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REGULAR ARTICLE

Correspondence between $\delta^{13}C$ and $\delta^{15}N$ in soils suggests coordinated fractionation processes for soil C and N

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Abstract

Background and aims Although a number of different factors influence C and N isotopic fractionation of organic matter, the $\delta^{13}C$ and $\delta^{15}N$ values of soil organic matter both tend to increase with soil depth, following similar trajectories. This similarity has not been investigated at the global scale. As microbial decomposition increases organic matter $\delta^{13}C$ and $\delta^{15}N$ values, soil isotopic values are hypothesized to generally increase with depth across local and global scales.

Methods Soil $\delta^{13}C$ and $\delta^{15}N$ values for 16 soil depth-profile sites were used for local-scale investigation, and 5447 global single-depth sites were used for global-scale investigation of the correspondence between $\delta^{13}C$ and $\delta^{15}N$. Correlative and boosted regression tree analyses were used to determine the main drivers of the variance in soil $\delta^{15}N$ globally and also the environmental association of variability in the correlation with depth between $\delta^{13}C$ and $\delta^{15}N$ at a number of sites.

Results Strong positive correlations between $\delta^{13}C$ and $\delta^{15}N$ values through soil profiles were found at a number of sites and were found to be independent of vegetation type. Globally, soil $\delta^{13}C$ and $\delta^{15}N$ values were also found to be significantly positively correlated across a wide range of climates and biomes.

Conclusion The global correspondences between $\delta^{13}C$ and $\delta^{15}N$ values may suggest a mechanistic link between $\delta^{13}C$ and $\delta^{15}N$ through the process of SOM decomposition and microbial processing and highlight the importance of soil-related processes in determining isotopic signals in soils. The variability in these soil processes should be considered when interpreting soil isotopic values of $\delta^{13}C$ and $\delta^{15}N$ as indicators of ecosystem sources of soil C and N and inferring vegetation inputs.

Keywords $\delta^{15}N \cdot \delta^{13}C \cdot$ Decomposition · Microbial · Soil profiles · Soil organic matter

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Introduction

Soil $\delta^{15}N$ values tend to decrease with increasing mean annual precipitation (MAP) and decreasing mean annual temperature (MAT) across a broad range of climate and ecosystem types (Amundson et al. 2003). To some extent, this variation in soil $\delta^{15}N$ values is associated with vegetation inputs, given that foliar $\delta^{15}N$ values range over 35‰ across plants globally (Craine et al. 2009). Soil $\delta^{15}N$ values, however, increase with decreasing soil organic C as global soil organic C

concentrations also decline with increasing MAT and decreasing MAP (Craine et al. 2015b). As a consequence, the dependence of soil $\delta^{15}N$ on MAP and MAT has been ascribed to this association of soil C with environmental variables and the consequences of these for microbial transformation of both C and N. Furthermore, soils with greater clay concentrations often have higher soil $\delta^{15}N$ values. The dependence of soil $\delta^{15}N$ on soil C and clay is through fractionation associated with decomposition of soil organic matter that might at least partially be due to better water retention by clay, further linking it with environmental variables (SOM; Craine et al. 2015b).

Like soil $\delta^{15}N$, global patterns of soil $\delta^{13}C$ values are correlated with MAP and MAT (Lu et al. 2004), but also with soil texture (Sollins et al. 2009). The largest influence on soil $\delta^{13}C$ values, however, is the $\delta^{13}C$ value of the input of C to the soil organic carbon (SOC) pool, which is either directly or indirectly derived from primary productivity (Kuzyakov and Domanski 2000). As a consequence, soil $\delta^{13}C$ has been used as a proxy for historical vegetation shifts in the distribution of C_3 and C_4 vegetation (Swap et al. 2004; Gillson et al. 2004; Kuzyakov et al. 2006; Gillson 2015). Despite these clear geographic differences, changes in soil $\delta^{13}C$ with depth do not necessarily reflect historic changes in the relative inputs of C_3 and C_4 vegetation. Turnover processes during soil development also contribute to changes in soil $\delta^{13}C$ (Cerling 1984; Balesdent et al. 1993; Qiao et al. 2014) with more decomposed SOC having higher $\delta^{13}C$ values (Boström et al. 2007). Thus both soil $\delta^{15}N$ and $\delta^{13}C$ values are, at least partially, determined by soil processes (i.e. decomposition and mineralization via microbial processing of OM), which may link the patterns of fractionation of these isotopes in the soil. If soil N and C isotope patterns are at least partially linked through common soil processes (i.e. decomposition and mineralization), then we may expect coordinated changes in $\delta^{15}N$ and $\delta^{13}C$ values with depth through a soil profile.

The $\delta^{13}C$ values of SOM through soil profiles commonly increase by 1–3‰ as depth increases below 0.2 m relative to that of the surface litter layer (Chen et al. 2005; Boström et al. 2007). The enrichment of ^{13}C with depth has been shown to occur in tropical, temperate and boreal systems (Hobbie and Ouimette 2009). Although atmospheric $\delta^{13}CO_2$ has declined by 1.5‰ over the past 100 years, this has been shown to contribute only marginally to the enrichment of soil $\delta^{13}C$ with depth (Ehleringer et al. 2000; Esmeijer-Liu et al. 2012). At least four hypotheses have been proposed for C isotope fractionation through soil profiles. Firstly, kinetic discrimination against ^{13}C during respiration may result from microorganisms preferentially respiring CO_2 that is ^{13}C–depleted relative to the substrate, resulting in ^{13}C enrichment of the remaining SOC (Ågren et al. 1996). Although some studies show large ^{13}C depletion of the CO_2 formed (e.g. Fernandez et al. 2003), others show no or only minor isotopic fractionation (e.g. Ekblad and Högberg 2000). Secondly, microorganisms are ^{13}C–enriched by 2 to 4‰ compared to plant material (Hobbie et al. 1999) and thus influence SOM, resulting in decreasing C:N ratios with soil depth (Wallander et al. 2003), and compound-specific shifts in soil organic matter to higher $\delta^{13}C$ values in products of microbial origin (Huang et al. 1996; Ehleringer et al. 2000). Thirdly, variable mobility (e.g. fulvic acids; Heil et al. 2000) and sorption of isotopes of dissolved organic C on soil particulates (especially clay) may contribute to soil $\delta^{13}C$ profiles (Craine et al. 2015b), although some authors have questioned the significance of these mechanism (Boström et al. 2007). Finally, although preferential utilization of ^{13}C–depeleted compounds has been suggested (Boström et al. 2007), the more recalcitrant C fractions of plant biomass (e.g. lignin, lipids and cellulose) that accumulate at depth (Rovira and Vallejo 2002) are ^{13}C–depleted relative to the whole plant (Wilson and Grinsted 1977), and thus cannot contribute to increased ^{13}C–enrichment with depth (Wynn et al. 2006). Apart from this, some, or all, of these processes may thus contribute to determining soil $\delta^{13}C$ values to variable extents in different ecological contexts.

