Evidence for nitrogen accumulation: the total nitrogen budget of the terrestrial biosphere of a lowland agricultural catchment.

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ABSTRACT

Several national-scale studies have shown that reactive N is accumulating in developed countries even when only the terrestrial biosphere is considered. However, none of these studies was able to consider the total N budget and so any discrepancy in budgets could be dismissed as being accounted for by N_2 exchange. This study considered a large (9948 km^2), mixed agricultural catchment where records of N flux, land use, climate and population go back at least to 1883. The N inputs were: biological nitrogen fixation, food and feed transfers, atmospheric deposition and inorganic fertilizers. The N outputs were atmospheric emissions (NH_3, N_2O, NO, N_2), direct waste losses and fluvial losses at the soil source. The results showed that, prior to the large-scale use of inorganic fertilizers, the total N budget of the catchment was at steady state with only a small net loss of total N. After the widespread introduction of inorganic fertilizers, the balance of the catchment shifts in favour of the net accumulation. Even accounting for losses to groundwater, the catchment was found to

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have accumulated 315 ktonnes N (315 tonnes/km^2) at a rate of 5.5 tonnes N/km^2/yr (55 kg N/ha/yr) over 35 years since 1973. We propose that the accumulation of N could be occurring in subsoils of the catchment.

Keywords: Total N; N_2; fluvial nitrogen; nitrate

1. Introduction

Several N balance studies have been conducted for individual countries and regions, e.g. UK (Lord et al., 2002, Worrall et al., 2009), Finland (Salo et al., 2007), Canada (Janzen et al., 2003) and even for the entire European Union (de Vries et al., 2011). However, these studies, even the most recent (e.g. Sutton et al., 2011, Ti et al., 2011) have been limited to considering reactive nitrogen species only (N_r). Billen et al. (2012), when considering the N imprint of Paris, do consider N_2 uptake but did not consider gaseous releases of N to the atmosphere of any species of N. Schlesinger and Bernhardt (2013) have outlined the global total N cycle. There are a number of reasons for budgets being restricted to N_r mainly the difficulty of including all possible uptake and release pathways for N_2. For example, Lord et al. (2002) suggested that estimates of denitrification to N_2 were too uncertain to include in their analysis of the N balance of all UK agricultural land. Indeed, several N balance studies have gone on to assume no long-term net accumulation or depletion in the terrestrial biosphere or at the country level (Galloway et al., 2004, Ayres et al., 1994) because it was assumed that there is steady-state with regard to total N balance and that any imbalance in N_r would be balanced by N_2 fluxes. For example, Kroeze et al. (2003), in their consideration of the N budget of The Netherlands, showed an equivalent N_r sink of 469 ktonnes N/yr in 1995 across the entire country, which they assumed was balanced by aquatic and terrestrial denitrification to N_2; however, they did not estimate either pathway. Equally, a meta-analysis of 217 field studies by Gardner and Drinkwater (2009) which suggest that on average 29% of applied inorganic N fertilizer was in the soil after one year, and Sebilo et al. (2013) have shown that applied inorganic fertilsiers in French soils upto 15% of applied N fertilizer was still present after 30 years.

Worrall et al. (2009) calculated a N_r budget for the UK from 1974 to 2005 and showed that, not only is the UK a “hotspot” for fluvial N_r flux, with higher exports of dissolved nitrogen than any other region of comparable size in the world, but that increasing fluvial fluxes were occurring at time when inputs were steady or declining, i.e. the UK remained a net sink of N_r but the size of that sink was diminishing, However, Worrall et al. (2009) could estimate neither aquatic nor terrestrial denitrification. Although they did consider atmospheric emissions from industry of N_r species, they did not consider the atmospheric emission, or consumption. of N_2 from or by industrial sources and so could not give the total N balance of the UK. Worrall et al. (in review) have endeavoured to estimate the first total N budget for a nation by estimating fluxes of N_2 from aquatic and terrestrial denitrification and from industrial emissions of N_2 and show that the UK is a net source of total N, although the size of this source has shrunk significantly since 1990.

Budgets for a nation or region are dominated by the largest input and the largest output; in the case of most European countries these would be the input of inorganic fertilizer and emission of N to the atmosphere, respectively. Of course, the first of these is an input to the terrestrial biosphere whereas the other is an output largely from fossil fuel burning. In other words, unlocking of long-term geological storage of N is influencing the contemporary N budget. If the current national or regional budget is only a net source because of releases from geological sources, then the terrestrial biosphere could be a net sink of total N. Howden et al. (2011) have modelled the export of nitrate from the Thames catchment and so doing have suggested that the terrestrial biosphere of the catchment has been a net sink of N_r for many decades. However, they did not consider a full N_r or total N budget and so could not confirm whether the terrestrial biosphere was indeed accumulating N or not.

Therefore, this study aims to be the first to estimate a total N budget for the terrestrial biosphere of a region (defined here as the River Thames drainage basin – see below). Furthermore, by constructing budgets over series of years, the long-term trend in total N balance can be established.

2. Approach & Methodology

This study has included all major N input and output pathways for the terrestrial biosphere over a length of time set by the length of the shortest record. The terrestrial biosphere defined for the study area was bounded laterally by the watershed of the catchment and the river network, i.e. once water containing nitrogen enters the stream network, it was considered to have left the terrestrial biosphere. In the vertical profile the terrestrial biosphere was taken as bounded by the atmosphere above and the bottom of the soil profile below. Although the bottom boundary was not fixed, we consider water below the water table and the unsaturated zone of the geology of the catchment to be outside the terrestrial biosphere. The lateral extent of the terrestrial biosphere was taken to stop at the boundary with the fluvial network.

