Environmental Science
Processes & Impacts

Environmental Impact statement.

Statistical models of nutrient concentrations in all 140 UK catchments, combined with river flow data, gave estimates of nutrient export loads to coastal seas 1993-2003. Nitrate concentrations were stable while orthophosphate declined in many catchments. The N:P ratios in export loads revealed that most catchments in Scotland, Wales and southwest England were potentially P limited, very few catchments were potentially N-limited, while those in central and eastern England were seasonally variable- potentially N-limited during summer and P-limited during winter. This provides crucial data needed to respond to the Water Framework Directive which requires management of nutrients at catchment level. The UK N and P export loads to the North Sea were small (<3%) when compared to inputs from continental estuaries and from the north Atlantic.

UK catchment nutrient loads 1993-2003, a new approach using Harmonised Monitoring Scheme data: temporal changes , geographical distribution , limiting nutrients and loads to coastal waters.

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Abstract

The work provides robust estimates of nutrient loads (nitrate and phosphate) from all UK catchments: as as required by the Water Framework Directive to monitor catchments' health , and to inform management of these environments. To calculate nutrient loads, data for nutrient concentrations and water flow are combined. In the UK, flow data are typically available at hourly intervals at more than 1300 gauging stations but concentration data are collected less frequently (roughly weekly) and at fewer locations (about 280). The sparseness of the concentration data limits the occasions for which load can be calculated, so a mathematical model was derived which was used to interpolate the concentrations between measurements. The model's parameters provide useful information about the annual nutrient concentration cycles within any catchment, and permitted improved estimates of both the annual loads of N and P, and of the N:P ratios, from mainland UK catchments. Data from 1993-2003 showed nitrate loads from UK catchments were generally constant, while orthophosphate loads generally declined. N:P ratios suggested that most catchments in the north and west of the UK were potentially P-limited although a few were potentially N-limited, while many in central and eastern UK oscillated seasonally between N and P limitation. Knowledge of the nutrient which is potentially limiting to biological productivity is a key factor for management of a catchment's nutrient loads. Calculations of nutrient export loads to coastal regions showed that UK catchments contributed only about 16.5% of total fluvial loads of nitrate to the North Sea, or about 3% of the total N loads when inputs from the Atlantic were included. Orthophosphate loads from the UK catchments into the North Sea were only 1.7% of the total P inputs from rivers and the Atlantic but did not include riverine inputs of P adsorbed to particles.

Key words:, nitrate, phosphate, Redfield ratios, nutrient loads, , eutrophication, catchments.

1. Introduction

Nitrogen (N) and phosphorus (P) are essential nutrients for biological primary production, but anthropogenic enrichment of nutrients (nutrification) can result in changes in the biological communities (eutrophication) in the rivers, estuaries and marine ecosystems receiving the nutrients ([1,2]). Enhancement of N can lead to increased phytoplankton growth and biomass, and to depletion of silicate as it is assimilated by diatoms, with the consequence that with any further increase of N load diatoms decrease in relative importance due to Si limitation while microflagellates become increasingly dominant ([3,4,5]). As diatoms form the basis of grazing food chains leading to commercially important species, whereas flagellates and microflagellates are the basis of microbial food chains, such changes induced by nutrification can be of great ecological and commercial importance ([6]). Concern for the consequences of nutrification has led to legislation at both national and international levels to regulate and minimise the impact of loading of nutrients to water bodies. In Europe, the Water Framework Directive (2000/60/EC) requires the development of management plans to control and limit the discharge of nutrients to catchments, in order to maintain biological populations within acceptable limits ([2]). However, such management plans are only possible with understanding of the sources and magnitudes of the loads of nutrients in a catchment.

Typically, aquatic primary producers such as microalgae and diatoms consume nutrients from the environment in the Redfield Ratio (atom:atom) of 106C : 16N : 16Si : 1P. As nutrients are assimilated by algal growth, the nutrients in the water may become depleted until one becomes limiting to further growth (biomass production). An environment is said to be limited by a particular nutrient when that nutrient is used up, but enough of the other nutrients remain to potentially support more biological activity. It also assumes that production is not limited by other variables such as light. In addition to nutrient concentrations, changes in the ratios of the limiting nutrients can have significant impact on the structure of communities. The Redfield Ratio provides a useful comparison to the nutrient ratios actually observed in rivers and estuaries and indicates which elements, in the presence of non-limiting sunlight, will potentially limit the growth of the microalgae. Primary production in rivers and lakes is usually P-limited ([7, 8]) but can be N limited or oscillate seasonally between P or N limitation.. However, coastal waters tend to be N-limited ([9]), although the general evidence for this marine limitation is not as conclusive as for freshwaters. Furthermore, discharge of treated sewage effluent, which has high P content, can change the receiving waters from P-limited to N-limited (e.g.[8]). Not all nitrogen in river water is biologically available (dissolved organic nitrogen, DON, may not be 'bioavailable', e.g. [10]) so that considering only the biologically available compounds may give a better indication of which nutrients will be limiting primary production. Moreover, some biologically available compounds are used in preference to others (e.g. ammonium preferred to nitrate by algae ([11,12]) when both are available), suggesting that the Redfield Ratio can be an oversimplification of the true situation. Again, if all nutrients occur at high, saturating concentrations (typically $\geq 2 \mu g\ l^{-1}$ for algae e.g. [7]), the nutrient ratios may be irrelevant, as all nutrients will be in excess and growth rates maximal. Hessen, ([13]) also warns against the traditional assumption that if primary production is well correlated with a single nutrient concentration, then that nutrient must be limiting. The arguments against this assumption are 1] that there is a time lag between nutrient loads increasing and primary production following, 2] that the water (especially in lakes) may not be well mixed, or 3] that light may be limiting rather than a nutrient. Furthermore, there is enough variation in nutrient uptake between organisms that the exact ratio of nutrient requirement is imprecise. However, , the levels of N and P give important information on the status of a body of water that is useful in its management.

Catchments nutrient loads are derived from measurements of water flow rate and nutrient concentration. Across UK rivers a network of more than 1300 gauging sites provide real-time measurements of water flow (see the UK National River Flow Archive at http://www.ceh.ac.uk/data/nrfa/index.html). Nutrient concentrations in water from 277 selected sites sampled since 1975 are available under the Harmonised Monitoring Scheme (HMS) ([14, 15]) for which data are held at the U.K. Environment Agency Data Centre, Twerton, U.K. While these data bases provide a potentially important resource, there has been only limited use of the data to understand the magnitudes of nutrient loads from UK catchments, or seasonal or regional changes in loads or nutrient ratios. Littlewood et al. ([16]) described the estimation of mass loads of solutes in the HMS data sets, and the problems associated with it, while Nedwell et al. ([8]) reported N and P loads from UK catchments for the 95 major UK estuaries with data averaged from 1995 and 1996. Littlewood and Marsh ([17]) presented time series from 1975-1994 of annual mass loads of suspended solids, total nitrogen and orthophosphate to UK estuaries, and to the coastal areas around the U.K. The record of the exact combination of gauging stations used by Littlewood and Marsh ([17]) is not now available, but a similar list, compiled in 1997, was provided by I. G. Littlewood (personal communication, Jan. 2006). In the present work we use the data from all available gauging and monitoring sites with adequate data sets, over an 11 year period to detect trends of change in nutrient loads, seasonal changes and changes of ratios for all monitored UK catchments.

