

## APPLIED ISSUES

# The determination of total nitrogen and total phosphorus concentrations in freshwaters from land use, stock headage and population data: testing of a model for use in conservation and water quality management

PENNY JOHNES,\*† BRIAN MOSS\*‡ AND GEOFFREY PHILLIPSS

*\*Department of Environmental and Evolutionary Biology, University of Liverpool, Liverpool L69 3BX, U.K.*

*‡National Rivers Authority, Eastern Region, Ipswich, U.K.*

*†Present address: Department of Geography, University of Reading, Whiteknights, Reading, U.K.*

*‡Author to whom correspondence should be sent*

### SUMMARY

1. Nutrient concentrations (particularly N and P) determine the extent to which water bodies are or may become eutrophic. Direct determination of nutrient content on a wide scale is labour intensive but the main sources of N and P are well known. This paper describes and tests an export coefficient model for prediction of total N and total P from: (i) land use, stock headage and human population; (ii) the export rates of N and P from these sources; and (iii) the river discharge. Such a model might be used to forecast the effects of changes in land use in the future and to hindcast past water quality to establish comparative or baseline states for the monitoring of change.

2. The model has been calibrated against observed data for 1988 and validated against sets of observed data for a sequence of earlier years in ten British catchments varying from uplands through rolling, fertile lowlands to the flat topography of East Anglia.

3. The model predicted total N and total P concentrations with high precision (> 95% of the variance in observed data explained). It has been used in two forms: the first on a specific catchment basis; the second for a larger natural region which contains the catchment with the assumption that all catchments within that region will be similar. Both models gave similar results with little loss of precision in the latter case. This implies that it will be possible to describe the overall pattern of nutrient export in the UK with only a fraction of the effort needed to carry out the calculations for each individual water body.

4. Comparison between land use, stock headage, population numbers and nutrient export for the ten catchments in the pre-war year of 1931, and for 1970 and 1988 show that there has been a substantial loss of rough grazing to fertilized temporary and permanent grasslands, an increase in the hectareage devoted to arable, consistent increases in the stocking of cattle and sheep and a marked movement of humans to these rural catchments.

5. All of these trends have increased the flows of nutrients with more than a doubling

of both total N and total P loads during the period. On average in these rural catchments, stock wastes have been the greatest contributors to both N and P exports, with cultivation the next most important source of N and people of P. Ratios of N to P were high in 1931 and remain little changed so that, in these catchments, phosphorus continues to be the nutrient most likely to control algal crops in standing waters supplied by the rivers studied.

## Introduction

Water quality is important in the management of freshwater bodies. It is also difficult to define because a large number of variables may be used to describe it, dependent on the needs of the user. For direct human use, amenity and conservation the quality needs to be the highest and such quality approximates most closely to an absolute, practicable standard. Such a standard should be the yardstick against which current quality is assessed for monitoring purposes.

In practice, no such yardstick comparison is usually made, though for flowing waters the River Invertebrate Prediction and Classification System (RIVPACS) approach (Wright, Furse & Armitage, 1993) and the riparian, channel and environmental inventory model of Petersen (1992) contain this philosophy, which is referred to as a 'state-changed' approach. We have argued (Moss, Johnes & Phillips, 1996) for such an approach to the monitoring of standing waters and have proposed a system for doing this, based on comparisons of the contemporary values of a number of variables with values hindcasted for a baseline state of the water body.

The baseline state is a more subtle concept than that of a simple establishment of the state of the water in the absence of human interference. Lake systems change even in pristine conditions and there is no landscape in north-western Europe that is not used by humans. The baseline state for such regions thus must take account of the activities of people but these must be indefinitely sustainable. There are approaches to land use that are more likely to be sustainable than others. First, they will reflect the natural topography, geology, soils and climate, rather than be responses to differential subsidies (of cash, energy or materials) for particular uses over other, perhaps more environmentally appropriate, ones. Second, they will reflect the availability of technology to prevent the discharge of deleterious substances such as toxins and nutrients in effluents from urban areas and intensive stock units.

The problem of defining a baseline water quality

standard, specific to each water body, is then one of defining sustainable land use for the catchment and of determining the values of water quality variables that will reflect such a state. 'Sustainability' is as difficult to define as 'quality' but a pragmatic approach may help. The transition from a land use reflecting natural constraints to a land use heavily dependent on cash, chemical or energy subsidies occurred in the U.K. after the Second World War. Prior to the 1940s, land use was much less intensive. If sustainable land use is taken to mean that which is naturally, rather than artificially, constrained, the immediate pre-war period therefore provides a cameo of use that also accepts the need for agriculture over much of a densely populated country.

Data are available from this period that allow calculation of past water quality sufficient to establish a baseline in the absence of directly measured data. Such a baseline state can also form a reference for monitoring of current changes in standing waters and an estimate of the best achievable target for attempts to improve water quality.

The credibility of such an approach depends on the method available to establish the baseline state. It must be reasonably precise, inexpensive and readily applicable to some tens of thousands of water bodies. It thus must be robust, for it cannot take into account the many details of nutrient movement and transfer *within* catchments. The approach tested here depends on export coefficient modelling (Omernik, 1976; Beaulac & Reckhow, 1982; Rast & Lee, 1983), modified by Johnes (1990, 1996).

Key to the approach is the determination of the nutrient chemistry (total N and total P) of the inflow water to the lake in the baseline state. Total concentrations of N and P are used because they show much less seasonal variation than concentrations of the chemical species (nitrate, nitrite, ammonium, dissolved and particulate organic N, soluble reactive (inorganic) phosphorus, dissolved organic phosphorus, colloidal

and particulate phosphorus) that comprise them and are therefore more reliable indicators of change in nutrient loading from year to year (Vollenweider, 1968; Moss *et al.*, 1996). Total N and P are also the units used in the literature on loss of N and P from different types of land use and stock.

The hypothesis tested here is that total N and total P concentrations in water draining from a catchment can be determined, within acceptable error, from the loadings (total amount delivered per year) of N and P and the annual discharge of the stream. In turn the sub-hypothesis is that these loadings can be calculated from the nature of the land use with allowances for local climate, topography and management (particularly the intensity of fertilizer application), the numbers of different sorts of farm livestock and the human population.

This paper describes how these variables may be determined through an export coefficient model simple enough to be practicable. It describes how the model may be calibrated against observed data and then independently validated by testing against further observed data. This process has been carried out for ten British rivers.

## Materials and methods

### *Outline of the approach to modelling*

The procedure (Fig. 1) is first to determine from existing databases (the annual agricultural censuses and the 10-yearly population censuses held in the Public Record Office) the land use of the catchment and the numbers of livestock and humans. Rates of N and P export from each type of land use are then selected initially from the available empirical literature, which is reviewed below. The nature of the terrain is taken into account in the selection of these export rates. To allow for changing rates of nitrogen application, a coefficient for percentage loss of fertilizer is incorporated. Similar coefficients cannot yet be applied for P but may be available in the future. The rates are then applied to the actual area of each land use in the lake catchment to give the load exported from these sources.

Similarly, annual rates of excretion and defecation of N and P from the major kinds of stock (cattle, pigs, sheep, poultry, as appropriate) are determined from the literature with reference to major breed character-

istics (largely upland *v* lowland). Allowance is made for the proportions exported and applied to the headage of stock in the catchment to give the loads exported.

A similar calculation is made for humans. In some instances loads may also need to be calculated for industrial sources. Finally the direct load from rain and snow is determined, and an estimate of N fixation included. The total load is calculated and divided by the annual stream or river discharge to give mean annual concentrations of total N and total P.

These calculated concentrations are then compared with observed concentrations for a test year. If the fit between them is reasonably close ( $< \pm 5\%$ ), no further adjustments are made. If there is a serious discrepancy, the export rates used are inspected and adjustments made, within the empirically determined range, to those that dominate the total loads, until acceptable correspondence is obtained. See Crow, Ghermnazien & Pathak (1983), Kirkby *et al.* (1987) and Johnes (1990, 1996) for use of such sensitivity analyses.

At this stage (calibration) there is an element of experience and judgement in selecting appropriate rates for the catchment and nutrient source concerned. This subjectivity is removed by the next stage (validation) in which the export rates are not further adjusted but are used to predict the concentrations for a different set of years for which independent records of land use and management, numbers of livestock and people and observed water quality are available. If, at this validation stage, these concentrations are predicted with acceptable precision ( $< \pm 10\%$ ), the model is accepted and can be used to calculate concentrations for years for which no observed data are available. If the precision is unacceptable, there is a return to the calibration stage.

