The prediction of peak nitrate concentration from annual nitrate load at the field and catchment scales

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Abstract An approach to predict peak nitrate concentrations in rivers draining agricultural catchments is described. Regression relationships were derived from field-drainage experiments on different soils, relating peak nitrate concentration in drainage to annual nitrate load. Regression coefficients ranged from about 1.3 for a sandy soil over limestone to 0.25 for a structured clay with mole drainage. A 1.0 coefficient means that 100 kg N ha⁻¹ yields a maximum concentration of 100 mg NO₃-N l⁻¹. This range reflects variability in soil-water capacity and degree of preferential flow through the soil. Similar relationships were derived from river data in England and Wales. Regression coefficients derived from river data were smaller than those of field data. This nitrate dilution was larger in western catchments and was assumed the effect of runoff from farmed uplands, denitrification, and baseflow contributions. Such factors should be included if soil regression relationships are used for a catchment-scale nitrate-leaching model.

INTRODUCTION

The European Communities (EC) Nitrate Directive (Commission of the European Communities, 1989) requires that the concentration of nitrate N in surface waters used for domestic supplies should be below 11.3 mg l⁻¹. In the UK, nitrate concentrations in rivers have been rising for a number of years (National Rivers Authority, 1992), with peak concentrations in several of them exceeding this limit. A major objective of the environmental policies of national governments within the EC is the optimization of land use and farming intensity to enable compliance with the Directive. A second feature of

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the Directive is the setting up of designated areas where water resources are particularly vulnerable to nitrate pollution. In these nitrate sensitive areas (NSAs), a detailed programme of monitoring land use, fertilizer application rates, and nitrate concentrations of rivers and groundwater has been initiated.

The planning for changes in land use and management that might be required to enable compliance with the Nitrate Directive will involve the use of models that are able to predict nitrate concentrations in waters draining agricultural land at the catchment and regional scales. A number of catchment nitrate leaching models already exist (e.g. Cooper *et al.*, 1992), but these are very complex and require detailed input parameters that often do not exist at the spatial resolution required. For management purposes models are required that operate at the level of complexity commensurate with the availability of the input data and the level of expertise of the intended user.

Much of the data from UK nitrate-leaching experiments have been in the form of a load, expressed in kg N ha⁻¹ year⁻¹ because it has been conceptually convenient to consider leaching as part of an annual budget for an agricultural system. However, the value of annual nitrate load is generally derived by integration of the plot of concentration and drainage volume so that with long-term experiments the opportunity exists to derive relationships between peak concentration and nitrate load. Therefore, if an existing model could be used to calculate the annual nitrate load, then such relationships could be applied to derive a model output in terms of concentration.

Support for this empirical approach has been provided by the results of some recent field drainage experiments (Scholefield *et al.*, 1993), where it was found that peak nitrate concentrations in the drainage water could be accurately predicted from the total nitrate load leached from the soil. In the present paper, the results from further field scale leaching experiments are presented in order to examine the possibility of extending

Location	Soil type	Agriculture	а	b	r^2	n
Ogbourne St George	Sandy loam over limestone	Arable	0.0	1.37	0.86	70
Bourne Brook	Loamy sand	Arable	3.0	0.92	0.93	48
Bourne Brook	Loamy sand	Grass	6.6	0.9	0.88	41
Bourne Brook	Loamy sand	Arable	10.0	0.7	0.89	16
Hurley,Bristol, Jealotts Hill	Loamy sand	Grass	-1.4	0.99	0.90	19
	Loam	Grass	3.5	0.62		
North Wyke	clay/clay loam good drainage	Grass	5.6	0.25	0.91	24
North Wyke	clay/clay loam poor drainage	Grass	3.8	0.4	0.84	24
Brimstone Farm	clay, good drainage	Arable	28	0.89		8
Brimstone Farm	clay loam over chalk	Arable/grass	6.8	0.34	0.91	13

Table 1 Regressions of peak concentration in leachate on annual nitrate load in the soil for different soil/crop combinations. Peak (mg N l^{-1}) = $a + b \times load$ (kg N ha^{-1}).

the relationships to a variety of different soil and crop conditions. The same empirical approach is employed at the catchment scale to predict nitrate concentrations in rivers draining land with particular soil-crop combinations.

