Journal Pre-proof

A spatial total nitrogen budget for Great Britain

Xiangwen Fan, Fred Worrall, Lisa M. Baldini, Tim P. Burt

PII: S0048-9697(20)32381-0

DOI: https://doi.org/10.1016/j.scitotenv.2020.138864

Reference: STOTEN 138864

To appear in: *Science of the Total Environment*

Received date: 15 February 2020

Revised date: 15 April 2020

Accepted date: 19 April 2020

Please cite this article as: X. Fan, F. Worrall, L.M. Baldini, et al., A spatial total nitrogen budget for Great Britain, *Science of the Total Environment* (2020), https://doi.org/10.1016/j.scitotenv.2020.138864

A spatial total nitrogen budget for Great Britain

Xiangwen Fan[1], Fred Worrall[2*], Lisa M. Baldini[3] and Tim P.Burt[1]

[1]Dept. of Geography, Science Laboratories, South Road, Durham University, Durham, DH1 3LE, UK
[2]Dept. of Earth Sciences, Science Laboratories, South Road, Durham University, Durham, DH1 3LE, UK
[3]Dept. of Science, School of Health & Life Sciences, Teesside University, Middlesbrough, TS1 3BX, UK

Abstract

Understanding nutrient budgets makes it possible to predict where and by how much nutrients are accumulating in the environment. Previous studies have considered this problem for nitrogen (N) but have limited themselves to reactive N species (i.e. excluding N_2) or have considered total N (including N_2) but have been limited to regional or national scales. In this study the spatially-distributed total nitrogen (N) budget of Great Britain (GB) was estimated at a 1 km^2 grid scale. The inputs of N considered were: biological N fixation; atmospheric deposition; food and feed transfer; and inorganic synthetic fertilizer. The outputs of N considered were: atmospheric emission; terrestrial denitrification; fluvial loss from the soil; gaseous emissions from sewage treatment plants; direct sewage flux loss; and groundwater loss. All pathways were considered over a number of years. This study constructed a spatially-differentiated total N budget for GB, which not only includes all major N pathways but also distributes the N budget to various land uses with a 1 km^2 spatial resolution. The results showed that both sink and source areas exist across GB, although the majority of 1 km^2 grid squares were identified as sources. Based on a mass balance model calculated for 2015, total N exhibited a net flux of a source of -1045 (±244) ktonnes N/year. The spatial N budget across GB ranged from -21 (±3) tonnes N/year to 34 (±5) tonnes N/year, where 66%

* Corresponding author: Fred.Worrall@durham.ac.uk; tel. no. +44 191 334 2295.

of grid squares were source areas and 34% were sink areas. Urban and arable land use were predominantly source areas: 97% of total urban land use and 98.5% of total arable land use. 65% of grassland was a sink area. The total amount of N released to the environment by human activity in 2015 was -16.65 kg N/ca/yr.

Keywords: Reactive nitrogen · Total N · National budget · Spatial analysis · Land use change

Introduction

The increase in anthropogenically-sourced N has greatly altered the N cycle at a global scale; thus, each input or output of N has received considerable attention (Galloway et al. 2008; Schlesinger et al. 2009). Maintaining the balance between N input and output is essential to ensure the optimal use of this important resource while limiting pollution problems; the N budget has been considered as a priority agri-environment indicator by many countries (OECD, 2007). As a result of its importance, several national and regional scale N budget studies have been published for a wide range of locations: the Republic of Korea (Bashkin et al. 2002); Canada (Janzen et al. 2003); The Netherlands (Kroeze et al. 2003); the catchment area of the North Atlantic Ocean (Galloway et al. 1996); Brazil (Filoso et al. 2006); New Zealand (Parfitt et al. 2006); Finland (Salo et al. 2007); France (Billen et al. 2012); China (Ti et al. 2012); the agricultural land of Asian counties (Shindo 2012); a forested catchment area in New Hampshire, USA (Yanai et al. 2013); forest ecosystems (see the review by Johnson et al. 2014); and the grasslands of south-east Scotland (Jones et al. 2017). Although these studies contributed to an improved understanding of N pathways, none of them provided a total N budget, for a number of reasons, as summarised by Worrall et al. (2016a). The reasons for incomplete N budgets include different boundaries of study system (Ti et al. 2012;

Worrall et al. 2015), missing industrial N_2 quantifications (Kroeze et al. 2003), and not have reflected current processes but changes in legacy stores and sinks (i.e., due to N reserves and reservoirs having different time constants - Addiscott, 1988).

Previous studies (e.g. Galloway et al. 2004; Worrall et al. 2009; Worrall et al. 2015) have calculated the N budget based on reactive N (N_r) alone, which was justified since excess N_r can affect the environment quickly. However, to fully understand how N cycles through the environment, a total N budget that includes both N_r and N_2 is critical. Worrall et al. (2016a) calculated the UK National scale total N budget in 2016 by including industrial emissions of N_2 as well as both terrestrial and aquatic denitrification, to give the total N budget at the national scale. The total N budget for the UK was estimated to have declined from -1941 ktonnes N/year in 1990 to -1446 ktonnes N/year in 2012, which meant that the UK was a net source of total N, with the magnitude of this source having declined since 1990 and was expected to decline until at least 2020. Although the study of Worrall et al. (2016a) is important for providing a total N budget for the UK, a key limitation of the study was that the total N budget was not spatially distributed. Other studies (Lord et al. 2002; Bouwman et al. 2005; Ti et al. 2012) have developed a spatially-distributed N_r budget but not calculated a spatially-distributed total N budget.

Most of previous studies (Galloway et al. 2004; Worrall et al. 2009; Worrall et al. 2015) have just focused on N_r budgets but have only derived the nitrogen surplus or deficit at an individual catchment or national level. However, in many countries, nitrogen surplus or deficit could be highly variable spatially, meaning that some areas could be severely affected by excessive nitrogen gain or loss, but others not. Therefore, a spatially-distributed nitrogen budget provides a more powerful N balance indicator than any single national N budget result. In addition, previous spatial N budget studies (Lord et al. 2002; Bouwman et al. 2005; Ti et al. 2012) excluded some major N pathways (i.e., N_2); therefore, and were therefore incomplete. This study fills this gap in the literature by not only including flux of all major N pathways but also distributes the N flux of each pathway by land use and soil type to construct a spatial N budget across Great Britain (GB). It aims moreover to present spatially-differentiated total N budget that includes a comprehensive list of N inputs (biological N fixation, atmospheric deposition, food and feed transfer, and inorganic synthetic fertilizer) and outputs (atmospheric emission, terrestrial denitrification, fluvial flux loss from the soil, gas emissions from sewage treatment plants, direct sewage flux loss, and groundwater loss). Although decomposition of organic matter was not considered as a separate pathway in the present study, gaseous N produced through organic decay was accounted for in the total N emission pathway and the dissolved organic N was accounted for in the fluvial N loss pathway. The approach means that it is possible to identify the N balance (sink or source) for different land uses and so to analyse the impact of land use change on the N budget of GB.

Approach & Methodology

Data and study area

GB is an ideal place to construct a spatial total N budget. Firstly, according to Worrall et al. (2009), GB is a hotspot for fluvial N_r flux and the export of dissolved N from the GB (275 - 758 ktonnes N/yr) is higher than any other region of same size in Europe. Secondly, it has already been demonstrated that there are detailed records of N inputs and outputs for GB (Worrall et al. 2016a; Bell et al. 2011).

Due to the availability of land use and soil type data across GB (England, Scotland and Wales) but limited availability elsewhere in the UK (i.e., Northern Ireland), the present study will develop the spatial total N budget at a 1 km^2 grid scale for GB only and not for the entire United Kingdom (UK).

Methodology

The GB total N budget was estimated based on the gross nitrogen balance methodology (OECD, 2007) which calculates all inputs and outputs from each 1 km^2 area. The present study examined all possible pathways of N (Fig. 1). The input pathways considered were: biological N fixation; atmospheric deposition (wet and dry include N fixed from lightning); food and feed import; and inorganic fertilizer. The output pathways considered were: atmospheric emissions; terrestrial denitrification; food and feed export; fluvial losses from the soil; gas emissions from sewage treatment plants; direct sewage flux loss; and ground water loss. Because GB is a net importer of food and feed, these were considered here as an input pathway (Worrall et al. 2015).

N inputs

Biological N fixation is a major input of N to land, occurring in both agricultural and natural ecosystems. In GB, the major N-fixing crops are legumes (beans, peas) and clover. For agricultural ecosystems, biological N fixation rates were assumed to be 4 tonnes N/km^2/yr for beans and peas; and 15 tonnes N/km^2/yr for clover (Smil, 1999). For agricultural land, the land areas of the respective crops were obtained from the June Agricultural Census (DEFRA, 2001 – 2015). Therefore, total biological N fixation in agricultural ecosystem was estimated by scaling the nitrogen fixation rate of the identified crops by their areas, respectively. For natural ecosystems (i.e. non-agricultural lands), the UK was divided into classes of forest and grassland; these areas were identified from the Centre for Ecology & Hydrology (CEH) land cover map (https://www.ceh.ac.uk/services/land-cover-map-2015). Nitrogen fixation in temperate forests is well studied (Cleveland et al. 1999) and there is no substantial difference in rates of biological N fixation between coniferous and deciduous forests (Boring et al. 1988). Therefore, the rates of N fixation in temperate forests can be used as average rates of

N fixation for all forests in GB. Forest and grassland biological N fixation rates were obtained from Cleveland et al. (1999), who assumed a constant value of 0.04 tonnes N/km^2/yr for forest and 4.70 tonnes N/km^2/yr for grass. Note the study of Cleveland et al. (1999) did include values from the UK. An estimated uncertainty in biological N fixation of ±25% was calculated from published ranges (Smil 1999; Cleveland et al. 1999).

