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3Catchment nutrient loads: temporal changes and geographical distribution in UK river

4systems, and loads to coastal waters 1993-2003.

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2Abstract

3Robust estimates of nutrient loads (nitrogen and phosphorus) from catchments are
4required to monitor the health of aquatic ecosystems, and to inform management of
5these environments. To calculate nutrient loads, data for nutrient concentrations and
6water flow are combined. In the UK, flow data are typically ~~collected~~ [available](#) at
7hourly intervals at more than 1300 gauging stations but concentration data are
8collected less frequently (roughly weekly) and at fewer locations (about 280). The
9sparseness of the concentration data limits the occasions for which load can be
10calculated, so a mathematical model has been derived which can be used to
11interpolate the concentrations between observations. The model is constructed so that
12the parameters estimated provide useful information about the annual nutrient
13concentration cycles within the catchment. The model permits improved estimates of
14both the annual loads of N and P, and of the N:P ratios, from mainland UK
15catchments. Over the 11 years of data from 1993-2003 nitrate loads were generally
16constant, while orthophosphate loads generally declined. Most UK catchments would
17seem to be P-limited although a few are N-limited while others oscillate seasonally
18between N and P limitation.

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20Key words: macronutrients, nitrate, phosphate, [Redfield ratios](#), nutrient loads,
21nitrification, eutrophication, catchments.

11. Introduction

2Nitrogen (N) and phosphorus (P) are essential nutrients for biological primary
3production, but anthropogenic enrichment of nutrients (nutrification) can result in
4changes in the biological communities (eutrophication) in the rivers, estuaries and
5marine ecosystems receiving the nutrients ([Giraud et al., 2008; Grizzetti et al., 2008](#))
6~~{Giraud, et al., 2008; Grizzetti, et al., 2008}~~). Enhancement of N can lead to
7increased phytoplankton growth and biomass, and to depletion of silicate as it is
8assimilated by diatoms, with the consequence that with any further increase of N load
9diatoms decrease in relative importance due to Si limitation while microflagellates
10become increasingly dominant ([Franzs, 1986; Humborg et al., 1997; Kocum et al.,](#)
11~~2002a~~){[Franzs, 1986; Humborg, et al., 1997; Kocum, et al., 2002a](#)}. As diatoms form
12the basis of grazing food chains leading to commercially important species, whereas
13flagellates and microflagellates are the basis of microbial food chains, such changes
14induced by nutrification can be of great ecological and commercial importance ([Justic](#)
15~~et al., 1995~~){[Justic, et al., 1995](#)}. Concern for the consequences of nutrification has
16led to legislation at both national and international levels to regulate and minimise the
17impact of loading of nutrients to water bodies. In Europe, the Water Framework
18Directive (2000/60/EC) requires the development of management plans to control and
19limit the discharge of nutrients to catchments, in order to maintain biological
20populations within acceptable limits (~~{Grizzetti et al., 2008}~~){[Grizzetti, et al., 2008](#)}.
21However, such management plans are only possible with understanding of the sources
22and magnitudes of the loads of nutrients in a catchment.

1 Typically, aquatic primary producers such as microalgae and diatoms consume
2 nutrients from the environment in the Redfield Ratio (atom:atom) of 106C : 16N :
3 16Si : 1P. As nutrients are assimilated by algal growth, the nutrients in the water
4 may become depleted until one becomes limiting to further growth (biomass
5 production). An environment is said to be limited by a particular nutrient when
6 that nutrient is used up, but enough of the other nutrients remain to potentially
7 support more biological activity. It also assumes that production is not limited by
8 other variables such as light. In addition to nutrient concentrations, changes in the
9 ratios of the limiting nutrients can have significant impact on the structure of
10 communities. The Redfield Ratio provides a useful comparison to the nutrient
11 ratios actually observed in rivers and estuaries and indicates which elements, in
12 the presence of non-limiting sunlight, will potentially limit the growth of the
13 microalgae. It is generally held that primary production in rivers and lakes is P-
14 limited ([Hecky and Kilham, 1988](#); [Nedwell et al., 2002](#))~~([Hecky and Kilham, 1988](#);~~
15 ~~[Nedwell, et al., 2002](#))~~ and this might therefore also be the case at the top of
16 estuaries. However, coastal waters tend to be N-limited ([Howarth, 1988](#))~~([Howarth,](#)~~
17 ~~[1988](#))~~, although the general evidence for this marine limitation is not as conclusive
18 as for freshwaters. Furthermore, discharge of treated sewage effluent, which has
19 high P content, can change the receiving waters from P-limited to N-limited (e.g.
20 [Nedwell et al., 2002](#))~~([Nedwell, et al., 2002](#))~~). Not all nitrogen in river water is
21 biologically available (e.g. dissolved organic nitrogen, DON, may not be
22 'bioavailable' e.g. ([Agedah et al., 2009](#))) so that considering only the biologically
23 available compounds may give a better indication of which nutrients will be
24 limiting primary production. Moreover, some biologically available compounds
25 are used in preference to others (e.g. ammonium preferred to nitrate by algae

