EUROHARP 5-2004

Catchment Report:

Yorkshire-Ouse, England

Trend Analysis, Retention and Source Apportionment

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The Project: The EC funded EUROHARP project encompasses 22 research institutes from 17 European countries (2002-2005). The overall objective of the EUROHARP work is to provide end-users with guidance for an appropriate choice of quantification tools to satisfy existing European requirements on harmonisation and transparency for quantifying diffuse nutrient losses, e.g. to facilitate the implementation of the Water Framework Directive and the Nitrates Directive. The project includes both the assessment of the performance of individual models and the applicability of the same models in catchments with different data availability and environmental condition throughout Europe. The basis for the performance and applicability studies is the compilation of a harmonised GIS/database for all catchment data and the analysis of these data (trends, watercourse retention).

Key words: Nutrients. Trend analysis.Retention.Source apportionment. Diffuse losses. Water Framework Directive. Nitrates Directive.

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Executive Summary

The first primary objective of the EUROHARP project is to provide end-users (national and international European policy-makers) with a throrough scientific evaluation of nine contemporary quantification tools and their ability to estimate diffuse nutrient (N,P) losses to surface water systems and coastal waters, and thereby facilitate the implementation of the relevant policy instruments (eg. EC Water Framework Directive; EC Nitrates Directive). EUROHARP will contribute substantially to improve the comparability, transparency and reliability of the quantification of nutrient losses from diffuse sources, and thereby to improved efficiency of abatement strategies related to the implementation of e.g. the Nitrates Directive and the Water Framework Directive.

The Water Framework Directive and Nitrates Directive demand analyses of the main sources of nutrient pollution at the river basin scale. European River Basin District Authorities thus need tools for quantification of the discharges and losses from point and diffuse sources of nitrogen and phosphorus in catchments. Such tools could also be the combined trend analysis, nutrient retention and source apportionment, as described in this report. The report analyses nutrient pressures, nutrient retention and nutrient trends at the outlet station from the Yorkshire-Ouse catchment in England, applying standardised methodological approaches as described in four separate Annexes.

Kendall’s seasonal trend test with flow-adjustment reveals that the Yorkshire-Ouse experiences an upward non-significant trend for nitrate nitrogen concentrations and a downward significant trend for ammonium nitrogen concentrations during the period 1990-2000. Total reactive (molybdate) phosphorus concentrations experienced an upward significant trend during the period 1990-2000. The average annual nutrient retention in lakes and streams in the Yorkshire-Ouse catchment has been calculated at 1483 tonnes N and 5.36 tonnes P, applying the Tier 1 EUROHARP retention tool. The source apportionment was conducted on the entire catchment using data on point source discharges from 1989. Moreover, both the measured total reactive (molybdate) phosphorus load and a corrected total phosphorus load were used for source apportionment. Source apportionment showed that diffuse sources represent the main nutrient source in the catchment, contributing an average of 90% to dissolved inorganic nitrogen, 50% to total reactive phosphorus and 67% of estimated total phosphorus loads during the three-year period 1998-2000. The average losses of dissolved inorganic nitrogen, total reactive phosphorus and estimated total phosphorus from agricultural areas amounted to 36.1 kg N ha^{-1}, 0.23 kg P ha^{-1} and 0.78 kg P ha^{-1} respectively, during the period 1990-2000.

1. Introduction

Identification of pressures and assessment of impacts in River Basins is the first task in the implementation of the EU Water Framework Directive (WFD) to be completed before 22 December 2004. Member States shall collect and maintain information on the type and magnitude of significant anthropogenic pressures on water bodies leading to ecological impacts. Among these pressures are the diffuse losses of nutrients. Excess nutrient loadings into rivers, lakes, reservoirs and estuaries lead to eutrophication which, through algae growth, can severely impact freshwater and marine ecosystems.

The River Basin District Authorities (RBDA) have to conduct an analysis for each catchment, based on existing data on catchment characteristics such as land use, pollution sources and on water monitoring data. Such an analysis can be performed in a stepwise manner following for example the DPSIR concept, see diagram below.

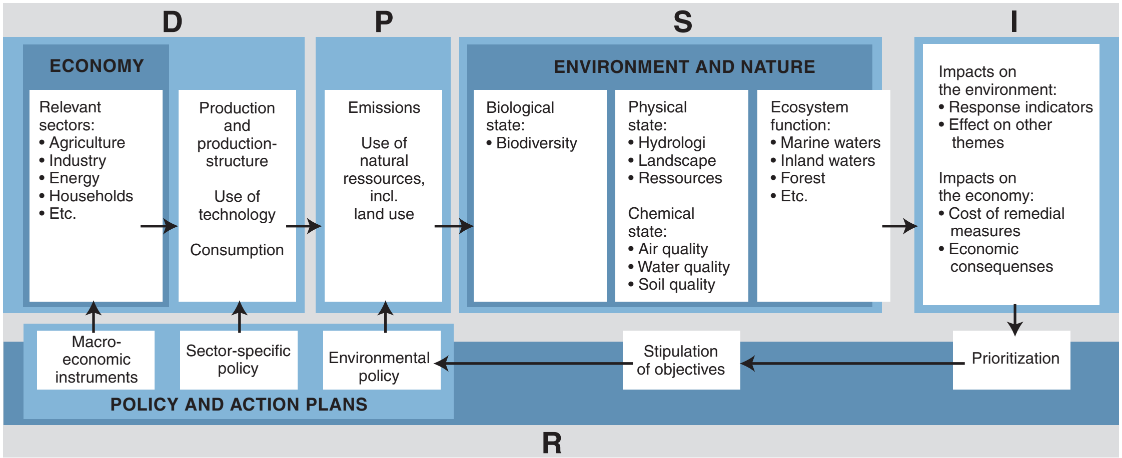

Diagram of the DPSIR concept

In the case of nitrogen and phosphorus, the RBDA will have to analyse existing monitoring data in water bodies for trends, and investigate the main nutrient pressures by conducting a source inventory quantifying the importance of the main nutrient sources, viz:

- Point sources, such as waste water discharges from wastewater treatment plants, industrial plants, scattered dwellings and fish farms.
- Diffuse sources, such as background nutrient loses, nutrient losses from agricultural activities, atmospheric deposition of nutrients and nutrient losses from forestry.

The information gathered on pressures and their impacts should be used in deciding environmental objectives for the water bodies and in the development of River Basin Management Plans. The quantitative aspect is important, especially to evaluate the precise needs for pollution control to make each water body meet its environmental objectives.

Most of the required WFD activities mentioned above depend on a detailed knowledge of the anthropogenic pressures and their impacts on the aquatic ecosystems. This knowledge is acquired mainly through the existing monitoring programmes implemented for the aquatic ecosystems and for the most important pressures.

The RBDA have to fulfil the requirements of monitoring of surface and groundwaters under the WFD by establishing a monitoring network designed to provide a coherent and comprehensive overview of the ecological and chemical status within each river basin. The WFD includes three different monitoring programmes: surveillance monitoring, operational monitoring and investigative monitoring. The monitoring programmes should be tailor-made according to the information required and the problem to be solved. The WFD monitoring programmes have to be implemented by 22 December 2006.

Following the pressure/impact analysis and the implementation of the WFD monitoring programmes, the RBDA shall ensure that a river basin management plan is produced for each basin before 22 December 2009.

The information contained in this Catchment Report results from EUROHARP, Work Package 5 activity on analysing existing catchment data following the DPSIR concept. The following three EUROHARP tools have been applied:

- Trend analysis of flow and nutrient concentration data (see Annex 3).
- Source Apportionment of nutrient sources (EUROHARP QT9) (see Annexes 1 and 2).
- Nutrient retention estimates for streams, rivers, reservoirs and lakes by applying the EUROHARP quantification tool for retention in surface waters (see Annex 4).