N_r in the atmosphere was mainly from fossil fuel combustion, N fertilizer application and agricultural development, with 70 - 80% N_r in atmosphere deposited to land surface and surface water by dry deposition and wet deposition (Asman 1998; Goulding et al. 1998). The other 20-30% of the atmospheric N_r remained in the atmosphere or was transported offshore (Asman 1998; Goundling et al. 1998). Because most of the N_r emissions would be deposited to the land surface or surface water, previous studies have constructed a relationship between N deposition and atmospheric N emissions (Asman 1998; Goulding et al. 1998). This relationship can be used to estimate N deposition when atmospheric N emissions data are available, but this relationship was not suitable for a distributed assessment at the national scale. For GB, consistent atmospheric deposition data have been recorded since 2004 at a 5 km^2 resolution (http://www.pollutantdeposition.ceh.ac.uk/data). For the purposes of this study, these data were converted to a 1 km^2 grid scale. Specifically, atmospheric deposition at 5 km^2 resolution are based on a grid-average of multiple land classifications. In ArcGIS, the point data of atmospheric N deposition were created from 5 km^2 raster data using a point to raster tool. The raster data at 5 km^2 resolution were then converted to the polygon data at 5 km^2 resolution using the Raster to Polygon tool. To get the deposition polygon data at 1km^2 resolution a new fishnet and fishnet point at 1 km^2 resolution was generated using create fishnet tool and spatially joined with the polygon deposition data of 1 km^2 resolution using the spatial join tool. Atmospheric deposition data were reported by Fowler et al. (2005). However, neither their data nor current atmospheric deposition monitoring data include the deposition of dissolved organic nitrogen (DON). Previous studies only provide precipitation DON concentration but do not provide the amount of total wet DON deposition for the UK. However, the Moor House upland monitoring site in the UK (https://www.ceh.ac.uk/our-science/monitoring-site/moor-house-enabling-long-term-uplands-research) reports annual DON deposition between 1992 and 2003 (Worrall et al. 2012a). DON deposition reported by Worrall et al. (2006) as being between 0.01 and 0.15 tonnes N/km^2/yr was quite low when compared to the deposition of the other compounds of N at Moor House such as inorganic N (0.87~4.26 tonnes N/km^2/yr). Thus, DON deposition measured at Moor House was applied across GB. In addition, it was also possible to estimate the C/N ratio for atmospheric deposition at Moor House. This was used to estimate DON deposition from sites where DOC deposition data are available. There were 3 sites with recorded DOC deposition. DOC deposition values reported in Worrall et al. (2006) were also quite low (0.73 to 4.83 tonnes C/km^2/yr). Given a C/N ratio of 25, DON deposition would vary from 0.02 to 0.19 tonnes N/km^2/yr. Therefore, the total atmospheric N deposition could be estimated for each 1 km^2 across GB. Because neither Fowler et al. (2005) nor current atmospheric deposition monitoring data were accompanied by an error estimation, an uncertainty of ±80% was ascribed as a credible error for atmospheric deposition in this study.

For N in food and feed transfers as well as seed and plant transfers, the UK's Department of Environment, Food & Rural Affairs (Defra) has recorded trade data in food, feed, and drink including indigeneity and degree of processing, since 1988 (Defra, 2015). The key commodities of the Defra data were: whisky, wine, cheese, poultry meat, poultry meat product, beef, veal, wheat, lamb (mutton), pork, breakfast cereals, milk, cream, bacon, ham, butter, egg, egg product, fresh vegetables, fresh fruit and salmon. The commodity trade data in food, feed and drink can be converted to N trade data by reference to the average N contents of food, feed and drink by means of the McCance and Widdowson (Food Standards

Agency, 2014) composition of foods integrated dataset (CoFID). Worrall et al. (2009 and 2016a) used commodity trade data to estimate the amount of food and feed transfer for the UK, but this method cannot spatially distribute the amount of food and feed transfer to a 1 km^2 resolution. To calculate the amount of food and feed transfer at a 1 km^2 resolution, the food and feed transfer was divided into livestock N balance, human N balance, and crop N balance. In this study, the livestock N balance and crop N balance were quantified, following the N surplus method used by Lord et al. (2002) who estimated all fluxes of input and output for livestock and crops. The approach of Lord et al. (2002) was used to calculate the N balance for each category of livestock (sheep, cattle, pig and poultry) and crop (crop and non-crop) at a 1 km^2 resolution. In addition, the human N balance can be estimated from the difference between human demand and human output using the approach of Boyer et al. (2002). The human output was considered as sewage flux which would be accounted for in fluvial loss and gas emission from sewage treatment plants. In this step, the human balance is considered as the input per human. Human input flux was assumed to be entirely due to human N consumption from an average diet which was taken from the Food and Agriculture Organization of the United Nations (FAO: http://www.fao.org/home/en/). The N surplus of crop, livestock and human N consumption are only reported within government or published data sources. The uncertainty provided by each individual source was accepted. The uncertainty of crop and livestock were estimated to be ±80% based on Lord et al. (2002). The uncertainty of human N consumption (also ±80%) was provided by the FAO.

The amount of inorganic N fertilizer application in the UK was obtained from the British Survey of Fertilizer Practice which has recorded synthetic inorganic fertilizer inputs from 1992 to 2015 (British Survey of Fertilizer Practice, 1992~2015). For the period 1990-1992, the fertilizer input rates were obtained from Mattikalli and Richards (1996). The reports of the British Survey of Fertilizer Practice not only provided overall N consumption per hectare for each year but also provided average field rates for major tillage crops. Based on that study, the average field rates can be used to estimate N fertilizer application across GB when considered in conjunction with the CEH land cover map and June Agricultural Census (DEFRA, 2001 – 2015). The British Survey of Fertilizer Practice reported an uncertainty of ±9% in the input of inorganic fertilisers.

N outputs

Atmospheric emissions considered here include: NH_3 volatilisation, NOx (NO, NO_2 and N_2O) and industrial emissions of N_2. The record of nitrogen gases (NH_3, NOx), including those emissions from agriculture and industrial sources across GB, was obtained from UK's National Atmospheric Emission Inventory (NAEI). The UK's NAEI provides NH_3, NOx (NO, NO_2 and N_2O) emission maps at a 1 km^2 resolution across GB, but does not include terrestrial or aquatic denitrification to N_2 nor emissions of N_2 from industrial sources. Because industrial N_2 emissions include factory N emissions as well as N emissions from traffic, although there are no records of industrial emissions of N_2 for GB, industrial N_2 emissions can be calculated from estimates of industrial carbon emissions (i.e., because hydrocarbon fuel when combusted releases both N and C in known proportions). UK greenhouse gas carbon emissions have been recorded since 1990 (Jackson et al. 2009; Jones et al. 2017). If the C/N ratio for each carbon-based fuel is known, then the total amount of N from industrial sources can be estimated. From previous reviews, solid fuel values have been estimated for bituminous coal (C:N = 0.011 to 0.020; Burchill and Welch, 1989); petrols (C:N = 0.001 to 0.024; Rickard 2008); and natural gas (C:N= 0.000 to 0.071; Neuwirth, 2008). Using these estimates, the N_2 released from industrial activities can be calculated as the difference between total N predicted in the combustion of fossil fuels and the recorded industrial emissions (nitrogen oxides and ammonia). During the combustion process, only high-temperature burning of fuels (typically greater than 1600 ℃) can fix atmospheric N_2 to NOx, but this process only has an effect on nitrogen species and causes no additional nitrogen release or uptake from atmosphere. This study is primarily concerned with the total N budget and not the individual species; high temperature conversion of N_2 to NOx does not alter the mass of atmospheric N. Due to a lack of information concerning the distribution of industrial N_2, here we assume that industrial N_2 is directly related to population. Therefore, the total amount of industrial N_2 emissions for GB was divided by the total GB population to estimate the industrial N_2 emission per person. The spatial distribution of industrial N_2 emissions was then calculated from the spatial distribution of the GB population. Because the NAEI emissions data are not accompanied by uncertainty estimates, here we used a conservative uncertainty estimate of ±80%. Uncertainty of industrial N_2 emission calculated from the variation in C/N ratio of carbon-based fuels was estimated at ± 50%.

In this study, denitrification includes both terrestrial denitrification and aquatic denitrification. Van Breemen et al. (2002) provided fixed rates of terrestrial denitrification for a range of land uses and estimated that denitrification rates represented 35% of N input to the atmosphere. However, because different land uses have different rates of denitrification, any spatially differentiated total N budget should consider denitrification rates for different land uses. Barton et al. (1999) examined 95 studies of N_2 flux from natural systems and calculated a value of annual N_2 flux specific to land use. This study uses the results of Barton et al. (1999) to calculate the amount of N_2 denitrification across GB for a range of common land uses (forest, grazing land, grassland and crop land). The amount of terrestrial denitrification to N_2 was estimated by the annual N_2 denitrification rate for different land uses multiplied by the areas of different land uses. Throughout this study, it is assumed that the eventual product of denitrification is N_2, even if the initial emission was the less reduced form N_2O. The uncertainty of denitrification emissions reported by Barton et al. (1999) was ±96%.

The concentrations of different N species and river discharge have been recorded at the tidal limit as part of the UK's Harmonised Monitoring Scheme (HMS; Bellamy and Wilkinson, 2001). These data can be used to calculate the flux of different N species at the tidal limit. If N losses which occur between terrestrial sources and the end of the fluvial network (in-stream loss) is known, the N loss at the terrestrial source can be estimated by subtracting the in-stream loss from the N flux at the tidal limit. Using the method of Rodda and Jones (1983), Worrall et al. (2012b) calculated the flux of different N species for each catchment (all rivers with annual discharge greater than 2 $m^3\ s^{-1}$ in UK). Using these data, the relationship between different N species fluxes and catchment characteristics (including soil type and land use) were established through multiple linear regression analysis. This statistical approach can provide the value of in-stream loss and, therefore, the fluvial loss at the terrestrial source. Worrall et al. (2012b) classified dominant soil into mineral soil, organic-mineral soil, and organic soil based on the classification system of Hodgson (1997). The present study uses the method of Worrall et al. (2012b) to map GB at a scale of 1 km^2 based on soil type and land use:

$$TDN\ flux = 5.6Urban + 4.3Grass + 1.4Arable + 4.9Mineral + 6.4OrgMin + 5.9Organic - 0.8Ksheep - 5.4Area \qquad \text{Eq. 1}$$

where TDN flux is total annual average N flux (tonnes N yr^{-1}), Urban is the area of urban area in the catchment (km^2), Grass is the area of grassland in the catchment (km^2), Arable is the area of arable land in the catchment (km^2), Mineral is the area of mineral soils in the catchment (km^2), OrgMin is the area of organic-mineral soils in the catchment (km^2), Organic is the area of organic soils in the catchment (km^2), Ksheep is the number of 1000 head of sheep (the equivalent sheep per hectare was calculated based on published nitrogen export values of the respective livestock giving a ratio of 3.1 sheep per cow (Johnes and Heathwaite, 1997)), and Area is the area of the catchment (km^2). Equation (1) was used to calculate the flux of different dissolved N species at the tidal limit and soil source.