1 (~~Dortch, 1990; Kocum et al., 2002b~~)(~~Dortch, 1990; Kocum, et al., 2002b~~)) when
2 both are available, suggesting that the Redfield Ratio can be an oversimplification
3 of the true situation. Again, if all nutrients occur at high, saturating
4 concentrations (typically $\geq 2\mu\text{g l}^{-1}$), the nutrient ratios may be irrelevant, as all
5 nutrients will be in excess and growth rates maximal. (~~Hessen, 1999~~)(~~Hessen,~~
6 ~~1999~~) also warns against the traditional assumption that if primary production is
7 well correlated with a single nutrient concentration, then that nutrient must be
8 limiting. The arguments against this assumption are 1] that there is a time lag
9 between nutrient loads increasing and primary production following, 2] that the
10 water (especially in lakes) may not be well mixed, or 3] that light may be limiting
11 rather than a nutrient. Furthermore, there is enough variation in nutrient uptake
12 between organisms that the exact ratio of nutrient requirement is imprecise.
13 However, these possible reservations apart, the levels of N and P may give
14 important information on the status of a body of water that is useful in its
15 management.

16

17 Loads of nutrients from catchments are derived from measurements of water flow rate
18 and nutrient concentration. Across UK rivers a network of more than 1300 gauging
19 sites provide real-time measurements of water flow (see the UK National River Flow
20 Archive at <http://www.ceh.ac.uk/data/nrfa/index.html>). Nutrient concentrations in
21 water from 277 selected sites sampled since 1975 are available under the Harmonised
22 Monitoring Scheme (HMS) (~~Hurley et al., 1994; Simpson, 1980~~)(~~Hurley, et al., 1994;~~
23 ~~Simpson, 1980~~) for which data are held at the U.K. Environment Agency Data
24 Centre, Twerton, U.K. While these data bases provide a potentially important
25 resource, there has been only limited use of the data to understand the magnitudes of

1 nutrient loads from UK catchments, or seasonal or regional changes in loads or
2 nutrient ratios. ([Littlewood et al., 1998](#))[~~Littlewood, et al., 1998~~] described the
3 estimation of mass loads of solutes in the HMS data sets, and the problems associated
4 with it, while ([Nedwell et al., 2002](#))[~~Nedwell, et al., 2002~~] reported N and P loads
5 from UK catchments for the 95 major UK estuaries with data averaged from 1995 and
6 1996. ([Littlewood and Marsh, 2005](#))[~~Littlewood and Marsh, 2005~~] presented time
7 series from 1975-1994 of annual mass loads of suspended solids, total nitrogen and
8 orthophosphate to UK estuaries, and to the coastal areas around the U.K. The record
9 of the exact combination of gauging stations ~~that they used~~ [by Littlewood and Marsh](#)
10 [\(2005\)](#) is not [now](#) available, but a similar list, compiled in 1997, was provided by I. G.
11 Littlewood (personal communication, Jan. 2006). In the present work we use the data
12 from all available gauging and monitoring sites with adequate data sets, over an 11
13 year period to detect trends of change in nutrient loads, seasonal changes and changes
14 of ratios for all monitored UK catchments.

