Catena 246 (2024) 108366

Contents lists available at ScienceDirect

Catena

journal homepage: www.elsevier.com/locate/catena

Uncovering nitrogen accumulation in a large mixed land-use catchment: Implications for national-scale budget studies and environmental management

Xiangwen Fan [a], Fred Worrall [b,*], Lisa M. Baldini [c], Tim P. Burt [a]

[a] Dept. of Geography, Science Laboratories, South Road, Durham University, Durham DH1 3LE, UK
[b] Dept. of Earth Sciences, Science Laboratories, South Road, Durham University, Durham DH1 3LE, UK
[c] School of Health & Life Sciences, Teesside University, Middlesbrough, Tees Valley TS1 3BX UK

A R T I C L E I N F O

Keywords:
Total N budget
Spatial analysis
N accumulation
Land use change
C/N ratio

A B S T R A C T

Accurately quantifying the location and extent of nitrogen accumulation is crucial for mitigating its severe impacts on climate and the environment. Here we estimated a spatial total N budget and its input/output fluxes from different land uses on a 1 km^2 grid scale across the whole of a large, mixed land use catchment (Trent, UK). With a long history of water quality monitoring, the Trent catchment provides a unique and ideal test bed for developing a detailed nitrogen budget and determining where N accumulation occurs. In 2015, a significant 35 ($\pm$5) ktonnes N accumulation was found, with 31 % of the area acting as a net source and 69 % as a net sink. The spatial budget ranged from −16 ($\pm$5) to 45 ($\pm$7) tonnes N/km^2/year. Using this budget, we identified N accumulation and loss areas under diverse land uses and conducted strategic soil sampling and C/N analysis. Notably, grassland subsoil exhibited nitrogen buildup compared to arable land, spotlighting intricate land use, nitrogen, and soil dynamics. The study emphasizes the need for targeted nutrient management to prevent potential environmental repercussions linked to subsoil nitrogen accumulation, especially in grassland contexts.

1. Introduction

Human activities, including the application of nitrogen-based fertilizers and fossil fuel burning, perturb the global N cycle by introducing excess N into terrestrial ecosystems (Galloway et al., 2004,2017; Sutton et al., 2011; Zhu et al., 2020; Liu et al., 2020). Excess N exacerbates a range of environmental impacts including: the greenhouse effect (e.g., Vitousek et al., 1997; Change et al., 2021), acid rain (Van Drecht et al., 2003), surface water pollution (Craswell et al., 2021) and groundwater pollution (Choudhury and Kennedy, 2005; Yu et al., 2019). To mitigate these impacts, estimates of N flux dynamics are needed that cover a range of scales from catchment to global. This requirement can be fulfilled using N budgets (e.g., farm scale – Hayakawa et al., 2009, regional – Van Breemen et al., 2002; Howden et al., 2011, national scale – Worrall et al., 2016, and global scale – Van Drecht et al., 2003). Studies at the farm or catchment scale provide more detailed datasets that improve the accuracy of N flux estimates, enhancing our understanding of human impacts on the N cycle as well as our ability to mitigate those impacts through data-driven and well-informed environmental management practices.

Several studies have calculated a catchment-scale N budget including studies of: the Seine, Somme, and Scheldt catchments (France, Belgium, the Netherlands, respectively) (Billen et al., 2009); the Changjiang, Huanghe, and Zhujiang catchments of China (Xing and Zhu, 2002); the Hubbard Brook Experimental Forest catchment in New Hampshire, USA (Yanai et al., 2013); and the Weser catchment, Germany (Sarrazin et al., 2022). Although these studies vary across orders of magnitude in size, it is difficult to consider all potential pathways of N flux in a total N budget and all of the aforementioned studies have assumed a balanced total N budget on inter-annual timescales. Worrall et al., (2015) constructed a total N budget at the catchment scale for the UK's River Thames catchment (9948 km^2). Whilst this study included denitrification to N_2 in the N budget, it did not include the spatial distribution of the N budget across the catchment, nor did it identify locations of N sink or loss. In this study, we advance on this approach and include the spatial distribution of the total N budget. The total N budget for the present study was defined to include N inputs (atmospheric deposition; biological nitrogen fixation; inorganic fertiliser; and feed

* Corresponding author.
E-mail address: Fred.Worrall@durham.ac.uk (F. Worrall).

https://doi.org/10.1016/j.catena.2024.108366
Received 31 August 2023; Received in revised form 29 August 2024; Accepted 4 September 2024
Available online 15 September 2024

and food transfer) and outputs (terrestrial denitrification; atmospheric emission; fluvial loss from the soil; gas emissions from sewage treatment plants; groundwater loss; and direct sewage flux).

Across a whole catchment, where there are mixed land uses and N sources, the N accumulation or loss per unit area of land is likely to be highly variable, with some areas affected by N accumulation and others affected by N loss (Fan et al., 2020). Using long records of N flux, Howden et al., (2011) estimated a total N budget for the Thames catchment that revealed temporal N accumulation but was unable to identify hotspots of N accumulation due to the lack of a spatial element to the study. A spatial N (e.g., spatial distribution of N) budget is a much more powerful tool for analysing the interactions between agriculture and the wider environment (OECD, 2007).

Although many studies have assessed the spatial variability of soil total nitrogen, these studies have not considered as many possible N pathways and identified where N accumulation is occurring (Gao et al., 2019; Wang et al., 2021; Bukpmba et al., 2022; Smith et al., 2022). Accurate estimation of N budgets at high spatial resolution is a considerable challenge due to the scarcity of spatial data for important pathways such as industrial N emissions and groundwater loss (De Vries et al., 2011) and uncertainty about N loss due to ammonia volatilization and denitrification in soil and water. For these reasons, high spatial resolution N budgets that evaluate N accumulation and loss across a single, multi-land use catchment are needed to fill a gap in the literature.

To calculate a total N budget, it is important to consider all major inputs and outputs for N sink and source areas (Fan et al., 2020). The most straightforward way to judge where N accumulation or loss is occurring (e.g., identifying N sinks and sources, respectively) is typically by resampling the same location over several years. Van Meter et al., (2016) used the 'resampling method' to calculate present-day total N in the Mississippi River Basin (USA) compared to the total N at the same location in the mid-1990 s. This study provided evidence of N accumulation in the root zones of agricultural soils. In the absence of long-term soil N data, the present study uses the carbon/nitrogen (C/N) ratio on select soil samples (the soil sample located at N loss and N accumulation areas) as opposed to the resampling method to assess N accumulation or loss. The C/N ratio is the ratio of total C and total N in the organic matter and an indicator of the status of soil nutrients (e.g., a change in the C/N ratio is related to the accumulation or loss of nutrients) (Tian et al., 2010; Fazhu et al., 2015). A high C/N ratio (mass of carbon /mass of nitrogen > 25) is likely to increase the immobilization process (by which nitrate and ammonium are taken up by soil organisms and become unavailable to crops) indicating that organic matter accumulation rate is greater than its decomposition rate (Fazhu et al., 2015). Change in the soil C/N ratio also can be used to explain the status (accumulation or loss) of C and N stock in the soil. Thus, the aim of this study was to determine the nitrogen budget of a catchment area spanning thousands of square kilometers and encompassing multiple land uses. The spatially-distributed N budget for the catchment was further constrained through targeted soil sampling and measurement of C/N ratios to confirm where nitrogen accumulation and loss were occurring.

