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Long term simulations of macronutrients (C, N and P) in UK freshwaters

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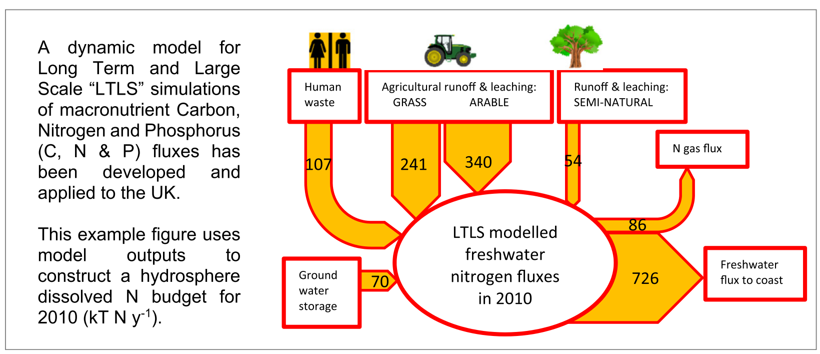
HIGHLIGHTS

- A national-scale dynamic model of freshwater macronutrients has been created.
- We reconstructed river/coastal fluxes back to 1800 using available historical data.
- From ~1900, macronutrient fluxes increased with population and industrial growth.
- The majority of macronutrients from terrestrial sources export to coastal waters.
- Measured coastal macronutrient fluxes from rivers may neglect groundwater fluxes.

GRAPHICAL ABSTRACT



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ABSTRACT

Over the last two centuries, the landscape of many industrialised nations has been transformed by the spread and intensification of agriculture, by atmospheric pollution, by human waste (rising in line with population growth), and now by changes in the climate. The research presented here aims to understand and quantify how these long-term changes have impacted UK freshwaters and the flux of macronutrients to the sea. The Long Term Large Scale (LTLS) Freshwater Model presented here used readily-available driving data (climate, land-use, nutrient inputs, catchment topography) to understand and quantify how changes in the UK's macronutrient histories have impacted on freshwater stores and fluxes. Model-reconstructed sources and fluxes of carbon, nitrogen and phosphorus (C, N and P) from 1800 to 2010 indicate that the rapid increase in the use of agricultural fertilisers after the second world war, and the rising human population, led to a rapid rise in N & P fluxes to rivers. During this period, the modelling shows that the dominant source of N in rivers changed from improved grassland to arable, the dissolved N export to rivers quadrupled, and P from human waste increased by ~600%, despite waste water treatment. The simulations also indicate a net storage of nitrates in groundwater between the 1940s and 1990s, and a net release to coastal waters post-1990; but groundwater retention and later release of C&P are less significant. Overall, modelling indicates that >75% of C, N and P entering freshwaters goes directly to the coastal waters, with 15–20% of C & N removed in river processes. These results constitute the first process-

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based integrated modelling assessment of freshwater macronutrient change at a national scale. The LTLS approach provides a methodology to develop fully-coupled global models of terrestrial, freshwater, atmospheric and marine processes that can take account of changes in land-management and climate.

1. Introduction

Over the last 200 years, pools and fluxes of macronutrients (carbon (C), nitrogen (N) and phosphorus (P)) in UK ecosystems have been transformed by the spread and intensification of agriculture, by atmospheric pollution, by human waste (rising in line with population growth but to some extent mitigated by wastewater treatment), and more recently by changes in the climate. The aim of the research described here is to understand the effects of anthropogenic and climatic influences on UK freshwaters and the consequent changes in nutrient delivery to the sea. The research forms part of the Macronutrient Cycles Long Term Large Scale (LTLS) project which aimed to understand the major changes to terrestrial and freshwater pools and fluxes of macronutrients (C, N and P) that have occurred over the last two centuries, and to develop a validated model able to forecast future changes.

Although a high proportion of the UK's terrestrial and freshwater C, N and P passes directly to coastal waters, significant amounts are stored for several years, even decades, in soils (Davies et al., 2016a), river sediments and floodplains (e.g. Walling et al., 2003), lake sediments (Dean and Gorham, 1998) and groundwater (e.g. Wang et al., 2012). Long term observations of such stores and fluxes are sparse in the UK (and internationally), and typically available only for the last 50–60 years and at selected locations, so the aim was to develop a suite of simple process-based models in order to reconstruct them at a national scale. The LTLS project as a whole (www.ltls.org.uk) undertook an integrated modelling analysis (the LTLS Integrated Model, or "LTLS-IM"), encompassing atmospheric, soil, crop and freshwater models, which aimed to explain observable pools and fluxes in different UK catchments in terms of their nutrient enrichment histories. The modelling analysis was supported by historical records and assessed with respect to observational data where available. The LTLS approach emphasised the use of process-based models and understanding to interlink the cycles of C, N and P in soils and rivers, and a model design that reflects the availability of large scale data. By taking account of historical and present day inputs and fluxes the new approach aimed to address important contemporary issues including: transfers of nutrient species and dissolved organic carbon to the sea, competing priorities between food production and water quality & quantity, the management and re-use of human waste, and long-term trends in carbon storage, as affected by climate and nutrient interactions.

The LTLS freshwater model component of the LTLS-IM provides a method of dynamically linking anthropogenic land-management practices and fluxes of nutrients/pollutants to freshwater and coastal ecosystems. This capability is important as it allows us to understand how anthropogenic-modification of atmospheric and terrestrial nutrient cycling affects freshwater and coastal ecosystems, enabling targeting of policy interventions. Very few, if any, models are currently available to satisfy this requirement. The land-surface components of whole earth system models (e.g. the land-surface model JULES (Clark et al., 2011) in UKESM (Sellar et al., 2019), CLM (Lawrence et al., 2019) and ORCHIDEE (Guimberteau et al., 2018)) aim to simulate the complexity of interactions and feedbacks between multiple environmental systems including atmospheric processes, oceans, ecosystems, vegetation and water cycles. However, few are able to comprehensively and dynamically link the nutrient fluxes between land-surface and marine systems via freshwater, although ORCHIDEE can simulate carbon fluxes from soils to freshwaters. One of the most widely used sources of nutrient fluxes to coastal waters is from the Global NEWS project (NEWS 2: Mayorga et al., 2010), which provides steady-state global estimates of river export of dissolved and particulate C, N and P under current conditions and future scenarios. Global NEWS provides steady state annual exports of dissolved and particulate C, N and P based on landuse data, agriculture and wastewater statistics, and atmospheric deposition model estimates. However, plant-soil nutrient dynamics are not dynamically represented, with soil retention and release estimates derived through a simple export coefficient approach (Johnes, 1996; Worrall and Burt, 1999; Alexander et al., 2002), while nutrient retention in sediments and water bodies is included via retention fractions estimated through calibration to observed fluxes. Loss of nutrients from river water through biogeochemical processes and losses or gains from long-term groundwater storage/release are ignored.

The LTLS Freshwater Model (or "LTLS-FM") presented here provides a dynamic, large-scale model of macronutrient C, N and P fluxes consisting of simple process-based models to understand and quantify how changes in the UK's macronutrient histories have impacted on stores and fluxes in UK freshwaters over the past 200 years.

2. Methodology: the LTLS modelling approach

The LTLS Integrated Model (LTLS-IM) combines UK-wide atmospheric, terrestrial and freshwater models of macronutrients (C, N and P). Terrestrial soil-vegetation models for semi-natural areas (N14CP: Davies et al., 2016a, 2016b) and agricultural areas (Roth-CNP: Muhammed et al., 2018) provide spatially distributed estimates of soil macronutrient storage and runoff, and other estimates such as leaf area index (LAI) required by the erosion model. These are used as input to a dynamic freshwater hydrological model (LTLS-FM: Section 4.2) of soil-moisture, runoff, river flows and nutrient fluxes. These models are driven by weather variables such as rainfall and potential evapotranspiration (PET), all on a 5 km×5 km national grid. Nutrient deposition from the FRAME atmospheric chemistry model (Dore et al., 2015; Tipping et al., 2017) is input directly to the terrestrial models, and estimates of nutrients from human waste (Naden et al., 2016) are input to the river component of the freshwater model. Fig. 1 presents a schematic of the LTLS-IM, highlighting the linked model components and data flow between them. All the models share driving datasets of weather, the landscape (soil, terrain and land-cover history) and management (grazing density, fertiliser, human waste), and provide extensive model outputs consisting of soil and freshwater macronutrients (dissolved and particulate), crop yield, erosion, gaseous fluxes of nitrogen and CO_2 and estimates of chlorophyll load in lakes and rivers.

The driving datasets are summarised in Section 3, and model components including the new LTLS freshwater model are summarised in Section 4. Typically, LTLS-FM output consists of spatial grids of macronutrient fluxes across the UK which vary in time from 1800 to 2010. For grid-cells corresponding to the locations of freshwater monitoring sites, model estimates of macronutrient fluxes can be compared to observations. This analysis (Section 5) provides an assessment of how well the LTLS-FM is able to simulate observed freshwater macronutrient fluxes, from 1974 onwards, for a wide range of catchments across Britain. The LTLS historical analysis of modelled changes in the sources, losses and fluxes of UK macronutrients from 1800 to 2010 is presented in Section 6, and the results are discussed in the context of other published studies in Section 7.

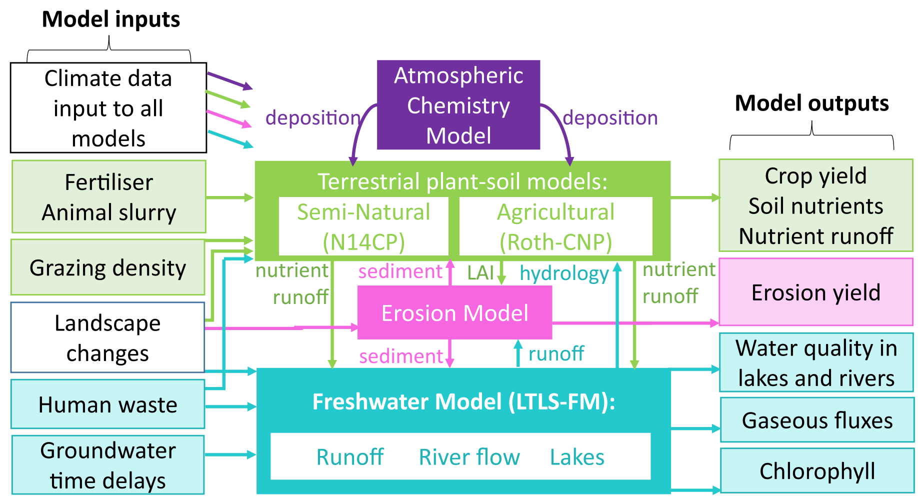


Fig. 1. Schematic of the full LTLS-IM, with arrows indicating where output from one model or dataset is input to another. Freshwater model (LTLS-FM) components are shown in blue.

3. Freshwater model driving data and observations

The full LTLS-IM (Fig. 1) comprises a set of linked models each with specific spatio-temporal data requirements. Although these data requirements vary between models, they share a common landscape and climate history from 1800 to 2010. This section briefly summarises the datasets used directly in the freshwater model.

A spatially-distributed historical scenario of significant changes in land-cover was reconstructed for the period 10,000 BCE to 2010 CE from (often limited) available data. The post-1800 historical land use scenario assumes a change from pre-1800 non-intensive agriculture (Thirsk, 1987), to more intensive and widespread agriculture by the early 20th century based on land-cover information from the Dudley Stamp Land Utilisation Survey (Stamp, 1937, 1948). The land-cover reconstruction also includes two phases of conifer plantations during the 20th century, and present-day land-cover from LCM2007 (Morton et al., 2011). Example maps showing change in dominant land-cover in each grid-cell between 1800 and 2007 are presented in Fig. 2. These maps highlight the increase in agricultural land at the expense of semi-natural, particularly rough grassland, over the last 200 years.

