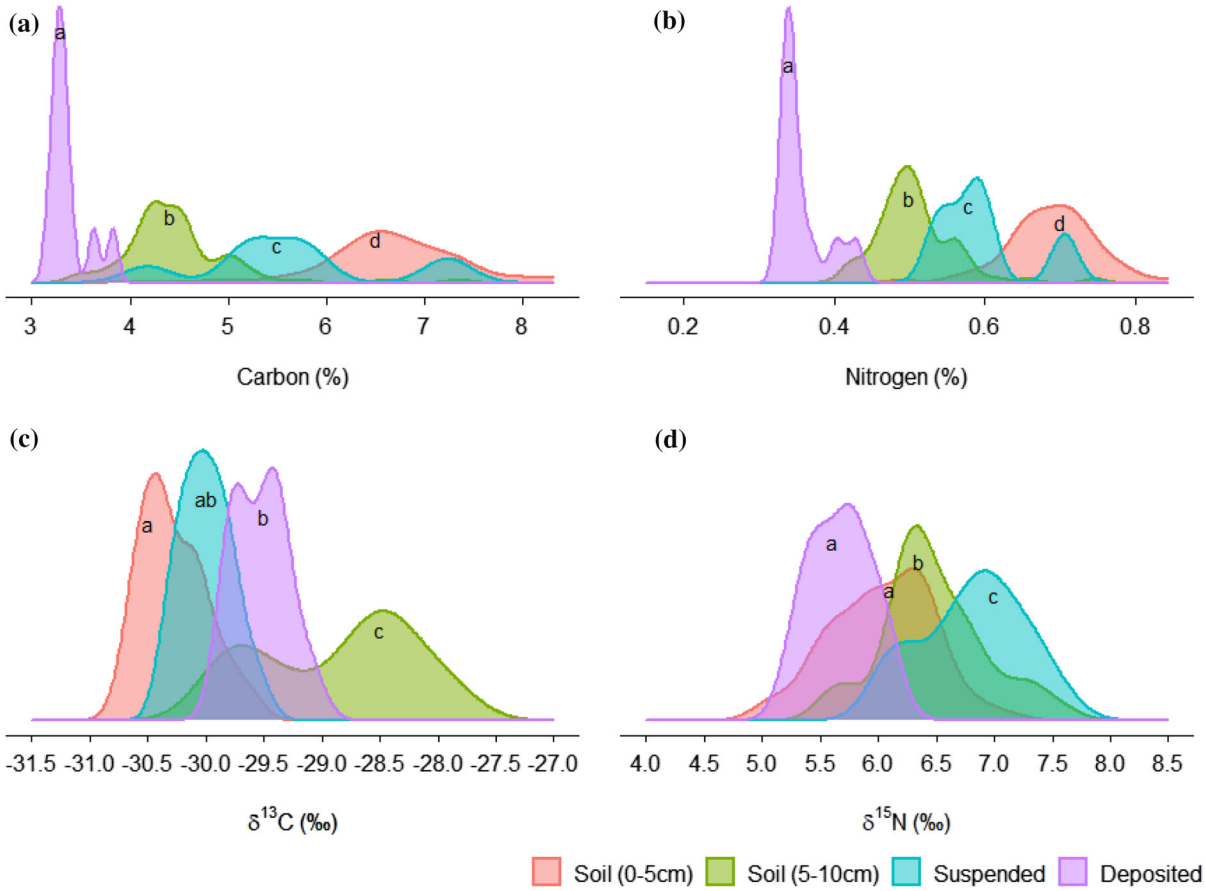

Fig. 3 Density plots and statistical significance tests for **a** %TC, **b** %TN, **c** δ^{13}C, and **d** δ^{15}N, for the source soil and target sediment samples. Significance differences are indicated by letters

were only significantly different to the 5–10 cm layer soils. Deposited sediment was significantly different to both soil layers (Fig. 3c). The Δ^{13}C values were − 0.3 ± 0.4‰ and − 0.8 ± 0.4‰ for suspended sediment and deposited sediment samples, respectively, compared to the 0–5 cm soil layer (Fig. 4b). The slope of the regression line fitted between δ^{13}C and ln (C%) across the target sediment types was − 0.65 (Fig. 5a).