2. Methodology

2.1. Study area

The river Trent is the third longest river in the UK and flows from a source just north of Stoke-on-Trent to the North Sea through the Humber Estuary (Fig. 1). The Trent catchment (including all River Trent tributaries) covers an area of 8,231 km^2 flowing through several counties (including Staffordshire, Derbyshire, Leicestershire, Nottinghamshire, and Lincolnshire) with 70 % of land used as agriculture (e.g., non-urban landscapes including arable, forest, grassland, wetland, and so on). The most intensive mixed farming occurs at the centre of the Trent catchment. Urban land use makes up 30 % of the Trent catchment and includes the major urban centres of Birmingham, Derby, Nottingham, Leicester, Burton-on-Trent, Stafford, Stoke-on-Trent, Cannock, and Lichfield, giving a whole-catchment human population of approximately six million people. Within these urban areas, industrial activities include vehicle manufacturing, engineering, pottery production, and electricity-generating power stations (consuming N fossil fuel). As an N study area, the Trent catchment has several advantages including: (i) decadal-long records of surface water and groundwater quality that are available across the catchment; (ii) the catchment consists of both sink and source areas as estimated in Fan et al., (2020) (an updated version is presented in Fig. 2, herein); and (iii) land use and soil type vary considerably across the catchment with both extensive areas of organic and mineral soils present, and at least 70:30 agriculture:urban area split as detailed above.

Fig. 1. Location and outline of the River Trent catchment in the UK.

2.2. Data

2.2.1. Spatially-distributed total N budget of the study catchment

Herein, a new and improved spatial total N budget for the Trent catchment was calculated. As in Fan et al., (2020), the total N budget considers the following major pathways of N loss and accumulation: atmospheric N deposition (wet and dry including fixed from lightning),

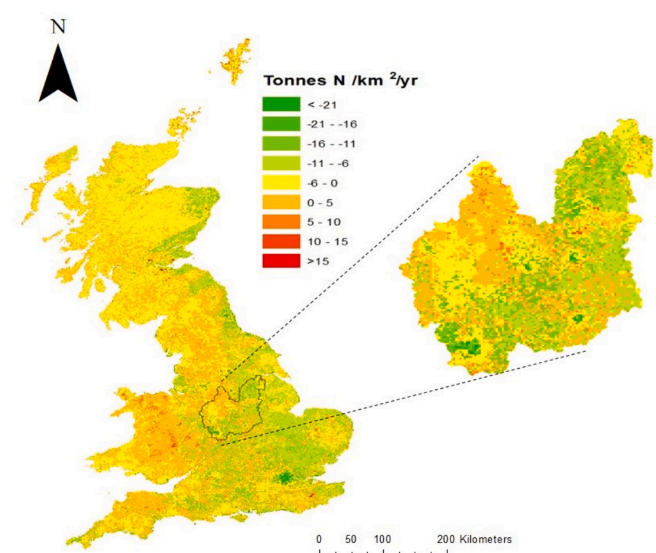

Fig. 2. The spatial total N budget for Great Britain with the Trent catchment total N budget enlarged (modified from Fan et al., 2020).

biological fixation, feed and food import, inorganic synthetic fertilizer, atmospheric N emissions, terrestrial denitrification, feed and food export, fluvial losses from soils, emissions of N gases from sewage treatment plants, groundwater N loss, and direct sewage N flux loss. However, in contrast to Fan et al., (2020), the present study utilised local catchment area data to improve the estimation of fluvial and groundwater N fluxes (that were previously based on catchment characteristics involving some uncertainty).

2.2.2. Catchment-scale fluvial and groundwater loss data

Whilst catchment-scale N activity flux data used previously (Fan et al., 2020) were sufficiently resolved for a national-scale study, the present study makes use of local monitoring data, for example, river discharge and river N concentrations, allowing for a more precise and customised N budget for the Trent catchment. Water quality data were used to calculate fluvial N flux (NO_3, NO_2, NH_4, dissolved organic nitrogen (DON) and particulate organic nitrogen (PON)) at the sub-catchment scale. Measured NO_3, NO_2 and NH_4 data were obtained directly from the Environment Agency (https://environment.data.gov.uk). The sourcing of DON and PON data, however, was somewhat less direct. Because the Environment Agency do not directly measure concentrations of DON and PON, DON was estimated from monitored dissolved organic carbon (DOC) using the average C/N ratio for UK fluvial dissolved organic matter (8:1) (Hillier. 2001). Similarly, Hillier, (2001) reported the organic carbon content of UK fluvial particulate organic matter (POM), and so POM flux was estimated using suspended sediment, mineral concentration, and river flow data. Equally, PON was estimated from the average C/N ratio of suspended sediment (8:1) and the concentrations of suspended sediment monitored by the Environment Agency. The uncertainty in the estimation of DON and PON is indicated by the standard errors reported in equations 1–7.

For every sub-catchment (Fig. 3), for which data were available, the fluxes of dissolved N species were calculated using the available river discharge and river N concentration data. River discharge data were obtained from the National River Flow Archive (NRFA; https://nrfa.ceh.ac.uk/data/search) and N species (NO_3^-, NO_2^-, NH_4^+ and DOC) concentration data were obtained from the Environment Agency (https://environment.data.gov.uk/water-quality/view/landing). The flux of N species was calculated (using the method of Worrall et al., (2013)) only for sub-catchments where both river discharge and river N concentration data were available (Fig. 3). By comparing the flux of each determinand (NO_3^-, NO_2^-, NH_4^+ and DOC) with the physical characteristics (including soil type and land use) of each sub-catchment, the determinand flux of surface water was predicted, based upon the distribution of soil type and land use across the whole Trent catchment. This comparison between N species flux and catchment properties was calculated by multiple linear regression. To improve accuracy of the net groundwater N flux estimate, local monthly total rainfall, daylight hours, and air temperature data were obtained from the UK Met Office (https://www.metoffice.gov.uk) and used to estimate groundwater recharge. Groundwater recharge was calculated as the difference between rainfall and actual evapotranspiration (AET) using the Grindley model (Grindley, 1970). The N species flux to groundwater was predicted based on the distribution of land use and soil type following the same technique as described above for surface water.