2. Driving Forces in theYorkshire-Ouse Catchment

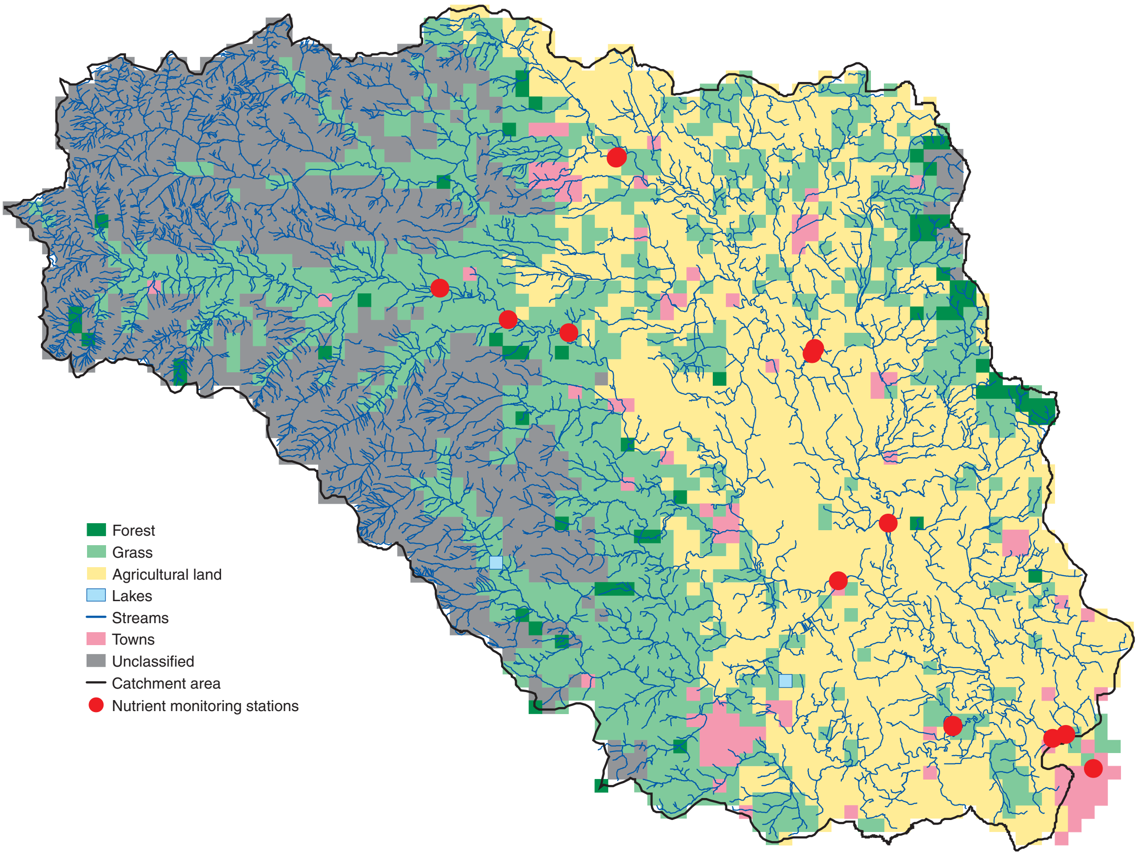

Figure 1: Map showing land use and river network characteristics for the Yorkshire-Ouse catchment, Norway, and existing water quality monitoring stations in the catchment.

Main characteristics of the catchment:

Catchment area:	3314 km^2
Precipitation:	923 mm
Land use:	Dominantly grassland and arable land

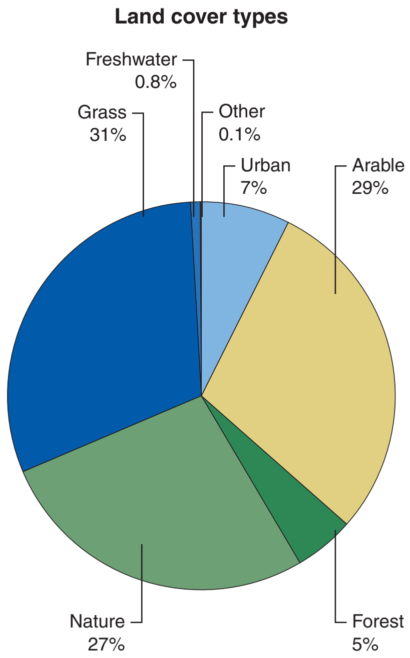

Figure 2: Main land use classes in the Yorkshire-Ouse catchment.

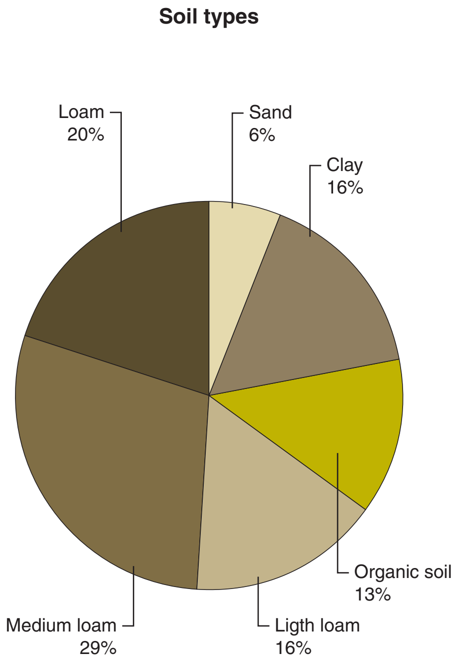

Figure 3: Main soil types in the Yorkshire-Ouse catchment.

Soil types:	Predominantly loamy soils	
Population:	323,000 inhabitants	
Number of WWTP's:	39 plants	
Livestock:	355,000 cattle, 472,000 pigs, 1,326,000 sheep, 2,021,000 poultry	
Agricultural land:	1995 km^2 (arable land and intensive grassland)	
Fertiliser use:		
<u>Winter wheat</u>		
Chemical (year 2000):	193 kg N ha^{-1}	29.7 kg P ha^{-1}
Manure (year 1995):	36.7 kg N ha^{-1}	13.4 kg P ha^{-1}
<u>Winter barley</u>		
Chemical (year 2000):	146 kg N ha^{-1}	27.9 kg P ha^{-1}
Manure (year 1995):	36.7 kg N ha^{-1}	13.4 kg P ha^{-1}
Number of lakes < 5 ha:	0	
Number of lakes > 5 ha:	24	
Stream network density:	1.39 km km^{-2}	

3. Analysis of Nutrient Pressures

3.1 Point sources

Point sources in the Yorkshire-Ouse catchment include:

- Waste Water Treatment Plants (WWTPs).
- Discharges from industrial plants.

The annual discharge of total nitrogen and total phosphorus from WWTPs is shown in Figure 4. However, the most recent data reported is from 1989.

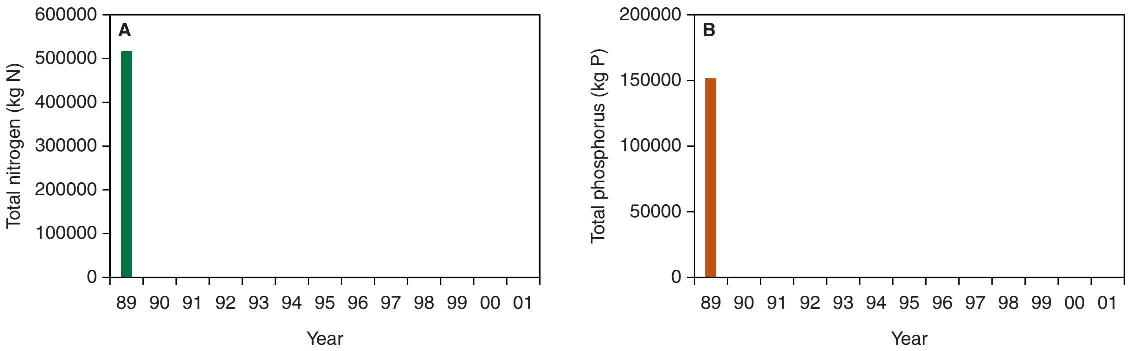

Figure 4: Annual discharge of total nitrogen and total phosphorus from WWTPs in the Yorkshire-Ouse catchment.

3.2 Background yields of nutrients

Table 1 show estimated average annual background losses of total nitrogen and total phosphorus applied for the Yorkshire-Ouse catchment.

Table 1: Average annual background export coefficients of total nitrogen and total phosphorus.

	Export coefficient
Total nitrogen	1.7 kg N ha^{-1}
Total phosphorus	0.06 kg P ha^{-1}

3.3 Catchment hydrology and losses of nitrogen and phosphorus

Discharge and nutrient transport data for the monitoring station at the catchment outlet (station name: Nether Popplleton: water chemistry and Skelton: discharge) has been reported for the period 1990-2000. The method applied for transport estimation is described in Annex 1.

The runoff, dissolved inorganic nitrogen transport, total reactive (molybdate) phosphorus and estimated total phosphorus transport vary considerable from year to year, depending especially on the annual climate (Fig. 5). Total phosphorus transport was estimated from calculated total reactive P-loss (TRP) by conversion of TRP first to dissolved reactive P (DRP) (conversion factor TRP/DRP=0.92) followed by conversion of DRP to total P (conversion factor TP/DRP=1.51).