The δ^{15}N of the source soils and target sediment samples exhibited the opposite trend to those of the δ^{13}C. While δ^{15}N values of the two target sediment types were significantly different ($p < 0.001$), the deposited sediment was more akin to the 0–5 cm soil layer. The δ^{15}N of the deposited sediment was lower than that of the soils and the δ^{15}N of the suspended sediment was higher than both soil depths (Fig. 3d). The sediment samples in this case sit 'outside' the range of the values measured for the two source soil sampling depths. The Δ^{15}N values were − 0.8 ± 0.6‰ and 0.4 ± 0.5‰ for suspended and deposited sediment, respectively (Fig. 4b). The slope of the regression line fitted between δ^{15}N and ln (N%) was 2.2 across both target sediment types. Importantly, δ^{13}C values of surface source soil and suspended sediment were not affected by grain size in this study (Table S2). In contrast, ^{15}N showed a different trend across the particle sizes in surface soil (remaining stable) compared with suspended sediment (depleted in the fine fraction i.e., < 32 µm compared to the bulk sample i.e., < 106 µm).

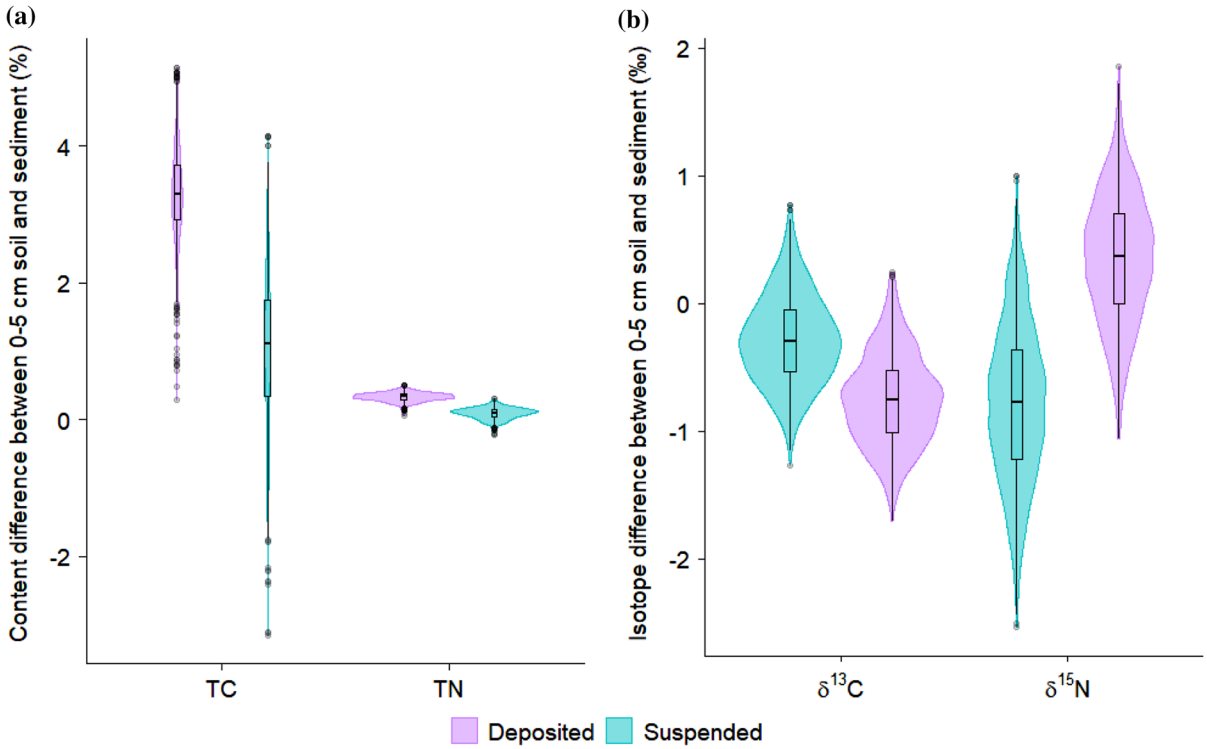

Fig. 4 Violin and box plots showing tracer differences between the 0–5 cm layer source soil, and the deposited and suspended sediment samples: **a** %TC and %TN, and; **b** δ13C and δ15N

