



Methods to predict the agricultural contribution to catchment nitrate loads: designation of nitrate vulnerable zones in Northern Ireland

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Abstract

The European Court of Justice has ruled that the Nitrates Directive places an obligation on EU member states to designate the catchments of eutrophic waters as Nitrate Vulnerable Zones (NVZs), where agriculture is a significant source of nitrate pollution. Recently, the European Commission has indicated that NVZs should be designated when agriculture can be shown to contribute more than 20% of the overall nitrate loading to those waters. Two methods have been used to identify catchments in Northern Ireland, where this condition is met. The first method employs a GIS to predict diffuse losses of nitrate from agricultural land to surface waters based on livestock data and a leaching factor to apportion the annual fertiliser usage and manure between all major catchments. The second method is based on export coefficient modelling. In the first method, allowances for denitrification losses, together with inputs of N from the atmosphere and domestic sewage to surface waters, were made to apportion the total nitrate load to each major river and thus determine if the catchment satisfied the 20% criterion to be designated as a NVZ. Both methods were validated against existing river monitoring data and offered a level of prediction that provides adequate information for a preliminary screening of those catchments to be targeted for designation. Apart from the River Lagan catchment, which includes the city of Belfast and where agriculture only contributed about 8.5% to the nitrate load, the agricultural contribution in the remaining catchments ranged from 33 to 86%. This implies that, if eutrophication is present in the latter surface waters, most of Northern Ireland should be designated a NVZ.

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1. Introduction

Despite the adoption of the Nitrates Directive (91/676/EC) throughout the European Union (EU) by Member States in 1991, the nitrate concentrations of many rivers in the United Kingdom (UK), including

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Northern Ireland, have continued to increase over the period 1991–2001 (DEFRA, 2001). In 1991, the emphasis on application of the Nitrates Directive in the UK was the concern over human health but the emphasis has now shifted to concerns over eutrophication of surface waters due to diffuse losses from agriculture. The Nitrates Directive requires Member States to designate as nitrate-vulnerable zones (NVZs) all known areas of land that drain into surface and groundwaters, where nitrate concentrations exceed $50 \text{ mg NO}_3 \text{ l}^{-1}$, where nitrate concentrations are showing a rising trend or, where there is evidence of eutrophication and a significant amount of the nitrates present come from agricultural sources. In Northern Ireland, only a total of 1580 ha of land (0.1% of the land area) has, to date, been designated as NVZs, affecting a mere 87 of the approximately 30,000 farmers in the Province. This contrasts with England, Scotland and Wales who have currently designated 55, 13.5 and 3% of their land area, respectively. Northern Ireland, along with the rest of the UK, is currently involved in an advanced Article 228 infraction case for failure to implement properly the Nitrates Directive. The infraction case relates to failure to identify and designate all surface and ground waters with elevated nitrate concentrations. However, it has recently become clear that Northern Ireland is failing to comply with the Nitrates Directive on a much larger scale by failing to designate the catchment areas of certain surface waters, which are eutrophic.

In order to comply with the European Court of Justice (ECJ) ruling, the UK must adopt one of two options: to apply the Action Programme measures designed to reduce nitrate losses to surface and ground waters to either the whole country or to designate *all* river and lake catchments, where nitrate concentrations exceed $50 \text{ mg NO}_3 \text{ l}^{-1}$, where there is a rising trend in nitrate concentrations or, where there is evidence of eutrophication. Thus far, Great Britain and Northern Ireland have opted to implement the Nitrates Directive using the designation approach. Recently, the European Commission has indicated that NVZs should be designated when agriculture can be shown to contribute more than 20% of the overall nitrate loading to surface waters (DOE-DARD, 2002). This presents the problem of how to estimate the agricultural contribution of nitrate to surface waters.

The present paper applies and compares two approaches to overcome this problem. For each major river catchment in Northern Ireland, diffuse losses of nitrate from agricultural land to surface waters were predicted based on both estimates of nitrate fertiliser applied to land using (a) ‘the DCE method’, where livestock data were used to apportion the annual fertiliser usage between catchments (Jordan et al., 1994), and (b) by using a method based on nitrate export coefficients (Jordan et al., 2000). Complementary data on inputs of N from the atmosphere and rural population to surface waters were also used to estimate the total nitrate load to each catchment (excluding point sources other than domestic sewage) and thus to determine if the catchment satisfied the 20% agricultural contribution criterion to be designated as a NVZ.

Member States may use a number of criteria to justify a derogation for permitting manure N application rates greater than $170 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ in any designated NVZ. One of these criteria is the presence of soils with an ‘exceptionally high denitrification potential’. As Northern Ireland is dominated by soils with impeded drainage and which remain wet throughout the year (Higgins, 1997), denitrification is likely to play a significant role in reducing the nitrate nitrogen (NO_3N) available for leaching to watercourses. The extent of this loss process was predicted on a catchment basis for Northern Ireland using a simple GIS-based model with minimal data requirements. These data were also used to calculate the net NO_3N load and concentration in each major river in the study area.