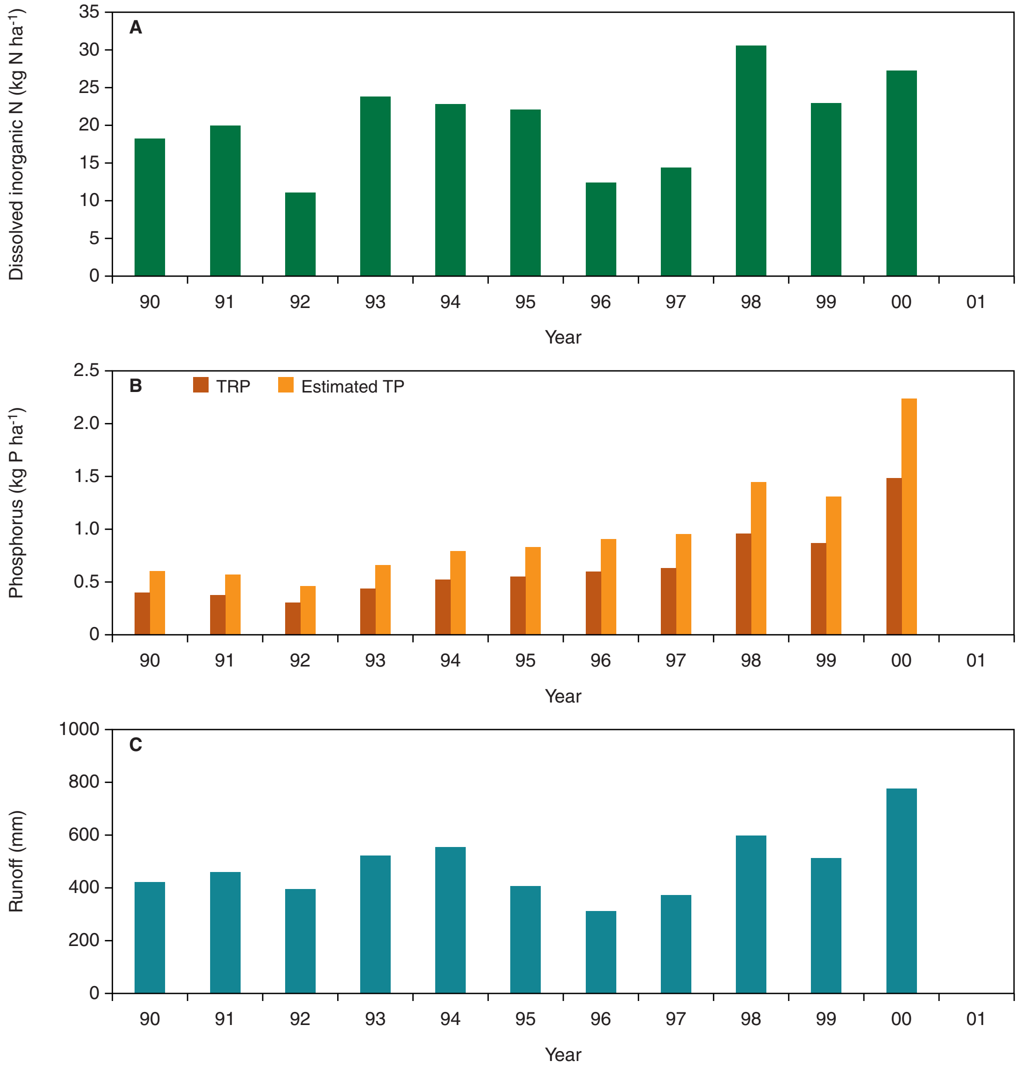

Figure 5: Annual runoff and losses of total nitrogen and total phosphorus from the catchment.

Annual average runoff (1990-2000):	410 mm
Annual average dissolved inorganic nitrogen loss (1990-2000):	20.5 kg N ha^{-1}
Annual average total reactive phosphorus loss (1990-2000):	0.55 kg P ha^{-1}
Annual average estimated total phosphorus loss (1990-2000):	0.98 kg P ha^{-1}

3.4 Nutrient retention in the catchment

Nutrient retention estimates with the EUROHARP Nutrient Retention Tool include the processes of denitrification and sedimentation in surface water bodies in the catchment. The Retention Tool operates at catchment scale and its application produces quantitative estimates of longer-term annual permanent nutrient retention (see Annex 4). The nutrient retention estimate does not comply to a specific year (dry/wet), but is expressed as an average annual estimate of the retention capacity in a specific catchment. A comprehensive description of the Nutrient Retention Tool regarding input data needs and retention rates and models will be developed and presented as a Handbook at a later stage in the EUROHARP project.

The Retention Tool requires descriptive information on water bodies in the catchment. Specific hydromorphologic information is needed for all lakes and reservoirs larger than 5 hectares. Moreover, information on total area of lakes < 5 ha, total areas of streams < 6 m and total areas of rivers > 6 m is required.

Input data for nutrient retention calculation about streams, reservoirs and lakes, and the resulting average annual nutrient retention in the Yorkshire-Ouse catchment is shown in Tables 2-4. The retention calculation for the Yorkshire-Ouse Catchment was conducted by applying a combination of the Tier 1 and Tier 3 retention tool, the latter being used for the large lake in the lower part of the catchment.

Information on water bodies in Yorkshire-Ouse, England
There are 24 reservoirs in the catchment.

Table 2: Length and estimated areas of streams and rivers.

Watercourses	Length	Area
Streams: < 6 m wide	3819 km	611 ha
Rivers: > 6 m wide	780 km	906 ha
Total	4599 km	1517 ha

Table 3: Number and areas of lakes and reservoirs in the river network.

Lakes	Number	Area
1-5 ha	0	
5-20 ha	14	122.2 ha
20-100 ha	9	272.3 ha
> 100 ha	1	126.1 ha
Total	24	520.6 ha

Nutrient retention estimates

Table 4: Long term annual nitrogen and phosphorus retention in water bodies for the entire catchment.

Water body type	Total nitrogen	Total phosphorus
Streams: < 6 m wide	513 t N	-
Streams: > 6 m wide	761 t N	2.492 t P
Lakes & reservoirs: > 5 ha	208 t N	2.864 t P
Lakes & reservoirs: < 5 ha	0 t N	0 t P
Total	1483 t N	5.357 t P

3.5 Source Apportionment of Nutrient loads

A source apportionment has been conducted on the annual nutrient export from the catchment, taking into consideration the average annual calculated nutrient retention in surface waters during the period 1990-2000 (Fig. 6). However, discharges of nutrients from point sources were only given for the year of 1989. Any trends in the discharge of nutrients from point sources during the 1990'ies will therefore greatly influence the results presented in Fig. 6. Moreover, point source discharges of nutrients are reposted as total N and total P, whereas measured nutrient concentrations and estimated loads in the river are as dissolved inorganic N and total reactive (molybdate) P (TRP). Applying the source apportionment method on the catchment (described in Annex 2) will therefore espicially for phosphorus create erronomous results. This is also seen in Fig. 6B where the P-loss from agricultural land becomes negative. The transport of TRP has been converted to total P (TP) and applying TP in the source apportionment produces more realistic losses from agricultural land (Fig. 6C).

The main nutrient pressures in the catchment can be identified from Figure 6.

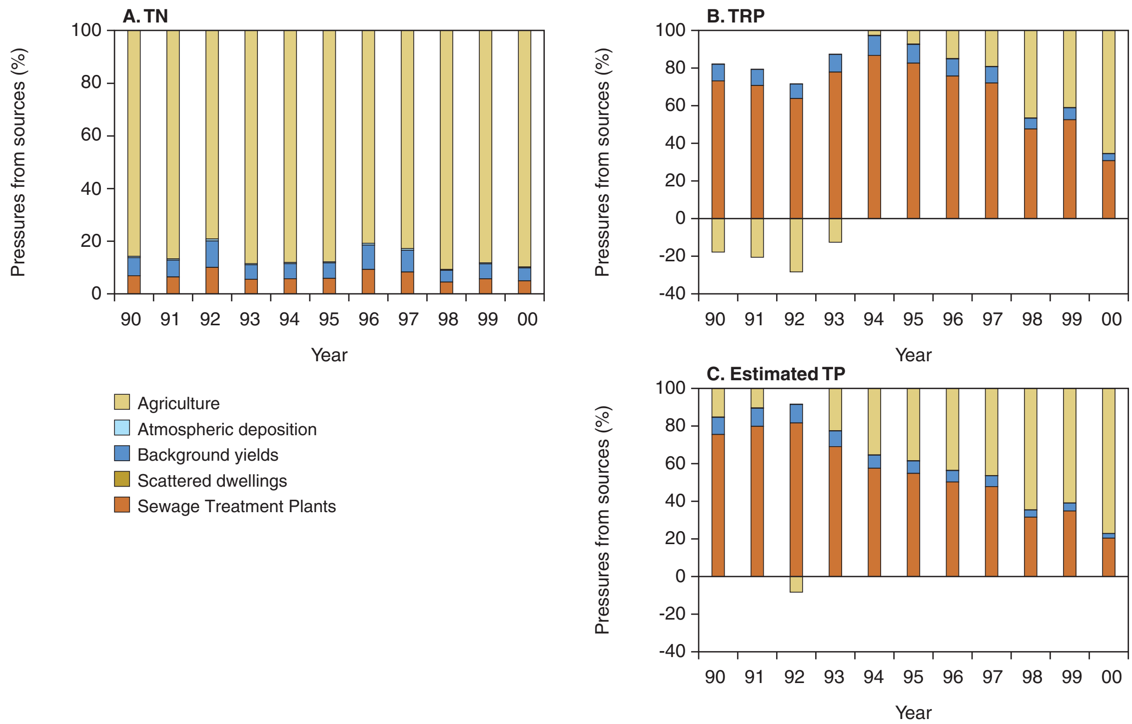

Figure 6: Source apportionment of annual dissolved inorganic nitrogen, total reactive (molybdate) phosphorus and estimated total phosphorus exports from the catchment.

The diffuse losses of total nitrogen, total reactive (molybdate) P and estimated total phosphorus from agricultural land in the catchment are shown in Figure 7. The diffuse loss of phosphorus from agricultural land is estimated based on both the measured total reactive (molybdate) phosphorus concentrations and loads (Fig. 7B) and the estimated total phosphorus loads (Fig. 7B).