As with $\delta^{13}C$, $\delta^{15}N$ values usually increases with soil depth, although occasionally maximum $\delta^{15}N$ is evident at an intermediate depth possibly as a result of increased volatilization in this soil zone (Hobbie and Ouimette 2009) followed by a subsequent decline at greater depths. The degree of enrichment that $\delta^{15}N$ undergoes through a soil profile can have a much broader range than $\delta^{13}C$. In arid and semi-arid systems where soil pH is high, surface $\delta^{15}N$ values can be elevated by as much as 7‰ relative to deeper soils (Pataki et al. 2008). There are six potentially important mechanisms that influence $\delta^{15}N$ values within soil profiles. Firstly, depletion of ^{15}N by mycorrhizal fungi and transfer of that ^{15}N–depleted N to plants (Hobbie and Ouimette 2009) results in the accumulation of ^{15}N–enriched N derived from mycorrhizal fungi (Hogberg 1997; Hobbie and Ouimette

2009). Secondly, depletion of ^{15}N through enzymatic hydrolysis (Silfer et al. 1992), ammonification, nitrification, or denitrification and the associated fractionation during gaseous loss of ^{15}N–depleted N-containing gas or leaching loss of ^{15}N–depleted NO_3^- and the preferential utilization of ^{14}N by plants, drives soil $\delta^{15}N$ values up (Handley and Raven 1992; Austin and Vitousek 1998). Thirdly, mixing of soil N among different soil layers through bioturbation (Gabet et al. 2003) and trophic fractionation (i.e. faunal processes; Ponsard and Arditi 2000) could alter soil $\delta^{15}N$ profiles. Fourthly, soil texture (i.e. clay) may moderate ^{14}N gaseous loss pathways and/or the differential retention of ^{15}N–enriched SOM (Craine et al. 2015b). Fifthly, preferential microbial utilization of ^{14}N compounds could contribute to accumulation of ^{15}N–enriched compounds deeper in the soil (Boström et al. 2007). Finally, N deposition has been shown to decrease $\delta^{15}N$ values of soils because deposited N is typically depleted in ^{15}N, although this effect is relatively small (Liu et al. 2017; Esmeijer-Liu et al. 2012).

SOM decomposition is thus common to both $\delta^{13}C$ and $\delta^{15}N$ fractionation in soil. At the global scale, climate influences decomposition through both temperature and moisture (Gholz et al. 2000). The SOM composition and nutrient concentrations (especially N) also strongly affect decomposition (Parton et al. 2007). Although most SOM is derived from plants, only a small fraction of the yearly litter and root inputs are incorporated into the stable organic matter pool, most of it after repeated processing by soil microbes (Lerch et al. 2011). SOM transport through soils is generally downward through advection and soil development, and thus the effects of decomposition on soil $\delta^{13}C$ and $\delta^{15}N$ values are more noticeable deeper in the soil profile. With increasing depth, SOM is more highly processed by microbes (Trumbore 2009) with lower C:N ratios (Marin-Spiotta et al. 2014) and increasing $\delta^{13}C$ and $\delta^{15}N$ values (Heil et al. 2000; Billings and Richter 2006). This change in $\delta^{13}C$ and $\delta^{15}N$ is often modelled as "Rayleigh distillation", which predicts soil $\delta^{13}C$ and/or $\delta^{15}N$ values based on the soil [C]/[N] in order to account for microbial isotopic enrichment of SOM during decomposition (Mariotti et al. 1981; Baisden et al. 2002; Wynn et al. 2005; Fischer et al. 2008). This enrichment results from the kinetic fractionation during microbial processing (Dijkstra et al. 2006) with subsequent stabilization of products by fine mineral particles in soils (Wynn et al. 2006). This Rayleigh distillation model, however, only pertains to closed systems, potentially ignoring continuous inputs (Fry 2006) that do occur in soils.

Although a number of different factors influence the isotopic fractionation of C and N isotopes, $\delta^{13}C$ and $\delta^{15}N$ values both increase with soil depth and commonly follow similar trajectories. We hypothesized that changes in soil $\delta^{13}C$ and $\delta^{15}N$ values are coordinated, possibly through decomposition-related processes, and that the scale of decomposition related changes in $\delta^{13}C$ may confound interpretation of soil $\delta^{13}C$ as indicative of prior C_3 or C_4 vegetation. Although the initial isotope composition of the organic matter is indisputably important, subsequent soil fractionation may result in $\delta^{13}C$ and $\delta^{15}N$ following similar trajectories in space and time. We therefore predict that changes in $\delta^{13}C$ and $\delta^{15}N$ values correspond with each other both locally through soil depths at a site and globally due to the extent of decomposition and other soil processing. In order to test these predictions, we compiled data from soil depth profiles from sixteen widely distributed sites and also conducted an analysis of global $\delta^{13}C$ and $\delta^{15}N$ variations in surface soils in order to determine relationships between soil isotopes with climate and soil properties.

Methods

Data sources

Data for soil $\delta^{13}C$ and $\delta^{15}N$ values were acquired from literature and by contacting individual researchers known to have collected soil isotope data in the past. Soil depth-profile data included $\delta^{13}C$ and $\delta^{15}N$ for mineral soils at multiple depths at a single site. A second independent dataset included both mineral soil $\delta^{13}C$ and $\delta^{15}N$ values at a single depth at a number of geographic locations. For each site, climate data were taken from the original source and also, using the geographic coordinates, from the 50-year climatic means (1950–2000) obtained from www.worldclim.org (accessed Sep 2014) at ca. 1 km^2 resolution. Variables included were mean annual temperature (MAT), mean annual precipitation (MAP) and 17 other derived climatic variables (Supp. Table 1).

Potential evaporation (PET) was obtained from Trabucco and Zomer (CGIAR Consortium for Spatial Information, 2009. Accessed: http://www.csi.cgiar.org)

in which PET was modelled using the method of Hargreaves et al. (1985) with data from Hijmans et al. (2015) and verified by comparison with separate data sources. From the climatic data, the monthly PET was subtracted from monthly precipitation to obtain an index of water availability (P–PET) and averaged to obtain the annual average. Normalized difference vegetation index (NDVI) data was obtained from eMODIS TERRA (US Geological Survey Earth Resources Observation and Science Center), which is corrected for molecular scattering, ozone absorption and aerosols. The NDVI data spanned between 19/12/2009 to 18/12/2012 and was at a spatial resolution of 250 m. The data was averaged to obtain monthly and annual average values using the "raster" (Hijmans et al. 2015) and "RCurl" (Lang and Lang 2016) packages in R.

The fraction of the vegetation with C_4 photosynthesis was obtained from Berry et al. (2009) in which the percentage of vegetation within each one degree by one degree grid cell of the land surface which possesses the C_4 photosynthetic pathway was determined using 'C_4 climate map' from Collatz et al. (1998), 'Continuous fields of vegetation characteristics' from DeFries et al. (2000) as well as 'Cropland fraction distribution' from Ramankutty and Foley (1998). Where necessary, the component fields were re-sampled to bring them to a common one degree by one-degree spatial resolution.