FIELD-SCALE EXPERIMENTS

Well-fitted linear relationships between annual nitrate load in the soil and the peak concentration in the drainage were first found by Scholefield *et al.* (1993) for drained and undrained clay loam soils (non-calcareous pelosols) of the Hallsworth series, under grassland in experimental plots at North Wyke, Devon, UK. Similar relationships derived from additional data sets are now presented for a range of soil-crop combinations (Table 1) at other sites within the UK (Fig. 1), including well-drained sandy loam soils under grassland management at Jealotts Hill (Barraclough *et al.*, 1983), Hurley, and Bristol (Rodda, 1993), and from more limited data for a cracking clay under arable management at Brimstone Farm (Cannell *et al.*, 1984). At all sites except Ogbourne St George, water for the determination of nitrate concentration was sampled either from field drains or from ceramic cups at depths of 85-90 cm. At this site the soil was shallow and consequently the samplers were placed at depths of less than 30 cm.

CATCHMENT-SCALE EXPERIMENTS





Fig. 1 Locations of nitrate leaching experiments (italics) and Water Authority Areas.

concentrations in rivers was assessed by deriving similar linear regressions from independent data for rivers. These were selected from a national data base comprising measurements of nitrate concentration and discharge for more than 800 rural catchments obtained during the period 1974-1987 (Betton, 1990). Rivers were selected on the criteria that the average annual concentration of nitrate N was greater than 2 mg l^{-1} , and that there were sufficient data to provide accurate estimations of the N load. This was calculated on an annual basis using an interpolation technique employed in the Harmonized Monitoring Scheme (Simpson, 1978):

$$L = K \sum_{i=1}^{n} \frac{C_i Q_i}{n} \tag{1}$$

where Q_i and C_i are the instantaneous measurements of river discharge (m³ s⁻¹) and nitrate N concentration (mg l⁻¹), respectively, K is the time factor (i.e. number of seconds in a year), and n is the number of measurements. This technique has been widely used for the calculation of contaminant, nutrient, and suspended-sediment loads (Walling *et al.*, 1992). At least one measurement per month was required to generate a sufficient level of accuracy in the load calculation. Rodda (1993) has shown that with 12 instantaneous measurements per year, this equation estimated load to an accuracy of 5.6% at the 95% confidence level.

Data were discarded from years that did not show typical patterns of nitrate concentration over time or contained very sharp peaks in concentration, which were assumed due to point sources or leaching of spring-applied fertilizer. The typical annual pattern of river Nitrate N concentration is shown in Fig. 2, where the peak concentration was reached approximately one month after the soil was returned to field capacity.

A further selection criterion was the amount of drainage required to leach the load of nitrate from the different soils. The results from the field experiments indicated that for light sandy soils at least 150 mm of drainage is required, whereas in clay and clay loam soils around 300 mm of drainage is necessary to leach at least 70% of the load.



Fig. 2 Typical annual pattern of nitrate concentration for a small river draining an agricultural catchment (Thames Water Authority area).

Drainage volumes, taken as hydrologically effective rainfall (HER), were obtained from the MORECS square archive (Thompson *et al.*, 1981) for the appropriate 40-km square grid for each of the years of record. A total of 196 catchment-years were used from 46 rivers. The catchments were grouped according to the old Regional Water Authority Areas (Fig. 1). This was because the original data base was already grouped accordingly, but also because it associated catchments with generally similar geology, climate, soils, and agriculture.

RESULTS AND DISCUSSION

Field-plot scale regressions

The regressions (Fig. 3; Table 1) show that a steeper slope is associated with lower clay content of the soil. This may be explained by the combined effects of two soil characteristics that change with clay content. One is the water-filled pore space at field capacity, which determines the concentration/load relationship at the onset of drainage. The second is the degree of preferential flow during drainage, which determines the degree of displacement of antecedent water containing the dissolved nitrate by "new" water flowing preferentially through macropores.

Catchment-scale regressions

A regression of maximum nitrate N concentration on total N load using the full data set explained only 22% of the variance, but much closer relationships were obtained for individual Water Authority Areas (Fig. 4; Table 2). Regressions for drier, more easterly



Fig. 3 Regressions of peak nitrate concentration in drainage on annual nitrate load for three soil conditions; \blacksquare sandy loam, \bigcirc drained clay loam, \blacksquare undrained clay loam.