Methods

Flow Measurements. Flow data are available as hourly or daily mean values from the National River Flow Archive (see the UK National River Flow Archive at http://www.ceh.ac.uk/data/nrfa/index.html). Examples of time series for two gauging stations are shown in Figure 1.

Concentration measurements. Concentrations in river water are measured much less frequently than flows (typically just once or twice a month, often using water samples gathered manually) to monitor levels of up to 80 properties of the water in each location, including six factors directly relevant to nitrogen and phosphorus concentrations. Measurements are sporadic, although the largest rivers are generally sampled at least fortnightly, but sampling has, if anything, decreased in frequency over the last decade (see for example, nitrate and phosphate data from the River Rother in Figure 1). Under the HMS, four different measurements are taken of chemicals containing nitrogen, along with two measurements concerning phosphorus (Table 1). Table 1 shows the annual average number of determinations made for each variable during the 1993-2003 period of this work. For nitrogen, ammoniacal nitrogen, nitrite and nitrate measurements are all made with a similar frequency. The possibility of summing two or more of these N variables in estimating total N loads was considered but rejected as this could only be done where a single sample had been analysed for each of the determinands, which would significantly reduce the number of usable observations. However, nitrate concentrations are usually at least one order of magnitude larger than the other measurements, typically >90% of the total dissolved inorganic nitrogen (DIN) concentration.

As well as orthophosphate, the total phosphorus measurements appear to give the data required to calculate phosphorus loads, but these measurements are taken rarely compared to the orthophosphate measurements. Furthermore, (see Table 1) the average concentration measurement for orthophosphate is often higher than the average measurement of total phosphorus, which is impossible. This could be due to differences in the analytical methodology used to derive the results or due to space-time sampling bias in the sites at which total phosphorus measurements are made, or a combination of both factors. Therefore, the orthophosphate measurements were used in calculating P loads as soluble orthophosphate is the biologically available form of phosphate. We note that this is likely to underestimate the total P load because of adsorption of phosphate to exported particulate material ([18, 19]).

Validation of the concentration data

Before concentration data could be used for calculating loads, it needed to be assessed for reliability. Some data may be unreliable for the following reasons:

- Some concentration data were duplicated on the database with more than one observation for the same day. This could be due to more than one sample being taken, more than one analysis of the sample, or duplicate data entry. All measurements taken on the same day at the same site were converted to a single measurement given by the average.
- Some of the concentration data were recorded as "<LOD" (less than the Limit of Detection) where the value was below the minimum value that could be detected by the chemical analysis. The LOD may vary over time, even at the same gauging station, reflecting changed analytical methods, changed equipment, or analysis being performed in different laboratories. Samples marked as "<LOD" were rejected, after comparing results for including them as LOD or LOD/2, and finding that the calculated loads were similar (within

5% in 96% of catchments). Littlewood and Marsh ([17]) arbitrarily calculated mass loads using <LOD data as LOD/2.)

- At some stations the concentration data are quantised, that is, they take one of very few distinct values. This would suggest that rounding errors will play a larger part in these stations than in general (see below).

In general, the analysis of trends in the nutrient concentration will be more robust, allowing for detection of subtler trends, if more data are included. Data from the period 1993-2003 were initially validated and then used in our analysis as this represented a period long enough to be able to detect temporal changes in concentration, and included the most recently available (2003) data at the time that this work was started.

While calculation of loads requires knowledge of both flow rate and concentration, the different frequencies of measurement of each variable limits precision of load estimates. Much of an export load from a catchment may occur during periods of high flow which may be missed by the infrequent sampling for measurement of nutrient concentration ([20]), but the more frequent measurements of flow rates may, however, detect such episodic events. To permit more precise estimates of nutrient loads from catchments, therefore, we adopted the strategy of modelling nutrient concentrations from existing concentration data which could then be combined with the frequent measurements of flow to provide a much more robust estimate of catchment nutrient loads, including episodic events detected by flow. Littlewood et al ([16]) also advocated the use of interpolation of HMS data where sampling is irregular.

Seasonal cycles in N and P concentrations. Initially, to get a robust picture of the temporal variation in fluvial nitrate and phosphate concentration over Britain, concentration data from all the selected catchment gauging stations were amalgamated into one time series. To allow for the differences in magnitude of concentration at each site, each measured concentration was normalised by dividing by the average for that site. These values were then averaged by month to reduce all the observations to 132 values (one for each of the 12 months for 11 years). The presence of seasonal cycles for N and P and a long-term temporal trend for P in the logged aggregated data (see Results) motivated the subsequent choice of model for individual catchments.

Seasonal and long term trends in N and P concentrations in catchments. To investigate the seasonal and long term trends in nutrient concentrations, those HMS sites were selected which had sufficient data, and were close to an NRFA gauge that could be used to calculate load. The requirements were that: 1] at least 60 of the months in the 11 years' data should have acceptable concentration measurements (typically the actual number averaged 100.); 2] more than ten distinct values of concentration should be recorded – sites with fewer distinct values may be especially biased by rounding errors.

For the 140 catchments judged to have adequate nitrate concentration data by the previous criteria, and for the 119 catchments with adequate phosphate concentration data a statistical model which reflected the seasonally cyclical concentrations and had the following properties was fitted to the concentration measurements:

- It allowed concentration to be estimated for days when there was no measured concentration.
- It allowed outliers in the concentration data to be identified and removed. Outliers were removed by identifying individual points that changed the fit of

the model significantly (F test, P<0.0001), and iteratively removing them one at a time until no such points remained.

- It encapsulated the most important features of the data in a small number of parameters that have ecological relevance.

The questions of ecological relevance that the model should be able to consider are:

1. How big is the average nutrient concentration ?
2. Is the concentration increasing or decreasing over time ?
3. How much larger is the peak seasonal concentration in proportion to the annual average concentration ?
4. At what time of year does the peak concentration occur?

To meet these requirements we used the following statistical model:

$$C = \exp(\alpha(1 + \beta t + \gamma \cos(2\pi[t - \tau]))) \qquad (1)$$

where C is the expected concentration, α, β, γ and τ are the parameters to fit the model and t is the time in years (taking the midpoint of the study period as 0). The parameter α is the average log concentration and β is the proportional annual change in log concentration relative to mean log concentration. The term $\gamma\cos(2\pi[t - \tau])$ in the model represents the annual cycle of nutrient concentrations (see Fig 2) as described by both magnitude (γ) and time of year (τ: see Fig 3 for interpretation of this value) of the seasonal peak. γ is the proportional magnitude of the annual seasonal variability relative to mean log concentration The α, , and γ components of the model were chosen to be orthogonal over the study period, meaning that they can be interpreted independently of one another, and improving the optimiser performance compared to alternative parameterisations. This model has an infinite number of values of γ and τ that give the same fit due to the periodicity of the cosine wave, so the following restrictions are placed on the parameters:

$\gamma \geq 0; 0 \leq \tau < 1$ (2)

The concentration data for each catchment with an acceptable concentration data set was fitted to the statistical model by choosing α, β, γ and τ to minimise the least squares difference between observed and modelled concentrations on a log-scale using the software package R (R Development Core Team, 2007).