2. Study area

The study area comprises all river catchments in or draining into Northern Ireland. This includes an area of 3934 km^2 in the Republic of Ireland (Jordan et al., 2000). Northern Ireland is comprised of six counties viz. Antrim, Down, Armagh, Fermanagh, Tyrone and Londonderry. The total area of the Province is $14,120 \text{ km}^2$ of which $13,480 \text{ km}^2$ is land and 640 km^2 is ascribed to inland waters, predominantly Loughs Neagh and Erne (Fig. 1). Over 17% of the land area is above 200 m while nearly 6% is above 300 m. A maximum altitude of 850 m is found in the

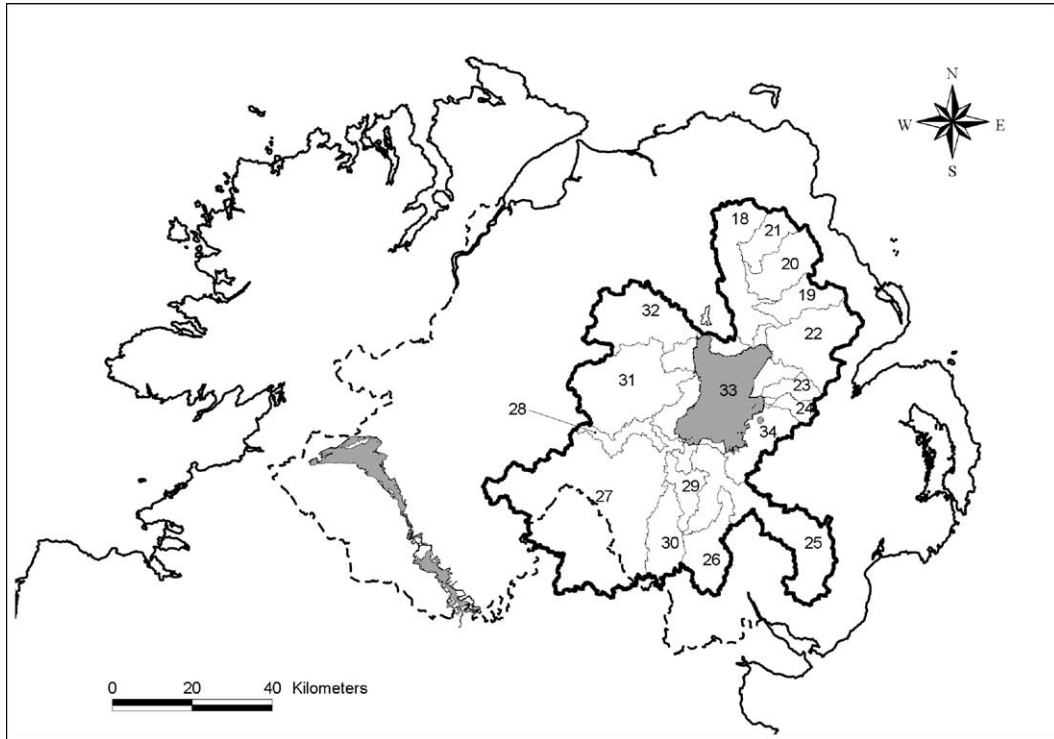


Fig. 1. River catchments draining into Lough Neagh. The names, ids and areas of each catchment are detailed in Table 1. The two largest surface waters in the Province are also shown shaded—Lough Neagh is located centrally while Lough Erne lies to the west of Northern Ireland. The international border between Northern Ireland and the Republic of Ireland is shown as a broken line.

south-east. The Province has a long-term (1961–90) mean daily air temperature of 8.7 °C, a mean annual rainfall of 1113 mm and a mean annual potential evaporation loss of 384 mm (Betts, 1997). Since agricultural land accounts for 80% of the total area of Northern Ireland and this is dominated by grassland (72%) and rough grazing (18%) with only 6% under crops and 1% in woodland, the dominant land cover class in most river and lake catchments is pasture of one form or another.

The dominant soil parent materials are drifts and glacial tills derived from basalts, Silurian shales, mica-schist and carboniferous-age rocks. The major soil subgroups are climatic peat above 200 m (14%), with acid brown-earths (13%) and gleys (56%) at lower elevations. The mineral soils have a mean bulk density of 1.03 g cm⁻³ and a mean organic C content of 5.0% (Cruickshank, 1997).

The Province has a total human population of nearly 1.6 million of which 18% are recorded as

belonging to the rural population (DFP, 1992). The land mass is divided into six counties and, due to the geological and climatic conditions in Northern Ireland, surface water is the dominant source of public water supply with groundwater estimated to provide only 8% of the total public water supply (EHS, 2000). The hydrology of the study area is dominated by the Lough Neagh and Lough Erne drainage systems. Lough Neagh is situated centrally, occupies a total area of 382 km² and, with a total catchment area of 4483 km², the lake and its catchment account for 43% of the surface area of Northern Ireland. Six major rivers flow into Lough Neagh, draining 88% of the total catchment of Lough Neagh (Fig. 1, Table 1). Mean annual rainfall in the Lough Neagh catchment is 997 mm. Lough Erne lies in the west of the Province, is an important tourist attraction and its catchment area includes much of County Fermanagh. Mean annual rainfall for the component of the Lough Erne catchment in Northern Ireland is 1153 mm.

Table 1
Names, ids and areas of all major river catchments flowing into Lough Neagh

Catchment ID	River name	Catchment area (km ²)
18	Main	291
19	Main-Kells Water	127
20	Main-Braid	189
21	Main-Clogh	108
22	Six Mile Water	302
23	Crumlin	62
24	Glenavy	46
25	Upper Bann	470
26	Upper Bann-Cusher	186
27	Blackwater	1154
28	Blackwater-Torrent	76
29	Blackwater-Tall	93
30	Blackwater-Callan	169
31	Ballinderry	434
32	Moyola	313
33	Lough Neagh surface	382
34	Lough Neagh & Peripherals	463

The first name is the primary basin and, where present, the hyphenated name is a sub-basin of the primary catchment (see Jordan et al. (2000)).