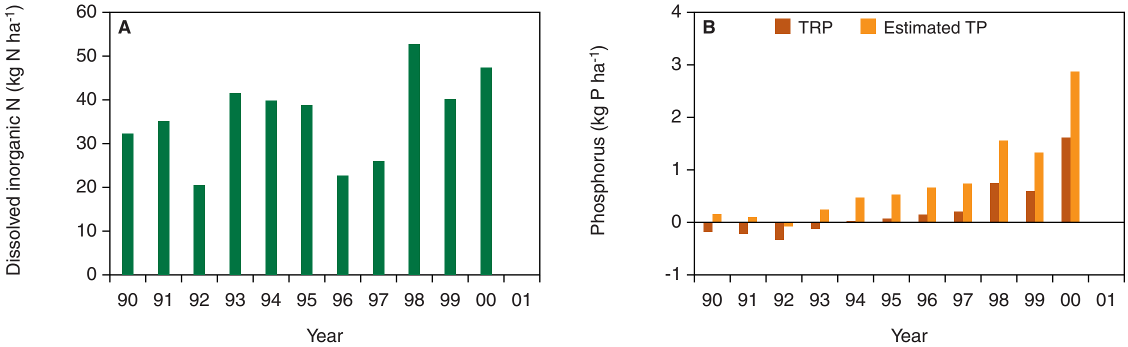

Figure 7: Annual diffuse losses of dissolved inorganic nitrogen, total reactive (molybdate) phosphorus and estimated total phosphorus from agricultural land within the catchment.

Average annual dissolved inorganic nitrogen loss from agricultural land: 36.1 kg N ha^{-1}

Average annual total reactive (molybdate) P loss from agricultural land: 0.23 kg P ha^{-1}

Average annual total phosphorus loss from agricultural land: 0.78 kg P ha^{-1}

4. Analysis of Nutrient State

The time series of flow and nitrogen and phosphorus concentrations from the monitoring station at the catchment outlet have been analysed for trends, applying Kendall's seasonal test. Before applying the test, the measured concentrations were flow-adjusted applying a robust curve fitting procedure (see Fig. 14). The statistical procedures are described in Annex 3.

The seasonal variations of runoff, nitrate (NO3-N), ammonium (NH4-N) and total reactive (molybdate) phosphorus concentration are shown in Figure 8. The time series of nitrate (NO3-N), ammonium (NH4-N) and total reactive (molybdate) phosphorus at the catchment outlet are shown in Figures 9-11. The time series of ammonium nitrogen and total reactive (molybdate) phosphorus show homogenous trends (Table 5). An upward trend was detected for nitrate nitrogen (*P*=20%). The mean annual trend was estimated to 0.045 mg N l^{-1} for the period 1990-2000. A significant downward trend was established for ammonium nitrogen (*P=0.76%*), whereas a significant upward trend was established for total reactive (molybdate) phosphorus (*P*=1.2%). The mean annual trend was estimated to –0.006 mg N l^{-1} in the case of ammonium-N and 0.010 mg P l^{-1} in case of total reactive P for the period 1990-2000. No significant trend was identified for the runoff measurements (Fig. 12).

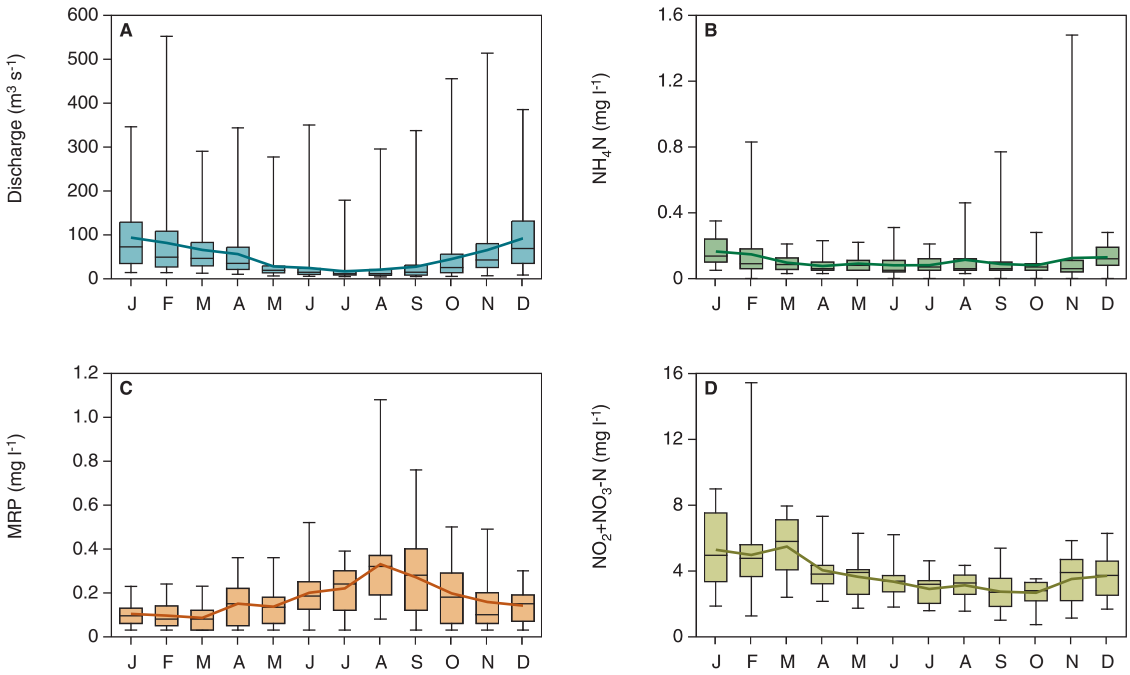

Figure 8: Box-Whisker plots showing the variation in runoff, nitrate-N (NO3), ammonium-N (NH4) and total reactive (molybdate) phosphorus (MRP) concentrations in the catchment.

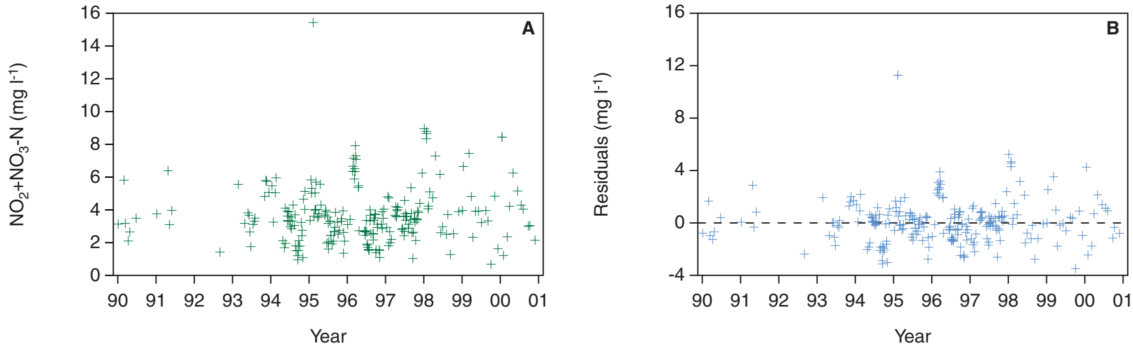

Figure 9: Time series of concentrations of nitrate-N (NO3) and the flow-adjusted concentrations (residuals) during the period 1990-2000. Average concentration of nitrate nitrogen is 3.63 mg l^{-1} (CV=48%).

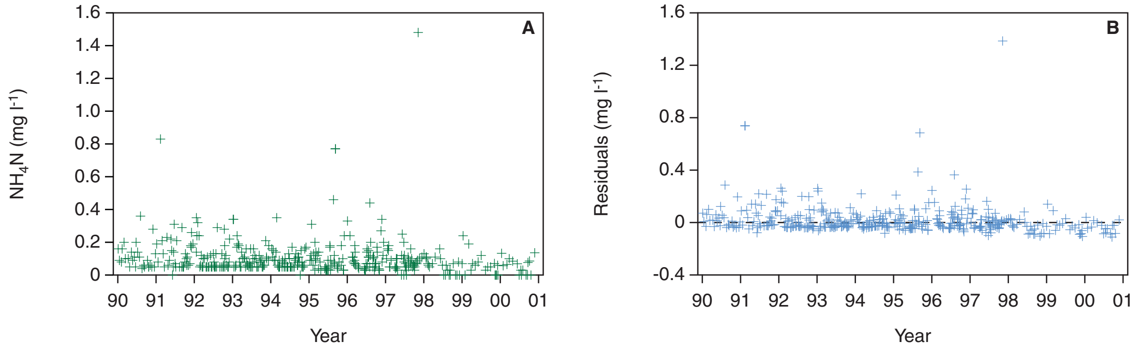

Figure 10: Time series of concentrations of ammonium-N (NH4) and the flow-adjusted concentrations (residuals) during the period 1990-2000. Average concentration of ammonium-N is 0.11 mg l^{-1} (CV=103%).