The "SoilGrids1km" global soil data product (Hengl et al. 2014), which has mean soil information at 1 km resolution for six soil depths to 1.5 m deep (ISRIC – World Soil Information 2013), was averaged across the full depth by depth weighted-averaging. The environmental data included in the models is shown in Supp. Table 1.

Soil depth data

Data for 9 sites, which include 4 sites in Africa (Paulshoek, Pretoriuskop, Satara, Hluhluwe) and sites in Alaska, France, Sweden, New South Wales and the Amazon in Brazil were compiled from a number of publications (Table 1). These made up a total of 16 different sampling groups within distinct vegetation types and included data for 79 soil profiles at multiple depths. As most sites were represented by repeated sampling of different vegetation types, the average value of the N and C isotopes at each depth for each vegetation type, as well as the confidence intervals, were determined for each site. As the ranges of $\delta^{13}C$ and $\delta^{15}N$ values through soil profiles were different in magnitude, the actual measured values were scaled using the "scale" function in R (z-transformation). This allowed both the N and C isotope patterns through the soil profiles to be plotted on the same set of axes for comparison using the 'ggplot2' package (Wickham 2009) in R. A Pearson correlation test was then performed on the scaled data. This correlation was then treated as a derived variable. As one of the locations, Hluhluwe, consisted of a number of different vegetation types, each vegetation type at the site was plotted separately rather than averaging across the site.

Global analysis of surface soil

In order to determine the main global correlates of soil $\delta^{15}N$ values, the dataset from Craine et al. (2015b), which included soil and climatic data for sites around the globe, was re-analysed. Records that did not include a depth or mineral soil components were removed leaving a total of 5447 sites for the analysis. As the $\delta^{13}C$ and $\delta^{15}N$ values were from single depths only, the dataset was used to determine the global correlation of soil $\delta^{13}C$ and other variables with $\delta^{15}N$.

Boosted regression tree analyses

Boosted regression tree models were used to determine how differences in soil and environmental conditions influence the correlation between $\delta^{13}C$ and $\delta^{15}N$ values for soil depth-profiles, as well as the main drivers of $\delta^{15}N$ at the global scale. Boosted regression tree analysis is a form of non-linear modelling that uses machine learning (Elith et al. 2008). The modelling entails decision trees splitting the data into two homogenous groups, a process repeated many times (boosting) so as to improve the prediction of the response variable. Models are parameterized by adjusting their learning rates, tree complexity and bag fraction (Elith et al. 2008). We used a cross-validation procedure to identify the optimal number of trees and tree size for the model, and to guard against over-fitting (Hastie et al. 2001). Initially, the data set was randomly divided into 10 mutually exclusive subsets of equal size, 9 of which were used as a training set to create the boosted tree while the remainder was used as a test set to determine the predictive accuracy of the model. The data in the training sets were fitted using trees of different sizes (range = 2 to 10) by incrementally adding trees in sets of 50. For each combination of tree size and number of trees,

Table 1 List of sites used in determining the correlation between soil $\delta^{13}C$ and $\delta^{15}N$ values through soil profiles. Variables included are mean annual temperature (MAT), mean annual precipitation (MAP), $\delta^{15}N$, $\delta^{13}C$, the dominant vegetation at the site, the Pearson correlation coefficients between $\delta^{13}C$ and $\delta^{15}N$ through soil profiles with significance values (bold where significant, $p < 0.05$). Values for $\delta^{13}C$ and $\delta^{15}N$ are include the 5 percentiles, (means) and 95 percentiles of the soil profile data

Site	MAT (°C)	MAP (mm)	$\delta^{15}N$ (‰)	$\delta^{13}C$ (‰)	C_3/C_4 dominant	Pearson correlation	*p*-value	Reference
Alaska	−4.1	405	−1.9 (0.1) 1.1	−27.0 (−24.4) -25.3	C3	0.98	**0.003**	Pries et al. 2012
Amazon	24.1	2134	8.2 (9.8) 11.1	−27.6 (−26.7) -25.9	C3	0.95	**0.000**	Ometto et al. 2006
Kruger - Satara OC	22.3	565	3.2 (6.1) 7.4	−13.7 (−12.3) -11.6	C4	0.94	**0.000**	February and Higgins 2010
Kruger - Satara UC	22.3	565	4.1 (6.0) 7.0	−15.0 (−13.0) -12.0	C4	0.92	**0.000**	February and Higgins 2010
Kruger - Pretoriuskop UC	21.0	734	2.0 (5.3) 6.9	−20.8 (−16.6) -14.5	C4	0.87	**0.000**	February and Higgins 2010
France - Natural	9.0	1280	1.7 (3.5) 4.7	−28.4 (−27.8) -27.2	C3	0.85	**0.071**	Zeller et al. 2007
Hluhluwe - Thicket	21.2	892	5.3 (6.5) 7.6	−18.0 (−16.4) -15.0	C4	0.72	**0.000**	Grey 2011
Sweden - Plantation	5.8	617	2.5 (5.8) 7.5	−27.8 (−27.4) -26.8	C3	0.68	0.136	Boström et al. 2007
Hluhluwe - Forest	21.2	892	6.8 (7.3) 7.9	−20.0 (−17.4) -15.5	C4	0.61	**0.000**	Grey 2011
Hluhluwe - Savanna	21.2	892	5.6 (6.5) 7.2	−15.0 (−13.8) -12.3	C4	0.58	**0.000**	Grey 2011
Kruger - Pretoriuskop OC	21.0	734	2.2 (5.1) 6.4	−17.6 (−14.8) -13.3	C4	0.50	**0.000**	February and Higgins 2010
Hluhluwe - Grassland	21.2	892	7.4 (8.1) 9.0	−15.5 (−13.9) -12.7	C4	0.49	**0.001**	Grey 2011
New South Wales - Grove	17.6	259	8.9 (10.0) 10.6	−22.1 (−18.8) -13.4	C4	0.46	0.297	Macdonald et al. 2015
France - Plantation	9.0	1280	1.0 (3.2) 5.2	−27.2 (−26.9) -26.7	C3	0.29	0.641	Zeller et al. 2007
New South Wales - Inter grove	17.6	259	8.5 (9.1) 9.5	−22.8 (−18.3) -13.2	C4	0.25	0.586	Macdonald et al. 2015
Karoo - Paulshoek	18.9	118	8.6 (9.2) 9.6	−21.2 (−21.0) -20.7	C3	−0.40	**0.007**	Edmund February unpublished

the predictive accuracy of the model was determined by comparing values in the test set with those predicted by the model. This procedure was repeated 10 times so that all groups were used as cross-validation groups, and the mean predictive error calculated across all subsets for each level of complexity. The combination of tree size and tree number that produced the lowest predictive error was chosen for all subsequent analyses. Performance was evaluated by expressing the predictive deviance of 10-fold cross validation as a percentage of the null deviance.