The total N budget of the terrestrial biosphere of a catchment was defined as the balance between the following inputs and outputs:

$$N_{total} = N_{dep} + N_{bnf} + N_{food} + N_{fert} - N_{atm} - N_{fluv} - N_{ground} - N_{direct} \qquad \text{(i)}$$

where: N_x = the flux of total N due to x, where x is dep = atmospheric deposition; bnf = biological nitrogen fixation; food = trans-boundary food and feed transfers; fert = inorganic fertilizer; atm = atmospheric emissions; fluv = losses to the fluvial network; ground = losses to groundwater; direct = losses from sewage and waste effluent.

The inputs considered are: atmospheric deposition of nitrogen (wet and dry and would include N fixed from lightning); biological fixation; net trans-boundary food and feed transfer across the catchment boundary; and synthetic inorganic fertilizer applications. The vast majority of animal wastes in the UK are returned to the land on the same farm as they are produced (or on nearby farm units), so represent an internal transfer; this study has assumed that there is no net loss or gain of animal wastes across the catchment's watershed. Equally, by taking the boundary of the study system as the watershed of a catchment, there is no need to consider trans-watershed exchanges of surface and ground water. Clearly, this assumption could not be applied in cases where significant inter-basin transfers are evident or where the system boundary was defined politically rather than hydrologically.

This study considers the following output pathways:

(1) Atmospheric emissions (including: NH_3 volatilisation, N_2O, NO and N_2 emissions) from agricultural land use (including forestry) but not emissions from industrial sources. It was assumed that all industrial emissions come from geological sources (geosphere) and there are now fossilfuel sources currently being extracted in the study basin..

(2) The fluvial flux of N species is made up of several components. Firstly, the flux of N species from the terrestrial biosphere as it leaves the soil and enters the

fluvial network. Secondly, some of the nitrogen entering the fluvial network will be lost to the atmosphere; this aquatic denitrification is a loss to the atmosphere. The N species considered within the fluvial fluxes include: nitrate, nitrite, ammonium, dissolved organic nitrogen (DON), and particulate organic nitrogen (PON).

(3) Flux to groundwater was labelled a loss from the terrestrial biosphere in Equation (i). Although nitrogen recharging to groundwater may well eventually return to the river and be included in estimating the flux from the river of the catchment at its outlet at the tidal limit, the groundwater only represents a significant source or sink if the concentration of the N in the groundwater is changing; otherwise it is just a just a stable reservoir of N. Stuart et al. (2007) have shown a significant increase in nitrate concentrations in UK groundwater over recent decades. Further, because the lag time represented by flow through groundwater in the study catchment has been shown to be of the order of 35 years (Howden et al. 2011), large lag times would exist that net changes in groundwater storage of N would not necessarily be reflected in surface water monitoring within the timescale available to this study.

(4) The study includes direct waste effluent from sewage treatments works as loss from the terrestrial biosphere of the study catchment. The direct waste effluent flux was included because the fluvial flux of N species was considered at the point it left the soil profile and entered the fluvial network and so does not include N flux into the fluvial network from sewage outfalls. Further, sewage effluent represents the reprocessing and return of food and feed transfers. The difference between the human consumption of N and the direct waste effluent is

the amount of N lost in sewage treatment to the atmosphere or the amount returned to land.

A schematic diagram of the flows and fluxes considered by this study is shown in Figure 1.

The management of crop residues could represent a flux of nitrogen within the catchment. The UK Government banned the burning of crop residues in 1993 and most residues are now left in field after harvest. However, the extent to which this will impact the terrestrial nitrogen budget is currently not known and values of what this represents in terms of N transfer to the soil were not available. Smil (1999) recognized that records of crop residues are not maintained by any country and so this cannot be estimated here either.

The quality of the individual records varied and so this study attempted to assess the uncertainty in each input or output. Most of the nitrogen fluxes needed for a complete N budget were only reported within Government and other published data sources: hence published values were used, rather than being calculated within this study. Since the original data were not available, it was necessary to accept the error estimation provided by each individual source. In some cases, no error or uncertainty estimate was given or the error estimate was not credible. In other cases, although the reported flux error was given as a range, it was not always clear what this error actually represented (e.g. range, inter-quartile range, confidence intervals). The uncertainty estimation associated with the calculation of each pathway is discussed with each pathway. Where no credible error was available for an individual pathway, a default value of ±20% was used – this value was chosen as it represented a median of the credible uncertainty values. Given the uncertainty associated with each input and output, the total N budget for any year was calculated as the sum of individual inputs and outputs and the uncertainty in that estimate was calculated where 500 values for each input or output pathway taken at random from within the range that can be defined for each input or output. In this way estimates of the annual total N balance were calculated together with an estimate of the level of uncertainty involved.

2.1. Study site

The River Thames is the second largest river basin in the UK with a catchment area of 9948 km^2 at the Kingston gauging station in south west London, close to the tidal limit at Teddington (Figure 2). There are two important aquifers in the basin: groundwater supplies from the Cretaceous Chalk provide the majority of London’s water supply. Further north, Jurassic limestones form locally important aquifers. In between these two aquifers are clay vales where surface runoff is much more important; large areas were drained post-World War II to enable poorly-drained meadows to be converted to arable land. At present, urban areas comprise 16% of the catchment area and include the major settlements of Swindon, Oxford and Reading; the gauged area studied here lies largely upstream of London. About 8% of the basin is forested. The great advantage of the Thames catchment is that, not only has there been a very long period of water quality monitoring, but there are also extensive records of potential driver variables. The following records were used:

Water quality: monitoring at Kingston has been ongoing since 1867 making it the longest water quality record for anywhere in the world. With respect to this study, Howden et al (2010) have established the nitrate concentration and flux record over this period and the DOC concentration record (for DON) at the catchment outlet has been reconstructed. For PON flux the suspended solids records for the catchment from HMS records (outlined below) were examined.

