Hutchins, Michael G.. 2012 What impact might mitigation of diffuse nitrate pollution have on river water quality in a rural catchment? *Journal of Environmental Management*, 109. 19-26. 10.1016/j.jenvman.2012.04.045

What impact might mitigation of diffuse nitrate pollution have on river water quality in a rural catchment?

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Abstract

Observations of river flow, river quality and solar radiation were collated to assess the degree to which light and nutrients may be limiting phytoplankton growth at seven sites in the River Ouse catchment in NE England under average conditions. Hydraulic information derived from river network model applications was then used to determine where river water has sufficient residence time above the tidal limit to facilitate bloom development. A nitrate model (NALTRACES) was developed to estimate the impact of land management change on mean river nitrate concentrations. Applications of this model showed that although agricultural activity contributes substantially to nitrate loads in the Ouse it is likely to have little impact on phytoplankton growth, which could still occur extensively in its absence given favourable sunny and dry conditions. As an example of a means of controlling light availability, establishing full riparian tree cover would appear to be a considerably more effective management scenario than suppressing inputs to the river of nitrate or phosphorus. Any actions should be prioritised in headwater areas such as the upper reaches of the Swale and Ure tributaries. These conclusions are in broad agreement with those arising from more detailed simulations at daily resolution using the QUESTOR river quality model. The combination of simple modelling approaches applied here allows an initial identification of suitable spatially-targeted options for mitigating against phytoplankton blooms which can be applied more widely at a regional or national level.

Keywords: nitrate, phytoplankton, river water quality, catchment modelling, pollution mitigation, policy

1. Introduction

The contribution that diffuse runoff sources make to freshwater nitrate loads is known to be sensitive to the extent and management of agricultural land in the upstream catchment (Cherry et al., 2008; Heathwaite et al., 2005). Effort to reduce these loads is being made in the context of various legislative requirements such as the EC Nitrates Directive (including Nitrate Vulnerable Zone designation) and the EU Water Framework Directive (WFD). Mathematical models play a central role in this process (Arnold et al., 1998; Dunn et al., 2004; Heathwaite, 2003; Hutchins et al., 2009; Wade et al., 2002). Some modellers (e.g. Anthony et al., 2009; Bouraoui et al., 2002) have made such applications in the River Ouse (Yorkshire, UK), the subject of research in the present study. Agriculture also makes an important contribution to diffuse sources of phosphorus, but these are harder to reduce substantially unless micro-management interventions are specifically prescribed (Haygarth et al., 2009). Importantly the WFD also covers a more overarching requirement to ensure the health of freshwater ecosystems and to avoid eutrophication.

It has been widely assumed that nutrients control eutrophication, one of the key manifestations of which are phytoplankton blooms. Whilst the importance of nutrient supply is clearly demonstrated in lakes (Reynolds et al., 2001) where residence times are long, in rivers the interactions with hydrology make for a distinctly different and less tractable set of controls (Hilton et al., 2006). Applications of detailed process models of the river channel help achieve better understanding of the controlling factors. In this respect, an example of such a model, QUESTOR, has been applied to the River Ouse catchment (Hutchins et al., 2010a) illustrating that phytoplankton biomass is far more sensitive to changes in flow rate, light and water temperature than to nutrients, which are considerably in excess throughout the year.

For the development of strategies to protect river ecosystems, initial risk assessments need to be performed rapidly to encompass large areas. Therefore to ensure effective guidance of the decision-making process it is important to distil the complexities embodied in process-based models such as QUESTOR into simpler approaches whose application is straightforward with lesser data requirements. It is accepted that for applications where predictions of greater detail are required a more complex model would be more accurate and better suited. Undertaking model simplification may involve aspects of process representation, spatial variability and/or temporal resolution, the process often also providing benefits by reducing model uncertainty without greatly impairing performance (Hutchins et al., 2007; Lindenschmidt, 2006; Snowling and Kramer, 2001). Whilst initial risk assessments have been undertaken for nutrient leaching (e.g. Johnes, 1997) they have not been extended to consider potential phytoplankton impacts. In this regard in the present study, a novel method using coarser temporal resolution was developed which assessed on a site-specific basis the extent to which average nutrient and light conditions will potentially limit river phytoplankton growth. The method allowed the impact of future possible changes in nutrient loads, incident light and water temperature to be assessed easily, upon which more detailed analysis with complex models can follow. An example of such a preliminary analysis was illustrated for the Yorkshire Ouse catchment in NE England, highlighting in particular the interventions of land use change and riparian tree planting.

Using an example of 7 sites within the Yorkshire Ouse catchment, the present study:

- Assessed the potential extent to which phytoplankton growth is being limited by (i) nutrients, using mean annual concentrations from periodic regulatory monitoring. programmes, and, (ii) light, using solar radiation data and suspended sediment monitoring.
- Identified the sites where the river water has sufficient residence time to the tidal limit to facilitate development of phytoplankton blooms.
- Developed and applied a model of mean nitrate concentration sensitive to land use change.
- In applying this model, assessed nitrate limitation under a hypothetical situation where agriculture is absent to determine how much scope there is for agricultural mitigation measures to curtail phytoplankton growth. This scope was considered relative to the alternative (or additional) measure of planting riparian trees to reduce light incidence.

2. Methodology

2.1. Study area

The Yorkshire Ouse catchment in NE England covers an area of 3315 km^2 and is fed by three main tributaries, the Swale, Ure and Nidd. Less than 10 km downstream the tidal limit is reached, the river draining via the Humber estuary (Figure 1) into the North Sea. More detail is provided elsewhere (Hutchins et al., 2010a). The analysis carried out in the present paper was focused on 7 river flow and quality monitoring sites within the catchment namely (5 figure site IDs and 8 figure NGRs in brackets): Cod Beck at Dalton Bridge (27085: 4422 4766), River Swale at Catterick (27090: 4226 4993) and Crakehill (27071: 4425 4734), River Ure at Kilgram Bridge (27034: 4190 4860) and Boroughbridge (27007: 4356 4671), River Nidd at Pateley Bridge (27005: 4141 4683), and the catchment outlet of the River Ouse at Nether Poppleton (27009: 4568 4554) near the city of York.

2.2. Assessment of potential riverine phytoplankton growth limitation

The state of understanding of controls on phytoplankton growth in rivers has been captured and summarised in a number of river quality models (Hutchins et al., 2010a; Reichert et al., 2001; Scharfe et al., 2009; Whitehead et al., 1997) which typically, due largely to a paucity of observations, represent a mixed phytoplankton population rather than differentiating between functional groups and their specific environmental requirements. Rather than conduct applications of physically-based models at daily time step, the present study sought to demonstrate the use of the principles behind the phytoplankton component of such models to enable a rapid estimation of the factors most likely to be limiting growth. In making this simplification, the analysis did not cover consequences of the mechanism of prolonged bloom development whereby the phytoplankton themselves become significant nutrient sinks. In reality, a given N or P concentration, whilst not limiting at the onset of a period of growth, may nevertheless become limiting during persistent and severe blooms.