Two different models were used, either to explain the correlation of $\delta^{13}C$ and $\delta^{15}N$ values at the local scale across soil depths (BRTlocal), or to explain the value of $\delta^{15}N$ at the global scale for a single soil depth (BRTglobal). The climatic and soil variables listed in Supp. Table 1 were used as the predictor variables. The 'select07' function (Dormann et al. 2013) in R, was used to identify collinear predictors. In cases where the predictor variables were found to be strongly collinear with each other, the variable with either the strongest correlation with the response variable, or the most biologically relevant, was retained. Following an initial run (learning rate = 0.01, tree complexity = 5, bagging fraction = 0.5), a simplification procedure was implemented (Elith et al. 2008) to eliminate variables with low influence (such as NDVI and PET). Both models were run ten times using the libraries 'gbm' (Ridgeway et al. 2013) and 'dismo' (Hijmans and van Etten 2014) packages in R. Model outputs were used to ascertain the relative influence and relationship of each predictor with the correlation between $\delta^{13}C$ and $\delta^{15}N$ at the local scale or $\delta^{15}N$ at the global scale.

To account for C_3 and C_4 vegetation input into the SOM pool, global soil $\delta^{13}C$ values were analyzed for bimodality using libraries 'diptest' (Maechler 2015) in R and cutoffs were calculated using the 'mixtools' (Benaglia et al. 2009). $\delta^{13}C$ for C_3 and C_4 were then treated as separate sets of data on which BRT modeling for global $\delta^{15}N$ values were independently reanalyzed.

Results

Isotopic variation with soil depth

For 11 out of 16 sampling groups analyzed, the variation in average soil $\delta^{13}C$ and $\delta^{15}N$ values with depth were significantly positively correlated with each other (Fig. 1, Table 1). For many of these sites, both $\delta^{13}C$ and $\delta^{15}N$ values increased with depth, with the majority of the increase occurring in the upper 10–20 cm of the profile. The range of variability for both isotopes was ca. 2–8‰ through the soil profiles and this range was independent of the average $\delta^{13}C$ and $\delta^{15}N$ signature for the sites (Table 1). Within the relatively small geographic area of the Hluhluwe Nature reserve, the significant positive correlations between $\delta^{13}C$ and $\delta^{15}N$ values were independent of vegetation types comprising forest, grassland, savanna and thicket sites. Across all of these distinct vegetation types, $\delta^{13}C$ and $\delta^{15}N$ values increased similarly with depth (Fig. 2, Table 1). For these sites the range of variability for both isotopes was also ca. 2–8‰ with the majority of the increase in $\delta^{13}C$ and $\delta^{15}N$ values occurring within the upper ca. 20 cm of the soil. Although most sites had significant positive correlations between $\delta^{13}C$ and $\delta^{15}N$, for 5 of the 16 sampling groups, changes in average soil $\delta^{13}C$ and

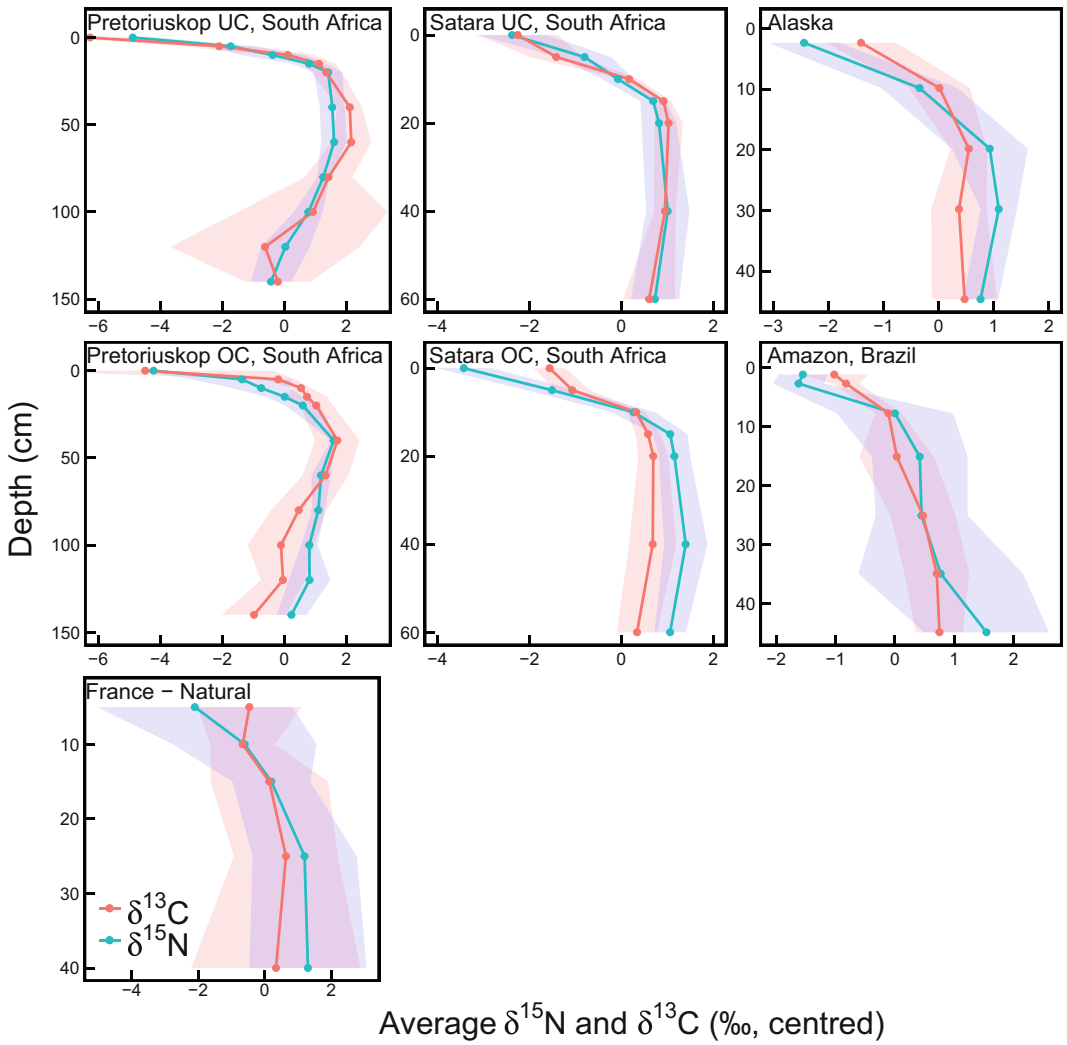

Fig. 1 Variation with soil depth of $\delta^{13}C$ and $\delta^{15}N$ values for sites in which $\delta^{13}C$ and $\delta^{15}N$ are significantly correlated with each other (Table 1). The data was averaged for each depth and the confidence interval is represented by the coloured bands. The $\delta^{13}C$ and $\delta^{15}N$ data were independently centred on 0 so as to allow comparison of the variation of these within a site and thus the range of the data corresponds to that of the original data. Sites designated OC and UC are from open-canopy and under-canopy, respectively