For each catchment the modelled concentrations generated by the statistical model were checked by comparison with the actual measured concentration values for the same day. Overall, the modelled concentrations versus actual measured values for the same day had a slope coefficient of 1.003 ± 0.003 ($P<001$) for nitrate and explained 83% of variance; while for phosphate was 1.008 ±0.004 ($P < 0.001$) and accounted for 74% of variance.

Estimation of loads. Nutrient loads (L) can be estimated as the product of water flow rate (F) with the nutrient concentration (C), although there are several ways of calculating loads with different degrees of precision (see [16, 20, 21]). Generally, precision increases by measuring nutrient loads over shorter periods of time, and summing the loads; rather than averaging over longer periods, which may underestimate peak loads. In our work, for each catchment daily nutrient load was calculated as the product of the measured daily average flow from the NRFA, and the concentration value obtained from Equation 1 fitted to the concentration data for that particular catchment. Daily loads were then summed to get annual loads. It was a requirement that HMS sites for concentration data were within 20 km of NRFA gauges. This 20km limit may seem large, but in practice the mean distance was 6.6km and 75% of the pairs were located within 5km of one another. Where HMS sites measured a sub-catchment of another HMS site, only the larger catchment was used to avoid doublecounting. This gave 140 sites selected for nitrate and 119 for phosphate loads. In comparison, Littlewood et al ([16]) reported 150 sites with both HMS and NRFA data.. (There was no reliable flow data for the River Great Ouse draining central England into the North Sea due to unmeasured cross pumping between parallel channels near the mouth, although the concentration data were adequate.)

In order to estimate nutrient loads to estuaries and coastal seas the catchments flowing to each coast of the U.K., and catchment areas for gauging stations were deduced from the CEH Digital Terrain Model ([22, 23]; and see [17]). The total load to each coastal region was calculated by summing the loads from the catchments that flow into that region, and dividing by the proportion of the area draining to that region that is within the modelled catchments. This accounted for ungauged catchments, areas downstream of gauging stations, and catchments with inadequate data by assuming that they export the same load per unit area as the neighbouring gauged areas flowing into that coastal region. This gave estimates of total nutrient loads to the North Sea, the Irish Sea, Celtic Sea, Atlantic coast and the English Channel.

Results and Discussion

Aggregated and normalised data for all catchments. The log transformed aggregated concentration data from all catchments (Fig 2) showed significant annual cycles in both N and P concentrations, informing the annually cycling model subsequently used for concentrations, and a significant temporal decrease over 11 years 1993-2003 in P concentrations, but not in N concentrations. Littlewood et al ([16]) also reported decrease of orthophosphate loads to UK estuaries for the period 1985-90.

U.K. wide variations in nutrient concentrations. Figures 3(A) and 4(A) illustrate the values of the parameters *α,* (the logarithm of average concentration, in mg N or P l^{-1}) from the nitrate and phosphate concentration models. The catchments shaded in grey are those which have inadequate concentration data sets while the white areas indicate regions where data are not available. Lack of data may result from gauging stations not being at tidal limits and thus some parts of the catchments being below a gauging station yet above tidal limits. Some small catchments are not gauged, such as those in northern Scotland which would require a large effort to monitor relative to their small size and nutrient load, and so measurement effort is focused on larger, more accessible catchments.

Figure 3(A) shows results for nitrates. The highest values of α are in the Midlands and the south-east of England, while the lowest are in northern Scotland and the west of Wales. The spatial coherence of the concentrations indicates that there are underlying factors (such as geology or land use) influencing the loads, rather than simply random differences between catchments. (We will consider elsewhere the underlying causes of these catchment loads (Earl et al, in preparation)). The high values of α in the Midlands and South East suggest that nitrates are dependent on a combination of human population density and agriculture as reported previously ([24]), as these areas have the highest population densities and most intensive agriculture. Neither factor alone adequately explains the concentration, as the catchments with high nitrate concentration in the south east of England (in North Norfolk, for example) have a relatively low population density, whereas the catchments around Liverpool and London have high nutrient concentrations despite being areas with little agriculture.

Figure 4(A) shows the log of average phosphate concentration. Phosphate concentrations were highest in the catchments which include major urban areas such as London and Merseyside, suggesting that the main source of phosphate is from sewage.

Long-term trends in nutrient concentrations. Figures 3B) and 4(B) show the corresponding results for the parameter β, which is the proportional change in the log concentration per year. Therefore, a value of ±0.05 represents a compound change in concentration of over 70% in the 11-year period being studied. Only those catchments where β is statistically significant ($P<0.05$) are coloured. Figure 3(B) shows that for much of Britain (86/140catchments) the nitrate concentrations have not changed significantly during the study period, which agrees with the aggregated national data illustrated in Figure 2. However, there are some exceptions:-

- In Northern Scotland, a cluster of catchments showed an apparently significant increase during 1999-2001 in nitrate concentrations at gauges 11002 (River Shin), 11003 (River Conon), 11004 (River Beauly) and 11005 (River Ness), where concentrations were approximately double that of previous years. The geographically consistent nature of this anomaly suggested that there had been an analytical data processing or entry error, or a change in analytical procedure, rather than a real change.
- The River Mersey showed a highly significant increase in nitrate concentration over 1993-2003, which does not arise from any obvious anomalies and indicates a real change. This might be the effect of improvements in the sewage treatment works achieving greater nitrification, resulting in a decrease of ammonium and corresponding increase of nitrate. The River Thames showed a significant decrease of nitrate over the period, largely driven by high nitrate concentrations in 1996 and 1997. As these were

both years of low rainfall and low flow in the Thames, and hence low dilution, it seems plausible that these high measurements were a true reflection of the change of nitrate concentrations in the river.

When the concentration model was applied to phosphate concentrations there were significant (at the 0.05 level) changes in 68 of the 119 catchments with useful data. The change of P with time (Figure 4(B)), illustrates a trend of general decrease of phosphate concentrations (and see https://www.gov.uk/government/uploads/system/uploads/attachment_data/file/69592/pb13811-waste-water-2012.pdf) over 1993-2003, with very few catchments increasing. The decrease in phosphate may be attributable to decreasing use of polyphosphates in detergent, or increase in phosphate stripping in sewage treatment works (e.g. [25,26]) since the introduction of the Urban Waste Water Treatment Directive in 1991. The two catchments (16007 & 16008) with apparent steep increases of P in Western Scotland may result from change in measurement accuracy, or local changes in agriculture or sewage treatment provision.

Seasonal variations in nutrient concentrations. Figure 3(C) shows results for nitrate of parameter γ, (the magnitude of the seasonal variation of nitrate concentrations) and Figure 3D shows parameter τ (the timing of the peak nitrate concentration). In both cases they are coloured only if γ is significant (τ is meaningless in the absence of significant seasonal variation). Of the 140 catchments to which the model was fitted, 128 had significant ($P < 0.05$) seasonal variation. For nitrate concentrations (Fig 3D) the majority of catchments have a value for τ around 0.1-0.2, indicating the peak of nitrate concentrations in February, suggesting that high rainfall in this winter period washes out of the catchment soil nutrients that may have accumulated over the year. The catchments that appear in green have the opposite trend of highest concentration in August, suggesting that they are dominated by nitrates from sewage which is diluted at times of high rainfall but concentrated during the summer months.