Flow: daily mean flow records for the Thames at Kingston from 1883 were obtained from the UK National Rivers Flow Archive (NRFA: http://www.ceh.ac.uk/data/nrfa/; station number: 39001). Thus, N flux records can be calculated from 1883 onwards.

Land use: annual agricultural census returns have been compiled for each English parish since 1868 until 1988. In 1989 the UK Government moved to annual, national-scale reporting with reporting for supra-parish units in 1990, 1995 and 1999. From the year 2000 to present, the UK Government returned to reporting annually but only for supra-parish units. Therefore, in order to provide a consistent and coherent record across the period of water quality monitoring, the land-use records were compiled across the entire period 1868-2007 for the UK and for the Thames catchment for all possible years. The two records were then compared so that land use in the Thames catchment in unreported years could be estimated. The annual agricultural census does not cover woodland areas and so the area of woodland, including all forestry types, both commercial and semi-natural, was taken from statistics held by the Forestry Commission (Forestry Commission, 2007) for the years 1924, 1947, 1965, 1980, 1990, 1998 – 2002, and 2008. Linear interpolation was used to derive an annual estimate of national woodland area. In order to estimate the area of woodland in the Thames catchment, national data were rescaled to Thames catchment area. The area of urban land in the catchment was taken to be the area left unaccounted for by agricultural land or forestry. For simplicity and for comparison with other models (Worrall et al., 2012a), land use was summarised as arable land, grassland (including permanent and temporary pasture; as well as rough grazing), woodland and urban areas. Livestock numbers (overwhelmingly sheep and cattle) were derived from the same sources to give an annual time series of livestock numbers in the catchment. Of particular note with regard to land use is that Thames catchment under went a considerable land use change with the onset of the Second World War in 1939. The land use of the catchment, which had previously been dominated by grassland, underwent conversion to arable (Howden et al., 2010 – Figure S1).

Population: census returns were available for every English county for every decade from 1841, with additional projected numbers from 2001 to 2007 (http://www.ons.gov.uk). The population for the Thames catchment was then estimated as a weighted proportion of the area of each county within the catchment. Linear interpolation was used between census years in order to get an estimate of the Thames catchment population in each year of the study.

Climate: detailed rainfall and temperature records have been maintained at Oxford in the centre of the Thames basin, since the 18th century (Burt and Shahgedanova, 1998; Burt and Howden, 2011).

2.2. N inputs

Consistent atmospheric deposition records for the UK have only been maintained since 1986 (Fowler et al., 2005). However, the fluxes reported by Fowler et al. (2005) were not complete with respect to wet and dry deposition of either reduced or oxidized forms of nitrogen. Therefore, this study extended the record of dry deposition by linear interpolation of the ratio of wet to dry deposition in those years where both were reported. Fowler et al. (2005) only give records to 2001 but further records were available from the Centre for Ecology and Hydrology (CEH: www.ceh.ac.uk) for 2004 to 2006. In order to get flux estimates for 2002 and 2003, linear interpolation was used. Neither Fowler et al. (2005) nor CEH quote an error for their deposition values, but CEH quotes deposition to 2 decimal places implying the error to be of the order of ±1%: this study did not consider this a credible error, therefore we have ascribed an error of ±20%. No national depositional data were available after 2006. None of the atmospheric deposition estimates of Fowler et al. (2005), Simpson et al. (2011) or CEH (www.ceh.ac.uk) included an estimate of the atmospheric DON or PON. There is no national-scale monitoring of DON in either wet or dry deposition; however, there is at least one site in the UK where DON in total deposition has been monitored since 1992, although the site is in the north of England some 300 km north of the Thames catchment. Annual figures of DON deposition for this one site have been calculated for period of 1992 to 2003 by Worrall et al. (2006) and this can be extended through to 2007. Total deposition estimates were then rescaled for the area of the Thames catchment. It is acknowledged that the rates of DON deposition in the north of England could be very different from those further south. In order to understand deposition back over the entire period of the study, it is necessary to assume a background level of deposition and at what point in time this began to be exceeded. Howden et al. (2011), by considering the long-term history of nitrate flux from this catchment, suggested that, given very little trend in stream nitrate concentrations prior to the outbreak of WWII, the catchment was at a steady state with respect to N_r species (though not necessarily with respect to total N) and so this study has assumed that there was no significant change in atmospheric deposition to the catchment before 1936. This study has assumed linear decline in atmospheric deposition from the existing monitoring data (1986-2006) back to the year 1936 and then a constant value back to 1867.

Biological nitrogen fixation can occur in all ecosystems and can represent a significant input of nitrogen to the terrestrial biosphere. For agricultural systems the approach of Smil (1999) was used; although updates to this method have been published by Herridge et al. (2008), their updates are for crops and land use types not found in the UK. The area of nitrogen-fixing crops for the Thames catchment was considered to consist exclusively of legumes (predominantly beans and peas) and clover, as part of crop rotation. The area of each of these was available from the land-use records for the catchment. For both clover and legumes, the middle estimate of N fixation as reported by Smil (1999) was used. For biological fixation in natural ecosystems, as opposed to agricultural systems, the approach of Cleveland et al. (1999) was used. It should be noted that Vitousek et al. (2013) has suggested these values are an exaggeration. For the Thames it was assumed that the majority of natural ecosystems fell into the classes of temperate forest or temperate grassland as defined by Cleveland et al. (1999). The area of the study catchment that was not under forestry, or under clover or under peas and beans, was taken as equivalent to temperate grassland as defined by Cleveland et al. (1999). The error in the biological nitrogen fixation was calculated by using the ranges in fixation published by Smil (1999) and Cleveland et al. (1999).