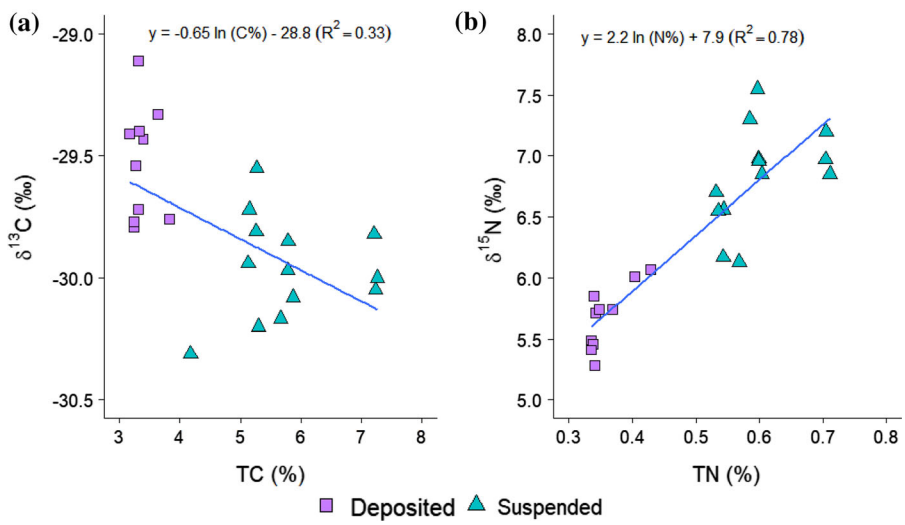

Fig. 5 Linear regression showing changes in **a** δ^{13}C vs ln (C%) and **b** δ^{15}N vs ln (N%) in the deposited and suspended sediment samples

Sensitivity to informative priors and discrimination factor adjustment in un-mixing model predictions of sediment source contributions

The origin of target sediment in the edge-of-field flume can be identified by comparing the δ^{13}C and δ^{15}N of the sediment samples with those of its potential sources. In this grassland field case study, two potential sediment sources were considered i.e., surface (0–5 cm) and sub-surface (5–10 cm) soil layers. Biplots of δ^{13}C, δ^{15}N and C/N ratios are presented in Fig. 6. The relationships between δ^{13}C, δ^{15}N and C/N ratios demonstrated that the δ^{13}C versus δ^{15}N plot effectively discriminated between the two soil layers. Qualitatively, 0–5 cm soil was the primary source of target sediment samples collected at the edge-of-field flume (Fig. 6). This qualitative finding was supported by the MixSIAR model outputs (Table 1, Fig. S4, S5) which showed that the probability distributions for the proportional contribution of target sediment from the 0–5 cm soil layer varies with the MixSIAR model formulation. A formulation based on an uninformative prior and an assumption of conservative tracer behaviour estimated that 63% (CI 41–85%) and 56% (CI 27–88%) of suspended and deposited sediment originated from the 0–5 cm soil layer, respectively. Both target sediment types were predicted to predominantly (i.e., > 95%) derive from the 0–5 cm soil layer (i.e. > 95%) when an informative prior was included, and the potential tracer alteration factor was adjusted in MixSIAR. Overall, our results showed that the un-mixing model with "informative prior and adjusted discrimination factor" is preferable (lowest LOO and highest weight) over the other models which neglect this important information in Bayesian tracer un-mixing model formulation (Table 1).

Discussion

Variability of carbon and nitrogen isotopic signatures across the plant–soil–sediment continuum

Carbon and nitrogen in grassland soils are mostly derived from grass roots (Amelung et al. 1999; Collins et al. 2019; Li et al. 2017; Szpak 2014) since above ground biomass is often removed from the field for silage. In addition to grass roots, the influence of dung (δ^{13}C = − 30.9 ± 0.4‰, δ^{15}N = 6.2 ± 0.7‰) and urine from grazing livestock as well as deciduous tree leaf litter (δ^{13}C = − 29.9 ± 0.5‰, δ^{15}N = − 0.1 ± 0.6‰) on δ^{13}C and δ^{15}N values measured in this grassland soil cannot be neglected.