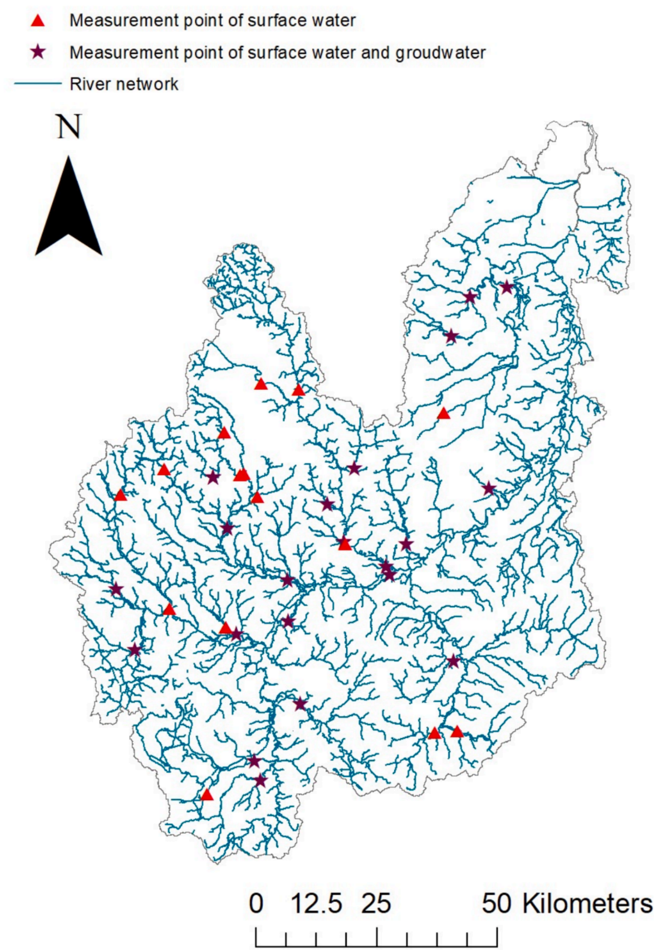

Fig. 3. Sub-catchment N Species Flux Calculation Points: Purple stars for surface and groundwater flux, red triangles for surface water only. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

2.3. Field sampling and C/N ratio

Consistent with previous studies of subsoil N dynamics (e.g., Wang et al., 2016; Novak et al., 2015; McDowell et al., 2004; Burt et al., 2003), catchment subsoils play an important role in regulating nitrogen dynamics and can act as both sources and sinks for nitrogen. Whereas all major N pathways of the Trent catchment could be calculated from existing data, temporally-resolved soil data are scarce. Thus, we used our spatially differentiated N budget for the Trent catchment (Fig. 2) to identify areas of estimated N accumulation and N loss under different land uses and targeted these end member sites for detailed soil sampling and C/N analysis across each soil profile. The hypothesis of this study was that the two-way interaction term between N status (accumulation or loss) and soil depth would be significant for the C/N ratio. The expectation is that the change in C/N ratio with increasing soil depth will be less pronounced, i.e. the magnitude of the gradient would be lower, in areas designated as nitrogen sinks compared to areas designated as nitrogen sources. If the analysis supports the expectation, it would suggest that there is nitrogen accumulation in the subsoil in areas that are nitrogen sinks. It is important to note that the key point is not whether the C/N ratio is necessarily lower at greater depths in nitrogen sink areas compared to nitrogen source areas. Instead, the focus is on the difference in how the C/N ratio changes with depth between these two types of areas.

For a statistically robust experimental design, 24 locations were chosen based upon the total N budget map (Fig. 4a). Three locations were selected from each combination of four factors: soil type (with two 'levels': mineral and organo-mineral soils, organic soils were not included as they never showed a contrast in their N accumulation status), land uses (with two levels: arable and grassland), soil depth (with two levels: topsoil and subsoil), and accumulation status (with two levels: sink or source). Two levels of each of the four factors were selected for sampling and samples were obtained in triplicate, resulting in 24 sample locations (Fig. 4). The site-specific soil data (soil types) were identified and extracted from soil maps series (Falloon, 2002) whilst land use (arable or grassland) at each of the 24 locations was

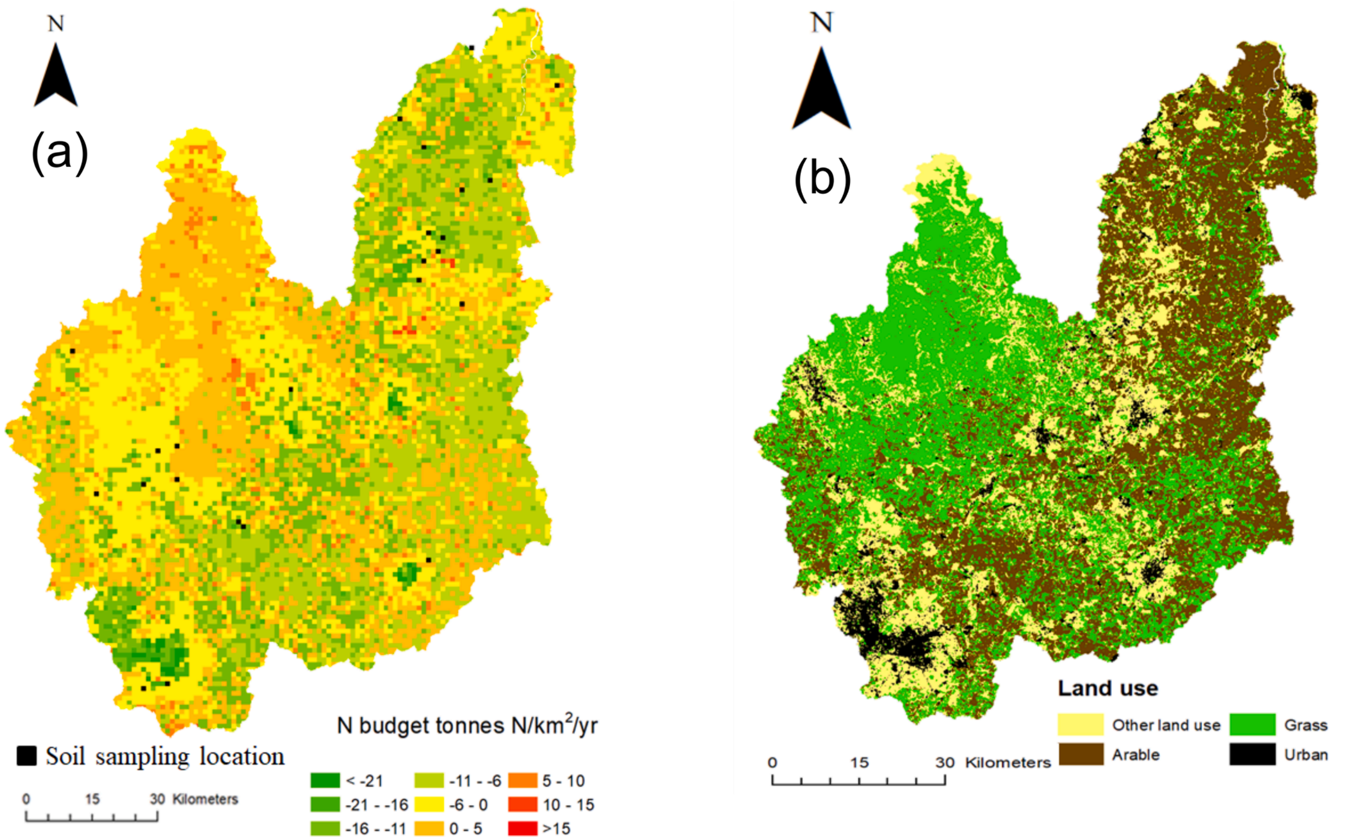

Fig. 4. (a) Spatial total N budget of the Trent catchment and 24 soil sampling locations within 1 km^2 grid squares (black squares) compared to (b) land use of the Trent catchment.

identified from Centre for Ecology & Hydrology CEH land cover data (https://www.ceh.ac.uk/services/land-cover-map-2015).

