

# EUROHARP 4-2004

## Catchment Report: Enza, Italy Trend Analysis, Retention and Source Apportionment

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**Catchment Report: Enza, Italy**  
**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.

The report may also be downloaded from the EUROHARP web site: [www.euroharp.org](http://www.euroharp.org)  
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## Executive Summary

The Water Framework Directive and Nitrates Directive demand analyses of the main sources of nutrient pollution at the river basin scale. European catchment managers thus need tools for quantification of the importance of point sources and diffuse sources of nitrogen and phosphorus in catchments. Such tools could be the combined trend analysis, nutrient retention and source apportionment as described in this report. This report analyses nutrient pressures, nutrient retention and nutrient trends at the outlet station from the Enza catchment in Italy, applying standardised methodological approaches as described in four separate Annexes.

Kendall's seasonal trend test with flow-adjustment reveals that the Enza experiences a downward significant trend for dissolved inorganic nitrogen concentrations and a downward but non-significant trend for total phosphorus concentrations during the period 1991-2000. The average annual nutrient retention in lakes and streams in the Enza catchment has been calculated at 113 tonnes N and 0.25 tonnes P, applying the Tier 1 EUROHARP retention tool. A source apportionment showed that diffuse sources represent the main nutrient source in the catchment, contributing an average 58% of dissolved inorganic nitrogen and 60% of total phosphorus loads during the two-year period 1999-2000. The average loss of total nitrogen and total phosphorus from agricultural areas amounted to 15.4 kg N ha<sup>-1</sup> and 1.74 kg P ha<sup>-1</sup> respectively, during the period 1991-2000.

# 1. Introduction

Identification of pressures and assessment of impacts in River Basins are 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 have to conduct an analysis for each catchment, based on existing data on catchment characteristics such as land use, pollution sources and monitoring data. Such an analysis can be performed in a stepwise manner following for example the DPSIR concept, see diagram below.

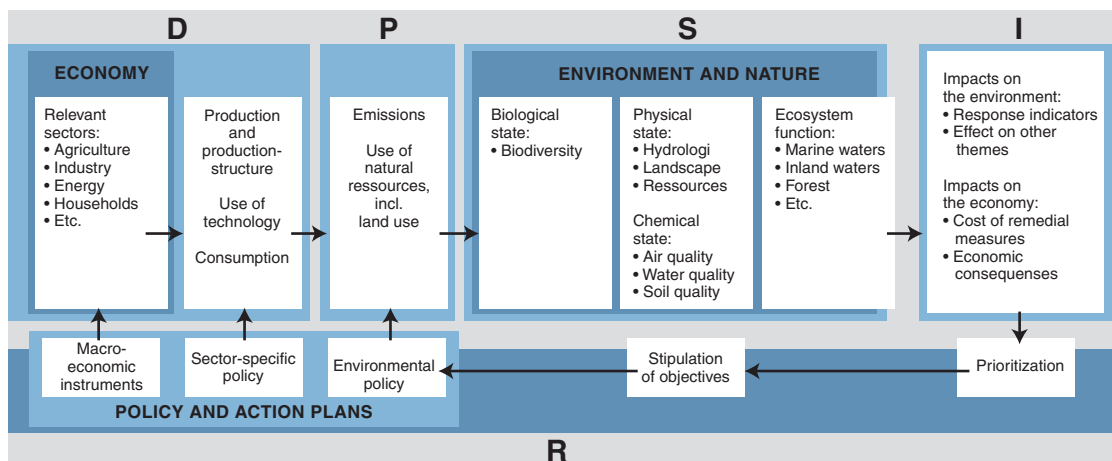


Diagram of the DPSIR concept

In the case of nitrogen and phosphorus, the catchment manager 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 waste water treatment plants, industrial plants, scattered dwellings and fish farms.
- Diffuse sources, such as background nutrient losses, nutrient losses from agricultural activities, atmospheric deposition of nutrients and nutrient losses from forestry.

The information gathered on pressures and their impacts on water bodies should be used in deciding environmental objectives for the water bodies and 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 significant pressures.

The River Basin District Authorities have to fulfil the requirements of monitoring of ground water and surface waters under the Water Framework Directive in 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 programme has to be implemented by 22 December 2006.

Following the pressure/impact analysis and the implementation of the WFD monitoring programme, the River Basin District Authorities 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.
- Source Apportionment of nutrient sources (EUROHARP QT9).
- Nutrient retention estimates for streams, rivers, reservoirs and lakes by applying the EUROHARP quantification tool for retention in surface water.