Similarly, Figures 4C and 4D illustrate the seasonality of the phosphate concentrations : 106 of the 119 of the catchments have a significant seasonality, with peaks typically in July-October. This seasonal trend is consistent with phosphate sources being dominated by a relatively constant P input which is diluted most during the winter and concentrated most in periods of low flow during the summer.

Ratios of nutrients. The continuous time series of nitrate and phosphate concentrations can be plotted against one another as N:P (atom:atom) ratios to indicate whether a catchment is generally likely to be N- or P-limited. This does not imply that primary production in each catchment is actually limited by that nutrient as it is only when the potentially limiting nutrient becomes depleted in concentration that biological production becomes growth rate limited, but it is the potentially limiting nutrient which is the first target nutrient which needs to be managed and reduced to limit biological production and eutrophication, as required by the Water Framework Directive. The N:P ratios were plotted over the 11 years of the study for the 119 catchments where both N and P concentration time series had been successfully created. While the use of solely soluble orthophosphate will underestimate the total P load because of P adsorption to particulates ([18, 19]), soluble orthophosphate is the biologically available form of P and therefore appropriate for calculating the N:P ratio. (In contrast, nitrate does not adsorb to particles.) Examples are shown in Figure 5 for the HMS site 7004 (River Rother, Kent) and HMS site 1010 (River Wyre at St Michael's, Lancashire) catchments. The cycles in the data reflect the annual nitrate and phosphate concentration cycles over 11 years, with successive annual cycles differing slightly because of the long term trends in the nutrient concentrations, particularly in the case of phosphate. The broken line shows the Redfield Ratio in which these nutrients are used by a ‘typical’ phytoplankton, while the black point represents the overall average N:P ratio that is often used to decide whether the river is N- or P-limited. The Rother catchment appears to be always P-limited because the N:P ratio is always above and to the left of the line indicating the Redfield Ratio. In the River Wyre, though, while the average N:P ratio indicates potential P-limitation, the seasonal cycle of N:P shows that the catchment is P-limited from September through the winter until the end of April but during the summer months the river is N-limited. As algae and higher plants need light for primary production, the N-limitation during the summer months when sunlight intensity is high is considerably more ecologically important than the P-limitation over winter when light is low, and so the overall annual average value of N:P may be deceptive.

The distribution of the N- and P-limited catchments is shown in Figure 6. Of the 119 catchments that had adequate data for both nitrate and phosphate, the majority (83) appeared to be potentially P-limited, while only 7 were potentially N-limited. It is note-worthy that the potentially N-limited catchments generally occurred in the large metropolitan areas (London, Birmingham, Liverpool, Manchester) where discharge of P-rich treated sewage effluent would tend to increase the probability of N-limitation (e.g. [8]). The wide-spread occurrence of P limitation would imply that control of point sources of P, such as sewage treatment works, in such catchments would facilitate limitation of eutrophication, as required by the Water Framework Directive. Of the remaining cases, 28 had an annual cycle that changed from N-limited in the summer to P-limited in the winter over the annual cycle , and the other two changed from N-to P-limited over the 11 year period, but not on an annual cycle. It may be that the seasonal oscillation of N or P limitation in some catchments is because high winter rains washing out nitrate from catchments (see Fig 2) increases the N:P ratio whereas P loads predominantly from STWs do not increase. Catchments in Scotland, Wales and western England are almost entirely P-limited, whereas central and southern England catchments oscillate over the annual cycle. The spatial coherence of the limiting nutrient suggests that there is an underlying pattern, which could be due to the terrain or land use (although the two factors are closely connected); for example, the P-limited catchments are generally in the more rural areas where sewage inputs are lower. [The Supplementary Material has a spread sheet which shows for each named and numbered UK catchment the element which appears to be potentially limiting to primary production, and hence most important in nutrient management.]

Estimated annual loads. Figure 7 shows the annual nitrate and phosphate loads derived from the modelled concentrations and the measured flow, normalised by catchment area. The lowest nitrate loads per unit area are observed in the sparsely populated areas of northern Scotland. There is an area of high nitrate loads in central England, corresponding with the area around the cities of the midlands and the north west. The large area of white in central eastern England for the catchment of the River Ely Ouse is the result of unreliable flow measurements for this catchment. Parallel channels between which ungauged cross flow at Denver Sluice can occur at different times of the year make load estimates highly problematic although concentration data are satisfactory. The phosphate loads are highest in a region encompassing the urban areas of the midlands and north-west. This adds weight to the generally accepted hypothesis that population density (via sewage) is the major cause of high phosphate loads.

Significance of UK east coast nutrient loads to North Sea. Table 2 shows the estimated loads from UK estuaries to each coast (as defined by PARCOM), averaged over the 11 years of the study.

- the East Coast into the North Sea from Cape Wrath to the Thames estuary
- the Channel Coast from the Thames estuary to Lands End
- the South-West Coast into the Celtic Sea
- West coast into the Irish Sea.
- The Atlantic Ocean from the North Channel to Cape Wrath.

Clearly, the greatest loads from the U.K. are into the North Sea. The proportion of gauged to non-gauged catchments calculated for each coast were identical to those given by Littlewood et al ([16,17]), and the total loads cited in Table 2 were derived by dividing the figure for any gauged catchment area by the proportion of gauged area in the total catchment. Bootstrap analyses gave 95% estimates for the annual export load from UK to coastal waters of 22933-30458 Mmol N and 701-1391 Mmol P, although the estimate for P will be solely for soluble orthophosphate. The 95% ranges of annual loads from each U.K. coastal region are shown in Table 3.

The average annual N and P area export loads to each coast were (in Mmol N or P km^{-2} y^{-1} for N and P loads respectively), North Sea catchments 0.117 and 0.005; English Channel catchments 0.149 and 0.0025; Celtic Sea catchments 0.165 and 0.004; Irish Sea catchments 0.141 and 0.007; Atlantic Ocean catchments 0.089 and 0.0074. Our values for nitrate loads compare closely with those for total N (of which the majority will be nitrate) given by Littlewood and March ([17]) as mean values for 1975-94

The magnitude of the U.K. N load to the North Sea. By comparison with the UK loads to the North Sea (1.3 x 10^4 Mmol N y^{-1} or 1.9 x 10^5 tonnes N y^{-1}) , the Scheldt alone exports 7.28 x 10^4 tonnes N y^{-1} (5.2 x 10^3 Mmoles N y^{-1}) ([27]), the Seine 9.24 x 10^4 tonnes N y^{-1} (6.6 x 10^3 Mmol N y^{-1}) (Billen et al, unpublished data cited in [28], and the Rhine/Meuse had a load of about 4 x 10^5 tonnes N y^{-1} (2.9 x 10^4 Mmoles N y^{-1}) between 1985-95 ([29]). Laane et al. ([30]) estimated total fluvial inputs to the North Sea of 10^6 tonnes N y^{-1} (7.2 x 10^4 Mmoles N y^{-1}), and Howarth et al., ([28]) gave a similar value of 1.22 x 10^6 tonnes y^{-1} (8.7 x 10^4 Mmoles y^{-1}), of which 34% was attributed to STW inputs. The entire UK N load to the North Sea is therefore equivalent to 1.3 x 10^4/8 x 10^4 Mmoles y^{-1}, or at most 16.5 % of the total fluvial N load to the North Sea.