The soil texture data used by the terrestrial nutrient models and the hydrological model (Section 4) were obtained from the Harmonised World Soil Database (HWSD) (FAO, 2012) which provides soil property and texture classes on a ~ 1 km × 1 km resolution. In the LTLS-FM, landscape and freshwater properties such as soil texture (e.g. sand/silt/clay), slope, river/lake/reservoir dimensions and locations, floodplain extent, river network properties and bankfull flow are assumed unchanged (time-invariant) over the period 1800 to 2010. These assumptions are expected to have had negligible impact on national-scale freshwater simulations over the last 200 years, particularly when uncertainties in the historical reconstructions of weather, land-cover and anthropogenic influences are taken into account. Anthropogenic changes to the hydrological function of the landscape, such as agricultural field drains and flood defences, are not currently included in the LTLS-FM. The spatial datasets required to configure the hydrological model (section 4.2) are generated from a hydrologically corrected 50 m Digital Terrain Model (Morris and Flavin, 1990, 1994). Further lake data were obtained from the UK Lakes Portal (https://eip.ceh.ac.uk/apps/lakes/) which is a GIS-based inventory of lakes for Great Britain (Hughes et al., 2004). UK lake coverage is shown in Fig. 2 alongside the river network.

The driving data required by the LTLS-FM consist of daily precipitation, near-surface air temperature, and monthly potential evaporation (PE) estimates. These data are readily available from the mid 20th century onwards: rainfall from CEH GEAR (Keller et al., 2015), air temperature from the Met Office (Perry et al., 2009) and PE from MORECS (Hough and Jones, 1997). However, similar data for the earlier period (pre ~1960) were pieced together from a range of available datasets including sparse historical daily raingauge data and the WATCH forcing dataset (Weedon et al., 2011).

For the assessment of model performance, in-situ observations of water quantity and quality are available from ~1970 onwards. Measured daily river flows were obtained from the National River Flow Archive (NRFA: http://nrfa.ceh.ac.uk/) for gauging stations across Britain, and were used to assess the ability of the LTLS-FM to simulate observed river flows. Observation-based estimates of river nutrient loads and their uncertainty were derived following Cooper and Watts (2002) from the Harmonised Monitoring Scheme (HMS) network (Simpson, 1980) which supplies measurements of nutrient concentrations at approximately 230 sites across England, Wales and Scotland (Fig. 2) at approximately weekly to monthly intervals from 1974 to the present day. For a small number of UK sites, observations of freshwater macronutrient concentrations are available before 1970. This additional data has been obtained for three sites with long-term continuous measurements: the River Frome in Dorset, for which observations of nitrate-N, phosphorus, ammonium and calcium are available from 1965 to 2009 (Bowes et al., 2009, 2011); the River Tweed in Scotland, for which there are nitrate observations from 1961 to 1994 (Robson and Neal, 1997); and the River Thames at Kingston, where nitrate concentrations are available back to 1883 (Howden et al., 2010).

Further information about these and other datasets required only by the sub-models (e.g. models of agricultural, semi-natural land or human waste), is provided in Supplementary material (Appendix A and Table A1).

4. Freshwater and nutrient modelling

4.1. Nutrient inputs to freshwater systems

4.1.1. Atmospheric nutrients (deposition and emissions)

Nutrient deposition from the atmosphere to the landscape is a key input to the two terrestrial soil-vegetation models N14CP and Roth-CNP (Sections 4.1.2 and 4.1.3) which in turn provide estimates of nutrient runoff to the LTLS-FM. The LTLS freshwater model receives the majority of nutrient deposition to soil indirectly via the terrestrial runoff budget, and only requires atmospheric deposition as a direct input to lakes (direct deposition to rivers is neglected). The atmospheric deposition data consist of annual estimates of ammonium (NH_4-N),

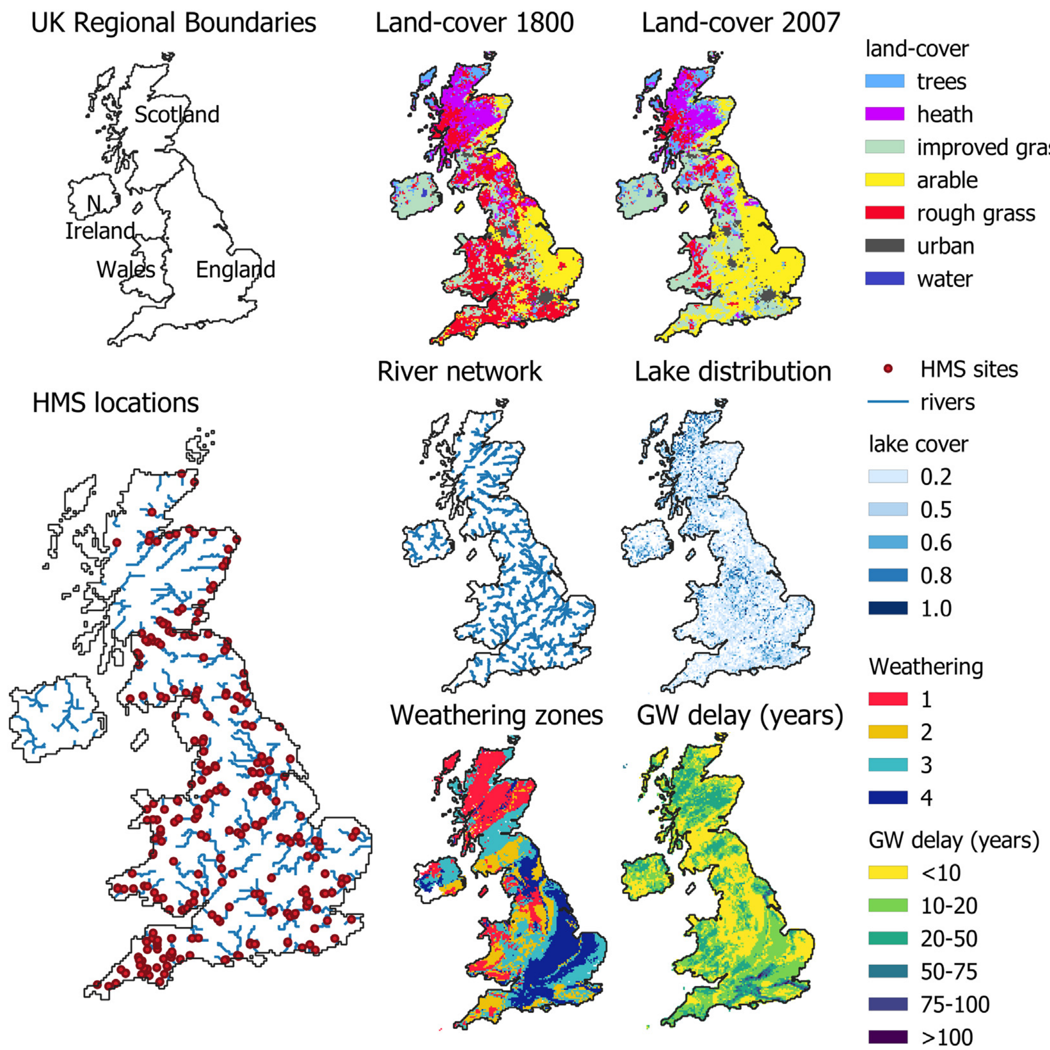


Fig. 2. Maps of the UK showing regional boundaries, land-cover in 1800 and 2007, HMS monitoring locations (red dots), river network, lakes (fraction per grid-cell), geological weathering susceptibility classes (ranging from 1:4) and derived groundwater (GW) travel time (years).

nitrate (NO_3-N) and sulphate (SO_4-S) (g m^{-2} $year^{-1}$) on a 5 km × 5 km grid resolution (Tipping et al., 2017). Atmospheric phosphorus deposition is not included here, but can be significant (Tipping et al., 2014). Further work could provide national estimates for input to the LTLS-IM.

4.1.2. Semi-natural soils

Estimates of macronutrient runoff and leaching from semi-natural areas across the UK are provided by the soil-vegetation model, N14CP (Davies et al., 2016a, 2016b; Tipping et al., 2017, 2019). The model is based on an earlier model of C and N cycles, N14C (Tipping et al., 2012), but extended to include long-term P weathering and the impact of available P on nitrogen fixation.

For semi-natural areas, N14CP simulates stoichiometrically linked C, N and P pools representing nutrients in plant biomass, coarse decomposing litter, and soil organic matter (SOM) in two layers (A and B horizons) representing the top 15 cm of soil and everything below this depth respectively. N14CP is applied on the LTLS 5 km × 5 km square grid across the UK, and is driven by the same national climate and soil data, modelled N, P and S atmospheric deposition, and estimated land cover history used in other sub-models, as described in Section 3.

For the LTLS freshwater model simulations, N14CP provides quarterly estimates of macronutrient fluxes from semi-natural soils for the dissolved (A and B horizon) and particulate (A horizon only) nutrients as listed in Table B1, with the exception of ammonium-N which is assumed to be zero from semi-natural land. Nutrients released from the soil A horizon are associated with surface runoff and nutrients from the B horizon are associated with sub-surface runoff (leaching). For use in the LTLS-IM the seasonal fluxes are post-processed to a monthly time-step using surface-runoff estimates from the LTLS freshwater model (Section 4.2.1).

4.1.3. Agricultural soils

The Roth-CNP model (Muhammed et al., 2018) was developed for the LTLS-IM to simulate crop yields and grass above-ground biomass, SOC stocks and macronutrient fluxes from UK agricultural land on a 5 km × 5 km grid. In the LTLS-IM, agricultural areas are subdivided into improved grass and arable crops using information from LCM2007 for the present day and the LTLS landscape historical reconstruction (Section 3). Inputs required by Roth-CNP consist of monthly weather data, initial states for soil C, N and P (from N14CP), annual atmospheric deposition of N (NH_4-N and NO_3-N) (Section 4.1.1), land-cover (Section 3), livestock numbers, fertiliser and manure application rates (Table A1), soil texture and profile depth, and hydrological inputs (soil-moisture, drainage, surface and sub-surface runoff, evaporation) supplied by the LTLS-FM (Section 4.2.1).

Roth-CNP output consists of monthly gridded estimates of dissolved and particulate nutrients, as shown in Table B1, the particulate nutrients being associated with the erosion volumes simulated by the LTLS erosion scheme (next section).

Calcium and DIC for agricultural soil are not output directly from the model, but were estimated assuming the chemical composition of soil water to be dominated by $CaHCO_3$, with $pCO_2 = 0.01$ and $pH = 6.5$ for England and Wales (National Soil Resource Institute, 2013) or $pH = 6.0$ for Scotland (Soil Survey of Scotland Staff, 1981). This yielded dissolved Ca and DIC concentrations of 12.0 g m^{-3} and 13.8 g m^{-3} respectively for soils of England and Wales; the corresponding values for Scottish soils were 4.0 g m^{-3} and 8.9 g m^{-3}.

Monthly estimates of crop leaf area index (LAI) from Roth-CNP are used as input to the LTLS erosion model to calculate the vegetation cover in arable areas at any time during the simulation.

4.1.4. Soil erosion and particulate nutrients

The LTLS erosion model bridges the hydrological and terrestrial models (as shown in Fig. 1), using runoff estimates from the hydrological model, removing nutrients in particulate form from the terrestrial models and delivering this as a sediment load and associated nutrients to the river model. The erosion scheme, summarised in Appendix C, is semi-empirical and runs on a monthly land-use fraction basis. It assumes erosion production is related to soil type, vegetation cover, and the kinetic energy provided by overland flow and slope.

4.1.5. Sewage and wastewater

For the LTLS-FM, annual estimates of the different forms of nitrogen, phosphorus and organic carbon from sewage sources were estimated from 1800 to 2010 at a 5 km × 5 km grid resolution. (Naden et al., 2016). Historical events that impacted on these estimates included the introduction of the water closet (flush toilet) in the 1830s, along with population growth, urbanization, connection to sewer, improvements in wastewater treatment and use of phosphorus in detergents. In the case of sewage treatment, there is a lack of historical evidence for when changes were implemented in different places. Naden et al. (2016) represented changes in water treatment practices as a series of assumed national step changes to indicate the impact of sewage treatment, instead of attempting to reconstruct a spatial and temporal trend. A detailed description of the approach, including a comparison of derived estimates of nutrient emissions with measurements is provided by Naden et al. (2016), and only a brief description of recent period and historical application in the LTLS-FM is provided here.