### *Factors affecting the magnitude of export rates*

A range of factors may affect export rates of nutrients both immediately at source and at the point of delivery to a watercourse (Table 1). The rates of export of N and P to surface waters from land uses, stock and humans have been determined in many studies. For land uses, these have often involved monitoring experiments carried out in large lysimeters (Kolenbrander, 1972; Dowdell & Webster, 1980) or experiments at the field or small catchment scale (Jackson *et al.*, 1973; Neilson & Mackenzie, 1977; Jacobs

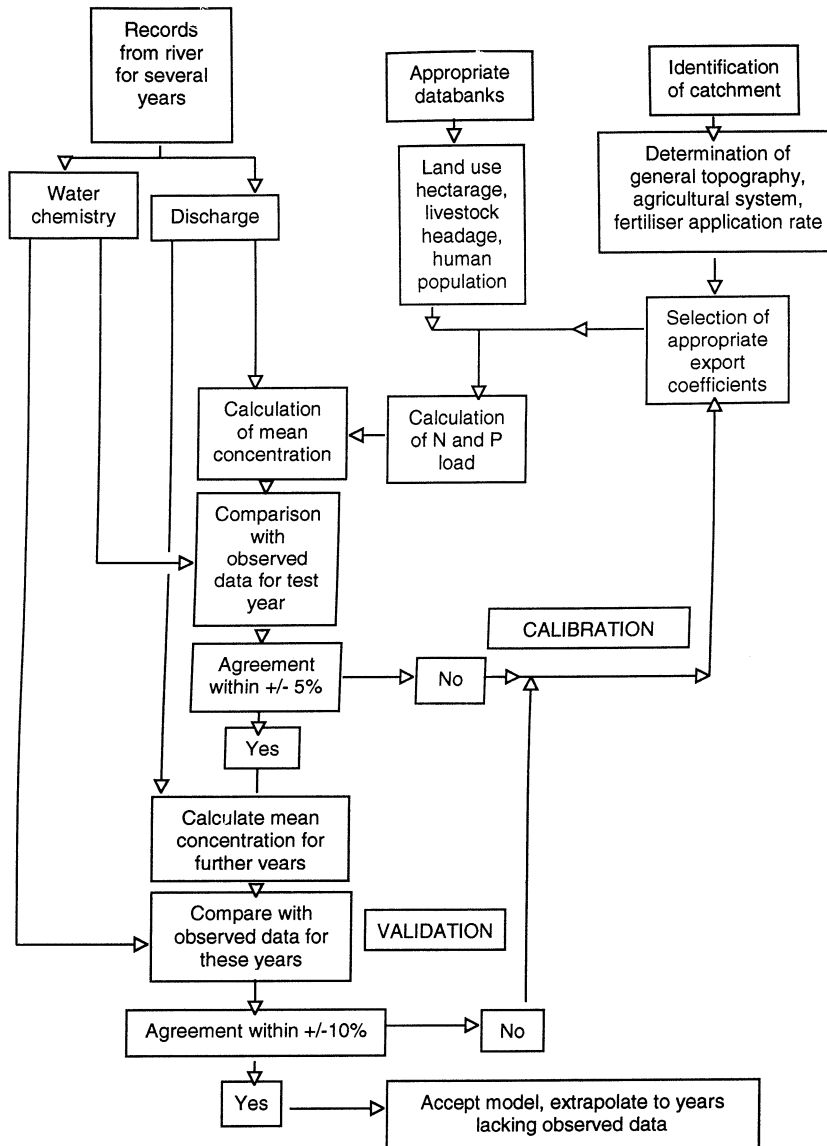


Fig. 1 Flow diagram of the model.

& Gillam, 1985; MacDonald *et al.*, 1989). Examples of the range obtained for north temperate regions are shown in Table 2.

The variations in nutrient export are linked with differences in soil type and structure, extent and timing of crop cover and fertilizer application and rainfall (Royal Society, 1983). Open-pored sandy soils, for example, lose much more nitrogen by leaching than clay or organic-rich soils (Kolenbrander, 1972; Royal Society, 1983). High rainfall and steeply sloping land, as in western Britain, will also lead to higher erosion rates and nutrient losses than in the flatter, drier east.

Fertilizer application rates may also be important (Williams & Jackson, 1976; Garwood, Salette &

Lemaire, 1980) with losses of 2–5% at rates applied of  $< 250 \text{ kg N ha}^{-1}$  and 10–40% at  $500 \text{ kg ha}^{-1}$ . Nutrient exports are higher from arable than from grassland because the soil is bare for part of the year. Absence of biomass leads to greater run off and erosion whilst the breakdown of oilseed rape litter in the soil leads to greater export than the decomposition of cereals (Addiscott, Whitmore & Powelson, 1991). Direct grazing of arable fodder crops by stock increases export rates because of compaction of the soil and greater run off as well as mobilization of nutrients in faeces and urine (Heathwaite, Burt & Trudgill, 1990; Heathwaite & Johnes, 1996).

Livestock (Table 2) are responsible for much nutrient

**Table 1** Factors potentially affecting the rates of delivery of nitrogen and phosphorus from the land surfaces (export rates)

Climate	Temperature and period soils are unfrozen; intensity, seasonality and distribution of rainfall; wind speed and direction (in affecting evaporation)
Geology	Determination of topography, soils and hydrological characteristics; presence and behaviour of underlying aquifers
Topography	Steepness of hillslopes; presence of floodplain
Soils	Type and distribution; structure and intrinsic stability; nutrient retention capacity
Hydrology	Pathways linking land–stream network; seasonal variation in routing of pathways; connectivity of aquifers with surface waters; under drainage; irrigation and other human interference
Land management	See hydrology; timing of fertilizer applications; application of sewage sludge and animal manures and slurry; cultivation of legumes; cultivation of crops with high residues (e.g. oilseed rape); fodder cropping; intensity of production system—stocking density on grassland; breed of livestock; multiple cropping of land in 1 year
Sewage treatment	Proportion of population on septic tank systems; degree of sewage treatment; use of phosphorus stripping
Spatial location of nutrient sources in the catchment	Proportion of population on septic tank systems; degree of sewage treatment; use of phosphorus stripping
Spatial location of nutrient sources in the catchment	Proximity and connectivity of nutrient sources to hydrological pathways

loss to water, especially in the wetter west of Britain where animal numbers, run off and slope angles are often high. There is a logarithmic relationship between nutrient voidance and body weight such that cattle void sixteen times, pigs twice, sheep one and a half times and poultry one-seventh as much as a human (Vollenweider, 1968; Cooke, 1976; Owens, 1976). There is some variation with breed and the systems used for keeping the animals. Nutrients are readily washed out of manure dumps in farmyards, urine patches or droppings in the fields and manure spread on the land (Cooke & Williams, 1970; Sheehy, 1988).

The practices used in storage and application of manure to the land also influence export rates. On average virtually all the faeces and urine of sheep and about half those of cattle are voided directly to the land (Cooke, 1976; Gostick, 1982; Royal Society, 1983). Richardson (1976) and Gostick (1982) estimate that about 70% of cattle wastes, 50% of pig, and 90% of poultry wastes are collected and reapplied to the land and that 10–20% of nitrogen in collected slurry may be lost as volatile compounds to the atmosphere. In surveys carried out in Devon and the Cotswolds (Johnes & O'Sullivan, 1989; Johnes, 1990, 1996; Johnes & Heathwaite, 1996) farmers were found to apply all livestock wastes to their own or adjacent land.

In this paper we have assumed (based on surveys of farmers; Johnes, 1990) that 95% of cattle wastes, 85% of pig wastes, 100% of sheep wastes and 90% of

poultry wastes will be applied to the land either directly by the animals or after stock house collection and mechanical reapplication. We have used coefficients of 17% of N and 3% of the P applied to the land for export to streams (Vollenweider, 1968; Cooke, 1976; Gostick, 1982; Johnes & O'Sullivan, 1989). The compounded percentages result in ranges between 14.5 and 17% of N and 2.55 and 3% of P in various animal manures reaching the streams. For upland catchments with more extensive vegetation cover, smaller animals and lower compaction through reduced stocking densities, these coefficients have been halved.

Humans (Table 2) contribute nutrients through excretion and defecation and through their use, from the 1950s onwards, of phosphate-containing detergents. The rate of nutrient loss is determined by body weight, diet, rate of detergent use and type and extent of sewage treatment. In the last 10 years there has been a considerable decline in the use of phosphate detergents as the major manufacturers have marketed both phosphate and non-phosphate formulations. Removal of solids at treatment works reduces export rates by 85–90% with further retention in filter beds. Tertiary treatment involving phosphorus precipitation may remove 90–95% of the remaining P (Jorgensen, 1980; Technical Standard, 1982). Septic tanks behave differently from mains sewerage and export rather lower quantities of P but sometimes greater amounts

**Table 2** Examples of variation in export coefficients (% of input) and rates (kg ha<sup>-1</sup> for land use and rainfall or kg head<sup>-1</sup> for stock and people) in north temperate farming systems. References: 1, Reckhow & Simpson (1980); 2, Beaulac & Reckhow (1982); 3, Kolenbrander (1972); 4, Sonzogni *et al.* (1980); 5, Loehr (1974); 6, OECD (1972); 7, Royal Society (1983); 8, Garwood *et al.* (1980); 9, Batey (1982); 10, Foster, Cripps & Smith-Carrington (1982); 11, Owens (1976); 12, Wilkinson & Greene (1982); 13, Cooke (1976); 14, Heal, Swift & Anderson (1982); 15, Vollenweider (1968); 16, Gostick (1982); 17, Richardson (1976); 18, Omernik (1976); 19, Smith (1976); 20, Stewart, May & Tuckwell (1976); 21, Stewart, Preston & Christofi (1982); 22, Alexander & Stevens (1976); 23, Soderlund, Granat & Rodhe (1988)