The Hillsborough experimental study site, where field denitrification rates were determined and used to calibrate the predicted denitrification rates, lies 15 km south west of Belfast at Irish grid reference 324,300 Easting, 357,800 Northing. The Hillsborough soil type is a clay-loam in an area receiving 880 mm rainfall annually. Chemical and physical characteristics of this site are detailed in Garrett et al. (1992).

3. Materials and methods

A number of the databases used in this study have been fully described in previous work relating to the study area (Jordan et al., 2000). Where this is the case, only brief details are provided below. Readers should refer to Jordan et al. (2000) for full details of the DEM, river catchments and CORINE databases for the study area.

3.1. GIS

ArcView V3.2a software, complete with the Spatial Analyst V2.0a software extension, running on an Intel PC was used for all GIS work described in the present study (ESRI, 1999). This software allowed the integration and analysis of vector and raster data formats.

3.2. DEM data

A DEM (digital elevation model) for the study area, giving elevation data at 50 m intervals in the easting and northing directions, was acquired from the Ordnance Survey of Northern Ireland (OSNI, 1999).

3.3. Catchment boundaries and stream networks

Northern Ireland was divided up into 84 catchments comprising 56 major catchment areas each with its own constituent river. For consistency with previous work in this study area, the scheme used in Jordan et al. (2000) was also used in this paper to number the catchments. Catchment areas were named according to the name of the major river contained within each catchment. For those 15 catchments lying partially within the Republic of Ireland (RoI) (catchments 1, 3, 5, 27, 65, 68–72, 77, 79–81 and 84; Jordan et al., 2000), animal and population numbers for the whole catchment were derived by increasing the values for the Northern Ireland portion of the catchment pro-rata by the area in the RoI. The total area contributing to flows within the Northern Ireland river network was 18,054 km². Catchment names and location within the study area are shown in Table 1 and Fig. 1 for the Lough Neagh catchment only.

3.4. CORINE database

Full details of the CORINE land cover database for the northern portion of Ireland, including the study area, are available in Cruickshank and Tomlinson (1996). For the purpose of deriving export coefficients, all rural land was regrouped into five main land cover classes: arable, improved grassland, non-improved grassland, coniferous forest and moor/heath as described in Jordan et al. (2000). Grassland in one form or another dominates land cover in

Northern Ireland and accounts for a total area of 8786 km² of which 4277 km² is improved grassland.

3.5. Catchment land cover statistics and NO₃N export coefficients

A breakdown of land cover with their associated areas were determined for each river catchment by overlaying the catchment boundaries layer on the CORINE land cover dataset using ArcView. These data were summarised by catchment using Microsoft Excel'97. The mean and range of diffuse NO₃N loads exported from each river catchment were predicted from the land cover statistics for each catchment using Eq. (1).

$$\text{NO}_3\text{N LOAD} = \Sigma(\text{LAND COVER AREA} \times \text{NO}_3\text{N COEFFICIENT})/10 \quad (1)$$

where NO₃N LOAD is in tonnes N yr⁻¹ and LAND COVER AREA and NO₃N COEFFICIENT are expressed in km² and kg N ha⁻¹ yr⁻¹, respectively. The export coefficients for NO₃N were derived using backward, stepwise regression of CORINE land cover and river NO₃N concentrations monitored weekly throughout 1990 in sub-catchments of the River Upper Bann and River Colebrooke catchments (catchment-ids 25 and 76 in Jordan et al., 2000) using the methodology of McGuckin et al. (1999). Mean NO₃N export coefficients for arable land, improved grassland and non-improved grassland were 69.3, 24.4 and 13.3 kg N ha⁻¹ yr⁻¹, respectively.

3.6. Meteorological data

Long-term (1961–90) annual mean rainfall (RAIN) and potential evapotranspiration (PE) data were received from the Meteorological Office on a 1 km grid for Northern Ireland (Meteorological Office, 1999).

3.7. Rainfall deposition of N

Since January 1985, rainfall chemistry, including N fractions, has been measured every 2 weeks at 4 remote stations in Northern Ireland using standard bulk (wet+dry) precipitation collectors (Jordan,

1997). These stations formed part of the UK rainfall deposition network (Vincent et al., 1996). Rainfall-weighted mean values for NO₃N at these stations for the period 1989–1991 were calculated and used to create an interpolated NO₃N concentration map. This data layer was then multiplied by the RAIN grid to give a distribution map of mean annual NO₃N deposition. Overlay of the deposition layer by the river catchment boundaries gave an estimate of the NO₃N deposited annually in each catchment.

The amounts of NO₃N leached across the study area are of the order of 5 kg N ha⁻¹ yr⁻¹, the same as that predicted by Smith and Stewart's (1989) NO₃N leaching model. Rainfall across the study area contained similar amounts of NO₃N and ammonium-nitrogen (NH₄N) but only the NO₃N was considered to be leachable as NH₄N is effectively immobilised in contact with soil. Moreover, NH₄N is taken up preferentially by perennial ryegrass, the dominant grass type in the study area, so that the opportunities for nitrification are minimal (Watson, 1986, 1987). This conclusion was supported by monitoring work in 1990 on 1011 ha of upland grazed by sheep in a remote part of the south-east of Northern Ireland, where no fertiliser was applied. The loss rates of NO₃N and NH₄N were found to be 5.2 and 0.3 kg N ha⁻¹ yr⁻¹, respectively, while the corresponding deposition rates for the same location were 4.8 and 3.8 kg N ha⁻¹ yr⁻¹, respectively. For the reasons just described, the NO₃N deposition rate in a catchment was taken to be equivalent to the background loss rate of NO₃N for each catchment.

