A STATISTICAL APPROACH TO ESTIMATE NITROGEN SECTORIAL CONTRIBUTION TO TOTAL LOAD

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ABSTRACT

This study describes a source apportionment methodology for nitrogen river transport. A statistical model has been developed to determine the contribution of each source (punctual and diffuse) of nitrogen to river-mouth transport. A non-linear regression equation was developed, relating measured nitrogen transport rates in streams to spatially referenced nitrogen sources and basin characteristics. The model considers applied fertilizer, atmospheric deposition and point discharges as sources, and winter rainfall, average air temperature, topographic wetness index and dry season flow as basin characteristics. The model was calibrated in an area of 8913 km^2 in East Anglia (UK). In the studied area, the average contribution of agriculture to the nitrogen load is estimated around 71%. Point sources and atmospheric deposition respectively account for 24% and 5% of the exported nitrogen. The model allowed the estimation of the contribution of each source to nitrogen emissions and the nitrogen retention in soils and waters as influenced by basin factors.

KEYWORDS: nitrogen, retention, source apportionment, statistical modelling.

INTRODUCTION

Excessive input of nitrogen is responsible for water quality degradation and eutrophication in rivers and coastal waters. Negative impacts include oxygen depletation, mortality of benthonic organisms and increased phytoplankton blooms. Human activity has increased the transfer of N through rivers to estuaries and coastal oceans (Vitousek et al. 1997), and constitutes the dominant control of NO_3 export at the global scale (Caracao and Cole, 1999). In Northern Europe, nitrogen in rivers originates mainly from the leaching of agricultural soils and from urban wastewater discharge. In the North Sea, rivers discharges account for 65 to 80% of the total nitrogen inputs (OSPAR Commission, 2000), and the riverine nitrogen fluxes from North Sea drainages have increased by 6 to 20 fold from pre-industrial times (Howarth et al., 1996). OSPAR convention established a reduction of 50% in inputs of nitrogen into areas where these inputs are likely to cause pollution. In the European Community, the Nitrates Directive (91/676/EEC) aims at controlling nitrogen export into waters, by implementing agricultural strategies in the areas directly responsible for waters nitrogen pollution. The evaluation of new regulations or alternative strategies requires preliminary modelling studies to assess the impact of these new policies and management options. Models constitute thus valuable tools for policy support. A variety of methods have been used to model the transport of nitrogen in river basins. Deterministic models describe nitrogen transport and loss according to mechanistic functions. They allow predictions and better understanding of processes, but data and calibration requirements are important and increase with basin size. Statistical methods have the advantage of being readily applied in large watershed, but they do not describe the spatial variability of nitrogen transport and transformation processes. Smith et al. (1997) proposed a statistical method including spatial variation of basin properties that influence nitrogen fate, allowing the estimation of the nitrogen loss rate in stream and on the landscape. In statistical models, the spatial variation of nitrogen sources and attenuation processes improve the accuracy of estimates of stream export and source contribution (Alexander et al., 2002). This study presents a statistical approach to estimate the nitrogen river loads, considering physical and climatic basin characteristics.

METHODS

The model

The model, inspired by the SPARROW model (Smith et al., 1997), consists in a non-linear regression equation, where the river nitrate load is related to the sum of the different nitrogen sources reduced by the retention processes occurring in soils and water. As nitrogen sources, the model considers applied fertilizer (artificial and manure), atmospheric deposition and point discharges. For downstream sub-basins, as they receive nitrogen loads from upstream sub-basins, the model includes a further source, which consists in measured nitrate load at the up-stream sub-basin outlet. The model considers two steps in nitrogen sources reduction: processes occurring during the transport from land to the river (modelled by a Basin Reducing Factor, B) and processes taking place during the transport inside the river (represented by a River Reducing Factor, R). The load at the outlet of sub-basin *i* is expressed as:

$$\mathrm{L}_i = \left(x_{1,i}\mathrm{B}_i\mathrm{R}_i + x_{2,i}\mathrm{B}_i\mathrm{R}_i + x_{3,i}\mathrm{R}_i + x_{4,i}\mathrm{R}_i\right) + \mathring{a}_i \tag{1}$$