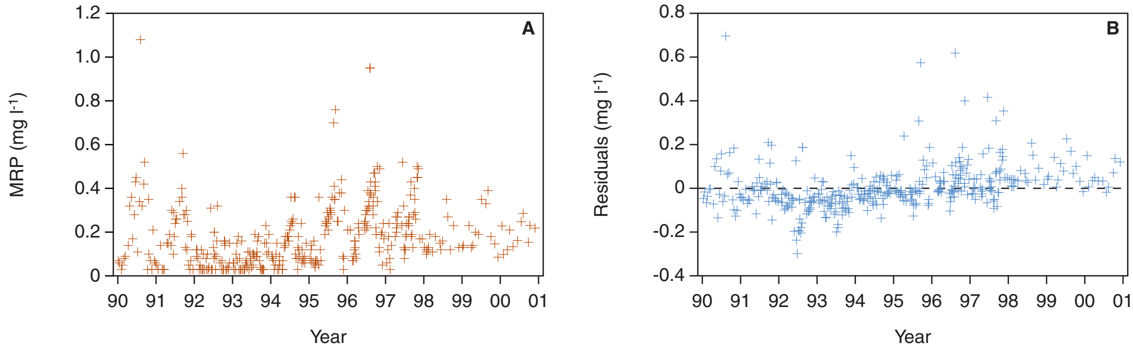

Figure 11: Time-series of flow-adjusted concentrations of total reactive (molybdate) phosphorus and the flow-adjusted concentrations (residuals) during the period 1990-2000. The average concentration of total reactive phosphorus is 0.18 mg l^{-1} (CV=78%).

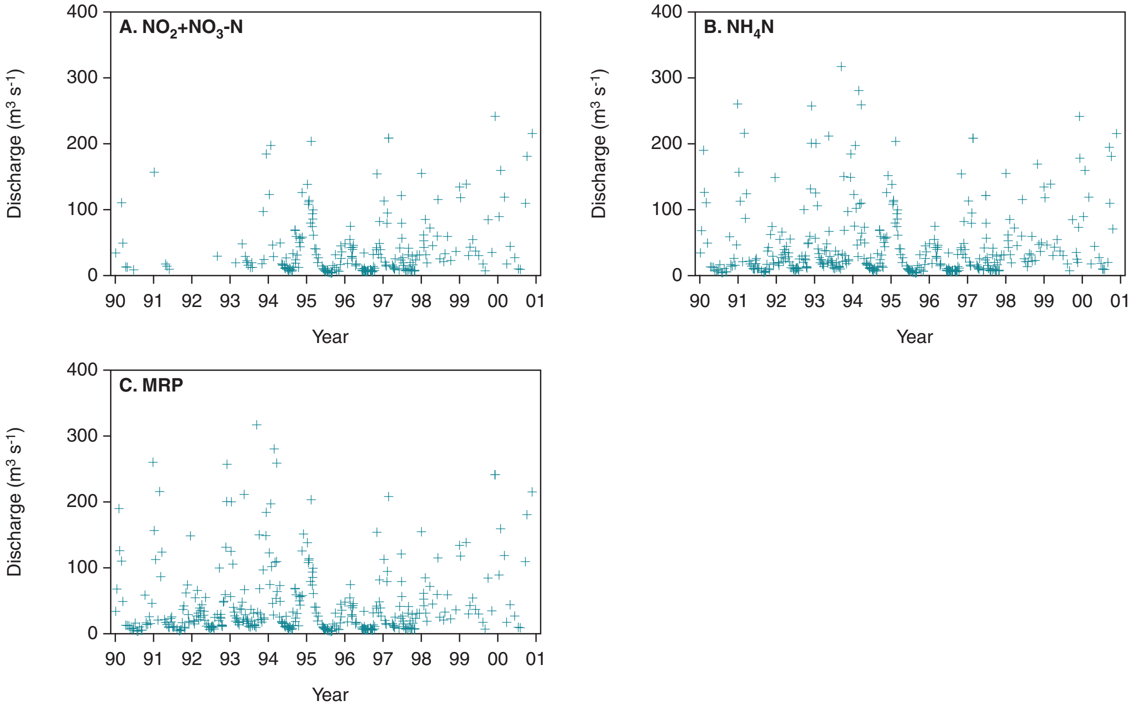

Figure 12: Mean daily discharge at the days of water sampling during the period 1988-2000. Figure 11A shows discharge at measurement days for nitrate-N, Figure 11B discharge for measurement days for ammonium-N and Figure 11C discharge for measurements days for total reactive phosphorus.

Tabel 5: Results from Kendall's seasonal trend analysis together with slope estimates and 95% confidence limits for these estimates.

	Test of homogeneity	Test probability (%)	Test statistic (Z)	Test probability (%)	Slope estimate	95%-confidence limits for slope
Runoff [$l\ s^{-1}$] (nitrate)	10.3	50	1.29	20	2.12	[-1.14;5.73]
Nitrate nitrogen [$mg\ l^{-1}$]	10.2	51	1.28	20	0.045	[-0.031;-0.150]
Runoff [$l\ s^{-1}$] (ammonium)	0	100	1.23	22	0.881	[-0.795;3.38]
Ammonium nitrogen [$mg\ l^{-1}$]	20.22	4.2	-2.67	0.76	-0.006	[-0.012;0.001]
Runoff [$l\ s^{-1}$] (phosphorus)	782	0	1.13	26	0.887	[-0.880;3.47]
Total reactive (molybdate) phosphorus [$mg\ l^{-1}$]	0	100	2.52	1.2	0.010	[0.003;0,019]

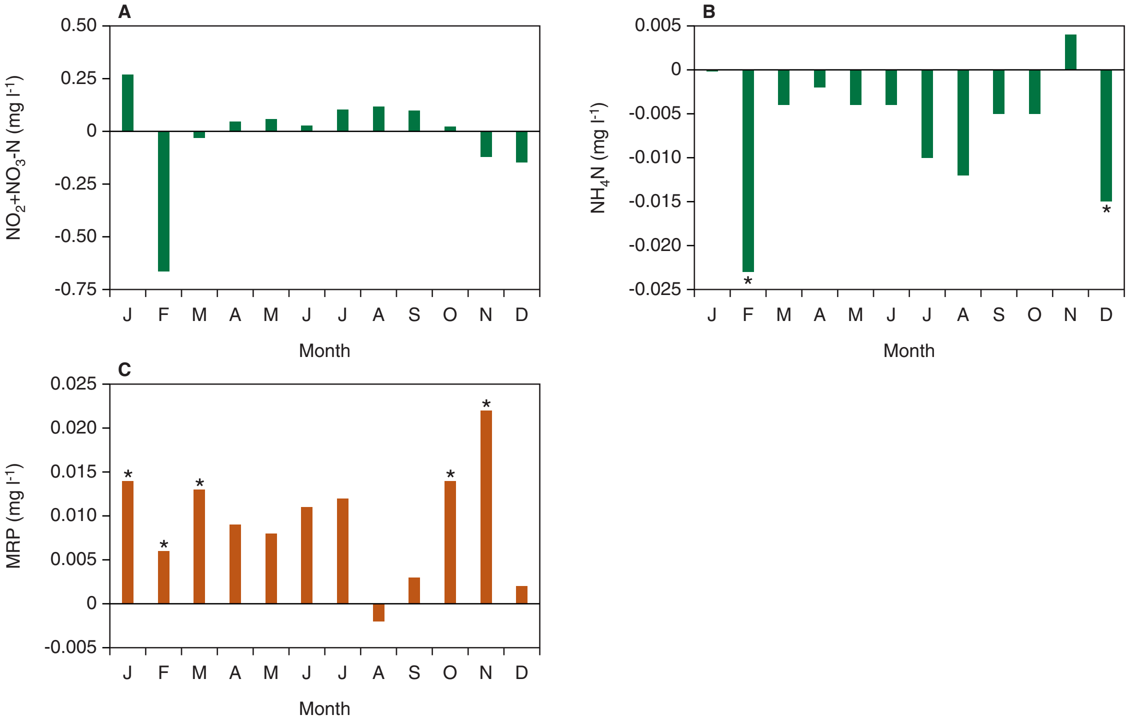

Figure 13: Monthly trend calculated on an annual basis in the concentration of nitrate nitrogen, ammonium nitrogen and total reactive (molybdate) phosphorus during the period 1990-2000. (*Significant at *P*=5%)