For more recent LTLS-FM simulations (1970 to 2010, Section 5), available wastewater treatment works (WWTW) measurements from 1990 to 2005 were used extensively. Before 1970, WWTW measurements were not available and estimates of nutrient fluxes arising from sewage required for long-term simulations (1800–2010, Section 6) are instead based on population data from UK Census Returns (1801, 1911, 1951, 1971, 1991 and 2011). In both cases, the impact of water treatment is included in the estimates of wastewater fluxes to freshwater following Naden et al. (2016). A similar approach is used to estimate nutrient losses from septic tanks, which were introduced in the 1890s, but are much less common today except in sparsely populated rural areas.

The nutrient fluxes derived from WWTW measurements and from population data are applied uniformly through the year (g / time-step) and are applied as a 5 km × 5 km grid of nutrient emissions to the LTLS-FM river network. Naden et al. (2016) provide broad indications of the uncertainties in their estimates, noting that the lack of co-location between population and sewage outfalls is a major contributing source of uncertainty in population-derived estimates of sewage-derived nutrient emissions.

4.1.6. Groundwater nutrients

The LTLS-IM makes the assumption that nutrient transport in groundwater is conservative, and estimates of organic nutrients in groundwater model stores are provided by the leaching from soil-vegetation models (N14CP and Roth-CNP) and the LTLS human waste model. While groundwater denitrification can be locally important, at a national scale there is low potential for groundwater denitrification in the UK (Rivett et al., 2007). However, the unsaturated zone is an important temporal store of nitrate (Ascott et al., 2016), and this can, therefore, be a significant source of nutrient flux to rivers for future years (Stuart and Lapworth, 2016). In the LTLS project, these data have been incorporated in the freshwater modelling as a temporal delay (years) between macronutrients leached from the LTLS soil-vegetation and human waste models, and their eventual contribution to river flows (Section 4.2.6).

Background groundwater values of Ca, SO_4 and DIC associated with deep groundwater weathering processes were obtained from baseline susceptibility classes (Edmunds and Kinniburgh, 1986), which group UK soil nutrient contamination into four background concentration classes (Fig. 2). The categories run from 1 (high susceptibility, low weathering, Ca = 2 mg l^{-1}, SO_4-S = 0.19 mg l^{-1}, DIC = 7.5 mg l^{-1}) to 4 (low susceptibility, high weathering, Ca = 100 mg l^{-1}, SO_4S = 9.6 mg l^{-1}, DIC = 59.3 mg l^{-1}).

4.2. Freshwater modelling of flows and nutrient fluxes (LTLS-FM)

4.2.1. The hydrological model: water quantity

The LTLS-FM hydrological model is based on a 5 km × 5 km implementation of the hydrological modelling framework (HMF, Crooks et al., 2014), which operates on a 2 h time-step at a national scale, and uses a kinematic wave lateral flow routing scheme, similar to that used in the first implementation of the Grid-to-Grid (G2G) model (Bell et al., 2007). The runoff-production scheme used here is similar to that implemented in the G2G (Bell et al., 2009), which maintains a continuous representation of water stored in a soil column by balancing inputs from rainfall with "losses" from evaporation, soil drainage, and runoff from surface and sub-surface. Each 5 km × 5 km soil column is configured using hydraulic properties (saturation and residual water contents) to provide estimates of maximum and residual water storage. The hydraulic parameters are derived using a Van Genuchten scheme (Van Genuchten, 1984) applied to spatial datasets of soil texture (Section 3). In order to ensure that each grid-square generates realistic quantities of saturation-excess surface runoff even when it is not fully saturated, the probability-distributed soil moisture store formulation of Moore (1985, 2007) has been invoked within each grid-square (Bell et al., 2009).

Following Bell and Moore (1998) and Bell et al. (2007), 1-D kinematic wave (KW) flow routing is applied to a river network in two-dimensions, routing both land and river flows. It uses surface and sub-surface runoff estimates as input, and they are routed separately assuming a different wave speed for land and river, and surface and sub-surface pathways (four wave-speed parameters in total). A return flow term allows for flow transfers between the sub-surface and the surface pathways in river channels, providing a spatially continuous way of combining fast and slow components of flow. The KW model equation in 1-dimension is as follows:

$$\frac{\partial Q}{\partial t} + c\frac{\partial Q}{\partial x} = c(u + R) \tag{1}$$

where Q is either surface or subsurface flow (m^3s^{-1}), R denotes return flow per unit path length (water transfer between subsurface and surface pathways), and u represents lateral inflows per unit path length, which include runoff generated by the runoff-production scheme. The wave speed (celerity) c can vary with the pathway (surface or subsurface) and surface-type (land or river) combination. In practice, a forward difference approximation (Jones and Moore, 1980) to the derivatives in Eq. (1) is used

$$Q_k^n = (1-\vartheta)Q_{k-1}^n + \vartheta\left(Q_{k-1}^{n-1} + u_k^n + R_k^n\right) \tag{2}$$

where k and n denote positions in discrete time and space respectively, the dimensionless wave speed $\vartheta = c\Delta t/\Delta x$ and $0 < \vartheta < 1$. This is a simple, explicit numerical formulation for the kinematic wave equation, and the discrete formulation has the advantage of introducing attenuation and diffusion, an effect noted by Cunge (1969). The kinematic wave routing scheme is also computationally efficient as it expresses flow in a river reach or grid-cell in terms of the flow at the previous time-step.

For hydrological modelling of runoff and flow, short grass land-cover is assumed everywhere except for grid-squares with an urban/suburban fraction where available soil storage is reduced by 50%. This reduction in urban/suburban soil storage is a simplification of the 70% and 30% reductions applied to urban and suburban areas respectively by Bell et al. (2009), and will have the effect of increasing runoff, particularly surface runoff, in built-up areas leading to a faster hydrological response to rainfall.

4.2.2. Nutrient routing in river systems: water quality

A parallel approach has been adopted for the water quality modelling component, for which we make the fundamental assumption that dissolved and particulate nutrients travel with the water, and with the same wave-speed. Specifically, and in exactly the same way as the KW routing "moves" water between grid-cells, it is assumed that

$$(N_Q)_k^n = (1-\vartheta)(N_Q)_{k-1}^n + \vartheta\left((N_Q)_{k-1}^{n-1} + (N_u)_k^n + (N_R)_k^n\right) \tag{3}$$

where N_Q is either surface or subsurface nutrient flux (gm^{-3} s^{-1}), N_R denotes return flow of nutrients, and N_u represents lateral inflows of nutrients per unit path length, which include surface or sub-surface nutrient runoff generated from agriculture or semi-natural areas. The nutrient flux, N_Q, can represent any of the 10 dissolved or 12 particulate nutrients in Table B1. By making the assumption that nutrients, like water, are routed using the kinematic wave formulation, the scheme minimises spatial fluctuations in nutrient concentration that could arise from routing water and nutrients at different speeds, however, the implicit assumption that nutrients move through rivers with a celerity wave may in practice underestimate the retention time of nutrients in rivers.

4.2.3. In-river nutrient processes

The LTLS-FM within-river nutrient biogeochemistry model estimates primary production, organic matter decomposition, nitrifying activity and oxygen balance. Both dissolved and particulate nutrient processes are simulated, and while nutrients are conserved through the routing scheme, losses to the river system through storage in river sediments, denitrification and decomposition are included. Most processes are simulated using first-order temperature-dependent (Q10) reactions, and some are also pH-dependent, so both pH and temperature are calculated at every time-step for each river grid-cell model, along with oxygen and chlorophyll growth. A summary of the LTLS-FM in-river processes is provided in Fig. 3, and a full description is provided in Appendix D.

As many of the in-river biogeochemical processes are water temperature-driven, a model to estimate daily mean river temperatures is required. Here, a simple relationship between air temperature and river water temperature has been implemented following Webb et al. (2003), who investigated air-water temperature relationships for rivers in Southwest Britain. Following Mohseni et al. (1998), they fitted a non-linear relationship of the form

$$T_w = T_{w\_min} + \frac{T_{w\_max} - T_{w\_min}}{1 + e^{\gamma(\beta - T_a)}}, \tag{4}$$

where T_w is estimated water temperature (°C), T_{w_min} and T_{w_max} are estimated minimum and maximum water temperatures, T_a is the measured air temperature (°C), and β and γ are constants. As a first approximation this relationship has been applied across Britain, using the parameter values derived by Webb et al. (2003) for the River Exe. Further work using available measurements nationwide could generalise this approach for use in rivers across the UK, though it is important to note that the LTLS-IM requirement is for an estimate of the mean river temperature across a 5 km × 5 km grid-cell, not at a particular site.

4.2.4. Sediment loss to floodplain

Transfers of river sediment to the floodplain are modelled using an approximate relationship derived by Nicholas et al. (2006). This relates overbank sedimentation rate per unit length of reach (D, m^3 s^{-1} km^{-1}) to sediment concentration, discharge and floodplain geometry:

$$D = \begin{cases} \mu\, C\, W_0^{\theta}(Q - Q_{bf})^{0.5}, & Q > Q_{bf} \\ 0, & Q \le Q_{bf}, \end{cases} \tag{5}$$

where C is sediment concentration (local absolute concentration divided by the main channel concentration, dimensionless), Q and Q_{bf} (m^3 s^{-1}) are flow and bankfull flow respectively, W_0^{θ} (m) is the maximum width of the floodplain, and μ and θ are constants. Floodplain area, A_0, (km^2) for each 5 km × 5 km grid square is defined by the 100-year flood envelope (based on Environment Agency Flood Map for Planning (Rivers and Sea) - Flood Zone 3 (https://data.gov.uk/dataset/) for England, and IH130 elsewhere (https://www.ceh.ac.uk/services/ih130-digital-flood-risk-maps)), and $W_0 \approx 1000A_0/5$ (m). The model constants μ and θ are assumed to be 0.012 and 0.45 respectively, based on average values derived for UK catchments (Nicholas et al., 2006). Losses of sediment and associated nutrients to floodplains are assumed to be true losses, whereas in reality, they contribute to the soil budgets in floodplain areas. For the national scale modelling undertaken here, it is assumed that this simplification will have a negligible impact on nutrient fluxes compared to other approximations.

4.2.5. Nutrient processing in lakes and reservoirs

The presence of a freshwater body (lake or reservoir) reduces nutrient transport through a landscape. Lakes and reservoirs efficiently trap

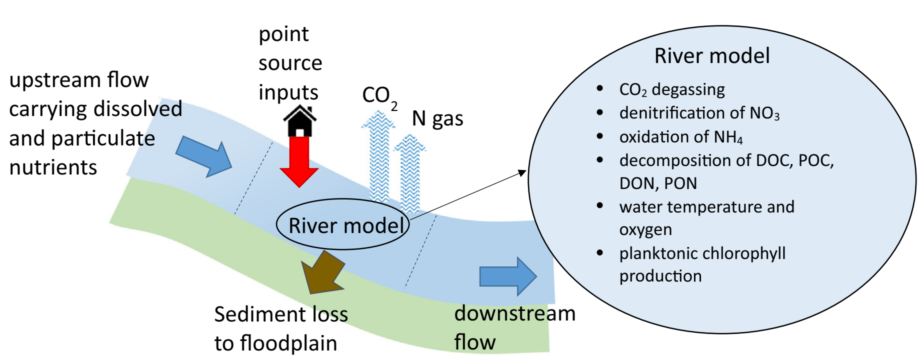


Fig. 3. Schematic of the in-river model processes.

fluvially-transported particles and nutrients, retaining these in bed sediment which can provide information on past nutrient loadings.