## 2. Driving Forces in the Enza Catchment

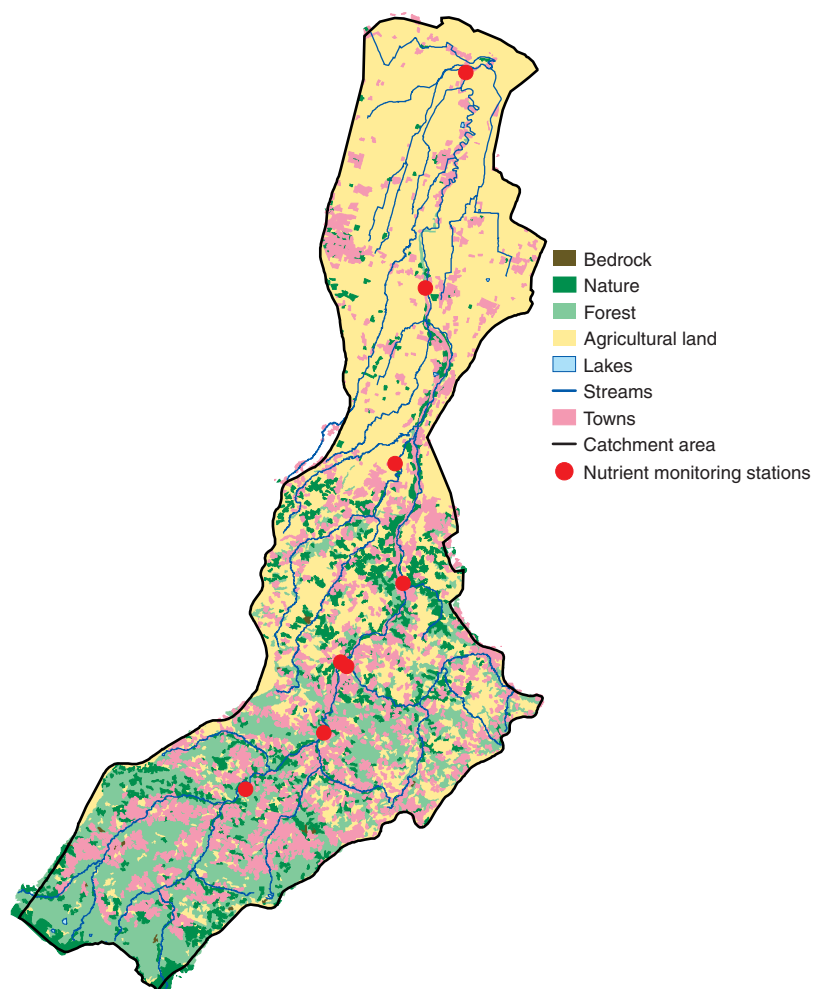


Figure 1: Map showing land use and river network characteristics for the Enza catchment, Italy, and existing water quality monitoring stations in the catchment.

*Main characteristics of the catchment:*

Catchment area:	901 km <sup>2</sup>
Precipitation:	1000 mm
Land use:	Dominantly agricultural

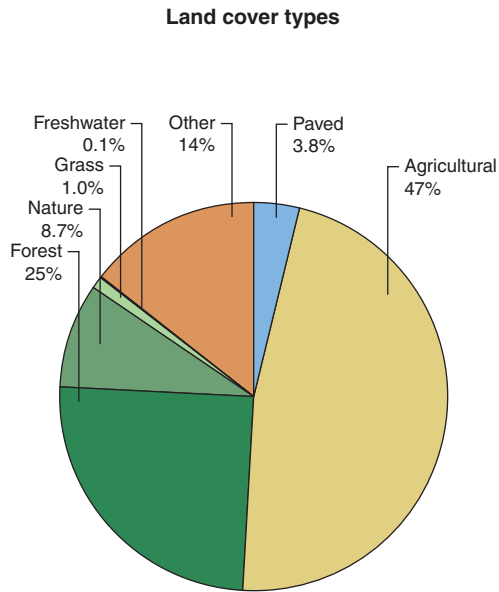


Figure 2: Main land use classes in the Enza catchment.

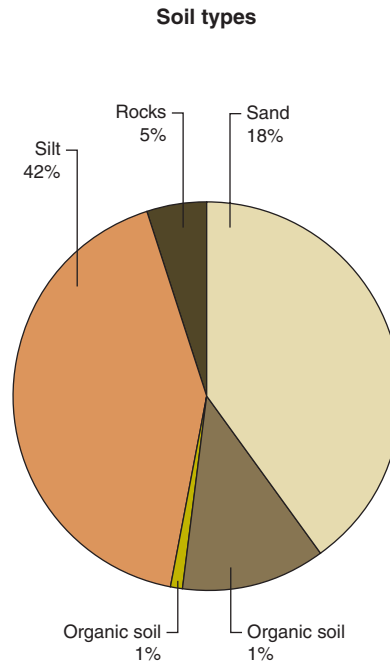


Figure 3: Main soil types in the Enza catchment.