3.8. Predicted river flows

The 1961–90 annual average RAIN and PE datasets were imported to ArcView for analysis. Hydrologically effective runoff (HER) for an area can be predicted from the difference between the rainfall and evapotranspiration values for that area (Gustard et al., 1992). The difference between the RAIN and PE layers was calculated using ArcView and used to create a (RAIN-PE) layer. Mean annual flows were then predicted for the major river within each catchment from data produced by overlaying the catchment boundaries on this (RAIN-PE) layer to give an estimate of the annual HER (Eq. (2)).

$$\text{HER} = \text{RAIN} - \text{PE} \quad (2)$$

where HER, RAIN and PE are in mm yr^{-1} .

Multiplying the annual HER value by the area for each river catchment gives an estimate of the mean annual flow for each river (Eq. (3)).

$$\text{FLOW} = \text{HER} \times \text{AREA} \quad (3)$$

where FLOW is in l yr^{-1} , AREA is in m^2 and HER is in mm yr^{-1} .

3.9. Measured RIVER Nitrate and FLOW data

Annual mean NO_3N concentrations at or near the outflows of each major river catchment in Northern Ireland were provided by the Environment and Heritage Service of the Department of the Environment for Northern Ireland, DOE(NI), from their statutory river monitoring database for the years 1989–1996. Mean annual flows for 22 river catchments, varying in catchment area from 62 to 1492 km^2 , were also calculated from individual rating curves for these rivers by the Northern Ireland Department of Agriculture and Rural Development's Rivers Agency using recorded water levels at 30 min intervals over a period of at least 10 years up to and including 1997. The NO_3N concentration and flow datasets were used to validate predicted flows and NO_3N loads.

3.10. Sewered and unsewered population data

The number of persons connected to sewers in each river catchment was calculated from the '1991 Population Census—Small Area Statistics' database. The 2001 Population Census could not be used for this purpose as it did not collect information relating to whether or not a property was connected to a sewer. The 1991 database holds, amongst other data, records of the number of households and persons normally resident together with the number of households and persons sewered in each 1 km^2 across Northern Ireland (DFP, 1992). By overlaying the catchment boundaries on these data within the GIS, the number of persons sewered and unsewered in each catchment were calculated. The data indicate that, in Northern Ireland, at least 82% of the human population are connected to a principal sewer. The NO_3N load from

the sewered population in each catchment was calculated using Eq. (4a):

$$\text{SEWAGE-N} = \text{SEWERED POPULATION} \times 6.7 \times 365/10^6 \quad (4a)$$

where SEWAGE-N is in tonnes N yr^{-1} and 6.7 is the number of grams of NO_3N per capita output daily from the sewage works in that catchment (Smith, 1976). Smith (1976) also gives the total-N daily output from the sewage works as 9.1 g of N per capita. However, because sewage works are designed to nitrify as much N as possible, it is unlikely that the extra 2.4 g N per capita output will be subsequently nitrified in the receiving river system. Moreover, in the 78,000 households (around 267,000 persons) in the study area not connected to sewers, human waste is collected in a septic tank. Septic tanks discharge about 0.3 m below the surface through a soakaway to the soil or, in the permanently saturated soils in the West of the Province, directly to a stream or drain (Patrick, 1988). Thus, most septic tank discharges end up in the surface water network. Ammonium-N is the major form of N in the effluent from the septic tank and it is assumed that most of the NH_4N is nitrified to NO_3N on its journey through the soil to a surface water or in the well-oxygenated receiving water itself. In the absence of experimental data for NO_3N losses from septic tanks, we can assume that the loss of NO_3N per capita from a septic tank to a watercourse is the same as that from a sewage works. Thus, the total NO_3N load discharged to surface waters by the human population can be calculated for any catchment, in tonnes N yr^{-1} , using Eq. (4b).

$$\text{HUMAN-N} = \text{HUMAN POPULATION} \times 6.7 \times 365/10^6 \quad (4b)$$

Moreover, it should be pointed out that the export coefficients for NO_3N used in the present study were derived for catchments that had a mean rural population density of 0.4 persons ha^{-1} . Thus, when calculating the total NO_3N load to surface waters using the export coefficient method, an allowance had to be made for the NO_3N discharged by the 'additional' population (over and above 0.4 persons ha^{-1}) using Eq. (4b).

3.11. Excreta-N

Livestock numbers from the 1993 DARD Farm Census were extracted for each major river catchment using the GIS. These data were combined with excreta-N production rates by animal type (DEFRA, 2002; MAFF, 2000b) to calculate the quantities of excreta-N generated for each river catchment. Cattle slurry was found to dominate annual excreta-N production in Northern Ireland with cattle, sheep, poultry and pig manures calculated to contribute 75, 12, 7 and 6%, respectively, of annual excreta-N production. Due to the dominance of cattle slurry, a figure of 30% of all excreta-N was assumed to be available for leaching and denitrification (MAFF, 2000a,b).

3.12. Prediction of denitrification loss rates

Relative denitrification rates for each major river catchment were modelled within the GIS using surrogate databases for the main factors that determine denitrification losses viz. soil moisture, soil temperature, soil carbon and soil NO_3N . These data were then calibrated using measured data from the Hillsborough study site. All datasets for denitrification modelling were created on a 1 km grid starting at Irish Grid coordinates 180,000 Easting, 300,000 Northing.