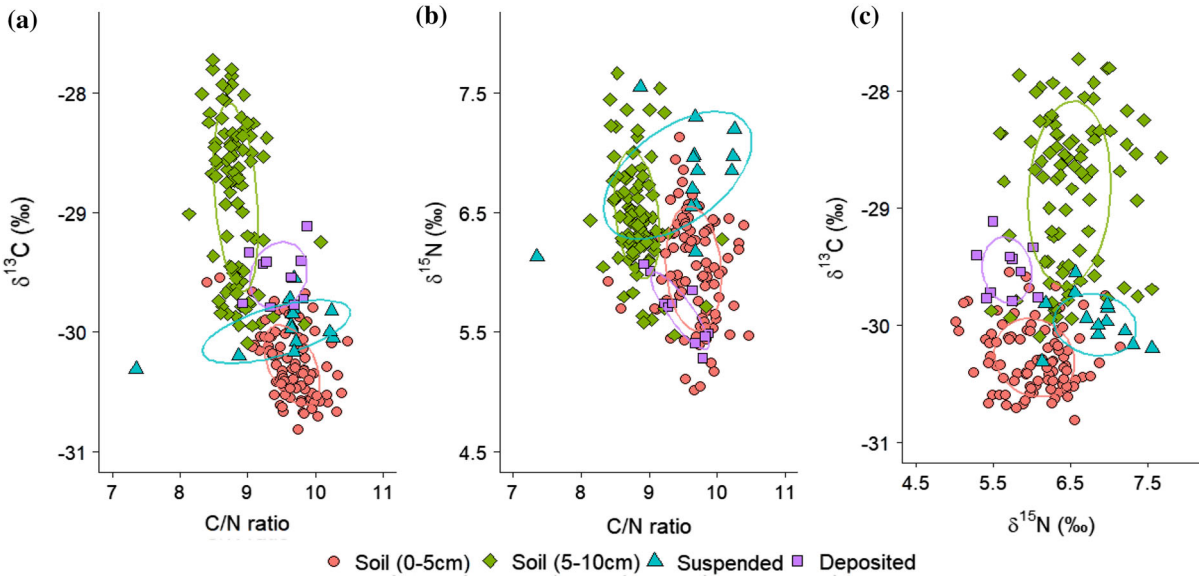

Fig. 6 Biplots of **a** δ^{13}C vs C/N ratio, **b** δ^{15}N vs C/N ratio and **c** δ^{13}C vs δ^{15}N for potential source soils and target sediment types. The ellipse represents 50% of the data points

Table 1 Proportional contribution of surface vs subsurface soil in the edge-of -field sediment samples for different MixSIAR mixing model fits

Sediment type	Informative prior	Tracer discrimination factor adjustment	Predicted source contribution Mean (95% CI)		Model fit criteria				
			0–5 cm soil layer	5–10 cm soil layer	LOO	SE (LOO)	dLOO	SE (dLOO)	Weight
Suspended	No	No	0.63 (0.41–0.85)	0.37 (0.14–0.58)	66.0	4.3	19.6	4.8	0
	Yes	No	0.74 (0.45–1)	0.26 (0–0.54)	68.8	4.0	22.4	5.4	0
	No	Yes	0.93 (0.81–0.99)	0.07 (0–0.18)	47.7	7.3	1.3	1.1	0.343
	Yes	Yes	0.99 (0.94–1)	0.01 (0–0.05)	46.4	6.6	0	–	0.657
Deposited	No	No	0.56 (0.27–0.88)	0.44 (0.11–0.73)	47.5	3.4	6.7	2.0	0.027
	Yes	No	0.80 (0.35–1)	20 (0–64)	45.8	3.5	5.0	1.6	0.064
	No	Yes	0.87 (0.56–0.99)	0.12 (0–0.43)	40.8	3.8	0	–	0.78
	Yes	Yes	0.99 (0.91–1)	0.01 (0–0.08)	44.4	3.5	3.6	1.5	0.129

dLOO is the difference in leave-one-out cross-validation (LOO) between each model and the model with lowest LOO. The "informative + discriminative" model had the lowest LOO and received 66% of the Akaike weight, indicating a 66% probability that it is the best mixing model for the target sediment samples collected at the edge-of-field flume

However, the isotopic abundance of ^{13}C and ^{15}N in grass leaves and roots (Fig. 2) were within the reported range for C_3 non-nitrogen fixing plants (Craine et al. 2009; Hobbie and Hogberg 2012). The $\delta^{15}N$ value offset (0.7 ± 1.5‰) between grass and roots (5–10 cm soil layer) suggested that mycorrhizal colonisation has not directly significantly influenced the grass N capture (Craine et al. 2009). The $\Delta^{15}N$ values ($\delta^{15}N_{grass} - \delta^{15}N_{soil\ (0–10\ cm)}$) were negative (− 2.6 ± 1.5‰) which further suggests that N uptake by the plant may have responded mainly to mineral fertilizer rather than the cycling of organic nitrogen (Kahmen et al. 2008; Robinson 2001). Overall, the $\delta^{13}C$ and $\delta^{15}N$ values of soil reflected contributions from very dense root systems and other-soil-related processes (e.g. SOM decomposition) within the soil which are integrated over time.