Two replicate soil cores were taken at each of the 24 locations across Trent River sub-catchments using a 6 cm diameter and 0.5 m length gouge corer. Each core was subdivided into 4 samples based on the soil profile (two in the topsoil layer and two in the subsoil) resulting in a total of 192 soil samples. Samples were subdivided in the field and the sample name, date, location, and depth were recorded. Samples were air dried to reduce weight and shipped to the Durham University Department of Geography's laboratory for analysis.

2.4. Laboratory analysis of Trent catchment subsoils

In the laboratory, all samples were dried in a 105 °C oven over night to remove remaining moisture. Once dried, loss on ignition (LOI) was used to determine the organic matter content of each soil sample – LOI was used as a covariate in the analysis. A sub-sample of each soil sample was freeze-dried, ball-milled, and 20 mg weighed into tin containers for elemental analysis. The elemental analysis was performed on a Thermo Scientific Flash 2000 Organic Elemental Analyser and NC (Nitrogen Carbon) Soil Analyser. The elemental combustion system used a pneumatic autosampler and the computer software, EAS Clarity (DataApex Ltd, Prague, Czech Republic). For both C and N analyses, calibration curves of $r^2 > 0.999$ were created using acetanilide as a standard. An acetanilide standard was included in each run and each sample was analysed in triplicate as quality control measures. The C and N concentration of each sample was then used to calculate the C/N ratio as a proxy for N store.

2.5. Statistical analysis

To evaluate the relationship between C/N ratio and four soil sample parameters (e.g., accumulation status, soil depth, soil type, and land use), we used a four-factor analysis of variance (ANOVA) with C/N ratio as the response variable. A four-factor ANOVA is a better choice than a Student's *t*-test or Mann-Whitney *U* test because there are more than two groups to compare and multiple factors may influence the outcome (Maxwell and Delaney, 2004). The accumulation status (herein referred to as 'Status') was identified from the estimated total N budget and this had two levels – sink and source. The soil depth factor (herein referred to as 'Depth') was divided into two levels – topsoil (0–10 cm and 10–20 cm) and subsoil (20–30 cm and 30–40 cm). The soil type factor (herein referred to as 'Soil') had two levels – mineral ('mineral') and organo-mineral ('orgmin'). Finally, the land use factor (herein referred to as 'Land Use') also had two levels – grass and arable. Given the nature of the experimental design, it was possible to consider two-way interactions and three-way interactions between these factors. The hypothesis (change in C/N ratio with depth is significantly greater in sink areas compared to the change C/N ratio with depth in source areas) was tested by considering the interaction terms and not the single factors. The expected result was that the two-way interaction term between Status and Depth would be significant and in which case the C/N ratio should decrease less with depth in the subsoil in the sink areas compared to source areas. If supported by the data, this would suggest N accumulation in the subsoil. The C/N ratio is a necessary but not sufficient condition to test our hypothesis, thus, the C and N content of the sampled soils were also assessed separately. Furthermore, because organic matter plays a significant role in influencing the carbon-to-nitrogen (C/N) ratio of soils, LOI data was included as a covariate in the ANOVA.

Before any ANOVA was performed, the data were Box-Cox transformed to assess for outliers and the Anderson-Darling test was used to normality (Anderson and Darling. 1952). The homogeneity of the variance was tested using the Levene test (Levene, 1960). If necessary, the data were log-transformed and re-analysed – further transformation did not prove necessary. The generalised ω^2 (Olejnik and Algina, 2003) was used to measure the magnitude of effect sizes of each significant factor and interaction and values are presented as least-square means – known also as marginal means. The Tukey test was used to assess post hoc significant differences between levels of significant factors and interactions. Unless otherwise stated, significance was assessed refer to the effect being different, or not, from zero at the probability of 95 % – 5 % chance of being zero. Power analysis was performed to assess adequacy of the samples size and probability of Type 2 errors (GPower 3.1 software; Faul et al. 2007; http://gpower.hhu.de/). *A priori* the acceptable power was set at 0.8 (a false negative probability $\beta = 0.2$) and degrees of freedom = 1, n = 192 with the significance (α) set at 95 %.

3. Results

3.1. Fluvial N flux

The DON flux was calculated for 19 Trent sub-catchments with total land use and soil type data using calculated DOC flux (estimated by concentration data and river discharge). The best-fit regression equation ($R^2 = 0.92$, df = 18) for DON was:

$$DONflux = \underset{(0.09)}{0.49}arable + \underset{(0.05)}{0.20}grass + \underset{(0.08)}{0.32}urban \tag{1}$$

where, *DON flux* = average annual DON flux (tonnes N/yr); *arable* = area of arable land (km^2); *urban* = area of urban land use (km^2); and *grass* = area of grassland (km^2). The numbers in the brackets underneath Eq. (1) are the standard error of each coefficient. Note there is no constant term in Eq. (1) as it was found not to be significantly different from zero at a 95 % probability.

In the calculation of nitrate (NO_3^-) N flux, a total of 28 sub-catchments were considered. The best-fit equation ($R^2 = 0.94$, df = 27) for nitrate flux was:

$$Nitrateflux = \underset{(2.27)}{9.19}arable + \underset{(2.58)}{10.71}grass + \underset{(2.45)}{9.94}urban - \underset{(2.13)}{6.27}Area \tag{2}$$

where, *Nitrate flux* = average annual nitrate flux (tonnes N/yr); *Area* = area of whole catchment (km^2). All other variables are as defined for Eq. (1) above. The numbers in the brackets underneath Eq. (2) are the standard error of each coefficient.

To calculate ammonium (NH_4^+) N flux, a total of 33 catchments were considered and the best-fit equation ($R^2 = 0.52$, n = 33) determined to be:

$$NH_4flux = \underset{(0.04)}{0.20}grass + \underset{(0.18)}{0.41}urban - \underset{(0.07)}{0.24}Mineral \tag{3}$$

where *NH_4 flux* = the average annual NH_4^+N flux (tonnes N/yr); *Mineral* = the area of mineral soil land (km^2). All other terms are as defined for Eq. (1) above. The numbers in the brackets underneath Eq. (3) are the standard error of each coefficient.

PON flux was calculated using data available from 20 Trent sub-catchments. The best-fit equation ($R^2 = 0.91$, n = 20) is:

$$PONflux = \underset{(0.02)}{0.12}grass + \underset{(0.01)}{0.09}urban \tag{4}$$

where PON flux = the average annual PON flux (tonnes N/yr). All other terms are as defined for Eq. (1) above. The numbers in the brackets underneath Eq. (4) are the standard error of each coefficient.

