REPORT

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Methods for the assessment of diffuse nutrient pollution in rural catchments

Project acronym: AQUISAFE 1

by

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Abstract

The Aquisafe project aims at mitigation of diffuse pollution from agricultural sources to protect surface water resources. The first project phase (2007-2009) focused on the review of available information and preliminary tests regarding

(i) most relevant contaminants,
(ii) system-analytical tools to assess sources and pathways of diffuse agricultural pollution,
(iii) the potential of mitigation zones, such as wetlands or riparian buffers, to reduce diffuse agricultural pollution of surface waters and
(iv) experimental setups to simulate mitigation zones under controlled conditions.

The present report deals with (ii), presenting existing diagnostic methods for agricultural diffuse pollution on a river basin scale. The report focuses on methods with low to moderate data requirements and analytical effort. Generally no numerical models but mostly GIS based approaches have been considered. The described methods were distinguished along two questions:

1. Does diffuse agricultural pollution play an important role in a given catchment?
2. Which areas within the catchment contribute highly to diffuse pollution of the receiving river, i.e. which areas are critical source areas (CSAs)?

Question 1 can be answered by using nutrient measurements, mass balance approaches or land use based methods. For most catchments some nutrient measurements and land use data are available, which allow a first assessment whether diffuse pollution could play a role.

For question 2, the identification of CSAs, a number of GIS-based methods was found in scientific literature. Since most available methods focus on nutrients and since spatial data on other contaminants, such as pesticides, are typically not available, the report outlines methods for the two critical nutrients nitrogen and phosphorus. Each method can be looked up separately, as they are summarized in a similar structure. Moreover Table 8 in Appendix G provides a quick overview of all the presented methods. All the described approaches focus on nutrients, as they are a major concern and often in the focus of research projects. In general the presented methods consider three aspects to assess the risk of pollution from an area within a river basin:

1. The *source of nutrients* on agricultural land is included through fertilizer application, livestock numbers or indirectly via land use.
2. *Transport* to the river is mainly assessed via soil type, land cover, elevation and distance to the river
3. In addition several methods take *retention* processes into account during transport to or within the river

It is important that different contaminants show different behaviour. For instance, phosphorus is pre-dominantly particle-bound, enters rivers via soil erosion and can be retained by adsorption or plant export. Nitrate, the dominant form of nitrogen, is very well soluble, is lost mostly through leaching and most efficiently retained by denitrification. Consequently, methodologies for the assessment of CSAs for phosphorus and nitrogen were looked at separately.

While many promising methods with limited data requirements and analytical efforts were identified in the report, few concepts (such as the Universal Soil Loss Equation for phosphorus) seem to be well established. Most literature concerns specific local or regional case studies. As a result, transferability to other catchments is questionable. The highest potential is seen in qualitative, multi-criteria methods (such as the scoring approach by Trepel and Palmeri, 2002), which can be adapted by the user depending on the diagnostic aim as well as local data availability.

In summary, it is recommended to test several of the presented GIS methods on one or two catchments to gain experience in their handling and their transferability.

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Chapter 1
Introduction

1.1 Background

Nutrient and pesticide input into surface waters can lead to the deterioration of aquatic ecosystems. Moreover, they may contaminate valuable drinking water sources directly or indirectly and therefore be a threat to human health. The various substances have different adverse effects on organisms.

Nitrate can cause methaemoglobinaemia in infants (WHO, 2007) and is regulated by the Nitrates Directive (EU, 1991) and the Raw Water Directive of the European Union (EU, 1975), which has set a maximum permissible concentration of 50 mg-NO_3/L. In the US, the drinking water maximum contaminant level is set at 10 mg/L N-NO3/L. It may also cause eutrophication in nitrogen-limited surface water, commonly observed in marine ecosystems and also increasingly implicated in freshwater ecosystems. Ammonia (NH_3) is mainly toxic to fish in surface waters (e.g., Rossi et al., 2004).

High phosphorus concentration is the dominant reason for eutrophication in freshwater but also many marine systems (Guildford and Hecky, 2000). Eutrophication-related algal blooms can cause O_2 shortages through decomposition in or close to the sediment, which limit the habitat for aquatic organisms (e.g., Kalff, 2002). Blooms of toxic algal species can be a threat to human and animal health (Chorus & Bartram, 1999).

While a reduction of point source pollution has been achieved in many industrialized countries, diffuse pollution remains a problem in many catchments (e.g. Campbell et al., 2004). The present report aims at assessing methods for (i) the identification of river basins, which are subject to diffuse pollution and (ii) the identification of diffuse pollution hotspots within such river basins. If feasible, such methods shall be applied at a later stage of the Aquisafe project for the placement of mitigation measures. The main focus of the report is on nutrients, i.e. phosphorus and nitrogen, although some approaches may also hold for other substances, such as pesticides. However, little information on diagnostic methods for pesticides is found in scientific literature. Moreover, methods would require information on the use of specific pesticides in a watershed. Information on pesticide use is difficult to get on national or regional scale, let alone at field resolution within a watershed.

In this report, as in many other publications, the terms “non-point pollution” and “diffuse pollution” are used synonymously for all sources that are not classified as point sources.

One starting point for the assessment of pollution is to identify, whether pollution from point or diffuse sources predominates in a given catchment. Methods to address this question are presented in Chapter 2. If diffuse sources are important it is crucial to identify pollution hotspots, so-called critical source areas (CSAs) in order to focus mitigation measures. CSAs are areas within the catchment, which contribute most to the pollution loads in the river system. These methods are discussed in Chapter 3.

In a previous study of the Aquisafe project, physically based numerical models with high data requirements have been assessed. These models are commonly used in a scientific context for the assessment of processes involved or for detailed scenario analysis (Skop & Sörensen, 1998). The present report gives an overview of alternative methods, which are less data and time consuming. The presented methods allow easier assessment of nitrogen and phosphorus sources in rural and semi-urban catchments. They are based on simpler models, such as mass balance models, intensive monitoring, multi-criteria analysis and statistical regression.

Both approaches have advantages as well as disadvantages. Complex numerical models reflect better actual transport and transformation processes of the substances in the catchment. As a result they may be used for process understanding or careful prediction of future scenarios. However, the high data requirements and time-consuming model implementation result in high costs. It might therefore be more cost and time efficient to determine CSAs with a simple method and concentrate further investigations on these "hotspots".

1.2 Differences between nitrogen and phosphorus transport

Even though nitrogen and phosphorous are often addressed jointly as nutrients, they differ significantly in their chemical characteristics and therefore their transport pathways within a catchment. As methods for nitrogen and phosphorus analysis are discussed in this report, these differences will be pointed out in the following section.

1.2.1 Forms of nitrogen and phosphorus

In analyses phosphorus is usually subdivided into particulate and dissolved phosphorus, which together make up the total phosphorus (TP) load. Dissolved phosphorus is usually dominated by inorganic phosphates (PO_4^{3-}). Total phosphorus (TP) is measured as an indicator of P pollution, even though not all TP is bioavailable, i.e. relevant for eutrophication (Strobl et al., 2006).
In the case of nitrogen, total nitrogen (TN) is composed of organic nitrogen and inorganic nitrogen (ammonia, nitrate). Nitrate (NO_3^-) is the most relevant form regarding surface water pollution and eutrophication.
The key difference between the predominant dissolved forms of P and N, PO_4 and NO_3^-, is their mobility in water. Whereas PO_4 adsorbs to soil particles and precipitates with iron under aerobic conditions, NO_3^- is highly soluble and easily transported through soil matrices.

1.2.2 Transport pathways

Nitrate from diffuse pollution enters streams mainly in dissolved form via baseflow.
Most phosphorus losses on arable land are in particulate form, while on grassland mostly dissolved phosphorus is lost, since the vegetation impedes particulate transport (McGuckin et al., 1999). According to Strobl et al. (2006) erosion and surface runoff are the main transport pathways of phosphorus, while subsurface flow has a lower relevance. However, this may be somewhat different in ditched and drained areas, where a component of phosphate is delivered more readily.

1.2.3 Retention processes

During transport from land to surface waters as well as in the streams and lakes different processes of attenuation take place. This is due to the different chemical characteristics of the two nutrients. NO_3^- is subject to denitrification by microbiological processes resulting in gaseous N_2 or N_2O. In these forms nitrogen is released to the atmosphere and therefore removed from the aquatic ecosystem. On the contrary volatilization of P (e.g., as phoyphines) is very low, which makes adsorption the main way of P retention.

Chapter 2

Methods for the assessment of diffuse vs. point source pollution

In order to assess pollution in a catchment a first step should be to investigate which pollution sources (point or diffuse) dominate in the area. Several methods exist to address this question. Taking into account that the purpose of this first step is to check if the catchment is generally affected by diffuse pollution, the method should be as simple as possible, requiring little data and time. On the basis of this quick assessment one should be able to decide, if quantification of diffuse pollution is necessary in this catchment or if point sources are to be addressed first.

2.1 Methodology

A literature study was performed in order to assess existing methods for source apportionment of nutrient pollution in rural catchments. The governing criterion for the inclusion of a method was low data requirements.

2.2 Level of urbanization

One way to obtain a rough first hand screening of the relative contribution of point and non-point sources is through the proportion of urban areas, assuming that point sources dominate here while diffuse pollution dominates in rural areas. Possible approaches look at

(1) the N:P ratio in the river water
(2) land use versus population density of the catchment

2.2.1 N:P ratio

The influence of urban areas can be assessed using N:P ratios. In Table 1 typical N:P ratios of nutrient sources for freshwater systems are given. It is shown that the N:P ratio of agricultural sources is generally higher (N:P 44 to 166) than the one of urban sources (N:P 6 to 14) (Kalff, 2002). In order to illustrate this relation, the N:P ratio of a river draining an agricultural catchment (Meu, France) were compared with the one of an urban catchment (Spree, Germany). As expected, the Meu has a more than 5 fold higher N:P ratio than the Spree (Table 2). Moreover, the observed N:P ratios are in good agreement with literature values in Table 1.
A drawback with this method is that it is not possible to determine a critical N:P ratio as a threshold for the classification as a rural catchment, which in turn is assumed to be subject to diffuse pollution. From Table 1 and Table 2 the great range of possible N:P ratios can be seen, which allows only a rough estimation of the influences of point versus diffuse sources. Another disadvantage is that limited river monitoring data are necessary. On the other hand, this method can give a quick estimation if diffuse pollution is an issue in a certain catchment if the data are readily available. If additional information on urbanization are available (see sections 2.2.2 and 2.2.3) the N:P ratio can be used to double-check the expected dominant pollution pathway using water quality data of the river.

Table 1 Molar N:P supply ratios of potential nutrient sources for freshwater systems (assembled by Kalff, 2002)

Source	N:P
Runoff from unfertilized fields	547
Export from medium fertility soils	**166**
Export from forested areas	157
Export from rural areas and croplands	**135**
Export from fertile soil	**74**
Groundwater pristine	63
Precipitation	54
Tropical forest	52
Export from agricultural catchments	**44**
River water (Mississippi)	27
Macrophytes/crops	24
Algae	22
Fertilizer	17
Phytoplankton	16
Macrozooplankton excreta	15
Sewage	**14**
Sediments, mesotrophic lake	12
Pasture land and urban runoff	10
Bacterioplankton protoplasm	10
Septic tank effluent and sewage	**6**
Sediments, eutrophic lake	6
Gull feces	2
Sedimentary rock	2
Earths crust	<0.2

Table 2 Comparison of N:P ratios of river water in two catchments in Germany (Spree) and France (Meu)

	Meu	Spree	Meu/Spree
N-NO_3 [mg-N/L]	5.80	1.35	4.3
TP [mg-P/L]	0.14	0.17	0.8
P-PO_4 [mg-P/L]	0.06	0.08	0.7
ratio N-NO_3/P_{tot} molar	93.28	17.73	5.3
ratio N-NO_3/P-PO_4 molar	225.30	38.26	5.9

2.2.2 Land use maps & population density

A second possibility to determine the influence of urban areas is to look at land use maps to identify which land use types dominate in the catchment. If agriculture dominates the catchment, diffuse agricultural pollution is presumably an issue, although the local application of best management practices may reduce this impact significantly. If urban areas dominate (using population density as a measure of urbanization) a higher contribution of nutrient loads from point sources, i.e. mainly wastewater treatment plants, but also from diffuse nutrient loads from urban impervious surfaces would be expected.

The influence of agricultural versus urban nutrient loads can be assessed broadly by using average export coefficients, as defined in detail for watersheds with a high level of point source treatment by Zobrist and Reichert (2006). They found export coefficients of 2.9 g-N/m^2/yr and 0.03 g-P/m^2/yr for agricultural areas and 2.1 kg-N/inh/yr and 0.04 kg-P/inh/yr for inhabitants. Table 3 exemplifies the use of these coefficients for the EU and compares this EU average to one agriculturally dominated and an urban watershed. The method is obviously much too rough to assess reliable nutrient loads in a specific watershed,

but it can serve as a first screening of relative importance of agricultural versus urban sources.
Most methods described later in this report need information on land use, so gathering of this information is probably necessary in a later step anyhow. Land use data is available for all of Europe, so – if applied in Europe or other regions with existing land use data – no field work is necessary. Most governments work with land use information for planning purposes and the EU-wide project “CORINE land cover” provides land use data at a scale of 1:100000 or larger. This project has the aim to provide consistent land use information for Europe. Maps are available for the years 1990, 2000 as well as for the changes between the two datasets. The data are updated every 10 years and the following 32 countries are covered: Albania, Austria, Belgium, Bosnia and Herzegovina, Bulgaria, Croatia, Cyprus, Czech Republic, Denmark, Estonia, Finland, France, Germany, Greece, Hungary, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, Montenegro, Netherlands, Poland, Portugal, Romania, Serbia, Slovakia, Slovenia, Spain, Sweden and the United Kingdom (European Environmental Protection Agency, n.d.). These data can be downloaded at no costs from the European Environment Agency for non-commercial use if a download agreement is signed (http://dataservice.eea.europa.eu/download.asp?id=17938&filetype=.zip). CORINE land cover data of Germany can be acquired from the German Remote Sensing Data Center at the German Aerospace Center (Deutsches Zentrum für Luft- und Raumfahrt, n.d.).
In the US there are also numerous landuse data sets available free of charge and without signing any agreements, e.g., via the US Department of Agriculture or directly from most US states.
Population density is often available on a catchment level. For instance in Germany detailed information on population number and area is available from municipalities, which can easily be aggregated to calculate population density in a river basin. The data availability in other countries is not known but expected to be similar.

Table 3: Application of nutrient export coefficients

	Ic (France)	**Spree (Germany)**	**EU-27**
Agricultural area [km^2]	71	4,110	1,616,180
Inhabitants	12,000	4,100,000	499 676,300
Inhabitants/Agricultural area [inh/km^2]	169	1,000	309
N-loadagriculture/N-loadinhabitants	8.1	1.4	4.5
P-loadagriculture/P-loadinhabitants	2.1	0.4	1.2

2.3 Regression Analysis

Non-parametric regression (e.g. Albek, 2003) requires more effort than the methods introduced in Chapter 2.2. Stream monitoring data of flow (Q) and water quality parameters are used to carry out regression analysis between these data. Some studies show that the relationship between Q and the measured parameters indicate if point or non-point sources dominate in the catchment (Albek, 2003). It is generally assumed that concentrations from diffuse sources increase with Q, as pollutants leach during rain events. On the other hand, point sources such as treatment plants have a more constant load. As a result concentrations from point sources are diluted at high Q.
However, an example from the Ic catchment in France shows that an observed decrease of the concentration of pollutants with the increase of flow does not necessarily point out the importance of point sources (as there is no sewage treatment plant draining into the river). Here this relationship was due to the contribution of groundwater as a major pathway of

nitrate pollution. The method may also be critical if cities in the watershed are drained via combined sewer systems, since nutrient loads may increase during heavy storm events as a result of combined sewer overflows.
In the study by Albek (2003) two monitoring stations in a Turkish catchment were chosen; one draining a mainly rural, agricultural area and the other one being situated downstream of a major city with 130000 inhabitants where urban wastewater enters the river. At the urban station the relationship between Q and concentration of pollutants is inversely proportional, as expected for point sources (Figures 1b and 1d). The rural station shows no significant relationship between Q and water quality parameters (Figures 1a and 1c), because diffuse pollution enters the stream both during precipitation events and via baseflow. This coincides with the observations in the Ic catchment in France, where an inverse relationship is not due to point sources, but to groundwater contribution. If nitrate/phosphorus were only associated with surface runoff, the concentration would increase with flow.