Location	Ref.	Nitrogen (kg ha <sup>-1</sup> )	Nitrogen (%)	Phosphorus (kg ha <sup>-1</sup> )	Phosphorus (%)
<b>Arable</b>					
USA	2	2.8–26.9	–	0.68–5.77	–
Netherlands	3	–	–	0.06–0.72	–
USA	4	–	–	0.25–1.25	–
USA	5	–	–	0.06–2.9	–
UK	10	25–70	–	–	–
UK	11	13	–	–	–
UK	12	30–120	–	–	–
UK	13	–	5–50	0.5–5.0	–
<b>Cereals</b>					
USA	2	0.67–72.5	–	0.02–2.1	–
UK	13	–	12	0.06–0.7	–
<b>Grassland</b>					
USA	2	2.41–18.1	–	0.1–0.7	–
USA	2	0.15–9.2	–	0.02–4.9	–
Netherlands	3	–	3–5	0.2–0.3	–
USA	4	–	–	0.05–0.6	–
USA	5	–	–	0.05–0.6	–
Europe	6	4.0	4	0.22	–
UK	7	–	1–5	–	–
UK	9	3–6	–	–	–
UK	11	8	–	–	–
UK	12	12–30	–	–	–
UK	13	–	5	0.2	–
UK	8	–	10–40	–	–
<b>Forest</b>					
USA	1	–	–	0.02–0.4	–
USA	5	1.0–6.3	–	0.01–0.88	–
Europe	6	0–6	–	0.01–0.06	–
UK	14	13	–	–	–
<b>Bare fallow</b>					
USA	5	0.5–6.0	–	0.05–0.25	–
<b>Rough grazing</b>					
UK	7	6.4	–	–	–
UK	10	<10	–	–	–
UK	11	4	–	–	–
UK	12	3–6	–	–	–
<b>Stock</b>					
<b>Export from manure applied to land</b>					
Netherlands	3	–	1–25	–	–
Europe	15	–	17	–	3
Cattle	–	–	7.2–16.2	–	1.3–2.85
Pigs	–	–	7.2–14.5	–	1.3–2.55
Sheep	–	–	8.5–17.0	–	1.5–3.0
Poultry	–	–	7.7–15.3	–	1.35–2.7

Table 2 Cont.

Location	Ref.	Nitrogen (kg ha <sup>-1</sup> )	Nitrogen (%)	Phosphorus (kg ha <sup>-1</sup> )	Phosphorus (%)
Manure voided					
Cattle	15,16,13 11,17,18	44.4–74.8	–	7.65–17.6	–
Pigs	11,17,18	6.6–18.8	–	1.4–5.63	–
Sheep	11,17,18	7.0–10.1	–	1.47–1.8	–
Poultry	11,17,18	0.2–0.9	–	0.1–0.3	–
People	1,11,19,20 21,15,4,6,22	1.86–8.6	–	0.3–3.9	–
Mean		4.0	–	1.18	–
Rainfall input					
USA	1	–	–	0.15–0.5	–
UK	23	24	–	–	–
UK	7	20	–	–	–
UK	11	8.7–19	–	0.2–1.0	–
UK	13	17	–	–	–
UK	12	10	–	–	–

per person of N. Inputs to treatment facilities have been estimated as 3.94 kg N per head and up to 1.16 kg P per head, and average exports to streams, allowing for the widespread use of septic tanks in rural areas, as 2.14 kg N and 0.38 kg P per head except in one catchment where most of the population was served by main sewage treatment works and another where phosphorus stripping is installed.

*Modification and testing of the general procedure to give a robust practicable system for routine operational use*

Many factors thus affect export rates and if all are taken into account, the model can give extremely precise results (predictions within 0.5–2% of observed data; Johnes, 1990, 1996; Johnes & Heathwaite, 1996). The data collection, calculations and calibrations are, however, very time consuming and unsuitable for routine use where a large number of assessments must be made.

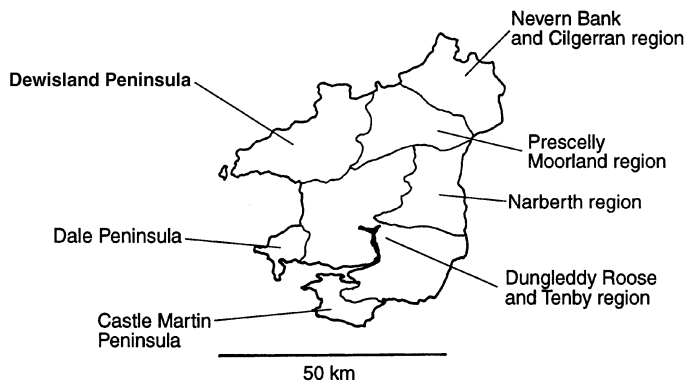
This paper thus tests the accuracy of simplifications of the model which potentially convert it to routine operational use. These use the land use categories of the annual agricultural censuses (permanent grass, temporary grass, cereal crops, root crops, field vegetables, oilseed rape, rough grazing, woodland and orchards, small fruit, and fallow land) but ignore the spatial distribution of these uses within the catchment

and the nuances of different cultivation practices by individual farmers.

Selection of export rates does, however, take into account the average fertilizer application rate for the land use concerned, as published by the Ministry of Agriculture, Fisheries and Food (MAFF) for several years between 1969 and 1985, and the general nature of the terrain (flat, rolling, upland). The nature of stock management (intensive *v* extensive) is taken into account to that extent. Further simplifications include no differentiation between stock breeds other than hill farm breeds and lowland stock and no differentiation between humans served by mains sewerage or septic tank or other systems.

Beyond these assumptions, we test two approaches: first, the predictions made on an individual catchment basis (catchment-specific approach), for which a unique calculation is made for a particular site. The second approach (land use region approach) uses natural regions, for which calculations assume that all bodies of water within the region would be similar in their baseline states. The regions chosen are those delineated by Dudley-Stamp (1941) in a complete survey of British land use made during the 1930s. They recognize natural features of geology and topography, which at the time of the surveys were strongly linked with farming systems. Some examples of land use regions are shown in Fig. 2.

(i) Pembrokeshire



(ii) Somerset

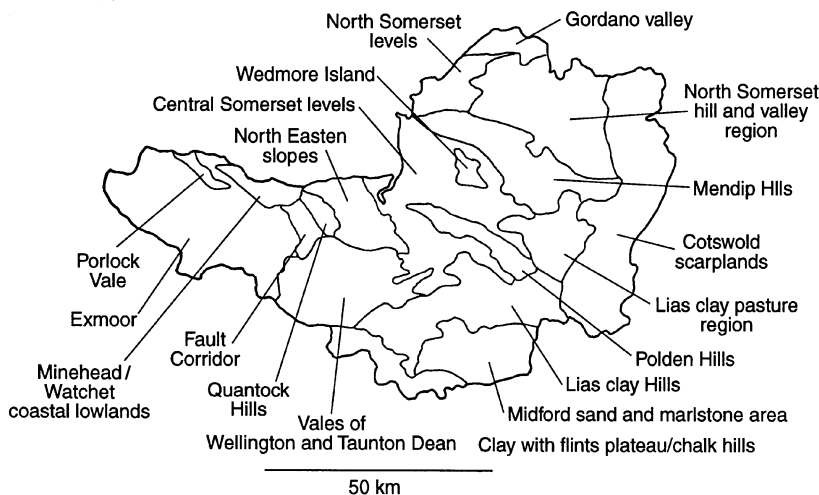


Fig. 2 Examples of Dudley-Stamp's (1941) division of English counties into natural land use regions.

*Choice of catchments and available data*

Ten catchments representative of the range of terrain in Britain were chosen. The sites used are shown in Fig. 3 and their general characteristics in Table 3. The specific choices were determined by the existence of adequate recent sets of data in National River Authority files. In practice no sets that included total N were available, but measurements of nitrate (or total dissolved oxidized nitrogen) had been made and were converted to total N estimates using literature data (Johnes, 1990; Johnes & Burt, 1991). Details are given under individual sites. Total P data were also unavailable for all but one site, though there were adequate sets of soluble reactive (inorganic) phosphorus concentrations. These also were converted to total phosphorus using literature data.

These conversions were inevitable, not only because total N and total P are the better indices of availability

of these nutrients to biological communities within natural waters (see above), but also because the export rates available in the literature are given in terms of total N and total P. The year 1988 was used for calibration because this was the latest year for which the annual agricultural census returns were available in the public domain. Observed data were available for 1985, often for 1980, and sometimes for 1975 and 1970. These years were used for validation of the calibrated model. Hindcasts were made for the pre-war year 1931.

For each of the years concerned, the records of land use were obtained from the Public Record Office at Kew. The land use records are given on a parish basis (though they are collected on a farm by farm basis). The total areas of each land use and the stock headage were recorded for each parish that contained part of the specific catchment concerned and appropriately apportioned to the catchment area. For the land use



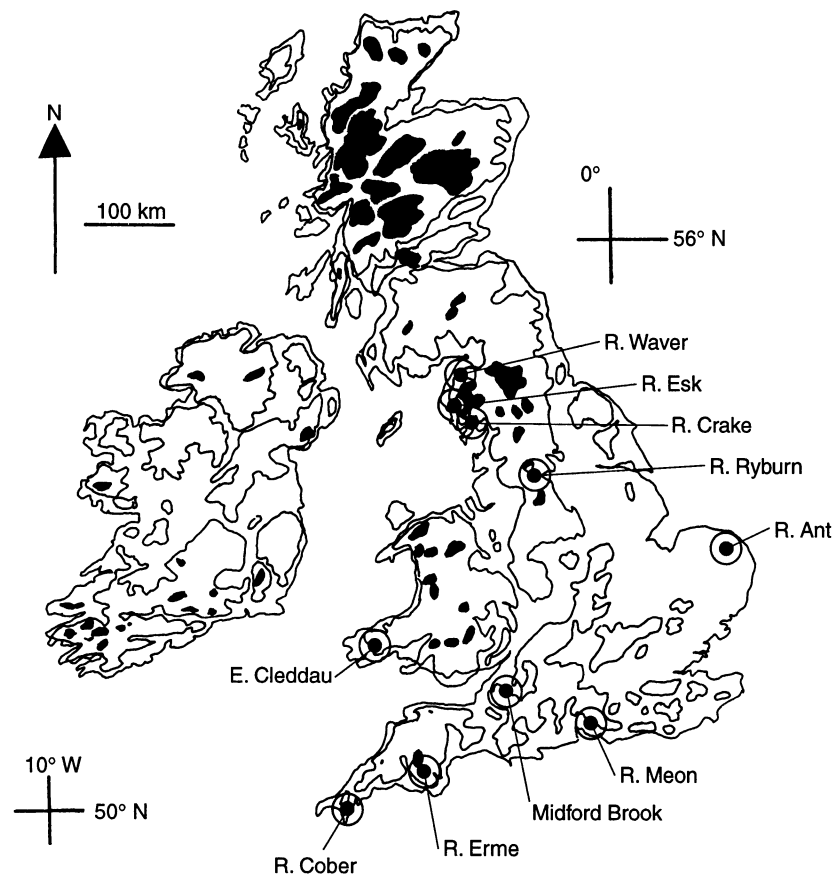


Fig. 3 Locations of the ten catchments discussed. Contours shown are at 100 m and 550 m (dark shaded) above sea level.