In respect of the principles underpinning understanding of phytoplankton growth, photosynthetic rate is limited by a multiplicative formulation of nutrients (f(Nutrients): minimum of N and P: a hyperbolic relationship as defined by Michaelis Menten kinetics (Equation 1)) and light (f(Light)). For light limitation, (i) attenuation (γ) with depth is described by the Beer-Lambert law (including effects of suspended sediment (SS) and the phytoplankton (Phy) themselves) (Equation 2), and (ii) photolimitation, with respect to autotroph-specific optimum intensities, is represented by the Steele (1962) formulation (Equation 3). Phytoplankton are assumed to be exposed to depth-averaged light. The limitation factors, f(N), f(P) and f(Light) hold values between 0 (full limitation) and 1 (no limitation). It should be noted that the maximum photosynthetic rate is first order with respect to biomass and is temperature dependent (via the Arrhenius equation) although this was not to be considered in the present paper.

$$f(Nutrients) = \min[f(N), f(P)] = \min\left[\frac{N_{\text{var}}}{N_{\text{var}} + k_N}, \frac{P_{\text{var}}}{P_{\text{var}} + k_P}\right] \quad (1)$$

where: k_N = 0.1 mg N L^{-1}; k_P = 0.01 mg P L^{-1}; N_{var} and P_{var} are concentrations in mg L^{-1} of nitrate-N plus ammonium-N and inorganic-P plus organic-P respectively.

$$\gamma = \gamma_{base} + L_{ss} SS_{\text{var}} + L_{Phy} Phy_{\text{var}} \quad (2)$$

where: SS_{var} (suspended sediment) and Phy_{var} (phytoplankton biomass determined from a Chl-a surrogate (Hutchins et al., 2010a) using the stoichiometric ratio of 1:50:10:1 for Chl-a:C:N:P) are concentrations in mg L^{-1}; γ_{base} (0.01 m^{-1}) is the light extinction coefficient in clean water; L_{ss} (0.01 m^{-1} mg^{-1} L) and L_{phy} (10 m^{-1} mg^{-1} L) represent light attenuation due to SS and Phy respectively. Values of the constants are from Bowie et al. (1985).

$$f(Light) = \frac{2.718}{\gamma d}\left[e^{-\frac{R_s L_1 L_2}{L_{opt}} e^{-\gamma d}} - e^{-\frac{R_s L_1 L_2}{L_{opt}}}\right] \quad (3)$$

where: R_s = radiation at the surface not reflected (W m^{-2}); d = water depth (m); L_{opt} (60 W m^{-2}) is the optimum light intensity for phytoplankton; other terms being the fraction of incoming radiation that is visible light (L_1) and the fraction of that visible light that is useful for photosyntheisis (L_2). Values of constants are from Bowie et al. (1985).

Light and nutrient limitation factors were calculated at each of the 7 sites of interest. In order to estimate light limitation, photosynthetically-active radiation was required (determined at daily resolution using weather station data for the Cawood site (NGR 4575 4375) held at the NERC British Atmospheric Data Centre). A shading reduction factor (DeWalle, 2008) was applied to these data to mimic the effect of riparian tree cover. Tree cover was estimated using satellite imagery. Light limitation factors were calculated based on typical conditions in the spring/summer growing season. River depths were determined from flow data at median flow as estimated using an existing

QUESTOR application (Hutchins et al., 2010a). An indicative chlorophyll-a concentration of 0.015 mg L^{-1} was applied for estimating the self-shading effect of phytoplankton on light availability.
In terms of nitrogen and phosphorus, limitation factors were calculated based on average annual conditions. These were based either on (i) observations of soluble reactive phosphorus (SRP), total phosphorus (TP), ammonium-N (NH_4-N) and nitrate-N (NO_3-N) from the Environment Agency (EA) periodic monitoring programme, or (ii) in the case of the NO_3-N component, based on a model of annual mean concentration that is sensitive to land use. In this second case it was then possible to illustrate the influence agricultural nitrate may have on potential for phytoplankton growth.

Historic chlorophyll-a data are scarce, although Neal et al. (2006) report spring/summer means for 16 UK sites (including 4 in the Ouse), and linear regression of these against estimates of upstream residence time (Soballe and Kimmel, 1987) reveal a strong relationship ($r=0.68$, $P<0.001$). As residence time and dilution are of key importance in rivers, the manifestation of limitation factors in terms of phytoplankton population are seen downstream of the sites themselves. Therefore, for each site the downstream travel time to the tidal limit was calculated under two conditions: (a) mean flow and (b) 90th percentile (low: Q90) flow. Travel times along a river stretch were derived via the calculation of flow velocity (Round et al., 1998) at a succession of points where data are available. Progressive dilution from sources joining the river stretch was also calculated for each of the 7 cases. Data on residence time and dilution were generated using the Low Flows 2000 software.

2.3. Modelling river mean nitrate-N concentrations

In this study a river nitrate-N model (NALTRACES: <u>N</u>itrate <u>A</u>vailable for <u>L</u>eaching, <u>T</u>ransport to <u>R</u>ivers <u>A</u>nd <u>C</u>hannel <u>E</u>xports and <u>S</u>inks) was first developed and tested against observed monitoring data. Then it was used to calculate phytoplankton growth limitation factors under hypothetical scenarios as well as present day (baseline) conditions. Four components comprise the modelling of nitrate-N concentrations by NALTRACES which is also portrayed schematically (Figure 2):

- The calculation of soil nitrate-N available for leaching (NAL) from diffuse sources to waterbodies (Sections 2.3.1 and 2.3.2)
- A hydrological nitrate-N transfer function to be applied to diffuse sources of nitrate-N (Section 2.3.3)
- Estimation of point source nitrate-N loads (representing effluents from sewage works and industry) (Section 2.3.4)
- Estimation of in-river sinks of nitrate-N due to denitrification and biological uptake (Section 2.3.4)

In terms of establishing a benchmark for "present day" conditions and for testing the model against observations the period 1st September 1999 – 31st August 2003 was considered. Model performance was evaluated in terms of (i) mean concentrations across the four year period, (ii) year-specific mean concentrations, and (iii) mean concentrations (1999-2003) in 17 additional headwater catchments (< 300 km^2) in other basins draining to the Humber. The third aspect of testing focused solely on catchments of short residence time thereby providing additional testing of the first three components of NALTRACES.

2.3.1. Input data required for estimating diffuse sources of nitrate

A profile of land-use and soil combinations was prepared and statistically summarised at the level of hydrological response units (HRU). In the Ouse catchment, 539 of these HRU were delineated, each representing hydrologically-isolated units of approximately 5 km^2 (Hutchins et al., 2010b). As Posen et al. (2011) describe, the profiles were based on best estimates of observed land-use (made by integrating landcover (CEH Land Cover Map 2000: Fuller et al., 2002) and 2004 Department for Environment Food and Rural Affairs (Defra) Agricultural Census data (available online at http://www.edina.ac.uk)) prior to combination with a soil classification based on hydrological properties (HOST: Boorman et al., 1995).