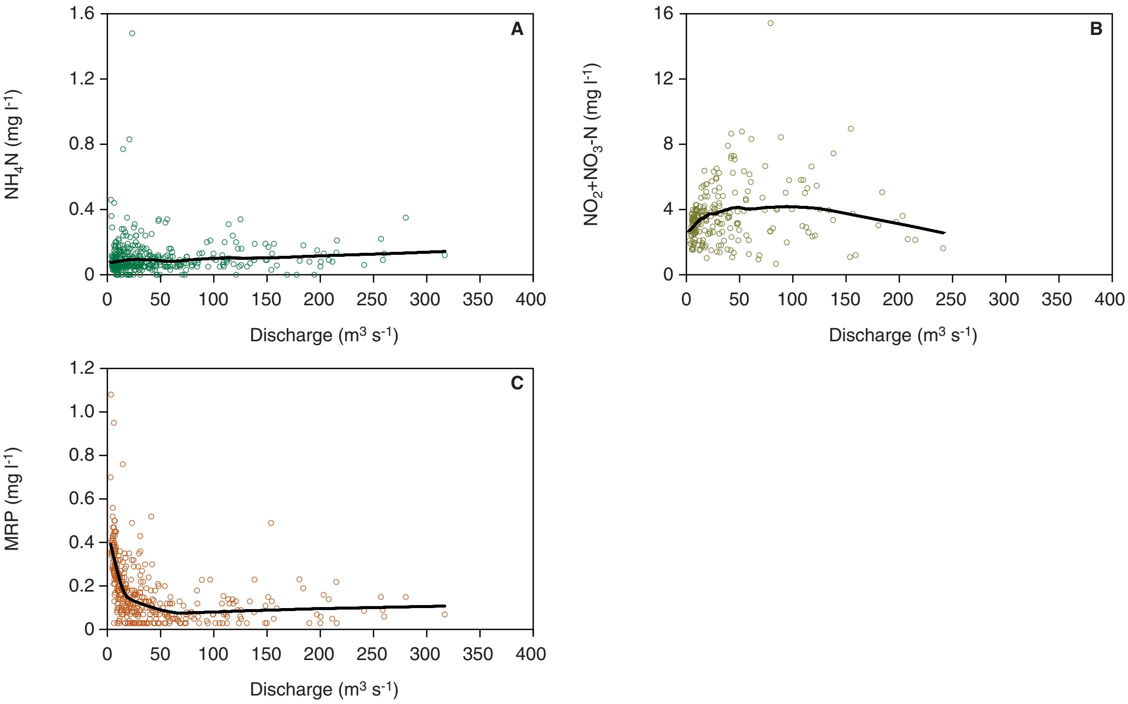

Figure 14: Relationships between discharge and concentrations of nitrate nitrogen, ammonium nitrogen and total reactive (molybdate) phosphorus, established applying the LOWESS fitting procedure (see Annex 3).

Annex 1: Methodology for Nutrient Transport Estimation

Determination of river transport (load) of nutrients is an integral component of monitoring programmes. The transport estimates are essential when establishing N and P mass balances for lakes and coastal waters, and in general for source apportionment.

The method used in the EUROHARP project for estimating transport on an annual basis is an interpolation method. It is assumed that concentrations of nutrients have been measured a number of times during a given year. Normally, the dates of measurement should be more or less evenly distributed in the given year. It is further assumed that daily runoff values exist for the selected measurement site. The method then utilise interpolated concentration values at days were nutrients have not been measured. The definition of the method is as follows.

The nutrient concentrations are measured at the days denoted by $t_i, i = 1,2,\ldots,n$. Concentrations are denoted $c_i, i = 1,2,\ldots,n$. Let t_0 and t_{n+1} be the start, respectively the end of the year. The assumption is made that $c_0 = c_1$ and $c_{n+1} = c_n$.

Then the transport is estimated by

$$\hat{L} = \sum_{i=0}^{n-1} \sum_{t_i < t \le t_{i+1}} q_t \frac{c_i \cdot (t_{i+1} - t) + c_{i+1}(t - t_i)}{t_{i+1} - t_i} \quad (1),$$

where

$\sum$: denotes summation, i.e.

$\sum_{i=0}^{n-1}$: denotes summation of values for the index in the interval 0 to *n-1*, and

$\sum_{t_i < t \le t_{i+1}}$: denotes summation of values for *t* in the interval t_i to t_{i+1}, but t_i is not included in the interval

t: denotes a day between two measurement days

q_t : is daily runoff for day *t*.

The assumption that $c_0 = c_1$ results in $c_{interpolated} = c_1, \text{ for } t_0 < t \le t_1$, and the assumption $c_{n+1} = c_n$ results in $c_{\text{interpolated}} = c_n$, for $t_n < t \le t_{n+1}$.

Concentrations are given in mg l^{-1}, runoff as l s^{-1}. To obtain a transport per day multiply the estimate by 0.0864.

The principle of estimating nutrient transport is shown in the following three figures.

Illustration of calculations:

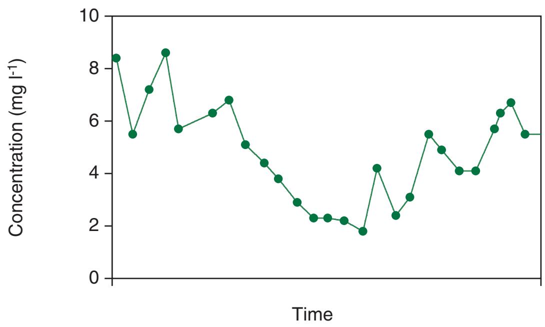

Figure 1: Measured concentrations and interpolated concentrations.

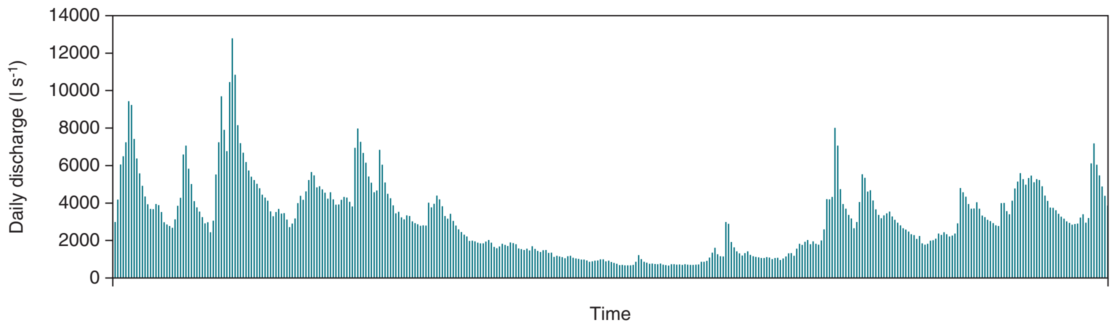

Figure 2: Daily runoff values.

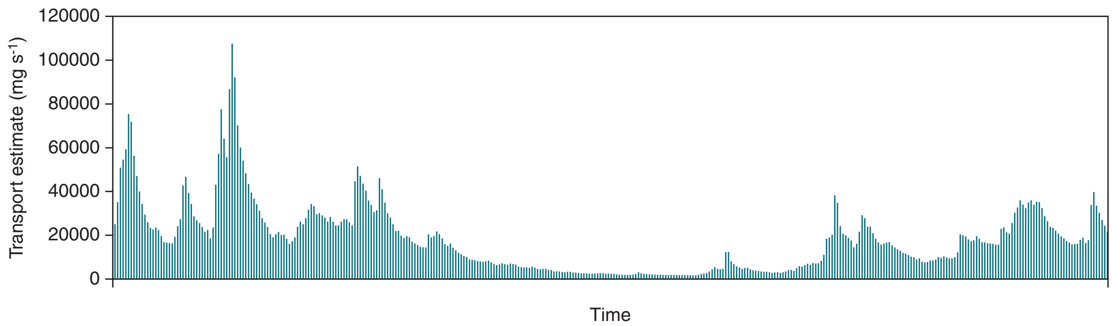

Figure 3: Daily estimated fluxes (product of runoff and estimated concentration).

Annex 2: Methodology for Source Apportionment

The source apportionment method is based on the assumption that the nutrient (total nitrogen or total phosphorus) transport at a selected river measurement site (L_{river}) represents the sum of the components of the nutrient discharges from point sources (D_P), the nutrient losses from anthropogenic diffuse sources (LO_D) and the natural background losses of nutrients (LO_B). Furthermore, it is necessary to take into account the retention of nutrients in the catchment after the nutrients have been discharged to surface waters (R). This may be expressed as follows:

$$L_{river} = D_P + LO_D + LO_B - R \quad (1)$$

The aim of the source apportionment is to evaluate the contributions of specific point and diffuse sources of nutrients to the total riverine nutrient load, i.e. to quantify the nutrient losses from diffuse sources (LO_D) as follows:

$$[LO_D = L_{river} - D_P - LO_B + R] \qquad (2)$$

The importance of the different sources may be expressed as:

$$\text{Proportion of } LO_B = (LO_B / L_{river} + R) \cdot 100\% \qquad (3)$$

$$\text{Proportion of } D_P = (D_P / L_{river} + \quad R) \cdot 100\% \qquad (4)$$

$$\text{Proportion of } LO_D = (LO_D / L_{river} + R) \cdot 100\% \qquad (5)$$

The method outlined above requires:
Measurements at the selected river measurement site in order to determine L_{river}, which represents the riverine transport. The riverine transport is the quantity of a determinant carried by a watercourse (natural river or man-made watercourse) per unit of time. The transport estimator applied is described in Annex 1.

Determinations of the nitrogen and phosphorus point source discharges (D_P) and natural background losses of nitrogen and phosphorus (LO_B) in the river catchment area concerned, as well as the quantification of the retention of nitrogen and phosphorus (R) in surface waters are needed. For this purpose, there are different methodologies available.

For most of the EUROHARP catchments there are more than one monitoring station and hence source apportionment can be performed for sub-catchments. Furthermore source apportionment is made on an annual basis at each site.