<b>Soil types:</b>	Predominantly silt-sandy soils	
<b>Population:</b>	293,300 inhabitants	
<b>Number of WWTP's:</b>	9 plants	
<b>Livestock:</b>	105,000 cattle, 138,000 pigs, 6200 sheep	
<b>Agricultural land:</b>	431.0 km <sup>2</sup>	
<b>Fertiliser use:</b>		
Chemical:	170 kg N ha <sup>-1</sup>	19 kg P ha <sup>-1</sup>
Manure:	70 kg N ha <sup>-1</sup>	2 kg P ha <sup>-1</sup>
<b>Number of lakes &lt; 5 ha:</b>	10	
<b>Number of lakes &gt; 5 ha:</b>	2	
<b>Stream network density:</b>	0.46 km km <sup>-2</sup>	



### 3. Analysis of Nutrient Pressures

#### 3.1 Point sources

Point sources in the Enza catchment includes:

- Waste Water Treatment Plants (WWTP).
- Discharges from industrial plants.
- Discharges from scattered dwellings with less than 30 Person Equivalents (PE).

The annual discharge of total nitrogen and total phosphorus from WWTPs is shown in Figure 4.

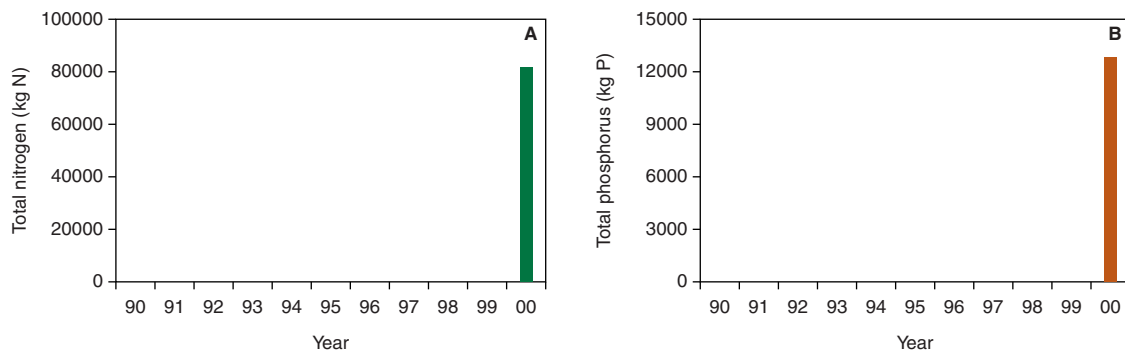


Figure 4: Annual discharge of total nitrogen and total phosphorus from WWTPs in the Enza catchment.

#### 3.2 Background yields of nutrients

Table 1 shows estimated average annual background losses and flow-weighted concentrations of total nitrogen and total phosphorus in the Enza catchment.

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

	Export coefficient
Total nitrogen	1.93 kg N ha <sup>-1</sup>
Total phosphorus	0.18 kg P ha <sup>-1</sup>

### 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: Coenzo) has been reported for the period 1991-2000. The method applied for transport estimation is described in Annex 1.

The annual runoff, dissolved inorganic nitrogen transport and total phosphorus transport vary considerable from year to year, depending especially on the annual climate (Fig. 5).