Daily rainfall on a 1 km^2 grid was derived from data available from the UK Meteorological Office network of raingauges. Monthly potential evapotranspiration (PET) was accessed from a MORECS 40x40 km grid (Thompson et al., 2002). For both rainfall and potential evapotranspiration, data were aggregated to the annual level and representative values chosen for each HRU.

Atmospheric nitrogen deposition was derived from a 5 km^2 grid (based on a modelled interpolation from 32 UK monitoring stations (Fowler et al., 2005)) and representative values assigned for each of the 7 sub-catchments (Table 1). Likewise, for these 7 areas, geographically-specific inputs were defined for modelling (i) the soil nitrogen cycle in grassland systems using NCYCLE (Scholefield et al., 1991) and (ii) contributions to available nitrate-N from livestock manure applications to arable land as quantified using MANNER (Chambers et al., 1999) (see below).

2.3.2. Calculation of soil nitrate available for leaching (NAL)

The input datasets described above permit estimation of crop and soil-type specific NAL values. Aggregated annual NAL values were derived in the same way as carried out previously on a monthly basis (Hutchins et al., 2010b) whereby arable and grassland values were calculated separately. As before a constant NAL value of 6 kg ha^{-1} yr^{-1} was used for all non-agricultural land, reported values tending to be slightly higher for woodland and slightly lower for open moorland respectively (Silgram et al., 2005). Crop rotation was not explicitly accounted for but was assumed to occur within the statistical assemblage of crops defined on an HRU-basis.

There were a number of key departures from a previously published method (Hutchins et al., 2010b) of estimating NAL values for arable land:

(a) Representation of mineralization of recalcitrant (mainly humic) material as a source of NAL was modified to use the approach adopted in SOIL-N, a widely-tested field-scale model of agricultural soil nitrogen dynamics (Johnsson et al., 1987). Undertaking an extensive survey and analysis of soils was logistically inappropriate for this study. Therefore, estimates of soil organic carbon content, necessary for the determination of NAL, were assigned to soils based on the HOST classification (Boorman et al., 1995) using data from the SEISMIC database (Hallett et al., 1993), a national-scale source of physico-chemical data allowing soil properties to be assigned to mappable units.

(b) A change in the estimation of direct nitrate-N losses from livestock manure. Whilst being mindful of the substantial simplifications involved and inevitable loss of detail involved, the principles of apportioning livestock wastes, as applied by Dunn et al. (2004), was adapted. In our study, cattle manures were assigned to grasslands based on stocking densities of 2.7 and 2.0 livestock units per hectare for dairy and beef systems respectively (Nix, 2000). This component was then accounted for, as an input to NCYCLE, in the modelling of leaching from grasslands. Any leftover waste was then assigned to arable crops, the N content determined and the MANNER model used to determine the fraction made available for leaching. The fate of N from pig and poultry manures was also determined using MANNER, though in these cases it was assumed that all waste was applied to arable land. In each component sub-catchment, a single average figure per hectare for all cropland was used given uncertainty in the location of manure spreading (in particular from pig and poultry units) and the prevalence of manure trade between enterprises.

(c) Including provision for direct nitrate-N losses from fertiliser applications. Virtually all fertiliser is locked up as plant uptake by June. As stressed by Davies and Sylvester-Bradley (1995) the likelihood of losses is only significant when crops are spring-sown, applications being negligible in autumn (e.g. 3 kg N ha^{-1}). Therefore it was assumed that between April and July approximately 10% of the applied fertiliser is potentially available for leaching (Lord and Bland, 1991): adding, for example, to the April NAL, approximately 5 kg N ha^{-1} depending on the type of crop.

(d) Inclusion of topsoil denitrification in the soil nitrogen cycle, based on well-founded concepts described by Boyer et al. (2006). Rates were calculated at a monthly time-step (Equation 4):

$$DN_{soil} = NO_3(1 - \exp(-w\lambda_T C_{org} t)) \quad (4)$$

Where: DN_{soil} = monthly soil denitrification rate N (kg ha^{-1}); NO_3 = monthly available soil nitrate-N (kg ha^{-1}); C_{org} = topsoil organic carbon (%) (see part (a) above); t = 1 (i.e. a single monthly time step); w = dimensionless reduction factor for water content (w = 0 at field capacity, w =1 at saturation); λ is a van't Hoff expression representing exponential increase in denitrification with temperature ($\lambda = Q10^{(T-Tref)/10}$ (where Q10 = 2.28; Tref =21 and T = observed soil temp). Coefficients defining the van't Hoff temperature relationship were taken from mean values of a review of model structures and their parameterisation (Heinen, 2006).

The modifiers to denitrification rate based on temperature (λ_T) and water content (w) were calculated as follows. Mean monthly values of soil temperature in the topsoil were derived from research by Green and Harding (1979). A mean monthly reduction factor on denitrification due to water content was assigned on an HRU basis. All 17 EA flow gauging stations falling within the Ouse catchment (as shown on Figure 1) have a published PROPWET characteristic (Centre for Ecology and Hydrology, 2003), defined as the proportion of time when soil moisture deficits are less than 6 mm. These 17 values were used as an index of soil wetness, although there is not much change on a small spatial scale, values being in part derived from MORECS 40 x 40 km cells. After soils become "wet" it was assumed that *w* changes from 0 to a maximum value over a 30 day period. The maximum value was determined from soil properties of the dominant soil HOST class in each of the 17 sub-catchments, being the ratio of water content at field capacity to water content at saturation. Likewise, at the end of the "wet" period, a change in reverse at the same rate was assumed.

2.3.3. Transfer function model of nitrate leaching from land to watercourse

For agricultural grasslands and the non-agricultural land-uses all the NAL was assumed leached each year. In the case of arable crops, a formulation was used to calculate the fraction of NAL that is actually leached on an annual basis (Anthony et al., 1996; Lord and Anthony, 2000). Anthony et al. (1996) show this formulation to successfully mimic field-scale model output from the more complex Solute Leaching Intermediate Model (Addiscott and Whitmore, 1991). The formulation requires values of hydrologically effective rainfall (HER) to be calculated for each HRU using rainfall, PET and a soil categorisation based on hydrological properties. The model also requires the field capacity (FC) to 90 cm depth of all soils to be estimated. The soil hydrological properties were assigned using a combination of the HOST classification (Boorman et al., 1995) and data from the SEISMIC database. The two values, HER and FC, were combined to generate an indicator of "drainage efficiency" which acts as the dependent variable in a non-linear (cubic) regression relationship to determine the fraction of nitrate-N leached. It was assumed that (i) all nitrogen leached reaches watercourse in the form of nitrate, (ii) groundwater of long residence time contributing to river flow is neither enriched nor depleted in nitrate relative to water from near-surface sources.