A process-based model (Tipping et al., 2016) was developed to calculate the impact of lakes and reservoirs on landscape CNP flux. Tipping et al. (2016) provide a formal description and assessment of the model, and highlight the simplifications made and processes neglected. In the LTLS-FM, water-bodies of all sizes within each 5 km × 5 km grid-cell are spatially aggregated into a single conceptual “lake” with area equal to the total water-body area in the grid-cell, and an area-weighted depth. Only lakes connected to the river system are considered, and the few un-connected lakes in the UK are treated as terrestrial land. Fig. 2 shows the distribution of lakes in the UK on the 5 km × 5 km grid, highlighting that although the larger UK lakes are situated in Scotland and Northern Ireland (to the north and west of the UK), there are small lakes connected to rivers across most of the country. Every lake is assumed to be completely mixed and of constant volume, with outflow of water equal to inflow. Inflowing water brings in particulate matter from upstream rivers, derived principally from soil erosion, and containing organic matter comprising C, N and P, as well as particulate inorganic P. It also brings solutes, namely dissolved inorganic nitrogen (DIN), dissolved inorganic phosphorus (DIP), and dissolved organic matter (DOM), which contains C, N and P. Water leaving the lake contains the same components (although generally at different concentrations), together with algal biomass generated within the lake by photosynthesis (Tipping et al., 2016).

4.2.6. Groundwater nutrient sources and transport

Nitrate concentrations in UK groundwaters have increased since the 1950s following the post-war growth in agricultural fertiliser use, peaking during the 1980s and early 1990s. Since then changes in agricultural practice under the European Nitrates Directive (Council Directive, 1991) have led to a reduction in groundwater concentrations which can now be observed at some sites in the more rapidly responding aquifers, such as the Quaternary gravels and the Lincolnshire Limestone. However, for Chalk aquifers, the thick unsaturated zone means that these improvements may not be seen for some decades in places, and the unsaturated zone remains an important store of nitrate (Ascott et al., 2016).

Wang et al. (2012) were able to quantify this temporal “delay” in nitrate concentrations in the water table using a simple conceptual model implemented in a GIS. The modelling work led to the development of a UK-wide map of travel times in the unsaturated zone from the surface to the water table for nitrate (and other conservative tracers). These data have been incorporated in the LTLS-FM as a temporal delay between macronutrients leaching from soil to their contribution to subsurface flows. A UK-wide 5 km × 5 km resolution spatial grid of macronutrient travel times through the unsaturated zone was prepared, assuming the temporal delays derived by Wang et al. (2012) apply to all solutes. The map of delays (shown in Fig. 2) confirms that for much of the UK, particularly Northern and Western Britain and Northern Ireland, the delay in nitrate travel times is less than 25 years (the mean travel time is ~15 years), but for some areas of the South and East, the travel time can exceed 50 years, and reaches over 100 years in some areas of chalk aquifer. Here, these data have been used to delay estimates of all dissolved nutrients leaching from soils (both semi-natural and agricultural) by the time delay appropriate for each grid-cell location. In most areas, the effect on fluvial nutrient fluxes is minimal, but in other areas, such as catchments in the Thames Basin (in south east Britain), the effect of the delay is more apparent.

5. Results: LTLS Freshwater Model assessment (1970–2010)

5.1. The model output

The LTLS-FM was run across the whole UK at once on a 5 km × 5 km grid resolution for periods spanning decades to centuries, and applied “blind”, i.e. with no calibration (parameter adjustment) to observations of freshwater macronutrients or river flows at individual sites.

Output from the freshwater component (LTLS-FM) consists of monthly or annual dissolved or particulate freshwater macronutrients (listed in Table B1, column 1), together with estimates of sediment load, water temperature, oxygen, pH, chlorophyll and a range of hydrological variables (soil-moisture, drainage, surface and sub-surface runoff, evaporation, river flow). Many other variables can be output for analysis, but are not produced routinely (e.g. sediment loss to flood plain, gaseous fluxes from lakes and rivers, lake physical and macronutrient variables) as there are few readily available observations with which to compare them.

The spatially-consistent configuration of the LTLS-FM model provides estimates and temporal simulations of nutrient fluxes at both gauged and ungauged locations, i.e. at locations where information on flows or nutrients are not routinely available. Model output can be analysed as monthly or annual UK-wide spatial grids, and at country, regional or catchment scales. Alternatively, time-series of nutrient fluxes can be compared directly to observations at gauged locations, or used as input to coastal, ocean or estuary models.

Although the LTLS-FM was designed to simulate long-term macronutrient fluxes at large (national) scales, it is important to compare simulated and measured freshwater fluxes to understand the uncertainty in the model estimates. Model estimates have been compared to observations at HMS monitoring sites across Britain for which annual nutrient loads and 95% confidence intervals can be estimated (Section 3). Fig. 4(a-b) presents observed and modelled annual fluxes of nitrate and TDP for 3 UK sites, one each from England, Scotland and Wales: Thames at Teddington Weir (HM site 6010; HMS catchment area 9959 km^2), Dee at Maryculter Bridge (HMS 12007; 2007 km^2) and Conwy at Cwm Llanerch (HMS 10023; 340 km^2). Simulated dissolved nitrate (NO_3-N) fluxes generally fall within, or are close to the observation confidence interval (shown as a grey bar above and below the expected value), and for some sites the model can reproduce trends in the observations in this 40-year period. Temporal simulations of TDP fluxes are much less variable than observed, though often fall within confidence bounds of the observation.

Generally, large scale fluxes of the main macronutrients simulated by the model correlate with observations. Fig. 4(c) compares model estimates of fluxes (tonnes/year) with all available observations for all 224 HMS sites for the period 1970 to 2010 and for 4 determinands: nitrate, TDP, DOC and DIC. Both axes are on a logarithmic scale, and although the model takes into account major influences on nutrient fluxes, a large proportion of the accuracy in prediction of nutrient flux estimates arises from good model estimates of the river flows. Overall, nitrate and DOC fluxes compare reasonably well with simulated, with values tending to lie around the 1:1 agreement line. The figures indicate that compared to observations, the LTLS-FM tends to underestimate DIC fluxes in rivers, but overestimate DOC fluxes and lower values of TDP (though higher TDP values are reasonably well simulated).

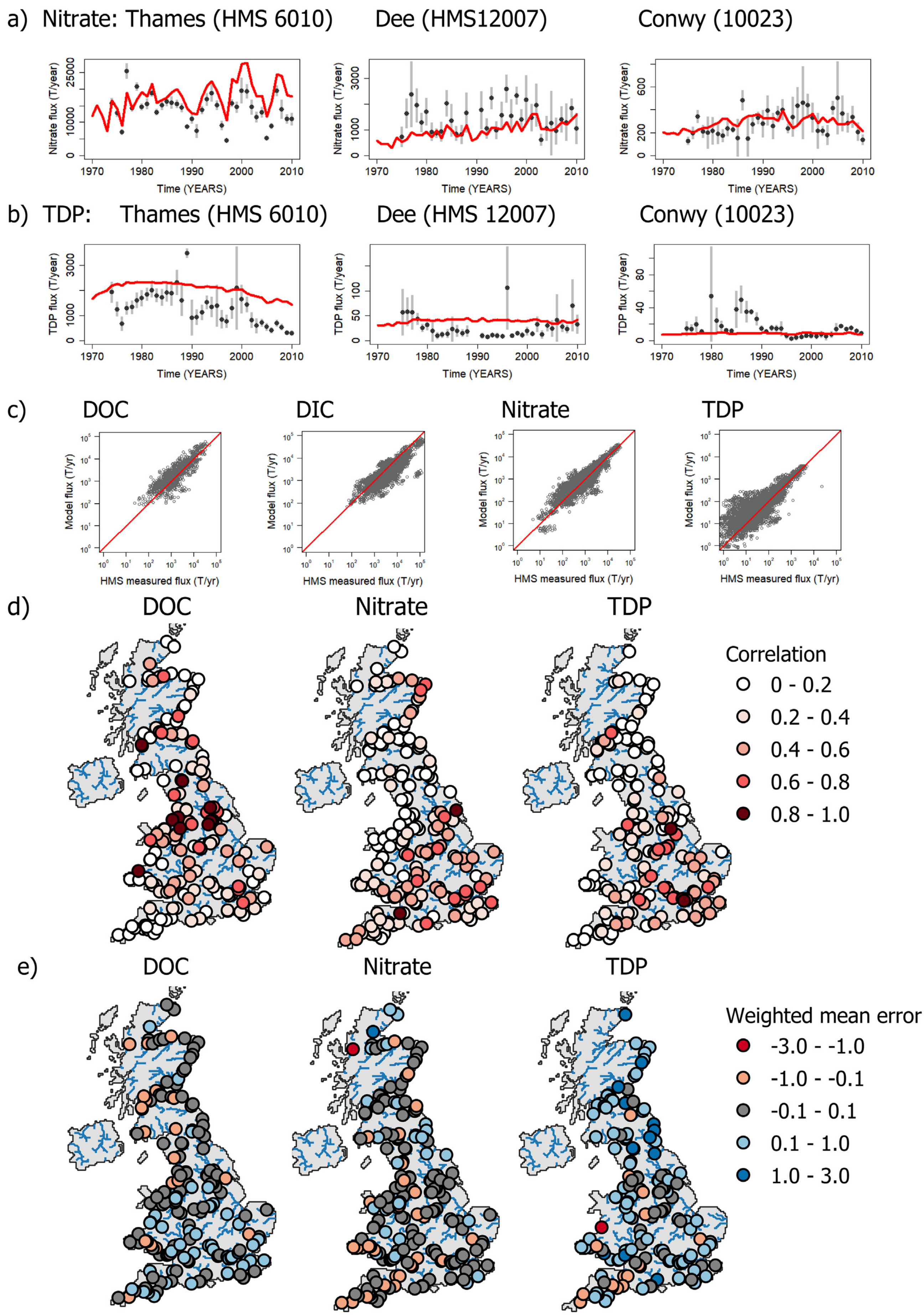
5.2. Variation in performance across the UK

Model performance for 224 HMS sites has also been quantified using two statistical measures:

- Pearson Correlation, r
- A weighted mean log error, *wme*, based on the difference between modelled (m) and observed (o) nutrient fluxes, but weighted in favour of observations with less uncertainty (i.e. observations associated with a smaller confidence interval, $C_I(o)$):

$$wme = \frac{\overline{C_I(o)}}{n_{obs}} \sum_{n=1}^{n_{obs}} \frac{(\log_e(\mathrm{m}) - \log_e(\mathrm{o}))}{C_I(o)}$$

Pearson's correlation coefficient, r, provides a standard measure of the linear correlation between observed and modelled nutrient fluxes


a) Nitrate: Thames (HMS 6010)
Dee (HMS12007)
Conwy (10023)
Nitrate flux (T/year)
Time (YEARS)
b) TDP: Thames (HMS 6010)
Dee (HMS 12007)
Conwy (10023)
TDP flux (T/year)
Time (YEARS)
c) DOC
DIC
Nitrate
TDP
Model flux (T/yr)
HMS measured flux (T/yr)
d) DOC
Nitrate
TDP
Correlation
0 - 0.2
0.2 - 0.4
0.4 - 0.6
0.6 - 0.8
0.8 - 1.0
e) DOC
Nitrate
TDP
Weighted mean error
-3.0 - -1.0
-1.0 - -0.1
-0.1 - 0.1
0.1 - 1.0
1.0 - 3.0

($r = 1$, 0 and -1 indicate positive, zero and negative linear correlations respectively), and values of r can be compared across a range of sites. The *wme* statistic provides a measure of the extent to which the model is over- or under-estimating fluxes, while taking account of the confidence in the observations (of which there are n_{obs} at each site). The use of logarithms also ensures that the *wme* statistic is not excessively biased by errors in high fluxes. For sites where $|wme| < 0.1$, the ratio of modelled to observed fluxes will be below 1.11, but for larger values of *wme*, for example $0.1 < wme < 1.0$, modelled fluxes could be typically 2.7 times higher than observed.