L_i average annual nitrate loss (t N/yr);
B_i basin reducing factor (dimensionless);
R_i water reducing factor (dimensionless);

$x_{1,i}$ fertilizer application (t N/yr);
$x_{2,i}$ atmospheric deposition (t N/yr);
$x_{3,i}$ points discharges (t N/yr);
$x_{4,i}$ up-stream input (t N/yr);
ε_i residual

The Basin Reducing Factor considers all nitrogen losses including soil denitrification, volatilisation, plants consumption and soil storage. The River Reducing Factor explains nitrogen losses due to in-stream denitrification, volatilisation and plants consumption and includes net sedimentation. The diffuse sources (fertilisers and atmospheric deposition) are reduced by both factors, while point sources and up-stream input are affected only by the River Reduction Factor, as they reach directly the stream. Basin Reducing Factor is assumed to be a function of rainfall, temperature and basin topography. River Reducing Factor is related to water flow. Both factors are parameterised as exponential decreasing functions:

$$\mathrm{B}_i = \exp\left(-(\alpha_{\mathrm{P}} x_{5,i} + \alpha_{\mathrm{T}} x_{6,i} + \alpha_{\mathrm{B}} x_{7,i})\right) \tag{2}$$

$$\mathrm{R}_i = \exp\left(-(\alpha_{\mathrm{Q}} x_{8,i})\right) \tag{3}$$

$x_{4,i}$ measured sources (t N/yr);
$x_{5,i}$ normalized winter rainfall (October-April) (dimensionless);
$x_{6,i}$ normalized temperature degrees (dimensionless);
$x_{7,i}$ normalized topography wetness index (dimensionless);
$x_{8,i}$ normalized water flow of dry season (June-September) (dimensionless);
α_P rainfall coefficient (dimensionless);
α_T temperature coefficient (dimensionless);
α_B topography coefficient (dimensionless);
α_Q water flow coefficient (dimensionless);

The model considers precipitations from October to April, as in northern regions they are responsible for groundwater recharge. In fact, during winter, soil moisture content can reach saturation and rainfall can easily cause nitrogen loss by leaching or surface and subsurface runoff. Temperature controls plant growth and bacterial activity, influencing nitrogen removal by plant consumption and denitrification. In particular denitrification rate increases with temperature and drops at about 10°C (Germon et al., 1983). The model considers the degrees temperature that are the sum of the average temperature of all days with an average air temperature higher than a threshold value, which was fixed to 10°C. The topography wetness index (TWI) (Beven and Kirkby, 1979) was introduced in the model to take into consideration the physical characteristics of the basin. High values of this index are typical of saturated areas, where surface and subsurface runoff tends to concentrate and where consequently the conditions are more suitable to runoff generation (Beven and Kirkby, 1979) and denitrification process. The model relates the in-stream retention processes to low water flow, which occurs during the period from June to September in the studied region. Sedimentation and water residence time increase at low flow rates. Characteristics having a positive influence on nitrogen losses (rainfall and water flow) were taken as inverse values. In order to compare different parameters, all characteristics were normalised by their maximum value before being entered in the model.

The studied area

The study was performed over an area of 8913 km^2, which partially covers the river basins of Great Ouse, Nene, Welland and Witham, in East Anglia (UK) (Fig.1). In this region the average air temperature is 4°C in winter and 17°C in summer. Precipitation ranges between 528 and 695 mm/yr, increasing with altitude. Agriculture and husbandry are intense all over the region and constitute potential diffuse source of pollution for both groundwater and surface water. Discharges from treatment plants contribute to the river nitrogen loads. In 2002 the entire region was declared Vulnerable Zone according to the Nitrates Directive (91/676/EEC). The Nitrates Directive defines a Vulnerable Zone as an area of land that drains into waters containing more than 50 mg/l nitrates. In these areas good agricultural practices are required to contain nitrogen loss in water. The plains near the sea (Felland) lie almost below sea level. They are drained and most of the channels are artificial. Since data was not available, this area was not included in the present study.