2.3.4. Calculation of river nitrate concentrations

For calculation of nitrate-N loads from point sources, the method adopted was to estimate population numbers and apply to these a set of per capita coefficients as defined by Johnes (1997). Population data from the 2001 Census were acquired and resolved spatially at the level of HRU assemblages (aggregate HRUs, of which there are 157 in the Ouse catchment). A characterisation of the type of population representative as being predominant in each HRU assemblage was made. Three classes were used: urban, village and rural. Urban populations were assumed to be connected to sewage treatment works and an annual value of 2.09 kg NO_3-N capita^{-1}, as used by Johnes (1997), was assumed. A higher annual value of 2.49 kg NO_3-N capita^{-1} was assumed for the other two classes of population, which are considered typically served by septic tanks.

An empirical model (Equation 5) formulated from an extensive world-wide database of observations (Seitzinger et al., 2002) was applied to calculate river sinks of nitrate-N on a reach-by-reach basis. Here, the percentage of nitrogen removed is related to the hydraulic load of the river reach. Hydraulic load is defined by water depth and travel time:

$$DN_{river} = 88.45 \left(\frac{D}{T}\right)^{-0.3677} \quad (5)$$

where: DN_{river} = removal of NO_3-N load in the river reach (%); D = depth (m); T = travel time (yr)

To facilitate this calculation, a previous application of the QUESTOR model to the Ouse (Hutchins et al., 2010a) was made use of to represent the river system as a 325 km network above Site 27009 (Figure 1) divided into 189 connected reaches. Into these reaches, 93 spatially distinct inputs of nitrogen were specified, representing all the diffuse and point sources described above. Quantification of the river nitrate-N sink was made on a reach-by-reach basis. QUESTOR estimates a daily water flow time-series for each reach from which properties of the flow duration curves were calculated to allow modelling of nitrate-N sinks at low, median, mean and high flows. Clearly the size of the sink is strongly related to water flow. Rather than use the Manning equation, which requires information on river hydromorphology not readily available, simple non-linear hydraulic relationships between flow and velocity (Leopold and Maddock, 1953) are used by QUESTOR on a reach-specific basis. Employing these, in conjunction with estimates of river widths taken from UK national river habitat surveys (Raven et al., 1998) allowed calculation of travel times and depths, and hence nitrate-N sinks. The nitrate-N sink calculations at mean flow were deemed most appropriate and applied for the estimation of mean annual river loads of nitrate-N at the 7 sites.

Finally, annual flow data (compiled from the EA flow records and held in the CEH National Water Archive) were used to derive mean annual nitrate-N concentrations from the modelled mean annual loads for the 7 sub-catchments. Where available, the nitrate-N concentration data, as collected nearby by the EA under routine fortnightly or monthly resolution monitoring, were used for evaluation of NALTRACES model performance.

3. Results: river basin characteristics, growth limiting factors, and model outputs

Catchment characteristics in terms of land use statistics and nutrient (N and P) outputs reveal large variations across the Ouse basin (Table 1), reflecting the differing land-use composition. Water quality observations during the period were typically made at monthly intervals although Site 27071 was usually sampled twice a month. Atmospheric nitrogen inputs are less variable (Table 1). The residence time calculations (Table 1) suggest that river water at the 3 sites furthest from the tidal limit (27005, 27090 and 27034) will have sufficiently long residence time in the freshwater river environment at low flows (Q90) to foster significant phytoplankton growth. However the volumetric contribution from Site 27005 to the Ouse at the tidal limit is not substantial.

Under present day conditions airborne imagery suggests riparian shading is at 25% of capacity on average across the Ouse basin. In conjunction with incoming solar radiation data, a typical April-August daily flux at the water surface was estimated to be 155 W m^{-2}. Across the 7 sites mean SS between April and August is 3.2-27.9 mg L^{-1}, suggesting SS could cause the light limitation factor (f(Light)) to vary considerably between sites. River water depths at conditions between median and low (Q90) flows broadly representative of April-August were estimated to be 0.2-0.84 m across the 7 sites. Using these ranges of values, f(Light) was estimated to lie between 0.46-0.49. When compared to values of f(N) and f(P) (Table 1) this demonstrates that throughout the Ouse, incident light is likely to be limiting phytoplankton growth far more than nutrients.

Mean simulated annual nitrate-N concentrations are given under present day conditions (Table 2) and when compared with observations (Table 1) an indication of model skill is given. For the extended dataset of mean nitrate-N concentrations (y) from 17 other sites in the wider Humber basin (mean nitrate-N range: 1.28-11.05 mgL^{-1}) a regression analysis against model simulations (x) revealed a good fit (y=0.90x, r^2=0.64, P<0.001), the slight overestimation likely being due to in-channel retention which was not quantified in these cases. For individual years, simulations and observations for the sites with the three largest catchment areas in the Ouse are displayed graphically (Figure 3). Comparison of the mean annual nitrate-N simulations in the Ouse with estimates of nitrate-N concentrations under the hypothetical scenario in which agriculture is absent (Table 2) illustrates the large contribution of agricultural sources to river nitrate loads throughout the basin, with the exception of the upland extremities to the north and west (e.g. Site 27005). However these agricultural sources appear to make little contribution to the nutrient limiting factor (f(N): Table 2). In contrast, limitation due to light may be increased to a considerable extent by establishing riparian shading at full capacity (estimated f(Light) at 100% canopy coverage: 0.34-0.37).

4. Discussion: model performance, and prioritising the choice and location of interventions

The wide spatial variability of mean nitrate-N concentrations prevalent in the Ouse catchment (Table 1) is captured by NALTRACES. However, although simulations at the Ouse catchment outlet (27009) and the largest sub-catchment (27071) are within 10% of observations, there are cases of larger under- or over-estimation at individual sites (Table 2). In the Ure (27007) a source of N appears to be missing and cannot be explained in the context of uncertainties in either diffuse or point sources. Additional observations along the river (at lower temporal frequency) suggest the unexplained source appears in the vicinity of Aysgarth Falls (NGR 4018 4888). High concentrations observed in small sub-catchments (e.g. Cod Beck: 27085) may be poorly simulated as in such cases if population N sources are discharged via sewage works into streams across a sub-catchment boundary there will be a significant impact on total nitrate-N load and mismatches will become apparent. When considering specific years (Figure 3) the response of the model is generally satisfactory although there are difficulties in simulating Sept 2000-Aug 2001, a period during which there was prolonged exceptionally high rainfall and associated flooding (in November 2000, York suffered its worst flooding for 400 years). Consequently, the lowest concentrations of the 4 years were simulated in 2000-01 due to high dilution, yet other processes and sources of N associated with severe flooding that are not represented in NALTRACES (e.g. combined sewer overflows) are likely to have been important, elevating loads. Furthermore, in spring 2001, a food and mouth disease outbreak greatly affected agricultural activity. When focusing on individual years, imprecision is introduced when making the necessary use of national survey data from satellite imagery (land-cover) and censuses (agricultural, human population); and NALTRACES has not been primarily designed to account for year-on-year variability, despite being responsive to year-specific climate. It should also be noted that in using the nitrate leaching transfer function based on total annual HER (Anthony et al., 1996) the simulation of individual river observations is not feasible.