Nitrogen is redistributed across boundaries with food and feed transfers as well as plant and seed transfers. Boyer et al. (2002) have estimated the food and feed transfer flux of nitrogen for the eastern USA by considering human and animal demand relative to production within the region. Alternatively, Worrall et al. (2009) used commodity trade data to estimate the nitrogen export or import for the UK. For the Thames catchment, this study used the approach of Lord et al. (2002). The agricultural census data for the Thames for cattle and sheep was used and scaled according to average values of the amount and N content of livestock outputs (meat, wool, milk) and values of feed inputs. Equally, the values of amount and N content for crop off-take of N were taken from Lord et al. (2002) combined with land use data for the Thames catchment: input to crops were considered under fertilizers (see below). Any consideration of food and feed transfer must also consider human consumption and human sewage outputs. In terms of total human consumption of nitrogen, an average of daily N intake (FAO/WHO, 1973) multiplied by the population of the Thames catchment was used. The human sewage is then returned via waste treatment. The N in waste treatment either discharges to the fluvial network; is denitrified and lost as atmospheric emissions; or is returned to land as sewage sludge (the fate of the human consumption as sewage is discussed under outputs below). By considering the input and outputs of each of crop, livestock and humans within the catchment, it was not necessary to consider what proportion of the agricultural output was used within the catchment. In the absence of other means of uncertainty estimation the error in the food and feed transfers was considered as ±20%.

Figures for the use of synthetic inorganic fertilizer in the UK were derived for the period 1962 to 2007 from surveys published by the Fertilizer Manufacturers Association and the Environment Agency of England and Wales (British Survey of Fertilizer Practice, 2008). The use of fertilizer in the UK peaked in 1987 and showed a steady, approximately linear, rise to this year from the beginning of the record in 1962. To convert the annual total fertilizer use in the UK to inputs of fertilizer per hectare for each land-use type in the study catchment, the recommended values from the UK Fertilizer Best Practice manual (British Survey of Fertilizer Practice, 2008) were used to scale the total annual fertilizer use for any individual year to the average that would be applied for each land-use type for each year. The values of annual fertilizer input are reported with an estimated standard error of ±9%. Before, 1962, N-fertilizer inputs were estimated using data from Mittikalli and Richards (1996), who collated average rates of nitrogen fertilizer use on arable and grassland in England and

Wales between 1943 and 1989 based on data published in Cooke (1975), ADAS (1979), Church (1979) and MAFF (1983). Data were reported by Mittikalli and Richards (1996) for "arable" and "grassland" in 1943, 1950, 1957 and 1962 and linear interpolation was used to estimate the values for years in between these dates. Prior to 1943 values of fertilizer inputs were estimated by linear interpolation decreasing backward through time until they equalled a value of 25 kg N/ha/yr for all fertilised land. The value of 25 kg N/ha/yr is the input expected from organic manures based on evidence from export coefficient models (Worrall and Burt, 2001).

2.3. N outputs

No estimates of N from industrial sources or any fossil fuel burning were estimated in this study as it was only the terrestrial biosphere that was being considered. Therefore, this study only considered denitrification from non-industrial sources to both N_2O and N_2; and the emissions of NH_3 from livestock within the catchment. Since net transfers of food and feed across the catchment boundary were included in the budget, it is not necessary to assume that all livestock consume food from within the catchment.

Terrestrial denitrification to N_2 was estimated using the review of Barton et al. (1999). They examined 95 studies of N_2 flux from natural systems and were able to establish significant differences between land uses in the annual N_2 export and so distinct land use types could be given an estimate and range of N_2 flux to the atmosphere. The distinct land uses considered were forestry, rough grazing land, fertilized grassland and cropland. In a similar fashion, it was possible to give estimates and ranges of N_2O flux from distinct land-use types based upon the UK model of Sozanska et al. (2002) and for NO emissions based upon ranges from

Davidson and Kingerlee (1997). Misselbrook et al. (2010) have estimated the range of NH_3 flux from a range of UK livestock types. Given the land use history for the study catchment reconstructed above, it was possible to give estimates of N_2, N_2O, NO and NH_3 flux to the atmosphere back to 1867.

The fluvial flux of N from the terrestrial biosphere and the aquatic denitrification cannot be directly estimated from available data. The flux of nitrate at the outlet of the study catchment has been calculated by Howden et al. (2010) back to 1883. The Thames water quality record at Kingston does not include DON but records of DOC, or its equivalent, for the river for the catchment have been recorded back to 1883. This study assumed that flux of DON can be derived from the flux of DOC, given a knowledge of the C/N ratio typical of fluvial DOC (Neal, 2003). Neal (2003) studied sediment from rivers with catchment areas from 373 to 8231 km^2; organic carbon contents varied from 5 to 17% with 11% as a preferred value. For ammonium it was possible to calculate a flux back to 1906. In 1906 the flux of ammonium was only 4% of the nitrate flux and so this percentage was assumed back to 1883. Given the pH of the River Thames over the course of the record, it was assumed that the flux of nitrite would be 1% of the nitrate flux (Patrick and Mahapatra, 1968).

After March 1974, the Thames at Teddington was included in the Harmonised Monitoring Scheme (HMS: Bellamy and Wilkinson, 2001) which includes the analysis of suspended solids. Therefore, the flux of suspended solids could be calculated for each year from 1974 to 2007. No significant trend was found for the flux of suspended solids over the period 1974 – 2007. The annual flux estimates of suspended solids were compared to the range of other known fluxes (nitrate, ammonia and DOC) and to annual water yield: a significant relationship was found with annual water yield and used in order to estimate flux of suspended solids back to 1883.