15

16 **Methods**

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

21 *Concentration measurements.* Concentrations in river water are measured much less
22 frequently than flows (typically just once or twice a month, using water samples
23 gathered manually); to monitor levels of up to 80 properties of the water in each
24 location, including six factors directly relevant to nitrogen and phosphorus
25 concentrations. Measurements are sporadic, although the largest rivers are generally

1 sampled at least fortnightly, but sampling has, if anything, decreased in frequency
2 over the last decade (see for example, nitrate and phosphate data from the River
3 Rother in Figure 1). Under the HMS, four different measurements are taken of
4 chemicals containing nitrogen, along with two measurements concerning phosphorus
5 (Table 1). For nitrogen, ammoniacal nitrogen, nitrite and nitrate measurements are all
6 made with a similar frequency. The possibility of summing two or more of these N
7 variables in estimating total N loads was considered but rejected as this could only be
8 done where ~~the a~~ sample had been analysed for each of the determinands, which
9 would significantly reduce the number of usable observations. **Cite Littlewood doing**
10 **the same.** However, nitrate concentrations are usually at least one order of magnitude
11 larger than the other measurements, typically >90% of the total dissolved inorganic
12 nitrogen (DIN) concentration.

13 As well as orthophosphate, the total phosphorus measurements appear to give the
14 data required to calculate phosphorus loads, but these measurements are taken rarely
15 compared to the orthophosphate measurements. Furthermore, (see Table 1) the
16 average concentration measurement for orthophosphate is often higher than the
17 average measurement of total phosphorus, which is impossible. This could be due to
18 differences in the analytical methodology used to derive the results or due to space-
19 time sampling bias in the sites at which total phosphorus measurements are made, or a
20 combination of both factors. Therefore, the orthophosphate measurements were used
21 in calculating P loads as soluble orthophosphate is the biologically available form of
22 phosphate. We note that this is likely to underestimate the total P load because of
23 adsorption of phosphate to exported particulate material (e.g. ([House et al., 1998](#);
24 [Prastka et al., 1998](#))/~~[House, et al., 1998](#); [Prastka, et al., 1998](#)~~).

25

12.3. Validation of the concentration data

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

- 4 • Some ~~of the HMS~~ concentration data were duplicated on the database with
5 more than one observation for the same day. This could be due to more than
6 one sample being taken, more than one analysis of the sample, or duplicate
7 data entry. All measurements taken on the same day at the same site were
8 converted to a single measurement given by the average.
- 9 • Some of the concentration data were recorded as “<LOD” (less than the Limit
10 of Detection) where the value was below the minimum value that could be
11 detected by the chemical analysis. The LOD may vary over time, even at the
12 same gauging station, reflecting changed analytical methods, changed
13 equipment, or analysis being performed in different laboratories. Samples
14 marked as “<LOD” were rejected, after comparing results for including them
15 as LOD or LOD/2, and finding that the calculated loads were similar (within
16 5% in 96% of catchments). [\(Littlewood and Marsh \(2005\) arbitrarily
17 calculated mass loads using <LOD data as LOD/2.\)](#)
- 18 • ~~There may be gaps in the concentration data when data were not recorded.~~
- 19 • At some stations the concentration data are quantised, that is, they take one of
20 very few distinct values. This would suggest that rounding errors will play a
21 larger part in these stations than in general.

22 In general, the analysis of trends in the nutrient concentration will be more robust,
23 [allowing for detection of subtler trends](#), if more data are included, ~~allowing for~~
24 ~~detection of subtler trends in the data~~. Data from the period 1993-2003 were used in
25 our analysis as this represented a period long enough to be able to detect temporal

1 changes in concentration, and included the most recently available data at the time
2 that this work was started.

3

4 While calculation of loads requires knowledge of both flow rate and concentration,
5 the different frequencies of measurement of each variable limits precision of load
6 estimates. Much of an export load from a catchment may occur during periods of high
7 flow which may be missed by the infrequent sampling for measurement of nutrient
8 concentration ([Walling and Webb, 1985](#)), but the more
9 frequent measurements of flow rates may, however, detect such episodic events. To
10 permit more precise estimates of nutrient loads from catchments, therefore, we
11 adopted the strategy of modelling nutrient concentrations from existing concentration
12 data which could then be combined with the frequent measurements of flow to
13 provide a much more robust estimate of catchment nutrient loads, including episodic
14 events detected by flow.