3.2. Groundwater N loss

To estimate groundwater N loss, DON flux was calculated for 22 sub-catchments that have total land use and soil data. The best-fit regression equation ($R^2 = 0.93$, n = 22) for DON was:

$$DONgroundwater = \underset{(0.01)}{0.03}grass + \underset{(0.01)}{0.08}urban \tag{5}$$

where: DON groundwater = the average annual DON flux (tonnes N/yr) loss to groundwater. All other terms are as defined above. The numbers in the brackets underneath Eq. (5) are the standard error of each coefficient.

A total of 22 sub-catchments were considered in the analysis of nitrate. The best-fit equation ($R^2 = 0.95$, n = 22) for nitrate flux was:

$$Ngroundwater = \underset{(0.19)}{1.32}Mineral + \underset{(0.33)}{1.33}Orgmin \tag{6}$$

where: N groundwater = the average annual nitrate flux (tonnes N/yr) loss to groundwater; Mineral = the area of mineral soil land (km^2); Orgmin = the area of OrgMin soil land (km^2). All other terms are as defined above. The numbers in the brackets underneath Eq. (6) are the standard error of each coefficient.

The NH_4^+ flux was analysed for 22 sub-catchments. The best-fit regression equation ($R^2 = 0.95$, n = 22) for NH_4groundwater flux was:

$$NH_4groundwater = \underset{(0.03)}{0.04}urban + \underset{(0.01)}{0.03}Orgmin + \underset{(0.02)}{0.07}Organic \tag{7}$$

where: NH_4 groundwater = the average annual NH_4^+ flux (tonnes N/yr) loss to groundwater; Organic = the area of organic soil in the catchment (km^2). All other terms are as defined above. The numbers in the brackets underneath Eq. (7) are the standard error of each coefficient.

3.3. Spatial N budget of the Trent catchment

The estimated N flux inputs and outputs and the percentage contribution of each to total N inputs and outputs in the Trent catchment in 2015 are reported in Table 1. The spatial total N distribution across the Trent catchment is presented in Fig. 4a. Chemical fertilizer N consumption is the largest N input in the Trent catchment, accounting for 64 % of the total N input in 2015. Due to variations in fertilizer applications according to arable versus grass land use, the broad flat plains located in the eastern Trent catchment had the highest fertilizer input (14 ± 2 tonnes/km^2/yr, where the value given is the mean and standard error). Conversely, the Peak District National Park area located in the north-western Trent catchment had the lowest fertilizer input (4 ± 1 tonnes/km^2/yr). The total estimated biological N fixation (BNF) was 19 ± 3 ktonnes N/yr which accounted for 17 % of the total N inputs to the Trent catchment in 2015 (Table 1). Atmospheric deposition input to the Trent catchment was 16 ± 2 ktonnes N/yr which accounted for 14 % of total input in 2015 (Table 1). Because gaseous N can migrate over a long

Table 1
Summary of calculated median values of N flux inputs and outputs for the Trent catchment in 2015; and percentage of total N inputs or outputs in 2015.

	Flux in 2015 (ktonnes N/yr)	Percentage of N inputs/outputs
Inputs		
Biological N fixation	19	16 %
Atmospheric deposition	16	13 %
Inorganic fertilizer	76	64 %
Net food and feed transfer	8	7 %
Sub-total	*119*	
Outputs		
Atmospheric emission	47	55 %
Terrestrial denitrification	9	11 %
Fluvial loss at soil source	28	33 %
Ground water loss	0.5	1 %
Sub-total	*85*	
Total N budget	**+35**	

distance, the atmospheric deposition rate changed little across the catchment. Net N input through food and feed transfer was 8 ± 3 ktonnes N/yr; it contributed 7 % of total N input. The Trent catchment is an agricultural region, and hence food produced in the Trent catchment is nearly adequate to meet the demand of that population, and hence the net food and feed transfer is relatively low compared to other N pathways.

Atmospheric N emission included NO, N_2O from agricultural land, NH_3 from livestock and fertilizer. The amount of atmospheric N emission was 47 ± 13 ktonnes N /yr which accounted for about 55 % of total N outputs in 2015 (Table 1). The highest atmospheric N emission occurred in the north-western Trent catchment where land use was predominantly forest and grassland (Fig. 4b). Fluvial N loss at soil source (N losses from soil source to fluvial system) was 29 ± 13 ktonnes N /yr, accounting for approximately 28 % of total inputs; the highest fluvial N flux loss was located at in the eastern Trent catchment where the land use was predominantly. The amount of denitrification was 9 ± 4 ktonnes N/yr, accounting for 9 % of total N output in 2015 with the highest denitrification output observed in the eastern Trent catchment. Conversely, the lowest denitrification output was observed in the north-west Trent catchment (forest and grassland). Groundwater loss was the lowest output observed, accounting for 9 % of total output in 2015. The distribution of groundwater loss varied little across the Trent catchment.

Across the catchment, 31 % of total areas were source areas and 69 % of total areas were sink areas. The source areas were mainly located in the north-west and central-south of the Trent catchment (Fig. 4a). The sink areas were mainly located in the south-west, north-east and the middle of the Trent catchment (Fig. 4a). The N accumulation status for each sampling point is provided in the Supplementary Material (Table S1).

3.4. C/N ratio

As described in Section 2.3, we used the spatial total N Budget for the Trent catchment calculated in this study (Fig. 2) to identify areas of estimated N accumulation and N loss under different land uses and targeted these end member sites for detailed soil sampling and C/N analysis across each soil profile. The spatial distribution of 24 sampling points is shown in Fig. 4a and box plots of the C/N ratios according to Land use (arable vs grass), Soil type (mineral vs OrgMin), and Status (source vs sink) are presented in Fig. 5 with supporting data in Table 2.

3.5. ANOVA

No outliers were identified and the distribution of C, N, and C/N data were found to be normally distributed. The power analysis suggested that the study’s experimental design could detect a difference between any of the levels greater than 0.55. The ANOVA for the C/N ratio, without the inclusion of LOI as a covariate, explained 20.7 % of the variance in the original dataset (Table 3). The largest effect on the data was the Land Use factor with arable sites exhibiting higher C/N ratios relative to grass sites. The difference between C/N for arable and grassland samples reflected a significant difference for each of the elements considered (C and N content) – e.g., the soil C/N under grassland

Table 2
The variation in C/N by the factors included in this study.