If Q-nitrate correlations show a positive correlation it can be inferred that diffuse pollution via surface runoff plays a major role in the catchment. However, if an inverse relationship is found no source apportionment is possible, since this observation could be due to groundwater influence or point sources. Consequently, it can be inferred that Q-nitrate correlations are not ideal for an assessment of pollution sources. In contrast, Q-phosphorus (total phosphorus or orthophosphates) correlations may work better, as agricultural loads are usually flow-dependent (e.g. Gächter et al. 2004). Nevertheless, phosphorus observations in a rural catchment by Albek (2003) show that this may not always be the case (Figure 1c).

An alternative to regression analysis is the use of load duration curves for doing a similar analysis that relates flow with N and P loads during different flow conditions (see EPA 2007 for methodology). Load duration curves relate measured loads to their percentage of occurrence. If the methodology is used for source identification, it has similar limitations as regression, since the classical dilution of point sources and increase in diffuse sources during (less-frequent) flood events, may not hold for some cases, as discussed above.

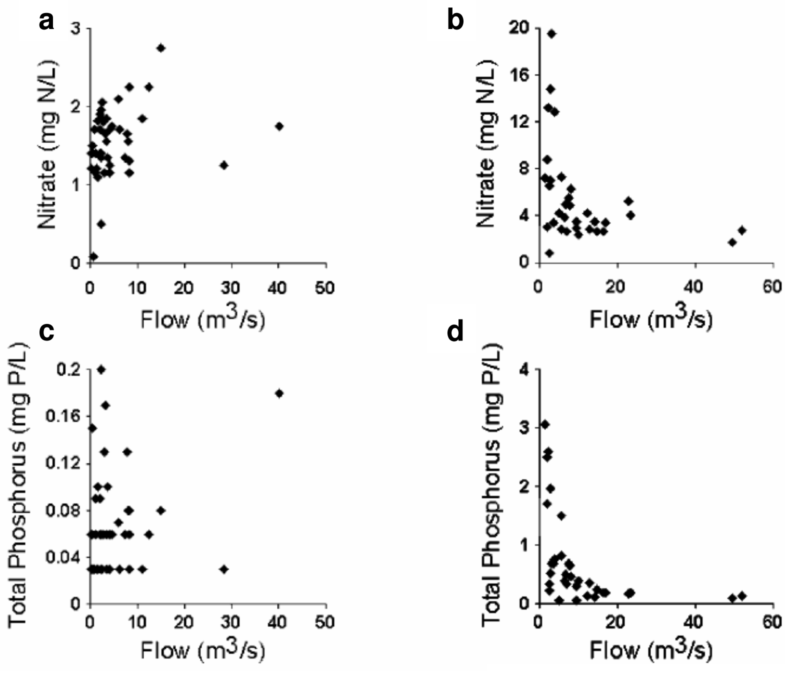

Figure 1 Relationship between flow (Q) and water quality parameters (NO_3 and total P) from Albek (2003); (a) and (c) showing the concentrations at the rural monitoring station; (b) and (d) showing the concentrations at the urban station.

2.4 Nutrient budgets

Behrendt (1999) compared seven different methods of source apportionment of nutrients to rivers for point and diffuse source pollution with respect to their suitability for load prediction. Of these seven methods only the first three are shortly described here, since methods four and five cannot be applied on the basis of the information that was available in the paper. Methods five to seven include factors determined specifically for the Baltic Sea catchment.

2.4.1 Mass-balance approaches

One simple method is the estimation of diffuse pollution by subtraction of point source emissions (PE_N, PE_P in tN/a and tP/a, respectively) from observed total load (L_N, L_P in tN/a and tP/a, respectively) (Salo et al., 1997). This method requires some field measurements of nutrient loads in the river as well as information on point sources in the catchment. In the study of Behrendt (1999), which aimed at predicting exact values for different sources, it did not yield good results, because retention processes in the river are not taken into account. However, it could be applicable if only relative contribution of diffuse and point sources are of interest, since retention is typically assumed to be the same for nutrients, irrespective of their source.

The second method described by Behrendt (1999) is similar to the first one, complemented by a parameter which accounts for the retention of nutrients in the river. This parameter is obtained by multiplying the surface water area (mainly lakes and rivers) by a coefficient which represents the mean retention per surface water area. Coefficients were determined in field studies in Denmark as $1.5 * 10^{-5} \pm 0.9 * 10^{-5}$ mg N/m²*d and $1.5 * 10^{-7} \pm 3.7 * 10^{-7}$ mg P/m²*d (Svendsen et al., 1995; Kronvang et al., 1996) and subsequently applied to catchments in northern Germany by Berendt (1999). The approach yielded better results than the first method, but was still not assessed as "good" by Behrendt (1999). Since the standard deviations of the coefficients for lake retention were quite high (61 % and 250 % for N and P, respectively), it seems not appropriate to apply an average value. Furthermore it is questionable if the coefficients determined in Denmark are applicable for other climate regions.

$$DE_N = L_N - PE_N + 1.5 \cdot 10^{-5} * A_S \tag{1}$$

$$DE_P = L_P - PE_P + 1.5 \cdot 10^{-7} * A_S, \tag{2}$$

where $DE_{N,P}$ = diffuse emissions [tN/a and tP/a]; $L_{N,P}$ = measured loads of N and P [tN/a and tP/a]; $PE_{N,P}$ = point source emissions [tN/a and tP/a] and A_s = area of surface water [m²].

2.4.2 Statistical relationships

In the third method used by Behrendt (1999), retention is accounted for by using a statistical relationship between nitrogen and the hydraulic loading (runoff per unit surface water area; HL in m/a) as well as phosphorus and the specific runoff (runoff per unit drainage area; q in $l*km^{-2}*s^{-1}$). This statistical relationship was determined empirically by Behrendt and Opitz (1999) in a study considering 100 river basins in Europe. The approaches explained 80 % and 65 % of observed variance, for phosphorus and nitrogen, respectively.

$$DE_N = L_N\left(1 + 5.9 * HL^{-0.75}\right) - PE_N \tag{3}$$

$$DE_P = L_P\left(1 + 26.6 * q^{-1.71}\right) - PE_P \tag{4}$$

where HL = hydraulic load [m/a] and q = specific runoff [$l*km^{-2}*s^{-1}$].

2.5 Conclusions

The main factor governing the choice of method is the availability of data in the given catchment. It is therefore not possible to suggest one preferable method here, but in each study the method should be selected depending on readily accessible data.

The easiest method would be the assessment of urbanization (Chapter 2.2) through land-use or population density. Determining N:P ratios of the river water from average values could be classified as a method of medium complexity, while regression (Chapter 2.3; only P) as well as the mass-balance approaches (Chapter 2.4.1) are most complex, because continuous measurements are necessary.

Since in most cases the method shall be as simple as possible, either a method to assess urbanization or, somewhat more elaborate, the simplest nutrient budget method (Chapter 2.4.1) suggested by Behrendt (1999) have high potential to be chosen. As mentioned before, land use data is quite easily accessible in Europe, which leads to the conclusion that the method using these data may often be preferred.

However, it is strongly suggested to combine the methods described in this chapter in order to obtain more detailed information on the sources of the pollution load. If, for example, land use maps are used, the result can be validated by taking additional data on point source emissions or average N:P ratios into consideration. For instance, the study by Albek (2003) has shown that even at an urban station with a typical inverse Q-nitrate relationship, a large share of nitrate was due to diffuse pollution. Therefore, it cannot always be concluded that pollution in an urban catchment comes mainly from point sources. Yet, a combined approach which reveals the presence of urban areas as well as point sources gives an important indication if diffuse pollution is a major source of nutrients.

If possible, experts with knowledge on the catchment should be consulted in order to take into consideration all available information. If experts with understanding of the area know that the catchment has a high percentage of agricultural land use, diffuse sources could be an important factor to consider.

An advantage of the method by Albek (2003) is that information on transport processes is acquired, which can be of high importance regarding the type of mitigation measures.

Chapter 3

Methods for identification of Critical Source Areas (CSAs)

After it has been determined that diffuse pollution in a given catchment is significant, further analysis is necessary in order to find out where CSAs (= hotspots) are situated. This assessment is important for an effective placement of mitigation measures.
One question to be addressed when evaluating different methods of CSA assessment is how they take into account the different transport processes for nitrogen, phosphorus and other substances. Especially when methods are designed for a wide group of substances – e.g. nutrients or pollution in general – this question is crucial in order to know how to interpret the results of the method.
Three methods have been found, which specifically address nitrogen leaching in particular via statistical or multi-criteria approaches (Chapter 3.2). Methods that can be applied for N and P, as well as other pollutants were classified into multi-scale intensive monitoring, multi-criteria analysis and statistical methods (Chapter 3.3). Finally, methods found that are specifically designed for the assessment of P loss from catchments are mainly based on multi-criteria analysis (Chapter 3.4). An overview of all the discussed approaches is given in tabular form in Appendix G.
Each method is presented along the following structure (where applicable):

- Background (why and where the method was developed)
- Method (description of method)
- Data requirements
- Required equipment
- Factors taken into account (sources, transport pathways and retention processes)
- Limitations and uncertainty (based on paper and own interpretations)
- Transferability to other catchments (based on paper and own interpretations)

3.1 Methodology

In order to compare existing methods a literature study has been performed. The aim of the literature study was to find methods for the localization of diffuse pollution sources in a catchment. The main criterion for the consideration of a method was its development for cases with low data availability. Generally numerical models were not considered, yet exceptions were made where simulations had very low data requirements and were designed for low data availability.
The methods were divided into (i) methods that work only for N, (ii) methods that work for N and P and (iii) methods that work only for P, based on the differences described in Chapter 1.2. Some methods placed in the first and third category might be suitable for both N and P, but the studies found were only applied for one substance.

3.2 Nitrogen

3.2.1 Statistical methods/Export coefficients

The methods presented in this chapter are based on statistical relationships between catchment characteristics. They differ in their way to account for diffuse N losses. Skop and Sörensen (1998) use NO_3^- leaching coefficients for different kinds of land use, soils and N-input. The "Dairy Cow Equivalent" (DCE) method by Jordan et al. (1994) bases the calculations on the amount of fertilizer used.
Both authors use mass balances in a combination with a Geographical Information System (GIS). Point sources and non-point sources are added and retention processes are taken into account in different ways depending on the method. Skop and Sörensen (1998) subtract retention, while Pieterse et al. (2003) include a factor for nutrient loss, which is related to the

flow. In this report, not the whole mass-balance is of importance, but only the part about diffuse pollution. Although the present report focuses on diffuse pollution, sections not related to diffuse pollution are described briefly in order to understand the methods to their full extent.

DCE method (Jordan et al., 1994)

Background

A study of Northern Ireland (Jordan et al., 1994) showed a good correlation between applied fertilizer-N and the amount of N leached in that area, which was taken as a basic assumption in this method. The amount of fertilizer applied is presumed to be proportional to the amount of cattle raised in an area. In this study it is stated that 15% of fertilizer-N applied are lost during leaching. Further studies are cited, which show similar results within the 95% confidence interval (e.g., Foy et al., 1982).

Method

In the study Northern Ireland was divided into 10 km² grid cells. Total nitrogen leaching from a cell was calculated as follows:

$$N = (0.15 * N_f) + N_s + N_t \qquad [tN*a^{-1}], \qquad (5)$$

where N = total N leaching from an area [$tN*ha^{-1}*a^{-1}$]; N_f = N in inorganic fertilizer [$tN*a^{-1}$]; N_s = N from sewerage [$tN*a^{-1}$] and N_t = N from precipitation [tN]. As shown in Equation 5, 15% of the fertilizer-N is assumed to leach in each grid cell.

Fertilizer input was calculated from the total inorganic fertilizer used and apportioned by the number of cattle in a grid cell, since most fertilizer in the area is used to produce grass for cattle raising. Because there are animals of different ages and types, the Dairy Cow Equivalent (DCE) was calculated according to Kirke and Hassard (1990). Only grazing animals are included since the fertilizer is used for grass production. The total fertilizer used in Northern Ireland was apportioned to the grids using the following equation:

$$N_f = \frac{DCE_f}{\sum DCE_f} \times F \qquad [tN*a^{-1}], \qquad (6)$$

where DCE = cattle number in Dairy Cow Equivalents and F = total annual amount of fertilizer used in Northern Ireland [$tN*a^{-1}$].

In the calculations for N from sewerage (N_s) it is assumed that all N that leaves the wastewater treatment plants is converted to NO_3^-. N_s was calculated by multiplication of discharged N per capita per day (9.1g $N*person^{-1}*d^{-1}$) with the population. A factor to account for partial or total discharge into to the sea was included which was set to 0 for coastline grids and 1 for all other grids, except for Belfast (0.18).

From other studies in Northern Ireland (e.g. Smith & Stewart, 1989) it seems that almost all the NO_3 deposited by precipitation (N_t) leaches to the surface waters. This was shown by measurements in regions without fertilizer input by the Department of Agriculture of Northern Ireland. About the same amounts of NO_3-N and NH_4-N are contained in the rain, but only the NO_3 is considered to leach, since NH_4 is taken up by perennial grass so that there is little nitrification.

The annual flow (Q) is calculated from the difference between precipitation and Penman potential evapotranspiration PT [mm]:

$$Q = \frac{(rain - PT) * A}{100} \qquad [10^6 L*a^{-1}], \qquad (7)$$

where A = land area [ha]. Comparison between predicted annual water discharge (*rain-PT*) and measured discharge show high agreement for the whole catchment as well as individual catchments. The total NO_3^- load and flow are finally converted into a concentration. Predicted and observed NO_3^- concentrations for 1990 and 1991 largely matched each other.

Data Requirements

For agricultural diffuse pollution:

- Digital map of the catchment (borders, coastline, watercourses, lakes, forestry, roads)
- Farm census data (amount of animals)
- Fertilizer usage for the whole catchment

Additionally for full method:

- Number of people and households (in the same resolution as the underlying map)
- Maps with annual rainfall isohyets
- PT: net radiation, density of water, latent heat of evaporation, relative humidity, wind speed at 2m above surface, saturation humidity at surface air temperature (same grid of squares as rainfall isohyets by interpolation). In this study PT values were provided by the Meteorological Office in Belfast.
- Rainfall chemistry data (N fractions; same grid of squares as rainfall isohytes by interpolation)

Required equipment

- TERRASOFT software or other GIS
- Water quality monitoring equipment for rainfall chemistry (if data not readily available)

Factors taken into account

- Sources
    - Fertilizer input
    - Atmospheric deposition (precipitation)
    - Point sources (sewerage)
- Transport
    - Export is considered as a bulk parameter
- Retention
    - Not taken into account

Limitations and Uncertainties

The main uncertainty in this method is the assumption that a constant percentage of 15% of fertilizer input is exported from agricultural fields. This value is based on several studies performed in Northern Ireland (Smith et al., 1992; Foy et al., 1982) which have shown that this number can vary between 11% and 19% in the Lough Neagh catchment in Northern Ireland. A study by Pieterse et al. (2003) in the Netherlands and Belgium (described in detail in Chapter 3.3.3) found that 5.5% of the applied N leached into surface waters, which affirms that the percentage leached has to be determined for each catchment or region separately. Differences in export coefficients from agricultural land are due to differences in the intensity of agriculture in the study area, vegetation cover and soil type. Especially the fact that soil and cropping factors are not taken into account leads to great uncertainties with respect to the amount leached even within a catchment. Similarly drainage characteristics, such as ditches and piping are not considered in the export coefficients.
Another major uncertainty is that fertilizer application is apportioned for the grid cells based on the amount of cattle. This can only be assumed in catchments dominated by cattle farming or dairy production, where most fertilizer is applied on grassland in order to produce cattle feed.