The anthropogenic diffuse nutrient loss from agricultural areas in the catchment can be estimated following equation 6:

$$[LO_{AG} = L_{river} - D_P - LO_B + R - LO_{AT} - LO_{SD}\ ] \ (6)$$

Where LO_{AG} is the anthropogenic loss of nutrients from agricultural areas entering surface waters; LO_{AT} is the nutrient load from atmospheris deposition directly on surface waters in the catchment and LO_{SD} is the nutrient load to surface waters from scattered dwellings in the catchment as defined in HARP Guideline 5 (WWW.EUROHARP.ORG).

Annex 3: Methodology for Trend Analysis

Trend analysis of time series of nutrient concentrations and runoff at river stations in the 17 European catchments was undertaken using Kendall's seasonal trend test with correction for serial correlation. This test is robust non-parametric site-specific statistical tests for monotone trends. It is robust towards missing values, values reported as "< detection limit", seasonal effects, autocorrelated measurements and non-normality (i.e. non-Gaussian data). The test was introduced in the papers Hirsch et al. (1982) and Hirsch and Slack (1984) and has become a very popular and effective method for trend analysis of water quality data. The statistical trend method can analyse both seasonal and annual data and provide a trend statistic, *P*-value and an estimate of the annual increase or decrease in nutrient concentrations.

A trend analysis starts with a time series plot (a graph showing observed concentrations versus time of observation) and a Box-Whisker plot (a graph showing the distribution of data for each calendar month). Such plots can give hints on possible trends, seasonality and extreme values.

Both total nitrogen and total phosphorus concentrations are highly depending on discharge. This substance-specific relationship can be modelled by the non-parametric and robust curve fitting method LOWESS (Locally Weigthed Scatterplot Smoothing, Cleveland, 1979). The nutrient concentrations must be adjusted for runoff in order to minimise the impact from climate and to prevent a deterioration of the trend detection thereby increasing the power of the test. To remove the effects of runoff calculate residuals, i.e.

$$r = x - \hat{x}_{(LOWESS)},$$

where $\hat{x}_{(LOWESS)}$ is the estimated concentration from LOWESS and x is the observed concentration. A time series plot of the residuals will reveal if the trend is still present in the adjusted values (residuals).

The trend method only operates with one value for each combination of season and year. Therefore an average value for the seasons with more than one observation is used. Let r_{ij} denote the average value of all adjusted measurements in year *i* and season *j*. It is assumed that there have been measurement in *n* years and *p* seasons, i.e. $i = 1,2\ldots,n$ and $j = 1,2,\ldots,p$. In EUROHARP applications the number of seasons *p* per year was set to 12 one for each month of the year. Some of the r_{ij} s can be missing if no measurement have been done in the relevant month and year.

The null hypothesis of the trend analysis is: for each of the *p* seasons the *n* data values are randomly ordered. The null hypothesis is tested against the alternative hypothesis: one or more of the seasons have a monotone trend. The trend test is done by calculating

$$S_g = \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} \operatorname{sgn}(r_{jg} - r_{ig}),$$

for $g = 1,2\ldots,p$, and where

$$\operatorname{sgn}(x) = \begin{cases} 1, & x > 0 \\ 0, & x = 0 \\ -1, & x < 0 \end{cases}.$$

If r_{jg} and/or r_{ig} is a missing value, then $\operatorname{sgn}(r_{jg} - r_{ig}) = 0$ per definition.

A combined test for all seasons (months) is done by first calculating

$$S = \sum_{g=1}^{p} S_g \ ,$$

and

$$\mathrm{var}(S) = \sum_{g=1}^{p} \mathrm{var}(S_g) + \sum_{g,h:g \neq h} \mathrm{cov}(S_g, S_h).$$

The variance for S_g under the null hypothesis can be calculated exactly by

$$\mathrm{var}(S_g) = \frac{n_g(n_g - 1)(2n_g + 5) - \sum_{j=1}^{m} t_j(t_j - 1)(2t_j + 5)}{18},$$

where n_g is the number of non-missing observations in season g. In the formula for the variance of S_g it is assumed that there are groups of observations with completely equal values, m groups in total and in the j th group there is t_j equal values.

It is not possible under the null hypothesis to calculate the covariance between S_g and S_h exactly, but it can be estimated by (Hirsch and Slack, 1984)

$$\mathrm{cov}(S_g, S_h) = \frac{K_{gh} + 4\sum_{i=1}^{n} R_{ig} R_{ih} - n(n_g + 1)(n_h + 1)}{3},$$

where

$$K_{gh} = \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} \mathrm{sgn}[(r_{jg} - r_{ig})(r_{jh} - r_{ih})],$$

and

$$R_{ig} = \frac{n_g + 1 + \sum_{j=1}^{n} \mathrm{sgn}(r_{ig} - r_{jg})}{2}.$$

The term R_{ig} is the ranking of x_{ig} amongst all observations in season g, and all the missing values get the value $(n_g + 1)/2$ as ranking.

The test statistic for the aggregate test is

$$Z = \begin{cases} \dfrac{S-1}{(\mathrm{var}(S))^{\frac{1}{2}}}, S > 0 \\ 0, S = 0 \\ \dfrac{S+1}{(\mathrm{var}(S))^{\frac{1}{2}}}, S < 0 \end{cases}.$$

The sign of Z indicates an increasing (+) or decreasing (-) trend. Both increasing and decreasing trends are interesting. The null hypothesis must be rejected if the numerical value of Z is greater than the $(\alpha/2)$-percentile in the Gaussian distribution with mean 0 and variance 1. Here α stands for the significance level, which typically is 5%. At the 5%-level all Z-values numerically greater than 1.96 are significant. The reason for evaluating Z in a Gaussian distribution is that under the null hypothesis, S has a Gaussian distribution with mean 0 and variance $\mathrm{var}(S)$ for $n \to \infty$. The Gaussian approximation is good if $n \geq 10$ (Hirsch and Slack, 1984). This means 10 years of data with one concentration measurement for each month.

The trend in each season can be tested by calculating

$$Z_g = \begin{cases} \dfrac{S_g-1}{(\mathrm{var}(S_g))^{\frac{1}{2}}}, S_g > 0 \\ 0, S_g = 0 \\ \dfrac{S_g+1}{(\mathrm{var}(S_g))^{\frac{1}{2}}}, S_g < 0 \end{cases}.$$

The null hypothesis of no trend is rejected if the numerical value of Z_g is greater than the $(\alpha/2)$-percentile in the Gaussian distribution with mean 0 and variance 1.

It is possible to calculate an estimate for the trend (a slope estimate) if one assume that the trend is constant (linear) during the period and the estimate is given as change per unit time (year). Hirsch et al. (1982) introduced Kendall's seasonal slope estimator, which can be computed in the following way. For all pair of residuals (r_{ij}, r_{kj}) with $j = 1,2\ldots,p$ and $1 \leq k < i \leq n$ calculate

$$d_{ijk} = \frac{r_{ij} - r_{kj}}{i - k}.$$

The slope estimator is then the median of all d_{ijk}-values and is robust, if the time series has serial correlation, seasonality and non-Gaussian data (Hirsch et al., 1982). A slope estimate for each season can be calculated in the same way.

A $100(1-\alpha)$% confidence interval for the slope can be obtained by the following calculations

- Choose the wanted confidence level α (1, 5 or 10%) and use

$$Z_{1-\alpha/2} = \begin{cases} 2.576, \ \alpha = 0.01 \\ 1.960, \ \alpha = 0.05 \\ 1.645, \ \alpha = 0.10 \end{cases}$$

in the following calculations. For the EUROHARP application we use a confidence level of 5%.

- Calculate

$$C_\alpha = Z_{1-\alpha/2} \cdot (\mathrm{var}(S))^{\frac{1}{2}} .$$

- Calculate

$$M_1 = \frac{N - C_\alpha}{2},$$
$$M_2 = \frac{N + C_\alpha}{2},$$

where

$$N = \frac{1}{2}\sum_{g=1}^{p} n_g (n_g - 1).$$

- Lower and upper confidence limits are the M_1 th largest and $(M_2 + 1)$ th largest value of the N ranked slope estimates d_{ijk}.

Using the modified Van Belle and Hughes test for homogeneity (1984) one can test the homogeneity of the separate season trend test. This homogeneity test must be non-significant in order to use the combined trend test.

Time series of daily runoff values also has to be tested for trends. The same trend test as described above can be used on the measured runoff values. Slope estimates and confidence intervals are computed following the methods described above. If no significant trends are detected in the runoff time series, any significant trend in the concentration time series is said to be anthropogenic in arigin.

References

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Annex 4: Methodology for Nutrient Retention Calculation

A retention group under the EUROHARP project has developed a new tool for calculation of nitrogen and phosphorus retention in streams, rivers, lakes and reservoirs. The tool developed consists of different Tiers, where the demand of input data from the catchment increases wit each Tier. The tool has been developed based on a review of existing international literature and existing mass-balance data for a great number of lakes and reservoirs.

Tier 1
Nitrogen retention in streams and rivers is calculted by applying an average annual retention rate for total nitrogen on the calculated total surface area of streams and rivers in the entire river basin. Similarly, phosphorus retention is calculated by applying an average annual retention rate for total phosphorus on the riparian area (only 5% of total river width is estimated to be riparian area) of rivers being more than 6 m in width. Nitrogen and phosphorus retention in lakes and reservoirs is calculated by applying an average annual retention rate for the total area of lakes and reservoirs in the river basin.