Factor	Level	Median	Inter-quartile range
Status	sink	11.14	3.18
	source	11.44	2.34
Land use	arable	11.82	3.38
	grass	10.98	1.96
Soil type	orgmin	11.88	3.88
	iineral	10.98	1.46
Depth	topsoil (0–10 cm)	11.36	1.01
	Topsoil (10–20 cm)	11.87	2.45
	Subsoil (20–30 cm)	11.85	3.37
	Subsoil (30–40 cm)	11.18	2.84

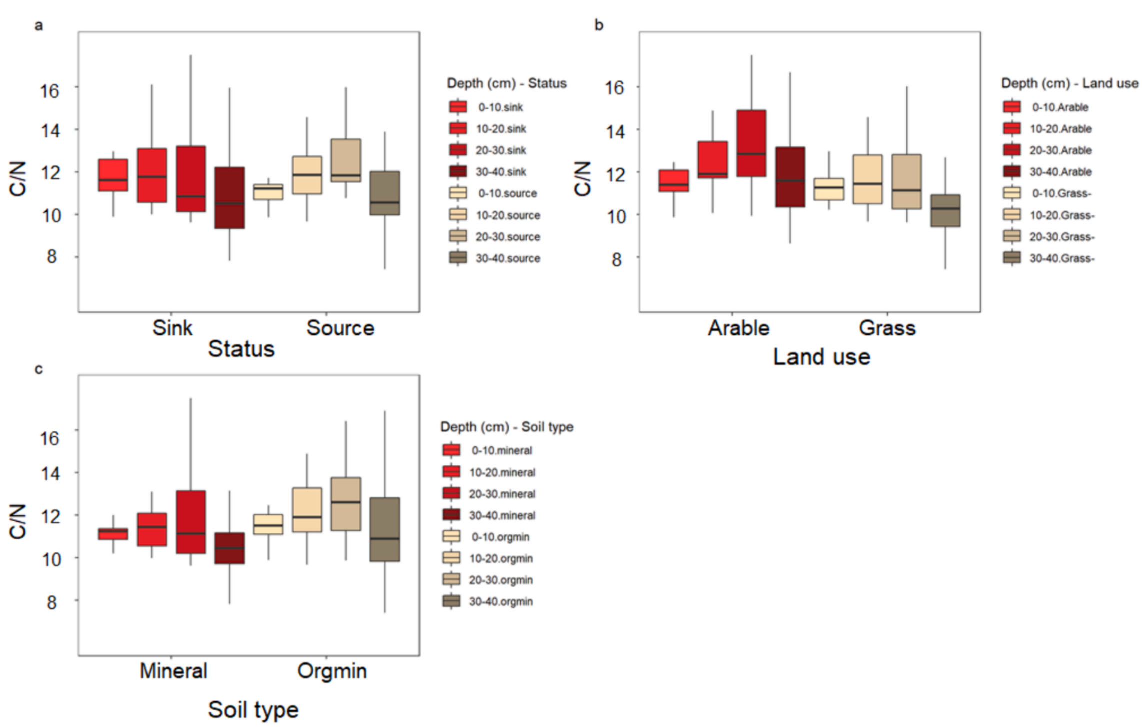

Fig. 5. Boxplot of the C/N ratio measured for the factors: a) Status — sink and source areas; b) Land use – Arable and Grass; and c) Soil type – orgmin and mineral. The upper and lower sides of the box plot are the 25 and 75% quartiles and the line inside the box represents the median of the data. The points outside the whiskers represent outliers beyond 1.5 times the inter-quartile range. The max and min values of the dataset (excluding outliers) are at the ends of the whiskers. Colour coding is defined in the legend of each graph.

Table 3
The percentage of variance (%) explained by each factor and interaction (excluding LOI as covariates). Significant (P<0.05) factors or interactions are highlighted in bold.

Source	C	N	C/N
Land use	**7.25**	**11.55**	**5.86**
Soil	**0.05**	**2.23**	**3.90**
Status	–	0.29	0.00
Depth	**15.19**	**17.68**	0.13
Land use*Soil	0.07	0.03	0.01
Land use*Status	0.17	0.02	**3.05**
Land use*Depth	**2.15**	**4.24**	0.02
Soil*Status	–	0.03	**2.20**
Soil*Depth	0.90	0.84	0.00
Status*Depth	0.06	0.01	0.32
Land use *Soil*Status	**3.85**	**3.41**	0.27
Land use *Soil*Depth	0.05	–	0.52
Land use *Status*Depth	0.24	0.19	**1.59**
Soil *Status*Depth	–	0.13	**1.97**
Land use *Soil*Status*Depth	0.17	0.46	0.68
Error	65.13	58.89	79.50

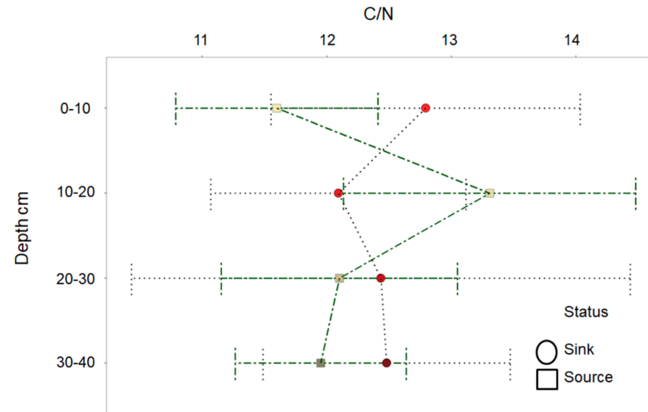

Fig. 6. The two-way interaction plot for the factors Status and Depth. The values are presented as least squares (marginal) means with their respective 95% confidence intervals. The colour scheme is the same as that used in Fig. 5 and corresponds to depth.

was lower than under arable due to both lower C and higher N content. Overall, the Land Use factor was the most important, explaining 5.9 % of the original variance in the C/N ratio results (Table 3). The Soil factor was the second most important factor explaining 3.9 % of the variance in the original dataset (Table 3) with the mineral soil having a significantly lower C/N ratio relative to C/N ratio of organo-mineral soil. The mineral soil was found to have a lower C/N ratio than OrgMin soil and this was reflected in significantly lower C and higher N content. No other single factors considered (i.e. Depth and Status) were found to have a significant effect on C/N ratio.

A number of the two-way interactions were found to be significant (Table 3). The most important interaction was between Status and Land Use which explained 3.1 % of the original variance (Table 3). For the identified N sink areas, grassland had a lower C/N ratio when compared to grassland associated with the identified N source areas. The second most important interaction was that between Status and Soil which explained 2.2 % of the variance in the original dataset (Table 3). For identified N sink areas, mineral soils had a significantly lower C/N – a reduction of 0.20. Conversely, for identified N source areas, the presence of mineral soil led to a reduction in C/N ratio by an average of 0.15.

The most important three-way interaction was the interaction between Soil, Status and Depth factors which explained 2.0 % of the original dataset variance (Table 3). The C/N ratio was significantly lower when samples were collected from identified N sink areas on orgmin soils or identified N source areas on mineral soils. Similarly, the C/N ratio was significantly lower at depth (subsoil) for identified N sink areas on OrgMin soil and significantly lower at depth for source areas on mineral soils. The least important, but still significant, three-way interaction was that between the Land Use, Status and Depth factors which explained 1.6 % of the original variance in the dataset (Table 3). The Depth factor had the effect of lowering the C/N ratio for samples collected from identified sink areas on grassland or identified source areas on arable land. The C/N ratio was lower in the subsoil of identified sink areas compared to identified source areas under grassland rather than arable land.