Retention processes are not taken into account specifically. However, retention during transport to the river is included implicitly in the empirical leaching factor. Evaluation of the predicted values shows that there is no overestimation of measured NO_3^--concentrations. If in-river retention processes were of importance in this catchment, the predicted values would be higher than the ones observed.
Flow is calculated as precipitation minus potential evapotranspiration. For long term studies this assumption is reasonable, but if shorter periods are considered the disregard of groundwater might be a source of error.

Transferability to other catchments

As this study does not account for soil type and climatic conditions, it might be difficult to employ the method to regions with different environmental conditions. The above factors are included in the black box of the model and cannot be adjusted easily. Consequently, the percentage of fertilizer-N leached needs to be determined experimentally for each catchment separately, as great differences between different river basins have been observed (see above). Methods to obtain these so-called export coefficients (ECs) are described more precisely in Chapter 3.3.3. Here they were obtained in small experimental scale as well as large-scale mass balance studies.
The amount of fertilizer in an area is assumed to be related to the DCEs, because most fertilizer in the study area is used for the production of grass for cattle raising. In catchments where this is not the case, this method cannot be used, since the DCEs are not a relevant parameter for the estimation of the amount of fertilizer used on the agricultural fields. For instance in a basin, which is dominated by crop land or pork production, the method would result in a wrong distribution of loads.
The information which is probably hardest to acquire is rainfall chemistry, farm census data (livestock numbers and fertilizer usage). Especially at remote sites these data might not be available. Rainfall chemistry data is measured on a regular basis for some parts of Germany (e.g. in Lower Saxony (Jankowski, n.d)); in other parts no data could be found. Precipitation contributed between 10 and 22% to the total loading of the rivers. If data for the catchment in question are not available, published average concentrations from similar areas could be applied. It can be assumed that the other required data are gathered on a regular basis by many countries.
The method cannot be applied without further information on the exact method of DCE calculations from Kirke and Hassard (1990), which was not readily available.

Advances in the method

Jordan & Smith (2005) expanded the above described approach (Equation 5) by the following extensions.

- Excreta from livestock and its leaching potential were considered (30% of all excreta-N), i.e. total NO_3^--N anthropogenic input was calculated as the sum of the DCE method and the excreta-N input.
- 1 km grids instead of 10 km grids were used.

Nitrate leaching coefficients (Skop & Sørensen, 1998)

Background

This study by Skop & Sørensen (1998) was performed in the agricultural Vejle Fjord catchment in Denmark. The method calculates diffuse pollution from nitrate leaching coefficients which are determined in experiments.
Both runoff from the topographic catchment and baseflow from the groundwater are considered to contribute to streamflow in the catchment.

Method

Total N-load for a studied time period is calculated as the sum of all contributing parameters as follows:

$$N_{tot} = \sum ps + \sum nps - \sum lr \qquad \text{[kg N]}, \tag{8}$$

where N_{tot} = total N-load at the outlet of each sub-catchment [kg N]; *ps* = N-load from point sources [kg N]; *nps* = N-load from diffuse sources [kg N] and *lr* = lake retention [kg N].
Industrial and sewerage outlets as well as fish farms are considered as point sources. Diffuse sources are agriculture and other land uses, as well as scattered houses:

$$\sum nps = \sum sd + \sum Nland \qquad \text{[kg N]}, \tag{9}$$

where *sd* = contribution from scattered dwellings [kg N] and *Nland* = N contribution from agriculture [kg N]. The amount of N from scattered dwellings was calculated following existing guidelines from the Danish Environmental Protection Agency (DEPA, 1992). Agricultural contribution is determined as follows, summing up the contributions from all cells in a subcatchment:

$$\sum Nland = \sum Nla * l + \sum Nlb * l \quad \text{[kg N]}, \tag{10}$$

where *Nla* = N-leaching from agricultural practice [kg N]; *Nlb* = N-leaching from natural background [kg N]; *l* = N-load factor [-], which accounts for the fraction of leached N that reaches the rivers.
NO_3^- leakage (*Nla*) is calculated with nitrate leaching coefficients, which are determined by experiments (Simmelsgaard, 1991) and are related to soil types, cropping pattern and nitrogen input (Skop & Shou 1996) for each cell (See Appendix A for results). N-leaching from background (*Nlb*) was assigned to 5 kg*ha^{-1}*a^{-1} based on literature values. *l* from Equation 10 is assumed to be distance-related and can be expressed for each cell j as

$$l_{ij} = (1 - p_i)_{ij}^{x} \qquad \text{[-]}, \tag{11}$$

where l_{ij} = N-loading factor accounting for the fraction of leached N that is not removed during the transport to the river; p_i = removal probability [m^{-1}]; x_{ij} = flow path length from an initial node to an end node; *i* = transport process index (runoff or baseflow) and *j* = cell index.
Probability factors were estimated by means of trial and error, i.e. comparing measured loads with modeled load for different probability values. In this study the probability factor for runoff was assigned to 0 m^{-1} (i.e. no N removal on the way to the river), while the one for baseflow was set to 0.00085 m^{-1}. This accounts for N removal during the transport through the soil.
Lake retention (*lr*) is calculated as a simple mass balance, subtracting the measured load at the inlet from the one at the outlet. Stream retention is neglected.

All the described model assumptions are implemented in a GIS. The catchment was divided into topographic and groundwater sub-catchments, which differ in some cases, so runoff and baseflow are considered separately. Sub-catchments are in turn split into a number of cells. The total N at the outlet of each sub catchment is the sum of the N-load from both pathways.
Seven steps are applied for calculations of the streamload from agricultural diffuse sources (∑*Nland*) as follows:

(1) Two flow distance grids are calculated in order to obtain the N-pathway distance from each cell to the nearest stream: one is following the topographic elevation, the other one is following the groundwater head gradients.
(2) For each cell N-leaching (*Nla*) for both pathways is calculated
(3) For each cell N removal for both pathways is calculated as N-loading factors (*l*), applying flow-distance grids

(4) N-load per cell is calculated as *Nla * I* plus *Nlb * I* (where *Nlb* = 5 kg*ha^{-1}*a^{-1}).
(5) N discharge in runoff at outlet of the sub-catchment: adding all cells within each topographic sub-catchment (Overlay of the topography with the N-load)
(6) N discharge in baseflow at outlet of the sub-catchment: adding all cells within each groundwater sub-catchments
(7) Total contribution of N at the outlet of sub catchment, ∑*Nland,* calculated as the sum of N-contributions of runoff and baseflow

In summary, this method relies on measurements of point sources in each sub-catchment, and the calculations of contribution from single dwellings. Agricultural and background leaching are estimated by means of a constant value and leaching coefficients determined in experiments in Denmark, respectively. Though the method mainly aims at calculation of N-loads, the cell-based implementation in GIS makes it possible to determine areas that contribute most to the stream load.

Data Requirements

For agricultural diffuse pollution:

- Nitrate leaching coefficients: soil type, cropping pattern, N input (which information exactly is needed could not be determined because the sources (Skop and Schou, 1996; Simmelsgaard, 1991) are not available))
- N-removal probability by trial and error
- Fluxes at in- and outlet of lakes
- Topographic map (for N-flowpaths in runoff)
- Groundwater head map (for N-flowpaths in baseflow)
- Two soil maps (topsoil and subsoil) for streamflow composition (Skop & Loaiciga, 1998)

Additionally for full method:

- Point source loadings
- Scattered dwellings (which information exactly is needed could not be determined because the source (DEPA, 1992) is not available)

Required equipment

- GIS software
- Water quality monitoring equipment (if data for lake retention not available)
- Equipment for determination of leaching coefficients

Factors taken into account

- Sources
    - Non-point source N leaching (Farm types, soils and N input considered)
    - Point source emissions
- Transport
    - Surface runoff (topography)
    - Baseflow (groundwater head level)
- Retention
    - Flow path distance to receiving river
    - Removal probability along this flow path
    - No retention in streams

Soil type is an important factor in this method as N leaching per unit area differs greatly among the various soil types. It is maximal on sandy soils, since crop biomass production and therefore the nutrient uptake is lower than on loamy soils. Usually this difference is not taken into account when fertilizer is applied and thus different amounts of N remain in the soil

after harvest. Furthermore, water retention is lower in sandy soils leading to more leaching than in loamy soils. On the other hand surface runoff is higher for loamy soils.
Differences in leaching are also observed due to farm sizes and types of farms, e.g. livestock dominated farms contribute more to leaching than part time and plant production farms (see Appendix A), which is a result of fewer livestock units (LU) per hectare and therefore less application of organic fertilizers. “Danish LUs” are a measure of the amount of N in manure, i.e. 1 LU is defined as the amount of N produced by one dairy cow in one year.
High leaching from an area does not imply that loads from this part of the catchment contribute most to the loading in the watercourses. Areas with lower export can add more to loadings because tile drainage can shorten travel times and reduce retention on the way to the river network. In this method catchment maps for N-loads reaching surface waters and N-leaching can be produced separately, accounting for this difference.

Limitations and Uncertainties

A comparison between measured and calculated N-loads shows deviations in the range of ± 17 %. N-leaching from pig farms seems to be underestimated by the model, since it assumes that farmers comply with the legislation concerning N-fertilizer application which is not always true. As pig farms have the highest livestock density these are most likely to defy regulations.
The following uncertainties arise with this method:

(1) N-removal in streams (assumed to be 0)
(2) The definition of the sub-catchment boundaries
(3) First-order removal process
(4) N-removal is calculated through estimated probabilities without experimental basis

In-stream retention is assumed to be 0, which is true considering an annual balance, but in the summer 12-16% of the N is retained. N reduction in buffer strips and riparian wetlands is not taken into account specifically (only via increased distance of agricultural land from river), neither are seasonality in drainage and other parameters.

Transferability to other catchments

For estimation of scattered dwellings this method uses method of the Danish Environmental Protection Agency, which was not available for this report. It is possible that this method makes assumptions, which only apply for Denmark. Nitrate leaching coefficients are determined by experiments and related to soil types, farming method and N input, so a study with different environmental conditions (e.g. climate) has to determine local nitrate leaching coefficients experimentally. An exact description of the experimental design is not given in the available study. For similar environmental conditions and agricultural practices, N-leaching determined for Denmark may be used.
In this method some in-field measurements are necessary. The information, which might be most difficult to acquire is soil type and information on farming sizes as well as cropping pattern. Moreover, separate mapping of topographic and groundwater sub-catchments are not readily available in most watersheds.
The exact information needed for the calculation of scattered dwellings influence and N-leaching coefficients could not be found in the literature, since the cited reports were not available. As the considered publication does not include all necessary calculations, the method cannot be used without external support.

3.2.2 Multi-criteria analysis

Multi-criteria analysis is an approach that links different parameters by logical operations to account for the influence of these parameters on nutrient export. In this chapter a multi-criteria method that has been designed for nitrogen is described, Chapters 3.3.2 and 3.4.1 take up this topic for all nutrients and only phosphorus, respectively.

Scoring System (Trepel & Palmeri, 2002)

Background

Trepel and Palmeri (2002) developed a scoring system in order to find best suitable locations for constructed wetlands, which can effectively retain nitrogen in a catchment. As stated before, the scope of the present report was to identify CSAs within a catchment that contribute most to pollution of surface waters and not to find sites for wetlands. But as the main purpose of the CSA identification is the future placement of mitigation measures, this scoring method presents an interesting approach. The most important conceptual difference compared to the other methods explained in this paper is that applicability factors are taken into account.
In the study by Trepel and Palmeri (2002) the method was performed in a catchment in northern Germany, the Neuwührener Au basin.

Method

A GIS is used to calculate the suitability for the placement of wetlands of each grid cell. A suitability value (*S*) for each cell is calculated using the following formula:

$$S = \frac{\sum_{i=1}^{n} li}{n}, \qquad [-] \qquad (12)$$

where n = number of data layers and li = score value of data layer i. Each layer can take a value between 0 and 1; a value of 1 representing a high suitability, a value of 0 no suitability. The eight data layers used in this study and its classes are shown in Table 4.

Table 4 Score values for the eight data layers (Trepel & Palmeri, 2002).

Soil substrate		*River distance [m]*	
Water	1.0	0-50	1.0
Peat	1.0	50-150	0.9
Glacial till	0.5	150-300	0.6
Sand	0.3	300-600	0.3
		>600	0.1
Land use		*Acceptability [cattle/person]*	
Water	1.0	<0.1	1.0
Mire, swamp	1.0	0.1-0.5	0.9
Grassland	0.8	0.5-1	0.7
Farmland	0.5	1-2	0.5
Forest	0.5	>2	0.3
Urban/industry	0.2		
Relief features		*Elevation [m above sea level]*	
Depressions	1.0	<30	1.0
Other	0.6	30-40	0.8
Slopes	0.1	40-50	0.6
		50-60	0.4
		>60	0.2
Slope (%)		*Historical wetlands*	
0.0-0.01	1.0	Fens, open water	1.0
0.01-0.02	0.9	Others	0.1
0.02-0.05	0.6		
0.05-0.1	0.3		
0.1-0.4	0.1		

Acceptability is calculated based on the amount of cattle per person in an area. This is due to the fact that in northern Germany the socio-economic restrictions against construction of wetlands depend mainly on the intensity of agriculture, hence the more cattle per person, the lower is the acceptability of wetland restoration. In a region where population density is the governing restriction for acceptability, i.e. in mainly urban catchments, the cattle per person index would not be a good indicator for acceptability.

Data Requirements

- Soil map
- Land use map
- Digital Elevation Model (DEM)
- Cattle per person (population density and cattle density) or other acceptability approach
- Historical maps

Factors taken into account

- Sources
    - No different sources considered
- Transport
    - Distance to the river
- Retention
    - Not considered
- Suitability for wetlands
    - Soil characteristics
    - Land use
    - Relief
    - Slope
    - Elevation
    - Socio-economic acceptability
    - Historical distribution of wetlands

The soil characteristics relate mainly to the suitability of the cell for the placement of a wetland, not to the leaching/substance removal characteristics.

Limitations and Uncertainties

The major uncertainties in this method are the choices of classes and values for the different factors. The authors do not state how they made the choice of the values for the different classes. It is assumed that these are selected on the basis of expert opinions and therefore mistakes could be made regarding the values assigned to different classes.
The method considers mainly factors with respect to suitability for wetland restoration of a grid. Pollution risk is only taken into account via distance from receiving water. Sources of pollution are not considered.