How significant are the UK east coast estuary loads relative to all N inputs to the North Sea, including those from the Atlantic ? Laane et al. ([30]) gave total N inputs to the North Sea as 6.48 x 10^6 tonnes y^{-1}, equivalent to 4.6 x 10^5 Mmoles N y^{-1}. Total fluvial N inputs to the North Sea (mean 8 x 10^4 Mmoles N y^{-1}) therefore represent only 19 % of the N inflow from the Atlantic. The relative load contributions of the entire east coast UK estuaries are, therefore, 1.3 x 10^4/4.6 x 10^5, or only about 2.9% of the total N load to the North Sea. According to Howarth et al., ([28]) the relative contribution of urban wastewater sources will be about 30% of that i.e. < 1%.

The P load. The total fluvial export of orthophosphate is 6.0 x 10^2 Mmoles P through the UK east coast estuaries. Laane et al., ([30]) cite a total P load to the North Sea of 1.3 x 10^6 tonnes P y^{-1}, equivalent to 4.2 x 10^4 Mmoles P y^{-1}. The North Sea Quality Status report ([31]) quotes 8 x 10^5 tonnes (2.7 x 10^4 Mmoles) phosphate from the Atlantic and fluvial inputs of 4.5 x 10^4 tonnes (1.5 x 10^3 Mmoles) y^{-1}: a total of 2.8 x 10^4 Mmoles y^{-1}. The mean of the two estimates is 3.5 x 10^4 Mmoles y^{-1}. Therefore, the annual orthophosphate load from UK east coast is equivalent to 6 x 10^2/3.5 x 10^4= 1.7 % of the total P load to the North Sea: although because of adsorption of P to suspended particles (which were not included in the present estimates of loads) this will be an underestimate of the total P load.

Acknowledgments. THE was supported by a CASE studentship (NER/S/A/2004/1228) from the Natural Environment Research Council, U.K., with additional financial support from the Centre for Environment, Fisheries and Aquaculture Science, Lowestoft.

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Table 1: Measured nitrogen and phosphorus variables taken under the Harmonised Monitoring Scheme. Measurement frequency refers to the total number of observations per year made across Britain during 1993-2003.

HMS Code	Description	Units	Measurement frequency per year	Average concentration. (see units column)
D125	Ammoniacal Nitrogen	mg N l^{-1}	5,000	0.36
D126	Nitrite	mg N l^{-1}	4,300	0.08
D127	Nitrate	mg N l^{-1}	4,900	5.2
D129	Ammonia (free)	mg NH_3 l^{-1}	1,600	0.0043
D212	Orthophosphate	mg P l^{-1}	4,800	0.64
D213	Total Phosphorus	mg P l^{-1}	880	0.5

Table 2. Annual export loads of nitrate (Mmol N y^{-1}) and orthophosphate (Mmol P y^{-1}) from UK catchments to coastal seas. Gauged percentages refer to the percentage of the area upstream of a gauging station used in this work compared to total catchment area. The directly gauged loads from the east coast to the North Sea excluded the Great Ouse catchment, for which flow data was unreliable, but the total North Sea load was adjusted proportionately to include the Great Ouse catchment area.

	gauged N load (Mmol N y^{-1})	gauged P load (Mmol P y^{-1})	N gauged percentage	P gauged percentage	Total catchment (km^2)	Total N load (Mmol N y^{-1})	Total P load (Mmol P y^{-1})
North Sea	8,565	312	65%	52%	112,000	13,177	603
English Channel	1,551	25	65%	62%	16,000	2,386	40
Celtic Sea	3,673	88	72%	72%	31,000	5,102	122
Irish Sea	2,666	101	65%	52%	29,000	4,101	193
Atlantic Ocean	429	29	30%	24%	16,000	1,431	119
Total					204,000	26,198	1,078

Table 3. Ranges (95%) of annual nitrate and phosphate export loads to U.K. coastal areas (Mmol N or P y^{-1}).

	Nitrate	Phosphate
North Sea	10011-16639	318-905
English Channel	1758-2892	24-65
Celtic Sea	4508-5544	42-169
Irish Sea	3141-5201	76-330
Atlantic Ocean	979-1738	49-157
Total	22933-30458	701-1391

Table 4. Annual export loads of N and P per km^2 of catchment area per year (L&M are values given by Littlewood and Marsh [16].)

	Mmol N km^{-2} y^{-1}	L&M values	Mmol P km^{-2} y^{-1}	L&M values
North Sea	0.0894-0.1486	0.114	0.0028-0.0081	0.0013
English Channel	0.1099-0.1808	0.138	0.0015-0.0041	0.0009
Celtic Sea	0.1454-0.1788	0.146	0.0014-0.0055	0.0015
Irish Sea	0.1083-0.1793	0.144	0.0026-0.0114	0.0017
Atlantic Ocean	0.0612-0.1087	0.098	0.0031-0.0098	0.0012

List of supplementary material.

Suppl 1. Reference list of named and numbered UK catchments with their limiting nutrient (N or P or seasonally variable), and annual loads, area-normalised loads, and the values of the concentration model parameters for each catchment.