Fig. 4 Regressions of peak nitrate concentration in annual nitrate load for rivers in three Water Authority Areas; ▲ Anglian, ■ Thames, □ Wessex.

Water Authority Areas, such as Anglia, Thames, and Southern had a greater slope. The areas characterized by high rainfall, impermeable underlying strata, and clay soils (South-West and Welsh) typically produced a more gentle slope. Restricting the data set to river-years with a HER greater that 150 mm removed a large cluster of points where a high concentration was associated with a small load, and this greatly improved the regression fit for the drier areas.

Subdivision of the data according to climate and geology also improved the regression fits. For example, the concentration was found to be almost independent of load in catchments over highly permeable limestone, and the regressions for rivers

Water Authority	а	s.e.	b	s.e.	r^2	р	River years
Thames	3.9	0.8	0.27	0.04	0.51	<001	48
Anglian	12.8	4.1	0.16	0.13	0.12	NS	5
Southern	2.8	0.7	0.23	0.04	0.39	<001	56
Wessex	4.6	0.8	0.15	0.03	0.37	<001	36
South-West	3.1	2.5	0.16	0.12	0.09	NS	8
Severn-Trent	6.1	4.1	0.17	0.16	0.13	NS	14
Welsh	1.8	1.1	0.12	0.04	0.21	0.007	29

Table 2 Regressions of peak concentration on annual nitrate load in rivers grouped by Water Authority Areas. Peak (mg N l⁻¹) = $a + b \times \text{load}$ (kg N ha⁻¹ of catchment).

NS = not significant

draining clay catchments were improved if areas receiving an annual rainfall of over 800 mm were excluded.

Comparison of the plot scale and catchment scale regressions

In general, the regression coefficients (b) for the rivers are lower than are the coefficients for the plot-scale experiments. The regression coefficients for the well-drained sandy loam soils are close to 1.0, which means that a peak concentration of 100 mg l^{-1} nitrate N would result from a load of 100 kg N ha⁻¹. The largest regression coefficient for the catchment-scale studies, those in the Thames Water Authority Area where the majority of soils are light and well drained, would give a maximum concentration of 27 mg l^{-1} nitrate N for a load of 100 kg N ha⁻¹. There is a similar discrepancy between the regression coefficients for field plots and catchments with clay and clay loam soils.

It may be assumed that these discrepancies might be accounted for by the effects of mixing the discharge from the agricultural areas with discharges from other sources. One of these effects is dilution with runoff from areas of the catchment low in nitrate, such as roads, paved surfaces, and land that is uncultivated and has received small inputs of N. This latter source would be expected to be particularly important in western Britain, where the headwaters that generate the greatest runoff are usually uncultivated moorland.

River baseflow from groundwater may also be an important source of dilution. In permeable catchments under chalk or sandstone, nitrate commonly moves very slowly through the unsaturated zone at a rate of 1-4 m year⁻¹ (Oakes, 1988). Nitrate concentrations in groundwater are therefore a function of the amount of leaching that occurred over previous decades and may not be as high as those currently measured in the leachate from agricultural land. Even if the nitrate concentration in baseflow is greater than that in the discharge from agricultural land, the nitrate peak:load ratio in the resultant mixture will be reduced from that in the discharge because the concentration in baseflow would remain constant, that is, with little or no peak.

The sharpness of the peak of concentration measured in the field experiment can also be smoothed on the catchment scale. Due to the distance of different fields from a stream channel and the different pathways by which the solute may reach the channel (e.g. rapid flow through field drains or a slower seepage through the soil matrix), the arrival at the river of the peak nitrate concentration from the individual fields is unlikely to be coincident.

Finally, biological processes can also be responsible for river nitrate concentrations being smaller than those in water draining fields. Denitrification, the reduction of nitrate to nitrogen oxides and dinitrogen gases in riparian buffer zones is well documented (e.g. Haycock & Burt, 1992) and could lead to a significant removal of nitrate from water prior to its entry into the stream channel. In addition, denitrification can also occur in groundwater, depending on the availability of oxygen and the amount of decomposable organic matter (Fustec *et al.*, 1991; Jarvis & Hatch, 1994).