Transferability to other catchments

The method can easily be applied in other catchments. If information for one of the layers is not obtainable, the calculations can be performed without this parameter. Since the method was developed mainly to find suitable places for wetland restoration, most factors are related to that question. However, the principle of the method can easily be applied with other aspects which can be included if they are of local importance. This makes the method very flexible, because it is suitable for a variety of data availabilities and local conditions.
Moreover, the values for the classes in each layer can be adapted for different catchments according to the present conditions. For instance, the elevation layer (Table 4) obviously needs to be adapted to the local situation. As stated above, the acceptability parameter has

to be adjusted to the general characteristics that restrict the socio-economic acceptability of the method, i.e. depending on the typical land use of the catchment.
Most information in this study was obtained from the Environmental Protection Agency of Schleswig-Holstein (Germany) and the Statistical Agency of Schleswig-Holstein. In Germany the information used is not difficult to access. Most difficult to acquire are data on soil characteristics and acceptability.
It might also be possible to adapt this method to account for the potential N-loss or pollution loss in general instead of the suitability for wetland restoration. Some factors would then have to be chosen in a different way. For instance, in the above method relief depressions get a high value, while higher slopes get low values, which accounts for suitability of an area for the placement of wetlands. If only leaching potential was considered, the values would have to be chosen the opposite way, since high slopes lead to more surface runoff which in turn results in high nitrogen export. The same is true for soil characteristics, where sandy soils are assigned a low value since they are not suitable for wetlands, but they have greatest leaching potential.

3.3 Nitrogen and Phosphorus

3.3.1 Multi-scale intensive monitoring

Background

Tang et al. (2008) performed intensive monitoring at high temporal and spatial resolution in China from 2001 until 2003 in order to assess hydrological pathways and source areas of P and N.

Method

Flows were measured at 10 minute intervals for rainfall, rivers as well as surface runoff. Water samples were taken regularly every week for surface runoff from paddy fields, stream water and groundwater as well as event-based during rain events for precipitation and surface runoff. Sediments from the uplands were also monitored event-based by installation of erosion plots. The study showed the importance of subsurface transport of N. The authors conclude that a combination of regular and intensive (event-based) monitoring is important in order to take into account nutrient transport during storm events. Assessment of data showed that there is an underestimation of N and P load of on average about 30 % and 50%, respectively, if only weekly sampling is taken into account. At the sub-catchment scale it is even 43% for N on average. Maximum discrepancy between only weekly and the additional intensive monitoring was 47% for N and 60% for P. The importance of rain events for the nutrient loads is confirmed by a number of studies (e.g., Moosmann et al. 2005).

Data Requirements

- No

Required equipment

- Sampling equipment

Limitations and Uncertainties

The method is extremely time consuming and expensive. In order to obtain export from all the areas in the catchment a very dense monitoring network is required.

Transferability to other catchments

This method can be applied in most catchments. However, the dense placement of monitoring stations in a large catchment is very expensive. Automated, flow-relative samplers cost in the order of 2000 € per piece (e.g. Teledyne Isco Sampler, pers. comm. B. Müller). More expensive is the collection and analysis of the samples. Moreover, it might not be possible to install monitoring stations at all reasonable locations.

Advances in the method

Moosmann et al. (2005) used data from three high resolution / flow-relative P sampling programs to assess required numbers of water quality samples (C) for a given uncertainty. Good results can be obtained, if quasi-continuous flow data (Q) are coupled with rating curves from C-Q-pairs. For instance an uncertainty in P-load of 10 % was reached if continuous flow data were combined with 40 to 200 random samples, depending on the river.

3.3.2 Multi-criteria analyses

Geocharacteristic Index (Bae & Ha 2005)

Background

The Geocharacteristic Index (GCI) addresses pollution in general, not only nitrogen and phosphorus. It was developed to include geomorphological properties in the assessment of pollution loads. It is based solely on risk of pollution (through distance to river) and retention capacity (based on land type). The study described here was performed in the central part of South Korea.

Method

The GCI is calculated in order to relate it to the pollution load in a river network. This relation is used to estimate loadings in catchments or sub-catchments, which are not monitored.
GCI is the product of the watershed form ratio (S_f) and the flow accumulation of pollution load (F_r). The higher the GCI the higher the susceptibility of pollution from a given cell.
The watershed form ratio (S_f) reflects the stream density in the catchment and shows therefore how easy pollutants can reach the watercourses. S_f is obtained by dividing the squared length of the drainage network by the area of the watershed. The exact formula can be found in Appendix B.
For the calculation of GCI the flow accumulation of pollution load (F_r) is obtained from the ratio FAV_W/FAV_N between the weighted flow accumulation value (FAV_W) and the non-weighted flow accumulation value (FAV_N). The flow accumulation value $FAV_{W,N}$ for each cell gives the direction of water flow from one cell to one of the neighboring cells based on the steepest slope from the DEM. The FAV_W is weighted by the geo-delivery impact factor which is gathered from literature research. The geo-delivery impact factor is a measure for the percentage of pollution load retained in each cell in the catchment depending on land use and slope (0 = complete retention, 1 = no retention, see Appendix B for details). The literature taken into account includes studies from various countries.

Data Requirements

- DEM
- Weighted geo-delivery impact factor
- Area of watershed
- Length of drainage network determined from the DEM

Required equipment

- GIS software

Factors taken into account

- Source
    - No
- Transport
    - Direction of flow in each cell depending on the topography of the catchment
- Retention
    - Proportion of drainage network in the catchment (watershed form ratio)
    - Land use and slope (Geo-delivery impact factor)

Limitations and Uncertainties

The main uncertainty is that the GCI does not account for chemical characteristics of different pollutants. Land use and slope are assumed to have the same influence on all contaminants. Different transport pathways, as runoff and baseflow, are not considered. The geo-delivery impact factors are based on a literature review, which can also be a source of uncertainty.
Moreover no source data is taken into account. The GCI only indicates a potential susceptibility of diffuse pollution.

Transferability to other catchments

This method has low data requirements. A problem for the application in other catchments could be that the geo-delivery impact factors were compiled in a literature review and might therefore not be applicable for all climatic regions. Even though the literature considered for this factor covers catchments from all over the world, the applicability of the used factors in other catchments remains unclear.
The cited study contains all information necessary to calculate the GCI. The only parameter, which might have to be adapted is the geo-delivery impact factor.
The method could be improved by overlaying the GCI with source data, such as fertilizer application.

3.3.3 Statistical Methods / Export coefficients approach

Another approach to model nitrogen or phosphorus export from diffuse sources is the usage of statistical models. Regressions between measured loads and certain basin characteristics (e.g. land use) are performed. These methods do not consider processes but are based on statistical relationships between different monitoring parameters. These relations have to be determined separately for different substances. One problem with this kind of method is that the statistical relations do not remain constant if climate or other conditions change (Grizzetti et al., 2005). As a result statistical methods may not be suited for predictions.
The export coefficient (EC) approach (e.g. Johnes, 1996; Jordan et al., 2005) assumes that for a given climate, nutrient losses in a catchment depend greatly on the land use types. The idea behind this method is that once the ECs have been determined they can be applied to other catchments with very little effort.
Hilton et al. (2002) have tested the use of ECs from the literature for the estimation of phosphorus pollution without adaptation to the specific catchment. For urban areas, where point sources contribute more to pollution than diffuse sources, good results were achieved while in catchments with mainly diffuse pollution the method was not applicable. This shows that ECs have to be adapted for each catchment (Vassiljev et al., 2008). Great differences in ECs for different catchments in various studies support this conclusion (McGuckin et al., 1999).
ECs are usually found empirically and are given in $kg*ha^{-1}*a^{-1}$ or percentage of load. The methods described in this section are (i) land use related backward stepwise regression by McGuckin et al. (1999), (ii) MESAW by Vassiljev et al. (2008) and (iii) input related regression (Pieterse et al., 2003)

Land use related backward stepwise regression (McGuckin et al., 1999)

Background

Multiple regression analysis was performed by McGuckin et al. (1999) in order to determine export coefficients of phosphorus for different land use types. The basis for the different land use types were the CORINE landcover data. Even though McGuckin et al. (1999) applied this method only for phosphorus, other studies show that the same procedure can be performed for NO_3^--N (Jordan et al., 2005) and other substances. The study by McGuckin et al. (1999) was performed in Northern Ireland and is described here exemplarily.

Method

A backward stepwise regression procedure was employed on the annual P loadings for the determination of export coefficients of different phosphorus fractions (total P (TP), total soluble P (TSP), soluble reactive P (SRP), soluble organic P (SOP) and particulate P (PP)) for each land use type. This method was chosen in order to make sure that independent variables are only included if they are significantly correlated with the dependent variable. Backward stepwise regression starts with a multiple linear regression against all possible independent variables in the model and removes the least significant variables stepwise. The goal is to explain a high fraction of the observed variance with a minimum number of independent variables.
The loading data were obtained from 30 monitoring stations within two catchments in Northern Ireland, each station draining a sub-catchment for which the areas of land use types have to be known. The annual loading [in kg] was used as dependent variable and correlated with the areas of CORINE land cover classes [in ha]. Sub-catchments with high contribution of point sources to the total load were excluded from the study.
The five CORINE land cover classes used are arable land, improved grassland, non-improved grassland, coniferous forest as well as moor/heath. The catchment boundaries of the sub-catchments were found with the software “WaterWay Version 1.4” in combination with a GIS. For each sub-catchment the percentages of each of the land use type were determined by overlay of CORINE land cover maps and the sub-catchment boundaries map.
Loss of different phosphorus forms (SRP, PP and SOP) from a range of land use types was determined. This differentiation can be of importance regarding the mitigation measures employed in the catchment.
The regression analysis between the loadings of the different phosphorus forms and the land use types was carried out with the Manugistics Statgraphics (Version 3) package, which could be replaced by any statistics program with the capability of performing backward stepwise (multiple linear) regression.

Data Requirements

- Measured loadings of multiple stations (twice per month) draining sub-catchments with different land use characteristics
- Areas of CORINE land cover classes
- Catchment boundaries (for the determination of the areas of the sub-catchments of each monitoring station)

Required equipment

- Software performing backward stepwise regression (here Manugistics Statgraphics Version 3)
- Software to determine sub-catchment boundaries (here WaterWay Version 1.4, could not be found online)
- Water quality monitoring equipment (if data not readily available)

Factors taken into account

- Sources
    - Land use classes
- Transport
    - No
- Retention
    - No

Limitations and Uncertainties

As mentioned before, the main problem with this method is that environmental conditions might change, which in turn leads to changes in ECs. If these conditions change without being noticed, estimated loads might differ from the actual ones.
The study was based on the loadings from one year. Since precipitation and therefore nutrient export varies throughout the years, the validity of the obtained ECs is questionable. Longer data series of nutrient loadings are needed in order to take variations between the years into account.
Nutrient loads in rivers depend on complex interaction of nutrient sources, transport processes and retention capacity. By correlating the ECs solely with land use only, differences in soil type, groundwater storage, mitigation areas such as buffer strips, etc. are neglected.

Transferability to other catchments

The method can be performed for each catchment that allows enough monitoring points and for which land use related areas are available. Attempts to apply ECs from literature studies on other catchments were not successful. A transfer of ECs might work better, if ECs were determined for nearby (sub-)catchments with similar climatic, soil and agricultural conditions.
The CORINE land cover data is easy to obtain. From the study it is not clear how many water quality monitoring stations are needed in general. Here 30 stations were included each draining a sub-catchment of 1.5 km^2 to 41 km^2, with 20 stations draining a catchment smaller than 10 km^2.. The measured P fractions (except for PP, TP and PO_4) are not standard parameters. In general the method can be applied for any substance, which is land-use dependent.
If the required software is available, the method can be performed with the information provided by the paper by McGuckin et al. (1999) and does not demand additional information.

MESAW/Non-linear regression (Vassiljev et al., 2008)

Background

The study area was situated in Estonia. Point sources as well as diffuse sources were assessed, but in this report only the part on diffuse pollution is described.

Method

The method for the determination of diffuse source export coefficients proposed by Vassiljev et al. (2008) is derived from a statistical method developed by Grimvall and Stalnacke (1996), which is based on non-linear regression. The statistical method was incorporated into the MESAW software which was developed by Vassiljev et al. (2008) in the MS Excel environment. In this software ECs are calculated for different land use categories and retention coefficients.

The major steps in this method are as follows (Liden et al., 1999):

(1) Estimation of loads at each monitoring station
(2) Determination of sub-catchments based on the location of the monitoring stations
(3) Calculations of relevant statistics regarding land use, soil types, point sources, lake area and other factors for each sub-catchment
(4) Non-linear regression with loads as a dependent and basin characteristics as independent variables.

The load at the outlet of each sub catchment is estimated as follows:

$$L_i = \sum_{j=1}^{n} (1 - R_{j,i}) L_j + (1 - R_1)(LU_i + LA_i) + (1 - R_2) P_i + (1 - R_3) D_i + \varepsilon_i \text{ [kg N]} \qquad (13)$$

where L_i = load at the outlet of the sub-catchment i; L_j = load at the outlet of the nearest upstream sub-catchment j; $R_{i,j}$ = retention on the way from the outlet of sub-catchment j to the outlet of sub-catchment i; n = number of sub-catchments located nearest upstream; LU_i = losses from different types of areas to water in the sub-catchment; LA_i = load from animals in the sub-catchment i; P_i = point source discharges in sub-catchment i; D_i = atmospheric deposition on surface waters in sub-catchment i; $R_{1,2,3}$ = retention in sub-catchment i for (LA +LU), P and D, respectively and ε_i = statistical error term. The terms LU, LA, P, D are either known or combinations of known and unknown variables. The unknown parameters are estimated by non-linear regression following the method by Grimvall and Stålnacke (1996).
Land use types covered are only arable land, forests and livestock. Other categories have been excluded, because they cover only small percentages of the studied catchments. In contrast to the study by McGuckin et al. (1999), the ECs for the different land use types are estimated by correlations using data of 10 years.
Dependency between annual depth of runoff (total runoff/area in mm/a) and ECs was found. For the load from animals ECs of 19% and 1.7% for N and P respectively were used, which were only obtained from a data set of one year.

Data Requirements

- Annual loadings of several years at each sub-catchment outlet
- Land use types
- Annual runoff
- Lake area
- Catchment area of the lakes

Required equipment

- MESAW software

Factors taken into account

- Sources
  - Point sources
  - Land use types
  - Animal loading
  - Atmospheric deposition
- Transport
  - Erosion (assessed in terms of annual runoff)
- Retention
  - For lakes and rivers (MESAW software)

Limitations and Uncertainties

The authors recognize that the ECs depend on topography and soil type, e.g. that N loss is lower in soils with clay. Yet, quantification of these dependencies is difficult with statistical methods and little data, which is why they are not taken into account.

Transferability to other catchments

As other statistical methods, this method is based on monitoring data from the studied catchment. There are no assumptions transferred from other studies, which could distort the results.
The most difficult aspect of this study is that quite long data series are required to obtain reliable statistical relationships. In the study by Vassiljev et al. (2008) data series of 10 years were used. The effort for the acquisition of data can be estimated similar to the one of the method by McGuckin et al. (1999).
The method needs the MESAW software. Since this software was not tested within this literature study it remains unclear if more parameters are needed for the application of the software. In any case, significant mathematical know-how is necessary to apply the above method.

Regression based on anthropogenic input (Pieterse et al., 2003)

Background

Pieterse et al. (2003) performed a study based on a mass-balance approach in order to assess the contribution of point sources and diffuse sources to the nutrient loading in the river Dommel catchment in The Netherlands and Belgium. In this chapter the part on diffuse pollution shall be described as an example for the quantification of diffuse pollution from a certain area.