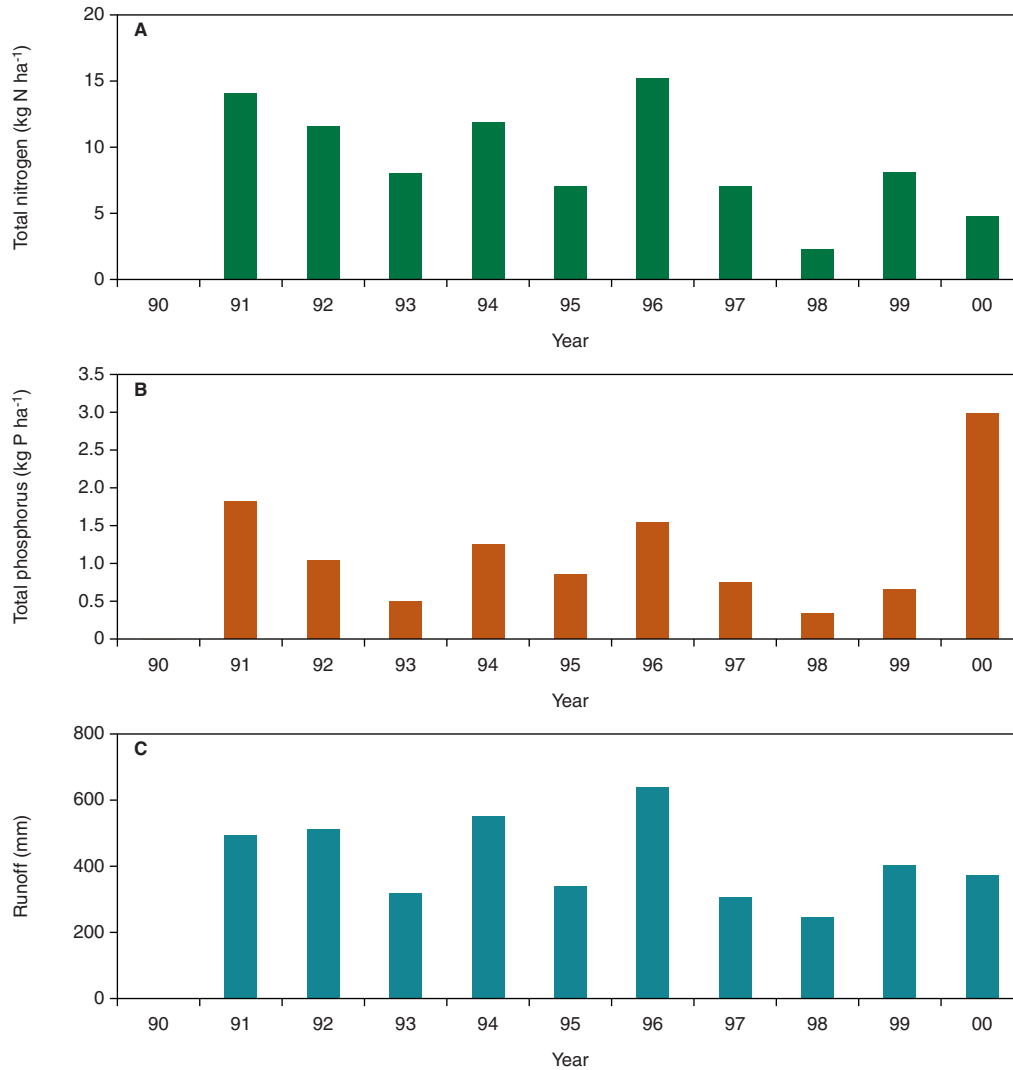


Figure 5: Annual runoff and losses of total nitrogen and total phosphorus from the catchment.

Annual average runoff (1991-2000): 418 mm  
 Annual average total nitrogen loss (1991-2000): 9.0 kg N ha<sup>-1</sup>  
 Annual average total phosphorus loss (1991-2000): 1.17 kg P ha<sup>-1</sup>

### 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. The nutrient retention estimate does not comply to a specific year (dry/wet), but 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 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 Enza catchment is shown in Tables 2-4. The retention calculation for the Enza Catchment was conducted by applying the Tier 1 retention tool.

#### Information on water bodies in Enza catchment, Italy

There are no reservoirs in the catchment.

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

Watercourses	Length	Area
Streams: < 6 m wide	345 km	55.3 ha
Rivers: > 6 m wide	71 km	76.6 ha
Total	416 km	131.9 ha

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

Lakes	Number	Area
0.001-0.1 ha	0	0
0.1-1 ha	0	0
1-5 ha	2	6.2 ha
5-20 ha	0	0
20-100 ha	0	0
> 100 ha	0	0
Total	2	6.2 ha

#### Nutrient retention estimates

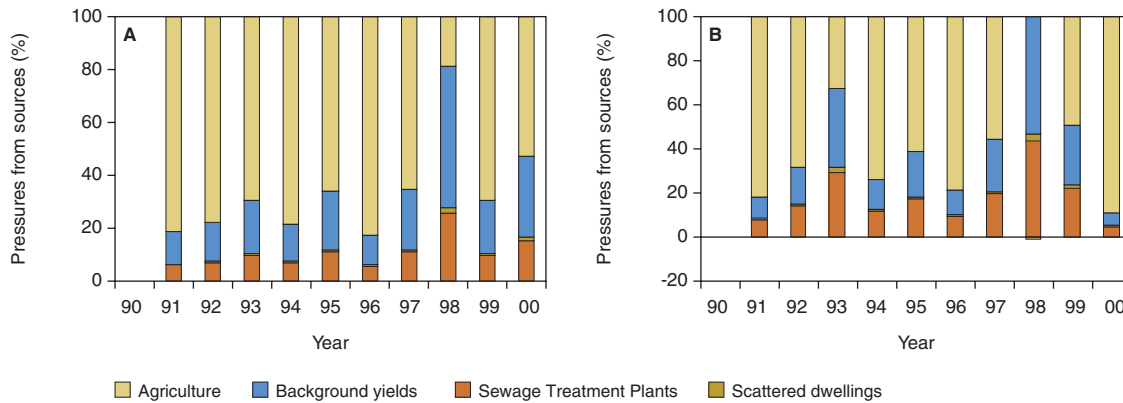
**Table 4: Long term annual nitrogen and phosphorus retention in water bodies for the entire catchment.**

Water body type	Total nitrogen	Total phosphorus
Streams: < 6 m wide	46.4 t N	0 t P
Streams: > 6 m wide	64.3 t N	0.211 t P
Lakes & reservoirs: > 5 ha	0 t N	0 t P
Lakes & reservoirs: < 5 ha	2.5 t N	0.034 t P
Total	113.2 t N	0.245 t P