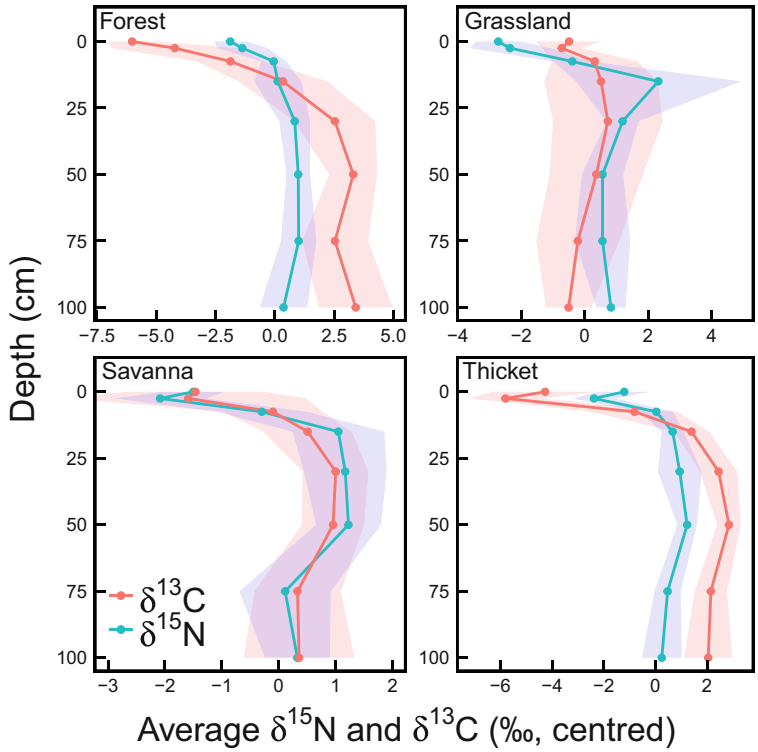

Fig. 2 Variation with soil depth of $\delta^{13}C$ and $\delta^{15}N$ values for sites in which the dominant vegetation types differ. The data was averaged for each depth and the confidence interval represented by the coloured bands. The $\delta^{13}C$ and $\delta^{15}N$ data were independently centred on 0 so as to allow comparison of the variation of these within a site and thus the range of the data corresponds to the original data

$\delta^{15}N$ values through the soil profiles were either not significantly associated or negatively correlated with each other (Fig. 3, Table 1). For these sites $\delta^{13}C$ and $\delta^{15}N$ values also increased with depth, with the exception of the Paulshoek site in which $\delta^{15}N$ initially increased before subsequently decreasing below ca. 10 cm. These sites also had a wider range of $\delta^{13}C$ and $\delta^{15}N$ values than those for which there were significant correlations between $\delta^{13}C$ and $\delta^{15}N$ (Figs. 1, and 2).

BRT analysis of the correlation between $\delta^{13}C$ and $\delta^{15}N$ values ranked CEC, mean diurnal temperature range, bulk density, MAT, clay and MAP as the top predictors (Fig. 4a), explaining 38% of the variance in the correlation between $\delta^{13}C$ and $\delta^{15}N$. Partial dependency plots, which show the effect of a variable on the response after accounting for the average effects of all other variables in the model, of the BRT analysis of the soil profile correlations between $\delta^{13}C$ and $\delta^{15}N$ values (Fig. 5), showed that this was strongest at sites with CEC < 20 cmol kg^{-1} and a mean diurnal temperature range < 13°C. Sites with bulk density above 1400 kg m^3 had strong correlation between soil $\delta^{13}C$ and $\delta^{15}N$ values. The influence of clay concentration on the correlation between $\delta^{13}C$ and $\delta^{15}N$ values was generally high. A number of sites with clay concentrations between 30 and 35%, however, had a relative low influence of clay on the correlation. These sites were arid, receiving <500 mm mean annual precipitation and had a relatively poor correlation compared to mesic sites (i.e. between 500 and 1000 mm) with a moderate influence in hydric sites (>1000 mm). The correlation between $\delta^{13}C$ and $\delta^{15}N$ values was stronger at sites with MAT >19°C (Supp. Fig. 4f).

Global geographic variation

Globally, soil $\delta^{15}N$ values of surface soils were significantly positively correlated with $\delta^{13}C$, MAT and the prevalence of C_4 photosynthetic vegetation and negatively correlated with CEC and diurnal T range (Table 2). Geospatial variation in global $\delta^{13}C$ and $\delta^{15}N$ values that were spatially averaged over 0.1° corresponded relatively well with each other at high latitudes (> 50°) where both $\delta^{13}C$ and $\delta^{15}N$ values were more negative compared to sites located nearer the equator (Fig. 5). Sites in which $\delta^{13}C$ values were relatively high (Fig. 5) were from more arid regions such as Southern Africa, Australia and North America and in which C_4 grass communities exist (Fig. 6).

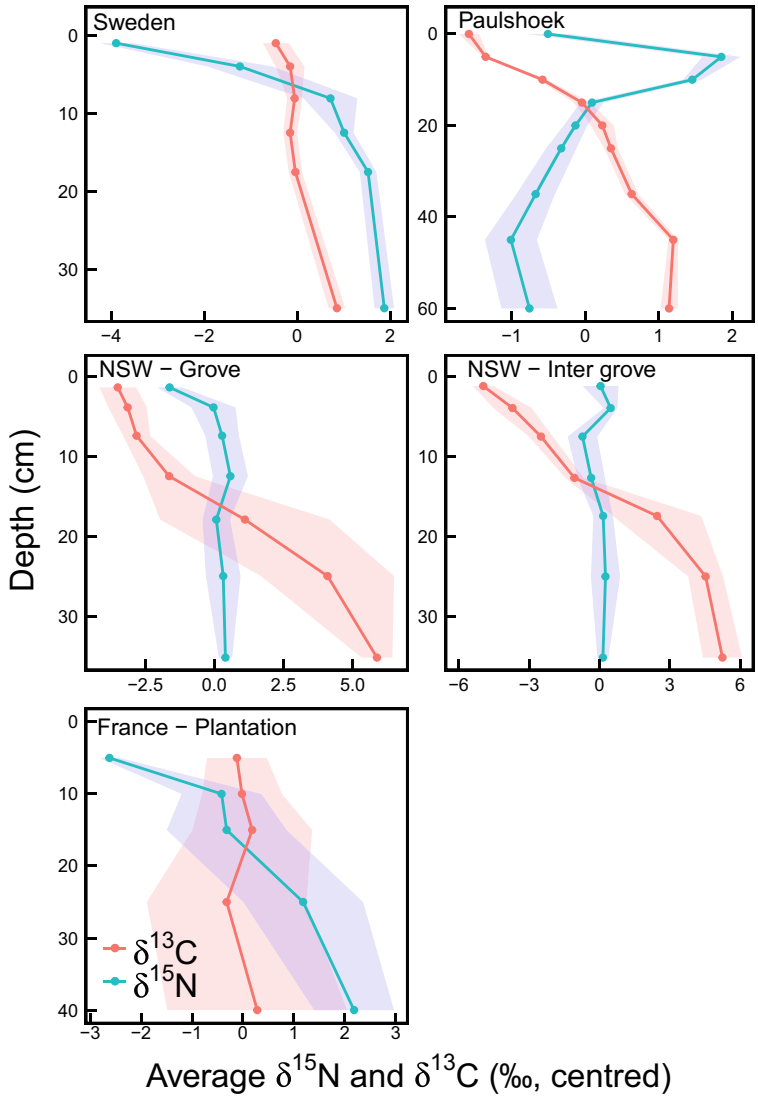

Fig. 3 Variation with soil depth of $\delta^{13}C$ and $\delta^{15}N$ values for sites in which $\delta^{13}C$ and $\delta^{15}N$ are poorly correlated with each other. The data was averaged for each depth and the confidence interval represented by the coloured bands calculated from the standard error. The $\delta^{13}C$ and $\delta^{15}N$ data were independently centred on 0 so as to allow comparison of the variation of theses within a site. The range of the data corresponds to the original data