Worrall et al. (2016b) constructed a statistical model of fluvial flux of particulate organic nitrogen (PON) using a similar method as described above. The statistical model used to calculate PON was:

$$PONflux = 213 + 0.4Grass + 0.4OrgMin + 5.0Organic - 0.13Area \qquad \text{Eq. 2}$$

The variable terms are as defined above. Equations 1 and 2 can be interpreted as an export coefficient model that was used to predict N fluvial losses at the source for each 1 km^2 grid square based on current land use and soil type maps. The uncertainty in this flux pathway was calculated from the fit of the regression equations, that is the standard error of each of the coefficients and constant were used to calculate the uncertainty in the flux. The uncertainty of fluvial flux based on different land use and soil types varied between ±28% and ±45% depending on the N species in the flux and the mixture of land use and soil types within any particular 1 km^2 grid square.

Although net in-stream loss calculated from Equation 1 will have included the N flux into groundwater, or indeed from groundwater to the stream network, a portion of N flux will be from the terrestrial biosphere via direct recharge to groundwater instead of entering the river network. Here direct recharge to groundwater was considered as a net N output pathway (loss to groundwater) because since 1990 nitrate concentrations have increased in UK groundwater (Stuart et al. 2007), and so the flux to groundwater was considered as a net N output even though some proportion of N in groundwater will contribute sooner or later to the fluvial flux. Stuart et al. (2007) calculated that the nitrate sink to UK groundwater occurs at a rate of 15 ktonnes N/yr which was considered here as the total amount of N loss to groundwater. To obtain groundwater N loss at a scale of 1 km^2, the total amount groundwater loss was evenly distributed at a 1 km^2 scale across all areas delimited in the aquifer map of GB (British Geological Survey). Stuart et al. (2007) reported an uncertainty estimate for groundwater N loss of ±50%.

The N flux from human sewage and industrial waste direct to the surrounding shelf sea were reported by the Oslo and Paris commission (OSPAR Commission, 2015). The direct N flux from tidal gauged areas has already been accounted for in the output pathway of fluvial N flux at soil source. The direct N flux from ungauged areas beyond the tidal limit were accounted for in this pathway (N direct loss). From OSPAR Commission (2015) report, values are reported for the upper and lower limits of direct loss of nitrate from GB to the surrounding shelf seas. The values of the upper and lower limits are considered to represent the range of the total amount of N flux direct loss to the surrounding shelf sea. Because the resolution of this study was 1 km^2, the total areas beyond the tidal limit were assumed to be the sum of the ungauged 1 km^2 area adjacent to the coastline of GB. The total amount of direct loss divided by total areas beyond the tidal limit was therefore calculated as direct loss per km^2. The uncertainty on this flux was reported by OSPAR as ±15%.

The majority of sewage produced in GB is treated within sewage treatment plants. Treatment of wastewater can lead to formation of N_2O (Parravicini et al. 2016). In this study, sewage was assumed to be generated by humans. Because the average healthy adult does not accumulate N in their body, N consumed in the average healthy adult diet was used as an estimate of human sewage output. The difference between human sewage output and fluvial loss in urban areas (as predicted by Equations 1 and 2) was used to estimate the gas emission from sewage treatment plants. The total gas emission from sewage treatment plants can be spatially distributed across urban areas using population estimates. No uncertainty estimates were available for this flux pathway, thus ±80% was used as the default uncertainty.

Uncertainty analyses in N budget

The uncertainty of the total N budget was considered for each 1 km^2 grid of GB using the individual uncertainties estimated for each pathway as detailed above. Monte Carlo simulations were used to quantify the overall uncertainty for all pathways for each 1 km^2 grid. A total of 1000 Monte Carlo simulations were performed using Matlab.

Results

Inputs of total N

The N fixation rates were determined to be: 4 tonnes N/km^2/yr for bean and pea crops; 15 tonnes N/km^2/yr for clover; 0.04 tonnes N/km^2/yr for temperate forest; and 4.70 tonnes N/km^2/yr for grass. The distribution of biological N fixation across GB (Fig. 2a and Supplementary Material Fig. S1) depends largely on land use; thus, higher values are observed in eastern England and the lowest values are observed in northern and western Scotland.

The total N deposition data were not vegetation-specific but were based on a grid-average of multiple land classes. Total N deposited to land ranged from 0.3 to 4.5 tonnes N/km^2/yr and averaged 1.3 tonnes N/km^2/yr. The high N deposition rate occurs in urban areas and areas with intensive agriculture (Fig. 2b and Supplementary Fig. S2). The high rate of N deposition found in the areas of the Scottish-English border, the Pennines and Welsh mountains can be ascribed to high annual precipitation in these regions. In addition, some areas close to intensive agriculture, such as East Anglia, also exhibit a high N deposition rates. In contrast, low N deposition rates (below 0.76 tonnes N/km^2/yr) are observed in north-west Scotland where there are few local industrial emission sources or urban areas.

The food and feed transfer was divided into livestock N balance, human N balance, and crop balance. N movement by wildlife is an internal N transfer (e.g., as there is generally no feed input to wildlife, the N produced on land is input to wildlife and subsequently returns to land through wildlife waste), therefore, this study has assumed there is no net N loss and gain via wildlife. As stated previously, the human N balance is equivalent to human N intake minus human N output. N intake (i.e., human N dietary consumption) was previously determined by the FAO to be 4.56 kg dry matter/yr (World Health Organization 1974). Because the human N output has already been accounted for in the sewage flux loss, human N balance can be represented by human N consumption alone. Therefore, the GB spatial distribution of human N balance is equivalent to the distribution of the GB population (Fig. 2c and Supplementary Fig. S3). The livestock N balance was determined to be an output from GB with values varying from 0.50 kg N/head to 10.50 kg N/head (Table 1). Maximum input from food and feed transfer were observed in grassland areas where livestock populations are the highest (Fig. 2d and Supplementary Fig. S4). Conversely, the livestock export was zero in urban areas.

Total N input of inorganic fertilizer was the largest N input into GB. The average fertilizer rate on different cropping varied from 3.0 tonnes/km^2 for peas to 21.1 tonnes/km^2 for oilseed rape. The average value of all crops and grass was 13.8 tonnes/km^2. The largest fertilizer input was in eastern England where land use is predominantly agricultural; conversely the values decrease to zero in the Highlands of Scotland where the land use comprises predominantly mountain, heath and bog (Fig. 2e and Supplementary Fig. S5).

Outputs of total N

Atmospheric N emissions account for the largest proportion of all N outputs. Combining the different types of N_r species and determining the spatial distribution of N_r revealed the highest N emission rates in agricultural areas (Fig. 3a and Supplementary Fig. S6). Conversely, lowest N emissions were observed in the semi-natural areas of western Scotland. The observed spatial distribution of N emissions across GB is in agreement with previous studies. Sozanska et al. (2002) constructed a GB model for N_2O flux based on different land use and predicted the highest fluxes of N_2O from grassland and arable land. Davidson and Kingerlee (1997) reported NO emissions from soil with the largest emissions associated with cultivated agriculture. In addition, NH_3 emission is dominated by livestock and N fertilizer application in agricultural areas (Davidson and Kingerlee. 1997). Therefore, the highest emissions of N_r species were observed in agricultural land (Fig. 3a and Supplementary Fig. S6). In agricultural land areas, the N species emissions were controlled by N applied and deposited within this land use, such as fertilizer and deposition.

The total industrial N_2 emission rate (included N emissions from industrial factories and traffic) for GB, according to NAEI estimates, was 262 ktonnes N/yr ±80%. Total amounts of industrial N_2 emission were distributed by population, giving an average emission of 0.004 tonnes N/ca/yr. Because the industrial N_2 emission was distributed by population, urban areas were determined to have the highest industrial N_2 emission output (Fig. 3b and Supplementary Fig. S7).

Terrestrial denitrification to N_2 according to different land use from Barton et al. (1999) varied from 0.00 tonnes N/km^2/yr to 1.34 tonnes N/km^2/yr (Table 2). The available land use data only provided a coarse 'grassland' classification rather than discriminating between 'improved' and 'unimproved' grassland – the latter having no fertilizer applied to it. As seen from Table 2, the value for terrestrial denitrification to N_2 on grassland was 0.93 tonnes N/km^2/yr calculated from the weighted mean of fertilizer grassland and rough grazing land based on Barton et al. (1999). The denitrification map reveals the spatial distribution of terrestrial denitrification to N_2 according to different land use across GB (Fig. 3c and Supplementary Fig. S8). Terrestrial denitrification to N_2 rates are highest in eastern England associated with arable land use and lower in western England grassland areas.

Total N fluvial flux at 1 km^2 according to different land use varies from 0.00 tonnes N/km^2 to 12.40 tonnes N/km^2 (Fig. 3d and Supplementary Fig. S9). The estimated uncertainty on the fluvial flux calculation is summarized in Table 3. Northwest England and western Wales reveal the largest fluvial export of total N. Most areas of northern and western Scotland have a lower biological N fixation rate ranging from 0.00 to 0.30 tonnes $N/km^2/yr$. The fertilizer input was also quite low, ranging from 0.00 to 3.00 tonnes $N/km^2/yr$. Although these input pathways are lower in the highlands of Scotland than eastern England (fertilizer input 4.51~13.73 tonnes $N/km^2/yr$, BNF 2.21~4.70 tonnes $N/km^2/yr$), the Scottish Highlands still export 4.50 to 6.50 tonnes N / km^2 and much of this is as DON rather than inorganic N.

Direct recharge to groundwater (i.e., groundwater N loss) per year in aquifer areas was previously reported by Stuart et al. (2007) as 15 ktonnes N /yr since 1990. The average value of groundwater loss in aquifer areas of 0.07 tonnes N /km^2/yr was calculated based on total ground water loss and aquifer area. Thus, the distribution groundwater N loss (Fig. 3e and Supplementary Fig. S10) necessarily follows the map of UK aquifers.

The total amount of direct N export beyond the tidal limit to marine areas was 58 (±9) ktonnes N in 2015 (OSPAR Commission. 2015). The value of direct N loss of 6.8 tonnes $N/km^2/yr$ was calculated from total N direct export to marine areas and total ungauged areas; the distribution of direct N loss is shown in Fig. 3f and Supplementary Fig. S11.

The N gas emission rates from sewage treatment plants was determined to be 0.0019 tonnes N/ca/year. Because all major sewage treatment plants are located in urban areas, land use maps were used to identify urban (rural) areas for inclusion in (exclusion from) the calculation (Fig. 3g and Supplementary Fig. S12).