Generally, it is clear that even with no contribution from agricultural activity, N concentrations would still be high enough, even in areas of large dilution due to high annual rainfall (>1100 mm yr^{-1} in sub-catchments 27034 and 27090), to facilitate phytoplankton growth (as evidenced by f(N) values in Table 2). Observed data suggest that N and P are limiting phytoplankton growth to a similar (if minimal) extent, except in the Nidd at the Gouthwaite Reservoir outlet (27005) where SRP concentrations are low. Analysis of the f(P) values generated from the observed phosphorus data is influenced by the introduction of P stripping between 1999 and 2002 at the larger sewage treatment works (STWs) in response to legislative requirements. Consequently TP concentrations in the Ouse network have been falling substantially. The effect of introducing tertiary treatment (with an effluent TP consent of 2 mg L^{-1}) has been simulated by Bowes et al. (2010) at 4 of the sites of interest. The benefits this measure may have on f(P) values (Table 2) appear to be similar, if slightly less, than the maximum achievable in terms of N limitation via the agricultural sector. For the upper Swale (27090), the predicted benefits in terms of potential reduction in phytoplankton growth are 25%, 5% and 4% under the scenarios of full riparian canopy cover, agricultural absence and a 2 mg TP L^{-1} STW effluent cap respectively.

The predicted changes in f(Light) and f(Nutrients) brought about by the scenarios considered are in line with those reported by Hutchins et al. (2010a) using a process-based modelling method (QUESTOR). Both modelling approaches show that establishing riparian tree cover at full capacity, although with inherent time delays for tree growth and requiring the cooperation of numerous stakeholders, is ultimately likely to be highly effective at suppressing phytoplankton growth. It is likely to be at least four times more effective than preventing all nitrate-N originating from agricultural sources from leaching (or capping the TP content in STW effluents at 2 mg L^{-1}). Furthermore, an additional cut of nitrate-N equivalent to the entire point source load would only slightly increase the beneficial curtailment of growth (to 8% at 27090). Hence, in this regard, there is clearly insufficient scope for realistic agricultural N mitigation measures alone to be effective. For example, in the upper Swale headwaters (27090), predictions using NALTRACES suggest that making landowners comply with an Environmentally Sensitive Area scheme (as administered by Natural England) may reduce nitrate-N concentrations by 11% but would lower f(N) by less than 1%. In a wider context, across England, the overall impact of the 2002 NVZ Action Programme is likely to only be a 5% reduction of nitrate-N leaching in designated areas (Lord et al., 2009).

The travel time calculations suggest that it is only in headwater areas where action of any sort is likely to provide water quality improvements, as development of phytoplankton blooms in the lower Ouse is due to water originating in upstream reaches that are sufficiently distant. Of these upstream rivers, the Ure is the most significant volumetrically, contributing over 25% to river flow at the tidal limit under low flow conditions. The research suggests that any blooms that do occur in the Ouse network will be ephemeral, as in all reaches the calculated flow velocities at mean discharge are sufficient to wash out any phytoplankton before substantial biomass can accumulate.

5. Conclusions

From the research, some key outcomes related to the Ouse case study are apparent:

- For suppressing phytoplankton blooms, establishing riparian shading in headwater areas is a far more effective mitigation option than curtailing nutrient inputs.
- It is unlikely that even the most drastic N-limiting or P-limiting strategies applied to agricultural and/or sewage sources would substantially curtail the development of phytoplankton blooms. However, reducing nutrient loads may allow persistent blooms, not currently seen in the Ouse, to be capped. Indeed, as stressed in Section 2.2, assessment of persistent blooms is outside the scope of the analysis presented in this study.
- Blooms will be ephemeral. Any actions should be focused in the sub-catchment of the upper Ure (27034) as it contributes substantially to downstream river flow, delivering water of sufficient residence time.

Of more general importance the research contributes the following:

- A nitrate model that is sensitive to land management practice (NALTRACES) captures the spatial variability of annual nitrate-N concentrations.
- An assessment of factors that potentially limit phytoplankton growth successfully mimics the output of more detailed dynamic modelling approaches.
- Therefore, given availability of data from national water flow and quality monitoring programmes coupled with nationwide atmospheric data on air quality and solar radiation, reliable rapid assessments can be carried out to establish the risk of phytoplankton growth in river networks.

Acknowledgements

Helen Davies (CEH) and Paulette Posen (UEA) are thanked for their help in preparing various input datasets for the nitrate model. Virginie Keller (CEH) obtained residence time and dilution data from the database underpinning the LF2000 software. Andrew Johnson (CEH) provided valuable comments on the text. River flow and quality data came from the Environment Agency who also provided funds which enabled the growth limitation and residence time calculations to be made. Defra/EDINA and BADC are acknowledged as the sources of the Agricultural Census statistics and solar radiation data respectively. The analysis undertaken in this article is stimulated in particular by the Catchment hydrology, Resources, Economics and Management (ChREAM) project, funded under the joint ESRC, BBSRC, NERC Rural Economy and Land Use (RELU) programme (award number RES-227-25-0024).

References

Addiscott TM, Whitmore AP, 1991. Simulation of solute leaching in soils of differing permeabilities. Soil Use and Management 7, 94-102.

Anthony SG, Quinn P, Lord EI, 1996. Catchment scale modelling of nitrate leaching. Aspects of Applied Biology 46, 23-32.

Anthony SG, Silgram M, Collins AL, Fawcett LE, 2009. Modelling nitrate river water quality for policy support. International Journal of River Basin Management 7, 259-275.

Arnold JG, Srinivasan R, Muttiah RS, Williams JR, 1998. Large area hydrologic modelling and assessment. Part 1: model development. Journal of the American Water Resources Association 34, 73-89.

Boorman DB, Hollis JM, Lilly A, 1995. Hydrology of soil types: a hydrologically-based classification of the soils of the United Kingdom: Report no. 126, Institute of Hydrology, Wallingford, UK.

Bouraoui F, Galbiati L, Bidoglio G, 2002. Climate change impacts on nutrient loads in the Yorkshire Ouse catchment (UK). Hydrology and Earth Systems Science 6, 197-209.

Bowes MJ, Neal C, Jarvie HP, Smith JT, Davies HN, 2010. Predicting phosphorus concentrations in British rivers resulting from the introduction of improved phosphorus removal from sewage effluent Science of the Total Environment 408, 4239-4250.

Bowie GL, Mills WB, Pocella DP, Campbell CL, Pagenkopf JR, Rupp GL, Johnson KM, Chan PWH, Gherini S, Chemberlain CE, 1985. Rates, constants and kinetic formulations in sourface water quality modelling: US Environment Protection Agency, Georgia USA.