Furthermore, the fit of any such relationship was also used to calculate the error on any estimate of the suspended solids flux. The flux of PON can be derived from the suspended sediment flux coupled with a knowledge of the organic carbon content and C/N ratio typical of suspended sediment (Hillier, 2001).

For the fluvial fluxes calculated directly from Thames water quality record using an interpolation method (Littlewood et al., 1995), then the error would be due to the sampling frequency: a minimum sampling frequency of monthly within the HMS means a maximum error of 14% (Worrall and Burt, 2007). For the PON flux, the error was both the error in the extrapolation method and, along with the estimation of DON and PON, the variation in the composition. The calculation of the DON and PON fluxes required use of literature estimates of the C/N ratio of the dissolved and suspended matter and the organic carbon content of the suspended sediment. Hillier (2001) studied suspended sediment throughout the River Don catchment in Scotland (area = 1320 km^2); the average C/N ratio was 8.1 with a range of 5.2 (n=13): this range was used here.

The fluvial flux as calculated above is the loss at the tidal limit and not the flux as the water enters the fluvial network. Therefore, the fluvial flux at the tidal limit will be an underestimate of the losses from the terrestrial biosphere as it does not account for in-stream losses and would include any in-stream gains in nitrogen. The processing of nitrogen species in streams was not considered by Smil (1999) or Boyer et al. (2002, 2005) but was by Marsh (1980). Nitrogen can be lost from rivers through immobilisation in the stream biomass or denitrification to the atmosphere. Rivers can themselves be sources of nitrogen as PON and DON and, given the definition of the terrestrial biosphere, i.e. confined to the soil profile and biomass upon it used in this study, then both groundwater influxes and direct sewage inputs represent in-stream sources. However, available methods for calculating in-stream losses of nitrogen species have differing approaches to distinguishing between these sources and some merely estimate loss of N within the stream network from whatever source. Here, the losses of N within the Thames estimated by four different methods. Firstly, Kroeze et al. (2003) reviewed N retention in surface waters, regardless of source, and their figures for rivers, rather than those for lakes, indicate that retention was between 11 and 50% of the input. Secondly, Seitzinger et al. (2002) proposed an empirical relationship relating %N removed to depth of water body and residence time: again regardless of source. Thirdly, Worrall et al. (2012a) have assessed the changes in the flux of DON, nitrate and ammonia for up to 169 catchments. By comparing differences in soil and land use between catchments with known dissolved N flux, it was then possible to assess the extent of net loss with increasing catchment size. Once the net loss was estimated, then the loss at the soil source was readily calculated – in this case a net loss in-stream across a catchment of 63%. The approach of was also independent of source as it considered a range of catchments with and without groundwater influence, and included urban land use which may be considered indicative of sewage inputs. Fourthly, Worrall et al. (2012b) have applied an export model to UK land use history since 1925 to estimate the flux of nitrate from UK soils at source. The export model applied across the UK can be applied to the Thames catchment and for the land use records back to 1867. The export model can only be applied to nitrate and not other N species in the fluvial flux – this would give an in-stream removal rate of 52%. Similarly, Worrall et al. (2007a) have proposed methods for the correction of DOC fluxes for in-stream losses; their method was used here to correct DON fluxes for in-stream losses. Worrall et al. (2009) have shown that nitrate and DON comprise over 90% of the total fluvial N_r flux. Worrall et al. (2014) have studied losses of POM from across 80 catchments across the UK using methods similar to those of Worrall et al. (2012a) and found an average in-stream loss of POM 33.5%. Given the C/N ratio outlined above it was then possible to calculate PON contribution to in-stream losses and PON flux at source. The error in the total fluvial flux at source for DON, nitrate, nitr~~i~~ate and ammonia was then taken as the variation between the local estimates of in-stream losses across a catchment (52 to 63% loss – an uncertainty of ±6.5%) and the error in the flux at the tidal limit (14%) giving a percentage error of 20.5%. Therefore, the method used to assess in-stream losses has implications for whether in-stream sources and losses from these sources need to be included, but given that these are independent of the in-stream sources, therefore this study does take the approach of considering groundwater and sewage fluxes as possible in-stream sources.

Groundwater can represent an important store for dissolved nitrogen and thus also a possible source of nitrogen to surface waters. A 1 mg N/l rise in average groundwater nitrate concentration since 1990 has been observed in the UK by Stuart et al. (2007). It was possible that large amounts of N are being stored in the aquifers underlying the catchment. In order to assess the amount of storage over the course of the study period, this study assumed that the input of nitrogen to the aquifer was dominantly in the form of nitrate but other forms of dissolved N could also be transported into the aquifer. For this study it was assumed that the time course of dissolved N species would be as predicted from the reconstruction of the loss at the soil source using the method outlined above. The aquifer was assumed to consist of two parts, saturated and unsaturated. In each case, the storage of nitrate (and other dissolved N species) was considered to be due to diffusion into the matrix of the aquifer from readily mobile transport pathways. The dissolved N diffuses from the fracture or cracks into the matrix and while there, no adsorption of dissolved N to aquifer materials was assumed, but denitrification was allowed. To estimate this sink, the problem was modelled as 1D-transport into water-filled porous media. The diffusion coefficient was taken as between 3.1 and 8.5 x 10^{-8} m^2/s (based on nitrate - Gooddy et al. 2007). The denitrification rate was taken as 0.5 to 3% per year based upon studies of aquifer denitrification by Hiscock et al. (2003). Fracture spacing was assumed to be between 10 and 12 cm (Bloomfield, 1996); this is large in comparison to the diffusion distance over the times of the model. The equation was solved by Crank-Nicholson method with a time step of 1 day for the period since 1883 and spatial step of 0.25 cm with an initial concentration of nitrate in the aquifer assumed to be 1 mg N/l (Limbrick, 2003). Once the concentration profile for the aquifer material had been calculated, it was possible to calculate the mass of material stored if the following were known: the porosity of the matrix, the percentage of the total porosity that is matrix, the thickness of the saturated zone and the area of the aquifers within the basin. The porosity of matrix was taken from measurements of Chalk as between 3 and 55% (Bloomfield et al., 1995) which also encompasses the range observed for the Jurassic limestones (Neumann et al., 2003). There are no published measurements of the proportion of fracture verses matrix porosity in the aquifers of Thames basin and so this study used values between 95 and 99% for Chalk elsewhere in the UK (Burgess et al. 2005). The thickness of the active aquifers within the basin was taken as up to 30 m. If both unconfined and confined aquifers within the Thames basin were considered, then between 50 and 100% of the catchment is underlain by aquifers that could act as sinks for dissolved N. Given the ranges outlined above, the calculation was performed 100 times drawing randomly from the ranges defined and assuming uniform distribution between the ranges and thus the uncertainty in the estimation was taken from the range of these 100 values. Equally, there would be storage in the unsaturated zone as well as in the saturated zone of aquifers. It was assumed that an unsaturated zone covers between 50% and 100% of the basin area with depth between 0 and 60 m and a moisture content between 5 and 95%. The dissolved N stored in the unsaturated zone can then be calculated as for the saturated zone.