The crop balance was the output from terrestrial biosphere. In this study, the grass removal rate was negligible as it has already been considered as an internal transfer with livestock. The average value of arable crop removal was determined to be 9.48 tonnes N/km^2. Therefore, the distribution of crop removal N output has just two values (9.48 tonnes N/km^2 for arable land use and 0.00 tonnes N/km^2 for non-arable land use) and the distribution follows that of arable land across GB (Fig. 3h and Supplementary Fig. S13).

Overall, the total N budget can be calculated by combining all major N input and output pathways across GB based on 1 km^2 resolution. Table 4 details the total N budget of GB based on the calculated values for each of the input and output pathways. Inorganic fertilizer was the largest nitrogen input to GB which accounted for 60% of total input. A spatially-distributed total N budget of GB was constructed by calculating the difference between all inputs of N and all outputs of N (Fig. 4). The 95% confidence interval of total budget is shown in Fig. 5a and Fig. 5b. Moreover, Fig. 6 which represent the distribution of sinks and sources that are 95% confident less or greater than zero. For the whole of GB, 66% of 1 km^2 grid squares are net sources while 34% of the 1 km^2 grid squares were estimated to be net sinks. On this spatial N map, the net sink of total N (input>output) represents N accumulation in the soil. Conversely, the net source of total N (input<output) represents N losses to the atmosphere and surrounding marine environment (Fig. 4). For each individual 1 km^2, there is considerable spatial variability in total N inputs, ranging from 0.68 ± 0.21 tonnes N/km^2/yr in northern Scotland to 73.86 ± 22.16 tonnes N/km^2/yr in London. The largest N output areas are also found in London where the mean value was -112.71 tonnes N/km^2/yr. The lowest value of total N output areas was -0.71 tonnes N/km^2/yr, found in north-west Scotland. At a national scale, the total N budget of 1 km^2 grid squares ranged from

-21 ± 3 tonnes N/yr to +34 ± 5 tonnes N/yr. Major sink areas were located in western England and northern Wales where fertilizer N application and biological N fixation rates are high and dominate the N input. Furthermore, high fertilizer application rates also result in high N deposition in those areas. The major N source areas are located in big cities, most notably London. The total N output is highly correlated with population density, indicating that high population may enhance N output. In addition, NO and NO_2 emissions released from those areas are higher than other areas due to fossil fuel combustion, particularly via natural gas combustion in domestic central-heating boilers and power stations.

Discussion

The population of GB increased from 54.38 million in 1971 to 64.17 million in 2015 and is very likely to continue to grow in the future (Office for National Statistics - https://www.ons.gov.uk/). In this study, industrial N_2 emissions, N gas emissions from sewage treatment plants and food input were assumed to have a direct relationship with population size whereas other pathways were not. To account for population influencing N fluxes, we conducted a correlation analysis between population and the total N budget for all 1 km^2 grid squares. A significant positive correlation between total N budget and population was found (r^2 = 0.83, p = 0.033) - as would be expected given the assumptions of this study. The implication is that increasing population may increase the total N budget. Furthermore, the total amount of N released to the environment by human activity in 2015 is estimated to be -16.65 kg N/ca/yr, suggesting that high population density areas are more likely to be source areas.

The evaluation of a land use change effect on N fluxes was discussed by Tecimen et al. (2017). Tecimen et al. (2017) concluded N fluxes was strongly influenced by land-use change and the land use type mainly determine the current N budget status. In this study, the proportion of N budget status (sink and source) for different land uses was not the same. The proportion of sink or source areas represented by each land use area is shown in Table 5. In urban land use areas, the mean value of the N budget was -19 (±2) tonnes /km^2/yr, ranging from -20.5 tonnes /km^2/yr to 1.2 tonnes /km^2/yr and 97% of urban land use areas were source areas. In grassland areas, the total N budget ranged from -2.4 tonnes/km^2/yr to 15.5 tonnes/km^2/yr with a mean value of 5.5 tonnes/km^2/yr. In total, 65% of grassland use areas were sink areas. For arable land, the mean value of the N budget was -11.8 tonnes/km^2/yr with only 1.5% of arable land use identified as a sink area; thus, arable land use in GB can effectively be considered as a source area. Therefore, on average, arable land use areas lose N to the surrounding environment whereas grassland areas store N in the soil. This distribution of sinks and sources by land use type is consistent with Lord et al. (2002) who concluded that the conversion of grass to arable would increase N losses; furthermore, the land use change itself was considered a major factor that affected the N budget given ploughing of grassland and resultant mineralisation. For urban land use, there is no inorganic fertilizer input or biological N fixation. Inorganic fertilizer was the largest N input, sequentially, followed by biological N fixation, for other land uses (grass and arable land use). Yoshida et al (2017) estimated spatial distribution of N input by different land use and concluded land use change may lead N input change. Because the different land use change N input, the status of N budget will change with land use change. In this study, the land use change was also changed the status of N budget. When grassland is converted to urban land use, the total N input will become less than the total N output; thus, these areas will become N source areas. When arable land use is converted to grassland use, ploughing to plant grass seed would initially result in mineralisation but thereafter the grassland would eventually become an N sink area.

In this study, every attempt has been made to include a comprehensive survey of all major N pathways. However, there is no absolute test as to whether our total N budget is complete or not. Van Meter et al. (2016) showed that reducing N loads through the Mississippi basin would take decades longer than expected as legacy N stores would sustain fluxes. The N flux from legacy N stores may miss in this study. Therefore, one potential limitation of the present study is that we could not consider the transfer of nitrogen from one year to the next or the possibility that lags can extend over several years and in effect act as a legacy reserve of nitrogen.

According to the distribution of the N budget across GB, it is necessary to consider where N accumulation is occurring, and similarly, where N loss is occurring (i.e. which reservoirs of N are being added to or depleted). In the case of industrial emissions of N, it is the organic fossil fuel N source that is being depleted, whilst for fertiliser use, the source of the N can be either natural gas or the atmosphere from which N is ultimately derived. Land use change could result in considerable accumulation or depletion of soil N reserves. Table 5 shows that grassland is more likely to be a sink of total N than either urban areas or arable land areas; therefore, conversion of grassland will result in the development of sources of N. Ploughing up of grassland will result in a loss of N in the form of organic N and the N release would follow the same trend as loss of carbon from soils (Bell et al. 2011; Barraclough et al. 2015). Alternatively, the N released from topsoil will feed into the subsoil which has not been disturbed and so could represent a location for accumulation. Therefore, accumulation in the subsoil represents an unexplored sink and potential "time bomb" of nitrogen in the vadose zone (Burt and Trudgill, 2003; Ascott et al. 2017). This study has not considered any processing within the groundwater sink; denitrification can occur in groundwater. Hiscock et al. (2003) measured denitrification rates in UK aquifers as between 0.5 to 3 N/km^2/yr; however, that would be of the order of 71 kg N/km^2/yr. For the source areas, N may be coming from denitrification of groundwater or groundwater recharge into soil. This study only considered the aquatic denitrification from the river surface not direct denitrification from groundwater or nitrate recharge into soil from groundwater.

The percentage of inputs and outputs in the different pathways reported are compared with other national N budgets in Table 6. N fertilizer application is seen to be the dominant N input in South Korea (Bashkin et al. 2002), China (Ti et al. 2012) and GB (data derived in this paper). The BNF (including both natural BNF and cultivation BNF) is the dominant N source in New Zealand (Parfitt et al. 2006). In the northeastern U.S.A, N deposition was previously found to be the largest N input (Van Breemen et al. 2002). For N output, the percentage of riverine N export was the highest of all N output pathways in South Korea (Bashkin et al. 2002), New Zealand (Parfitt et al. 2006) and GB (data derived in this paper). Denitrification and transfer to N storage were the largest N transfers in China (Ti et al. 2012) and the northeastern U.S.A (Van Breemen et al. 2002). The comparative percentage of different N pathways can give some indication that different countries may need to take different environmental management approaches to reducing N pollution.

N input from rock weathering has not been included in the spatial N budget of GB. Houlton et al. (2008) have calculated the N input from rock weathering for the Earth's surface and the N denudation flux was predicted to be between 11 and 18 Tg N/yr. According to the total N denudation flux of the Earth's surface and total surface area of the Earth, the average export from rock weathering would be between 21 to 35 g/ha/yr. Therefore, the export of N input from rock weathering is relatively low when compared to other N pathways and this N flux cannot be distributed to various land uses with a 1 km^2 spatial resolution. For this reason, the present study did not include the nitrogen input from rock weathering. The present study has also excluded N import from wood pellets because the calculated N flux cannot be spatially-distributed across GB. The Department of Energy and Climate Change (DECC) has published figures detailing UK imports and exports of wood pellets since 2008

(DECC, 2015). The available wood pellet data shows wood pellets to be an increasingly important fuel source in UK over the past decade. The importing of wood pellets from outside of the UK represents a new flux of N into the UK. The UK had a net import of 6447 ktonnes of wood pellets in 2015. The threshold values of nitrogen in wood pellets was between 0.3% and 1% (UK Pellet Council 2015). The new flux of N due to the net import of wood pellets would then be between 19 ktonnes N/yr to 64 ktonnes N/yr. Although there is no information that can be used to distribute the N flux from wood pellets to a 1 km^2 resolution, this N flux as export is already included in the values of industrial emissions to the atmosphere. However, other fuel types (excluding solids fuel, liquids fuel and gaseous fuel) have not been considered as imports into GB whereas wood pellets are coming from the terrestrial biosphere rather than the geosphere. The overall N budget of GB (including N flux from wood pellets) would become a net sink of 1087 ktonnes N/yr.

The sink and source areas across GB were calculated for each 1 km^2 area and not for the terrestrial biosphere as a whole. The major difference between a total N budget for the terrestrial biosphere and one for the whole of GB is industrial emissions of NO_X, NH_4 and N_2. Because there is currently inadequate spatial information about GB industrial emissions, this study used the population density to distribute industrial emissions across GB. For future studies, if a total N budget at the catchment scale is required, the spatial N budget presented here should be recalculated without industrial emissions. Some degree of uncertainty in our total N budget is introduced by considering industrial emissions equally across urban and rural areas according to population rather than excluding rural areas as an emissions source altogether; however, only 17.6 percentage of GB's population live in rural areas and a conservative uncertainty of ±80% is applied; thus, we assume the industrial N emission did not impact on the type of N budget (sink or source) for rural areas.