BRT analysis of global soil $\delta^{15}N$ values (BRTglobal) ranked MAT, $\delta^{13}C$, CEC, C_4, diurnal range and MAP as the top predictors of soil $\delta^{15}N$ (Fig. 4b), which explained 62% of the variation in $\delta^{15}N$ values. The partial dependency plots for the BRTglobal (Supp. Fig. 5) showed that as MAT increased, $\delta^{15}N$ values also increased. Sites with $\delta^{13}C$ values below ca. -30‰ had low $\delta^{15}N$ values, which increased rapidly with increased $\delta^{13}C$ values up until ca. -20‰, above which changes in $\delta^{15}N$ values were relatively small. Therefore, much of the change in $\delta^{15}N$ values associated with $\delta^{13}C$ values occurred in a range of $\delta^{13}C$ values considered to be characteristic of C_3 dominated sites (Supp. Fig 2). Sites with CEC values >10 cmol kg^{-1} had relatively low soil $\delta^{15}N$ values. $\delta^{15}N$ values were also low for sites with <75% C_4 vegetation. Soil $\delta^{15}N$ values were reduced with increases in mean diurnal temperature range and generally with increased MAP (Supp. Fig. 5f).

Global $\delta^{15}N$ values predicted from the full BRTglobal model, including both C_3 and C_4 sites, were strongly correlated with observed global $\delta^{15}N$ values (Supp. Fig. 1). There was, however, a degree of under-prediction of $\delta^{15}N$ values at low observed $\delta^{15}N$ values and over-prediction at high observed $\delta^{15}N$ values. Global soil $\delta^{13}C$ values were bimodal with two ranges of $\delta^{13}C$ values having peaks at −26.36‰ and −17.58‰, indicating that there were a number of sites dominated by either predominantly C_3 or C_4 plants (Supp. Fig. 2). BRT's predicting global soil $\delta^{15}N$ based on a subset of sites that were predominantly C_3 dominated ranked

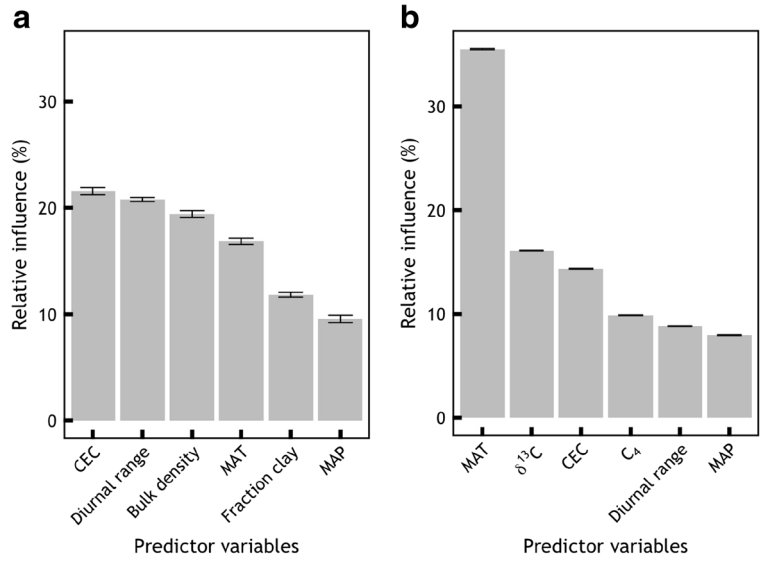

Fig. 4 Relative influence of variables in determining the correlation between global soil $\delta^{13}C$ and $\delta^{15}N$ as determined by BRT analysis (**a**) as well as the relative influence of variables in determining the global soil $\delta^{15}N$ as determined by BRT analysis (**b**). Values are the mean ± SE of 10 runs of each model. Error bars represent standard error