3.13. Soil wetness distribution

Soil wetness depends on both the amount of water falling on any given soil, the evapo-transpiration outputs and the hydrological response of that soil. HER can be calculated using Eq. (2) while the hydrological response of a soil can be summarised by its Hydrology Of Soil Type (HOST) class (Higgins, 1997). One quantitative measure of the soil HOST class is the standard percentage runoff values (SPR) assigned to each class (Boorman et al., 1995). The SPR value is the percentage of a standardised rainfall event, which causes a short-term increase in the river flow. In general, the less permeable the soil, the greater will be its SPR value and, consequently, its wetness. Other factors such as the presence of rock at shallow depths and the presence of peaty surface layers may also play an important role in determining soil wetness. Multiplying annual HER by the soil SPR

value gives a surrogate measure of the soil wetness at any given location. This calculation was carried out spatially within the GIS to map the distribution of soil wetness across Northern Ireland.

3.14. Soil temperature distribution

It is known that most denitrification takes place in the top 10 cm of a soil profile (Jordan, 1989) and that denitrification rates are very sensitive to changes in temperature (Brown et al., 2002; Jordan, 1989). Jordan (1989) showed that denitrification rates were insignificant for grassland soils in Northern Ireland at soil temperatures below 4 °C but that above this temperature there was an Arrhenius-like dependence viz. a doubling in the rate of denitrification for every 10 °C rise in temperature. Any temperature dataset used in the prediction of denitrification rates must, therefore, take the annual variation in daily soil temperature into account. Consequently, a simple distribution map of annual mean soil temperature at 10 cm would be inadequate to describe this variation. The grass-growing season was used as a surrogate for soil temperature at 10 cm depth as this was the only available data. The grass-growing season approximates to the period when soil temperature at 10 cm depth is consistently above 6 °C as this is considered the critical temperature threshold for grass growth (Betts, 1997; Keane, 1986). This is also the temperature above which significant denitrification takes place with grassland soils (Jordan, 1989; Ryden, 1983). A map of the length of the mean annual growing season (in days) over the period 1961–1990 shows that the growing season in Northern Ireland varies between 205 and 280 days with a mean of 245 days and a standard deviation of 17 days (Betts, 1997).

3.15. Soil carbon distribution

Previous work by Watson et al. (1994), using 22 agricultural soils sampled across Northern Ireland, reported soil carbon values ranging from 1.3 to 6.5%. These %C concentrations were associated with water-soluble C concentrations ranging from 198 to 450 $\mu\text{g C g}^{-1}$. Data from a recent complete soil survey of Northern Ireland reported the mean C content of agricultural soils in Northern Ireland to be 5.0% (Cruickshank et al., 1997). This value has a

standard deviation of 2.2% C associated with it so that 95% of all lowland (<200 m) soils have a %C value of 5.0 ± 4.3 . At these concentrations, the range of water-soluble C values is likely to be of the same order reported by Watson et al. (1994). Burton and Beauchamp (1985) showed that significant denitrification rates occur only for soils with water-soluble C concentrations above $40 \mu\text{g C g}^{-1}$. As this limit is likely to be grossly exceeded by all soils in Northern Ireland, denitrification losses from soils in Northern Ireland are not thought to be C-limited. Consequently, no allowance for soil C on denitrification rates was made in the present study.

3.16. Field denitrification rates at Hillsborough

Soil NO_3N concentrations are proportional to the amount of fertiliser N applied to the soil in mineral and organic forms. Jordan (1989) and Ryden (1983) showed that significant denitrification took place on agricultural soils when soil NO_3N concentrations were above $2\text{--}5 \text{ mg N kg}^{-1}$. Garrett et al. (1992) and Watson (2001) also showed that, at the Hillsborough study site, field denitrification rates were linearly related to annual N-inputs (Eq. (5)).

$$\begin{aligned} \text{N-DENITRIFIED} &= 0.1952 \times \text{N-INPUT}; \\ \text{df} = 3, \quad R^2 &= 0.922, \quad 0.001 < p < 0.01 \end{aligned} \quad (5)$$

where N-DENITRIFIED and N-INPUT are in $\text{kg N ha}^{-1} \text{ yr}^{-1}$. Measured denitrification rates used to derive Eq. (5) were calculated from observed N_2O concentrations in sealed jars in which intact soil cores were incubated for 24 h at field temperature in the presence of 4% acetylene to block denitrification at the N_2O stage (Ryden et al., 1987). All N_2O concentrations were determined by gas chromatography using a thermal conductivity detector (Watson et al., 1994).

3.17. The DCE method of estimating N inputs to agricultural land

In Northern Ireland, the dominant fertiliser-N used on grassland is calcium ammonium nitrate. Annual fertiliser-N applications for a river catchment area can be estimated from the annual Farm Census dataset (DARD, 2001) using aggregated animal numbers and

overall annual fertiliser-N usage (DARD, 2000) using the method of Jordan et al. (1994). In this method, numbers of animals of different types and ages are integrated using the concept of Dairy Cow Equivalents (DCE) (Kirke and Hassard, 1990). DCE values were calculated for each farm and aggregated by river catchment within the GIS. As these data were used to apportion annual fertiliser-N usage by catchment (Eq. (6)), and that fertiliser-N was to be used to increase grass yields, only grazing animals were included in the DCE calculation.

$$\begin{aligned} \text{FERTILISER-N}_{\text{catchment}} \\ = \frac{\sum \text{DCE}_{\text{catchment}}}{\sum \text{DCE}_{\text{NIreland}}} \times \text{FERTILISER-N}_{\text{NIreland}} \end{aligned} \quad (6)$$

where FERTILISER-N is in $\text{kg N ha}^{-1} \text{ yr}^{-1}$ and DCE is in livestock units. Total NO_3N -input to each 1 km grid square was calculated as FERTILISER-N from Eq. (6) plus 30% of excreta-N produced by animals within that grid square (see earlier). An example of calculated N-inputs by river catchment is shown in Table 2 for the Lough Neagh catchment. Use of Eq. (6) to calculate fertiliser inputs from DCE data will be referred to in the rest of this paper as the DCE method.