No account has been taken here of the potential effect of fertilizer application or the impact of excessive N deposition on increasing storage of N in agricultural soils. Recent studies (Gardner and Drinkwater 2009; Sebilo et al. 2013) have quantified the anthropogenic N (i.e. N fertilizer and N deposition) uptake by plants, export of N into the hydrosphere, and N retention in the soils using the N isotope method (stable isotope ^{15}N field experiments). Increasing N fertilizer use and excessive N deposition not only increased N export toward the hydrosphere but also increased N retention in soils. Sebilo et al. (2013) found that 12%-15% of fertilizer-derived N was residing in the soil and was predicted to remain in the soil more than a quarter of a century after fertilizer application. Further, Gardner and Drinkwater (2009) analysed 217 field studies which suggest that on average 29% of N fertilizer was still in the soil after one year. In this study, fertilizer application and N deposition accounted for 71% of total N input and parts of fertilizer application and N deposition will remain residing in the soil; it is therefore reasonable to assume that most of the storage of N in the soil is from fertilizer application and excessive N deposition. Thus, any increase in fertilizer application or N deposition can only increase the storage of N in the soils. Future research should focus on the sources of N accumulation in the soil.

Conclusions

This study has estimated the spatial total N budget across Great Britain and revealed the spatial pattern of N accumulation and loss. GB represents a net source of -1045 ±244 ktonnes N/yr. The total N budget at the 1 km^2 scale across GB ranged from -21±3 tonnes N/yr to +34 ±5 tonnes N/km^2/yr. Specifically, 66% of GB grid squares were source areas that export N to the surrounding atmospheric and marine environment, and 34% of GB were identified as sink areas that are accumulating N. Sink areas were predominantly in western GB and source areas of total N were predominantly located in eastern GB. For different land uses, 97% of urban areas and 98.5% of arable land use were sources of total N, whilst 34% of grassland was a net sink of total N. The total amount of N released to the environment by human activity in 2015 was -16.65 kg N/ca/yr.

References

Addiscott, T. (1988) Long- term leakage of nitrate from bare unmanured soil. Soil Use and Management, 4:91-95.

Ascott MJ, Gooddy DC, Wang L, Stuart ME, Lewis MA, Ward RS, Binley AM (2017) Global patterns of nitrate storage in the vadose zone. Nature Communications 8: Art. No. 1416.

Asman WA (1998) Factors influencing local dry deposition of gases with special reference to ammonia. Atmospheric Environment 32:415-421

Barraclough D, Smith P, Worrall F, Black H, Bhogal A (2015) Is there an impact of climate change on soil carbon contents in England and Wales? European Journal of Soil Science 66:451-462

Barton L, McLay C, Schipper L, Smith C (1999) Annual denitrification rates in agricultural and forest soils: a review. Soil Research 37:1073-1094

Bashkin V, Park S, Choi M, Lee C (2002) Nitrogen budgets for the Republic of Korea and the Yellow Sea region. In: The Nitrogen Cycle at Regional to Global Scales. Kluwer Academic, Netherlands, pp 387-403

Bell MJ, Worrall F, Smith P, Bhogal A, Black H, Lilly A, Barraclough D, Merrington, G (2011) UK land- use change and its impact on SOC: 1925–2007. Global Biogeochemical Cycles 25: Art. No. GB4015.

Bellamy D, Wilkinson P (2001) Ospar 98/3: An environmental turning point or a flawed decision? Marine pollution bulletin 42:87-90

Billen G, Garnier J, Thieu V, Silvestre M, Barles S, Chatzimpiros P (2012) Localising the nitrogen imprint of the Paris food supply: the potential of organic farming and changes in human diet. Biogeosciences 9:607-616

Boring LR, Swank WT, Waide JB, Henderson GS (1988) Sources, fates, and impacts of nitrogen inputs to terrestrial ecosystems: review and synthesis. Biogeochemistry 6:119-159

Bouwman A, Van Drecht G, Van der Hoek K (2005) Global and regional surface nitrogen balances in intensive agricultural production systems for the period 1970-2030. Pedosphere 15:137-155

Boyer EW, Goodale CL, Jaworski NA, Howarth RW (2002) Anthropogenic nitrogen sources and relationships to riverine nitrogen export in the northeastern USA. In: The Nitrogen Cycle at Regional to Global Scales. Kluwer Academic, Netherlands, pp 137-169

British Survey of Fertiliser Practice (1992-2015) Fertiliser use on farm crops for crop year 1992-2015. HMSO, London.

Burchill P, Welch LS (1989) Variation of nitrogen content and functionality with rank for some UK bituminous coals. Fuel 68:100-104

Burt TP and Trudgill ST (2003). Nitrate in groundwater. *Nitrate: Processes, Patterns and Management*, Wiley, 213-238.

Cleveland CC, Townsend AR, Schimel DS, Fisher H, Howarth RW, Hedin LO, Perakis SS, Latty EF, Von Fischer JC, Elseroad A (1999) Global patterns of terrestrial biological nitrogen (N_2) fixation in natural ecosystems. Global biogeochemical cycles 13:623-645

Commission OSPAR (1990) through 2015) Data report on the comprehensive study of riverine inputs and direct discharges (RID) in 1990-2015. OSPAR commission, Paris

Davidson EA, Kingerlee W (1997) A global inventory of nitric oxide emissions from soils. Nutrient cycling in agroecosystems 48:37-50

Defra (2001 through 2015). Agriculture in the United Kingdom. Department of Environment, Food and Rural Affairs. HMSO, London.

Department of Energy & Climate Change (DECC) (2015). Annex G: Foreign trade, Digest of United Kingdom Energy Statistics 2015: internet content only

FAO (1973) Energy and protein requirements. FAO/WHO, Geneva

Filoso S, Martinelli LA, Howarth RW, Boyer EW, Dentener F (2006) Human activities changing the nitrogen cycle in Brazil. In: Nitrogen Cycling in the Americas: Natural and Anthropogenic Influences and Controls. Springer, Dordrecht, pp 61-89

Food Standards Agency (2014) McCance and Widdowson's The Composition of Foods, 6th summary edition. The Royal Society of Chemistry, Cambridge

Fowler D, Smith RL, Muller JBA, Hayman G, Vincent KJ (2005) Changes in the atmospheric deposition of acidifying compounds in the UK between 1986 and 2001. Environmental Pollution 137:15-25

Galloway J, Howarth R, Michaels A, Nixon S, Prospero J, Dentener F (1996) Nitrogen and phosphorus budgets of the North Atlantic Ocean and its watershed. In: Nitrogen Cycling in the North Atlantic Ocean and its Watersheds. Springer, Dordrecht, pp 3-25

Galloway JN, Dentener FJ, Capone DG, Boyer EW, Howarth RW, Seitzinger SP, Asner GP, Cleveland CC, Green PA, Holland EA (2004) Nitrogen cycles: past, present, and future. Biogeochemistry 70:153-226

Galloway JN, Townsend AR, Erisman JW, Bekunda M, Cai ZC, Freney JR, Martinelli LA, Seitzinger SP, Sutton MA (2008) Transformation of the nitrogen cycle: recent trends, questions, and potential solutions. Science 320:889-892

Gardner JB, Drinkwater LE (2009) The fate of nitrogen in grain cropping systems: a meta -

analysis of 15N field experiment. Ecological Applications 19(8): 2167-2184

Goulding KW, Bailey NJ, Bradbury NJ, Hargreaves P, Howe M, Murphy DV, Poulton PR, Willison TW (1998) Nitrogen deposition and its contribution to nitrogen cycling and associated soil processes. The New Phytologist 139:49-58

Groffman PM, Altabet MA, Böhlke JK, Butterbach-Bahl K, David MB, Firestone MK, Giblin AE, Kana TM, Nielsen LP, Voytek MA (2006) Methods for measuring denitrification: diverse approaches to a difficult problem. Ecological Applications 16:2091-2122

Heathwaite AL, Johnes PJ, Peters NE (1996) Trends in nutrients. Hydrological processes 10:263-293

Hiscock K, Bateman A, Mühlherr I, Fukada T, Dennis P (2003) Indirect emissions of nitrous oxide from regional aquifers in the United Kingdom. Environmental science & technology 37:3507-3512

Hodgson J (1997) Soil Survey Field Handbook Describing and Sampling Soil Profiles. Soil Survey and Land Research Centre; Silsoe; England.

Houlton BZ, Morford SL, Dahlgren RA (2008) Convergent evidence for widespread rock nitrogen sources in Earth's surface environment. Science, 360: 58-62.

Jackson J, Li Y, Murrells T, Passant N, Sneddon S, Thomas J, Thistlethwaite G, Dyson K, Cardenas L (2009) Greenhouse Gas Inventories for England, Scotland, Wales and Northern Ireland: 1990-2007. AEA.

Janzen H, Beauchemin K, Bruinsma Y, Campbell C, Desjardins R, Ellert B, Smith E (2003) The fate of nitrogen in agroecosystems: An illustration using Canadian estimates. Nutrient Cycling in Agroecosystems 67:85-102

Johnes P, Heathwaite AL (1997) Modelling the impact of land use change on water quality in agricultural catchments. Hydrological processes 11:269-286

Johnson DW, Turner J (2014) Nitrogen budgets of forest ecosystems: a review. Forest ecology and management 318:370-379

Jones SK, Helfter C, Anderson M, Coyle M, Campbell C, Famulari D, Di Marco C, van Diik N, Tang YS, Topp CFE (2017) The nitrogen, carbon and greenhouse gas budget of a grazed, cut and fertilised temperate grassland. Biogeosciences 14:2069

Kroeze C, Aerts R, van Breemen N, van Dam D, Hofschreuder P, Hoosbeek M, de Klein J, van der Hoek K, Kros H, van Oene H, Oenema O (2003) Uncertainties in the fate of nitrogen I: An overview of sources of uncertainty illustrated with a Dutch case study. Nutrient Cycling in Agroecosystems 66:43-69

Lord E, Anthony S, Goodlass G (2002) Agricultural nitrogen balance and water quality in the UK. Soil Use and Management 18:363-369

Mattikalli NM, Richards KS (1996) Estimation of surface water quality changes in response to land use change: application of the export coefficient model using remote sensing and geographical information system. Journal of Environmental Management 48:263-282

McCance RA, Widdowson EW (2014) The Composition of Foods. HMSO, London

Neuwirth R (2008) Natural Gas Processing-Nitrogen Removal from Natural Gas: Technical and Economical Evaluation of Processes for Nitrogen Removal. VDM Verlag

OECD (2007) Gross Nitrogen Balance Handbook. OECD, Paris

Parfitt R, Schipper L, Baisden W, Elliott A (2006) Nitrogen inputs and outputs for New Zealand in 2001 at national and regional scales. Biogeochemistry 80:71-88

Parravicini V, Svardal K, Krampe J (2016) Greenhouse gas emissions from wastewater treatment plants. Energy Procedia 97:246-253

Rickard G (2008) The quality of aviation fuel available in the United Kingdom annual survey 2007. Report QinetiQ/08/01656, QinetiQ FLC, Cody Technology Park, Farnborough, UK GU14 0LX

Rodda J, Jones G (1983) Preliminary estimates of loads carried by rivers to estuaries and coastal waters around Great Britain derived from the Harmonized Monitoring Scheme. Journal of the Institution of Water Engineers and Scientists 37

Salo T, Lemola R, Esala M (2007) National and regional net nitrogen balances in Finland in 1990-2005. Agricultural and Food Science 16:366-375

Sebilo M, Mayer B, Nicolardot B, Pinay G, Mariotti A (2013) Long-term fate of nitrate fertilizer in agricultural soils. Proceeding of the National Academy Sciences 110(45):18185-18189

Schlesinger, W. H. (2009). On the fate of anthropogenic nitrogen. Proceedings of the National Academy of Sciences, 106(1), 203-208.