Method

This method determines diffuse contribution by the assessment of the anthropogenic input of nutrients based on the assumption that a constant fraction of this input leaches to the river network. The same assumption was made in the DCE method in Chapter 3.2.1. The anthropogenic input can be described by the following formula, separately for each type of land use:

$$AI_{XY} = Fix + Manure + Fert + Athm - Yield \tag{14}$$

where AI_{XY} = 30-year average diffuse anthropogenic input of N and accumulated anthropogenic input of P since 1945; *Fix* = fixation of atmospheric N (Phosphorus = 0); *Manure* = animal manure applied in agricultural land; *Fert* = artificial fertilizer applied; *Athm* = atmospheric deposition and *Yield* = nutrient uptake by crop. Units are $kg*ha^{-1}*a^{-1}$ for N and $kg*ha^{-1}$ (accumulated since 1945) for P. All parameters are put into a GIS database.
Nutrient retention in the river networks is taken into account by the parameter *a* in the following equation for the simulated overall riverine nutrient load (SL_{XY}), which includes point sources (PS_{XY}), scattered dwellings (ES_{XY}) and diffuse anthropogenic input (AI_{XY}).

$$SL_{XY} = a(PS_{XY} + ES_{XY} + (b * AI_{XY})) \tag{15}$$

b is the fraction of AI_{XY} that is delivered to the drainage network, corresponding to the term export coefficient (EC).

Equation 15 was rearranged into Eq. 16 for ten uncorrelated headwater tributaries without point source and only few residencies (*PS* = 0):

$$ML_{XY} - (a * ES_{XY}) = a * b * AI_{XY} \tag{16}$$

where ML_{XY} = 5 year average measured nutrient load on location x,y in the catchment [$kg*a^{-1}$]. From (16) the fractional export coefficient *b* was estimated for each tributary through linear regression and land use type.
Diffuse export to the river can be calculated through

$$Diffuse\ export = b*AI_{XY}, \tag{17}$$

Data Requirements

For diffuse pollution:

- Amount of N fixed (P = 0)
- Amount of N and P in manure applied on the fields
- Amount of N and P in fertilizer applied on the fields
- Atmospheric deposition of N
- Nutrient uptake by crops
- Average area specific runoff
- Various additional coefficients (see Appendix C)
- 5 year average measured nutrient load on location x,y

For the full method:

- Point source loading
- Loading of effluents from dwellings

Required equipment

- GIS
- Water quality monitoring equipment (if data not readily available)

Factors taken into account

- Sources
  - Anthropogenic input (including fixation of N, atmospheric deposition, manure and fertilizer input)
  - Point sources
  - Scattered dwellings
- Transport
  - General export from different land use types (no distinction of different processes)
- Retention
  - Related to annual flow (*q*) by empirical coefficients α and β
  - Nutrient uptake

Limitations and Uncertainties

The balance model does not take into account processes that determine the export of N from soils, i.e. the export is treated as a black box. When catchments are large, this is reasonable since variations in environmental conditions will be leveled out, but the smaller the catchment the bigger the influence of local variations.
Total N can be explained well by anthropogenic input even in small catchments. The authors do not provide a clear explanation for this observation, but one reason could be that fertilizer N generally exceeds the capacity of the soil. TP cannot be explained so well by fertilizer P, it is suggested that it may be because the retention capacity of the soil is not exceeded. Other factors, like erosion, can be important in some catchments, but have not been taken into consideration.
Regression coefficients can be expressed as land use specific export coefficients.

Transferability to other catchments

In the described study 5.5% of the applied fertilizer-N has leached to the river system. Other authors observed values ranging 5 % to 40 % (Pieterse et al., 2003). This variation makes it difficult to use the applied fertilizer as an indicator for N export across several catchments. Unaccounted factors, like soil type and climate, influence the amount of N that reaches the river network. It is therefore not recommended to assume that constant percentages of the nutrients applied with fertilizer are exported from agricultural fields.
In this study it was found that on a catchment scale point sources are more important, but on a smaller scale diffuse pollution is governing in many tributaries.
The empirical parameters α and β are provided for this case study but it is not described how they were obtained, therefore authors may have to be contacted in order to apply this method.

3.4 Phosphorus

Many methods have been found that are specifically designed for the assessment of phosphorus loss in catchments. Most of these models are based on the assumption that phosphorus is mainly transported in particulate form or adsorbed to particles during surface runoff due to erosion. In a study of 116 agricultural river catchments Prairie and Kalff (1986) found an average of 16 % of P not adsorbed to particles, which confirms the above assumption.

3.4.1 Multi-criteria analysis

Universal soil loss equation (USLE) (Wishmeier & Smith, 1965)

The universal soil loss equation (USLE) assesses soil erosion leading to sediment loads in the receiving river. It is presented here even though the formula itself does not directly evaluate P loss in a catchment. However, based on the above assumption, P loss is closely linked to erosion. Thus the USLE can be used to identify CSAs for phosphorus. Moreover the USLE is a basis for or component of many further methods explained in this and other chapters since it can be used for the assessment of phosphorus loss due to erosion.

Background

The USLE is an empirical model and was developed by Wishmeier & Smith (1965) in order to estimate the annual loss of sediments by erosion in a study area.

Method

(1) Original USLE (Wishmeier & Smith, 1965)

According to the USLE soil loss is estimated with the following formula:

$$A = R * K * L * S * C * P \, , \qquad (18)$$

where A = mean long-term annual soil loss [t*ha^{-1}*a^{-1}]; R = rain and surface runoff factor [a^{-1}]; K = soil erodibility factor [t*ha^{-1}]; L = slope length factor [-]; S = slope steepness factor [-]; C = vegetation cover factor [-] and P = erosion protection factor [-].
The method has been modified and incorporated in many methods since its development in 1965. In its original form this model did not comprise spatial aspects. It works best at farmland scales.

(2) USLE and GIS (Fistikoglu & Harmancioglu, 2002)

Fistikoglu & Harmancioglu (2002) performed a study in Turkey, which combined the USLE with a GIS. This has the advantage that outputs can be presented as maps. Each factor of

the USLE presents a single layer and the calculation of Equation 18 is performed by the overlay function.
With information on sediment erosion, the export of particulate bound contaminants can be calculated according to the "enrichment concept of contaminants to sediment yield" (Fistikoglu & Harmancioglu, 2002), e.g., for organic N:

$$ONY = 0.001(SY)(CON)(ER) \quad [\text{kg*ha}^{-1}] \tag{19}$$

where ONY = organic N runoff at subbasin outlet [kg*ha^{-1}]; SY = sediment yield [t*ha^{-1}]; CON = concentration of organic N in top soil layer [g*t^{-1}] and ER = enrichment ratio [-]
More information on the input parameters can be found in Appendix D.

Data Requirements (according to Fistikoglu & Harmancioglu (2002))

- Rainfall records (*R*)
- Soil types and their properties (*K*)
- Land use and management practices (*C* and *P*)
- Topographic information (*L* and *S*)

Required equipment

- GIS

Factors taken into account

- Sources
    - Land use
- Transport
    - Erosion via surface runoff (soil type, slope, length of slope, rainfall)
- Retention
    - Erosion protection (factor *P*)

Limitations and Uncertainties

The obvious shortcoming of the USLE is that it evaluates sediment loss and not nutrient loss. However, for primarily particle bound substances such as P it could be used as a simple measure of pollution risk. Using the enrichment concept introduced above substance loads could be inferred.
However, it has to be kept in mind that while erosion is the major transport pathway for P in many catchments, other pathways, such as SRP transport in tile drains (Gächter et al. 2004), may be important. Moreover, for the prevention of eutrophication in receiving lakes or the sea, the much smaller but directly bio-available P fraction of SRP may be more important than the P fraction bound to particles. However, SRP is not necessarily dependent on erosion.

Transferability to other catchments

The study by Fistikoglu & Harmancioglu (2002) showed that in Turkey most data required for the USLE were not available to a sufficient extent, which is assumed to be true for most transition and developing countries. On the other hand the above data should be available for most European countries.
If the USLE is used for the identification of CSAs for P, erosion needs to be the dominating transport pathway. Consequently, the method should not be used in areas with low erosion or intensive tile drainage.

Modified USLE (Sivertun et al., 1988)

Background

This method by Sivertun et al. (1988) is based on the assumption that the assessment of possible risk areas without exact quantification of sediment or pollutant loads should be the first step of pollution analysis. The difference compared to the original USLE is that the result does not give a pollution load, but information on the location of high risk areas. It is therefore similar to the score system method by Trepl and Palmeri (2002) presented in Chapter 3.2.2.
According to the authors transport of sediment and nutrients is linked to surface runoff, which should be reduced, while infiltration should be increased. It can be assumed that the term nutrients refers only to P and not nutrients in general.

Method

The method overlays 4 factor maps in a GIS according to the following equation:

$$P = K * S * W * U, \tag{20}$$

where P = product map (risk of pollution); K = soil factor map; S = slope factor map; W = watercourse factor map and U = land use factor map.

The factor maps are chosen along the terms of the USLE with some changes. The slope map takes only slope steepness into consideration, while in the original USLE slope length and steepness were considered. Moreover, no protection factor (P in USLE) is considered in (22). On the other hand the distance to the watercourse (factor map W) was introduced.
Classes of the individual maps are defined using integer values(Table 5). The classes can be adapted according to individual characteristics of the catchment. The method can be extended if more information is available, i.e. further classes can be chosen and maps can be changed without influencing the other factor maps.
The soil map is divided into different soil types, according to the prevailing grain size. The land-use map is based on a Landsat TM5 image and land cover information is complemented by land use information. The watercourse map shows the distance of every grid to the watercourse.
Finally ranges for risk classes are defined according to the results of the product map. This can be done based on the distribution of the product values, e.g. in Silvertun & Prange (2003) areas with values more than two standard deviations above the mean were classified as risk-areas.

Data Requirements

- Soil type maps
- Slope (DEM used)
- Land use (land cover + database on land use)
- Watercourse map

Required equipment

- GIS (ArcView with spatial analyst and 3D analyst)

Factors taken into account

- Sources
  - Land use
- Transport
  - Erosion via surface runoff (soil type, slope)
- Retention
  - Distance to river network (factor *W*)

Limitations and Uncertainties

The method has similar limitations as the USLE approach described above. However, it is very simple and has less data requirements. A limitation is that it works only for contaminants associated with erosion. Other processes than erosion are not taken into account.
The authors state that in this case study local analysis was not possible since the DEM was not accurate enough. With a finer resolution of the DEM a more detailed analysis is possible.
According to the authors a resolution of 30m for the DEM would be desirable and the vertical accuracy should be some centimeters. If the DEM resolution is finer, the land use map also needs a finer resolution. In Germany the highest resolution available is 12.5 m. (Landesvermessung und Geobasisinformation Niedersachsen, n.d.). However, the higher the resolution, the higher are the costs to access the DEM.
The slope map should exclude depositional areas; here this was only done for lakes and rivers.
The risk classes are based on the distribution of the results (standard deviation). Consequently, if pollution is high throughout a given catchment, no distinct CSAs can be defined.

Table 5 Values for the factor maps of the modified USLE (Silvertun & Prange, 2003)

Factor Map	Classification	USLE	GIS value
Soil (*K*)	Clays	0.45	5
	Silt/fine sand	0.38	4
	Sands	0.33	3
	Organic matter	0.30	3
	Gravel/hard rock	0.20	2
Slope (*S*) [in%]	>14		30
	11-14	2.07	21
	8-10	1.26	13
	5-7	0.78	8
	3-4	0.41	4
	1-2	0.23	2
	0	0.08	1
Land use (*U*)	Agriculture (exposed)	0.15	30
	Agriculture (harvested)	0.10	20
	Agriculture (perennial)	0.075	15
	Agriculture (covered)	0.05	10
	Clear, felled, pits, dump sites	0.04	8
	Urban areas	0.03	6
	Non-urban green	0.02	4
	Grassland	0.01	2
	Forests	0.005	1
	Water	0.00	0
Watercourse (*W*) [in m]	Zone 1 (0-50m)	1.00	10
	Zone 2 (50-200m)	0.60	6
	Zone 3 (200-1000m)	0.30	3
	Zone 4 (>1000m)	0.00	0

Transferability to other catchments

It is possible to perform a study with this method in different levels of detail depending on the availability of data.
The data requirements are low and there are no parameters that are only of importance for the catchment investigated in the published study. The values for the factor maps should be adjusted according to the resolution of the available data and the specific importance of the different parameters. The risk classes can be defined depending on specific needs in the

catchment, e.g. the level of protection that shall be reached. As only sediment transport is considered as a parameter for the export of phosphorus this method partly neglects soluble P fractions.

Further advances of the method (Sivertun & Prange, 2003)

Sivertun & Prange (2003) developed an improved version of the modified USLE, using the values of the original USLE for the factor maps (see Table 5). In the method described above integer values were used. The usage of the original values by Sivertun & Prange (2003) was possible due to advances in GIS technologies since 1988 when Sivertun et al. (1988) developed the modified USLE.
Major changes in the advances by Sivertun & Prange (2003) compared to the method by Sivertun (1988) were the following:

- Real values instead of integer
- Slope length component included in slope map (model developed by Mitasova & Mitas, 1999). This model also takes into account increased erosion in areas of concentrated water flow.
- Elevation model improved (higher resolution)
- Watercourse map has continuous cell values.

Potential Non-Point Pollution Index (Munafo et al., 2005)

Background

The Potential Non-Point Pollution Index (PNPI) was developed to detect and display areas that presumably contribute most to pollution in river networks. The method is based on GIS analysis and takes into account land use, geomorphology and distance to the river network. It was applied to the Tiber catchment in Italy.

Method

The pollution potential of a cell is calculated by three parameters: the land cover indicator (LCI), the run-off indicator (ROI) and the distance indicator (DI).
The LCI relates different land uses to pollution potential, by giving each land use a coefficient indicating the pollution potential. The coefficients are assigned by an expert system and the land use maps are obtained from CORINE land cover database.
The ROI of one cell is the average ROI along the path from the cell to the river. The run-off coefficient is calculated from soil permeability, land use and slope.
The DI is calculated from the theoretical route that water takes from each cell to the river in order to account for retention on the way.
The basis for ROI and DI is a DEM.
All three indicators are normalized between their highest and lowest values so that values between 0 and 1 are obtained. The PNPI is then calculated as follows

$$PNPI = 5 * LCI + 3 * DI + 2 * ROI \tag{21}$$

A MS Access Database is used for the calculations. The data for this database is obtained from the GIS analysis of the input maps.

Data Requirements

- Land use map (for LCI and ROI)
- Geological map (for ROI)
- Digital Elevation Model (for ROI and DI)
- Expert judgment of pollution risk for different land uses
- Expert judgement of the weighting of the three indicators

Required equipment

- MS Access
- GIS (ArcGIS with the three extentions 3D Analyst, Spatial Analyst and Hydrologic Modelling)

Factors taken into account

- Sources
  - Land use (LCI)
- Transport
  - Surface runoff (ROI, Flow rate and velocity)
- Retention
  - Hydraulic distance (DI)
  - Infiltration (ROI)

Limitations and Uncertainties

The quality of the method was not validated by water quality measurements. The authors state that the validation of the results by water quality measurements is not applicable for the PNPI. It therefore remains unclear if the results are reliable. However, the coefficients, which have been estimated by experts, were confirmed by a different group of experts, who came to similar results with low standard deviation.
Precipitation which governs the amount of runoff is not taken into account. This could be a source of error. However, since the precipitation in a studied area is likely to be evenly distributed and this method does not assess actual amounts of pollution but rather the contribution of different parts of the catchment, the neglect of precipitation might not have a significant influence on the (qualitative) results.

Transferability to other catchments

The importance of the factors governing pollutant export can vary. Therefore, the weighting of the three parameters might be different in different regions of the world. Moreover, local experts may have to estimate pollution risk for different land uses.
The main advantage of the study is that the data requirements are very low and the data are easy to obtain.
Unfortunately, this method cannot be applied using the information available in the study by Munafo et al. (2005) because it does not describe how exactly the three parameters are obtained. An example of values for the three parameters is given in Cecchi et al. (2007). Still, if the method is to be applied, one of the authors should be contacted for detailed information.