The direct flux of sewage and industrial wastes to the streams of the catchment was estimated using an export coefficient approach, i.e. a nitrogen load from sewage per head of population in the catchment was assumed based upon the review of export coefficients by Worrall et al. (2012b). The value of the per capita sewage export was 1.2 to 5.6 kg N/yr/ca (Worrall and Burt, 1999; Weber et al., 2006; Johnes, 1996; Johnes et al., 1996), with a preferred value of 4.5 kg N/yr/ca based on data from the smallest catchment. The population history of the catchment could be calculated from census returns; then the direct sewage inputs could be calculated back to 1861 with the error set by the range in the export coefficient. Gaseous emissions from sewage treatment were calculated based upon emissions factors published for the UK and Western Europe (IPCC, 2000). The difference between the amount of N input to the catchment via human consumption and the amounts lost from sewage treatment as either discharge to the river or predicted as emitted to the atmosphere was returned to land within the catchment as sewage sludge solids. It was assumed that there is no net transfer of sewage across the watershed and that all N discharged from sewage treatment within the catchment was discharged into the Thames and its tributaries, returned as sludge to land within the catchment, or lost to the atmosphere. The uncertainty in this pathway was estimated from range in the per capita sewage export coefficients and the range in the published emissions factors.

3. Results

There is not space within the manuscript to give the detail and time series of each input and output pathway and where the time series exist they are supplied in supplementary material.

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3.1. N inputs

The inorganic N deposition interpolated and extrapolated from values reported by Fowler et al. (2005) suggests a value of 15.6 ktonnes N/yr in 2006; no value was available for 2007, as discussed above. No reasonable error estimate can be provided from the original data and, given the assumption of a steady-state up to 1936, this would be an inorganic N deposition of 6.3 ktonnes N/yr – because this is extrapolated data no detailed time series is provided in the supplementary material. This value does not consider deposition of DON. The deposition of DON at the Moor House site was reported by Worrall et al. (2006) as being between 0.01 and 0.15 tonnes N/km^2/yr with no significant trend between 1993 and 2005. If the measured import at Moor House were re-scaled to the study catchment, then the input to the catchment would be 0.8 ± 0.7 ktonnes N/yr: therefore total N deposition in 2006 of 17.1 ktonnes N/yr (Table 1).

The biological nitrogen fixation (BNF) varied from 13 ± 3 ktonnes N/yr in 1883 to 10.4 ± 2.5 ktonnes N/yr in 2007 (Table 1 – supplementary material – Figure S2) with a peak year of 1960 when it peaked at 14.6 ± 3 ktonnes N/yr and has been declining ever since.

The trans-boundary transfer of food and feed to agriculture was an N input to the study catchment projected to have been 19.4 ± 3.9 ktonnes N/yr in 1867 but only

9.9 ± 2 ktonnes N/yr in 2007 (Table 1 – supplementary material – Figure S3). It was projected to have peaked in 1878 and there has been no significant trend on this transfer since 1994. Human consumption of N has increased in line with population growth in the catchment where in 1861 the population of the catchment was 911000 represented an intake of 22.1 ktonnes N/yr but by 2007 this had increased to an intake of 91.4 ktonnes N/yr based on a population of 3.77 million people. Working within the Seine catchment, Billen et al. (2012) found that the food and feed trtansfers represented a net export of N from the catchment.

The input of synthetic inorganic fertilizer was by far the largest nitrogen input into the basin, varying from an estimated 10.1 ktonnes N/yr in 1867 to a peak input in 1987 at 67.3 ktonnes N/yr, with values declining since then to 44.8 ktonnes N/yr by 2007 at a rate of 1 ktonnes N/yr^2, (Table 1 – Figure S4). At the national scale, the decline in inorganic fertilizer input has been occurring since 1984, but the particular land uses of the Thames basin means that fertilizer inputs peaked slightly later than the UK as a whole.