Boyer EW, Alexander, RB, Parton, WJ, Li C, Butterbach-Bahl K, Donner SD, Skaggs RW, Del Grosso SJ, 2006. Modelling denitrification in terrestrial and aquatic ecosystems at regional scales. Ecological Applications 16, 2123-2142.

Centre for Ecology and Hydrology, 2003. Hydrometric Register and Statistics 1996-2000. Wallingford, UK: Centre for Ecology and Hydrology

Chambers BJ, Lord EI, Nicholson FA, Smith KA, 1999. Predicting nitrogen availability and losses following application of organic manures to arable land: MANNER. Soil Use and Management 15, 137-143.

Cherry KA, Shepherd M, Withers PJA, Mooney SJ, 2008 Assessing the effectiveness of actions to mitigate nutrient loss from agriculture: a review of methods. Science of the Total Environment 406, 1-23.

Davies DB, Sylvester-Bradley R, 1995. The contribution of fertiliser nitrogen to leachable nitrogen in the UK: a review. Journal of Science, Food and Agriculture 68, 399-406.

DeWalle DR, 2008. Guidelines for riparian vegetative shade restoration based upon a theoretical shaded-stream model. Journal of the American Water Resources Association 44, 1373-1387.

Dunn SM, Vinten AJA, Lilly A, DeGroote J, Sutton MA, McGechan M, 2004. Nitrogen risk assessment model for Scotland. 1. Nitrogen leaching. Hydrology and Earth Systems Science 8, 191-204.

Fowler D, Smith RI, Muller J, Hayman G, Vincent K, 2005. Changes in the atmospheric deposition of acidifying compounds in the UK between 1986 and 2001. Environmental Pollution 137, 15-26.

Fuller RM, Smith GM., Sanderson JM, Hill RA, Thompson AG, 2002. The UK Land Cover Map 2000: Construction of a parcel-based vector map from satellite images. The Cartographic Journal 39, 15-25.

Green FHW, Harding RJ, 1979. Altitudinal gradients of soil temperatures in Europe. Meteorological Magazine 108, 81-91.

Hallett SH, Jones RJA, Keay CA, 1993. SEISMIC: a spatial environmental information system for modelling the impact of chemicals. In: Stebbing, A. R. D., Travis, K. & Matthieson, P.: Environmental Modelling: The Next 10 Years. Report of a Symposium at The Society of Chemical Industry, London, 16 Dec 1992, pp40-49.

Haygarth PM, ApSimon H, Betson M, Harris D, Hodgkinson R, Withers PJA, 2009. Mitigating diffuse phosphorus transfer from agriculture according to cost and efficiency. Journal of Environmental Quality 38, 2012-2022.

Heathwaite AL, 2003. Making process-based knowledge usable at the operational level: a framework for modelling diffuse pollution from agricultural land. Environmental Modelling and Software 18, 753-760.

Heathwaite AL, Quinn PF, Hewett CJM, 2005. Modelling and managing critical source areas of diffuse pollution from agricultural land using flow connectivity simulation. Journal of Hydrology 304, 446-461.

Heinen M, 2006. Simplified denitrification models: overview and properties. Geoderma 133, 444-463.

Hilton J, O'Hare M, Bowes MJ, Jones JI, 2006. How green is my river? A new paradigm of eutrophication in rivers. Science of the Total Environment 365, 66-83.

Hutchins MG, Dilks C, Davies HN, Deflandre A, 2007. Issues of diffuse pollution model complexity arising from performance benchmarking. Hydrology and Earth Systems Science 11, 647-662.

Hutchins MG, Fezzi C, Bateman IJ, Posen PE, Deflandre-Vlandas A, 2009. Cost-effective mitigation of diffuse pollution: setting criteria for river basin management at multiple locations. Environmental Management 44, 256-267.

Hutchins MG, Johnson A, Deflandre-Vlandas A, Comber S, Posen P, Boorman DB, 2010a. Which offers more scope to suppress river phytoplankton blooms: reducing nutrient pollution or riparian shading? Science of the Total Environment 408, 5065-5077.

Hutchins MG, Deflandre-Vlandas A, Posen P, Davies HN, Neal C, 2010b. How do nitrate concentrations respond to changes in land-use? A modelling case-study of headwaters in the River Derwent catchment, North Yorkshire, UK. Environmental Modelling and Assessment 15, 93-109.

Johnes PJ, 1997. Evaluation and management of the impact of land use change on the nitrogen and phosphorus load delivered to surface waters: the export coefficient modelling approach. Journal of Hydrology 183, 323-349.

Johnsson H, Bergstrvm L, Jansson PE, Paustian K, 1987. Simulation of nitrogen dynamics and losses in a layered agricultural soil. Agriculture, Ecosystems and Environment 18, 333-356.

Leopold LB, Maddock T, 1953. The hydraulic geometry channels and some physiographic implications. In: Geological Survey Professional Paper 252, Washington D.C.

Lindenschmidt KE, 2006. The effect of complexity on parameter sensitivity and model uncertainty in river quality modelling. Ecological Modelling 190, 72-86.

Lord EI, Bland G, 1991. Leaching of spring-applied fertiliser nitrogen: measurement and simulation. Soil Use and Management 7, 110-114.

Lord EI, Anthony SG, 2000. MAGPIE: A modelling framework for evaluating nitrate losses at national and catchment scales. Soil Use and Management 16, 167-174.

Lord EI, Anthony, SG, Gooday, RD, 2009. Assessing the impact of Nitrate Vulnerable Zones in England on nitrate loss from agricultural land. International Journal of River Basin Management 7, 233-243.

Neal C, Robson AJ, 2000. A summary of river quality data collected within the Land-Ocean Interaction Study: core data for the eastern rivers draining to the North Sea. Science of the Total Environment 251/252, 585-666.

Neal C, Hilton J, Wade AJ, Neal M, Wickham H, 2006. Chlorophyll-a in the rivers of eastern England. Science of the Total Environment 365, 84-104.

Nix J, 2000. Farm Management Pocketbook. Wye College Press, Ashford, Kent.

Posen P, Hutchins MG, Lovett A, Davies HN, 2011. Identifying the catchment size at which robust estimation sof agricultural land use can be made, and implications for diffuse pollution modelling. Applied Geography 31, 919-929.

Raven PJ, Holmes NTH, Dawson FH, Everard M, 1998. Quality assessment using River Habitat Survey data. Aquatic Conservation of Marine and Freshwater Ecosystems 8, 477-499.

Reichert P, Borchardt D, Henze M, Rauch W, Shanahan P, Somlyody L, Vantolleghem P, 2001. River Water Quality Model no. 1 (RWQM1): II. Biochemical process equations. Water Sci. Technol. 43, 11-30.

Reynolds CS, Irish AE, Elliott JA, 2001. The ecological basis for simulating phytoplankton responses to environmental change (PROTECH). Ecological Modelling 140, 271-291.