Table 3 Characteristics of the sites used in calibrating and validating the exporting coefficient model

Site	Nat. grid ref.	Catchment (ha)	Annual precipitation (mm)	Discharge ( $\text{m}^3 \text{s}^{-1}$ )
River Ryburn, Sowerby Bridge	SE059285	5100	1068	0.549
River Crake, Spark Bridge	SD306849	9400	1962	4.24
River Esk, Cropple How	SD131977	7160	2264	4.06
River Waver, Abbeytown New Bridge	NY184514	10 400	960	1.58
Midford Brook, Midford	ST763611	14 740	879	2.18
River Meon, Mislingford	SU541055	9300	920	1.0
River Erme, Sequer's Bridge	SX641531	10 775	1700	3.0
River Cober, Loe Pool outflow	SW642243	5375	1170	0.972
Eastern Cleddau, Canaston Bridge	SN072153	18 310	1420	5.98
River Ant at Barton Broad	TG362228	4930	660	0.32

region approach, data from all parishes contained within the appropriate natural region of the catchment concerned were recorded. In some cases the catchment covered more than one region.

For the land use region approach, the proportions of land use and stocking densities for the catchment were assumed to be those for the land use region concerned and, where the catchment fell into more

than one region, allowance was made for the proportions of the catchment that fell into each region. Catchment areas were determined by planimetry from suitably scaled maps and stream discharge from National Rivers Authority (NRA) records. Rainfall and actual evapotranspiration data were taken from the long-term averages given by the Meteorological Office (1989). Human population data were also obtained on

**Table 4** Export coefficients (% of input lost to water courses) and rates (kg lost ha<sup>-1</sup> year<sup>-1</sup>) for various land uses, stock types and people used in calculations for ten catchments in England and Wales

Catchment	Meon	Cober Erme (part)	Esk Crake Ryburn Erme (part)	Waver	Midford Cleddau	Ant
<b>Nitrogen</b>						
Permanent grass (%)	5	7.5	1	1	15	1.7
Temporary grass (%)	5	7.5	2	2	15	1.7
Cereals (%)	12	12	10	10	25	4
Root crops (%)	20	25	20	20	25	6.7
Field vegetables (%)	20	25	20	20	25	6.7
Oilseed rape (%)	30	25	20	20	25	6.7
Woodland (kg ha <sup>-1</sup> )	13	13	1	1	13	0.3
Rough grazing (kg ha <sup>-1</sup> )	13	13	1	1	13	0.3
People (kg head <sup>-1</sup> )	2.14	2.14	2.14	2.14	2.14	2.14
Cattle (%)	16.2	16.2	7.2	14.5	16.2	5.4
Pigs (%)	14.5	14.5	7.2	14.5	14.5	4.8
Sheep (%)	17	17	8.5	17	17	5.7
Poultry (%)	15.3	15.3	7.7	15.3	15.3	5.1
Rainfall	25	25	25	25	25	8.3
<b>Phosphorus</b>						
Permanent grass (kg ha <sup>-1</sup> )	0.1	0.4	0.3	0.1	0.8	0.03
Temporary grass (kg ha <sup>-1</sup> )	0.4	0.4	0.3	0.8	0.1	0.3
Cereals (kg ha <sup>-1</sup> )	0.65	0.6	0.6	0.6	0.9	0.22
Root crops (kg ha <sup>-1</sup> )	0.7	0.7	0.7	0.9	0.27	0.8
Field vegetables (kg ha <sup>-1</sup> )	0.65	0.6	0.6	0.6	0.9	0.22
Oilseed rape (kg ha <sup>-1</sup> )	0.65	0.6	0.6	0.6	0.9	0.22
Woodland (kg ha <sup>-1</sup> )	0.02	0.02	0.02	0.02	0.02	0.07
Rough grazing (kg ha <sup>-1</sup> )	0.02	0.02	0.02	0.02	0.02	0.07
People (kg head <sup>-1</sup> )	0.38	0.38	0.38	0.38	1.0	0.38
Cattle (%)	2.9	2.9	1.3	2.6	5.7	0.95
Pigs (%)	2.6	2.6	1.3	2.6	5.1	0.85
Sheep (%)	3	3	1.5	3	6	1
Poultry (%)	2.7	2.7	1.4	2.7	5.4	0.9
Rainfall (%)	25	25	25	25	25	8.3

a parish basis from the closest available 10-yearly census (1981).

For each site the reasons for selection of the rates and coefficients used (Table 4) are explained in the catchment descriptions (below). The choices were often in the upper part of the available (north temperate) range because of the high intensity farming frequent in the U.K. Similar rates and coefficients were used for broadly similar areas. Thus appropriate similar sets were used for the upland catchments of the Ryburn, Crake and Esk and the upland quarter of that of the Erme; for the intensive mixed farming regions of the Midford and Cleddau; and for the less intensive rolling catchments of the Cober and the lowland portion of the Erme.

The data required for the ten catchments included not only land usage, stock headage and human popula-

tions, but also data on the annual inputs (generally fertilizer use, derived from the MAFF annual surveys of fertilizer use, 1969–85) of N and P to each category, and that brought in from rain and nitrogen fixation. Input rates for 1931 are derived from MAFF (1968). For the model it is the export rates that are ultimately used but these are often conventionally expressed in the literature as percentages of the input. Where land is fertilized the input rates, particularly for nitrogen, not only have varied with land use but also with time during the period concerned. Export coefficients (% of input) are thus quoted. Because phosphorus is retained in soils to a much greater extent than nitrogen, export rates are much less dependent on fertilization rates and export rates are expressed as amounts lost per unit area rather than percentages of a varying input. The lower availability of agricultural data for

P as opposed to N also necessitates this more general approach.

#### *Calculation, calibration and validation*

We have not set out the detailed calculations as this would need very extensive tabulation. These details and tables are given in Johnes, Moss & Phillips (1994). For all sites, the initial calibration was made relative to 1988 data. Once this had been done, the rates used were not changed further and calculations for 1970, 1975, 1980 and 1985 represent validation of the model (cf. Kirkby *et al.*, 1987; James, 1993). Calculations for 1931, for which no direct measurements of water chemistry are available, represent extrapolation of the model.

#### **Catchment descriptions**

##### *River Ryburn*

The River Ryburn is an upland river draining Saddleworth Moor on the eastern edge of the Pennines in Yorkshire. It lies in the Pennine Moorland land use region. The human population is small and concentrated in two small towns.

Export rates used are low for the grassland, reflecting low intensity use, and low fertilizer application rates and stocking densities. Coefficients selected for arable uses are comparable with those of the lowlands because the steep slopes and high rainfall will lead to high erosion rates despite lower fertilization levels.

Export rates for livestock are half those used for lowland catchments reflecting the generally lower body weights of upland breeds and the coarse ground cover of upland rough pastures on which such stock feed for part of the year. Such ground tends to retain faeces to a greater extent than slopes of smoother grain.

Data were available only for nitrate-N and soluble inorganic phosphorus for the River Ryburn. These were scaled to total N and total P by taking nitrate as 35% and phosphate as 40% of the totals, respectively. The conversion factor for nitrogen is lower than that used as standard for lowland rivers to reflect the greater proportion of refractory organic nitrogen in the waters draining from peaty moorland soils.

##### *River Crake*

The River Crake drains south out of the English Lake District, running from Yew Tree Tarn and Tarn Hows in the north of the catchment, through Coniston Water to the sampling station near the basin outlet at Spark Bridge. It lies in the Lake District Central Dome land use region. The human population is concentrated in two villages and the catchment is largely upland with steep slopes and extensive livestock farming, although a small amount of more intensive dairy farming occurs in the southern quarter. Nutrient inputs and export rates used were the same as those for the Ryburn catchment.

Measurements of nitrate-N and inorganic dissolved P were converted to total values on the assumptions that nitrate-N was 55% of the total load and dissolved inorganic P 40% of the total P load. The latter value is that used for the River Ryburn, the former is higher and reflects the less peaty nature of the catchment.

##### *River Waver*

The River Waver drains north away from the lowland edge of the English Lake District into the Solway Firth. The catchment lies in the Solway Alluvial Strip and Wigton land use regions. There are no steep slopes and the catchment has a low altitude and is used intensively for livestock production, particularly dairying, with much higher stocking densities than on the adjacent upland lake district. In consequence higher input rates of N and P are found and higher export rates result.