The ^{13}C and ^{15}N enrichment with soil depth is the function of the signature of organic inputs from above- and belowground sources and loss of light isotopes due to organic matter decomposition processes. In this undisturbed permanent grassland, soil %TC and %TN decreased in content by 34 ± 13% and 28 ± 9% between the 0–5 cm soil and the 5–10 cm soil layers, while the $\delta^{13}C$ and $\delta^{15}N$ increased by 1.4 ± 0.7‰ and 0.4 ± 0.4‰, respectively. These findings are consistent with kinetic fractionation of ^{13}C; i.e., the Rayleigh distillation model and physical soil mixing processes that can result in increases of up to 2‰ and 1.5‰ in $\delta^{13}C$ values, respectively (Wynn et al. 2006). With increasing depth, microbially processed organic matter as well as necromass accumulate, soil C/N ratios tend to decline (Table S1) and $\delta^{13}C$ and $\delta^{15}N$ values often increase (Boström et al. 2007; Ehleringer et al. 2000). A linear relationship between the C content and its ^{13}C signature (Fig S3a) further suggests that physical mixing (i.e., old soil organic carbon with grass leaves and roots due to livestock trafficking and other bioturbation processes) could be the dominant process that enriches ^{13}C in the soil profile (Diochon and Kellman 2008; Wynn et al. 2006). The β value, (a proxy for the soil organic carbon turnover associated with decomposition and physical mixing; Acton et al. 2013) (Fig. S3a), is within the range of reported β values for grasslands across the world (Wang et al. 2018). A slight increase in $\delta^{15}N$ values with a decrease in inorganic N (Fig. S2 a) as well as TN in a soil profile (Fig. 3b) is consistent with the leaching of ^{15}N-depleted NO_3^- derived from nitrification (Hobbie and Ouimette 2009 and references therein) as well as addition of ^{15}N enriched microbial necromass (Dijkstra et al. 2006; Hobbie et al. 1999; Schmidt and Gleixner 2005). Although microbial necromass forms 50–80% of stable soil organic carbon (Liang et al. 2019 and references therein), its contributions to the degree of soil organic matter ^{13}C and ^{15}N enrichment with soil depth is still debatable.

Similar to the soil profile, potential mechanisms responsible for altering sediment isotopic composition are kinetic isotopic fractionation during hydrolysis (Silfer et al. 1992) and bacterial growth and preferential loss of isotopically distinct fractions (Acton et al. 2013; Boström et al. 2007; Lehmann et al. 2002; Robinson et al. 2012). The changes in δ^{13}C and δ^{15}N values between surface (0–5 cm) soils and the target sediments were greater in the deposited than the suspended sediment (Fig. 4b) although the C/N ratio was not changed. This can be attributed to coordinated degradation/removal processes for C and N by microbial-associated processing of organic matter during sediment mobilisation, transport to, and deposition at, the edge-of-field. The decrease in suspended sediment C content ($\sim$ 15%) compared to the 0–5 cm soil layer in this study fell at the low end of the magnitudes reported by Jacinthe et al. (2004) who found that up to 40% of total eroded C from grassland can potentially be decomposable. The increase in δ^{13}C is consistent with the results of other field experiments wherein sediment transport associated oxidation has been reported to lead to 1‰ ^{13}C-enrichment in runoff sediment compared to the source soils (Hu et al. 2016). It is reasonable to assume that the relative increase in lignin, cellulose and lipids content compared to carbohydrate and proteins (generally rich in ^{13}C) in the target sediment samples due to decomposition (Benner et al. 1987), can lead to a shift in the sediment isotopic signature towards a more ^{13}C poor direction. However, an insignificant C/N ratio shift between surface soil and target sediment suggests that refectory organic compounds (e.g., lignin) associated with silt and clay might not be mineralised during erosion processes due to unfavourable conditions for fungal growth and, therefore, lignin might not play a major role in the shift of isotopic signature in the target sediment types used in this study (Fig. 3).

Hydrodynamic sorting during sediment mobilisation and delivery to the edge-of-field most likely impacted less on the tracer alteration in this study due to the short sediment transport distance to the edge-of-field. However, the effectiveness of soil organic carbon protection mechanisms are weakened by the sediment transport process potentially leading to enhanced mineralisation (de Nijs and Cammeraat 2020), especially for labile carbon (Martínez-Mena et al. 2019), with estimates ranging from minor proportions up to 43% of the total carbon contained in eroded sediment (Xiao et al. 2018). Physical disturbance during sediment detachment and transport can expose mineral protected organic matter, yet, its impact on the alteration of N and its isotopic composition is far less understood compared to carbon. Soil erosion involves alternating detachment and transient deposition processes and the mixing of various pools (e.g., organic and inorganic N) at the catchment scale (Berhe and Torn 2017; Jensen et al. 2018). This implies that the isolation of the source of tracer alteration is not easy and straight forward, resulting in the need to treat erosion processes as a composite (de Nijs and Cammeraat 2020).