### 3.5 Source Apportionment of Nutrient loads

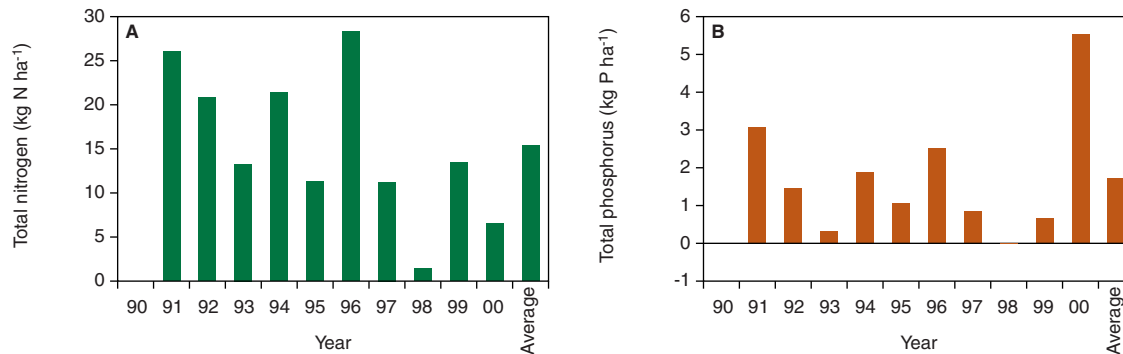
A source apportionment has been conducted on the annual nutrient export from the catchment, taking into consideration the average annual calculated nutrient retention in surface waters during the period 1991-2000 (Fig. 6). The source apportionment method is briefly described in Annex 2. However, data on point source discharges only existed from 2001 and these discharges were applied back in time.

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



**Figure 6: Source apportionment of annual dissolved inorganic nitrogen and total phosphorus exports from the catchment.**

The diffuse losses of total nitrogen and total phosphorus from agricultural land in the catchment are shown in Figure 7.



**Figure 7: Annual diffuse losses of dissolved inorganic nitrogen and total phosphorus from agricultural land within the catchment.**

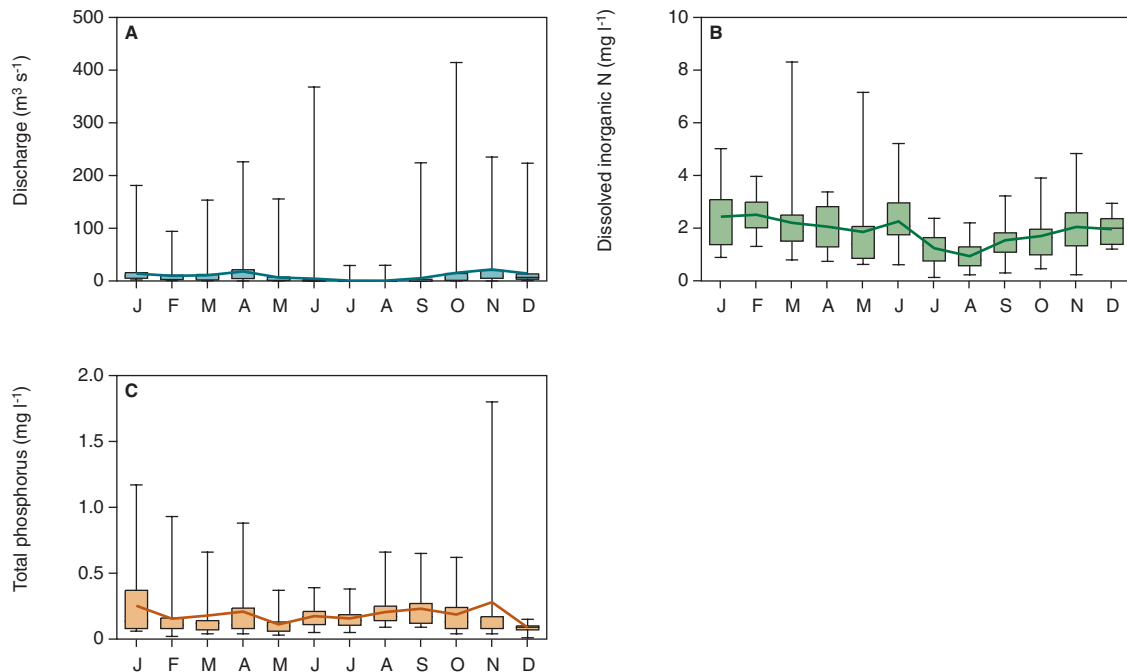
**Average annual total nitrogen loss from agricultural land:** 15.4 kg N ha<sup>-1</sup>

**Average annual total phosphorus loss from agricultural land:** 1.74 kg P ha<sup>-1</sup>

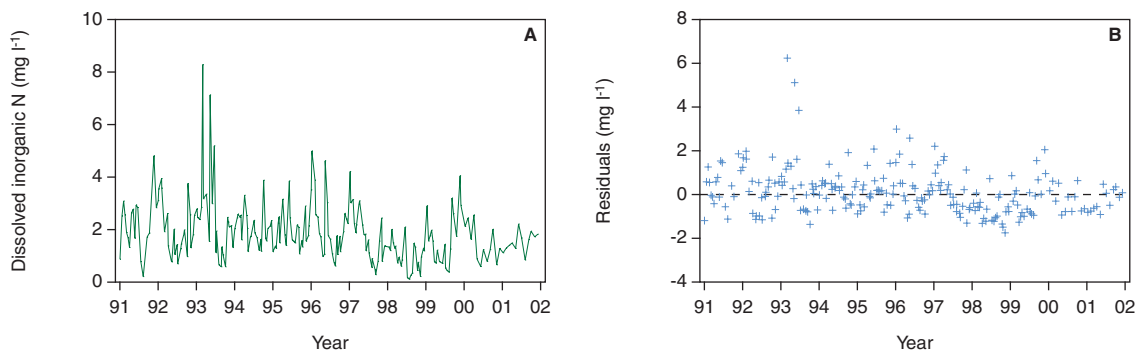
## 4. Analysis of Nutrient State

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. 13). The statistical procedures are described in Annex 3.