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

24 **Seasonal and long term trends in N and P concentrations in catchments.** To
25 investigate the seasonal and long term trends in nutrient concentrations, those HMS

1 sites were selected which had sufficient data, and were close to an NRFA gauge that
2 could be used to calculate load. The requirements were that: 1] at least 60 of the
3 months in the 11 years' data should have acceptable concentration measurements
4 (typically the actual number averaged 100.) 2] more than ten distinct values of
5 concentration should be recorded – sites with fewer distinct values may be especially
6 biased by rounding errors 3] the sites were within 20 km of NRFA gauges. This may
7 seem a large distance, but in practice the mean distance was 6.6km and 75% of the
8 pairs were located within 5km of one another. Where HMS sites measured a sub-
9 catchment of another HMS site, only the larger catchment was used to avoid double-
10 counting. This gave 139 sites selected for nitrate and 118 for phosphate. (In
11 comparison, Littlewood et al (2005) reported 150 sites with both HMS and NRFA
12 data.). ~~Plotting these revealed that data from only a small proportion of East Anglia
13 was included, despite it being an area known to export relatively high nutrient loads.
14 The reason for this is that the Ely Ouse catchment covers a large part of the region,
15 but flows within this catchment are not well measured for the purpose of load
16 calculation because of a complex system of drainage ditches and cross-pumping.
17 Consequently, although the modelling of both nutrient concentrations in this
18 catchment was performed, nutrient loads could not be calculated directly.~~
19 For the 140 catchments judged to have adequate nitrate data by the previous criteria,
20 and for the 119 catchments with adequate phosphate data a statistical model was fitted
21 to the concentration measurements which had the following properties:

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

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

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

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

6 1. How big is the average log nutrient concentration (α in the following

7 model)?

8 2. Is the concentration increasing or decreasing over time (β)?

9 3. How much larger is the peak seasonal concentration in proportion to
10 the annual average concentration (γ)?

11 4. At what time of year (τ) does the peak concentration occur? (See Table
12 2 for interpretation of this value.)

13 To meet these requirements we used the following statistical model:

$$14 \quad C = \exp(\alpha(1 + \beta t + \gamma \cos(2\pi[t - \tau]))) \quad (1)$$

15 where C is the expected concentration, α , β , γ and τ are the parameters to fit the model
16 and t is the time in years (taking the midpoint of the study period as 0). The parameter
17 α relates to the average concentration and β relates to annual change in concentration.

18 The term $\gamma \cos(2\pi[t - \tau])$ in the model represents the annual cycle of nutrient

19 concentrations (see Fig 2-~~or 3~~?) as described by both magnitude (γ) and time of year

20 (τ : see Table 2 for interpretation of this value.) of the seasonal peak. This model has

21 an infinite number of values of γ and τ that give the same fit due to the periodicity of

22 the cosine wave, so the following restrictions are placed on the parameters:

$$23 \quad \gamma \geq 0; 0 \leq \tau < 1 \quad (2)$$

24 **Estimation of loads.** Nutrient loads (L) can be estimated as the product of water flow

25 rate (F) with the nutrient concentration (C), although there are several ways of

1calculating loads with different degrees of precision (see [\(Littlewood et al., 1998;](#)
2[Vries and Klavers, 1994; Walling and Webb, 1985\)](#)~~[\(Littlewood, et al., 1998; Vries-](#)~~
3~~[and Klavers, 1994; Walling and Webb, 1985\)](#)~~). Generally, precision increases by
4measuring nutrient loads over shorter periods of time, and summing the loads; rather
5than averaging over longer periods, which may underestimate peak loads. In our
6work, for each catchment daily nutrient load was calculated as the product of the
7measured daily average flow from the NRFA, and the concentration value obtained
8from Equation 1 fitted to the concentration data for that particular catchment. Daily
9loads were then summed to get annual loads.

10In order to estimate nutrient loads to estuaries and coastal seas the catchments flowing
11to each coast of the U.K., and catchment areas for gauging stations were deduced
12from the CEH Digital Terrain Model ([\(Jenson and Domingue., 1988; Morris and](#)
13~~[Flavin, 1990\)](#)~~~~[\(Jenson and Domingue., 1988; Morris and Flavin, 1990\)](#)~~; and see
14[\(Littlewood and Marsh, 2005\)](#)~~[\(Littlewood and Marsh, 2005\)](#)~~). The total load to each
15coastal region was calculated by summing the loads from the catchments that flow
16into that region, and dividing by the proportion of the area draining to that region that
17is within the modelled catchments. This accounted for ungauged catchments, areas
18downstream of gauging stations, and catchments with inadequate data by assuming
19that they export the same load per unit area as the neighbouring gauged areas flowing
20into that coastal region. This gave estimates of total nutrient loads to the North Sea,
21the Irish Sea, Celtic Sea, Atlantic coast and the English Channel.