Interestingly, ^{15}N showed contrasting behaviour in target sediment, i.e., it increased by 0.8‰ in the suspended but decreased by 0.4‰ in the deposited sediment compared to surface soil (Table 2). Preferential degradation of protein and carbohydrates in sediment could be expected to have less effect on δ^{15}N values (Liu et al. 2020) but addition of ^{15}N-poor/rich microbial necromass and inorganic N transformation can alter the initial δ^{15}N values of source soils in target sediment samples (Bouillon et al. 2011; Lehmann et al. 2002). Therefore, the decrease in ^{15}N in deposited sediment can be explained by the preferential loss of ^{15}N rich less stable soluble nitrogenous compounds (e.g., protein, amino acids) or the addition of compounds depleted in ^{15}N originating from microbial cell lysis (Pörtl et al. 2007) facilitated by variable wetting and drying cycles, since the runoff from the field scale study catchment is intermittent, rather than continuous. Drying and wetting of sediment can change diffusion and both the physical and chemical properties of the sediment–water interface (e.g., pH) leading to release of adsorbed C (i.e., labile) and N (i.e., NH_4^+ and NO_3^-) from the sediment (Appel 1998; Borken and Matzner 2009; Shumilova et al. 2019) which could be responsible for decreasing $\sim$ 50% of the C and N content in the deposited sediments compared with surface soil (Fig. 3a, b). Related to these observations, Gomez et al. (2012) reported a loss of about 70% of sediment total organic matter and almost 100% of the NH_4^+-N content during natural desiccation of sediment. It should be noted that N mineralisation and NH_4^+sorption/desorption processes have little ($\sim \pm$ 1‰) to no isotope fractionation (Nikolenko et al. 2018). Nevertheless, the decline in δ^{15}N values in sediment has been reported in the literature (Lehmann et al. 2002) and attributed to

Table 2 Summary of $\delta^{13}C$ and $\delta^{15}N$ alteration during sediment transport and post-deposition in the literature and in this study

References	Land use	Scale	Soil type	Sediment type (fraction in μm)	Tracer	Source to sediment isotope alteration (‰)	Major processes
Bellanger et al. (2004)	Bare field	Field (30 m^2)	Ultisols	Runoff (< 50)	$\delta^{13}C$	− 1.4	NA
					$\delta^{15}N$	− 1.2	
	Coffee field	Field			$\delta^{13}C$	+ 0.4	
					$\delta^{15}N$	+ 0.5	
Hu et al. (2016)	Arable	Field	Luvisol	Runoff	$\delta^{13}C$	+ 1	1. Organic C mineralisation 2. Particle fining
This study	Permanent pasture	Field (6.7 ha)	Cambisol	Suspended (< 106)	$\delta^{13}C$	+ 0.3	3. Labile C leaching
				Deposited (< 106)	$\delta^{13}C$	+ 0.7	4. Organic C mineralisation 5. Addition/removal of microbial necromass
				Suspended (< 106)	$\delta^{15}N$	+ 0. 8	1. N leaching
				Deposited (< 106)	$\delta^{15}N$	− 0. 4	2. Organic N mineralisation 3. Adsorption/desorption of inorganic N 4. Addition/removal of microbial necromass

additions of ^{15}N organic matter from bacterial and/or algal growth sustained on ^{15}N-depleted nitrogenous compounds; i.e. NH_4^+ and N_2 from the atmosphere. Additionally, photo-heterotrophic interaction among the diverse biofilm community colonised in the bed gravel deployed in the sediment trap may promote utilisation of sediment organic carbon and nitrogen under the wet-dry conditions (Fabian et al. 2018), whereas it adds organic matter to the sediment concomitantly.

The offset of $\delta^{13}C$ and $\delta^{15}N$ values between the two target sediment types showed significant enrichment and depletion for ^{13}C (0.5‰) and ^{15}N (1.2‰), respectively. Significant differences between the tracer signatures of the two target sediment types (Fig. 4) and β values (Fig. 5) suggested that the assumption of conservative behaviour of these tracers to edge-of-field is questionable. In natural settings beyond the NWFP experimental site, sediment mobilised from key sources including eroding agricultural fields will be temporarily stored in multiple landscape locations where drying and rewetting will occur, including, amongst others, edge-of-field hedges, buffer strips and ditches. This will clearly increase the risk of alteration of original $\delta^{13}C$ and $\delta^{15}N$ signatures. The long-term alteration of tracer signatures in sediment could be larger than the observed magnitude in this study. Here, lab-based incubation experiments could be used to help evaluate environmental factors (e.g., temperature, moisture) associated with the transformation of sediment carbon and nitrogen isotopic composition and to help develop better understanding of the behaviour of widely used tracers across the sediment continuum within a catchment system as a whole.