Conversions of the available nitrate-N and soluble inorganic P data assume that the former was 50% of the total N load and the latter 35% of the total P load. These were the standard conversion factors used also for lowland mixed farming regions (see Rivers Meon, Erme and Cober).

##### *River Esk*

The River Esk drains westward from the English Lake District and is a predominantly upland catchment with a small human population scattered among isolated farms and villages. Like the River Crake, it falls in the Lake District Central Dome land use region and nutrient import and export rates are the same as those used for the Rivers Ryburn and Crake. There is

extensive livestock production over most of the catchment, except for the mountain outcrops in the north-east and more intensive livestock farming in the south-west. Data were available only for nitrate-N, which was taken as 35% of the total N load, and soluble inorganic P, 40% of total P, conversion factors similar to those used for the Ryburn catchment.

#### *Midford Brook*

The Midford Brook drains eastwards from the Mendips towards Bath and contains several towns and villages. The catchment has steeply sloping land with intensive arable cultivation and dairy production throughout and lies in the Chalkland and Jurassic Belt and Bath land use regions.

Observed data were confined to nitrate-N and soluble inorganic P which were assumed to comprise 55% of total N and 60% of total P. The N conversion is that used for all western dairying regions (see Crake, Cober, Eastern Cleddau), whilst that for P is higher than that used for other catchments to take account of the high human population density, gathered into urban areas served by main sewage treatment in the catchment. The export coefficient for P used for the human population was also higher than that for other catchments where the populations are served mainly by septic tank systems.

#### *River Meon*

The River Meon runs south-west off the South Downs and discharges into the English Channel. Its upper catchment is of chalk with an undulating topography of steeply sloping dry valleys. The lower part, which contains most of the human population in villages, is flatter. There is widespread cereal cultivation on the uplands and more intensive arable and livestock farming on the lowlands. This combination is similar to that of the Cotswolds, for one of whose rivers, the Windrush, the model has been examined in detail (Johnes, 1990, 1996). The export coefficients and rates developed for the Windrush were thus used for the Meon and appear to be generally applicable to any limestone or chalk catchment in lowland England.

Nitrate-N concentrations, the only available N data, were assumed to be 50% of the total N concentrations and similarly, dissolved inorganic P was taken to be 35% of the total P. These conversions were the standard

rates used for mixed farming regions in England and Wales (see Rivers Crake, Waver, Erme and Cober).

#### *River Erme*

The River Erme flows south from Dartmoor and then through the South Hams region of Devon. The upper quarter of the catchment is of waterlogged moorland lying over moderately steeply sloping land with low-intensity livestock production as in the Ryburn, Crake and Esk catchments. The lower part of the catchment contains most of the human population in scattered farms and villages. The land is steeply sloping in incised tributary valleys with poorly permeable bedrock, and supports intensive beef and dairy production mixed with some low intensity arable.

Different sets of export rates have been used for these very different parts of the catchment. For the upper part the same values as for the Ryburn were used, whilst for the lower part rates developed for the very similar catchment of Slapton Ley (Johnes & Heathwaite, 1996) were used. The catchment lies in two land use regions, the Dartmoor and the South Devon regions, and these were proportioned in the land use regions approach to the calculations.

Nitrate-N and dissolved inorganic P data were available and the conversion factors used were 50% for total N and 40% for total P. These rates were derived from measurements made in the Slapton catchment (Johnes & Heathwaite, 1996) and were used also for other lowland streams (see Rivers Crake, Waver, Meon and Cober).

#### *River Cober*

The River Cober flows south across Cornwall, through undulating land deeply incised by river valleys, into Loe Pool, a small coastal freshwater lake. The catchment lies in the Carnmellis and Western Coastlands land use regions of Dudley-Stamp (1941). Most of the human population is in the small town of Helston, and the farming is of mixed arable and dairy systems similar to those of the Slapton catchment and the lower part of the Erme catchment. The same export rates as for these catchments have thus been used.

Conversion of the available nitrate-N and soluble inorganic P data to total N and total P used factors of 55% and 40%, respectively, comparable with those used for the River Erme and other mixed farming

areas but slightly increased because of the greater point sources from the sewage treatment works serving Helston in this catchment.

#### *Eastern Cleddau*

The Eastern Cleddau flows south from the Preseli upland of northern Pembrokeshire. The land is moderately sloping and mostly used for intensive arable and dairy production. It lies in the Preseli Moorland and Narberth land use regions. Export rates used were similar to those of the agriculturally comparable Midford Brook catchment. No phosphate measurements are available for this river but nitrate-N concentrations have been taken to be 50% of total N in line with the value used for other intensive dairying catchments (see Waver and Midford Brook).

#### *River Ant*

The River Ant flows southwards through Norfolk, eventually to join the River Bure, having passed through Barton Broad. The human population is largely in one small town, North Walsham, plus a few small villages. The catchment is flat (Coward, 1926) and used largely for arable production. Livestock production is limited to the few remaining areas of undrained grazing marshes and is not intensive. The catchment lies in the Broadland land use region.

Because of the low annual precipitation and run-off and the flatness of the land, transport of nutrients to the river from diffuse sources is likely to be more limited than in areas with even moderate relief. Also the low river gradients allow rapid sedimentation of particulate nutrients once delivered to the river. Lower export rates have thus been used in this catchment than in others. A further complication is that sewage effluent from North Walsham was diverted direct to the sea in the early 1980s thus reducing the effective population from the point of view of the model. Official data, however, are very imprecise about the numbers of people whose sewage was so diverted.

Total P data were directly available and the available nitrate-N data were assumed to be 55% of total N in line with the standard conversions used for other lowland regions (see Crake, Waver, Midford Brook and Cober).

## Results

### *Model calculations compared with observed values*

Observed concentrations and, following calibration and validation, concentrations of total N and total P calculated on both catchment and regional bases for the group of ten rivers are shown in Fig. 4 and have been compared by regression. The equations for the catchment-based calculations were:

$$\text{observed total N (mg l}^{-1}\text{)} = 0.97 \text{ calculated total N (mg l}^{-1}\text{)} - 0.04 \quad (r^2 = 0.958, n = 33)$$

$$\text{observed total P (mg l}^{-1}\text{)} = 1.04 \text{ calculated total P (mg l}^{-1}\text{)} - 0.026 \quad (r^2 = 0.912, P < 0.0001, n = 30)$$

The fit of calculated and observed values of total P for the River Ant was much poorer than for the other nine rivers, for reasons discussed below concerning the quality of the human population data. When this clearly anomalous case is excluded, the regression becomes:

$$\text{observed total P (mg l}^{-1}\text{)} = 1.06 \text{ calculated total P (mg l}^{-1}\text{)} - 0.01 \quad (r^2 = 0.986, P < 0.0001, n = 27)$$

For the land region based calculations the relationships were:

$$\text{observed total N (mg l}^{-1}\text{)} = 0.92 \text{ calculated N (mg l}^{-1}\text{)} + 0.28 \quad (r^2 = 0.950, P < 0.0001, n = 33)$$

$$\text{observed total P (mg l}^{-1}\text{)} = 1.06 \text{ calculated total P (mg l}^{-1}\text{)} - 0.02 \quad (r^2 = 0.864, P < 0.0001, n = 30) \text{ (with River Ant)}$$

$$\text{observed total P (mg l}^{-1}\text{)} = 1.05 \text{ calculated total P (mg l}^{-1}\text{)} - 0.03 \quad (r^2 = 0.968, P < 0.0001, n = 27) \text{ (without River Ant)}$$

Consequently the relationships between catchment-based and land region-based calculations were also very close:

$$\text{calculated total N export rate (catchment, kg (ha a)}^{-1}\text{)} = 1.01 \text{ calculated total N export rate (regional, kg (ha a)}^{-1}\text{)} + 0.67 \quad (r^2 = 0.942, P < 0.0001, n = 60)$$

$$\text{calculated total P export rate (catchment, kg (ha a)}^{-1}\text{)} = 1.04 \text{ calculated total P export rate (regional, kg (ha a)}^{-1}\text{)} - 0.03 \quad (r^2 = 0.981, P < 0.0001, n = 60)$$

### *Changes in land use and nutrient budgets between 1931 and 1988*

Table 5 shows the relative changes in land use in 1998 compared with 1931 and Fig. 5 shows the total nutrient