Model parameterisation

In order to perform the model parameterisation, spatially referenced data of nitrogen sources and physic and climatic basin characteristics were processed by ArcView GIS 3.2 and some of its extensions (Olivera et al.,1998). 50 quality stations were selected, distributed over the region, for which time-series of flow and nitrate concentration measured are almost complete. Missing flow data were interpolated. A digital elevation model of 100*100 m grid size was available. It was processed by the softwere CRWR-PrePro (Oliveira, 1998), subdividing the region into 50 sub-basins so that each sub-basin outlet coincided with a water quality stations. For each sub-basin the annual value of nitrogen agricultural input and point discharges was computed using the inventories of sewage treatments plants and a 5*5km maps of artificial fertiliser and manure applications. Concerning the atmospheric deposition the average value of 10 kg N/ha/year (EMEP data) was used. A rainfall and a temperature gage were assigned to each sub-basin by the Thiessen polygon technique. 15 rainfall gages and 5 meteorological stations were available for the whole area. The average value of TWI, annual winter precipitations, degrees of temperature and low flow were computed for each sub-basin.

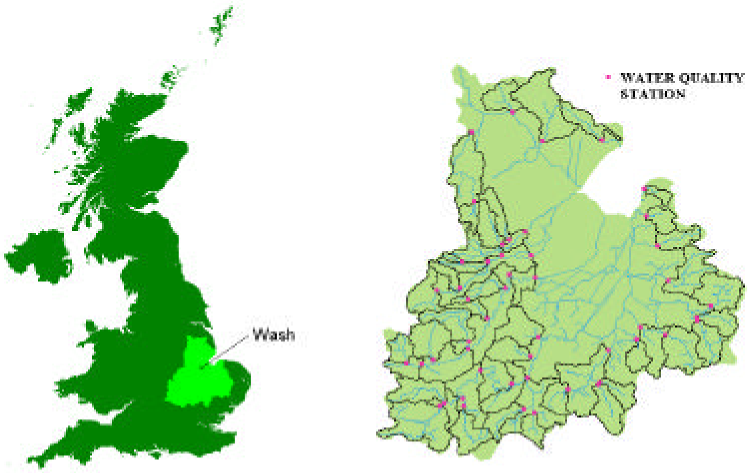


Figure 1. Location of the studied area.

Model calibration and validation

The estimation of mo del parameters was performed using the inverse modelling program UCODE (Poeter and Hill,1998). The parameter optimisation is achieved by minimising a weighted least-squared objective function using a modified Gauss-Newton method. The initial parameter values can influence the optimisation results, sometimes inducing convergence towards the closest local minimum. In order to avoid the influence of initial parameter values and the risk of a solution corresponding to a local minimum, a MonteCarlo approach was adopted. The MonteCarlo analysis consisted in performing 300 times the model calibration, by UCODE, using an initial set of parameter values extracted randomly from a given interval. The 300 sets of optimised parameters tend to concentrate in a unique interval of values, indicating an absolute minimum. The values of optimised parameter set are reported below.

Parameter	α_P	α_T	α_B	α_Q
Optimal value	3.29	0.28	0.77	3.96

The model was calibrated over a period of 5 years from 1995 to 1999. Then the model was validated over the period from 1990 to 1994. The lower number of points of validation, 67 compared to 248 of calibration, is due to missing data in time series, which prevented from including all sub-basins in each year of validation.

RESULTS AND DISCUSSION

Model performance

The Figure 2 shows the predicted nitrate loads versus the measured loads for calibration and validation. Several statistics of goodness of fit are reported in Table 1 to show the model performance. Values of the Nash-Sutcliffe coefficient (Nash and Sutcliffe, 1970) close to 1 indicate a good agreement between observed and predicted values. The higher value of the Nash-Sutcliffe coefficient for validation than for calibration can be explained by data accuracy. In fact, in validation only sub-basins with complete flow time-series were considered, and no flow data were interpolated. The modified Nash-Sutcliffe coefficient (Legates and McCabe, 1999) was reported, as it is less sensitive to extreme values. The model does not show any tendency to overestimation or underestimation as the mean bias is close to zero, both for calibration and validation. According to Willmott (1984) the Root Mean Squared Error (RMSE) can be subdivided into systematic ($RMSE_S$) and unsystematic ($RMSE_U$) Root Mean Squared Error, and the proportion between the two components $RMSE_S^2$ and $RMSE_U^2$ can be helpful in detecting model errors. $RMSE_S$, which indicates a systematic model error, should be relatively small, while the $RMSE_U$ should approach the total RMSE (Willmott, 1984). In the present study the proportion of $RMSE_U^2$ represents 91% and 87% of the $RMSE^2$ for calibration and validation respectively. According to goodness of fit statistics the model thus shows a good agreement between observed and predicted values, without significant model tendencies and systematic errors.