Shindo J (2012) Changes in the nitrogen balance in agricultural land in Japan and 12 other Asian Countries based on a nitrogen-flow model. Nutrient Cycling in Agroecosystems 94:47-61

Smil V (1999) Nitrogen in crop production: An account of global flows. Global biogeochemical cycles 13:647-662

Sozanska M, Skiba U, Metcalfe S (2002) Developing an inventory of N_2O emissions from British soils. Atmospheric Environment 36:987-998

Stuart M, Chilton P, Kinniburgh D, Cooper D (2007) Screening for long-term trends in groundwater nitrate monitoring data Quarterly. Journal of Engineering Geology and Hydrogeology 40:361-376

Ti C, Pan J, Xia Y, Yan X (2012) A nitrogen budget of mainland China with spatial and temporal variation. Biogeochemistry 108:381-394

Tecimen, H. B. (2017). Land use effect on nitrogen and phosphorus fluxes into and from soil. Eurasian Journal of Forest Science, 5(1), 8-12.

UK Pellet Council (2015). ENplus Handbook, Part 1 – General Part. Quality Certification Scheme For Wood Pellets. Brussels.

Van Breemen NV, Boyer EW, Goodale CL, Jaworski NA, Paustian K, Seitzinger SP, Lajtha K, Mayer B, Van Dam D, Howarth RW, Nadelhoffer KJ (2002) Where did all the nitrogen go? Fate of nitrogen inputs to large watersheds in the northeastern USA. Biogeochemistry 57:267-293

Van Meter KJ, Basu NB, Veenstra JJ, Burras CL (2016) The nitrogen legacy: emerging evidence of nitrogen accumulation in anthropogenic landscapes. Environmental Research Letters 11:035014

World Health Organization (1974). The work of WHO, 1973: annual report of the Director-General to the World Health Assembly and to the United Nations. Geneva.

Worrall F, Burt TP, Adamson JK (2006) Do nitrate inputs stimulate DOC production in upland peat bogs? Global Biogeochemical Cycles 20(3): GB3013.

Worrall F, Burt T, Howden N, Whelan M (2009) Fluvial flux of nitrogen from Great Britain 1974–2005 in the context of the terrestrial nitrogen budget of Great Britain. Global biogeochemical cycles 23:3017

Worrall F, Clay GD, Burt TP, Rose R (2012a) The multi-annual nitrogen budget of a peat-covered catchment - Changing from sink to source? Science of the Totel Environment 433:178-188.

Worrall F, Davies H, Burt T, Howden NJ, Whelan MJ, Bhogal A, Lilly A (2012b) The flux of dissolved nitrogen from the UK—Evaluating the role of soils and land use. Science of the Total Environment 434:90-100

Worrall F, Howden N, Burt T (2015) Evidence for nitrogen accumulation: the total nitrogen budget of the terrestrial biosphere of a lowland agricultural catchment. Biogeochemistry 123:411-428

Worrall F, Burt T, Howden N, Whelan M (2016a) The UK's total nitrogen budget from 1990 to 2020: a transition from source to sink? Biogeochemistry, 129: 325-340

Worrall F, Burt TP, Howden NJ (2016b) The fluvial flux of particulate organic matter from the UK: the emission factor of soil erosion. Earth Surface Processes and Landforms 41:61-71

Yanai RD, Vadeboncoeur MA, Hamburg SP, Arthur MA, Fuss CB, Groffman PM (2013) From missing source to missing sink: long-term changes in the nitrogen budget of a northern hardwood forest. Environmental science & technology 47:11440-11448

Yoshida, K., Tanaka, K., Noda, K., Homma, K., Maki, M., Hongo, C., Shirakawa, C., Oki, K. (2017). Quantitative evaluation of spatial distribution of nitrogen loading in the Citarum River basin, Indonesia. Journal of Agricultural Meteorology, 73(1), 31-44.

Table 1. Livestock export per head.

Item	Output (Total N tonnes)		Number (head)	N export for each category (kg N /head)
Sheep	Meat	22100	43304000	0.65
	Wool	6800		
Cattle	Meat	48100	11856000	10.50
	Milk	75200		
Pig	Meat	35500	7627000	4.65
Poultry	Meat	58500	142266000	0.50
	Egg	12500		

Table 2. Denitrification rates used in this study according to different land use.

	Land Use	Preferred value (tonnes N/km^2/yr)	
	Forestry		0.22
Grassland	Fertilizer grassland	1.34	0.93

Rough grazing land	0.32	
Crop		1.34
Other land use		0

Table 3. Summary of the source of information for every pathway; and the uncertainty on that pathway.

Input	Data source	Uncertainty
Biological nitrogen fixation	Smil (1999); Cleveland et al.(1999),MAFF(1987-2000); CEH	±25%
Atmospheric deposition	CEH: www.ceh.ac.uk	±80%
Inorganic fertilizer	British Survey of Fertilizer Practice	±9%
Human consumption		±80%
Livestock consumption		±80%
Output		
Atmospheric emission of NOx, NH_3	Naei.defra.gov.uk	±80%
Atmospheric emission of N_2	NAEI, Burchill and Welch (1989), Rickard and Fulker (1997), Neuwirth,2008.	±50%
Terrestrial denitrification to N_2	Barton et al. (1999), MAFF (1987-2000), Defra(2001-2013), Forestry Commission(2015)	±96%
Groundwater	Stuart et al. (2007),	±50%
Direct waste losses	OSPAR Commission	±15%
Fluvial N losses	Harmonised monitoring scheme; Worrall et al.2014; Neal and Davies,2003;	±28% to ±45%

Table 4. Summary of calculated median values of N inputs and outputs for 2015; and proportions of N inputs or outputs in 2015

	Flux in 2015 (ktonnes N/yr)	Proportions of N inputs/outputs
Input		
Biological N fixation	505	18%
Atmospheric deposition	306	11%
Food and feed import	295	11%
Inorganic fertilizer	1650	60%
Sub-total	2756	
Output		
Atmospheric emission	845	22%
Terrestrial denitrification	173	5%
Fluvial loss at soil	1823	48%

source		
Direct sewage flux	58	2%
Ground water loss	15	0.4%
Gas emission from sewage treatment plants	47	1%
Industrial emission	261	7%
Crop remove	579	15%
Sub-total	3801	
Total N budget	1045	

Table 5. The proportion of sink or source in the different land uses considered by the study.

Land use	Sink	Source
Urban land use	3%	97%
Grass land use	35%	65%
Arable land use	1.5%	98.5%
Total GB	34%	66%

Table 6. The percentage of inputs and outputs in the different N pathways of different countries. The source of data, 1. Bashkin et al. (2002), 2. Parfitt et al. (2006), 3. Ti et al. (2012), 4. Van Breemen et al. (2002), 5. Data derived in this paper. 6. Other N pathways just considered in this study, which included direct sewage N flux, ground water N loss, N gas emission from sewage treatment plants, industrial N emission and crop N remove.

	N pathway	South Korea [1]	New Zealand [2]	China [3]	Northeastern U.S.A [4]	GB [5]
N input	BNF	13%	60%	20%	30%	18%
	N deposition	8%	16%	24%	38%	11%
	Net food and feed import	24%	0%	3%	16%	11%
	Fertilizer	55%	24%	53%	16%	60%
N output	Atmospheric N emission	29%	22%	24%	3%	22%
	Fluvial N loss	40%	32%	18%	22%	48%
	Denitrification and soil stored	31%	31%	58%	75%	5%
	Net food and feed export	0%	15%	0%	0%	0%
	other N pathways [6]	0%	0%	0%	0%	25%

Figure Caption:

Fig. 1. Flow diagram of total nitrogen budget for each 1 km^2 gridded area. Red arrows denote nitrogen inputs while blue arrows denote nitrogen outputs.

Fig. 2. Nitrogen inputs via the different pathways identified in Figure 1 where food/feed transfer is the sum of the Human nitrogen consumption and Livestock inputs.

Fig. 3. Nitrogen outputs via the different output pathways identified in Figure 1.

Fig. 4. The total nitrogen budget of Great Britain.

Fig. 5. a) The lower limit of the asymptotic 95% confidence interval for N budget; and b) the upper limit of the asymptotic 95% confidence interval for N budget.

Fig. 6. The distribution of sink and source areas at a 95% probability for N budget.