In this study, we hypothesised that the two-way interaction between Status and Depth factors would be significant, and that the change in C/N ratio with depth should be less for areas identified as N sinks compared to the N source areas. There was no significant two-way interaction between the Status and Depth factors (Fig. 6 – Table 3), and so the hypothesis of this study was not met. However, the three-way interaction term (Land use, Status, and Depth) suggested that depth has a significantly different effect upon C/N ratio between sink and source areas under different land use (Fig. 7). Under grass land use in N sink areas, the C/N ratio decreased with depth compared to increased C/N ratio with depth for N source areas, i.e. N is concentrated at depth relative to C in N sink areas under grass but not in N source areas. Therefore, the measure used to test for N accumulation in this study did prove to be significant under grassland, but not under arable.

The ANOVA was also performed including the LOI as a covariate. When the C/N ratio was considered, the LOI was a significant covariate, explaining ~ 1 % of the variance (C/N ratio increased with organic matter content) (Table 4). Adding covariates improved the fit of the model and affected the results (variance explained by the model with LOI was larger than for the model without LOI). Although the fir of the ANOVA was improved by the inclusion of a covariate no further factors, or interactions were found to be significant, likewise no factors or interactions, found to be significant without the covariates, proved to be insignificant with the inclusion of the covariate. Therefore, the inclusion of LOI has not accounted for the significant, or insignificant, interactions identified above.

4. Discussion

In this study, we hypothesised that the change in C/N ratio with increasing soil depth will be less pronounced, the magnitude of the gradient being lower, in areas designated by our total spatial N budget as nitrogen sinks compared to areas designated as nitrogen sources. However, the result of ANOVA (Tables 3 & 4) found that only data from grassland supported this hypothesis whilst arable land use did not (e.g., the C/N ratio for arable land was higher in subsoil relative to the topsoil – Fig. 5b). There are likely several reasons why the hypothesis was not supported by the data from arable land. Firstly, in addition to the factors considered (Land Use, Soil, and Status), studies show that the C/N ratio can be influenced by a variety of factors, including the quality of organic matter (the quantity of organic matter having already been accounted for by inclusion of LOI in the analysis); the rate of decomposition of organic matter; the nitrogen mineralization rate; and the amount of nitrogen inputs from fertilizers or atmospheric deposition. Additionally, soil properties such as texture, pH, and moisture content can also affect the C/N ratio (Callesen et al., 2007; Miller et al., 2004). In general, the C/N ratio tends to decrease as the rate of nitrogen mineralization increases, indicating that nitrogen-rich organic matter is being broken down more rapidly relative to carbon-rich organic matter. Conversely, the C/N ratio tends to increase when there is a lower rate of nitrogen mineralization, indicating that carbon-rich organic matter is accumulating relative to nitrogen. Callesen et al., (2007) found the C/N ratio has a positive relationship with the percentage of sand, with higher C/N ratio observed in coarse-textured soils. Miller et al., (2004) developed a C/N model that showed the C/N ratio increases with increasing mean

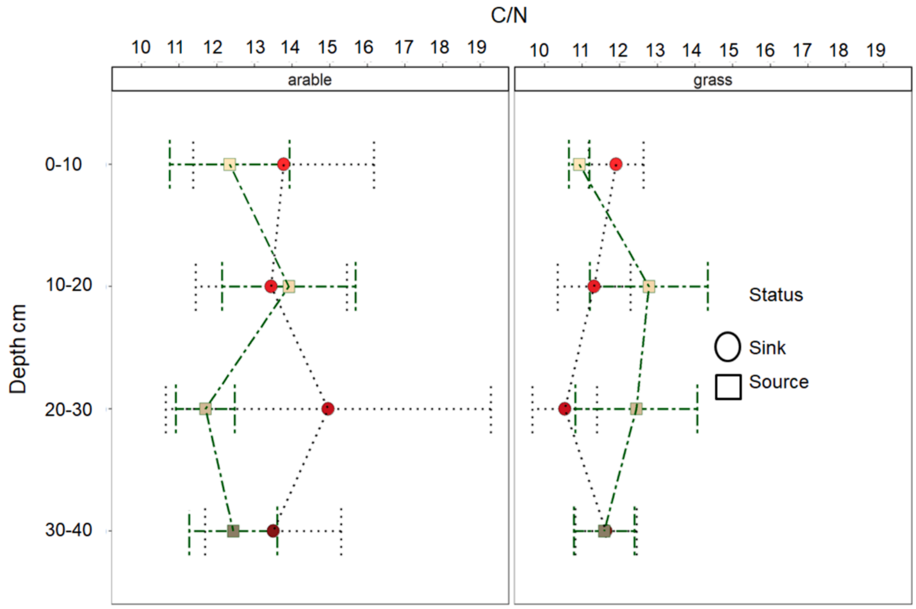

Fig. 7. The three-way interaction plot for the factors Status and Depth with different land use. The values are presented as least squares (marginal) means with their respective 95% confidence intervals. Given the size of the dataset each point and confidence interval is the equivalent of 13 datapoints. The colour scheme is the same as that used in Fig. 5 and corresponds to depth.

Table 4
The percentage of variance explained by each factor and interaction (including LOI as covariates). Significant (P<0.05) factors or interactions are highlighted in bold.

Source	C	N	C/N
LOI	**28.21**	**27.94**	**0.97**
Land use	–	0.39	**9.38**
Soil	0.41	–	**2.30**
Status	–	0.01	0.01
Depth	**1.94**	**2.84**	0.19
Land use*Soil	0.01	0.05	0.02
Land use*Status	0.07	0.09	**2.06**
Land use*Depth	0.22	**1.12**	0.16
Soil*Status	0.02	0.07	**2.91**
Soil*Depth	0.19	0.16	0.04
Status*Depth	–	0.09	0.33
Land use *Soil*Status	0.46	0.33	0.11
Land use *Soil*Depth	0.02	0.01	0.51
Land use *Status*Depth	0.03	0.01	**1.67**
Soil *Status*Depth	0.04	0.25	**1.60**
Land use *Soil*Status*Depth	0.02	0.16	0.64
Error	68.28	66.47	77.09

precipitation and decreasing mean annual temperatures. Therefore, soil texture and climate (precipitation and temperature) potentially explain why arable land did not fit the hypothesis (e.g., precipitation and temperature would change the C/N ratio of soil).

Another reason why arable land was not in agreement with our hypothesis may be due to the effects of ploughing on soil C/N ratio. Many farmers plough their arable land at least once a year for the crop rotation and to increase plough layer depth. Ploughing of arable land leads to the loss of N in the form of mineralisation of organic N and the N release would follow the same trend as loss of C from soils (Behera and Sharma, 2011; Barraclough et al., 2015). Large losses of soil organic C would lead to a decrease in soil C storage (Moreno, 2009). Therefore, it is possible that ploughing changed the distribution of C and N content in our arable land use samples, causing the C/N ratio in source areas to be lower than sink areas under arable land use. The study was unable to determine the total cultivation history of the sampled sites, including details such as the last time they were ploughed or their land rotation scheme. Furthermore, in the Trent catchment, crops vary across different regions. Different crops, owing to varying fertilizer application rates, are bound to affect soil nitrogen accumulation. However, this study did not consider the impact of different crops on nitrogen accumulation. In future work, we aim to address this aspect more comprehensively.