Round CE, Young AR, Fox K, 1998. A regionally applicable model for estimating flow velocity at ungauged river sites in the UK. Journal of the Chartered Institution of Water and Environmental Management 12, 402-405.

Scharfe M, Callies U, Blocker G, Petersen W, Schroeder F, 2009. A simple Lagrangian model to simulate temporal variability of algae in the Elbe River. Ecological Modelling 220, 2173-2186.

Scholefield D, Lockyer DR, Whitehead DC, Tyson KC, 1991. A model to predict transformations and losses of nitrogen in UK pastures grazed by beef cattle. Plant and Soil 132, 165-177.

Seitzinger S, Styles R, Boyer EW, Alexander RB, Billen G, Howarth R, Mayer B, Van Breemen N, 2002. Nitrogen retention in rivers: model development and application to watersheds in the northeastern USA. Biogeochemistry 57/58, 199-237.

Silgram M, Kirkham F, Mole A, Hutchins M, 2005. Nitrogen losses from non-agricultural land in England and Wales: a review. Final report to Defra. 55pp.

Snowling SD, Kramer JR. , 2001. Evaluating modelling uncertainty for model selection. Ecological Modelling 138, 17-30.

Soballe DM, Kimmel BL, 1987. A large-scale comparison of factors influencing phytoplankton abundance in rivers, lakes and impoundments. Ecology 68, 1943-1954.

Steele JH, 1962. Environmental control of photosynthesis in the sea. Limnology and Oceanography 7, 137-149.

Thompson N, Barrie IA, Ayles M, 1982. The Meteorological Office Rainfall and Evaporation Calculation System (MORECS). UK MetOffice, Hydrol. Memorandum No. 45, HMSO, London.

Wade AJ, Durand P, Beaujouan V, Wessel WW, Raat KJ, Whitehead PG, Butterfield D, Rankinen K, Lepisto A, 2002. A nitrogen model for European catchments: INCA, new model structure and equations. Hydrology and Earth Systems Science 6, 559-582.

Whitehead PG, Williams RJ, Lewis DR, 1997. Quality simulation along river systems (QUASAR): model theory and development. Science of the Total Environment 194/195, 447-456.

Tables and Figures

Table 1: catchment characteristics, including mean observed chemistry and phytoplankton growth limitation factors (f(N), f(P)) based on observations

Table 2: simulated mean chemistry (including scenarios) and phytoplankton growth limitation factors (f(N), f(P)) based on modelling

Figure 1: map of the Yorkshire Ouse river network, citing locations mentioned in the text

Figure 2: NALTRACES model schematic diagram

Figure 3: Comparison of observed and simulated mean nitrate-N concentrations for four individual years: (a) site 27071, (b) site 27007, (c) site 27009

Table 1

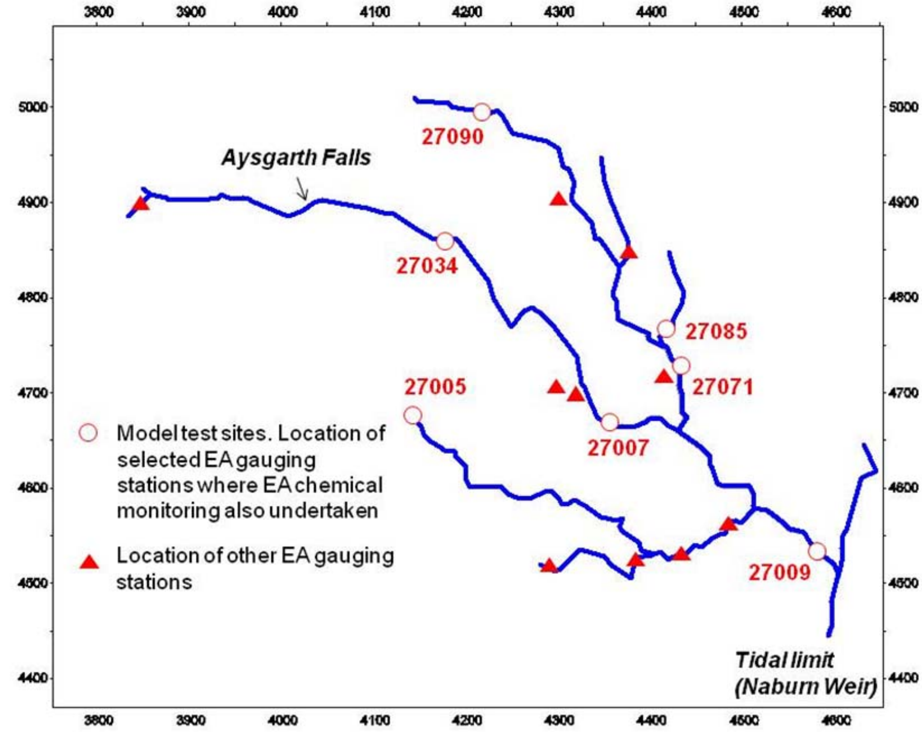
Site	Area (km^2)	Atmospheric deposition ($kg\ ha^{-1}\ yr^{-1}$)	% arable	% grass land	% urban	NO_3-N ($mg\ L^{-1}$)	NH_4-N ($mg\ L^{-1}$)	SRP ($mg\ L^{-1}$)	[a]TP ($mg\ L^{-1}$)	f(N)	f(P)	[b]Travel time to tidal limit (d)	[c]Contribution to flow at tidal limit (%)
27009	3315	32.1	31	44	2	3.61	0.07	0.17	0.24	0.97	0.97	0.9	100
27007	915	29.5	14	56	1	2.82	0.07	0.09	0.21	0.97	0.95	2.2	54
27005	114	28.5	0	52	0	0.83	0.04	0.02	0.03	0.90	0.76	5.1	6
27090	499	24.5	7	54	1	1.58	0.04	0.11	0.15	0.94	0.95	5.1	27
27071	1363	29.8	35	41	1	3.93	0.07	0.19	0.26	0.98	0.97	2.2	58
27034	510	29.5	2	71	0							4.6	26
27085	209	29.8	43	33	1	5.64	0.09	0.40	0.55	0.98	0.98	2.4	3