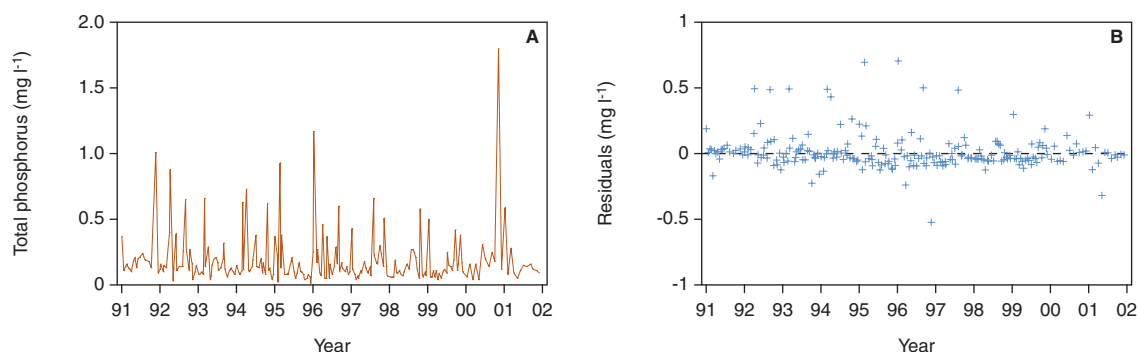
The seasonal variations of runoff, dissolved inorganic nitrogen and total phosphorus concentration are shown in Figure 8. The time series of total nitrogen and total phosphorus at the catchment outlet are shown in Figures 9 and 10. The time series of both nitrogen and phosphorus show homogenous trends (Table 5). A downward trend was detected for dissolved inorganic nitrogen ( $P=4.7\%$ ). The mean annual trend was estimated to  $-0.065 \text{ mg N l}^{-1}$  for the period 1991-2000. A downward trend was also established for total phosphorus ( $P=21\%$ ). The mean annual trend was estimated to  $-0.003 \text{ mg P l}^{-1}$  for the period 1991-2000. No trend was identified for the runoff measurements (Fig. 11).



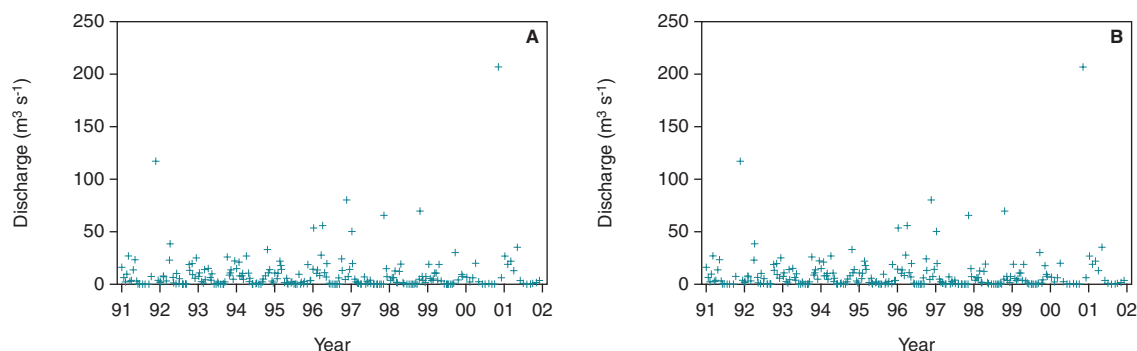
**Figure 8: Box-Whisker plots showing the variation in runoff, and dissolved inorganic nitrogen and total phosphorus concentrations in the catchment.**



**Figure 9: Time series of concentrations of dissolved inorganic N and the flow-adjusted concentrations (residuals) during the period 1991-2000. Average concentration of total nitrogen is  $1.99 \text{ mg l}^{-1}$  ( $CV=70\%$ ).**



**Figure 10: Time-series of flow-adjusted concentrations of total phosphorus and the flow-adjusted concentrations (residuals) during the period 1991-2000. The average concentration of total phosphorus is 0.23 mg l<sup>-1</sup> (CV=120%).**



**Figure 11: Mean daily discharge at the days of water sampling during the period 1991-2000. Figure 11A shows discharge at measurement days for dissolved inorganic nitrogen and Figure 11B discharge for measurement days for total phosphorus.**