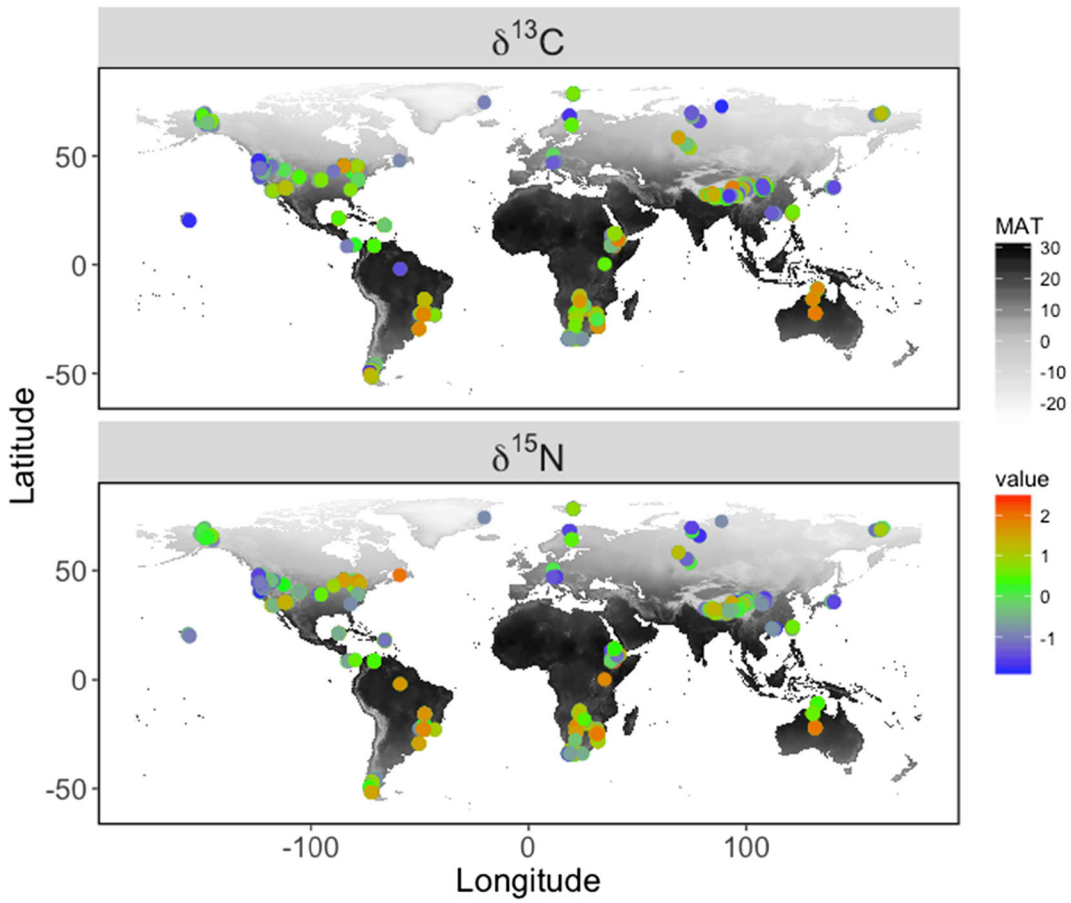

Fig. 5 The global variation in soil $\delta^{13}C$ and $\delta^{15}N$. The color of the points represents the site averages of $\delta^{13}C$ and $\delta^{15}N$ values standardized and centered to range between −1 and 1. Background fill colour represents mean annual temperature

Table 2 Bivariate ranged major axis (RMA) analysis results of top six predictors of global soil $\delta^{15}N$ with correlation coefficients (r) shown with *p*-values (bold where significant). All variables used in the prediction of global soil $\delta^{15}N$ are shown in Supp. Table 1

Predictor variables	n	r	p-value	Intercept	Slope
MAT	7461	0.48	**< 0.001**	1.13	0.21
$\delta^{13}C$	5501	0.48	**< 0.001**	14.16	0.43
CEC	7328	−0.2	**< 0.001**	7.07	−0.15
$\%C_4$	7415	0.43	**< 0.001**	2.99	0.05
Diurnal T range	7456	−0.1	**< 0.001**	5.82	−0.15
MAP	7474	−0.01	0.579	4.22	< 0.00

MAT, $\delta^{13}C$, CEC, bulk density, diurnal T range and MAP as top predictors (Supp. Table 2). The BRT developed for C_4 dominated sites ranked MAT, CEC, bulk density, MAP, diurnal range and $\delta^{13}C$ as top predictors. Although soil $\delta^{13}C$ was found to be a strong predictor of $\delta^{15}N$ for C_3 sites, it was a weak predictor in C_4 dominated sites.

Discussion

This study suggests that either common or coordinated processes contribute to fractionation of soil C and N isotopes. The link between soil $\delta^{13}C$ and $\delta^{15}N$ values may inform understanding of these processes due to this coordination of soil processes determining both C and N isotope fractionation. Our results suggest that although the initial isotope composition of the organic matter is indisputably important, subsequent fractionation via soil processes, such as decomposition and related processes, may result in correlations between $\delta^{13}C$ and $\delta^{15}N$ values in geographic space and commonly following similar trajectories with soil depth. More positive $\delta^{13}C$ and $\delta^{15}N$ values with soil depth (Fig. 1) must result from increasing fractionation or more prolonged fractionation in deeper soils relative to shallower soils.

The importance of the vegetation characteristics in determining C isotopic composition is apparent from the bimodal distribution of soil $\delta^{13}C$ values associated with C_3 (−22‰ to −32‰; Troughton 1979) and C_4 (−9.2‰ to −19.3‰; Hattersley 1982) vegetation (Fig. S2) whereas the variation in $\delta^{13}C$ within the C_3 and C_4 groupings is caused by climatic and geographical factors (Damesin et al. 1997). Likewise, global variation in soil $\delta^{15}N$ values (Fig. 5) is associated with variation in foliar $\delta^{15}N$ that varies with MAP, MAT, N availability, foliar N concentration, species composition and with the degree of N_2 fixation (Craine et al. 2009). Organic matter enters soils in a diversity of ways and this influences the initial isotopic signature of soil C and N (Eissfeller et al. 2013). The majority of SOM, however, enters the soil as plant-derived detritus, where it is utilized by soil microbes (Berg and McClaugherty 2008) and decomposer fauna (Hättenschwiler and Gasser 2005). Consequently, the isotopic values of the dominant vegetation and the variation in $\delta^{13}C$ and $\delta^{15}N$ values, both between and within species (Damesin et al. 1997; Craine et al. 2015a), strongly influence SOM isotopic composition.

Unlike for C, however, there are also strong ecosystem feedbacks between soil and vegetation N in determining ecosystem $\delta^{15}N$ values, because soil $\delta^{15}N$ also partially determines plant $\delta^{15}N$. Despite this dependence of SOM isotopic composition on that of OM and vegetation, the variations in $\delta^{13}C$ (range: −27.8 to −12.4‰) and $\delta^{15}N$ (range: −0.1 to 10.1‰) with depth in soil profiles were often strongly correlated with each other (Table 1). Likewise, geospatial variation in global $\delta^{13}C$ and $\delta^{15}N$ values also corresponded relatively well across a wide range of climates and biomes (Fig. 5). For example, C_3 and C_4 dominated sites showed similar patterns of $\delta^{13}C$ and $\delta^{15}N$ enrichment through soil profiles (Fig. 2), although the range of values was smaller with C_4 vegetation.

The correspondence between the increases of $\delta^{13}C$ and $\delta^{15}N$ values with depth is probably through processing of SOM, which is further supported by the most influential predictors in the BRT model for the correlation between $\delta^{13}C$ and $\delta^{15}N$ values through soil profiles (Fig. 4a), which themselves are related to microbial activity. Furthermore, soil $\delta^{13}C$ values were also strong determinants of $\delta^{15}N$ globally (regardless of soil and ecosystem type) while the remaining top predictors of $\delta^{13}C$ could be related to SOM decomposition (Fig. 4b). Processing of SOM is determined by characteristics of the SOM, such as the C and N composition (Fernandez et al. 2003), as well as by environmental factors including soil temperature, moisture and aeration (Gholz et al. 2000; Zhang et al. 2008). The reason for the positive correlation between MAT and both $\delta^{15}N$ and $\delta^{13}C$ values could therefore be due to microbial activity increasing with increasing temperature. Mean diurnal temperature range (e.g. Li et al. 2011), CEC and soil