The performance measures of correlation between observed and modelled fluxes are presented spatially for the UK in Fig. 4(d). The figures show that the LTLS-FM simulates observed nitrate and TDP with greatest accuracy in the South and East of Britain, and simulates DOC best in the North and West. Although there is considerable scatter in performance across the whole country there were no negative correlations. Over the period 1970 to 2010, sources of both nitrate and TDP have changed in response to wastewater management (TDP particularly) and agriculture, both factors that have been included in the modelling.

The *wme* performance criterion is better able to evaluate errors in the magnitude of the model estimates, and in Fig. 4(e), the maps show model over- and under-estimates in shades of blue and orange/red respectively. Good model performance is shown in grey. The LTLS-FM is not calibrated to individual sites, and the model performance would be expected to vary from catchment to catchment in line with our spatio-temporal understanding and representation of sources of C N and P across the UK. Across the UK, TDP is more often over- than under-estimated, particularly in northern rivers, which can most likely be attributed to over-estimates of TDP from human waste. The mean *wme* value for TDP fluxes across all sites and observations is 0.73, indicating that there are expected to be high errors in national TDP estimation of +108% (95% CI of 21 to 257%), however model performance will vary spatially and errors could be higher or lower in individual rivers. DOC fluxes tend to be simulated with greatest accuracy in the North and West, areas where peat soils export significant DOC to rivers. The mean *wme* errors of 0.093 in DOC and − 0.001 in nitrate at HMS locations are indicative of overall errors in national DOC and nitrate estimates of approximately 9% (95% CI of 2 to 17%) and − 1% (95% CI of ±3%) respectively.

6. Results: long term and large scale freshwater fluxes of C, N and P from 1800 to 2010 across the UK

6.1. Model configuration for historical simulations

For the 210-year historical simulation starting in 1800, the LTLS-FM was applied using a very similar configuration to that applied in the "present day" simulations in Section 5 but with the following important changes:

1. Estimates of nutrient fluxes arising from sewage were based on historical population data instead of measurements from wastewater treatment works (Section 4.1.5), and are shown in Fig. 5(b).
2. Fertiliser application rates used by the agricultural model Roth-CNP, changed dramatically over the period 1800 to 2010 and these are summarised in Fig. 5(c).
3. Reconstructed historical daily weather data were used to drive the terrestrial and freshwater model components (Section 3 and Appendix A).

Corresponding long term simulations of macronutrient fluxes in UK rivers presented in Fig. 5(d,e) reflect these changes in landscape and population. The graphs show the variation in fluxes of nitrate and phosphorus (tonnes/year) for three catchments for which longer observational records are available. The long-term trends in nitrate for the Thames and Frome are simulated well, indicating that the LTLS-IM has accounted for the main processes and influences, and in all four examples the LTLS model has simulated the correct historical trend. For these historical simulations, sewage inputs to rivers are calculated from population trends, and inaccuracies in sewage derived in this way have contributed to the overestimates of simulated TDP fluxes in the Frome (Fig. 5e). Simulations of TDP using observations from STWs (section 5) are more accurate in the Frome catchment. The historical model simulations show a large increase in freshwater macronutrient fluxes from around 1950 onwards, with the greatest increases in catchments with high populations (Thames). Decreased model performance in simulating present day observations (1970 onwards) in some catchments should be attributed not only to imperfect model process representation, but also to uncertainties associated with the reconstruction of spatial and temporal driving data for the 200-year period. It should also be noted that for these long-term simulations, estimates of nutrients from treated human waste are based on population numbers rather than observations, and fluxes to rivers will not necessarily correspond geographically to those from WWTW.

Observations of UK freshwater nutrients back to 1800 are not available to support a quantitative performance assessment, so LTLS historical estimates of freshwater nutrient fluxes can only be considered a scenario based on the historical evidence available. With that consideration in mind, and the reasonable model performance for present-day simulations (Section 5), long term and large scale assessments can be made about the storage and flux of nutrients in UK freshwaters from 1800 to present day.

6.2. Terrestrial macronutrient export to freshwater: 1800–2010

From 1800 to 2010, LTLS model estimates of terrestrial macronutrient export to UK freshwaters increased dramatically following industrialisation and population growth. Fig. 6(a) presents annual terrestrial exports of dissolved C (DOC + DIC), N (NO_3-N, NH_4 and DON) and P (TDP) to rivers for selected years between 1810 and 2010. All 3 charts indicate a rise in dissolved C, N and P from the early 19th century up to the mid- to late-20th century, during a period of growth in the human population and intensification of agriculture.

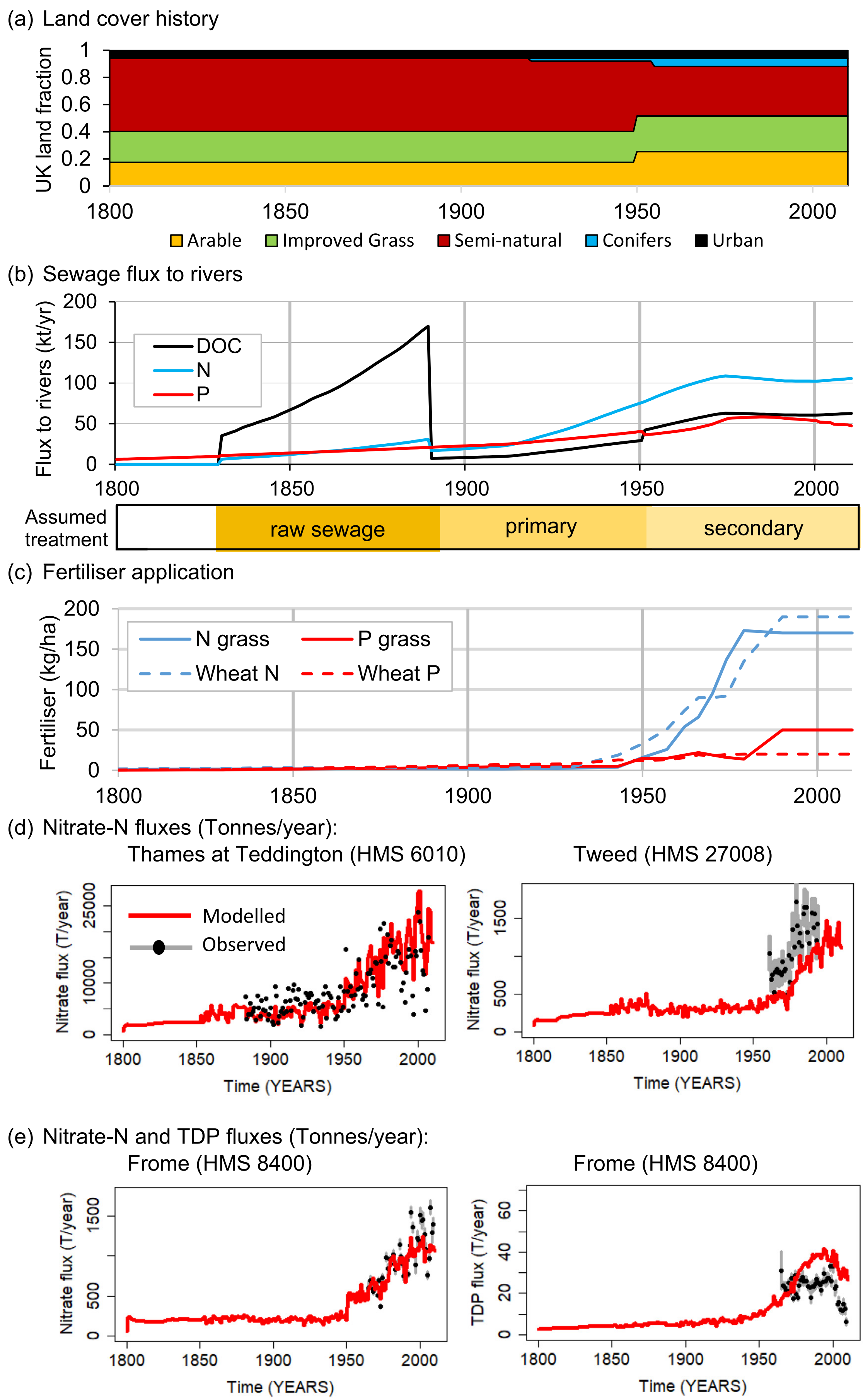
The LTLS-FM simulations in Fig. 6(a), all for dissolved macronutrients, indicate that between 1810 and 2010, carbon (DOC + DIC) export from terrestrial sources stayed relatively stable at approximately 4000 kT year^{-1}, of which approximately 25% was DOC. The estimated macronutrient flux from urban runoff was found to be negligible (approximately 1 kT year^{-1}C and 0.4 kT year^{-1} N). N export to rivers rose by just 14% between 1810 and 1900, but more than tripled over the next 80 years, reaching a peak of 964 kT year^{-1} before declining to 741 kT year^{-1} in 2010. Agriculture (improved grass and arable land) is the largest source to freshwaters, although N from sewage has increased by a factor of 5 since 1900. Most of the phosphorus (TDP) export to rivers comes from sewage (primarily from WTWW but also septic tanks), and across the UK was estimated to have increased from negligible quantities in 1800 to 4 kT year^{-1} in 1900. Total fluxes reached approximately 29 kT year^{-1} in the early 1980s, before declining following changes in the formulation of detergents and the implementation of P-stripping in WWTW (Naden et al., 2016).

6.3. UK Freshwater macronutrient fluxes: 1800–2010

6.3.1. Total fluxes to UK coastal waters

The estimates of dissolved macronutrient export to freshwaters in Section 6.2 consist of direct fluxes from terrestrial soils, and do not

Fig. 4. Model simulation performance for annual fluxes of a) Nitrate, and b) TDP fluxes for 3 UK sites, comparing model simulations (red line) and observations (black dot with 95% confidence bands in grey). Scatterplots (c) compare all model estimates and available observations for 224 HMS sites for the period 1970 to 2010. Maps (d) and (e) show the spatial distribution of LTLS-FM model performance (coloured circles) in simulating DOC, Nitrate, TDP and in terms of d) Pearson correlation and e) weighted mean error.


(a) Land cover history
UK land fraction
1
0.8
0.6
0.4
0.2
0
1800
1850
1900
1950
2000
Arable
Improved Grass
Semi-natural
Conifers
Urban
(b) Sewage flux to rivers
Flux to rivers (kt/yr)
200
150
100
50
0
DOC
N
P
1800
1850
1900
1950
2000
Assumed treatment
raw sewage
primary
secondary
(c) Fertiliser application
Fertiliser (kg/ha)
200
150
100
50
0
N grass
P grass
Wheat N
Wheat P
1800
1850
1900
1950
2000
(d) Nitrate-N fluxes (Tonnes/year):
Thames at Teddington (HMS 6010)
Tweed (HMS 27008)
Nitrate flux (T/year)
0
10000
25000
Modelled
Observed
0
500
1500
Time (YEARS)
(e) Nitrate-N and TDP fluxes (Tonnes/year):
Frome (HMS 8400)
Frome (HMS 8400)
Nitrate flux (T/year)
0
500
1500
TDP flux (T/year)
0
20
40
60
1800
1850
1900
1950
2000
Time (YEARS)