Influence of tracer modification on sediment source estimation

Sediment source apportionment using un-mixing models assumes that tracers remain conservative during erosion processes. Therefore, the effects of

any tracer alteration need to be explicit in sediment source apportionment procedures. Published studies have reported $\delta^{13}C$ and $\delta^{15}N$ transformation during erosion processes (Table 2) and our results also suggested that the isotope values of target sediment at an outlet (i.e., edge-of-field) sampling location cannot necessarily be compared directly to the isotopic composition of potential sources. In our study herein, sediment sample $\delta^{13}C$ and $\delta^{15}N$ values were found to lie within the observed ranges of $\delta^{13}C$ (− 30.8‰ to − 27.7‰) and $\delta^{15}N$ (5.0–7.6‰) of the source soil samples (Fig. 3c, d). Additionally, the sediment mean $\delta^{13}C$ values were also within the range of the source soil mean $\delta^{13}C$ values, but the mean $\delta^{15}N$ values of the two sediment types were outside of the range of the source soil mean $\delta^{15}N$ values. On this basis, $\delta^{15}N$ would be removed from the tracer set based on the conventional range or bracket test for screening out non-conservative tracers. The range test incorrectly identified $\delta^{13}C$ values as a conservative tracer due to a lack of sensitivity. Using the same conventional test, $\delta^{15}N$ values was correctly identified as a non-conservative tracer but, importantly, the test could not elucidate tracer transformation mechanisms due to lack of specificity.

The temporal order of mixing of sediment sources and tracer transformation differs with the spatial distribution of sediment sources, catchment size, tracer characteristics, residence times and depositional environment (Bellanger et al. 2004; Fox and Martin 2015; Hu et al. 2016). Conceptually, for spatially proximal sources, tracer (i.e., non-conservative behaviour) alteration follows mixing, while for spatially distant sources, mixing follows tracer alteration. In reality, tracer transformation patterns are highly complex at the catchment scale. Particle size selectivity during erosion and transport processes can alter the conservative behaviour of tracers. The impact of hydrodynamic sorting of sediment on the conservative behaviour of tracer values can be minimised by sieving the source soil based on the particle size distribution of the target sediments (Collins et al. 2020; Laceby et al. 2017; Upadhayay et al. 2020) but the impacts of different detachment and mobilisation processes on organic tracer alteration merit future research. Additionally, quantification and understanding of tracer alteration patterns due to complex biogeochemical transformation at the catchment scale is a prominent research gap to close in the future. Currently, the conventional range or bracket test is applied to identify non-conservative behaviour of tracers but this black-box approach can greatly reduce the number of tracers used in sediment source apportionment by not taking more explicit account of biogeochemical mechanisms controlling the source discrimination capability of tracers as well as the precision and accuracy of the estimated source contributions to target sediment samples (Martinez-Carreras et al. 2008). Clearly, the conventional black-box approach risks being problematic especially in complex catchment systems involving large source numbers and/or highly variable tracer concentrations.

Bayesian tracer un-mixing model formulation, such as incorporation of informative priors (Upadhayay et al. 2020), and adjustment of the tracer discrimination factor, can significantly influence the predicted sediment source contributions. In our new study herein, the un-mixing model which accounts for the "informative prior" and "discrimination factor" had the lowest LOO and received 66% of the Akaike weight, indicating a 66% probability that it is the best model for suspended sediment source apportionment,. In comparison, the "informative prior + adjusted discrimination factor" model was the best formulation (78% probability) for deposited sediment (Table 1). The changes in predicted sediment source proportions due to incorporation of the isotope alteration factor in the un-mixing model formulation (Table 1) supported our hypothesis that incorporation of a tracer alteration factor is important to estimate the true contributions of eroding soil to the target sediment sampled at the edge-of-field flume. This research shows, for the first time, that the accuracy of the source contributions would differ even for the same target sediment types purely due to the biogeochemical transformation of tracers if the tracer alteration factor is neglected during un-mixing model formulation.