CONCLUSIONS

This work has demonstrated that the use of empirical relationships, for different

agriculture and soil types, to predict nitrate concentration from total annual N load on a catchment and regional basis in the UK is a feasible approach, providing that the model using such relationships could account for dilutions from runoff low in nitrate, the effects of groundwater contributions and possible denitrification.

The results imply that compliance with a maximum of 11.3 mg l⁻¹ nitrate N in rivers would be associated with loads of about 40 and 75 kg N ha⁻¹ in eastern and western areas of England respectively. The smaller load is considerably less than the typical annual N loss from arable land. Therefore, to avoid exceeding the EC limit, substantial changes in land use and agricultural management may be required.

REFERENCES

- Barraclough, D., Hyden, D. M. & Davies, G. P. (1983) Fate of fertilizer nitrogen applied to grassland. I. Field leaching results. J. Soil Sci. 34, 483-497.
- Betton, C. (1990) Nitrate Levels in British Streams and Rivers. A Countrywide Perspective. Unpublished PhD Thesis, University of Exeter, Exeter.
- Cannell, R. Q., Goss, M. J., Harris, G. L., Jarvis, M. G., Douglas, J. T., Howse, K. R. & LeGrice, S. (1984) A study of mole drainage with simplified cultivation for autumn sown crops on a clay soil. 1. Background experiments and site detail, drainage systems, measurement of drainflow and summary of results. J. Agric. Sci. Cambridge 102, 539-5^A.
- Commission of the European Communities (1989) Intensive Farming and the Impact on the Environment and the Rural Economy of Restrictions on the Use of Chemical and Mineral Fertilizers. The Commission, Luxembourg.
- Cooper, D. M., Ragab, R., Lewis, D. R. & Whitehead, P. G. (1992) Modelling Nitrate Leaching to Surface Waters. MAFF/NERC Final Report, Institute of Hydrology, Wallingford, Oxfordshire.
- Fustec, E., Mariotti, A., Grillo, X. & Sajus, J. (1991) Nitrate removal by denitrification in alluvial groundwater: role of a former channel. J. Hydrol. 123, 337-354.
- Haycock, N. & Burt, T. P. (1992) Floodplains as nitrate buffer zones. NERC News 21, 28-29. Natural Environment Research Council, Swindon, Wiltshire, UK.
- Jarvis, S. C. & Hatch, D. J. (1994) Potential for denitrification at depth below long-term grass swards. Soil Biol. Biochem. 26, 1629-1636.
- National Rivers Authority (1992) The Influence of Agriculture on the Quality of Natural Waters in England and Wales. Water Quality series no. 6.
- Oakes, D. B. (1988) Modelling nitrate in groundwater systems. In: Report of the Special Topic Review on Nitrate Modelling. HMSO, London.
- Rodda, H. J. E. (1993) The Development and Application of a Nitrogen Cycle Model to Predict Nitrate Leaching from Grassland Catchments within the United Kingdom. Unpublished PhD Thesis, University of Exeter, Exeter, UK.
- Scholefield, D., Tyson, K. C., Garwood, E. A., Armstrong, A. C., Hawkins, J. & Stone, A. C. (1993) Nitrate leaching from grazed grassland lysimeters: effects of fertilizer input, field drainage, age of sward and patterns of weather. J. Soil Sci. 44, 601-613.
- Simpson, E. A. (1978) The harmonization of the monitoring of the quality of inland fresh waters. J. Inst. Wat. Engrs Sci. 32, 45-56.
- Thompson, N., Barrie, I. A. & Ayles, M. (1981) The Meteorological Office Rainfall and Evaporation Calculation System: MORECS. Meteorological Office Hydrological Memorandum no. 45, Bracknell, Berkshire, UK.
- Walling, D. E., Webb, B. W. & Woodward, J. C. (1992) Some sampling considerations in the design of effective strategies for monitoring sediment associated transport. In: *Erosion and Sediment Monitoring Programmes in River Basins* (ed. by J. Bogen, D. E. Walling & T. Day) (Proc. Oslo Symp., August 1992), 279-288. IAHS Publ. no. 210.