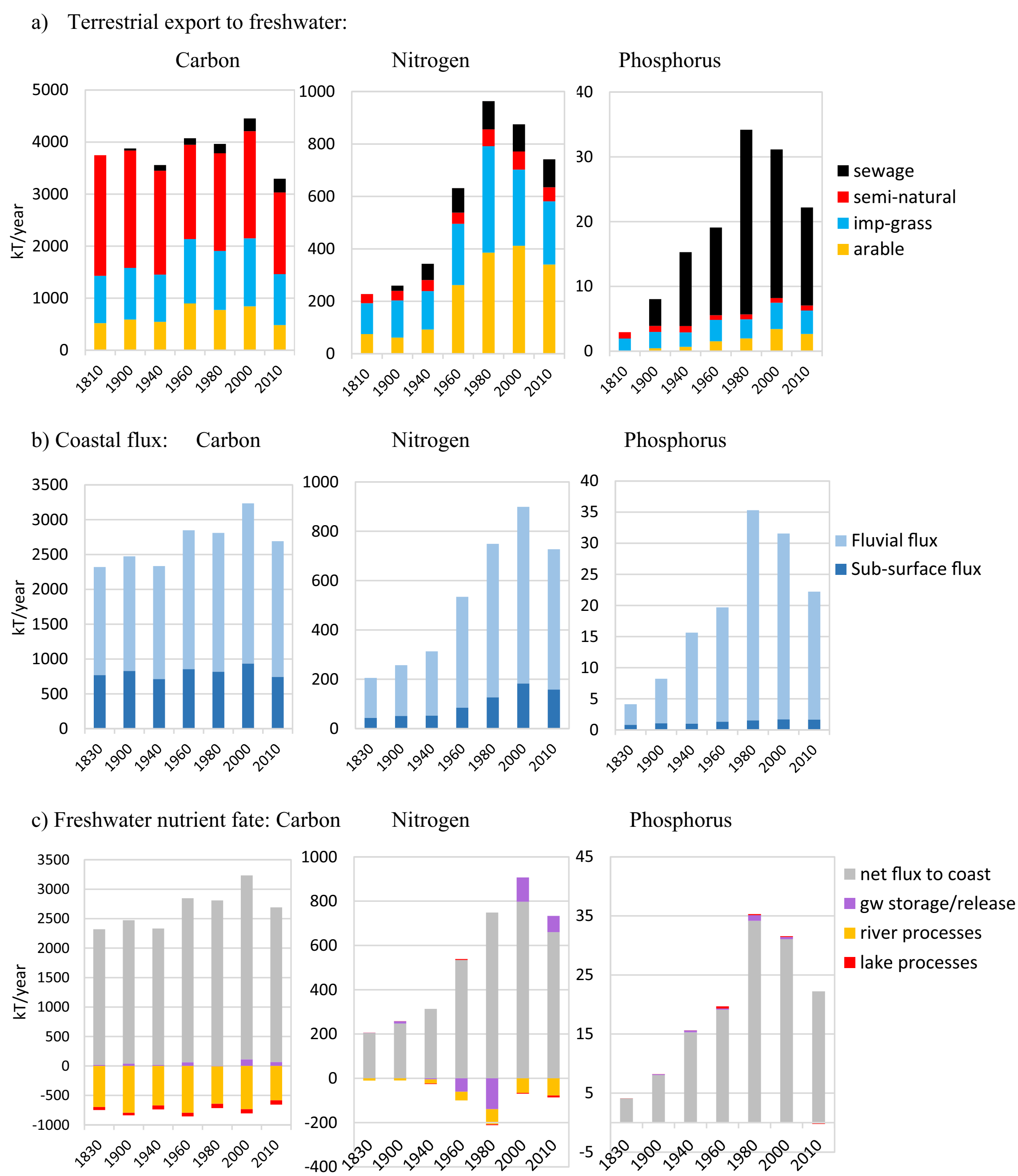


Fig. 6. UK dissolved macronutrient sources and fates: a) Total input to freshwater, b) Flux to coastal waters, and c) Fate of nitrogen (NO_3-N + NH_4 + DON), phosphorus (TDP) and carbon (DOC+DIC) (kT $year^{-1}$): 1800–2010. Negative values reflect "losses" from within-river/lake processes such as denitrification, and storage in groundwater (Section 6.3.2).

take account of indirect sources such as long-term storage of C and N in groundwater, or the impact of lake and river processes. The LTLS freshwater model then takes these macronutrient inputs and provides an estimate of direct fluxes to coastal waters, and the magnitude of losses/gains from freshwater processes.

For selected years from 1830 to 2010, Fig. 6(b) shows the modelled flux of dissolved nitrogen, phosphorus and carbon in fluvial (light blue shading) and sub-surface pathways (dark blue) to coastal waters, after including contributions/losses from stored groundwater and in-stream/lake processes. The total height of each bar shows the total coastal flux (fluvial + sub-surface) in kT $year^{-1}$. The first year displayed is 1830 to allow for model "spin-up", particularly relating to stored groundwater nutrients from preceding decades. It is apparent that while nitrogen inputs to freshwater peaked at around 1980 (Fig. 6a), the flux of nitrogen to coastal waters peaked approximately 20 years later. This delay is not apparent for C and TDP, for which the timing of nutrient inputs and outputs are similar.

For some macronutrients, a significant proportion is exported to coastal waters via sub-surface pathways, i.e., not from rivers or direct surface runoff. The LTLS freshwater simulations indicate that approximately 15% of DOC, 40% of DIC, 20% of NO_3 and 7% of TDP are exported to UK coastal waters from sub-surface pathways. Model estimates of total

Fig. 5. Timelines (1800 to 2010) of (a) UK-wide land-cover (fraction), (b) sewage flux to rivers (kT $year^{-1}$) and (c) fertiliser-application rates (kg ha^{-1}), and corresponding model simulations and long-term observations of (d) nitrate-N and (e) TDP (T $year^{-1}$). For observed fluxes, the expected value is shown with a black dot, and the 95% confidence bands (where available) are indicated with grey bars.

coastal export (surface + sub-surface fluxes) of N and P peak in the late 20th century, then decline following improved regulation of wastewater treatment and agricultural practices (declining fertiliser use and fewer livestock). By comparison, total C (DOC + DIC) export to coastal waters has stayed relatively stable over the 200 year period at approximately 3000 kT year^{-1}, of which approximately a third is DOC. However, annual estimates show considerable variability, particularly in DIC, and a modest increase of approximately 20% in DIC export between 1970 and 2010 (apparent in annual time-series output but less apparent in Fig. 6b).

Direct 'leakage' of freshwater to coastal waters via sub-surface pathways, also referred to as "Submarine Groundwater Discharge" or "SGD" has been recognised for centuries (Burnett et al., 2006) however, direct quantification remains challenging. LTLS model simulations indicate that the total UK flux of NO_3-N in SGD to coastal waters increased from 54 to 146 kT year^{-1} between 1950 and 2010, whereas fluxes of DOC and DIC in SGD have stayed relatively constant at approximately 140 and 650 kT year^{-1} respectively. Comparison of LTLS macronutrient fluxes with measurements (Section 5.2) indicates that the model tends to underestimate surface freshwater DIC fluxes, and in reality a lower flux of DIC might be transported as SGD. The model estimates of NO_3-N compare reasonably well with observations of nitrate fluxes in rivers (Section 5.2), supporting indicative estimates of 20% flux of nitrates to coastal waters via sub-surface pathways.

6.3.2. Impact of freshwater processes on UK macronutrient export

To understand the impact of lake, groundwater-delay and river-chemistry on model-estimated macronutrient fluxes to coastal waters, LTLS freshwater model simulations were run with different components enabled or disabled in order to quantify the relative impact of each on freshwater fluxes. Specifically, the different simulations were:

1. Standard LTLS-freshwater model, which includes lake and in-stream processes and groundwater storage delays
2. Standard LTLS-freshwater model, no groundwater storage delays
3. Standard LTLS-freshwater model, no lake processes
4. Standard LTLS-freshwater model, no lake or instream processes.

The differences between paired simulations (1 and 2, 1 and 3, and 3 and 4) provide an estimate of the impact of different freshwater processes. Fig. 6(c) shows the overall impact of LTLS-simulated freshwater processes on macronutrients fluxes, with different colours highlighting the loss/gain of long-term groundwater storage/ release (purple shading), lake processes (red), in-stream processes (yellow) on the coastal flux (net flux is shown in grey). The simulations provide only a first order estimate of the impact of the different processes, as they are likely to interact in non-linear ways, however, they provide a valuable overview of the fate of different macronutrients once they have entered UK freshwaters. Removal of nutrient fluxes from freshwater via groundwater storage, or by river/lake processes such as denitrification, are shown as "negative" fluxes.

The model simulations indicate that approximately 20% of total carbon inputs to freshwaters are removed by in-stream processes, the majority of which is through conversion of DIC to CO_2 gas. A negligible proportion of DIC is retained in groundwater stores, but DOC in stored groundwater contributed 3% of DOC flux to coastal waters in 2010. Approximately 10% of N in freshwaters was converted to N_2 by denitrification in rivers and lakes (yellow and red bars in Fig. 6c), and ~ 90% was exported directly to the coast. In 2010, an estimated 9% of nitrogen reaching freshwaters originated from long term groundwater retention. The estimated gain/ loss of N from stored groundwater is shown as positive/negative groundwater storage (purple bar). Only a small net balance of terrestrial nitrogen is held in groundwater storage over the whole 200 year period, but model simulations indicate a net storage of nitrates in groundwater between the 1940s and 1990s, and a net release to coastal waters post-1990. Thus the flux of N to coastal waters in 1980 is less than would have been expected as approximately 20% of terrestrial fluxes has been stored, whereas in 2000, the flux is 10% higher than expected as more nitrogen has been released from groundwater. Almost all TDP from terrestrial sources is exported to coastal waters, primarily because the LTLS river model (Section 4.2) does not include riverine loss processes for P. Most of the TDP in freshwaters originates from wastewater and discharges straight to rivers, with relatively little (1–2%) stored in groundwater. At a national scale, only a modest percentage is stored in lakes, but this percentage can be higher for catchments with extensive lake systems.

Although dissolved macronutrients are the main focus of the work reported here, a comparison with observations of annual fluvial fluxes of sediment at HMS sites indicates that the LTLS-IM tends to underestimate freshwater sediment fluxes, with a mean error of −8%, and a 95% confidence interval of −47 to 57% at HMS locations. For 2010, the LTLS-estimated UK terrestrial flux of suspended sediment to freshwaters was 740 kT, and the freshwater flux to coastal waters was 611 kT (95% CI: 324 kT to 959 kT), indicating an 18% loss within the fluvial system. In 2010, particulate C added 15% to the UK's terrestrial C export (an additional 490 kT: 37% from semi-natural soils, 37% from arable and 26% from improved grasslands). The LTLS-estimated coastal fluxes of particulate C, N and P in 2010 were 33, 0.8 and 0.3 kT respectively, however, it was a drier year than average and would have experienced less surface runoff (and LTLS-estimated erosion) than usual. By comparison, in 2000, a noticeably wetter year which resulted in extensive flooding across southern Britain, the LTLS-estimated UK sediment flux to coastal waters was nearly 3 times higher (1675 kT), of which terrestrial particulate C export (much of which comes from northern Britain) was significantly lower (133 kT) but particulate N export to rivers contributed an additional 1% to the annual export of N to freshwater. Further analysis of LTLS estimates of sediment fluxes and particulate nutrients is beyond the scope of this study, and will be explored in future work.

Based on the model simulations, UK hydrosphere macronutrient budgets can be constructed to summarise the main sources and fates. Fig. 7 presents example budget diagrams for a single year (2010), highlighting dominant sources and fluxes of dissolved N, P and C. The sizes of the arrows reflect the magnitude of the flux, though they are not exactly to scale. The dominance of semi-natural land as a source of DOC, agriculture as a source of nitrogen, human waste as a source of phosphorus and the in-river flux to coastal waters are immediately apparent.

6.3.3. Geographic variation and historical change

The summary of UK fluxes in Fig. 6 shows how national total fluxes of different macronutrients change in time, but gives no indication of the spatial variation of these historical changes. The maps of mean annual C, N, and P fluxes (T year^{-1}) in Fig. 8 highlight the geographic variation in freshwater fluxes for 3 decades: a) 2001 to 2010, b) 1901–1910, and c)1801–1810. Main rivers draining larger catchments in England and Wales, such as the Thames in the Southeast, the Severn in the west midlands, and the Yorkshire Ouse (draining to the east coast), have large fluxes of nutrients as expected but lower fluxes of N and P in Scottish rivers are also apparent. The maps, which are all on the same scale, highlight the relatively lower fluxes of P in Scotland, Wales and Northern Ireland, but also the high carbon fluxes in all regions.