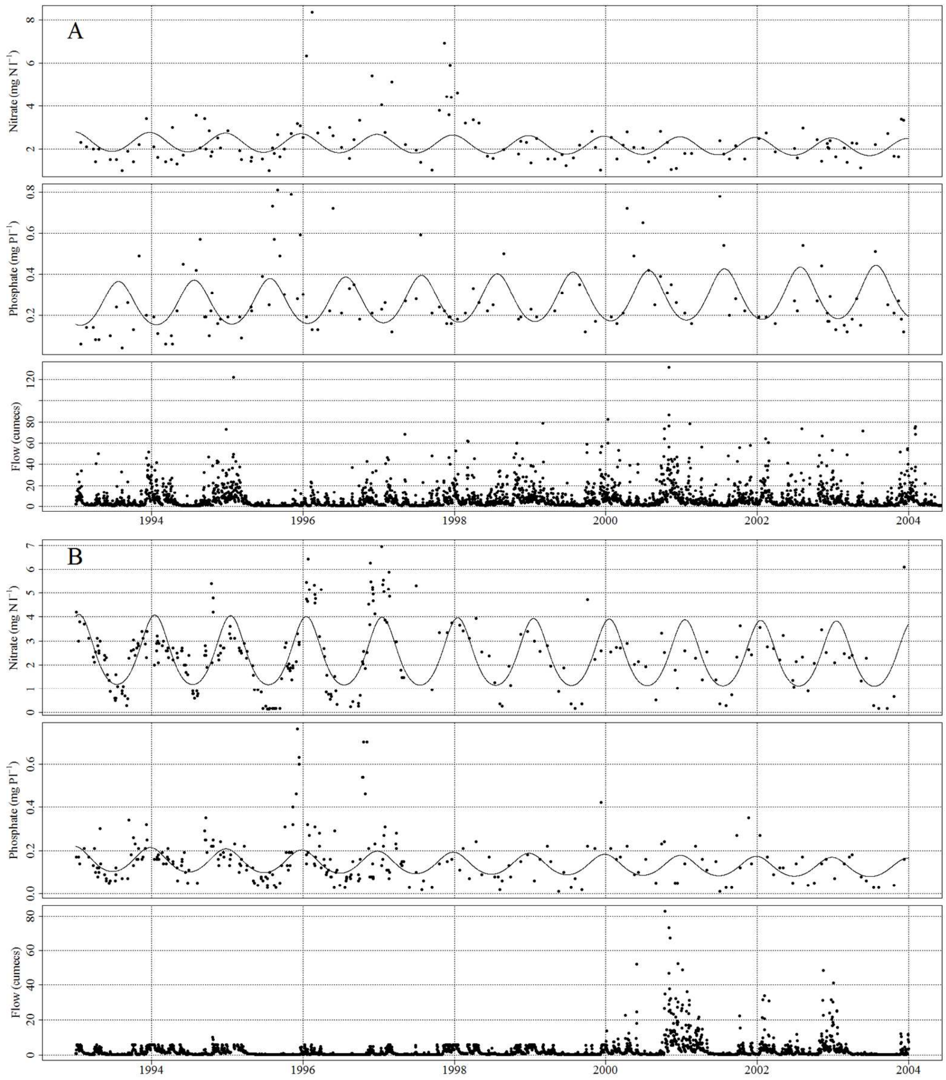

Figure 1: Example concentration and flow data from A. HMS site 1010 (River Wyre at St Michael's, Lancashire); and B. HMS site 7004 (River Rother, Kent). For each catchment, the plots show measured nitrate concentrations, phosphate concentrations and flow rate, with the modelled concentrations inserted for nitrate and phosphate.

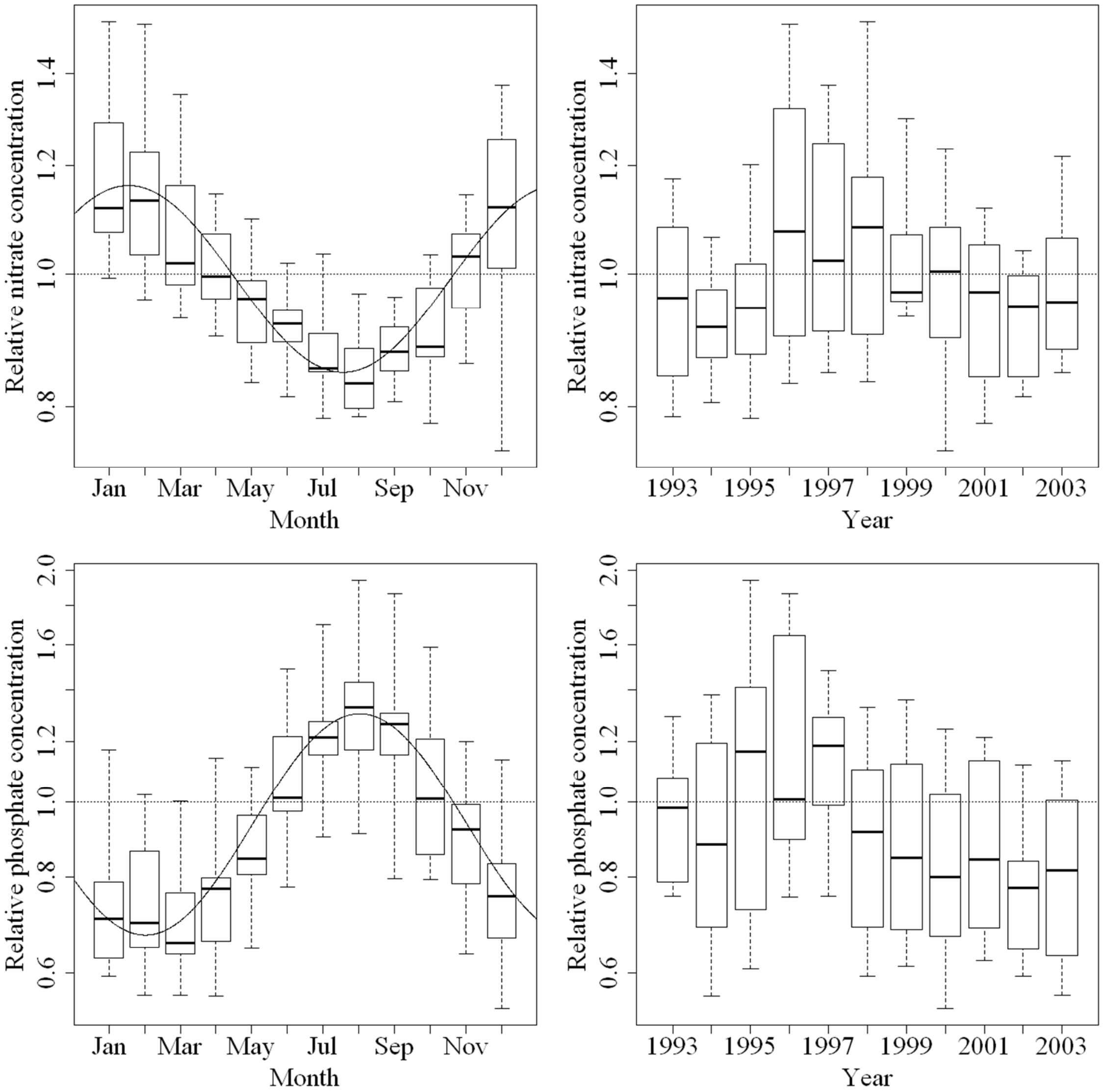

Figure 2: Aggregated standardised nutrient concentrations by month for all U.K.catchments with adequate data sets showing within year (left) and between years (right) variation in nitrate (top) and phosphate (bottom) concentrations.