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3.2. N outputs

The total N_2O emissions from the terrestrial biosphere track the projected inorganic fertilizer inputs projected to peak in 1987 at 2.9 ktonnes N/yr from a value of 0.5 ktonnes N/yr in 1867 and declining to 2.3 ktonnes N/yr by 2007 (Table 1 – Figure S5). The emissions of NH_3 were predicted to be largest at the beginning of study period at 7.5 ktonnes N/yr, declining to a minimum in 1932 at 4.1 ktonnes N/yr, rising to 5.0 ktonnes N/yr in 2007 (Figure S6). Terrestrial denitrification to N_2 was estimated as a minimum in 1904 of 3.3 ktonnes N/yr rising to a maximum of 5 ktonnes N/yr in the year 2000 (Figure S7). For NO emissions was estimated as a minimum of 0.8 ktonnes N/yr in 1913, and a maximum of 1.2 ktonnes N/yr in 1995 (Figure S8). In 2006 the total terrestrial atmospheric emissions were 13.1 ktonnes N/yr with an median $\frac{N_2O-N}{(N_2O-N+N_{2\cancel{-N}}-N)} =$ 0.31 within the ranges reported by Schlesinger (2009) for agricultural soils.

The total fluvial N flux at the tidal limit for 1904 (the first year for which complete records were available was 5.2 ktonnes N/yr (with the forms of fluvial N as 61:20:15:0.6 for nitrate-N, DON, PON, ammonia-N and nitrite-N respectively). There are two peak values: in 1977 the total fluvial N flux peaked at 27.3 ktonnes N/yr and then in 2001 at 36.6 ktonnes N/yr (equivalent to 3.7.tonnes N/km^2/yr, or 37 kg N/ha/yr) – Figure S9. In-stream losses of nitrogen follow those of the fluvial losses and are critically dependent upon the model used. However, using the model developed for the UK gives values of in-stream losses of total N from a minimum of 5.7 ktonnes N/yr in 1904 to the maximum in 2001 of 86.3 ktonnes N/yr. This means that the flux of total N from the soil source to the stream network in 2006 was 16.7 ktonnes N/yr.

The sink to the groundwater store is shown in Figure 3a and b shows that for most of the period of the record there was a net flux into groundwater storage in the saturated zone. Between 1883 and 1903, there was a net annual sink but this may be the result of not being able to know the concentration in the aquifer matrix in 1883 for which a uniform value of 1 mg N/l was assumed (Limbrick, 2003). After 1903, there was an approximately constant flux, i.e. near steady-state conditions occur once a period of establishment within the model has been achieved. The period of steady-state ends in 1939, i.e. at the beginning of the ploughing up of grassland with the onset of WWII. The flux into groundwater storage reached a maximum in 1972 at 66 ±33 ktonnes N/yr (Figure 3b); this sink has declined ever since with groundwater predicted to become a net source in 1993. The predicted sink in the unsaturated zone of the aquifers will parallel the time course of flux into the saturated zone where the maximum annual sink was between 1.4 and 5.5 ktonnes N/yr. The accumulated storage in the aquifers of the basin (both in the saturated and unsaturated zones) shows distinct changes (Figure 3a). The step changes can be associated with the step changes observed in the nitrate concentration of the River Thames as observed by Howden et al. (2010). The accumulated dissolved N in the aquifer peaks at a maximum of 1571 ± 608 ktonnes N between 2000 and 2004 and has since begin to decline. The approach here suggests that in 2006 the increase in concentration of N species in groundwater of the catchment represented a net additional store of 15.9 ktonnes N/yr.

The total flux of N from human sewage and industrial wastes has increased over the period in line with the population of the catchment from a low in 1867 of 3.1 ktonnes N/yr to 12.4 ktonnes N/yr in 2007 (Figure S10). Worrall et al. (2009) showed that due the implementation of the Urban Wastewater Directive (European Commission, 1991) the UK-wide direct flux of N declined by 50% between 1990 and 2003. The amount emitted to the atmosphere closely followed the population and by 2007 the amount released to the atmosphere from sewage treatment at 36 ktonnes N/yr with 42.5 ktonnes N/yr returned to land as sludge.

3.3. Total N budget

Given the uncertainties within each pathway, then the maximum annual source observed was in -59 ± 10 ktonnes N/yr (where the uncertainty is expressed as the inter-quartile range) and the maximum sink was in 2006 at +110 ± 26 ktonnes N/yr (Figure 4a and b) – the maximum sink was equivalent to 111 ± 27 kg N/ha. When preferred values are considered, then the maximum sink was 112 ktonnes N/yr. The total N balance can also be viewed as the cumulative sink or source over the course of the study period (Figure 4b), in which case it can be seen that within the range estimated for each flux pathway, the basin was a net source until somewhere between 1959 and 1973 when the cumulative curve reaches a minimum and between 1994 and 2004 the basin was a net accumulating sink and that accumulation increases to the present day and by 2007 was 315 ± 379 ktonnes N – which is equivalent to 32 tonnes N/km^2 or 320 kg N/ha, and accumulating at an average rate of 55 ktonnes N/yr since 1973 (the minimum in the accumulation time series – Figure 4b) - equivalent to 5.5 tonnes N/km^2/yr, or 55 kg N/ha/yr).

4. Discussion

The results predict a very large and ongoing storage of total N within the terrestrial biosphere of the Thames catchment. This raises a number of important questions. Firstly, is there evidence from other studies that such a storage could be happening? Several studies have concluded that developed countries are net sinks of reactive nitrogen (N_r – e.g. Sutton et al., 2011) and, indeed, this has been already demonstrated for this catchment (Howden et al., 2011), but those conclusions of these studies were not for the terrestrial biosphere nor for total N. When it comes to specific environments, then it is possible to assess total N budgets although there are a limited number of such studies to refer to. Hemond (1988) was the first to consider a total N budget for a specific environment - a peat bog; however, since the peat bog was a functioning sink of carbon, it is not too surprising that it was also a net sink of total N in line with the C/N ratio of the humified organic matter. Hemond (1988) recorded a net sink of total N of 0.58 tonnes N/km^2/yr. At a catchment scale, other studies have implied that the change in nitrate flux from the river over time is indicative of nitrogen storage within the catchment. Goolsby et al. (1999) estimated a net annual sink in the Mississippi Basin of 19 tonnes N/km^2 over a period of 40 years. Furthermore, Basu et al. (2010) showed a widespread occurrence of biogeochemical stationarity in large anthropogenically-disturbed catchments from a range sites across the northern hemisphere, but not for small undisturbed catchments (e.g. Hubbard Brook, New Hampshire, USA). This biogeochemical stationarity was ascribed to widespread saturation within anthropogenically-disturbed catchments meaning that, no matter what flow paths were operating, the result was the same. Therefore, although the sink predicted here is larger than those suggested by Goolsby et al. (1999) and Basu et al. (2010), this study did consider total N and not just reactive N.