The maps highlight that the largest increases in N and P occurred in England, Wales and Northern Ireland over the 20th Century, with annual P and N fluxes increasing in the lower Thames by approximately 90 and 170% respectively between the periods 1901–1910 and 2001–2010. Although nutrient fluxes have generally increased during the periods analysed, some rivers experienced decreases through the 19th and 20th centuries, particularly parts of Northern Scotland. This is likely to be due to the previously noted temporal variability in both carbon fluxes and river flows, which has led to model-estimated decreases in fluxes between the decades chosen for analysis.

7. Discussion

Despite not being calibrated to observations, LTLS freshwater model estimates have been shown to compare reasonably well to observations

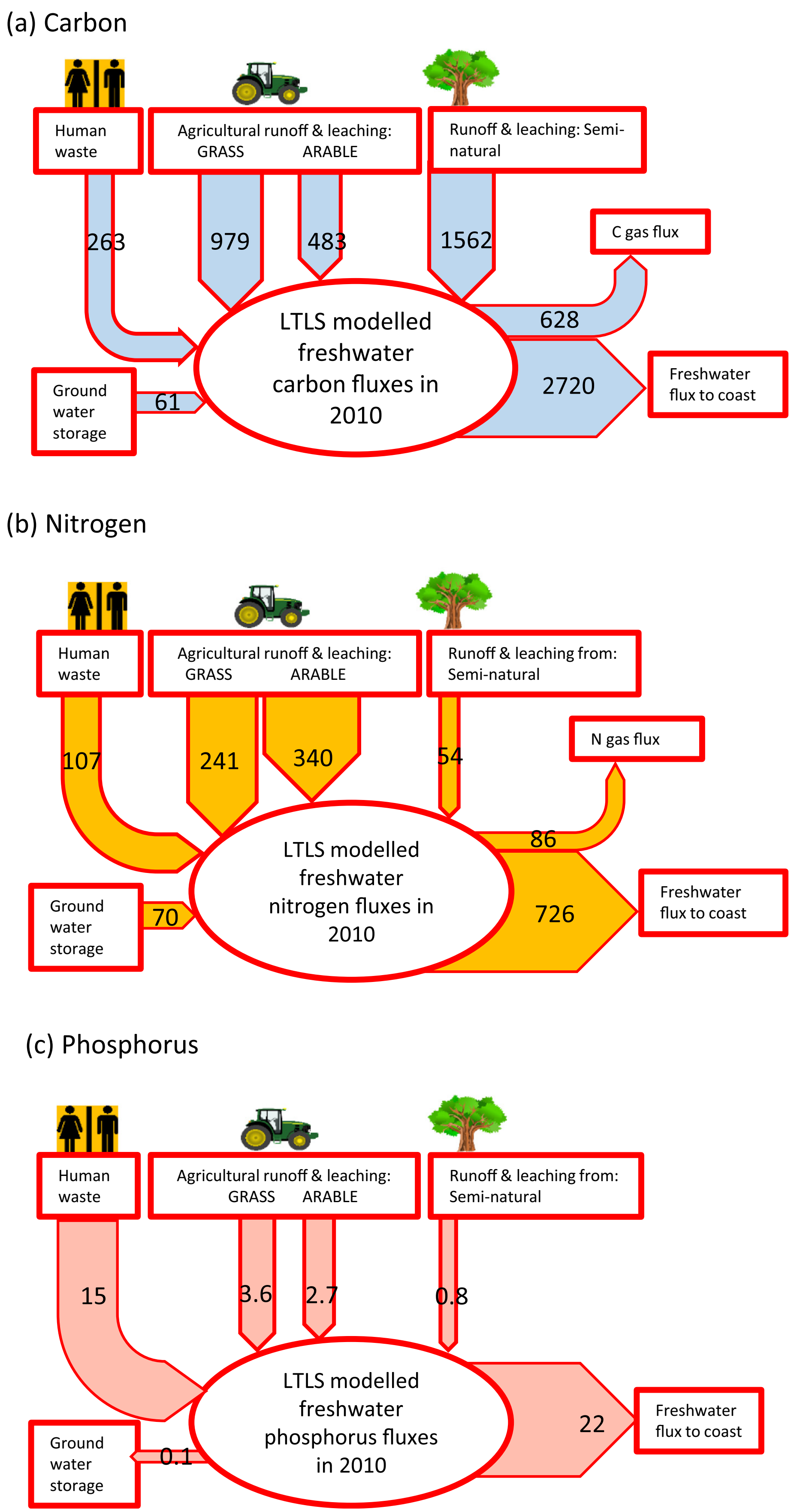


Fig. 7. Hydrosphere macronutrient budget (2010) providing estimated dissolved C, N and P flux from the LTLS-IM macronutrient model (kt yr^{-1}).

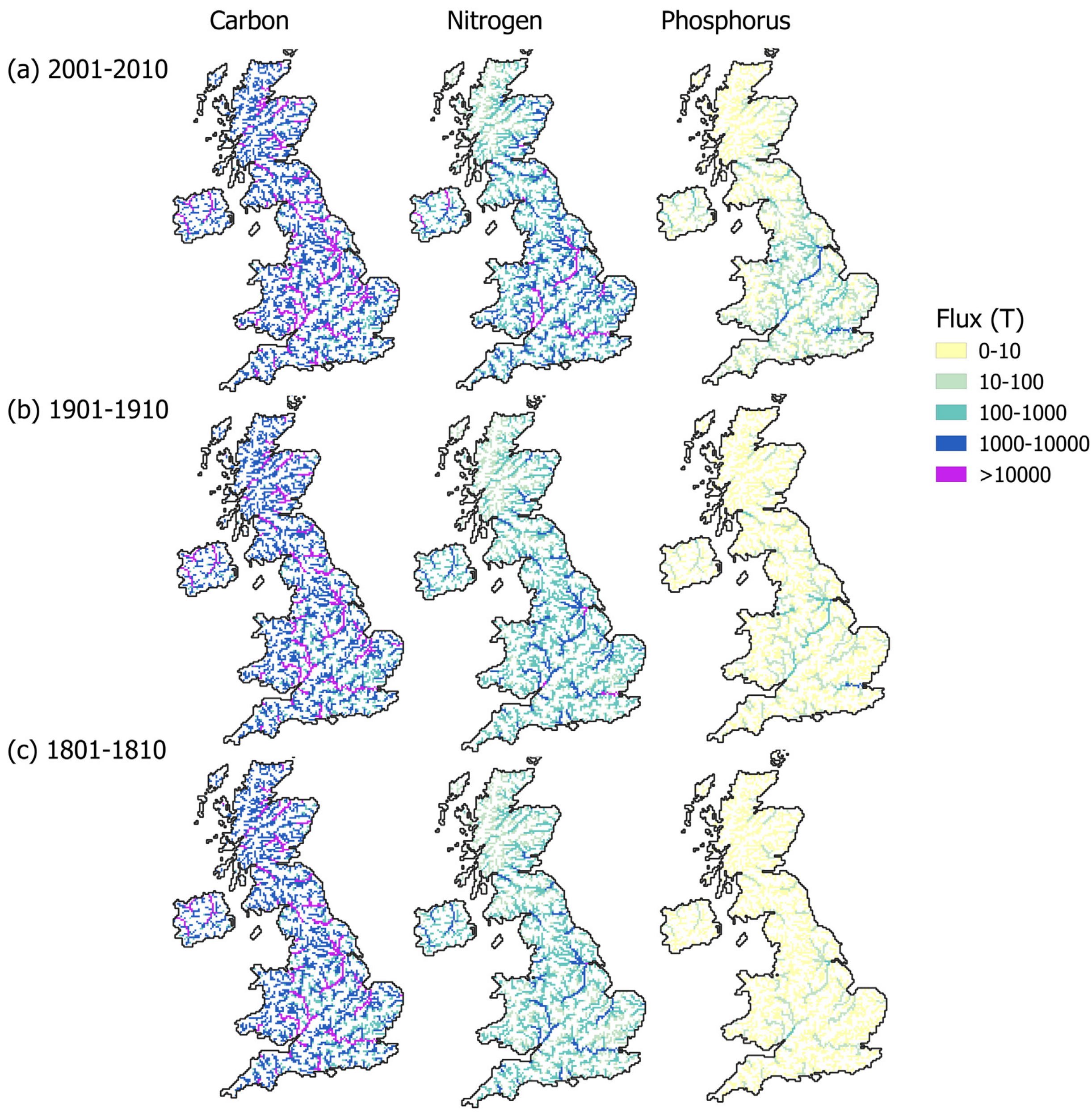


Fig. 8. UK maps of LTLS model estimates of mean annual dissolved C, N and P fluxes (T year^{-1}) for three historical 10-year periods (a) 2001–2010, b) 1901–1910 and c) 1801–1810.

at more than 200 HMS monitoring sites across Britain from the late 20th century onwards, and at a very small number of sites for which longer historical records are available. Based on these results, we have made the case that the freshwater component of the new integrated model (LTLS-IM) is able to reproduce the observed large-scale interrelationships between macronutrients in UK freshwaters. Using driving climate data and land-management information back to the 19th century, this new model provides a means to quantify and assess the interactions of C, N and P in freshwaters across the UK over two centuries from 1800 to 2010. The LTLS-IM also provides annual estimates of national-scale fluxes of C, N and P that can be compared with similar published estimates derived from observations and spatial extrapolation.

LTLS model simulations presented here indicate that between 1810 and 1980 the dominant source of N in rivers changed from improved grassland to arable and the dissolved N export to rivers quadrupled. Sewage N increased by a factor of 5 since 1900 and now contributes approximately 14% of dissolved nitrogen export to rivers. Present day LTLS-estimated dissolved N fluxes to UK coastal waters are broadly comparable with other published assessments. Applying (Section 5.2) estimates of 1% mean error (95% CI $\pm$3% error) in LTLS fluvial nitrate fluxes to total N fluxes, LTLS simulations indicate 727 $\pm$ 22 kT dissolved N flux to UK coastal/estuarine waters in 2010, which is comparable with the value of 791 kTy^{-1} estimated for the period 2001 to 2007 by Worrall et al. (2012a) using HMS measurements for 169 UK rivers. However, the LTLS simulations indicate that a much lower quantity (569 kT N) were exported to the coast via rivers in 2010, and the rest (22%) was exported via sub-surface pathways (SGD) and not measurable at HMS. LTLS model estimates also indicate 742 kT N terrestrial export to freshwaters in 2010, of which approximately 11% (86kT) was removed through in-stream processes. This percentage loss is within the range of previous literature estimates, for example Seitzinger et al. (2002) indicate 6–27% for the UK and Kroeze et al. (2003) suggest 11–50% for the Netherlands. Estimates by Worrall et al. (2012a) indicate 63% removed through in-stream processes such as denitrification, losses they noted were high compared to previous estimates.

Sewage is the dominant source of phosphorus (TDP) in rivers, particularly in England, and over the last century has increased with the UK's rising population to a peak in the early 1980s, before declining following improvements to wastewater treatment and changes to the formulation of detergents (Naden et al., 2016). Worrall et al. (2016) estimated fluxes of total phosphorus (TP), comprising both dissolved and particulate forms, for Great Britain (GB) between 1974 and 2012. Their estimates of 9 kTy^{-1} of total reactive phosphorus (TRP) flux from GB in 2011 are lower than the LTLS values of 22 kTy^{-1} TDP in 2010 estimated here for the UK, however LTLS TDP values are generally over-estimated and the true UK value would be expected to lie in the range 6 to 18 kT. Note that estimates for the UK should be ~6% larger than GB estimates because the UK is larger than GB, and TRP would be expected to be lower than TDP. LTLS simulations, which were compared with HMS measurements in Section 5 and Fig. 4, indicate that almost all TDP from terrestrial sources is exported to coastal waters, with relatively little (1–2%) stored long-term in groundwater or lake water, though retention of phosphorus in lakes can be more significant for catchments with extensive lake systems.