**Table 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 <sup>-1</sup> ] (nitrogen)	9.25	60	-0.606	54	-0.006	[-0.203;0.054]
Dissolved inorganic nitrogen [mg l <sup>-1</sup> ]	12.79	31	-1.99	4.7	-0.065	[-0.134;-0.0008]
Runoff [l s <sup>-1</sup> ] (phosphorus)	6.41	84	-0.467	64	-0.005	[-0.195;0.070]
Total phosphorus [mg l <sup>-1</sup> ]	15.22	17	-1.24	21	-0.003	[-0.007;0.002]

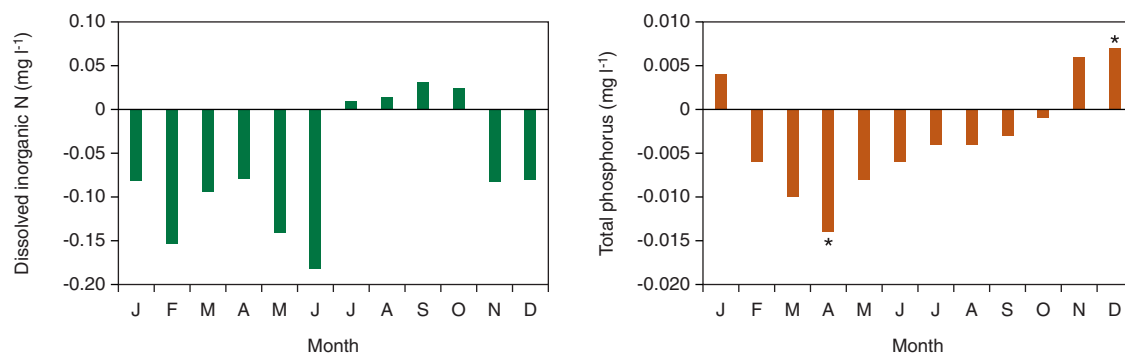


Figure 12: Monthly trend calculated on an annual basis in the concentration of dissolved inorganic nitrogen and total phosphorus during the period 1991-2000. (\*Significant at  $P=5\%$ )

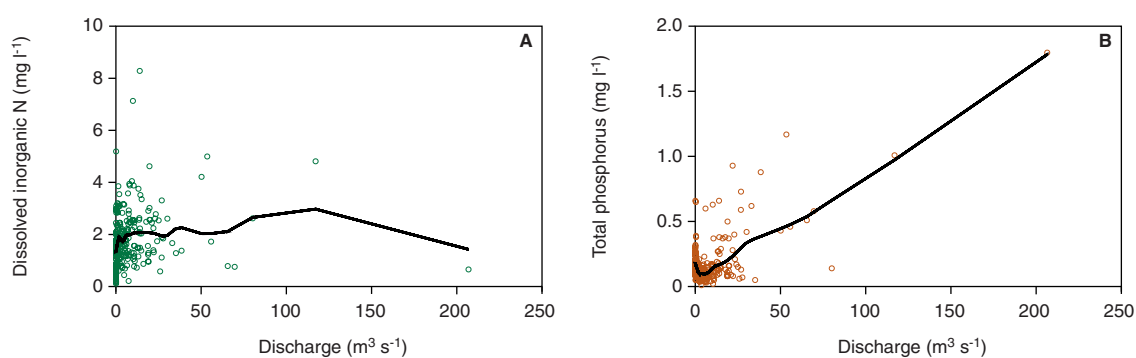


Figure 13: Relationships between discharge and concentrations of dissolved inorganic nitrogen and total phosphorus, established applying the LOWESS fitting procedure (see Annex 3).

## 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  $t_i, i = 1, 2, \dots, n$ . Concentrations are denoted  $c_i, i = 1, 2, \dots, n$ . 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

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

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

$\sum_{t_i < t \leq t_{i+1}}$  : 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  $t$ .

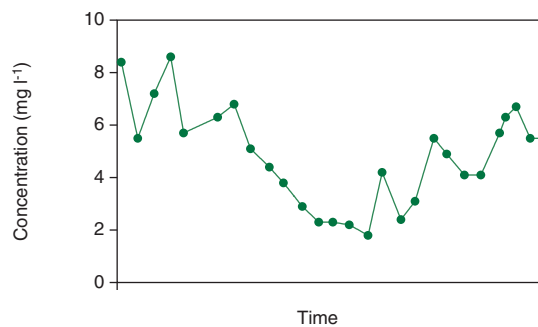
The assumption that  $c_0 = c_1$  results in  $c_{interpolated} = c_1$ , for  $t_0 < t \leq t_1$ , and the assumption  $c_{n+1} = c_n$  results in  $c_{interpolated} = c_n$ , for  $t_n < t \leq t_{n+1}$ .