Average annual nutrient retention rates in streams and rivers, and lakes and reservoirs.

Total Nitrogen	Average annual retention rates
Lakes and reservoirs	40 g N m^{-2} yr^{-1}
Streams and rivers	84 g N m^{-2} yr^{-1}
Total Phosphorus	
Lakes and reservoirs	0.55 g P m^{-2} yr^{-1}
Streams and rivers > 6 m width	5.50 g P m^{-2} yr^{-1}

Tier 2
Nutrient retention in lakes and reservoirs is calculated by applying average annual retention rates for total nitrogen and total phosphorus on the total area of lakes and reservoirs grouped into 5 classes having different hydraulic retention times.

Nitrogen and phosphorus retention in lakes having different hydraulic residence times (τ_W).

	Nitrogen retention		Phosphorus retention	
τ_W (years)	(mg N d^{-1})	(% of load)	(mg N d^{-1})	(% of load)
0.001-0.01	100	-	4.0	7
0.01-0.1	100 (30-200)	16	3.0 (1-9)	18
0.1-1	160 (50-300)	50	1.7 (0.5-4)	41
1-10	60 (10-120)	60	1.3 (0.2-3)	69
> 10	50	-	1.0	80

Tier 3

Nutrient retention in lakes and reservoirs is performed water body by water body by applying a nitrogen retention model incorporating depth and hydraulic residence time and a phosphorus model incorporation hydraulic residence time. Both models give the percentage retention of the incoming nutrient load to the water body that has to be known in order to calculate the annual nurient retention.

Annual total nitrogen retention in lakes and reservoirs as percentage of incoming load (D=average water depth (m); τ_W *= hydraulic residence time in years) (1).*

(1) $$N_{ret} = \left(1 - \frac{1}{\left(1 + \frac{7.3}{D} \bullet \tau_W \right)} \right)$$

Annual total phosphorus retention in lakes and reservoirs as percentage of incoming load (τ_W *= hydraulic residence time in years) (2).*

(2) $$P_{ret} = \left(1 - \frac{1}{1 + \sqrt{\tau_W}} \right)$$

Annex 5: Catchment Owner Questionnaire

Overall assessment

1. Is the report of any benefit for you as a catchment owner regarding eg. pressure/impact analysis for the Water Framework Directive or the Nitrates Directive ?

a) Yes, a great benefit ; b) Yes, a benefit ; c) Yes, but only to a minor degree ; d) Not of any use

If needed, please give detailed information on your opinion:

The report is of limited use (c) principally because as catchment owner we were the source of the catchment data provided by the report, and because the source apportionment technique does not provide any information on the physical processes of diffuse pollution so it is not helpful in identifying potential control mechanisms under the WFD or Nitrates Directive. Our catchment is physically and agricultural very diverse so it is very difficult to interpret bulk estimates of pollutant losses to identify targets for source control. The useful data in the report are the estimates of nutrient retention, especially of phosphorus, in the river and lake system.

Based on your knowledge of the catchment please indicate below your opinions on the content of the different sections of the report:

2. Driving Forces

Does the section adequately describe your catchment: Yes ☐ Partly ☒ No ☐

If you answered No, please specify any corrections below:

There are a number of issues of terminology that require correcting to give a better impression of the type of agriculture practised in our catchment. Firstly, the catchment is better described as approximately one third in each of arable, intensive pasture and extensive grazing (moorland and rough grass) rather than *dominantly grassland and arable land.* Also, we feel that the term *nature* is inappropriate for our extensive upland areas as they are still managed to some extent (heather burning, sheep grazing etc.) and are not pristine environments.

Given the environmental variability of the catchment, provided a rainfall range (600 to 2000mm) would also be better than providing a simple mean.

There are actually *c*. 260 lakes of less than 5ha, but we were asked to report only those greater than 5ha to you for the retention calculations. The surface area of these small lakes is 180.8ha.

3. Analysis of Nutrient Pressures - 3.1 Point Sources

Does the section adequately describe your catchment: Yes ☐ Partly ☐ No ☐

If you answered No, please specify any corrections below:

3. Analysis of Nutrient Pressures - 3.2 Background Yields of Nutrients

Does the section adequately describe your catchment: Yes ☐ Partly ☒ No ☐

If you answered No, please specify any corrections below:

The background export coefficients require some explanation as they appear to be added to losses calculated from all other diffuse sources.

3. Analysis of Nutrient Pressures - 3.3 Catchment Hydrology and Losses of Nitrogen and Phosphorus

Does the section adequately describe your catchment: Yes ☐ Partly ☒ No ☐

If you answered No, please specify any corrections below:

The use of conversion factors to calculate TP losses from TRP is clear, but it would be nice to see the measured TP data available for 1995 to 1997 to be included as visual validation of the methodology.

[The report is based on a time period that includes a number of droughts (1991 and 1994) hence is not necessarily representative of long-term conditions.]

[The total phosphorus loss estimated at Skelton (1990-2000) appears to be 50% less than data reported by House et al.]

3. Analysis of Nutrient Pressures - 3.4 Nutrient Retention in the Catchment

Does the section adequately describe your catchment: Yes ☐ Partly ☐ No ☐

If you answered No, please specify any corrections below:

Measurements of denitrification in UK river sediments have been measured in the laboratory in the range 6 to 60 mg N m^{-2} d^{-2} per mg N l^{-1} at 20°C (Toms *et al.*, 1975). Measurements in river systems based on mass balance studies have reported removal rates of 750 to 1400 mg N m^{-2} d (Owens *et al.*, 1972). Measurements of denitrification in the sediments of the Swale-Ouse system by the acetylene blockage method gave a maximal rate of between 12 and 110 mg N m^{-2} per hour, increasing upstream to downstream (Garcia-Ruiz *et al.*, 1998). Mean rates were in the range 14 to 100 mg N m^{-2} d^{-1} per mg N l^{-1} at ambient temperatures (Pattinson *et al.*, 1998; Garcia-Ruiz *et al.*, 1998b) and in the Wiske-Ouse system 14 to 100 mg N m^{-2} d^{-1} per mg N l^{-1} (Garcia-Ruiz *et al.*, 1998a). Modelling studies on the rivers Thames, Yorkshire and Bedfordshire Ouse and in UK reservoirs have used values in the range 20 to 60 mg N m^{-2} yr^{-2} per mg N l^{-1} (Whitehead and Toms, 1993; Thomson, 1979; Whitehead *et al.*, 1981).

Given mean nitrate concentrations of *c*. 5 mg N l^{-1} in the lower part of the Yorkshire Ouse system, the modelled and measured rates of denitrification are equivalent to an annual loss of 20 to 180 g N m^{-2}, which brackets the value of 84 g N m^{-2} used by the Euroharp Retention Tool for streams and rivers.

3. Analysis of Nutrient Pressures - 3.5 Source Apportionment of Nutrient Loads

Does the section adequately describe your catchment: Yes ☐ Partly ☒ No ☐

If you answered No, please specify any corrections below:

Figure 6 shows a very large decrease in the percentage contribution from point sources to the total phosphorus export from the catchment over 1990-2000. The point source inputs are a constant, so this can only result from a general increase in river flows and measure P concentrations with time (increasing the apparent diffuse source). We are not convinced that the trend should be as large as this and suspect that part of the apparent trend can be attributed to the method of interpolation and load calculation.

The reported annual losses of nutrients from agricultural land erroneously assumes that all losses come from only the intensive arable and pasture (only 2/3rds of the catchment). Nutrients are also lost from the extensive grazing areas (1/3rd of land area) and this should be included as part of the total agricultural land area over which the Skelton nitrogen loss is distributed. Taking this into account, the loss from all agricultural land is 28kgN/ha.

4. Analysis of Nutrient State

Does the section adequately describe your catchment: Yes ☐ Partly ☒ No ☐

If you answered No, please specify any corrections below:

Figure 11 shows a period of unusually low measured phosphorus concentrations in the river system in 1993 to 1995. Peak concentrations are c. 50% of those in 1990-92 and 1996-2000. These low concentrations may be the result of a single large sewage treatment works being taken off-line for upgrading or some measurement error. The measurements contribute significantly to the trend of decreasing sewage contribution with time (see above) and, more importantly, lead to a false identification of a positive trend in phosphorus concentrations in Section 4.

We are unsure of the validity of the flow-adjustment procedure before applying the seasonal Kendall's test. Observations in the UK show that flow-concentration relationships are different for each season, especially for nitrate. In autumn, there may be a positive correction with flow, and in spring / summer a negative correlation. It would have been better to fit a flow –concentration curve for each season.

Annex 1-4

Are the sections of any help for you: Yes ☐ Partly ☐ No ☐

If you answered No, please specify why below:

In parts of the catchment, the river regime is extremely flashy and concentrations change significantly on a time scale of 1-3 days, especially for phosphorus. The technique of linear interpolation between measurements that are 7 to 21 days apart is therefore likely to introduce significant error in the calculation of load. I would normally recommend calculation of a flow-weighted average concentration.

Name and affiliation of catchment owner filling in the Questionnaire:
Steven Anthony, ADAS , Laura Fawcett ADAS.