Declaration of interests

☒ 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.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Credit Author Statement

Xiangwen Fan: Investigation, formal analysis, Writing. Fred Worrall: Conceptualisation, Supervision, Writing- Reviewing and Editing, Lisa Baldini: Supervision, Writing- Reviewing and Editing. Tim Burt: Supervision, Writing- Reviewing and Editing,

Graphical abstract

Research Highlights

1) Only with a total N budget is it possible to know where N is being lost or gained
2) Study first to give both a total N budget and one that is spatially distributed
3) Great Britain represents a net source of -1045 ± 244 ktonnes N/yr.
4) 34% of Great Britain was a net sink of total N.
5) The total N budget of the UK is equivalent to an total N export of 16 kg/ca/yr

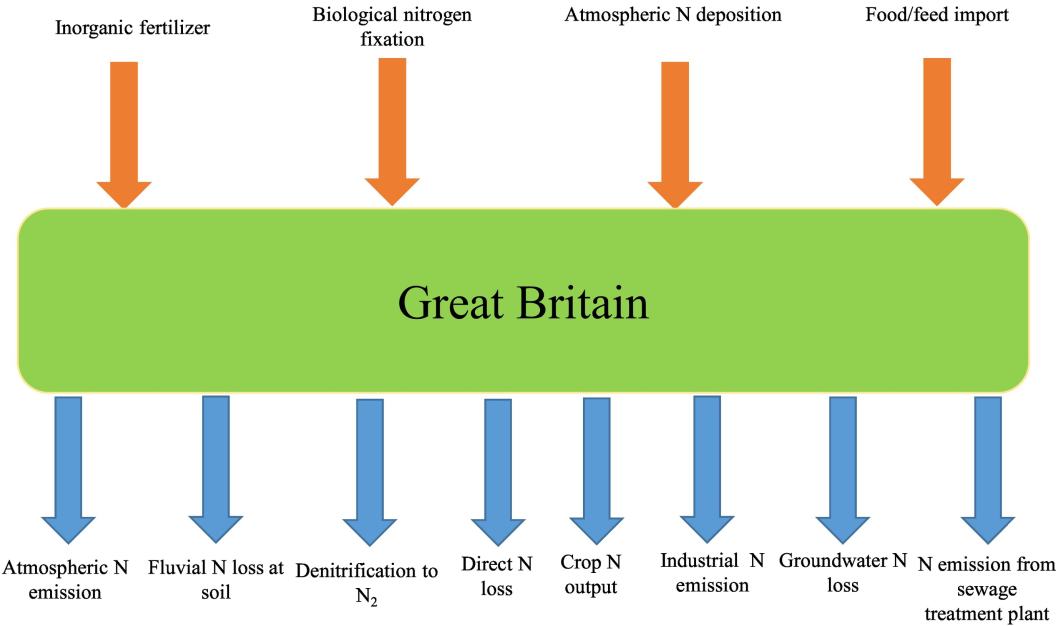
Inorganic fertilizer
Biological nitrogen fixation
Atmospheric N deposition
Food/feed import
Great Britain
Atmospheric N emission
Fluvial N loss at soil
Denitrification to N_2
Direct N loss
Crop N output
Industrial N emission
Groundwater N loss
N emission from sewage treatment plant

Figure 1

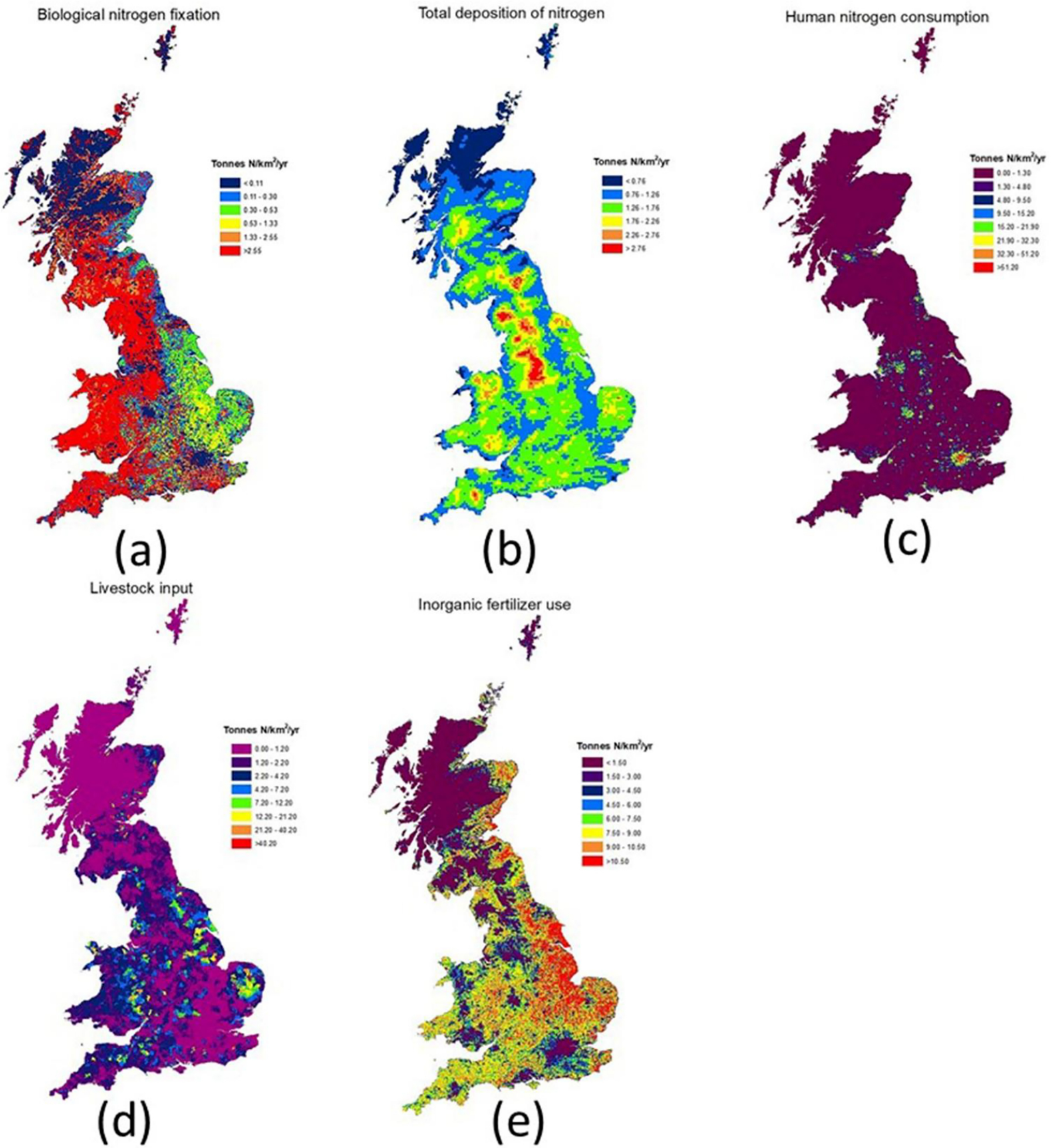
Biological nitrogen fixation
Tonnes N/km^2/yr
< 0.11
0.11 - 0.30
0.30 - 0.53
0.53 - 1.33
1.33 - 2.55
>2.55
(a)
Total deposition of nitrogen
Tonnes N/km^2/yr
< 0.76
0.76 - 1.26
1.26 - 1.76
1.76 - 2.26
2.26 - 2.76
> 2.76
(b)
Human nitrogen consumption
Tonnes N/km^2/yr
0.00 - 1.30
1.30 - 4.80
4.80 - 9.50
9.50 - 15.20
15.20 - 21.90
21.90 - 32.30
32.30 - 51.20
>51.20
(c)
Livestock input
Tonnes N/km^2/yr
0.00 - 1.20
1.20 - 2.20
2.20 - 4.20
4.20 - 7.20
7.20 - 12.20
12.20 - 21.20
21.20 - 40.20
>40.20
(d)
Inorganic fertilizer use
Tonnes N/km^2/yr
< 1.50
1.50 - 3.00
3.00 - 4.50
4.50 - 6.00
6.00 - 7.50
7.50 - 9.00
9.00 - 10.50
>10.50
(e)

Figure 2

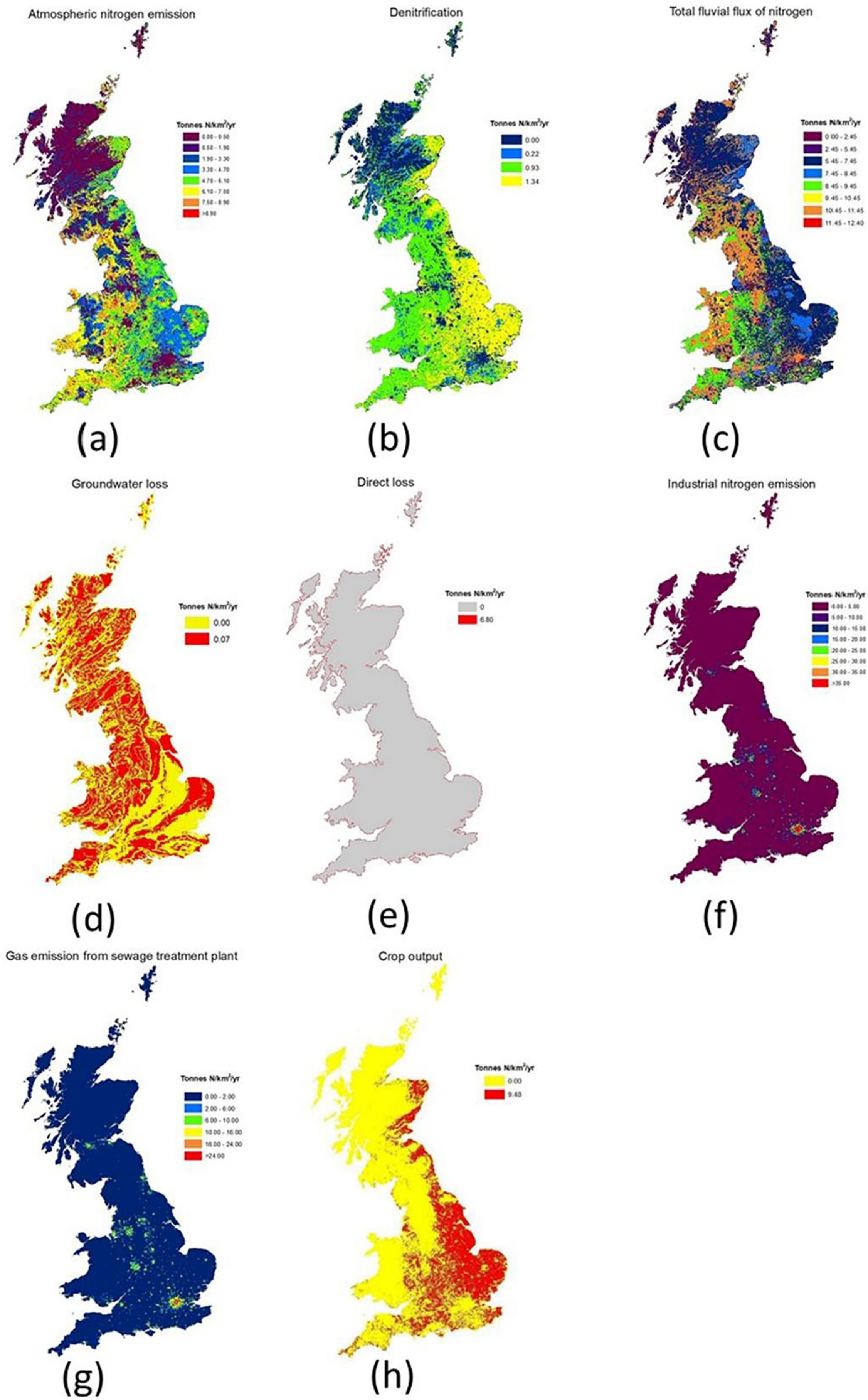
Atmospheric nitrogen emission
Tonnes N/km²/yr
0.00 - 0.50
0.50 - 1.90
1.90 - 3.30
3.30 - 4.70
4.70 - 6.10
6.10 - 7.50
7.50 - 8.90
>8.90
(a)
Denitrification
Tonnes N/km²/yr
0.00
0.22
0.93
1.34
(b)
Total fluvial flux of nitrogen
Tonnes N/km²/yr
0.00 - 2.45
2.45 - 5.45
5.45 - 7.45
7.45 - 8.45
8.45 - 9.45
9.45 - 10.45
10.45 - 11.45
11.45 - 12.40
(c)
Groundwater loss
Tonnes N/km²/yr
0.00
0.07
(d)
Direct loss
Tonnes N/km²/yr
0
6.80
(e)
Industrial nitrogen emission
Tonnes N/km²/yr
0.00 - 5.00
5.00 - 10.00
10.00 - 15.00
15.00 - 20.00
20.00 - 25.00
25.00 - 30.00
30.00 - 35.00
>35.00
(f)
Gas emission from sewage treatment plant
Tonnes N/km²/yr
0.00 - 2.00
2.00 - 6.00
6.00 - 10.00
10.00 - 16.00
16.00 - 24.00
>24.00
(g)
Crop output
Tonnes N/km²/yr
0.00
9.48
(h)