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

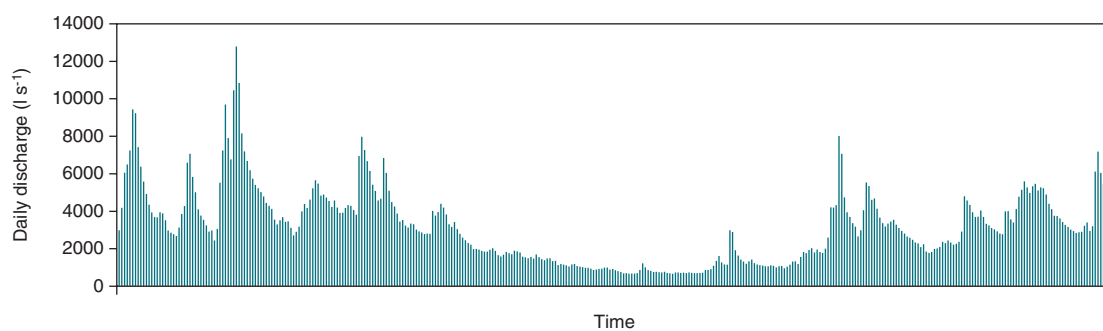
The principle of estimating nutrient transport is shown in the following three figures.



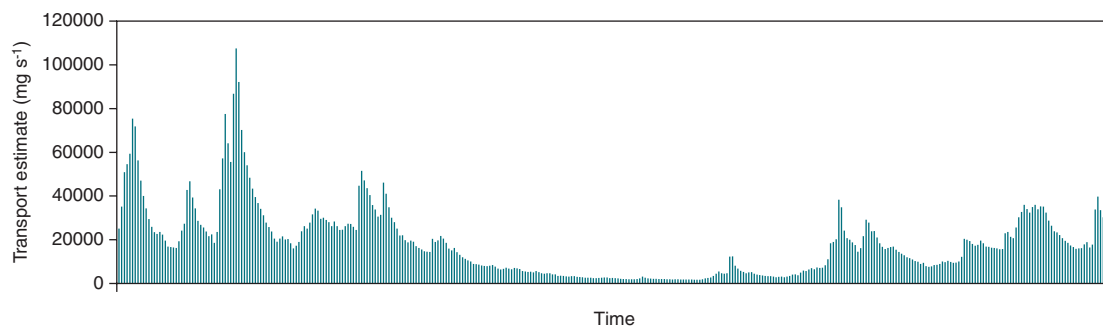
**Illustration of calculations:**



**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:

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

The importance of the different sources may be expressed as:

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

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

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

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:

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

Where  $LO_{AG}$  is the anthropogenic loss of nutrients from agricultural areas entering surface waters;  $LO_{AT}$  is the nutrient load from atmospheric 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 Weighed 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.  $i=1,2,\dots,n$  and  $j=1,2,\dots,p$ . 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

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

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

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

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

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

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

and

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

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

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

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)

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

where

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

and

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

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

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

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  $(\frac{\alpha}{2})$ -percentile in the Gaussian distribution with mean 0 and variance 1. Here  $\alpha$  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  $\text{var}(S)$  for  $n \rightarrow \infty$ . 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

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

The null hypothesis of no trend is rejected if the numerical value of  $Z_g$  is greater than the  $(\frac{\alpha}{2})$ -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  $j = 1, 2, \dots, p$  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  $\alpha$  (1, 5 or 10%) and use

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

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

- Calculate

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

- 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 origin.

## References

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van Belle, G. og Hughes, J. P. (1984): Nonparametric Tests for Trend in Water Quality. *Water Resources Research* 20(1), 127-136.

## 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 with 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 calculated 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 area of streams and 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 <sup>-2</sup> yr <sup>-1</sup>
Streams and rivers	84 g N m <sup>-2</sup> yr <sup>-1</sup>
Total Phosphorus	
Lakes and reservoirs	0.55 g P m <sup>-2</sup> yr <sup>-1</sup>
Streams and rivers > 6 m width	5.50 g P m <sup>-2</sup> yr <sup>-1</sup>

### 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 ( $\tau_w$ ).*

$\tau_w$ (years)	Nitrogen retention		Phosphorus retention	
	(mg N d <sup>-1</sup> )	(% of load)	(mg N d <sup>-1</sup> )	(% 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 nutrient retention.

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

$$(1) \quad N_{ret} = \left( 1 - \frac{1}{\left( 1 + \frac{7.3}{D} \cdot \tau_w \right)} \right)$$

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

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



## 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:

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**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:

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### 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:

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### 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:

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

Does the section adequately describe your catchment:    Yes    **X**    Partly        No   

If you answered No, please specify any corrections below:

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

Does the section adequately describe your catchment:    Yes        Partly    **X**    No   

If you answered No, please specify any corrections below:

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

Does the section adequately describe your catchment:    Yes    **X**    Partly        No   

If you answered No, please specify any corrections below:

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4. Analysis of Nutrient State

Does the section adequately describe your catchment:    Yes        Partly    **X**    No   

If you answered No, please specify any corrections below:

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Annex 1-4

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

If you answered No, please specify why below:

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Name and affiliation of catchment owner filling in the Questionnaire:

ANTONIO LO PORTO (IRSA-CNR) Catchment data owner