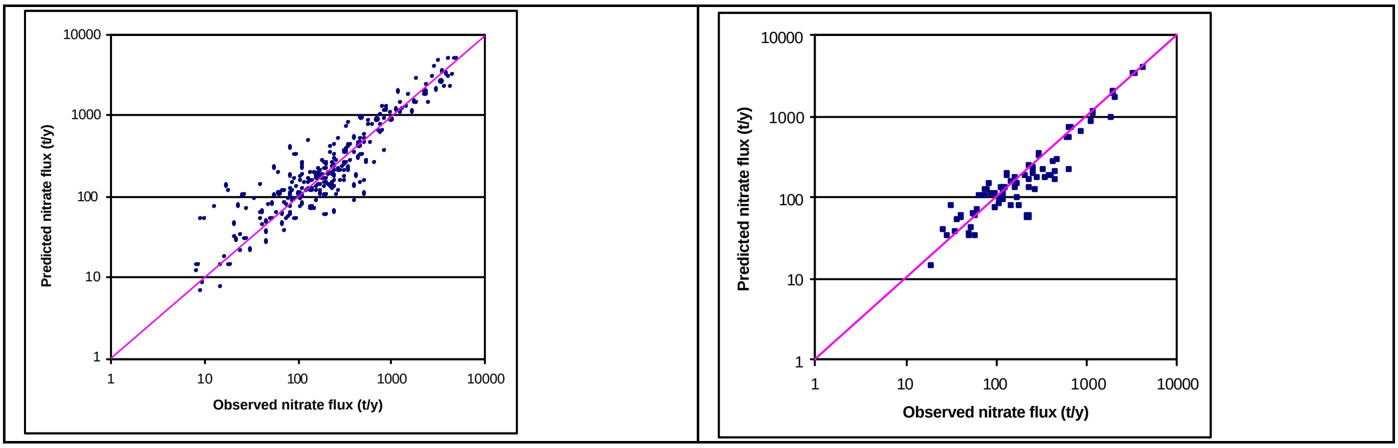


Fig.2. Predicted nitrate loads versus the measured loads for calibration (right) and validation (left).

Table 1. Goodness of fit statistics of calibration and validation.

Goodness of fit statistic	Calibration	Validation
Number of observations	248	67
Bias (t/y)	0.07	0.76
Proportion of unsystematic root mean squared error	0.91	0.87
Nash-Sutcliffe coefficient	0.72	0.81
Modified Nash-Sutcliffe coefficient	0.87	0.96

Spatial and temporal distribution of nitrogen removal

Once the model was calibrated, a weighted average of Basin and River Reducing Factors were computed allowing an estimation of basin and river retention (Tab.2). In the present study retention is defined as sum of permanent and temporary removal of nitrogen. In the studied area nitrogen delivered by fertiliser application and atmospheric deposition is reduced by 94% before reaching the stream. In surface waters, 6% of the nitrogen originating from diffuse emissions or direct discharges is retained. Annual variation of nitrogen retention is influenced by climatic conditions, especially precipitations (Fig.3 and 4). Basin retention decreases when winter rainfall increases, as it enhances nitrogen losses by surface runoff. The lowest value of basin retention occurs in 1998, the wettest year, while the highest value is recorded in 1997, the driest year. River retention is mostly connected to flow rate, decreasing when flow rate rises (Fig.3 and 4).

Table 2. Average basin and river nitrogen retention rate predicted by the model.