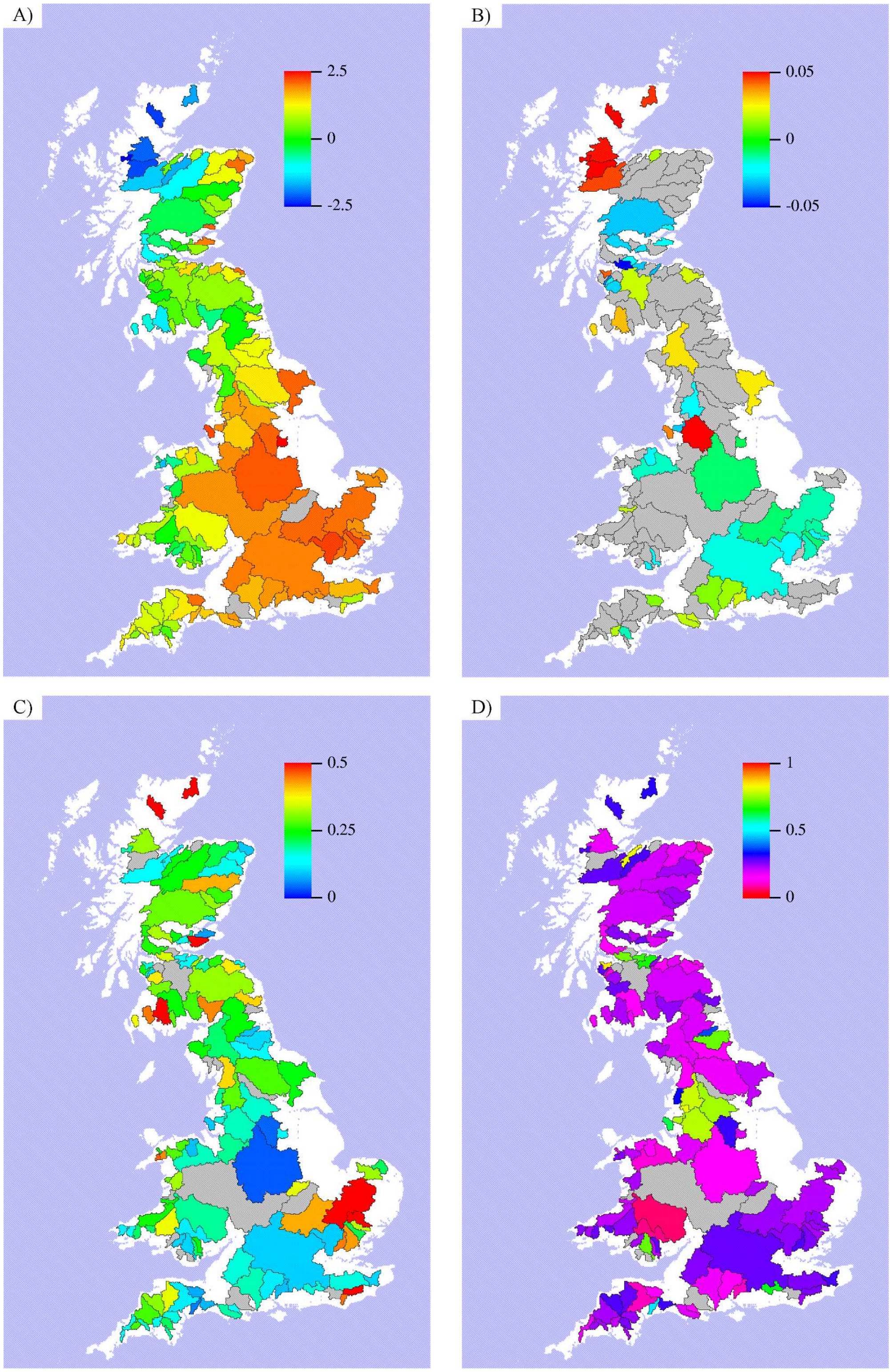

Figure 3: Nitrate model parameters for 140 UK catchments catchments A) α, mean log concentration in mg N l^{-1}. B) β, proportional change of concentration yr^{-1} . C) γ, proportional seasonal variation of concentration. D) τ, time of seasonal peak concentration (0= Jan, 0.25 = Apr, 0.5 = Jul, 1 = Oct). Grey catchments have inadequate data: white catchments areas have no data.

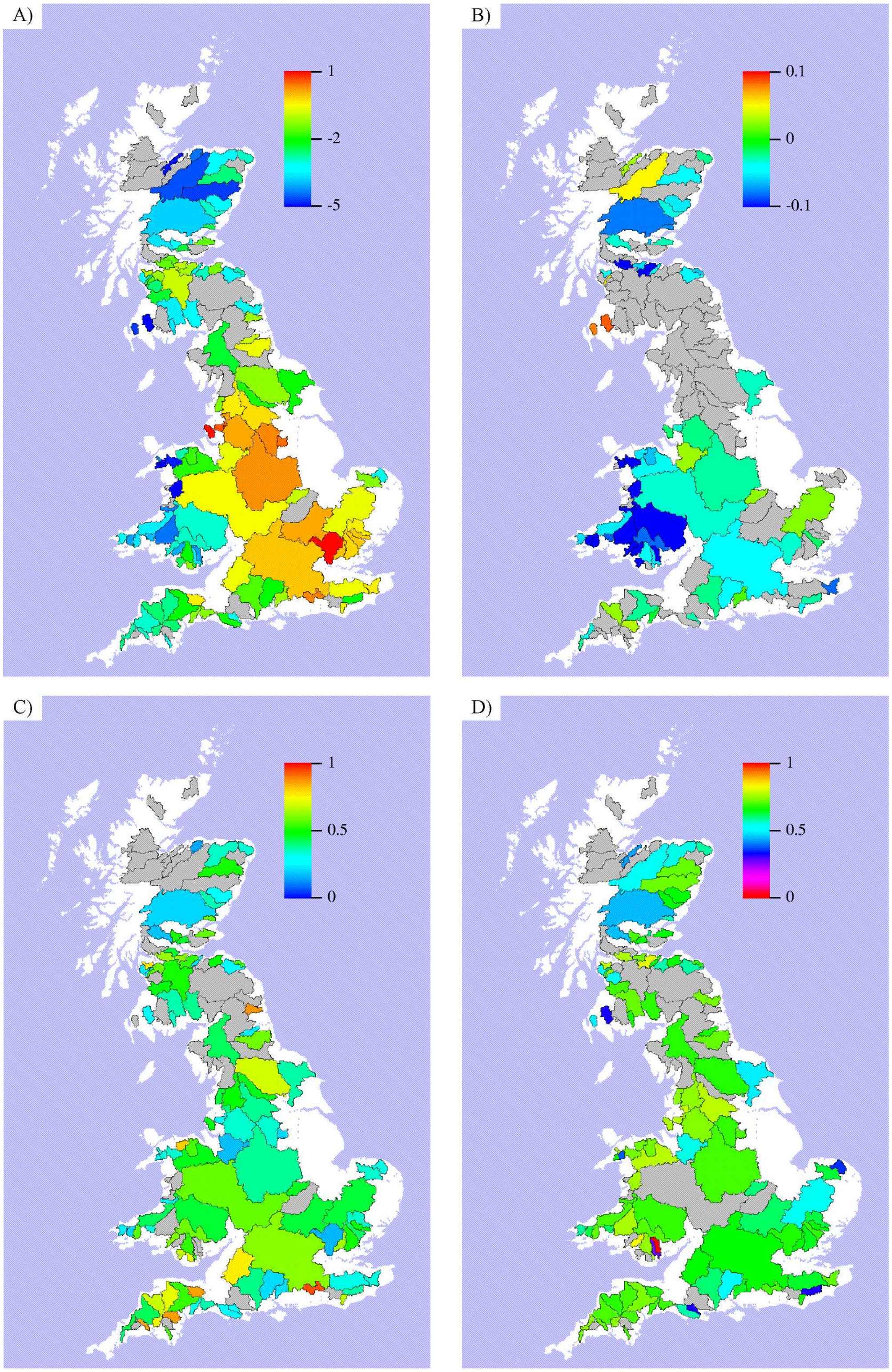

Figure 4: Phosphate model parameters for 119 UK catchments A) α, mean log concentration in mg P l^{-1}. B) β, proportional change of concentration yr^{-1}. C) γ, proportional seasonal variation of concentration. D) τ, time of seasonal peak concentration(0= Jan, 0.25 = Apr, 0.5 = Jul, 1 = Oct) . Grey catchments have inadequate data: white catchments areas have no data.