As the uncertainties around the source contribution estimates can increase due to non-conservative tracer behaviour, it is prudent to consider the tracer alteration factor in the un-mixing model to avoid the likelihood of erroneous interpretation of un-mixing analysis. This study showed that the mean uncertainty range of source contributions decreased with inclusion of the tracer alteration factor in the un-mixing model (Table 1, Fig. S4, S5). The extent of variability in the δ value (for whatever element of interest) alteration during sediment transport and post-

deposition must be estimated and its importance for robust estimation of sediment source contributions must be acknowledged explicitly. Importantly, an assumption of no alteration of isotopic tracers during erosion processes should not be blindly accepted since the application of sophisticated data analyses (for source discrimination and apportionment in this case) cannot overcome underlying flawed assumptions (Glibert et al. 2019). In fact, sediment source contributions can be either over- or under-estimated without accounting explicitly for the tracer alteration factor during un-mixing model formulation (Sherriff et al. 2015). Where tracer alteration is not accounted for explicitly and predicted source proportions are less robust, the cost-effectiveness of source-specific mitigation measures targeted using sediment source fingerprinting evidence is likely to be hampered. This, in turn, is likely to lead to a failure in achieving environmental objectives at the catchment scale despite increased investment in sediment management at source.

Overall, considerable progress has been made in assessing the potential impact of various processes on soil C and N stable isotopic composition, but the interpretation of these processes in terms of sediment δ^{13}C and δ^{15}N values hinges on a thorough insight into the underlying biogeochemical processes in the soil to sediment continuum and how they scale. It remains challenging to distinguish isotope fractionation due to preferential degradation of specific organic matter fractions by microbial-mediated processes when bulk isotopes are altered during sediment transport and deposition; i.e., early diagenesis (Liu et al. 2020). Our new study showed that TN transformations in sediment are more complex, when compared to C, with both biotic and abiotic process affecting the sediment δ^{15}N values (Baisden et al. 2002; Ford and Fox 2015; Jensen et al. 2018; Sánchez-Carrillo and Álvarez-Cobelas 2018; Silfer et al. 1992). We therefore strongly advocate that including bulk δ^{15}N as a tracer for sediment source apportionment requires very careful consideration despite its power to discriminate surface (agricultural top soils) vs subsurface (e.g., gullies) sediment sources in catchment systems (Mahoney et al. 2019 and references therein). This implies a need to determine catchment-specific discrimination factors for ^{13}C and ^{15}N experimentally and this is likely to be beyond the resources of many studies. Despite this resource challenge, sediment source tracing studies need to pay greater attention to exploring the conservative behaviour of organic tracers at intermediate locations as an additional procedural step in tracer shortlisting for conventional catchment scale applications which continue to expand in numbers globally (Collins et al. 2020).

Conclusions

Stable isotope measurements are inexpensive and highly accessible these days and, on this basis, have been increasingly used for sediment source apportionment purposes. This study demonstrated the alteration of the ^{13}C and ^{15}N isotope composition of source soils during sediment redistribution to edge-of-field. The variation in isotope alteration is likely to reflect decomposition of organic matter during sediment transport and deposition as well as the mixing of multiple organic matter pools. As sediment deposition exhibited a contrasting effect on C and N (deposited sediment enriched in ^{13}C but depleted in ^{15}N compared to suspended sediment samples), the widely assumed conservative behaviour of their isotopic signatures is questionable. Therefore, sediment fingerprinting procedures require explicit incorporation of alteration to ^{13}C and ^{15}N isotope composition during sediment transport and deposition in tracer unmixing models for robust source apportionment. In particular, this study highlights the unexpected behaviour of ^{15}N composition across the source (soil) to sediment continuum at edge-of-field scale. A very careful scrutiny of conservative behaviour of δ^{15}N values at smaller scales, based on our findings and existing knowledge of N biogeochemistry, is therefore recommended. We do acknowledge that it will be difficult to measure the tracer alteration factor in every catchment given the resource needs of undertaking work at intermediate scales along the sediment delivery cascade. A concerted collaborative effort to assess evidence for transformation in isotopic signatures at the edge-of-field in agricultural landscapes with different land use and climate needs to be undertaken to expand the work reported herein and to provide more strategic evidence on the risks of isotopic fractionation of organic tracers during sediment transport, deposition and re-distribution. More widely, this work points to the need for more edge-of-field scale testing of the conservative behaviour of

many more tracer types currently exploited at catchment scale in sediment source fingerprinting studies since this remains a strategic research need.

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Data availability The data that support the findings of this study are available from the corresponding author upon request.

Declarations

Conflict of interest The authors declare that there are no known competing financial or personal interests that can influence the data and interpretation of this paper.

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