In contrast with the rapid rise in dissolved N and P fluxes, LTLS estimates of coastal C fluxes (DOC + DIC) rose gradually from 2320 kTy^{-1} in 1800 to a peak of 3234 kTy^{-1} around the year 2000 (Fig. 6). The comparison with present day HMS observations in Section 5.2 indicated that LTLS-simulated DOC fluxes were typically overestimated by 2–17% and if the error in DIC error is similar, the total dissolved C flux to the coast around the year 2000 would lie in the range 2764 to 3170 kT. Appendix E in the Supplementary Materials separates the total dissolved C sources and fluxes shown in Fig. 6 into DOC and DIC components. The high proportion of DOC exported from semi-natural soils is apparent, though this proportion has decreased over time. The plots also highlight the greater temporal variability in DIC estimates compared to DOC. In the LTLS-FM terrestrial export of DIC is determined through estimates of weathering in agricultural soils and groundwater, processes which are weather-dependent and also likely to be spatially variable. Comparisons of modelled and observed DIC fluxes at HM sites (Fig. 4) indicate that the LTLS model simulates DIC reasonably well, but has a tendency to underestimation. Published assessments of UK total dissolved fluxes have tended to focus on DOC rather than total dissolved C (DOC + DIC). For example, Worrall et al. (2012b) estimated that the total terrestrial DOC flux to rivers between 2001 and 2007 was 3100 to 4000 kTy^{-1} using information from catchment properties and HMS measurements, of which 2200 to 3100 kTy^{-1} was removed by in-stream processes and 909 $\pm$ 354 kTy^{-1} was exported to coastal waters. Here, terrestrial DOC export to rivers in 2010 was estimated at 1112 kT, of which approximately 5% was removed by in-stream processes and 1054 kT was exported to coastal waters (892 kT in rivers and 162 kT via SGD). The LTLS estimates of coastal fluxes (1054 kT) are typically overestimated by 2 to 17% and the true value would be expected to lie in the range 900 to 1033 kT. These values are broadly in line with those of Worrall et al. (2012b) but once again, the LTLS model estimates indicate considerably lower terrestrial export to rivers and in-stream losses (by a factor of 3).

DOC terrestrial and freshwater fluxes to coastal and marine ecosystems are an important component of global carbon budgets, and there are concerns that the terrestrial biosphere has switched from being a sink to a source of carbon. Monteith et al. (2014) analysed DOC trends for 22 UK upland acid water monitoring sites between 1988 and 2008 and the majority showed a significant increase in DOC concentration over the period. Carbon losses have significantly increased post 1975 largely driven by drought and by reversal of soil acidification which is thought to have increased DOC export (Monteith et al., 2014). The N14CP model used here to simulate semi-natural soils and vegetation does not currently factor this in, although it does predict an increase in DOC export due to N fertilisation. Further work being undertaken by the ongoing NERC LOCATE project (Williamson, 2021 (in review)) seeks to address these issues.

Although particulate macronutrients are included in the LTLS-IM, dissolved nutrients have been the primary focus because they are more bioavailable and reactive than the particulate forms. However, preliminary particulate export budgets for recent years have been assessed, and they indicate that (as expected) terrestrial export of eroded sediments, and particulate macronutrients associated with them, to freshwaters is temporally and spatially dependent on the occurrence and location of heavy rainfall and surface runoff (Appendix C). Comparisons between LTLS and HMS flux estimates indicate that the LTLS model typically underestimates fluvial sediment fluxes by 8%, (95% confidence interval of −47 to 57%). Worrall et al. (2013) estimate UK terrestrial and coastal export of suspended sediments using a method based on HMS data, and their figures indicate a coastal flux of approximately 7500 kT in 2010, which is considerably higher than the LTLS model estimates of 611 kT (with the true value expected in the range 388 to 1144 kT). In a later paper, (Worrall et al. (2014) estimated that the C content of suspended sediment was 2.7 to 38% with a median value of 15.8%. Thus, the particulate C flux to coastal waters in 2010 would be in the range 202 to 2850 kT (expected value of ~1125 kT). In 2010, LTLS-estimated coastal flux of particulate C was 33 kT, which is again lower than the expected value of Worrall et al. (2013). Further work will investigate the reasons for this, which could include underestimation of peaks in surface-runoff, flows and erosion arising from the use of a relatively coarse model resolution (a 5 km $\times$ 5 km UK grid).

Macronutrient export from terrestrial ecosystems to coastal waters is not just dependent on direct export to rivers, as freshwater biogeochemical processes and groundwater retention/release over several decades can decrease or increase macronutrient fluxes to coastal waters, and to the atmosphere. In the UK, long term gain/loss of N from stored groundwater is relatively high, due in part to earlier high agricultural losses in areas of southern Britain which have resulted in significant groundwater storage. Results indicate that since the 1990s, release of stored groundwater from earlier decades has increased the N flux to coastal waters by ~10%. These LTLS estimates of groundwater nutrient release are based on, and in line with, a UK model of nitrate travel times (years) in the unsaturated zone (Wang et al., 2012). The results here also support other research (e.g. Allen et al., 2014; Wang et al., 2016) that suggests that historical nitrate leaching could take several decades to discharge to freshwaters, impacting on the ability of land managers to successfully implement targeted reductions in agricultural runoff to freshwaters. The conversion of grazed land to cropland during the Second World War is thought to have increased the flux of nitrate to groundwater which will take differing periods of time to re-emerge in surface waters depending on the intermediate geology (Whitmore et al., 1992).

The LTLS freshwater simulations indicate that significant proportions of nitrogen, carbon and, to a lesser extent, phosphorus, are exported to UK coastal waters from sub-surface pathways (i.e. not measurable in river-water). The UK has an extensive coastline and rivers typically extend up to a few hundred km before discharging to coasts and estuaries, allowing only limited time and opportunity for return-flow from sub-surface to surface waters to occur. This long coastline combined with significant groundwater storage may result in the UK exporting an unusually high proportion of groundwater to the sea by direct transfer. Water balance methods are widely used for estimating SGD at global scales, and reviews of such estimates (e.g. Taniguchi et al., 2002; Moosdorf and Oehler, 2017) indicate that SGD provides 0.01 to 10% of total freshwater inputs to coastal waters. Beusen et al. (2013) found that global SGD transport of nitrate (NO_3-N) to coastal waters increased from 1.0 to 1.4 Tg /year between 1950 and 2000 and expected an increase of another 20% in the following decades. The LTLS estimates of SGD of dissolved C (~30%) and N (~20%) are high compared to global estimates of up to 7.7% of the total coastal export (Luijendijk et al., 2020), though nutrient fluxes will vary with local geology and terrestrial sources. The model results presented here indicate however, that a significant flux of nutrients to UK coastal waters is currently neglected by routine freshwater monitoring, and potentially not accounted for by models of coastal eutrophication and ecosystem management. Although a range of methods are available for measuring SGD (e.g. Montiel et al., 2018), to our knowledge, measurements of macronutrient SGD to UK waters are not currently available, and we are therefore unable to assess the veracity of the LTLS model estimates.

8. Summary and conclusions

To understand and quantify long term and large-scale fluxes of macronutrients across the UK, the LTLS macronutrient modelling consortium has developed and applied a suite of relatively simple process-based atmospheric, terrestrial and freshwater macronutrient models over a historical period of more than 200 years. These models take account of the interlinked cycles of C, N and P in soils and rivers, include inputs from natural and agricultural terrestrial ecosystems, atmospheric deposition and sewage, and use best estimates of historical changes in climate, population and land-management.

The freshwater model outputs presented here provide realistic estimates of the increase in terrestrial macronutrient export to rivers through the 19th and 20th centuries following rapid industrialisation and population growth. Over the period 1800 to 2010, the LTLS modelling indicates:

- Terrestrial N and P export to rivers increased by factors of approximately 4 and 10 respectively, and dissolved C export increased by 20% before all started to decline in the late 20th Century.
- Dissolved N export to rivers reached a peak of over 900 kt year^{-1} in the 1980s before dropping to 741 kt year^{-1} in 2010.
- Agriculture (improved grass and arable land) is the largest N source, although N from sewage has increased by 400% since 1900.
- Most phosphorus (TDP) export to rivers comes from sewage, and across the UK was estimated to have increased from negligible quantities in 1800 to approximately 29 kT year^{-1} in the early 1980s, before declining to 22 kT in 2010.
- In contrast, LTLS simulations of carbon (DOC + DIC) export from terrestrial sources increased by just 20% from the early 1800s to a peak of 4454 kt year^{-1} in 2000.

The LTLS freshwater modelling indicates that the majority of C, N and P entering freshwaters from terrestrial sources is exported directly to coastal and estuarine waters. More specifically, the modelling indicates that:

- Nearly all of the TDP in freshwaters discharges straight to the sea, but approximately 20% of dissolved C and 10% of N is removed by in-stream processes, mainly through conversion to gaseous forms.
- Groundwater retention/release over several decades can decrease or increase macronutrient fluxes to coastal waters, and to the atmosphere. In the UK, long term gain/loss of N from stored groundwater is relatively high, due in part to earlier high agricultural losses in areas of southern Britain which have significant groundwater storage with long retention times.
- There was a net storage of nitrates in groundwater between the 1940s and 1990s, and a net release to coastal waters post-1990. Long term C and P storage and release is estimated to have been more modest (approximately 1–2%).
- A significant proportion of the UK's C and N export to coastal waters and estuaries (~20% ~30% respectively) is via sub-surface pathways (submarine groundwater discharge) rather than rivers, and measurements of macronutrients in rivers alone may underestimate total C & N export to the marine system.

The results presented here demonstrate how atmospheric, terrestrial and freshwater macronutrient models can be coupled in a simple but consistent way to provide long-term and national-scale estimates of the sources, pools and fluxes of macronutrients. Potential applications include providing national and regional nutrient budgets to support policy development, but also to provide a water quality benchmark of the impact population growth and agricultural development has had on UK freshwaters since pre-industrial times. The comparisons of present day and pre-industrial freshwater macronutrient fluxes in particularly polluted catchments or regions provide hydrologists and water managers with information to help set achievable environmental targets. Model development is an iterative process and the LTLS freshwater model will continue to be developed and improved. Further work is required to compare model outputs with other sources of freshwater quality observations (e.g. the Environment Agency WIMS database - https://environment.data.gov.uk/water-quality/view/landing), to develop and assess the estimates of particulate macronutrients, and potentially include estimates of macronutrient fluxes from industrial sources, which are not included here. Future application of the LTLS-FM at finer spatial resolutions, and use of higher resolution meteorological driving data (1 km and hourly are now available) will provide opportunities to explore the impact of hydrological extremes on freshwater quality and coastal macronutrient fluxes. The ability of the new model to provide continuous, spatially-distributed estimates of water and nutrient fluxes to coastal waters also provides new opportunities to develop fully-coupled global models of terrestrial, freshwater, atmospheric and marine processes that can take account of changes in land-management and climate.

CRediT authorship contribution statement

V.A. Bell: Writing, Visualization, Methodology, Investigation, Validation, Formal Analysis, Software. **P.S. Naden**: Conceptualization, Methodology, Validation, Formal Analysis, Software, Writing. **E. Tipping**: Conceptualization, Methodology, Funding acquisition, Supervision, Writing, Software. **H.N. Davies**: Data Curation, Visualization, Resources. **J. Davies**: Methodology, Investigation, Software, Investigation, Data Curation, Formal Analysis. **E. Carnell/A.J. Dore/ S. Tomlinson/ L. Wang/ L. Wu**: Investigation, Software. **U. Dragosits**: Investigation, Methodology, Formal Analysis. **D.J. Lapworth**: Methodology. **S. E. Muhammed**: Methodology, Investigation, Software, Investigation. **J. Quinton**: Conceptualization, Methodology. **M. Stuart**: Conceptualization, Methodology, Writing. **A.P. Whitmore**: Conceptualization, Methodology, Funding acquisition, Supervision.

Declaration of competing interest

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

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Supplementary data

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