Leaching of soluble high C/N organic compounds is another factor that may explain the lower C/N ratio in topsoil relative to the subsoil under arable land use. Diekow et al., (2005) showed that the C/N ratio increased with depth and explained that this trend might be due to high C/N soluble organic compounds leaching into deeper soil. In arable land use, the high C/N soluble organic compounds from crop residue would leach deeper into the soil and lead to a higher C/N ratio in the subsoil relative to the topsoil. Another potential explanation is that some of the data sets on denitrification and BNF collected from publications used to calculate the N budget were outdated (Smil, 1999; and Herridge et al., 2008). This could have led the N budget (sink or source status) to be wrong, especially for arable land.

Human activities have resulted in the production of an excessive amount of anthropogenic reactive N (Nr), which includes all nitrogen species except N_2. As a result, Nr is primarily responsible for altering the movement of nitrogen through the Earth's atmosphere, hydrosphere, and biosphere (Galloway et al., 1996). A considerable portion of the Trent catchment is agricultural where the anthropogenic N_r input was observed to be the dominant compared to other inputs. Total anthropogenic N_r input to the Trent catchment was estimated to be 14.5 tonnes $N/km^2/yr$, which is higher than other regions of similar area across the world (Table 5). This difference is due to its relatively high population, high livestock density, and a high proportion of arable land (Table 5). Because the overall N use for crops and grass was obtained from the British Survey of Fertilizer Practice (2015), the arable areas were assumed to have the same fertilizer application rate across GB. The Trent catchment has a high proportion of arable land and a high fertilizer application rate (fertilizer input was the largest N input) (Fan et al., 2020). However, according to Worrall et al., (2015), the flux of total N input in the Thames catchment was 17.4 tonnes N $/km^2/yr$ which is higher than the 14.5 tonnes $N/km^2/yr$ for the Trent catchment, observed herein. Because the Thames catchment has a high net import of food area, the high net N input through food/feed transfer results in a higher total N input for the Thames catchment relative to the Trent catchment. Furthermore, both the Thames and Trent catchments have a high

Table 5
Comparison of N inputs of Trent catchment with other regions with similar area across the world.

District	Area (km^2)	Arable percentage	Total N input per unit area (tonnes N/km^2)	Reference
Kennebel	13,994	6 %	1.1	Boyer et al.2002
Merrimack	12,005	8 %	2.2	Boyer et al.2002
Hudson	11,942	10 %	2.0	Boyer et al.2002
Androscoggin	8451	5 %	1.3	Boyer et al.2002
Mohawk	8935	28 %	3.6	Boyer et al.2002
Trent	8231	46 %	14.5	This study

proportion of arable land use with high fertilizer application rates compared to other similar area catchments. The high fertilizer application could result in high N gas emission, and most of the N gas would be deposited to the terrestrial biosphere. Therefore, the flux of N deposition in the Trent and Thames catchment is probably higher than for most other catchments in GB.

The predicted atmospheric N emission dominated the N output, accounting for 55 % of total N output in the Trent catchment. According to Skiba et al., (2012), fertilizer is the largest source of agricultural N emission. In their study, high atmospheric N emissions were caused by fertilizer application, manures, urine deposition and crop residues. In the Trent catchment, the average value of atmospheric N emission export was 4.3 tonnes N/km^2/yr which is higher than the average value estimated previously for the UK of 2.3 tonnes N/km^2/yr (Worrall et al., 2016). Several studies have quantified the relationship between atmospheric N emission and N deposition, finding that more atmospheric N emission leads to more N deposition (Asman, 1998, Goulding et al., 1998 and Kanakidou et al., 2016). Tonnesen et al., (2003) have claimed that high N deposition rates may take place in areas downwind of agricultural sources. The Trent catchment had higher predicted atmospheric N emission than reported by the National Atmospheric Emissions Inventory (2015) for other catchments such as the Thames. However, the N deposition in the Trent catchment was less than that estimated for the Thames catchment and lower than the average value of the UK. This difference is because previous studies only considered the relationship between total N deposition and total N emission rather than the N spatial distribution. That said, although there is a strong relationship between total N deposition and total N emission, this does not necessarily mean that all high atmospheric N emission areas have a high N deposition rate. Because atmospheric N gas can be transported by wind, high N deposition may not necessarily occur near N emission sources.

The United States Department of Agriculture (2011) reported that C/N ratios around 25 were considered optimal for microbial activity. Lower C/N (less than 25) ratios would decrease N immobilization potential, which increases the soil NO_3 concentration and may result in high N loss rates and low C sequestration rates. The average C/N ratio of the sink areas was lower than the source areas, which supports the view that N stores were larger in sink areas than in source areas. Cleveland and Liptzin, (2007) reported that the C/N stoichiometry in soil remains stable at 14 on the global scale. In the UK, Henrys et al., (2012) showed that the C/N ratios under arable land use varied between 9.37 and 17.22, with an average of 11.42 and the C/N ratio under grassland varied between 9.81 and 29.03, with an average of 15.32 (Table 5). Although similar, the present study's C/N ratio under grassland (15.32) was lower, and the C/N ratio under arable land (11.42) was higher, than that reported previously (Henrys et al., 2012).

Conclusions

The construction of nitrogen budgets has been widely used to describe the input, output, and internal cycling of nitrogen within an ecosystem. This study calculated a spatial total N budget, informed by monitoring data, for a mixed land use catchment (8231 km^2 – River Trent). According to the budget, 69 % of the catchment area was estimated to be net N sink areas whilst 31 % were identified as net N source areas. In 2015, the total N budget showed that the Trent catchment was accumulating total N, and the accumulation of total N in the catchment was estimated to be 35 ± 5 ktonnes N. Through strategic sampling guided by the spatial nitrogen budget, this study confirmed accumulation of N was occurring in the subsoil under grassland but found no significant N accumulation in the subsoils under arable land. These results have important implications for understanding nutrient dynamics and highlights the importance of managing nitrogen inputs such as fertilizers or organic matter to avoid excessive build-up and potential leaching to groundwater. Our observation of nitrogen accumulation in the subsoil under grassland as opposed to arable land underscores the complex interactions between land use, nitrogen accumulation, and soil dynamics. It emphasizes the need for context-specific approaches to nutrient management and highlights potential environmental consequences associated with nitrogen accumulation in subsoil, particularly under grassland conditions.

CRediT authorship contribution statement

Xiangwen Fan: Writing – original draft, Formal analysis. **Fred Worrall:** Writing – review & editing, Supervision, Project administration, Methodology. **Lisa M. Baldini:** Writing – review & editing, Supervision, Project administration. **Tim P. Burt:** Writing – review & editing, Supervision, Project administration.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgments

The authors thank the landowners for allowing access to their farmland for sampling. Dr Jin and Q. Jie are thanked for their assistance with fieldwork.

This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

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