3.18. Relative and field denitrification rate estimates

At the Hillsborough study site, soil NO_3N concentrations were linearly related to the N-input. It was assumed that over the range of surrogate values for soil moisture and temperature found across the study area, a 1:1 linear relationship existed between their values at any given location and the corresponding denitrification rate at that location (Eq. 5). The soil moisture and temperature data layers were calculated at each 1 km grid square across the study area relative to the Northern Ireland mean for each of these factors. Relative denitrification losses across Northern Ireland were then calculated for each 1 km grid square by multiplying the relative soil moisture and temperature layers by the actual soil N-input data. These relative denitrification rates for each grid square (1 km^2) were finally converted into field denitrification rates using Eq. (7) which is based on calibration data measured at the Hillsborough study site.

Table 2
Nitrate-N sources, sinks and predicted mean concentration by river catchment for the Lough Neagh catchment area, using DCE method

River catchment-id ^a	Flow (10 ⁶ m ³ yr ⁻¹)	Fertiliser-N (tonnes N yr ⁻¹)	Excreta-N (tonnes N yr ⁻¹)	Denitrification ^b (tonnes - N yr ⁻¹)	River NO ₃ N load (tonnes - N yr ⁻¹)	Fertiliser-N ^{c,d} (%)	Human-N ^d (%)	Background ^d (%)	Predicted mean NO ₃ N (mg l ⁻¹)
18	202.0	2766	4519	825	557	76.9	9.3	13.8	2.8
19	106.9	819	1489	272	172	75.1	4.8	20.0	1.6
20	149.8	1564	2945	353	404	67.3	19.6	13.0	2.7
21	107.0	934	1312	220	187	77.2	3.2	19.6	1.7
22	198.8	2629	3268	819	565	64.2	22.4	13.4	2.8
23	31.6	596	632	145	108	77.1	8.7	14.2	3.4
24	26.6	289	511	106	61	72.0	7.3	20.7	2.3
25	245.9	4422	5224	835	974	68.8	13.3	17.8	4.0
26	104.3	2150	2547	607	379	79.1	5.9	15.0	3.6
27	684.9	10,108	12,862	3231	1807	77.2	7.3	15.5	2.6
28	47.8	737	975	181	147	75.0	12.0	13.0	3.1
29	36.5	717	959	167	148	73.8	11.9	14.4	4.0
30	93.4	1443	1750	411	303	66.9	18.4	14.7	3.2
31	308.7	4492	5824	1321	815	78.4	7.3	14.3	2.6
32	275.6	2520	3796	647	539	72.6	9.5	17.9	2.0
34	179.6	3838	5067	853	837	70.0	17.7	12.4	4.7
Total	2799.4	40,024	53,680	10,993	8003	73.3	11.5	15.2	2.9

^a Full catchment names, location and areas are shown in Table 1 and Fig. 1.

^b Based on the whole land area of each catchment, not just the agricultural land area.

^c Includes both mineral fertiliser-N and excreta-N.

^d Percentage contribution to the total river NO₃N load.

FIELD DENITRIFICATION

$$= (\text{RELATIVE DENITRIFICATION}/100) \times 0.1952/0.786 \quad (7)$$

where FIELD DENITRIFICATION is in $\text{kg N ha}^{-1} \text{ yr}^{-1}$, RELATIVE DENITRIFICATION is in kg N km^{-2} , 100 is a factor to convert denitrification rates from kg N km^{-2} to kg N ha^{-1} , the factor 0.1952 is from Eq. (5) and 0.786 is the relative wetness times the relative temperature factor for the Hillsborough study site. Mean field denitrification loss rates for each major river catchment were derived by overlaying the denitrification dataset with the catchment boundary vectors within the GIS.

4. Results

In 2000, 130,900 tonnes of fertiliser-N and a further 168,800 tonnes of excreta-N were estimated to have been applied across the study area including the portions in the Republic of Ireland. If we assume 30% of the excreta-N is available for leaching and denitrification (see Section 3.11), the equivalent amount of fertiliser-N applied across the study area totalled 181,200 tonnes. The quantity of NO_3N leached into Northern Ireland rivers from all sources was estimated to be 27,500 tonnes of which 18,709 tonnes were agricultural in origin, 4293 tonnes were from human sewage and 4497 tonnes were from background sources (rainfall deposition). The total flow through the river network flowing into Northern Ireland (total contributing area of 18,054 km^2) was predicted to be 11,960 $\text{m}^3 \text{ yr}^{-1}$.

Predicted catchment denitrification rates ranged from 3 tonnes N yr^{-1} (Owenmore, catchment-id 4) to 3231 tonnes N yr^{-1} (Blackwater, catchment-id 27) with a mean denitrification rate of 455 tonnes N yr^{-1} . This equates to a total estimated denitrification loss of 37,300 tonnes N yr^{-1} for the whole study area or 20.7 $\text{kg N ha}^{-1} \text{ yr}^{-1}$. For Northern Ireland only, the average denitrification rate was 19.5 $\text{kg N ha}^{-1} \text{ yr}^{-1}$.