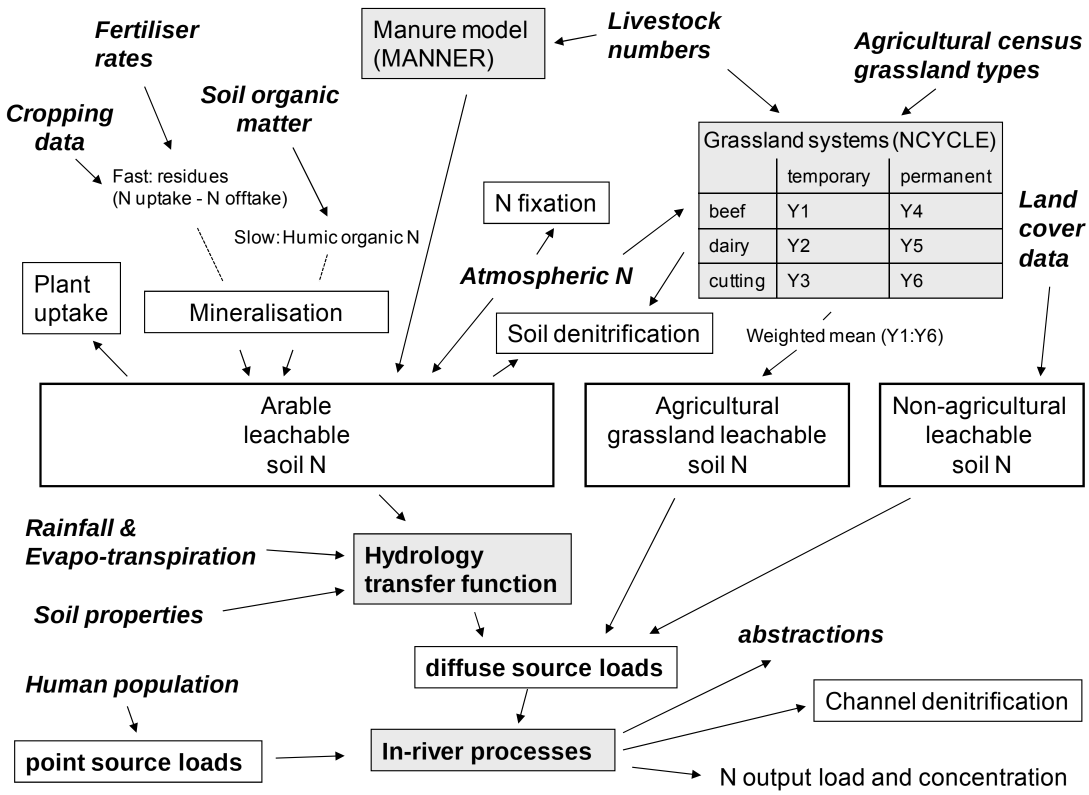
a) Total phosphorus data from EA in 1999-2003 are scarce, hence mean concentrations were estimated from mean observed SRP:TP ratio from samples collected under the LOIS programme (1993-97) (Neal and Robson, 2000) in conjunction with the mean observed SRP data from 1999-2003.
b) Travel time at low flow (Q90). Estimated travel times to the tidal limit at mean flows were all less than 3 days.
c) Flow contributions at low flow (Q90)

Table 2:

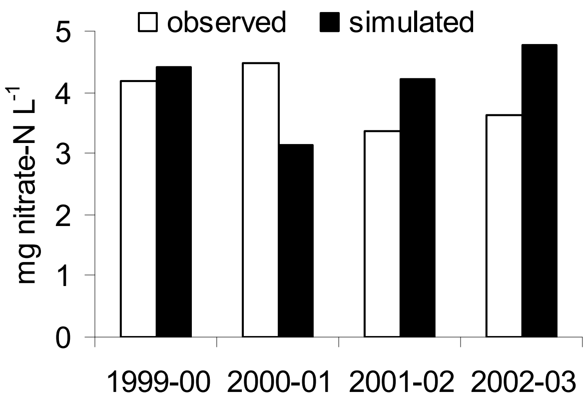
Site	NO_3-N (mg L^{-1}) (present day)	NO_3-N (mg L^{-1}) (agriculture absent)	f(N) (present day)	f(N) (agriculture absent)	[a]f(P) (prior to P stripping at STWs)	[a]f(P) (with STW effluents capped at 2 mg TP L^{-1})
27009	4.03	1.13	0.98	0.92	0.97	0.95
27007	1.83	0.66	0.95	0.88	0.95	0.93
27005	0.55	0.50	0.86	0.85		
27090	1.11	0.67	0.92	0.88	0.96	0.92
27071	3.76	0.98	0.97	0.91	0.97	0.95
27034	0.75	0.48	0.89	0.84		
27085	9.55	2.06	0.99	0.96		

a) Limitation factors generated using TP concentrations estimated by the LAM model (Bowes et al., 2010)

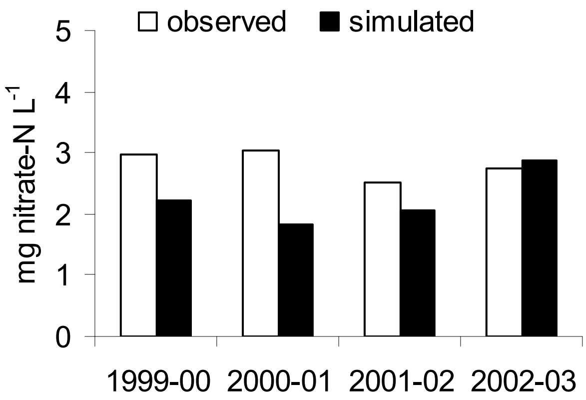

Aysgarth Falls
27090
27034
27085
27071
27005
27007
27009
Model test sites. Location of selected EA gauging stations where EA chemical monitoring also undertaken
Location of other EA gauging stations
Tidal limit (Naburn Weir)
3800 3900 4000 4100 4200 4300 4400 4500 4600
5000 4900 4800 4700 4600 4500 4400


Fertiliser rates
Manure model (MANNER)
Livestock numbers
Agricultural census grassland types
Cropping data
Soil organic matter
Fast: residues
(N uptake - N offtake)
Slow: Humic organic N
Grassland systems (NCYCLE)
temporary
permanent
beef
Y1
Y4
dairy
Y2
Y5
cutting
Y3
Y6
N fixation
Land cover data
Plant uptake
Mineralisation
Atmospheric N
Soil denitrification
Weighted mean (Y1:Y6)
Arable leachable soil N
Agricultural grassland leachable soil N
Non-agricultural leachable soil N
Rainfall & Evapo-transpiration
Hydrology transfer function
Soil properties
abstractions
diffuse source loads
Human population
Channel denitrification
point source loads
In-river processes
N output load and concentration

a)


observed
simulated
mg nitrate-N L-1
0
1
2
3
4
5
1999-00
2000-01
2001-02
2002-03

b)


observed
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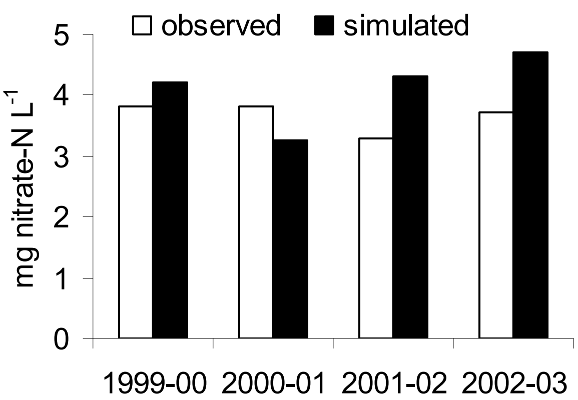
2002-03

c)


observed
simulated
mg nitrate-N L-1
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2001-02
2002-03