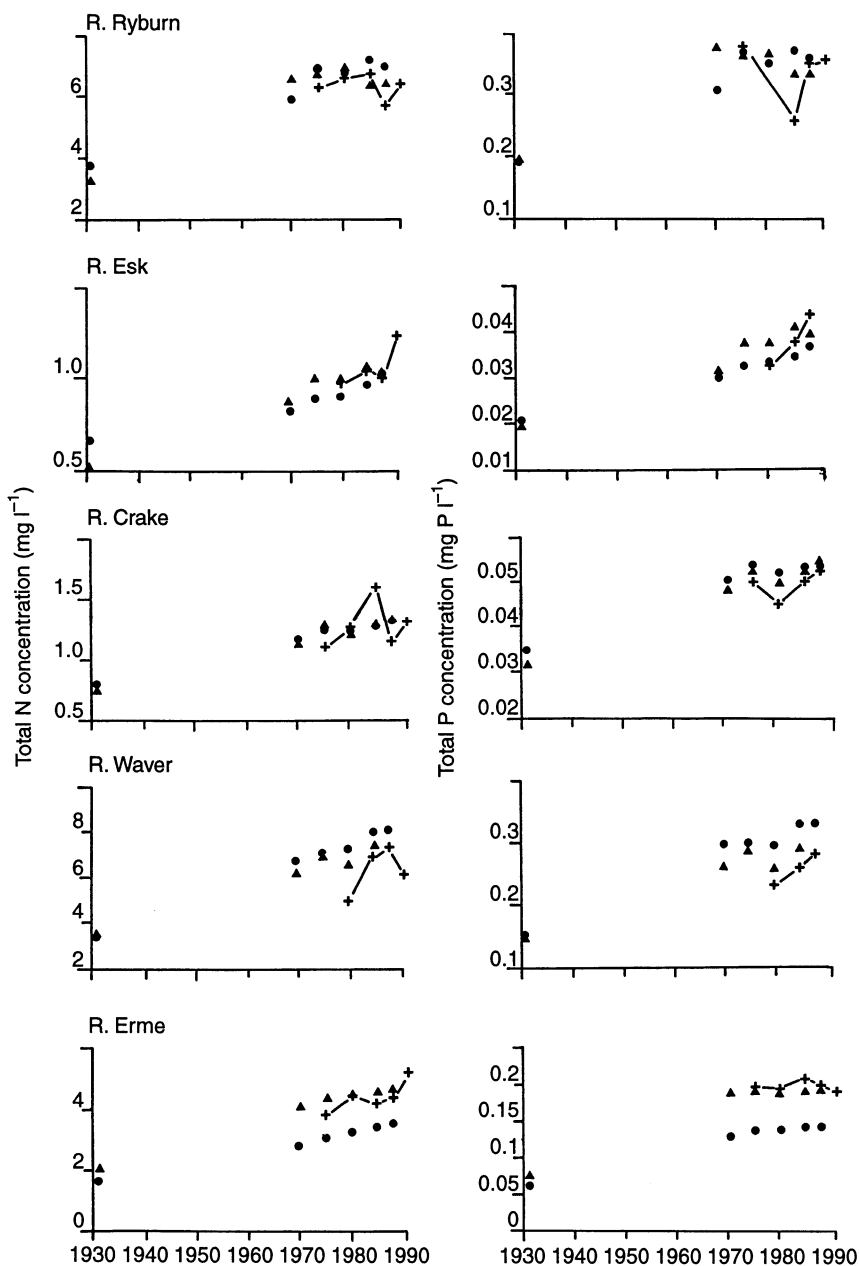


Fig. 4 Comparison among observed values for total P and total N (crosses and solid line) and those calculated by the specific catchment approach (triangular symbols) and the land use regions approach (circular symbols) for ten English catchments.

export rates and the proportions of the total nutrient loads attributable to the various sources for 1931, 1970 and 1988.

There are several general trends. First, there has been a loss of rough grazing and increases in cereal growing. The pattern of change has been complex within the categories of temporary and permanent grassland, as rough grazing has been converted to permanent grassland, permanent grassland to temporary grassland and both grassland types to cereals.

Cattle numbers have increased uniformly as, in general, have those of sheep. Pig numbers have declined in some catchments but increased greatly in others, whilst declines in poultry in most catchments are balanced by much greater increases in three catchments.

The trends in both land use and stock reflect the intensification and specialization in farming that has taken place since World War II under the influences of the Agriculture Act (1947) and the European Common Agriculture Policy. The trends are reflected particularly

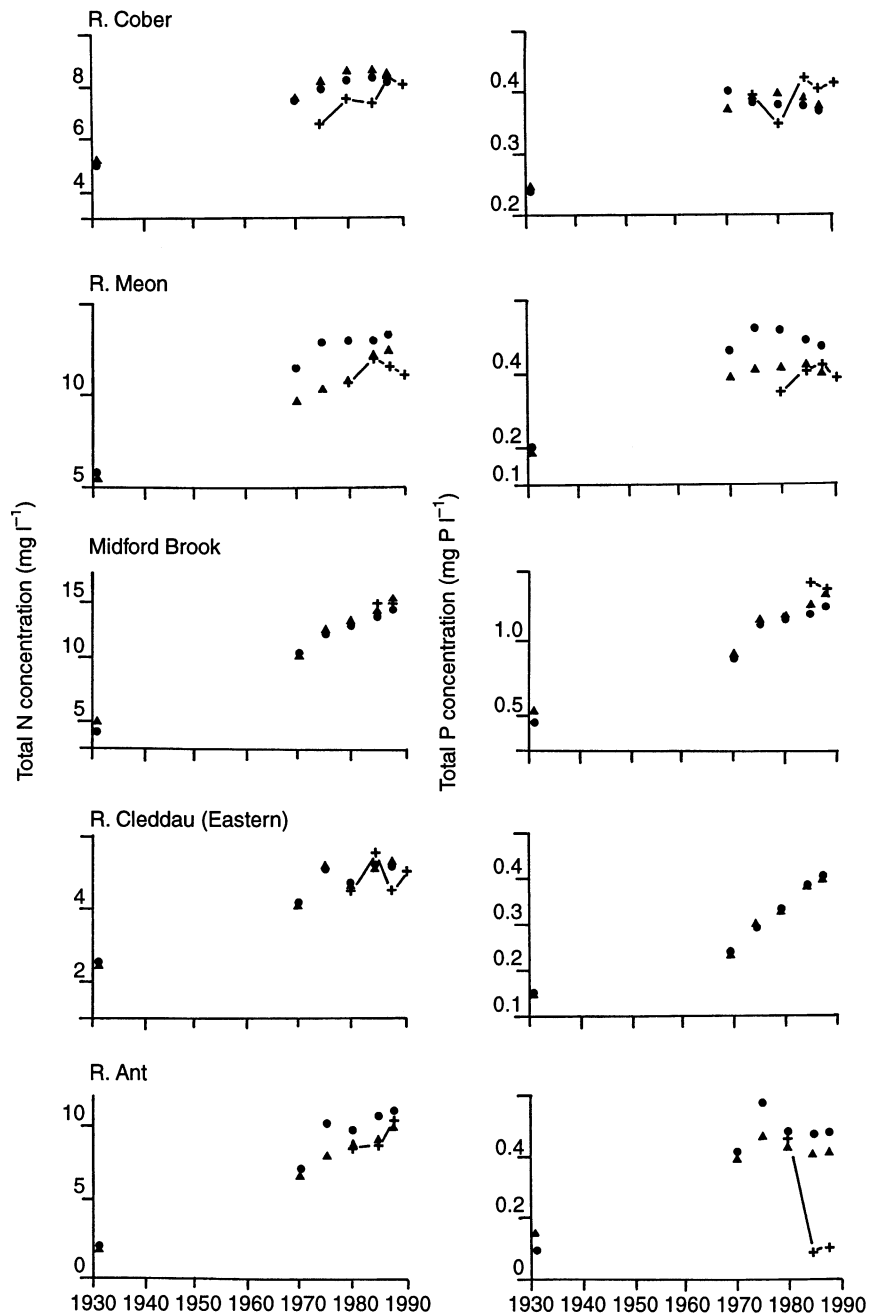


Fig. 4 Continued

in the increase in overall total N export, which has increased on average by a factor of 2.2, with the 1931 range of 4.36–25.1 kg (ha a)<sup>-1</sup> being succeeded by a range of 17.0–72.7 in 1988.

The human populations in these catchments have also increased markedly between 1931 and 1988, usually by over 10-fold. This reflects the drift of population from inner city centres to suburban estates and rural villages since the Second World War. With the increases in stock headage this is reflected in an increase by a

factor of 2.17 in P export rates, with the pre-war range of 0.35–2.02 kg (ha a)<sup>-1</sup> being replaced by a post war range of 0.71–6.35.

The parallel increases in both N and P loading have led to no change in N : P ratio on average, with a ratio by weight of 20.9 (47 by atoms) in 1931 and 22.1 (49.8 by atoms) in 1988. This would suggest that P was and remains very strongly the limiting nutrient to algal growth in standing water bodies served by rivers draining these catchments.