Figure 3

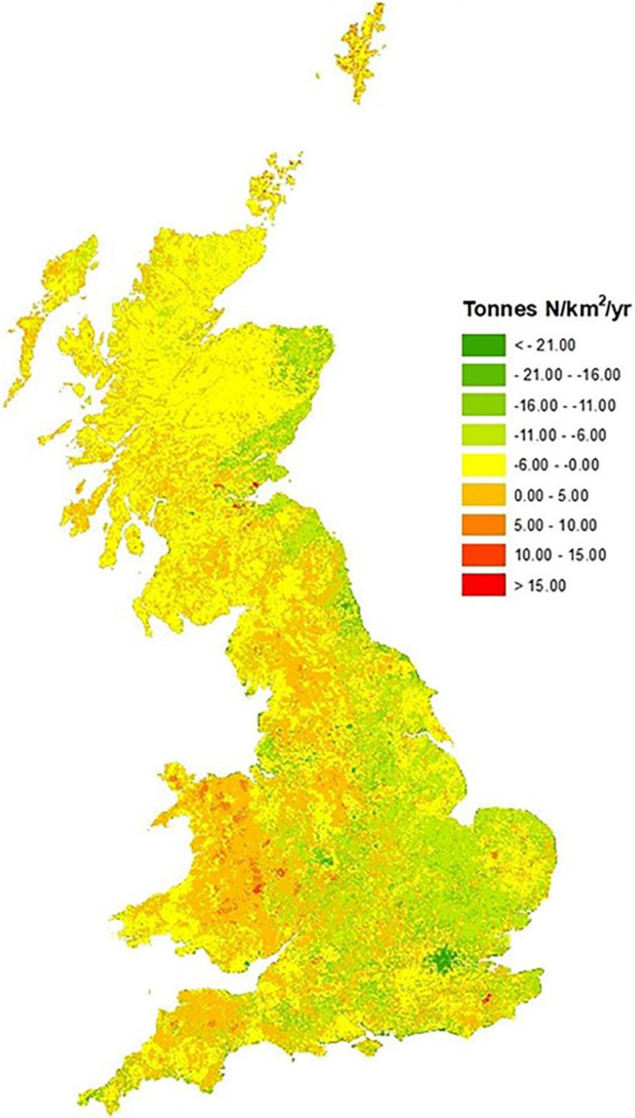
Tonnes N/km²/yr
< - 21.00
- 21.00 - -16.00
-16.00 - -11.00
-11.00 - -6.00
-6.00 - -0.00
0.00 - 5.00
5.00 - 10.00
10.00 - 15.00
> 15.00

Figure 4

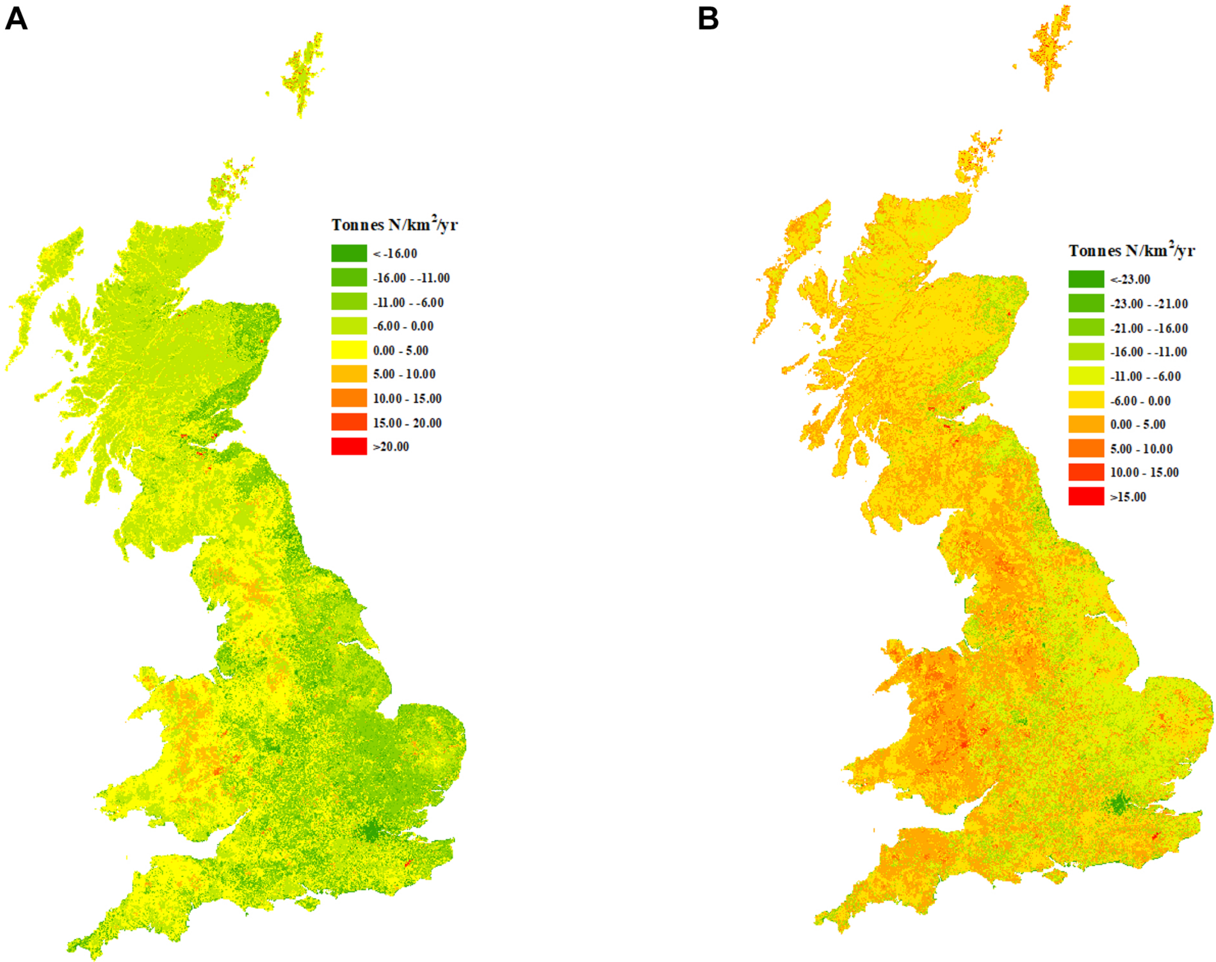
A
Tonnes N/km²/yr
< -16.00
-16.00 - -11.00
-11.00 - -6.00
-6.00 - 0.00
0.00 - 5.00
5.00 - 10.00
10.00 - 15.00
15.00 - 20.00
>20.00
B
Tonnes N/km²/yr
<-23.00
-23.00 - -21.00
-21.00 - -16.00
-16.00 - -11.00
-11.00 - -6.00
-6.00 - 0.00
0.00 - 5.00
5.00 - 10.00
10.00 - 15.00
>15.00

Figure 5

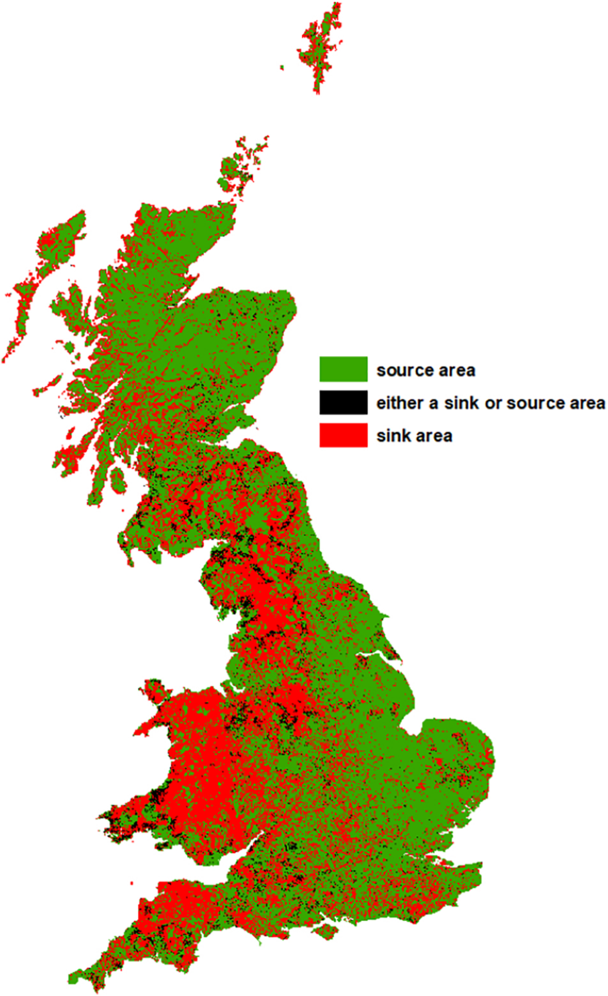

Figure 6