4.1. Validation of river flows

A comparison of GIS predicted mean annual flows for the major rivers in the Lough Neagh catchment, based on meteorological data, with those measured by the DARD Rivers Agency over the same period of time, showed that the GIS method is a good predictor of mean annual flow in a major river. Observed flows ranged from 30 to $860 \times 10^6 \text{ m}^3 \text{ yr}^{-1}$. Linear regression of the data showed that predicted mean annual flows were within 1% of the observed mean annual flows (Eq. (8)).

$$\begin{aligned} \text{Predicted flow} &= 1.0033 \times \text{Observed flow}; \\ df &= 20, \quad R^2 = 0.981, \quad p < 0.001 \end{aligned} \quad (8)$$

4.2. Validation of river NO_3N loads

Comparisons of NO_3N loads calculated using NO_3N export coefficients were made with NO_3N loads calculated from the DOE(NI) database using Eq. (5) and data for 32 river catchments known to have no major point sources of NO_3N pollution. Measured NO_3N loads ranged from 12 to 2354 tonnes $\text{NO}_3\text{N yr}^{-1}$. Linear regression of these data gave a highly significant correlation between the observed and predicted annual NO_3N loads with the prediction, using export coefficients, within 1% of the observed load (Eq. (9)).

$$\begin{aligned} \text{Predicted } \text{NO}_3\text{N load} \\ &= 0.988 \times \text{Observed } \text{NO}_3\text{N load}; \\ df &= 30, \quad R^2 = 0.942, \quad p < 0.001 \end{aligned} \quad (9)$$

Moreover, the average annual measured NO_3N load for the whole Lough Neagh catchment area (catchment-ids 18–34, inclusive, Table 1) for the period 1994–1999 was 8225 tonnes $\text{NO}_3\text{N yr}^{-1}$. Using the DCE method, the predicted total annual NO_3N loss rate to Lough Neagh was 8003 tonnes $\text{NO}_3\text{N yr}^{-1}$ or 97.3% of the observed load (Table 2).

4.3. Comparison of predicted NO_3N loads in rivers by export coefficient and DCE methods

A linear relationship was found between NO_3N loads (in $\text{kg N ha}^{-1} \text{ yr}^{-1}$) in rivers derived using the export coefficient methodology and that using the

DCE methodology (Eq. (10)).

$$\begin{aligned} \text{NO}_3\text{N}_{\text{DCE}} &= 0.906 \times \text{NO}_3\text{N}_{\text{export coeff}} + 37.6; \\ \text{df} &= 82, \quad R^2 = 0.953, \quad p < 0.001 \end{aligned} \quad (10)$$

Or, if the regression is forced through the origin (Eq. (11)),

$$\begin{aligned} \text{NO}_3\text{N}_{\text{DCE}} &= 0.960 \times \text{NO}_3\text{N}_{\text{export coeff}}; \\ \text{df} &= 82, \quad R^2 = 0.946, \quad p < 0.001 \end{aligned} \quad (11)$$

It is not unexpected that the DCE method predicts somewhat lower values of NO_3N exported because the export coefficient approach includes both diffuse losses and minor point sources.

4.4. Relative denitrification rates by county

Mean soil wetness, temperature and NO_3N values relative to the Northern Ireland annual mean were calculated within the GIS for each of the Province's 6 counties. These calculations show that there is little (3%) variation in soil temperature between the counties so this factor is likely to have little effect on overall denitrification rates. By contrast, there is significant variation in soil wetness and NO_3N concentrations. The wetter the soil and the greater its NO_3N concentration, the more denitrification we would expect to take place. The counties with the wettest soils lie to the west of Northern Ireland (Londonderry, Tyrone and Fermanagh) while those with the greatest mean soil NO_3N concentrations are found in the south-east (Down and Armagh) and are the most agriculturally intensive. The overall impact of soil wetness and NO_3N concentration is that County Tyrone soils show the greatest denitrification rate while the soils of County Armagh show the least denitrification rate.

4.5. Validation of field denitrification rate

The modelled field denitrification rates at Hillsborough and Castle Archdale of 29 and $58 \text{ kg N ha}^{-1} \text{ yr}^{-1}$, respectively, compared favourably with the field rates measured in 1989 of 25 ± 5 and $56 \pm 11 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ for Hillsborough and Castle Archdale, respectively (Jordan, 1989). Regression of the

field denitrification rates predicted by the present GIS study for 18 sites across Northern Ireland versus those published by Watson et al. (1994) gave a significant linear relationship between the two sets of data (Eq. (12)).

$$\begin{aligned} \text{Field Denitrification-rate}_{\text{GIS}} &= 0.370 \\ &\times \text{Denitrification-potential}_{\text{Watson}} + 6.05; \\ \text{df} &= 16, \quad R^2 = 0.633, \quad p < 0.001 \end{aligned} \quad (12)$$

where $\text{Field Denitrification-rate}_{\text{GIS}}$ is in $\text{kg N ha}^{-1} \text{ yr}^{-1}$ and $\text{Denitrification-potential}_{\text{Watson}}$ is in $\text{nmoles g}^{-1} \text{ h}^{-1}$.