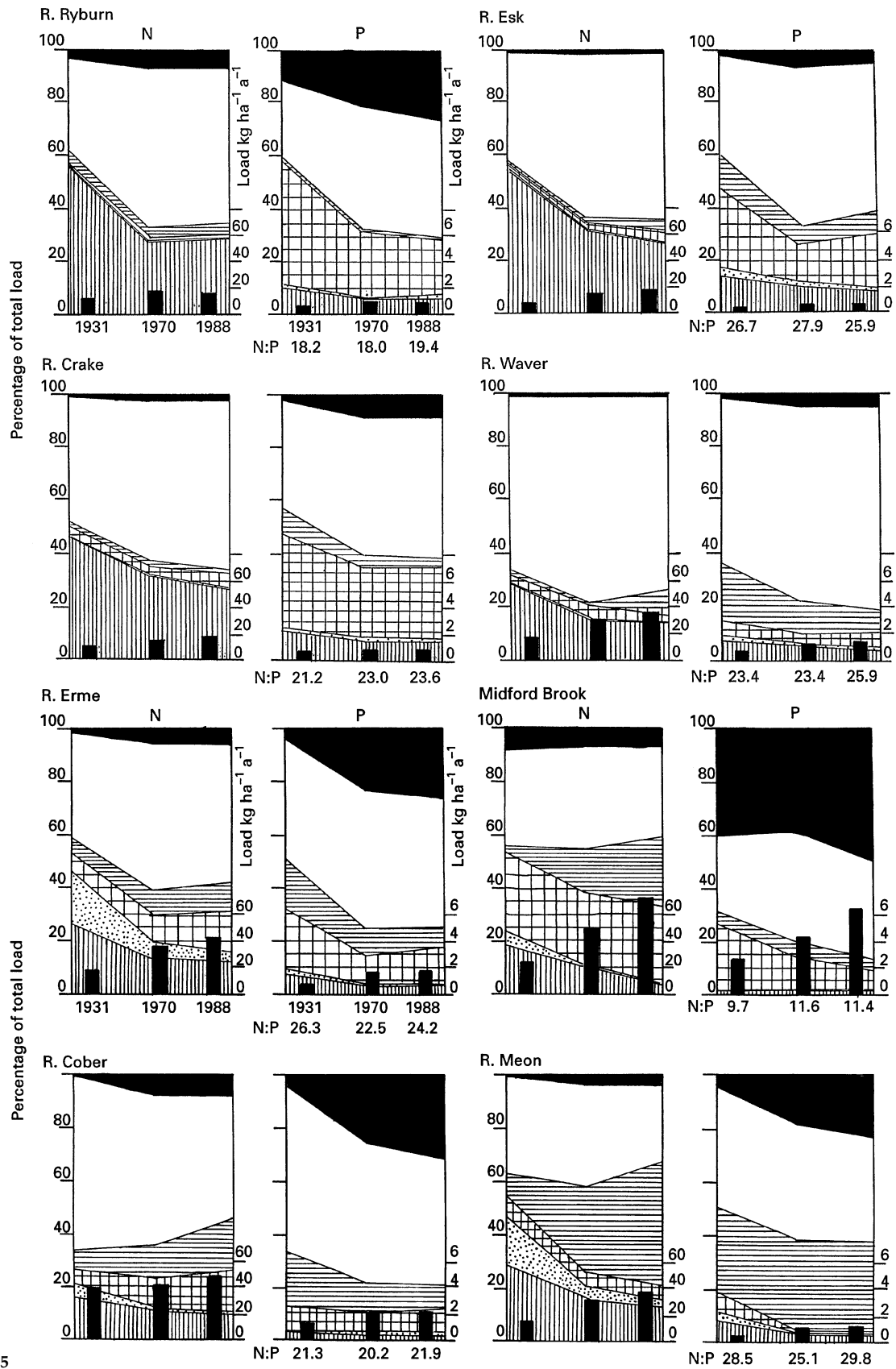


Figure 5



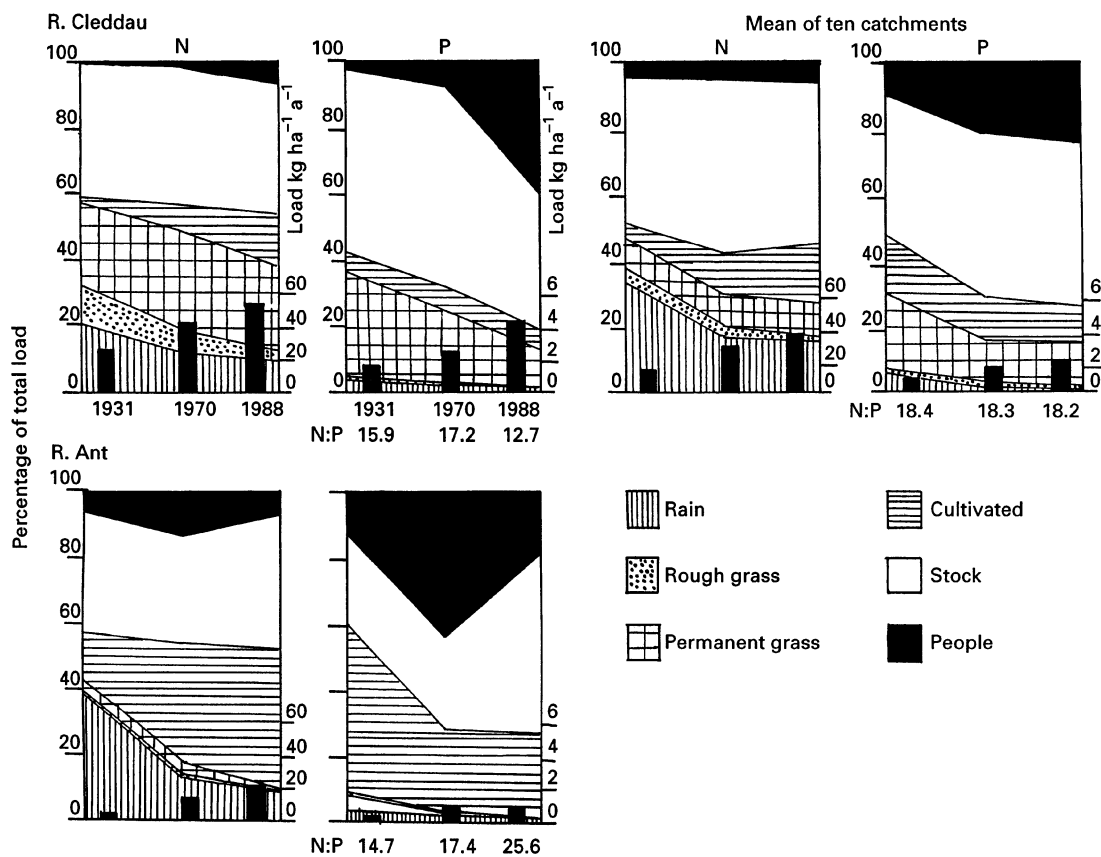
**Discussion**

*Overall success of the model*

No model is better than the data used for its construction, calibration and validation. For this model there are three sources of data: those obtained from the databases on land use, stock headage, population, fertilizer use and meteorology; the observed data necessary for calibration and validation; and those on export coefficients and rates coupled with the judgement necessary in their use. Any individual element in each of these could potentially be in error but the model is made up of so many elements, albeit a small fraction of the total number that could be incorporated, that it has a considerable robustness which potentially makes it particularly suitable as a practicable tool usable on a wide scale.

Some limitations of the data will be discussed below but because the value of a model lies in the validation stage, it can first be said that this is a very successful model in determining both total N and total P concentrations in freshwater streams and rivers draining catchments in England and Wales. The correlations between concentrations calculated, on both specific catchment and natural region bases, with observed concentrations are very high, with well over 95% of the variance in observed concentrations explained by the model. The results from catchment and regional calculations are also extremely close.

Comparisons were made between the recorded areas for the main land uses in the ten catchments, and those calculated on the assumption that a particular catchment faithfully reflected the average land use for its region. These showed that the land use region basis slightly underestimated the actual



**Fig. 5** Changes in the proportions of the N and P loads attributable to different sources in ten catchments in 1931, 1970 and 1988. Values (except for annual loads and N:P ratios) are in percentages of the total annual load. 'Rough grazing' encompasses fallow land and semi-natural habitats such as woodlands but also includes orchards which are not separated from woodlands in the records. 'Cultivated' includes temporary grassland, cereals, root crops, oilseed rape, field vegetables and soft fruit. Annual loads are shown as histograms at the bottoms of the panels.

**Table 5** Changes between 1931 and 1988 in land use, stock headage and human population for ten British river catchments. Change in land use is given as the difference in hectare used for each land use between 1988 and 1931 divided by the total hectare of the catchment and expressed as a percentage. Change in stock and human populations is expressed as the difference between numbers per ha in 1988 and numbers per ha in 1931 divided by numbers per ha in 1931 and expressed as a percentage. Means and standard deviations for the group of catchments are also shown

	Ryburn	Crake	Esk	Waver	Midford	Meon	Erme	Cober	Cleddau	Ant	Mean	SD
Perm. grass	4.4	17	15	13	-21	-18	21	22	0.43	-11	4.4	16
Temp. grass	3.5	0.18	8.0	0.14	12	2.4	-1.0	-16	11	-13	0.68	9.3
Cereals	0.27	-0.84	-1.4	-0.33	15	29	7.7	-4.2	2.3	0.65	4.9	10
Root crops	-0.03	-1.2	-1.5	-4.6	-2.6	-3.8	-2.7	1.6	-0.77	8.95	-0.66	3.8
Field veg.	-0.03	-0.01	-0.14	0.01	0.05	2.3	-3.2	2.2	0.2	14.9	1.6	4.9
Oilseed rape	0	-0.02	-0.14	0.41	0.78	3.8	0	-0.1	-0.54	0.51	0.47	1.22
Rough grazing	-6.3	-16	-17	-6.0	-1.1	-8.9	-17	-4.7	-13	-2.4	-9.2	6
Woods, orchards	-1.8	0.68	-3.2	-3.1	-3.2	-5.1	-4.8	-2.9	0.36	0.45	-2.3	2.2
Small fruit	0	-0.01	0	0	0.013	-0.32	-0.04	0	0.005	0.41	0.006	0.17
Fallow	0.02	0.47	0	0.048	-0.15	-1.5	-0.14	2.1	-0.02	0.16	0.1	0.86
Cattle	240	130	200	170	120	57	190	42	120	150	140	62
Pigs	-60	43	1800	-8	680	280	-50	85	90	1080	360	640
Sheep	inf	170	208	76	438	25	290	-10	96	0.3	144	149
Poultry	-58	-72	-96	-77	435	264	-66	-58	-77	346	54	207
People	310	980	400	1200	210	920	1300	1200	4200	507	1123	1153

usage in these catchments but that 89% of the variance in actual use was explained by the regional calculations:

hectarage (land use region calculation) = 0.833 hectarage (actual) + 280 ( $r^2 = 0.886$ ,  $P < 0.0001$ ,  $n = 72$ )

A similar comparison for stock numbers gave:

headage (land use region calculation) = 0.944 headage (actual) + 1572 ( $r^2 = 0.813$ ,  $P < 0.0001$ ,  $n = 72$ )

The ultimate comparison between concentrations, or overall export rates, obtained by the two methods showed even more of the variance explained. Total N export was underestimated by about 1% and total P underestimated by 3.7% by the land regions approach. This suggests that the less labour-intensive regional basis loses little in predictive ability compared with the labour-intensive 'gold standard' of calculations done on individual catchment bases for every water body studied. This makes the possibility of calculation of a set of overall export rates for each of perhaps one to two hundred land use regions in the British Isles eminently feasible.