	Basin Retention %			River retention %		
Year	Weighted average	25th	75th	Weighted average	25th	75th
1995	94	93	95	6	3	11
1996	96	95	97	10	5	19
1997	97	96	97	7	3	10
1998	91	90	92	5	2	9
1999	94	93	95	4	2	6
Average	94			6		

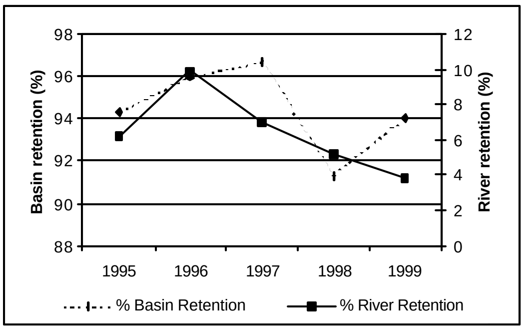


Figure 3. Annual basin and river nitrogen retention.

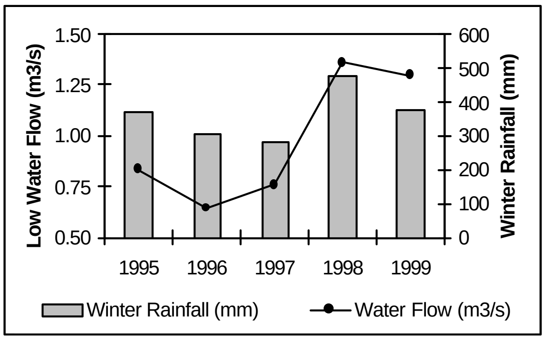


Figure 4. Annual average winter rainfall and water low flow.

The model provides an annual estimation of basin and river retention for each sub-basin, allowing a spatial distribution of retention values. In general basin retention declines with increasing slope (significance p<0.02), as runoff generation is enhanced. Nitrogen delivered by agriculture to river was estimated considering fertiliser application and basin retention rate. Maps of diffuse emission pressure were established, according to the model predictions, in order to identified areas more prone to nitrogen losses (Figure5).

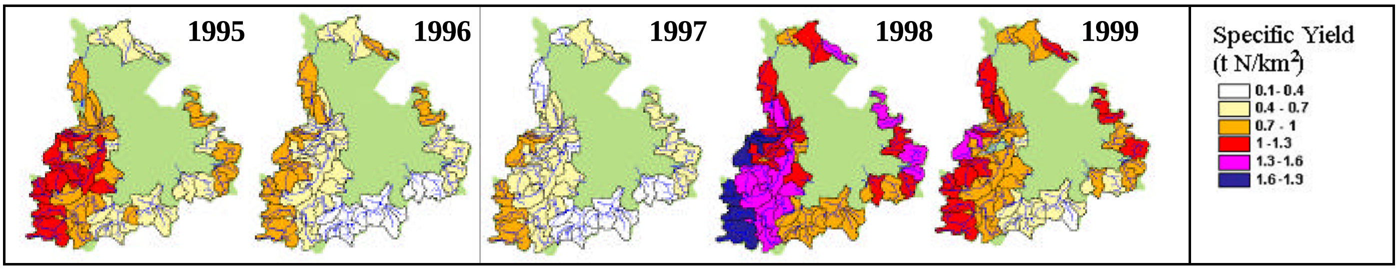


Fig.5. Spatial distribution of nitrogen specific yield.

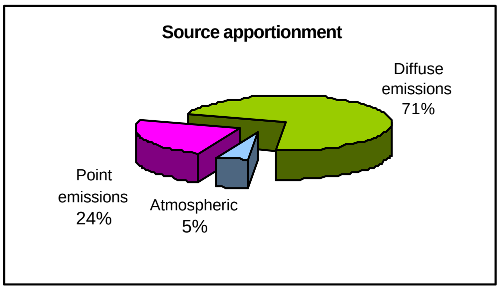
Concerning the river retention rate, the higher values occur especially in up-stream sub-basins. This is probably explained by the influence of channel size on in-stream nitrogen loss. Alexander et al. (2000) found a systematic decline in the rate of nitrogen removal from small streams to large rivers. Nitrogen removal by denitrification and settling decreases in deeper channels where exchange of stream waters with benthic sediments is reduced. At the basin scale, channel depth increases in downstream direction. River retention rate is directly related to slope (significance $p<0.01$), as in up-stream sub-basins slope is higher.