Emissions of N_2O arising from denitrification processes operating within UK agricultural soils have been modelled on a county basis by Brown et al. (2002). Using census and other data for 1990, they estimated that emissions of N_2O were greatest in the south-west of England and in Northern Ireland. For Northern Ireland, the mean N_2O loss rate estimated by Brown et al. was $5 \text{ kg N ha}^{-1} \text{ yr}^{-1}$. However, as the N_2O loss accounts for between one-third and one-quarter of the total nitrogen losses resulting from denitrification (Stevens and Laughlin, 2001; Ryden, 1983), the combined N_2 and N_2O loss for Northern Ireland, as a result of denitrification, was therefore estimated to be of the order of $15\text{--}20 \text{ kg N ha}^{-1} \text{ yr}^{-1}$. This agrees well with the total N loss from denitrification of $19.5 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ predicted for Northern Ireland in the present study. The latter values are at the lower end of the estimated denitrification losses of $21\text{--}32 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ reported for the Ayrshire Basin in Scotland based on reported N_2O emission rates of $7\text{--}8 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ (Lilly et al., 2003), an area similar to Northern Ireland in terms of its soil properties and agricultural intensity. Based on the present study, denitrification in Northern Ireland accounts for the loss of around 26,300 tonnes N yr^{-1} of which 6570–8760 tonnes is N_2O .

5. Discussion

Nitrate loads to a catchment in the study area were predicted equally well using either the export coefficient method or the DCE method. However,

the DCE method of prediction allows the source of the NO_3N load in the river water to be apportioned between background, agriculture and human contributions as well as providing an estimate of the significance of denitrification. Thus, of the 181,200 tonnes of NO_3N fertiliser (mineral and organic) applied annually across the study area, 37,300 tonnes NO_3N were estimated to have been lost to the atmosphere through denitrification. The remaining 143,900 tonnes NO_3N were available for leaching into the river network. Of the quantity of NO_3N entering into Northern Ireland rivers from all sources (27,500 tonnes), the agricultural (fertiliser including manures), human and background contributions were predicted to be 69, 13 and 18%, respectively. This loss of NO_3N has both environmental and economic consequences. Based purely on the cost of around £0.40 per kg, the loss of 27,500 tonnes NO_3N represents a loss of around £11,000,000 yr^{-1} for the Province as a whole, or nearly £8 $\text{ha}^{-1} \text{yr}^{-1}$ (all land).

Apart from the urban streams of the River Lagan catchment (catchment-id 47, Jordan et al. (2000)), where human-N was the dominant source of NO_3N leached (91.5%), the agricultural contribution to the NO_3N load in all catchments ranged from 33 to 86%. This is well in excess of the 20% limit 'suggested' by the EU as a criterion for NVZ designation i.e. *most* of Northern Ireland should be designated a NVZ. The EU Nitrates Directive restricts the application of excreta-N in nitrate-sensitive areas to 170 $\text{kg N ha}^{-1} \text{yr}^{-1}$. However, because Northern Ireland soils have a significant denitrification potential, the excreta-N restriction may be eased to 210 $\text{kg N ha}^{-1} \text{yr}^{-1}$. Either way, the introduction of an action plan to limit excreta-N application would have major implications for intensively-managed farms across the Province. Based on recent Farm Census statistics (DARD, 2001), an action plan to limit excreta-N applications to 170 or 210 $\text{kg N ha}^{-1} \text{yr}^{-1}$, respectively, would impact on around 14 and 7% of the 30,000 farms in Northern Ireland, respectively. Under the Nitrates Directive, there is also a provision requiring farmers to spread manure in a responsible manner. It is unlikely that farmers in Northern Ireland NVZs could operate their maximum herd size unless they had approximately 6 months storage capacity for slurry and it remains the case that farms in Northern

Ireland have an average of only 3 months storage capacity. One option would be for farmers to reduce their herd sizes but otherwise a significant increase in slurry storage capacity will be required.

The total flow through the river network flowing into Northern Ireland (total contributing area of 18,054 km^2) was predicted to be nearly 12,000 $\text{m}^3 \text{yr}^{-1}$. Thus, the weighted mean NO_3N concentration in Northern Ireland rivers was estimated to be around 2.3 mg l^{-1} , well below the guide (5.6 mg l^{-1}) and upper (11.3 mg l^{-1}) limits defined in the 'Drinking Water Directive' (75/440/EEC). Only one catchment (River Lagan, catchment-id 47, Jordan et al. (2000)) exceeds the 11.3 mg l^{-1} limit and this is due to the large contribution of sewage-N to the N-load of this largely urban catchment. A further single catchment to the east of the Province (north Down/Ards peninsula, catchment-id 59) is predicted to exceed the 5.6 mg l^{-1} guide limit. This catchment supports both intensively-managed livestock systems and significant arable production and thus has large N-inputs. Indeed, two parts of this catchment (near the town of Comber) were designated as NVZs in 1999 on the basis of monitoring of NO_3N concentrations in groundwaters (DOE-DARD, 2002).

6. Conclusions

In grassland-dominated catchments such as the present study area, the level of prediction offered by either the DCE or export coefficient method provides adequate management information for a preliminary screening of those catchments to be targeted for designation under the Nitrates Directive. In such catchments, the DCE method has the added advantage in that it allows attribution of NO_3N leached by source and thus more information on which to base management options for amelioration of the problem. However, in areas, where arable agriculture is a significant land use, the export coefficient method should offer the better predictive tool for prediction of NO_3N leached to a watercourse. As the latter method depends on coefficients, which represent the net export from the catchment, no attribution to source can be made and the significance of denitrification within the catchment is allowed for but cannot be assessed independently.

Apart from the River Lagan catchment, which includes the city of Belfast and, where agriculture only contributed about 8.5% to the nitrate load, the agricultural contribution in the remaining catchments ranged from 33 to 86%. This implies that, if eutrophication is present in the latter surface waters, most of Northern Ireland should be designated a NVZ.

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