Second, are the results sensitive to the considerable uncertainty in a number of the pathways being considered? The main features of the results is that they are not sensitive to the uncertainty or assumptions of the approach. The two main features of the study results are that there is now a large accumulated sink of total N within the terrestrial biosphere of the catchment and that there was an inflexion point in the behavior of the accumulated total N budget in the 1960s or early 1970s (Fig. 4). Any uncertainty would have to sufficiently large to change the scale of the accumulation or the time series of that accumulation. The largest source of uncertainty was in the terrestrial denitrification estimate but the study has already included that uncertainty and, even if the largest possible value of terrestrial denitrification was used, then all that would happen would be that the total accumulation would be lower by a value of approximately 800 ktonnes N by 2007, but this would only mean a slightly smaller rate of accumulation and the inflexion point would be offset by several years. The period of time for which information available to the study was the least uncertainty was the most recent period, i.e. the period when the largest net sinks and net accumulation were predicted. The most uncertain period was the period at the beginning of the record and so to offset the accumulation observed a larger source would have to be predicted in the second half of the record.

The time series that was most uncertain, as opposed to the uptake or release pathways, was the record of atmospheric deposition where it was necessary to assume a rate of increase from a period of steady-state and a year in which the steady state was broken (presently taken as 1936). Both of these assumptions have been based upon observations from the basin and so it would necessary to substantiate a different rate of increase; a different time at which the major increase started and value of the deposition during that period of steady-state. However, it should remembered that atmospheric deposition is an input and so to change the result it would have to be substantially lower, start increasing later than presently assumed and then increase faster the currently observed values.

Finally, it should be considered whether there was a flux pathway missing from the budget? It is always impossible to have a complete budget; however, in order to account for the estimated accumulation in the terrestrial biosphere suggested here, it would have had to have been a sink of the order of 100 ktonnes N/yr – it is just as likely that the study has failed to consider a source of total N. The major part of the terrestrial biosphere which we could not consider were the subsoils of the catchment where accumulation could be occurring.

If accumulation is occurring, then where is it accumulating? Conversely, if net loss were occurring then where was the loss coming from? In a catchment which was under intensifying agriculture, urbanization and climate change, it is easy to consider that the disturbance of soils stores means that there is a tendency to lose nitrogen just as there is to lose carbon (e.g. Bell et al., 2011, Barraclough et al., in press). Given the values of carbon loss predicted by Barraclough et al. (in press), this suggests that soils would be losing 1 tonnes N/km^2/yr (10 ktonnes N/yr for the Thames catchment). The average N loss from 1883 to 1959 predicted in this study was 20 ktonnes N/yr, i.e. 50% of the loss estimated by this study could be predicted by climate change alone, independent of intensification of agriculture or urbanization. Therefore, it is reasonable to assume that when accumulation does occur it is in the soils of the catchment and the so far this study has not considered the subsoils. It is easy to conceive that nitrogen released from topsoils could, in part, be absorbed in subsoils (if it were released in the form of DON) or stimulate biomass if it were released in inorganic forms.

5. Conclusions

The study has considered the total N budget of the terrestrial biosphere of a large mixed agricultural catchment dominated by mineral soils. The study shows that since the late 1950s the terrestrial biosphere and since 1973 has been accumulating total N at an average rate of 55 ktonnes N/yr (equivalent to 55 kg N/ha/yr), peaking in 2007 at 112 kg N/ha/yr. The accumulation of total N in the catchment was estimated to be 315 ktonnes N by 2007 (315 kg N/ha) even allowing for accumulation in groundwater. We propose that this accumulation is in sub-soils of the catchment.

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Table 1. Summary of preferred values of N inputs and outputs for 2006.

	Flux in 2006 (ktonnes N/yr)	Export in 2006 (kg N/ha/yr)
Input		
Atmospheric deposition	17.1	17.2
Biological nitrogen fixation	10.7	10.8
Food & feed transfers	99.2	99.7
Inorganic fertilisers	46.1	46.3
Sub-total	173.1	
Output		
Terrestrial atmospheric emissions	13.1	13.2
Fluvial loss at soil source	16.7	16.8
Groundwater storage	15.9	16.0
Sewage inputs	12.3	12.4
Sub-total	58.0	58.4
Total N budget	115.1	115.8

Figure. 1. A schematic diagram of the flows and fluxes considered by this study.

Figure 2. Location of the study catchment; study monitoring point at Teddington and location of the long term climate monitoring station at Oxford.

Figure 3.

a) The estimated accumulated groundwater store of total dissolved N over the course of the study period.

b) The estimated annual flux to groundwater of total dissolved N over the course of the study. The values are given as the interquartile range with a negative value being a a net discharge from ground to surface water.

Figure 4.

a) The estimated annual total N budget of the terrestrial biosphere of the catchment. The bar is given as the inter-quartile range based upon the stochastic combination within the uncertainties described.

b) The cumulative total N budget of the terrestrial biosphere of the catchment giving the median and inter-quartile range based upon range of annual values shown in Figure 4a.