P-index (Lemunyon & Gilbert, 1993)

Background

The P-index (PI) was developed as a simple tool for the assessment of P loss from agricultural fields accounting for different factors that govern phosphorus export. The first PI was developed by Lemunyon and Gilbert (1993), but many adopted indices have been developed since for different countries taking into account local conditions. For clarity reasons these adopted indices will not be discussed in detail here. Thus, the following section describes only the original PI by Lemunyon and Gilbert (1993). As a further example the Pennsylvania PI developed by scientists at the USDA-ARS Pasture Systems and Watershed Management Research Unit at University Park, PA and Penn State University College of Agricultural Sciences is illustrated (Beegle et al., 2006). A good overview of the many existing PIs is given in Buczko and Kuchenbuch (2007).

Method

The P loss parameters that are considered in the PI can be divided into source and transport factors. Eight factors are taken into account by simple addition weighted with weighting factors. The source factors are “P-content in the topsoil”, “fertilizer addition timing”, “manure addition timing”, “fertilizer mode of application” as well as “manure mode of application” while the transport factors are “soil erosion”, “irrigation erosion” and “surface runoff”:

$$PI(L\,\&\,G) = \sum_{i=1}^{n} \left(Ploss * wf\right), \tag{22}$$

where *PI(L&G)* = P-Index by Lemunyon and Gilbert (1993); *Ploss* = P loss ratings and *wf* = weighting factor. The weighting factors are estimated based on expert judgement. An example of how P loss ratings can be determined is given at the end of this section.

Data Requirements

- P-content in the topsoil
- Fertilizer amount (see Appendix E)
- Manure amount (see Appendix E)
- Fertilizer mode and timing of application (see Appendix E)
- Manure mode and timing of application (see Appendix E)
- USLE parameters for soil erosion
- Irrigation erosion
- Surface runoff

Required equipment

- P-content sampling equipment (if data not readily available)
- GIS (if spatial evaluation is desired)

Factors taken into account

- Sources
  - P-content of the soil
  - Fertilizer and manure application (amount, timing and mode of application)
- Transport
  - Erosion
  - Surface runoff
- Retention
  - Not considered

Limitations and Uncertainties

Stream bank erosion and retention in lakes is not considered in the PIs. Subsurface transport was previously considered to be of minor importance for phosphorus and therefore not included in the original PI. However, in recent PIs this factor is often considered. Similarly, the distance between the field and the receiving surface water was not considered in the original index.

Transferability to other catchments

Because the importance of different aspects of phosphorus sources and transport varies among the different regions of the world, many indices have been adapted to regional conditions. The original index was quite simple, so some factors which could be of importance were not included.
Since the PI includes the USLE or a variation of the USLE for erosion it definitely requires more effort than the USLE or the modified USLE explained above.

How easy data on manure and fertilizer application methods and timing can be collected depends very much on the country in question.
The original paper of Lemunyon and Gilbert (1993) was not available for this study. All information on the original PI was compiled from Buczko and Kuchenbuch (2007). How the parameters irrigation erosion and surface runoff were obtained originally cannot be obtained from this source. Nevertheless, there are many PI approaches, which are readily available. For instance the Pennsylvania PI, which is briefly introduced below is well documented.

A remark on further developments of the P-index

Besides the difference in factors taken into account, the PIs differ in the mathematical link of these factors (Figure 2). As described above the original PI simply added the different contributing factors. Another group of PIs (including the Pennsylvania PI described below) multiplies the source factor (*SF*) with the transport factor (*TF*), which are usually normalized between 0 and 1. SF and TF are each obtained by addition of the single source and transport factors. A third group of PIs adds three components (normally erosion, runoff and subsurface drainage), which are each calculated by multiplication of the single contributing factors.

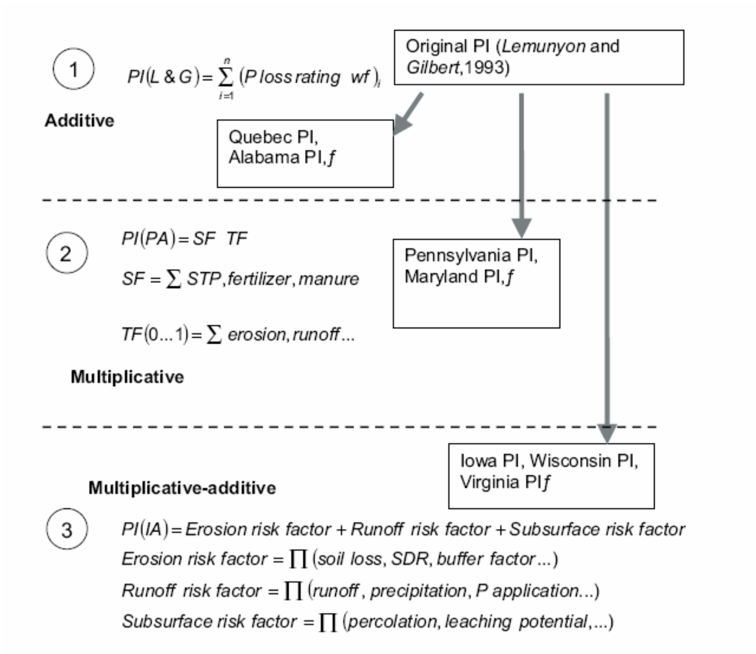

Figure 2 Different types of PIs with respect to their logical operations (Buczko & Kuchenbuch, 2007).

Example for a multiplicative P-Index: the Pennsylvania Index

The Pennsylvania PI was chosen to be explained in detail in this report because it is the basis for many of the PIs that have been developed in Europe.
As a first step the Soil Test P (STP) level and the distance from the river network are determined in order to find out if the STP level is greater than 200 ppm P or the distance is below 45 m from a water body. One of these conditions must be met for the PI to be calculated (see Appendix E). For cells with low soil P content and/or large distance from a receiving river, it is assumed that PI = 0, i.e. that there is no P loss risk from the cell in question.
If PI ≠ 0, the Pennsylvania PI is calculated as a type 2 operation in Figure 2. Figure 3 shows the different source and transport factors of the Pennsylvania PI. The source factors soil test rating, fertilizer rating and manure rating are added as well as the transport factors erosion, runoff potential, contributing distance and subsurface drainage. The sum of the single transport factors is multiplied by a factor accounting for modified connectivity, i.e. landscape characteristics which influence the transport such as riparian buffer strips, and finally divided

by 22. The resulting value is considered the transport factor. The summed source factor is multiplied by 2 and the transport factor.
Values for modified connectivity are 0.7 for riparian buffer strips, 1 for a grasses water way and 1.1 for a direct connection. Appendix E gives an overview of the parameters considered and how their values are chosen.
Exact information on each parameter can be found in Beegle et al. (2006) and downloaded from http://panutrientmgmt.cas.psu.edu/pdf/rp_PIndex_Guidance_Manual0605.pdf.

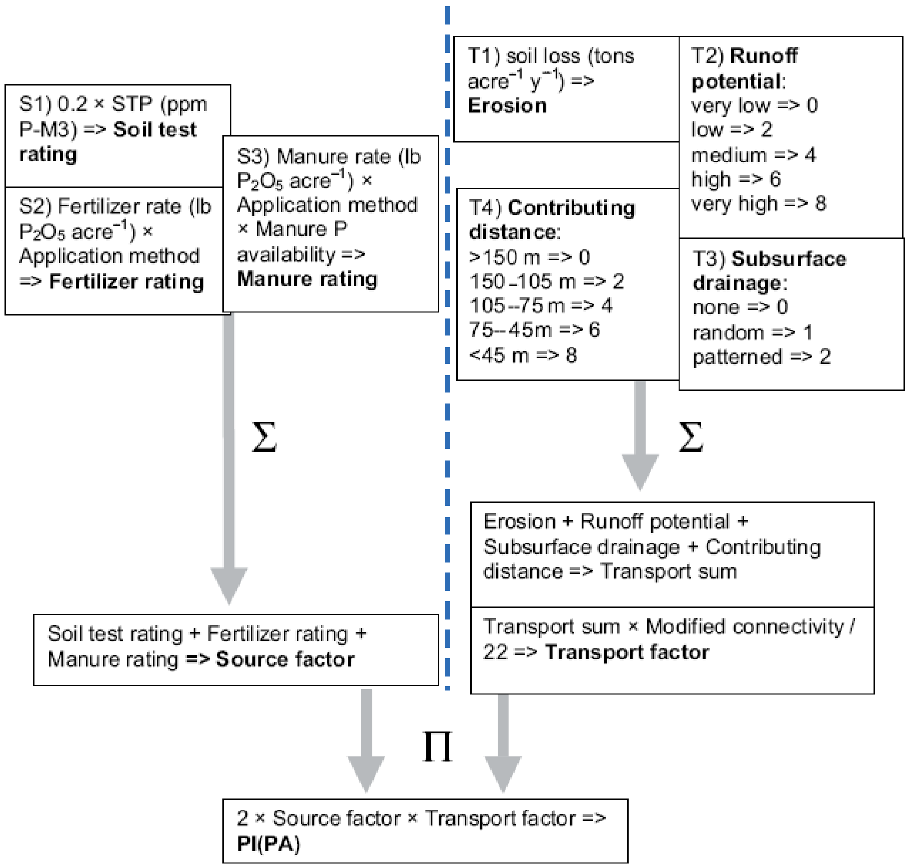

Figure 3 The components of the Pennsylvania PI (Buczko & Kuchenbuch, 2007).

Fuzzy decision trees (Schärer et al., 2006)

Background

The method was developed to predict annual P loss from agricultural catchments. To take uncertainty into account fuzzy logic was included in this method.

Method

The soluble P fractions ($TP_{<0.45}$, with reference to the use of a 0.45µm filter) and the particulate P fractions ($TP_{>0.45}$) are dealt with in two separate decision trees. Since the study by Schärer et al. (2006) showed only good results for the soluble fraction, only this part is described here (Figure 4).
The first step is the Baseflow Index (BFI). It is calculated as the ratio between base- and total flow and inversely related to both P fractions. Consequently the BFI is an inverse indicator of fast water flow, i.e. surface flow and macropore flow, which are mainly responsible for P export. In other words, a low BFI indicates high risk of P loss and vice versa.
The second set of branches refers to the annual rainfall, since the export of both P fractions is positively correlated to this parameter.

In the decision tree for $TP_{<0.45}$ the next step is the percentage of agricultural area within 50 m distance from the stream. The fourth step for $TP_{<0.45}$ is soil P, which influences the export of P from the soils. However, this parameter is only considered where the BFI is low (fast water flow) and the percentage of agricultural area is high.

Instead of just deciding between “low” and “high” (as shown in the basic decision tree in Figure 4) based on one threshold, two thresholds are defined for “low” and “high”, respectively, with intermediate “fuzzy sections”. Along a classical “fuzzy logic” approach low and high values are assigned with a value of 0 and 1, respectively, whereas linear interpolation is applied in between (Figure 5, more details in Appendix F). The approach was chosen to limit the extent of wrong decisions based on parameter uncertainty or “close calls”.

Observed $TP_{<0.45}$ loads in the receiving river are used to calibrate the fuzzy tree final outcomes. Only then can it be used to predict loads.

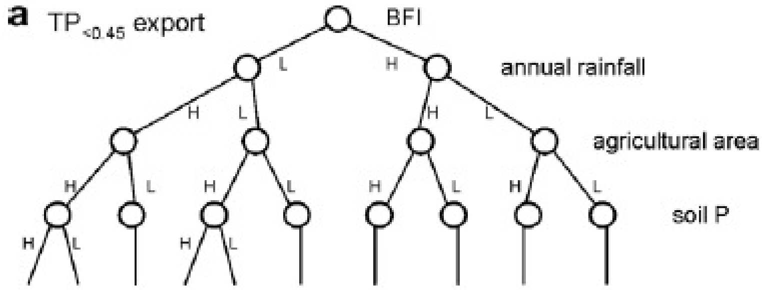

Figure 4 Decision trees to predict annual $TP_{<0.45}$ (taken from Schärer et al., 2006). H and L indicate that the factor at the last node is high or low, respectively.

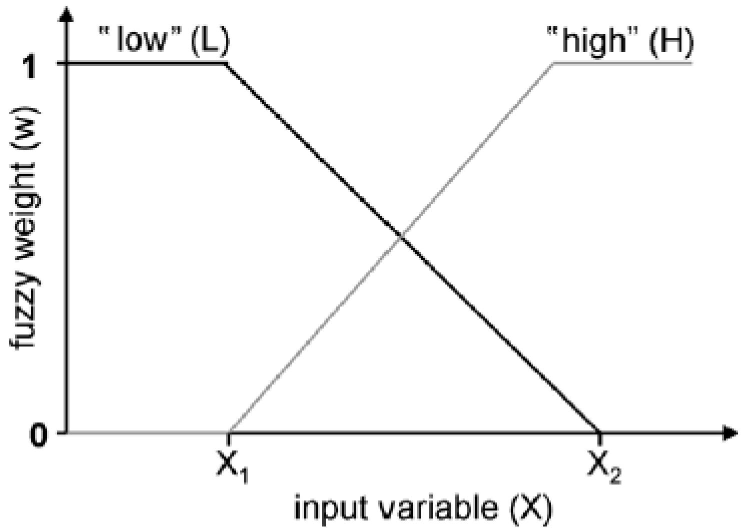

Figure 5 Fuzzy classification of input parameters (taken from Schärer et al., 2006)

Data Requirements

- Ratio between base- and total flow (Baseflow Index)
- Soil characteristics (to estimate Baseflow Index if no flow data available)
- Rainfall
- Soil P (only for areas with low BFI and high percentage of agriculture within 50 m of the streams)
- Land use maps
- Catchment borders
- Watercourse map
- DEM
- P loads in the receiving river for several years (to calibrate the fuzzy tree)

Material Requirements

- GIS
- Soil sampling and measurement equipment (if data not readily available)

Factors taken into account

- Sources
  - Soil P content
- Transport
  - Surface and macropore flow
  - Base flow
- Retention
  - Vicinity of agricultural fields to surface waters

Limitations and Uncertainties

The main limitation of the method is the river monitoring data needed for calibration. In fact, the loads in the river need to be known before the method can be used to (i) link the observed loads to the above factors and (ii) to predict loads in future years. In other words the fuzzy tree method is basically a second step, following intensive monitoring presented in Chapter 3.3.1.
Precipitation and fast flow (surface and macropore flow) are taken into account for both dissolved and particulate P. The effect of those factors on the export of the different P fractions should differ, but they are considered in the same way.
No seasonal variation of precipitation is taken into account. This has the effect that the high P losses due to single storm events are neglected. This can be a source of error and was the reason why the method did not work for particulate P.
The fact that agricultural area is only taken into account when within 50 m of the river can be a source of error in catchments that include fields in larger distance from the streams than 50 m with tile drainage or roads which can contribute to great extents to P loads.

Transferability to other catchments

If the thresholds for the different parameters are determined for each study area separately, this method could be applied to other catchments. However, the data needed to calibrate the fuzzy tree is only available for sites where intensive monitoring activities have been performed. Schärer et al. (2006) used the method for rivers where 14 years of continuous flow relative P data were available. Such a situation will only be met for very few river basins. As the errors of P load measurements are high even if a large monitoring effort is made (see Chapter 3.3.1) it is not suggested to use this approach based on sparse data. In contrast, the data needed for the decision tree itself is generally easy to obtain, especially because flow measurements to determine the BFI can be replaced by data on soil characteristics and multiple regression.