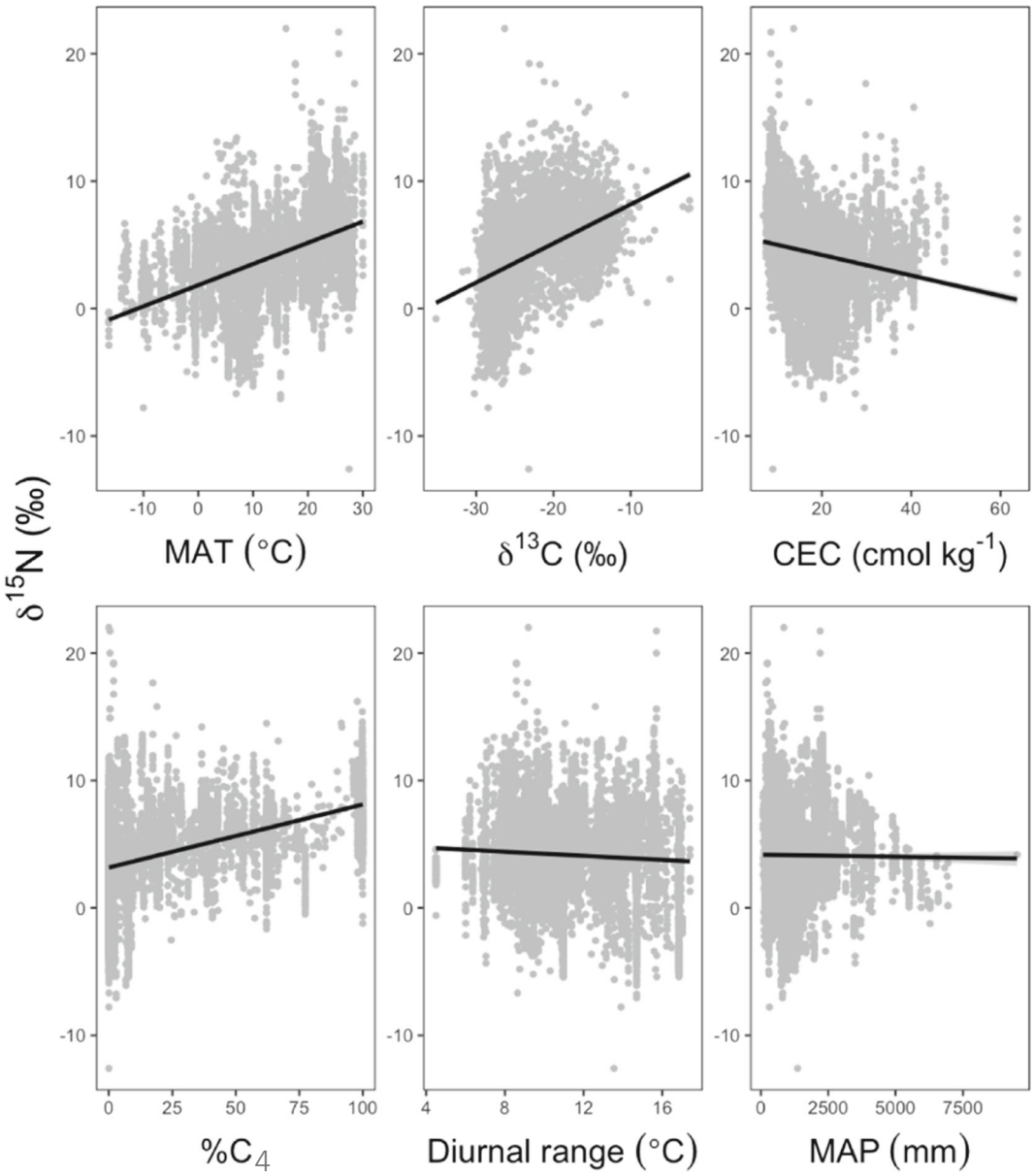

Fig. 6 Bivariate analysis of the top six predictors of global soil $\delta^{15}N$ against global soil $\delta^{15}N$. Lines indicate linear model function

fertility (Sikora 2013) may also be linked to SOM decomposition through soil microbial processes. Although favorable moisture conditions stimulate decomposer communities (Cotrufo et al. 2013), MAP was not significantly correlated with either $\delta^{13}C$ or $\delta^{15}N$ values at the global scale (Fig. 4b, Table 2). This is likely because many ecosystem properties depend on MAP obscuring clear relationships. For example, Craine et al. (2015a) related variation in global soil $\delta^{15}N$ to variation in clay concentrations. Further, there is the possibility that the limited range in MAP at the regional scale can obscure relationships between soil $\delta^{15}N$ and MAP as the increase in soil $\delta^{15}N$ with increasing MAP at the regional scale often breaks down at broader scales (Amundson et al. 2003; Austin and Vitousek 1998).

Despite strong global geographic correspondence between $\delta^{13}C$ and $\delta^{15}N$ and correspondence over soil depth (11 of 16 sites), some sites had non-significant (New South Wales, France, Sweden) or negative (Paulshoek) correlations between $\delta^{13}C$

and $\delta^{15}N$ (Fig. 3, Table 1). These sites indicate the complexity to the relationship between soil $\delta^{13}C$ and $\delta^{15}N$, and dependence on other factors. For example, the New South Wales sites had a large proportion of N_2-fixing microbes in the surface soil (Macdonald et al. 2015) resulting in $\delta^{15}N$ being close to 0‰. The non-significant Swedish and French sites were both associated with plantations (Boström et al. 2007; Zeller et al. 2007), whereas a corresponding natural site in France showed a significant relationship (Fig. 1). Paulshoek exhibited a maximum soil $\delta^{15}N$ value at intermediated depths, which is indicative of N-loss during nitrification and denitrification (Hobbie and Ouimette 2009). This is not surprising as Paulshoek is arid with high soil temperatures and sporadic rainfall (Table 1) and these conditions increase nitrification/denitrification rates (Craine et al. 2015b). Thus despite the general global relationship between $\delta^{13}C$ and $\delta^{15}N$, this correspondence does vary depending on local biotic, disturbance and environmental influences.

As a consequence of a link between soil $\delta^{13}C$ and $\delta^{15}N$, interpretation of soil $\delta^{13}C$ values as indicators of historical vegetation assemblages is complicated by the role of soil processes in determining soil $\delta^{13}C$ values, as also shown by Wynn et al. 2005. The ranges of $\delta^{13}C$ values with depth are commonly large (up to 11.0 ‰, Supp. Fig. 3) which overlaps the range of values commonly associated with vegetation change. For example, $\delta^{13}C$ values between −16 and −20‰ have been used to indicate mixed C_3 and C_4 vegetation and > −16% to indicate C_4 dominance (Gillson 2015). From our study, however, whilst the minimum $\delta^{13}C$ values of soils with C_3 and C_4 vegetation reflect the isotopic signature of the vegetation inputs, the maximum $\delta^{13}C$ values are indistinguishable. Since the maximum $\delta^{13}C$ values of soils supporting C_3 vegetation overlap with the minimum $\delta^{13}C$ values of C_4 vegetation, interpretation of intermediate $\delta^{13}C$ values (i.e. < ca. -15 ‰) as indicating historical vegetation characteristics should be approached with caution. Furthermore, in order to demonstrate that ancient $\delta^{13}C$ SOC values are indeed representative of ancient vegetation assemblages in samples of deep SOC, one must establish that the fraction of SOC remaining in the sample is very close to the original maximum concentration during soil formation and that fractionation has not been great (Wynn et al. 2006). This is because Rayleigh distillation and mixing processes vary with environmental and soil properties, with particularly strong effects associated with fine mineral particles (i.e. clay) in fine grained soils (Krull and Skjemstad 2003; Wynn et al. 2005) and should not be assumed to be constant everywhere.

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