22

23**5. Results and Discussion**

24**Aggregated and normalised data for all catchment trends.**

25The log transformed aggregated concentration data from all catchments (Fig 12)

1 showed a significant annual cycle in both N and P concentrations, and a significant
2 temporal decrease over 11 years [1993-2003](#) in P concentrations, but not in N
3 concentrations. Littlewood et al (1998) also reported decrease of orthophosphate loads
4 to UK estuaries for the period 1985-90.

5 **U.K. wide variations in nutrient concentrations.** Figures [23\(aA\)](#) and [34\(aA\)](#)
6 illustrate the values of the parameters α , (the logarithm of average concentration, in
7 **mg N or P l⁻¹**) from the nitrate and phosphate concentration models. The catchments
8 shaded in grey are those which have inadequate concentration data sets while the
9 white areas indicate regions where data are not available. Lack of data may result
10 from gauging stations not being at tidal limits and thus some parts of the catchments
11 being below a gauging station yet above tidal limits. Some small catchments are not
12 gauged, such as some in northern Scotland which would require a large effort to
13 monitor relative to their small size and nutrient load, and so measurement effort is
14 focused on larger, more accessible catchments.

15

16 Figure [23\(aA\)](#) shows results for nitrates. The highest values of α are in the Midlands
17 and the south-east of England, while the lowest are in northern Scotland and the west
18 ~~east~~ of Wales. The spatial coherence of the concentrations indicates that there are
19 underlying factors (such as geology or land use) influencing the loads, rather than
20 simply random differences between catchments. (We will consider elsewhere the
21 underlying causes of these catchment loads (Earl et al, in preparation)) The high
22 values of α in the Midlands and South East suggest that nitrates are dependent on a
23 combination of human population density and agriculture as shown previously
24 ([Peierls et al., 1991](#))[~~Peierls, et al., 1991~~], as these areas have the highest population
25 densities and most intensive agriculture. Neither factor alone adequately explains the

1 concentration, as the catchments with high nitrate concentration in the south east (in
2 North Norfolk, for example); have a relatively low population density, whereas the
3 catchments around Liverpool and London have high nutrient concentrations despite
4 being areas with little agriculture.

5

6 Figure 34(aA) shows the log of average phosphate concentration. Phosphate
7 concentrations were highest in the catchments which include major urban areas such
8 as London and Merseyside, suggesting that the main source of phosphates is from
9 sewage.

10

11 **Long-term trends in nutrient concentrations.** Figures 2(3bB) and 34(bB) show the
12 corresponding results for the parameter β , which is the percentage change in the
13 concentration per year. Therefore, a value of ± 0.05 represents a compound change in
14 concentration of over 70% in the 11 year period being studied. Only those catchments
15 where β is statistically significant ($P < 0.05$) are coloured. Figure 23(bB) shows that for
16 much of Britain (86/140 catchments) the nitrate concentrations have not changed
17 significantly during the study period, which agrees with the aggregated national data
18 illustrated in Figure 2. However, there are some exceptions:-

- 19 • In Northern Scotland, a cluster of catchments showed an apparently
20 significant increase during 1999-2001 in nitrate concentrations at gauges
21 11002 (River Shin), 11003 (River Conon), 11004 (River Beaully) and 11005
22 (River Ness), where concentrations were approximately double that of
23 previous years. The geographically consistent nature of this anomaly
24 suggested that there had been an analytical data processing or entry error, or a
25 change in analytical procedure, rather than a real change.

- 1 • The River Mersey showed a highly significant increase in nitrate
2 concentration over 1993-2003, which does not arise from any obvious
3 anomalies and indicates a real change. This might be the effect of
4 improvements in the sewage treatment works having achieved greater
5 nitrification, resulting in a decrease of ammonium and corresponding increase
6 of nitrate. (CEFAS, 2001)~~(CEFAS, 2001)~~ reported a trend of decreasing
7 ammonium loads after 1995.
- 8 • The River Thames showed a significant decrease over the period, largely
9 driven by high nitrate concentrations in 1996 and 1997. As these were both
10 years of low rainfall and low flow in the Thames, and hence low dilution, it
11 seems plausible that these high measurements were a true reflection of the
12 change of nitrate concentrations in the river.