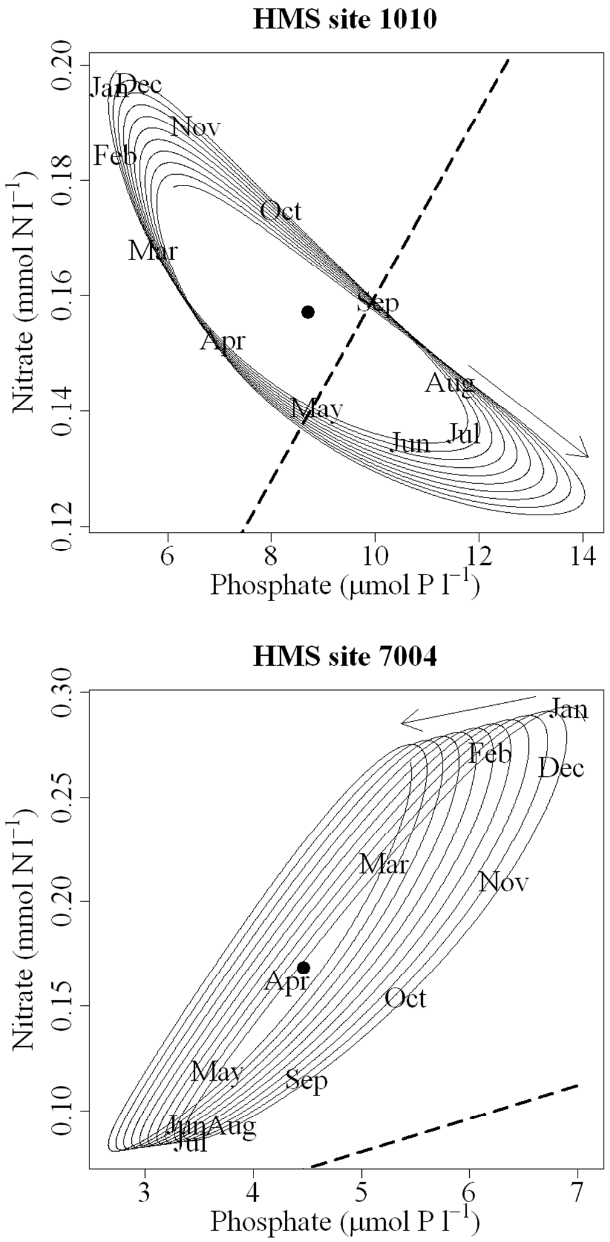

Figure 5: Example of annual cycles in modelled N:P ratios from HMS site 1010 (River Wyre at St Michael's, Lancashire; top) and HMS site 7004 (River Rother; bottom), also showing annual mean concentrations (black point) and the Redfield Ratio (broken line). The arrows indicate the change in annual cycle over successive years, and the first year (1993) is labelled with the months of the year. River Wyre oscillates seasonally between N limitation in summer and P limitation in winter, while River Rother is permanently P limited.

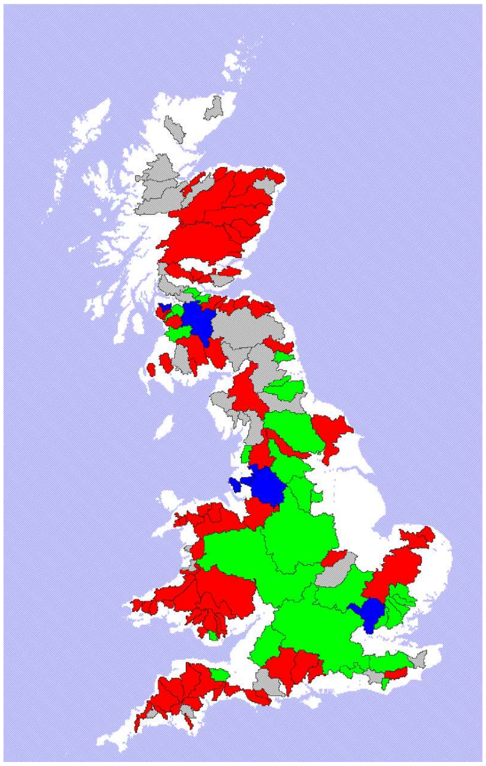

Figure 6: Potential nutrient limitation in catchments based on N:P atom ratios. Red catchments indicate potential P-limitation, blue catchments indicate potential N-limitation, and green catchments indicate oscillation of potentially limiting nutrient between P in winter and N in summer. Grey/white catchments have inadequate or no data.

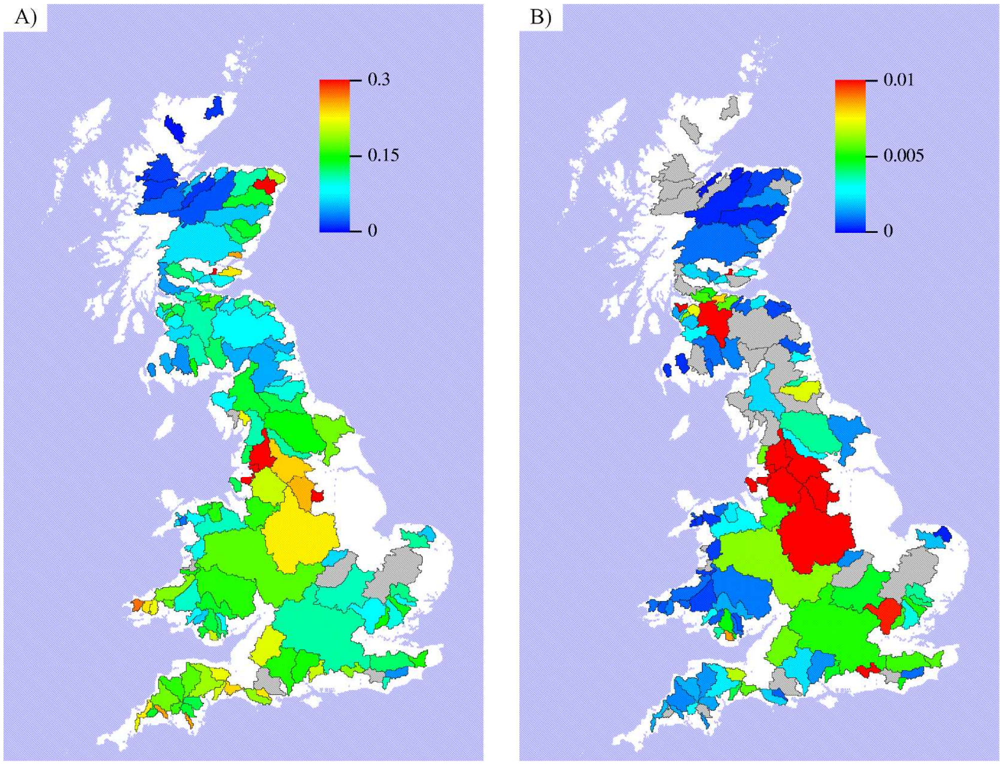

Figure 7: Nitrate (A) and phosphate (B) annual loads normalised for area (Mmol N or P km^{-2} yr^{-1}).