Source apportionment

The source apportionment of in-stream nitrate load was computed as surface weighted average of model estimated nitrogen source contribution at the 50 quality stations, during the period 1995-1999 (Table 3). Agriculture contributes to around 71% of the nitrogen load, and point discharges and atmospheric deposition account for 24% and 5% respectively. The Table 3 shows source apportionment values estimated according to the different river basins. The contribution of sewage discharges compared to agriculture is higher in areas belonging to the Great Ouse and Nene river basins than those of the Welland and Witham river basins, while atmospheric deposition has almost the same influence.

Table3. Source apportionment of in-stream nitrate load according to different basins.

River basin	Fertiliser	Sewage Works	Rainfall
Great Ouse	0.66	0.30	0.05
Nene	0.66	0.29	0.05
Welland	0.83	0.11	0.05
Witham	0.84	0.10	0.06
Partney Lymn	0.94	0.00	0.06
Babingly Brook	0.92	0.01	0.07
Heacham Stream	0.94	0.00	0.06
All studied area	0.71	0.24	0.05



CONCLUSION

The model was shown to be an attractive management tool, which allows estimating the contribution of each source to total nitrogen export, considering the role of retention in soil and in water. The model is able to represent the spatial and temporal variability of nitrogen retention, considering only four parameters: precipitations, temperature, topography and water flow. The interpretation of the physical meaning of model parameters allows a global estimation of nitrogen removal in soils and waters, without claiming to give a detailed quantification of physical processes involved. Moreover the model provides information about critical areas more prone to nitrogen losses.

REFERENCES

Alexander, R.B., Johnes, P.J., Boyer, E.W. and Smith, R.A., 2002. A comparison of modelsfor estimating the riverine export of nitrogen from large watersheds. Biogeochemistry, 57/58: 295-339.
Alexander, R.B., Smith, R.A. and Schwarz, G.E., 2000. Effect of stream channel size on the delivery of nitrogen to the Gulf of Mexico. Nature, 403: 758-761.
Beven, K.J. and FKirKby, M.J., 1979. A physically based, variable contributing area model of basin hydrology. Hydrol. Sci. Bull., 24 (1): 43-69.
Caracao, N.F. and Cole, J.J., 1999. Human impact on nitrate export: an analysis using major world rivers. Ambio, 28 (2).
European Community, 1991. Council Directive 91/676/EEC concerning the protection of waters against pollution caused by nitrates from agricultural sources. Official Journal L 375.
Germon, J.C., Pinochet, X. and Catroux, G., 1983. Relation between the kinetics of potential activity of denitrification and soil carbon, Third International Symposium on Microbial Ecology, East Lansing. Michigan, pp. 16 p.
Howarth, R.W. et al., 1996. Regional nitrogen budgets and riverine N & P fluxes for the drainages to the North Atlantic Ocean: Natural and human influences. Biogeochemistry, 35: 75-139.

Legates, D.R. and McCabe Jr, G.J., 1999. Evalueting the use of "goodness-of-fit" measures in hydrologic and hydroclimatic model variation. Water resour. res., 35 (1): 233-241.

Nash, J.E. and Sutcliffe, J.V., 1970. River flow forecasting through conceptual models. J. hydrol., 10: 282-290.

Olivera, F., 1998. CRWR-Prepro, 1998 ESRI User's Conference, San Diego, California.

Olivera, F., Maidment, D. and Reed, S., 1998. HEC-PrePro v. 2.0: An ArcView Pre-Processor for HEC's Hydrologic Modeling System, ESRI User's Conference, San Diego, California.

OSPAR Commission, 2000. Quality Status Report, 2000. Region II-Great North Sea, London.

Poeter, E.P. and Hill, M.C., 1998. Documentation of Ucode,A Computer Code for Universal Inverse Modeling. 98-4080, U.S. GEOLOGICAL SURVEY, Denver, Colorado.

Smith, R.A., Schwarz, G.E. and Alexander, R.A., 1997. Regional interpretation of water-quality monitoring data. Water resour. res., 33: 2781-2798.

Vitousek, P.M., Mooney, H.A. and Melillo, J.M., 1997. Human Domination of Earth's Ecosystems. Science, 277 (5325): 494.

Willmott, C.J., 1984. Spatial Statistics and Models. In: L. Gaile and C.J. Willmott (Editors), On the Evaluation of Model Performance in Physical Geography, Dordrecht, Holland, pp. 443-460.