This method might not be applicable in catchments where rainfall is very unevenly distributed during the year, because annual precipitation does not reflect the heaviness of single rainfalls, i.e. actual amount affecting the ground in the rainy season.
Fertilizer (organic and mineral) has not been included in the study, but it could be included if data are available for other catchments. The structure of decision trees makes it possible to include further parameters or modify the existing parameters to make the method more suitable for different catchments.
From the paper the method can be employed on other study areas. However, it needs to be said that fuzzy tree application requires mathematical background and may not be straightforward to use.

3.4.2 Area-related methods

Soil Sorption Capacity Measurements (Behrendt et al., 1996)

Background

The limited capacity of soils to store phosphorus is assumed to be the governing parameter responsible for the export of P from soils. Behrendt et al. (1996) tested this hypothesis in a catchment located in the East of Germany (Lake Schwielochsee).

Method

Phosphorus sorption capacity PSC [kg P $*ha^{-1}*cm^{-1}$] was measured, being a measure for the maximum amount of P that can be stored per volume of soil. The PSC was used to calculate the maximal storage of phosphorus by multiplication of the PSC with the depth of the groundwater table. This amount is divided by the difference between annual phosphorus input and uptake by crops in order to calculate the time period necessary to fill up the potential phosphorus reservoir. If the reservoir is unsaturated, leaching to the groundwater is very small or cannot be detected. If the reservoir is saturated, nearly the complete difference between P-inputs and P-uptake leaches to the groundwater.
In order to determine the time period of significant leaching the following parameters need to be specified: PSC, depth of the groundwater table, annual P-input/uptake balance.
The parameters are determined using a GIS.

- PSC: from measurements and a soil map of the major soil types in the study area
- Depth of GW table: difference between the topography map and the GW table map.
- Annual P balance:
    1. General P-surplus is determined by subtraction of the P-uptake by crops from the P-fertilizer application which is assumed to be equally distributed on the whole area.
    2. Manure is assumed to be unequally distributed with higher concentrations around livestock stables.
    3. Finally the general P-surplus and the P from manure are added to obtain the total P-surplus.

The maps are logically connected as described above in order to calculate the time to fill up the reservoir for the whole catchment. The resulting map shows the catchment with respect to the time needed for P-saturation in the different parts of the basin. In this study only a very small percentage of the agricultural area (1.3%) was likely to be P-saturated within a time span of 25 years. These areas are all situated in manure spreading areas, sandy soils and have a groundwater table below 0.3 m. Despite their small total area, they can contribute to significant amounts of groundwater loading and should be subject to mitigation measures.

Data Requirements

- P-sorption capacity of the soil
- Land use maps
- Soil type map
- Topography (Used to calculate depth of groundwater)
- Groundwater isohypses
- Map of water bodies
- Fertilizer used in the catchment
- Amount of livestock in order to calculate amount of manure.

Material Requirements

- GIS
- Soil sampling and measurement equipment (if data not readily available)

Factors taken into account

- Sources
  - P saturation (depending on the soil sorption capacity and the depth of the groundwater table)
  - P-input (mineral fertilizer and manure)
- Transport
  - Only leaching because of limited sorption capacity
- Retention
  - P uptake by crops

Limitations and Uncertainties

This method can only determine how sensible areas within the catchment are to P-leaching. It does not take into account the distance of these vulnerable areas to the surface waters, so the likelihood of P reaching the stream network is not taken into account; i.e. retention processes on the way to the streams and lakes are neglected. Surface runoff and particulate bound P are not considered either.

Transferability to other catchments

This method is not restricted to a certain region of the world. No assumptions are made that are exclusively relevant for this region. However, due to the fact that surface runoff and particulate bound P are not considered this method is only applicable to catchments with low slopes.
Local soil analysis is necessary for the transfer of the method. Otherwise, fertilizer usage might be the data least frequently available, but in general information required in this method is not difficult to obtain.
The method can be applied according to the descriptions in the study by Behrendt et al. (1996).

Localization of Critical Sampling Points (CSP) (Strobl et al., 2006)

Background

This method was developed in order to choose sampling points in a river network most effectively. Surface and subsurface areas that contribute most to the pollutant load can be allocated for each river reach. If these areas are known, sampling points in the streams can be placed in an effective way. Phosphorus was chosen as a sample substance.

Method

Surface and subsurface transport are treated separately in this method. Subsurface flow pollution potential includes only the factors groundwater, septic tanks, point sources and stream bank erosion. The first three parameters for subsurface flow pollution are included in the simulation model “Generalized Watershed Loading Function” (GWLF) and the latter was added to the original GWLF model.

Regarding surface flow the pollution potential is mainly connected to topographic and land use characteristics. The following parameters are included in detail:

- Slope (from DEM)
- Profile curvature (shape of slope in downward direction, from DEM)
- Plan curvature (shape of relief perpendicular to the line of maximum slope, from DEM)
- Potential solar radiation (from DEM and latitude)
- Topographic wetness index (measure of soil saturation, from DEM)
- Sediment transport index (effects of topography on soil loss, from DEM)
- Stream power index (measure of erosive power of overland flow, from DEM)
- Buffering potential of land uses (from land use)
- Flow path length (from DEM)
- Soil permeability

Fuzzy logic operations with 10 out of 11 surface process (all except landuse) variables are performed after assigning of weighting factors to each variable. The results are combined with the remaining land use variable.

By this means each cell gets an index which specifies the surface pollution potential of that cell. For each stream cell the index values of its surface contributing areas (SCA) in the catchment are added giving a summed index. These values are normalized to values between 0 and 1. The distribution of the phosphorus load is estimated by using the GWLF model again. It predicts the P load by incorporating all phosphorus sources in the catchment. This total P load from the GWLF model is distributed to the stream cells according to the potential surface pollution index of each cell.

$$SCLoad_i = \frac{PSurfPI_i}{\sum_{i=1}^{n} PSurfPI_i} * GWLFLoad_{sa}\,[\mathrm{kg}] \tag{23}$$

where $SCLoad_i$ = estimated TP surface load at stream cell i [kg]; $PSurfPI_i$ = potential surface pollution index at stream cell i [-] and $GWLFLoad_{sa}$ = TP load from all source areas [kg].

The potential subsurface pollution is estimated from the 4 parameters mentioned above. The pollution from septic systems is predicted by proportional allocation of urban areas in the catchment. The GWLF septic system load value is used for the determination of a loading from septic systems from each cell. Point source loads are directly allocated to stream reaches. Groundwater contribution to pollution is simulated by GWLF and evenly allocated to each catchment cell. The SCA are used to allocate the groundwater loading to the stream cells. For stream bank erosion the GWLF model is used and the simulated values are assigned evenly to the stream cells; local variations are not considered. Finally the four parameters for subsurface flow pollution are added.

Surface and subsurface components are added and the Potential Stream Pollution Index (PSPI) is calculated for each stream reach assigning the estimated total P loads proportionally. By ranking of all stream cells according to their potential loading, critical stream cells for sampling are identified. Subsequently logistic and financial restrictions are incorporated.

Data Requirements

- DEM (slope; aspect; area; elevation; for solar radiation: solar declination, latitude, hour angle of sunrise or sunset)
- Land use
- Soil permeability

Required equipment

- GWLF Software (free download at http://www.avgwlf.psu.edu/download.htm)
- GIS
- Water quality monitoring equipment

Factors taken into account

- Sources
  - Land use types
  - Point source (contributing to subsurface transport)
  - Septic systems (contributing to subsurface transport)
- Transport
  - Surface transport (slope, profile curvature, plan curvature, topographic wetness index, sediment transport index, permeability, stream power index, evapotranspiration)
  - Subsurface transport (groundwater loading, septic tanks, stream bank erosion, point sources)
- Retention
  - Flow path length
  - Land use (distance of source areas to streams)

Limitations and Uncertainties

Many parameters are needed in this method. However, those parameters can be obtained from few sources, e.g. the DEM. The weight put to each variable might be a source of error. Furthermore the ranking implies that there are stream cells with low pollution loading. In a catchment with high pollution everywhere, this is not necessarily true.
It is not clear how the GWLF model calculates the loads. However, even without this model a ranking of diffuse pollution source areas can be done, because the model is mainly used for calculation of subsurface contribution and to estimate the actual loading in the stream. For our purpose a ranking of the surface contributing areas (SCA) is sufficient, which can be done without the GWLF model.

Transferability to other catchments

The study does not include assumptions that are only valid in this catchment. However, the sediment transport index includes empirical values, which are not explained in the paper. The application to other geographical regions could be difficult. How these values are obtained is not explained.
The method includes many parameters, but most of these can be obtained from the DEM, which should be available for most catchments. The compilation of the different parameters might require some effort. Topographic properties can be used for the calculation of the topographic wetness index, the stream power index and the sediment transport index.
Data on soil permeability might be difficult to obtain. However, the authors suggest that values can be obtained from other secondary variables. Yet, they do not state how this could be done, so more information is necessary in case the data are not available.
The paper gives a detailed description of the method, however it remains unclear which input data is needed for GWLF model. More information on different case studies can be found in Strobl et al. (2007).

3.5 Conclusions

3.5.1 General Conclusions

General issues

Most of the described methods provide an interesting prospect for a qualitative evaluation of critical source areas (CSAs). Data and evaluation requirements for these methods are generally significantly smaller compared to numerical model approaches. Moreover most of the methods could be applied without the need of prior experience, apart from basic GIS skills. However, there are shortcomings, valid for almost all of the methods described in this report:

- Generally it can be concluded that in contrast to the more complex physically based models, the simpler methods are not very well established. Most of the methods presented in this report are based on one or few case studies of single working groups. However, it is difficult to assess how often these methods are applied, since the results of these applications are not necessarily published in scientific papers.
- Methodology was often not described in detail or the cited sources were not available online.
- A problem with many methods is that mostly average values of precipitation and loading are considered, which do not account for extreme events. However, those extreme events are usually responsible for critical situations, i.e. high nutrient or pollution concentrations.

General remarks on the choice of method

The choice of method for the identification of critical source areas depends very much on the question that is investigated. The first question is if (a) a prediction of the actual nutrient export or (b) a ranking of areas according to their risk of nutrient loss is aimed at. The table in Appendix G shows which of the described methods provide results on actual loadings and which ones give a ranking of source areas. If the aim is to find locations that contribute most to pollutant input in surface waters in order to place mitigation measures, no exact numbers are necessary but a ranking of areas is sufficient.

Data availability also plays a big role in the choice of a suitable method. Similar to more complex models, there is a clear trade-off between the reflection of processes and data requirements. The more data, the better natural processes can be taken into account. Regarding data the spatial scale of the study is of importance. The bigger the scale the lower input requirements and simpler models are sufficient. This is due to leveling out of differences in certain factors. In turn availability of data depends on the country/region of the case study; therefore no general conclusion about the extent of effort for data acquisition is possible. In many countries data can be accessed from Environmental Protection Agencies or statistical agencies. For instance, methods that include the Universal Soil Loss Equation (USLE) as a component may not be suitable in developing countries, because data requirements are too high. In Europe and other industrialized countries it should not be a problem to gather the data required by the USLE.

As a conclusion it can be stated that there is no universal method that is suitable for all cases, but in a specific case one method might be more appropriate than another. The choice of method is always a balancing act between exact representation of processes and amount of data needed.

The more data need to be collected the higher are the costs for the method. Moreover, the inclusion of more parameters does not necessarily result in more precise output, since the quality (i.e. accuracy and precision) of the data governs the quality of the outcome (Schärer et al., 2006). If the available data include a high uncertainty, it might be more adequate to use simpler models in order to avoid feigned precision. As natural processes are very complex a model is always a simplification and inclusion of parameters that have not been fully understood can be a source of error. Simpler models represent the governing processes

to a much more basic extent and it must be kept in mind that with changes in climate and other conditions model assumptions might have to be adapted.
In general, results could be improved by combining different approaches in a GIS. For instance a method, which is based on the risk of P loss such as USLE could be combined with a map of fertilizer application or livestock density to include source information.

Common characteristics of methods

Many of the methods used result in outputs in the form of maps. This has the advantage that areas of high export potential are easily visible to the user.

Sources

Some of the methods described in this chapter include the amount of fertilizer applied on the fields in the calculations. In a work from Germany (Behrendt et al., 2003) it is stated that the amount of mineral fertilizer can be a source of error since reliable data is only available on a national level. All values for smaller regions are based on the quantities of sales of fertilizer in that region, but these values only refer to the amounts sold to wholesale. Calculations of mineral fertilizer usage on regional scale are often done based on these numbers without knowledge of the actual amounts used (UBA 2004). A possibility to avoid these uncertainties is a survey among farmers. This is however, quite time-consuming and may not be representative. The authors suggest using mass balance calculations to obtain mineral fertilizer amounts.
Rain chemistry data is used by two methods, the DCE method and the nitrate leaching coefficients method. These data are usually not gathered on a regular basis, which is a limitation of methods that use precipitation input as an information. For methods assessing total N loads precipitation might be of importance, as in both studies the contribution of rain to N loads in surface waters was between 10 and 30% of the total N load, which indicates that neglecting this parameter would lead to wrong results. For P assessment rainfall P is generally assumed to be negligible. For methods that do not result in exact loadings of N precipitation does not play an important role, because the effect of rain contribution can be assumed to be even throughout the whole catchment.

Transport

Soil data is commonly used in the described methods but may be difficult to acquire. But even though soil characteristics is a parameter which might require some effort it can enhance the results of an analysis greatly since it is one of the major factors governing leaching of substances.
Groundwater maps are also not available for all areas, which is a limitation for the methods taking groundwater into account.

Retention

Some methods assess only the export of nutrients from fields, but do not account for the amount delivered to surface waters. Natural attenuation during transport can be accounted for by including the distance of fields from the watercourses and/or the land use surrounding the surface waters.

3.5.2 Nitrogen

The assumption of a constant fertilizer export from agricultural land as it is done by the **DCE method** seems to be a simple method for fertilizer export. Differences in soil characteristics and land use, however, are not taken into account here. Furthermore the assumption that all fertilizer used in the catchment is applied on grassland for production of food for cattle might be applicable for the investigated area (Northern Ireland), but cannot be transferred to catchments with different major agricultural products. This study accounts for rain data, which amounts to 30% of the NO_3 in some sub catchments.

The method by Skop & Sörensen (1998), which applies experimentally determined **N-leaching coefficients** and the export from scattered dwellings in order to estimate diffuse pollution, takes into account soil characteristics, farm types and N input. Compared with the DCE method it gives more detailed results; however the acquisition of data from experiments requires much higher efforts. Fertilizer amounts were assumed to comply with the legislation, which is not always the case.
The **scoring system** suggested by Trepel and Palmeri (2002) is a very promising method because of its simplicity and flexibility. While it is not suitable to calculate nutrient loads, it may be a highly transferable tool for the definitions of CSAs. However, for the purpose of identifying nutrient CSAs it should be adapted with a higher focus on the nutrient export rather than the suitability of a location for wetland restoration. Thereby other mitigation measures could be chosen in areas with high nutrient export but low suitability for wetlands.

3.5.3 Nitrogen and Phosphorus

A **multi-scale monitoring** as it was performed by Tang et al. (2008) is very cost intensive and only applicable on an experimental scale. This method was chosen to assess transport pathways within a catchment. If monitoring is applied in a larger catchment, sampling points should be chosen where pollution loads are likely to be highest. For example, the method of **localization of critical sampling points** (Chapter 3.4.2 on phosphorus) developed by Strobl et al. (2006) could be chosen here.
The **Geocharacteristic Index** (GCI) is a multi-criteria method. It is very general since it does not account for properties of different pollutants. Data requirements are not high but it remains unclear how some of the factors are calculated.
Some statistical methods have been found which relate the nutrient load at the monitoring station to a basin characteristic, usually using **regression analysis**. If water quality data of many years are readily available, these methods can easily be performed. McGuckin et al. (1999) use data of only one year, which should be avoided if possible because the export of nutrients depends very much on the weather, which differs between the years. Statistical methods can only reflect average export of nutrients. However, extreme conditions are usually governing critical pollution concentrations. This cannot be reflected by statistical methods.