#### *Quality of the data*

The quality of the data on which the model is based is clearly crucial. The land use and stock headage data are drawn from the annual agricultural censuses. These are obtained on a farm by farm basis by the MAFF and rely on accurate reporting by farmers. The latter may not always individually be strictly accurate but overall, because of the completeness of the sample, the picture is likely to be a very accurate one. The data are held in the Public Record Office on a parish basis and in examining the record over a historic period there may be difficulties caused by changes made to parish boundaries. These are usually small, however, and, in view of the results obtained here through the natural regions approach, unlikely to result in much additional error. The meteorological data used to determine rainfall are also highly reliable.

#### *Determination of export rates and coefficients*

The greatest difficulties come in the selection of appropriate export coefficients and rates, for although the literature contains a sufficient coverage of these to guide the use of the relevant range (see Table 2),

judgement and experience are necessary for selection of appropriate values if the process of calibration and validation is not to be prolonged into several iterations. However, in the ten catchments used here, despite their variety, we were conservative in our choice of values and kept them fixed for similar land use types in broadly similar topographies. Thus all the upland areas were allocated similar values, and the rates and coefficients already used in calibrating previous models of nutrient export in the River Windrush (Johnes, 1990) and the Slapton catchment in South Devon (Johnes & O'Sullivan, 1989) were used for the broadly similar Meon and the Cober and lower part of the Erme catchments, respectively. A greater degree of parsimony in choice of values may be possible than we originally anticipated for the acknowledged variety of British land surfaces.

Only one catchment has presented real problems in choosing coefficients and rates—the very flat catchment of the River Ant in Norfolk where values lower than elsewhere had to be used. The model was successfully run for N but with export rates lower than those noted in the existing literature. Studies elsewhere on nutrient export have concentrated on rolling or hilly land. There has been much less attention to the very low discharge eastern rivers in this respect.

Limnological studies in these rivers (Moss *et al.*, 1984, 1988) suggest that considerable denitrification may occur as water moves slowly into the side streams, through reed beds and over sediments frequently with low redox values at their surfaces. Although as much or more N may be applied to particular land uses as elsewhere, the rates of nitrate leaching may be much lower in the flatter and drier eastern regions than in the wet and steeply sloping areas of the west. The effects of denitrification in passage of drainage water to the river thus may result in considerably lower apparent export rates.

P moves into rivers in both particulate and dissolved forms and both contribute to the total P load. In slow-flowing, flat systems, loss to the sediments of particulate P derived from the land may also effectively reduce the export rates of P, necessitating the use of lower than usual values in calibration of the model for the River Ant. When these were applied the model worked poorly for 1985 and 1988. The latter was the calibration year but very poor correspondence between calculated values, derived from export rates that remained within literature ranges, and the

observed values was obtained. With use of these rates there was a good fit to observed data obtained in 1980.

After 1980 there was a marked fall in observed concentrations in the River Ant because the entire load of sewage effluent of a small town, North Walsham, in the catchment, was diverted away from the river and direct to the sea coast. Sewage effluent had been a major contributor to the P load delivered to the river and the calibration of the model was very sensitive to the number used for the human population in the catchment. There is frequently considerable uncertainty as to how many people are served by a particular sewage treatment works because many older works, such as that at North Walsham, have come to serve much larger populations than their design capacity, with consequent reduction in treatment efficiency. The latter number, however, is that contained in the records of the water company and supplied to us. If we have thus used a much larger number of people in the model post-1980 than were in fact discharging P to the river, the overtly high values of our calculations are explained.

This problem does not occur in the N calculations because a much smaller proportion of the N load to the Broadland rivers comes from effluent compared with agricultural sources. In a study of the River Bure, to which the Ant discharges, effluent accounted for 75% of the P and 10% of the N whilst all other (predominantly agricultural) sources accounted for 25% of P and 90% of N (Moss *et al.*, 1988).

In calculating export rates from particular land uses, there are two components: the input rate, essentially the amount of fertilizer put on the land, and the percentage of this lost by leaching. Input rates are now annually recorded on a regional basis by the MAFF and the fertilizer industry (Fertilizer Manufacturer's Annual Statistics) so as to monitor usage and predict future trends and demand. The quality of the data post about 1969 is thus good. For earlier periods such detailed information is not available though the general information available (MAFF, 1968) is sufficient to allow the use of the model for determination of past water quality. In this it is helped by the fact that before the 1940s fertilization levels were far lower than they have been in the post-World War II period. Thus the absolute error generated in using input rates in the model for this early period, which take less account of geographical variation than they can for recent years, is relatively small.

#### *Conversion factors for observed data*

An unexpected problem was in the availability of observed water quality records. We used those of the National Rivers Authority and found that although data on nitrate were widely available for recent years, there were no data for total N. Similarly total P data were lacking for all but the River Ant and even soluble reactive phosphorus data were not available for the Eastern Cleddau. In view of the concern that has prevailed since the 1960s about water quality and eutrophication in both mainland Europe and North America, this must suggest that a revision of the monitoring determinants in British rivers is needed.

For the present purposes we were forced to convert the available data on only one species of N or P compound to total values. For N, based on a very comprehensive data set obtained from the River Windrush and Slapton Ley (2100 samples), we used a standard conversion for all but a very peaty catchment where we allowed for a greater proportion of organic N compounds. For P, we used a conservative range which allowed for the greater contribution of sewage effluent (and hence a greater proportion of inorganic soluble phosphate) in well-populated catchments. There are thus certainly errors in the actual values of total P and total N against which we calibrated the model.

For the purposes of using this model these errors are immaterial, for the crucial test is not calibration—it is possible by adjusting the export rates and coefficients to calibrate to almost any value for the calibration year—but the validation step. Validation for these catchments was very successful and comparison of the relative changes in nutrient load and concentrations over time will be unaffected by the nitrate and phosphate conversion factors used. However, it would clearly be desirable to have improved absolute values through availability of directly measured total N and total P data.

There are too few studies relating nitrate to total N under a variety of circumstances to be able to estimate the error in absolute observed concentrations attributable to lack of total N data. For total P, however, more data are available. Series of contemporary mean annual soluble reactive P and total P values are available from small streams in Norfolk (B. Moss, unpublished) and in the West Midlands (Moss *et al.*, 1992). From available data on thirty-eight streams, a regression was

carried out relating soluble reactive P as a percentage of total P to mean annual soluble reactive P concentration:

$$\text{SRP (\% of total P)} = 25.01 \log \text{SRP } (\mu\text{g l}^{-1}) - 0.9$$

( $r^2 = 0.5$ ,  $P < 0.0001$ )

The values of total P used in calibration of the model (and derived from a conservative set of conversion factors) have been compared with those that would have been obtained through use of the regression. This resulted in a relationship between the values used in calibration and those that would have been derived from the regression above as follows:

$$\text{total P (calibration, } \mu\text{g l}^{-1}\text{)} = 1.19 \text{ total P (equation, } \mu\text{g l}^{-1}\text{)} + 40$$

( $r^2 = 0.965$ ,  $P < 0.0001$ ,  $n = 26$ )

The factors we used were appropriate in most cases but relatively low in some of the rivers that were relatively rich in P, so that the observed values for total P in these were probably overestimated. The regression itself, however, does not include data from upland catchments like those of the Crake, Esk and Ryburn.

#### *Trends over the period from 1931 to 1988*

Figure 5 shows the proportions contributed by different sources to the total loads of N and P in the catchments studied. It is striking that the contribution of livestock continues to be the dominant source of both N and P, with increasing secondary contributions of N from cultivated land and P from people. There is a general assumption that most N is contributed from arable agriculture and P from the human population and some detailed budgets (e.g. Moss *et al.*, 1988) do show this.

The ten catchments studied here were effectively randomly determined for selection depended on availability of observed water quality data subject to a requirement to cover a range from the uplands to the lowlands. They are thus probably representative of their general type—small rural catchments, from which the water supplies to many standing waters are derived. They are not representative of the larger rivers to which sewage effluent is exported from large cities and for which human-derived P supplies are almost certainly predominant and from which the major loads to coastal waters are derived.

The recent European Directive on Urban Waste Water Treatment will enforce P control at some large

sewage treatment works (> 10 000 person equivalents) but not at small ones. Because of the comparatively small number of works that will be improved even in the larger group (Carvalho & Moss, 1995), there will be only a modest decrease in loads to the sea and very little effect in the rural areas. Some standing waters that would benefit from phosphate removal from effluent will therefore not do so, but one major conclusion of the present survey of ten catchments is that control of nutrient export from livestock wastes is also urgently required if eutrophication problems in Britain are to be solved.

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