13

14 When the concentration model was applied to phosphate concentrations there were
15 significant (at the 0.05 level) changes in 68 ~~of the~~ 119 catchments with useful data.
16 The change of P with time (Figure 34~~(bB)~~), illustrates a trend of general decrease of
17 phosphate concentrations over 1993-2003, with very few catchments increasing. The
18 decrease in phosphate may be attributable to decreasing use of phosphates in
19 detergent, or increase in phosphate stripping in sewage treatment works since the
20 introduction of the Urban Waste Water Treatment Directive in 1991. The two
21 catchments (16007 & 16008) with apparent steep increases of P in Western Scotland
22 may result from change in measurement accuracy, or local changes in agriculture or
23 sewage treatment provision.

24 **Seasonal variations in nutrient concentrations.** Figure 23~~(eC)~~ shows results for
25 nitrate of parameter γ , (the magnitude of the seasonal variation of nitrate

1 concentrations) and Figure 23(dD) shows parameter τ (the timing of the peak nitrate
2 concentration). In both cases they are coloured only if γ is significant (τ is
3 meaningless in the absence of significant seasonal variation). Of the 140 catchments
4 to which the model was fitted, 128 had significant (TEST ? $P < 0.05$) seasonal
5 variation. For nitrate concentrations (Fig 23(dD)) the majority of catchments have a
6 value for τ around 0.1-0.2, indicating the peak of nitrate concentrations in February
7 suggesting that high rainfall in this winter period washes out of the catchment soil
8 nutrients that may have accumulated over the year. The catchments that appear in
9 green have the opposite trend of highest concentration in August, suggesting that they
10 are dominated by nitrates from sewage which is diluted at times of high rainfall but
11 concentrated during the summer months.

12 Similarly, Figures 34(eC) and (dD) illustrate the seasonality of the phosphate
13 concentrations : 106/119 of the catchments have a significant seasonality, with peaks
14 typically in July-October. This seasonal trend is consistent with phosphate sources
15 being dominated by a relatively constant P input which is diluted most during the
16 winter and concentrated most in periods of low flow during the summer.

17 **Ratios of nutrients.** The continuous time series of nitrate and phosphate
18 concentrations can be plotted against one another as N:P (atom:atom) ratios to
19 indicate whether a catchment is generally N- or P-limited. This was done for the 119
20 catchments where both N and P concentration time series had been successfully
21 created. While the use of solely soluble orthophosphate will underestimate the total P
22 load because of P adsorption to particulates (House et al., 1998; Prastka et al., 1998)
23 [House, et al., 1998; Prastka, et al., 1998]), soluble orthophosphate is the biologically
24 available form of P and therefore appropriate for calculating the N:P ratio. (In
25 contrast, nitrate does not adsorb to particles.) Examples are shown in Figure 4-5 for

1the HMS site 7004 (River Rother, Kent) and HMS site 1010 (River Wyre at St
2Michael's, Lancashire) catchments. The cycles in the data reflect the annual nitrate
3and phosphate concentration cycles over 11 years, with successive annual cycles
4differing slightly because of the long term trends in the nutrient concentrations,
5particularly in the case of phosphate. The broken line shows the Redfield Ratio in
6which these nutrients are used by a 'typical' phytoplankton, while the black point
7represents the overall average N:P ratio that is often used to decide whether the river
8is N- or P-limited. The Rother catchment appears to be always P-limited because the
9N:P ratio is always above and to the left of the line indicating the Redfield Ratio. In
10the River Wyre, though, while the average N:P ratio indicates potential P-limitation,
11the seasonal cycle of N:P shows that the catchment is P-limited from September
12through the winter until the end of April but during the summer months the river is N-
13limited. As algae and higher plants need light for primary production, the N-limitation
14during the summer months is considerably more ecologically important than the P-
15limitation over winter, and so the annual average value of N:P may be deceptive.

16 The distribution of the N- and P-limited catchments is shown in Figure 56. Of
17the 119 catchments that had adequate data for both nitrate and phosphate, the majority
18(83) appeared to be potentially P-limited, while only 7 were N-limited (~~details for~~
19~~each named catchment are given in the supplementary material~~). It is note-worthy that
20the N-limited catchments generally occurred in the large metropolitan areas (London,
21Birmingham, Liverpool, Manchester) where discharge of P-rich treated sewage
22effluent would tend to increase the probability of N-limitation (e.g. [\(Nedwell et al.,](#)
23[2002\)](#)~~[Nedwell, et al., 2002]~~. Of the remaining cases, 28 had an annual cycle that
24changed from N-limited in the summer to P-limited in the winter over the annual
25cycle , and the other two changed from N- to P-limited over the 11 year period, but

1not on an annual cycle. Catchments in Scotland, Wales and western England are
2almost entirely P-limited, whereas central and southern England catchments oscillate
3over the annual cycle. The spatial coherence of the limitationsing nutrient suggests
4that there is an underlying pattern, which could be due to the terrain or land use
5(although the two factors are closely connected); for example, the P-limited
6catchments are generally in the more rural areas where sewage inputs are lower. [\[The
7Supplementary Material shows for each named and numbered catchment the element
8which appears to be potentially limiting to primary production.\]](#)

9**Estimated annual loads.** Figure 6-7 shows the annual nitrate and phosphate loads
10derived from the modelled concentrations and the measured flow, normalised by
11catchment area. **The lowest nitrate loads per unit area are observed in the sparsely
12populated areas of nNorthern Scotland.** There is an area of high nitrate loads in
13central England, corresponding with the area around the cities of the midlands and the
14north west. The large area of white in central east England for the catchment of the
15River Ely Ouse is the result of unreliable river-flow measurements for this catchment.
16Parallel channels between which ungauged cross flow at Denver Sluice can occur at
17different times of the year make load estimates highly problematic although
18concentration data are satisfactory. The phosphate loads are highest in a region
19encompassing the urban areas of the midlands and north-west. This adds weight to the
20generally accepted hypothesis that population density (via sewage) is the major cause
21of high phosphate loads. **[Compare our average annual export load km⁻² wit those
22export coefficients from Johnes and Butterfield 2002 for England and Wales only.
23(Johnes and Butterfield, 2002){Johnes and Butterfield, 2002}]**

24

25**Significance of UK east coast nutrient loads to North Sea.** Table 3 shows the

1 estimated loads from UK estuaries to each coast (as defined by PARCOM **YEAR?**
2 **Reference ??**), averaged over the 11 years of the study.

3

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

9

10 Clearly, the greatest loads from the U.K. ~~were~~are into the North Sea. The proportion
11 of gauged to non-gauged catchments calculated for each coast were identical to those
12 given by Littlewood et al (2005), and the total loads cited in Table 3 were derived by
13 multiplying the figure for any gauged catchment area by the proportion of gauged area
14 in the total catchment. The average N and P loads km^{-2} were [GIVE VALUES TO
15 EACH COAST AND COMPARE WITH AVERAGE VALUES 1975-94 IN
16 LITTLEWOOD AND MARSH 2005]

17 **The U.K. N load to the North Sea.** By comparison with the UK loads to the North
18 Sea ($1.3 \times 10^4 \text{ Mmol N y}^{-1}$ or $1.9 \times 10^5 \text{ tonnes N y}^{-1}$), the Scheldt alone exports $7.28 \times$
19 $10^4 \text{ tonnes N y}^{-1}$ ($5.2 \times 10^3 \text{ Mmoles N y}^{-1}$) (Billen et al., 1985)[~~Billen, et al., 1985~~],
20 the Seine $9.24 \times 10^4 \text{ tonnes N y}^{-1}$ ($6.6 \times 10^3 \text{ Mmol N y}^{-1}$) (Billen et al, unpublished
21 data cited in (Howarth et al., 1996)[~~Howarth, et al., 1996~~]), and the Rhine/Meuse had
22 a load of about $4 \times 10^5 \text{ tonnes N y}^{-1}$ ($2.9 \times 10^4 \text{ Mmoles N y}^{-1}$) between 1985-95
23 (Nienhuis, 1996)[~~Nienhuis, 1996~~]. (Laane et al., 1993)[~~Laane, et al., 1993~~])
24 estimated total fluvial inputs to the North Sea of $10^6 \text{ tonnes N y}^{-1}$ ($7.2 \times 10^4 \text{ Mmoles N}$
25 y^{-1}), and (Howarth et al., 1996)[~~Howarth, et al., 1996~~] gave a similar value of $1.22 \times$

110⁶ tonnes y⁻¹ (8.7 x 10⁴ Mmoles y⁻¹), of which 34% was attributed to STW inputs.

2The entire UK N load to the North Sea is therefore equivalent to 1.3 x 10⁴/8 x 10⁴

3Mmoles y⁻¹, or at most 16.5 % of the total fluvial N load to the North Sea.

4

5How significant are the UK east coast estuary loads relative to all N inputs to the

6North Sea, including those from the Atlantic ? ([Laane et al., 1993](#))[~~Laane, et al.,~~

71993}] gave total N inputs to the North Sea as 6.48 x 10⁶ tonnes y⁻¹, equivalent to 4.6

8x 10⁵ Mmoles N y⁻¹. Total fluvial N inputs to the North Sea (mean 8 x 10⁴ Mmoles N

9y⁻¹) therefore represent only 19 % of the N inflow from the Atlantic. The relative load

10contributions of the entire east coast UK estuaries are, therefore, 1.3 x 10⁴/4.6 x 10⁵,

11or only about 2.9% of the total N load to the North Sea. According to ([Howarth et al.,](#)

121996)[~~Howarth, et al., 1996~~] the relative contribution of urban wastewater sources

13will be about 30% of that i.e. < 1%.

14**The P load.** The total fluvial export of DP-orthophosphate is 6. x 10² Mmoles P

15through the UK east coast estuaries. ([Laane et al., 1993](#))[~~Laane, et al., 1993~~] cite a

16total P load to the North Sea of 1.3 x 10⁶ tonnes P y⁻¹, equivalent to 4.2 x 10⁴ Mmoles

17P y⁻¹. The North Sea Quality Status report (NSTF 1993) quotes 8 x 10⁵ tonnes (2.7 x

1810⁴ Mmoles) phosphate from the Atlantic and fluvial inputs of 4.5 x 10⁴ tonnes (1.5 x

1910³ Mmoles) y⁻¹: a total of 2.8 x 10⁴ Mmoles y⁻¹. The mean of the two estimates is 3.5

20x 10⁴ Mmoles y⁻¹. Therefore, the annual DP-orthophosphate load from UK east coast

21is equivalent to 6 x 10²/3.5 x 10⁴= 1.7 % of the total P load to the North Sea: although

22because of adsorption of P to suspended particles (which were not included in the

23present estimates of loads) this will be an underestimate of the total P load.

24

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24

1

2Table 1: Measured nitrogen and phosphorus variables taken under the Harmonised

3Monitoring Scheme. Measurement frequency refers to the total number of

4observations per year made across Britain. **Where does this come from ? Give**

5**Reference ?**

6

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

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2Table 2: Interpretation of the concentration model parameters

3

Parameter	Interpretation
α	The average log concentration of the catchment (mg l^{-1})
β	The proportional change in concentration per year over the 11 year period
γ	The proportion of the load that changes due to seasonal variation
τ	The time of year when concentration is at a maximum
	0: 1st January
	0.25: 1st April
	0.5: 1st July
	0.75: 1st October

4

1

2Table 3. Annual loads of nitrate (Mmol N y⁻¹) and orthophosphate (Mmol P y⁻¹) from UK catchments to coastal seas. Gauged percentages refer to
3the percentage of the area draining into each ocean that is upstream of a gauging station used in this work. The directly gauged loads from the
4east coast to the North Sea excluded the Great Ouse catchment, for which flow data was unreliable, but the total North Sea load was adjusted
5proportionately to include the Great Ouse catchment area.

6

	N gauged Load (Mmol N y ⁻¹)	P gauged 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

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1List of Figures.

2

3Figure 1: [Example concentration and flow data from the River Wyre at St Michael's,](#)
4[Lancashire \(top\) and The River Rother, Kent \(bottom\). For each catchment, the plots](#)
5[show nitrate concentration, phosphate concentration and flow rate.](#)

6~~Fig 1. Nitrate and phosphate concentration data and flow rates from the Rivers Wyre-~~
7 ~~and Rother.~~

8

9Fig 2. Aggregated and normalised seasonal concentration data from all UK
10 catchments.

11

12Fig 3a-d. Nitrate model parameters

13

14Fig 4a-d Phosphate model parameters.

15

16Fig 5. Annual cycles of N:P ratios for Rother and Wyre.

17

18Fig 6. Distribution of N or P limitations in UK catchments.

19

20Fig 7. Area- normalised N and P loads for UK catchments.

21

22

23

24List of supplementary material.

25

26Suppl 1. Reference list of named and numbered UK catchments (we need to give the
27gauging station number and the corresponding HMS site number) with their limiting
28nutrient (N or P or seasonally variable), [N and annual loads, area-normalised loads,](#)
29and the values of the concentration model parameters for each catchment.