3.5.4 Phosphorus

The forms of P exported from a catchment depend very much on the land use; on arable land most P is lost in particulate form, while on grasslands and forestry soluble forms dominate in the leachate (McGuckin et al., 1999). In some of the described methods erosion is the only P export process taken into account. If this is the case, one must be aware that dissolved P is neglected which can be a great source of error.
Four multi-criteria methods which combine different parameters by different logical operations (multiplication and addition) have been found. All of these methods have low data requirements and the calculations are easy to use. One of these methods is the **modified USLE** which is based on the multiplication of four factor maps and similar to the scoring method for N by Trepel and Palmeri (2002). Both the modified USLE and the **PNPI** include distance from the river network as a factor in the calculations. The **P-indices** also work with multiplication of different parameters, but more parameters are considered so data requirements are higher. Moreover, the parameters are weighted according to their relative importance to P export. As many adaptations already exist it is likely that one can be found which is suitable in a catchment in question. It might also be possible to adapt PIs for a catchment to obtain better results. A drawback is that the PIs only consider sources and transport but not the likelihood of P reaching the streams. The **fuzzy decision trees** have very low data requirements and the results of the study were promising when compared to multiple regression. However, application of the method requires significant mathematical skills.
Furthermore two area related methods have been found. The method based on **soil sorption capacity measurements** as suggested by Behrendt et al. (1996) can give a first

estimate of areas that are susceptible to P leaching but retention processes on the way to the rivers are not considered.
As mentioned the method to locate **critical sampling points** can provide a ranking of which locations shall be chosen first for water quality monitoring because of their likelihood to be subject to high pollution.

3.5.5 Recommendations

When selecting a method (i) the answers needed and (ii) data availability need to be defined. It is suggested to start with a simple approach, e.g., a multi-criteria method. If results are not sufficient or validation is required a second simple or more complex approach can be applied.
Generally the multi-criteria methods seem to be most suitable for a basic CSA identification. The biggest advantage of these methods is their flexibility regarding data requirements and inclusion of different parameters. Since data availability differs to a great extent in many catchments, this characteristic makes the methods generally applicable.
For example, the scoring method by Trepel and Palmeri (2002) is a quite simple yet effective way to assess sites that not only contribute most to pollution but also are suitable for the placement of mitigation measures. If mitigation measures in the catchment should be performed, a method that takes factors for the suitability into account seems appropriate. A drawback with this method is that only wetlands are considered as mitigation measures. However, as stated above, the scoring method could be adapted to account for different mitigation measures. However, it has to be kept in mind that a scoring approach is difficult to validate and errors in assessment can easily be made if scores are not scientifically defined. As a result it is suggested to use only scores, which are well-funded in scientific literature, even if ranking itself is qualitative.

Appendix A

Nitrate leaching coefficients

Table 6 Calculated nitrogen leaching from farm types in the Vejle Fjord catchment (Skop & Sørensen, 1998)

Farm type[a]	N-leaching sand (kg N ha^{-1})	N-leaching loam (kg N ha^{-1})	Area sand (ha)	Area loam (ha)	Sum (weighted by area) sand (1000 kg N)	Sum (weighted by area) loam (1000 kg N)	Total (1000 kg N)
Part time farms	66	49	4674	9747	308	478	786
Plant production small	65	46	1554	4158	101	191	292
Plant production large	61	43	1180	3043	72	131	203
Cattle production small	79	67	3479	3724	275	250	524
Cattle production large	79	64	1676	3348	132	214	347
Pig production small	115	75	1258	2223	145	167	311
Pig production large	110	73	1424	6555	157	479	635
Total			15245	32798	1190	1909	3099

Mean annual figures based on the 1990/91–1992/93 period.

[a] Small: less than 80 ESU (Economic Size Units); Large: 80 ESU or more. The classification of ESUs is carried out from the farms standard gross margin. 1 ESU corresponds to a standard of 1200 ECU (European Currency Unit).

Appendix B
Geocharacteristic Index

$$S_R = S_f * F_r \tag{24}$$

$$S_f = \frac{D^2}{A} \tag{25}$$

$$F_r = \frac{FAV_W}{FAV_N} \tag{26}$$

Table 7 Geo-delivery impact factors (Bae & Ha 2005)

Land Coverage	Slope (%)				
	0 ~ 0.25	2.5 ~ 5	5 ~ 7.5	7.5 ~ 10	10 ~
Forest	0.075	0.115	0.155	0.195	0.235
Cultivate	0.150	0.188	0.225	0.263	0.300
Water body	1.000	1.000	1.000	1.000	1.000
Residential	0.950	0.950	0.950	0.950	0.950
Road	0.950	0.950	0.950	0.950	0.950

Appendix C

Regression based on anthropogenic input

The parameter a is described by the following formula:

$$a = \left(1 + \alpha * q_{R,XY}^{\beta}\right)^{-1} \qquad (27)$$

where $q_{R,XY}$ = average area specific runoff upstream of location x,y [$l*s^{-1}*km^{-2}$]; α [$s*km^2*l^{-1}$] and β [-] are parameters to describe the retention in the river network. Values for α and β can be obtained from de Wit (1999).

Appendix D
USLE

According to Fistikoglu & Harmancioglu (2002) can organic N pollution be assessed employing the “enrichment concept of contaminants to sediment yield” (Fistikoglu & Harmancioglu, 2002). In general, this concept can be used for particulate bound contaminants as PO_4, NH_4^+, metals and pesticides, but is not applicable for soluble contaminants as nitrate and some pesticides.

$$ONY = 0.001(SY)(CON)(ER) \text{ [kg*ha}^{-1}\text{]} \qquad (28)$$

where ONY = organic N runoff at subbasin outlet [kg*ha^{-1}]; SY = sediment yield [t*ha^{-1}]; CON = concentration of organic N in top soil layer [g*t^{-1}] and ER = enrichment ratio [-]
The sediment yield is the amount of sediment measured at a watershed outlet and described as follows

$$SY = A * DR, \qquad (29)$$

where A = total gross erosion computed from USLE and DR = sediment delivery ratio.
DR is assumed to be:

$$DR_i = 10 * \frac{R}{L} \qquad (30)$$

where R = difference in elevation between a land point and the point where the surface flow reaches the stream channel and L = length of the flow path between the point and the channel outlet.
The enrichment ratio (ER) is the concentration of contaminant in sediment divided by the one of parent soil (mostly with clay and OM)

$$ER = \frac{Cr}{Cs}, \qquad (31)$$

where Cr = contaminant concentration of runoff per gram sediment and Cs = contaminant content of the parent soil per gram.

Appendix E

Pennsylvania P-Index

Overview of the Pennsylvania P Index (Weld et al., 2007)

PART A: Screening Tool

		CMU/Field ID				
Is the CMU/field in a special protection watershed?	If the answer is yes to any of these questions, Part B must be used.					
Is there a significant farm management change as defined by Act 38?						
Is the soil test Mehlich 3 P greater than 200 ppm P? (Enter soil test value in ppm P.)						
Is the contributing distance from this CMU/field to receiving water less than 150 feet?						

PART B: Source Factors

						CMU/Field ID			
Soil Test	Mehlich 3 Soil Test P (ppm P)								
Soil Test Rating = 0.20* Mehlich 3 Soil Test P (ppm P)									
Fertilizer P Rate	Fertilizer P (lb P_2O_5/acre)								
Fertilizer Application Method	0.2 Placed or injected 2 inches or deeper (e.g., starter fertilizer)	0.4 Incorporated less than 1 week following application	0.6 Incorporated more than 1 week or not incorporated following application in April to October	0.8 Incorporated more than 1 week or not incorporated following application in November to March	1.0 Surface applied to frozen or snow-covered soil				
Fertilizer Rating = Fertilizer Rate x Fertilizer Application Method									
Manure P Rate	Manure P (lb P_2O_5/acre)								
Manure Application Method	0.2 Placed or injected 2 inches or more deep	0.4 Incorporated less than 1 week following application	0.6 Incorporated more than 1 week or not incorporated following application in April to October	0.8 Incorporated more than 1 week or not incorporated following application in November to March	1.0 Surface applied to frozen or snow-covered soil				
P Source Coefficient	Refer to: Test results for P Source Coefficient OR Book values from P Index Fact Sheet, Table 1								
Manure Rating = Manure Rate x Manure Application Method x P Source Coefficient									
Source Factor = Soil Test Rating + Fertilizer Rating + Manure Rating									

PART B: Transport Factors

						CMU/Field ID			
Erosion	Soil Loss (ton/acre/yr)								
Runoff Potential	0 Drainage class is Excessively	2 Drainage class is Somewhat Excessively	4 Drainage class is Well/Moderately Well	6 Drainage class is Somewhat Poorly	8 Drainage class is Poor/Very Poorly				
Subsurface Drainage	0 None		1 Random		2* Patterned				
Contributing Distance	0 More than 500 feet	2 350 to 500 feet	4 200 to 349 feet	6 100 to 199 feet OR less than 100 feet with 35-foot buffer	9‡ less than 100 feet				
Transport Sum = Erosion + Runoff Potential + Subsurface Drainage + Contributing Distance									
Modified Connectivity	0.85 50-foot Riparian Buffer Applies to distances less than 100 feet		1.0 Grassed Waterway or None		1.1 Direct Connection Applies to distances greater than 100 feet				
Transport Sum x Modified Connectivity / 24									

P Index Value = 2 x Source x Transport				

* OR rapid permeability soil near a stream
‡ "9" factor does not apply to fields with a 35-foot buffer receiving manure.

Appendix F

Fuzzy decision trees

Fuzzy weight (w_{low}) for low class:

$w_{low} = 1$, if $X < X_1$ (low range)

$w_{low} = 0$, if $X > X_2$ (high range)

$$w_{low} = \frac{X_2 - X}{X_2 - X_1}, \text{ if } X_1 < X < X_2 \text{ (intermediate range)}$$

The thresholds X_1 and X_2 are defined for each junction depending on the parameter contribution to P-loading.

Table 2 Input parameters and thresholds of the fuzzy membership functions used in the decision tree for $TP_{<0.45}$ and $TP_{>0.45}$

Parameter	Range	Median	X_1	X_2	Rule for different thresholds
BFI	0.54–0.77	0.60	0.61	0.64	
Annual rainfall/mm	819–1377	1150	950	1320	
Agricultural area/%	42–86	62	45	55	If BFI = low
			60	78	If BFI = high
Soil P/%	15–91	49	50	75	
Slope/%	3–45	17	12	17	If annual rainfall = high
			28	38	If annual rainfall = low

Schärer et al., 2006

Appendix G

All presented methods of Chapter 3

Table 8 Overview over all presented methods for the assessment of critical source areas

		Main characteristics	Advantages	Disadvantages	Ranking/load estimation	Applications
Nitrogen						
Statistical methods						
	Dairy cow equivalents (DCE) Jordan et al. 1994	• The method is based on the assumption that a constant fraction of the applied fertilizer is exported from a field • The amount of fertilizer applied on a field is estimated from the amount of grazing animals on this area • For total N loading point source and rainfall deposition are also considered	Simple calculations	• The exported fraction of fertilizer-N varies between catchments • The method can only be applied in catchments with cattle rising as a major fertilizer source	Load estimation	Northern Ireland
	Nitrate leaching coefficients Skop & Sörensen, 1998	• Diffuse pollution is calculated by means of nitrate leaching coefficients which are determined by experiments and related to soil types, farm types and N input • For total N loading point source and rainfall deposition are also considered	Takes into account soil characteristics, farm types and N input	• Applied fertilizer assumed to comply with the legislation • Some of the data might be hard to acquire	Load estimation	Denmark

		Main characteristics	Advantages	Disadvantages	Ranking/load estimation	Applications
Multi-criteria analysis						
	Scoring system Trepel & Palmeri, 2002	• This GIS based method assignes a "suitability value" to all cells on the watershed map by calculating the average of all contributing parameters • Contributing parameters include factors which take the suitability of the cell for wetland construction into consideration	• Very flexible in terms of data requirements • Suitability for wetlands taken into consideration	• How the values for the different parameters are obtained remains unclear • Most factors account for the suitability, not for the export from the catchment	Ranking	Germany
Nitrogen and Phosphorus						
Monitoring						
	Multi-scale intensive monitoring Tang et al., 2008	• Monitoring is performed weekly and during storm events • No other data is needed	Low data requirements	Expensive in terms of time consumption and material requirements	Load estimation	China
Multi-criteria analysis						
	Geocharacteristic Index (GCI) Bae & Ha, 2005	• The GCI is calculated in order to relate geocharacteristic properties to the pollution load in a river network. This relation shall be used to estimate loadings in catchments or sub-catchments which are not monitored. • Pollution in general is adressed, not only N and P	Low data requirements	Very general, because different substances are not considered	Load estimation	South Korea

		Main characteristics	Advantages	Disadvantages	Ranking/load estimation	Applications
Statistical methods						
	Land use related backward stepwise regression McGuckin et al., 1999	• Multiple regression between the annual loadings on the y-axis and the areas of the land use types on the x-axis	Low data requirements	• Measurements necessary for each catchment • Soil types and topography not taken into account	Load estimation	Northern Ireland
	MESAW / non-linear regression Vassiljev et al., 2008	• Non-linear regression with loads on the y-axis and a basin characteristic on the x-axis • For total N loading point source and rainfall deposition are also considered	Low data requirements	• Measurements necessary for each catchment • Soil types and topography not considered	Load estimation	Estonia
	Regression based on anthropogenic input Pieterse et al., 2003	• It is assumed that a constant fraction of the anthropogenic input leaches from the catchment • To obtain this fraction, regression analysis is performed	Retention is taken into account	More data intensive than the two methods above	Load estimation	Netherlands/Belgium
Phosphorus						
Multi-criteria analysis						
	Universal Soil Loss Equation (USLE) Wishmeier & Smith, 1965	• Basis for the estimation of soil loss in many methods that assess phosphorus loss from catchments • Multiplication of parameters considering precipitation, soil types, topography and land cover	Simple calculations	Quite data intensive	Load estimation	worldwide

		Main characteristics	Advantages	Disadvantages	Ranking/load estimation	Applications
	Modified USLE Sivertun et al., 1988	• Simplification of the original USLE • 4 factor maps considering soil types, slope, distance to watercourses and land use are multiplied in GIS • Assessment of high risk areas	• Simple calculations and prioritization of risk areas • Low data requirements	Only erosion as a transport process is taken into account	Ranking	Sweden, China
	Potential Non-Point Pollution Index (PNPI) Munafo et al., 2005	• The pollution potential of a cell is calculated by three parameters: the land cover indicator, the run-off indicator and the distance indicator	• Low data requirements • Simple calculations	The method has not been evaluated with water quality measurements	Ranking	Italy
	P-indices Lemunyon & Gilbert, 1993	• Logical operations of different source and transport factors influencing P export from catchments • Each factor is weighted according to its importance regarding P export	• Many adaptations possible depending on local conditions • Simple calculations	• Quite data intensive • Retention and subsurface transport not considered	Ranking	worldwide
	Fuzzy decision trees Schärer et al., 2006	• 4 parameters considering fast water flow, annual precipitation, agricultural area and soil P are set up in decision trees • Fuzzy classification is used	Simple structure of the method	• Only erosion as a transport process is taken into account • not storm events, but annual precipitation considered	Ranking	Germany (?)

		Main characteristics	Advantages	Disadvantages	Ranking/load estimation	Applications
Area related methods						
	Soil sorption capacity mesurements Behrendt et al., 1996	• The limited capacity of soils to store phosphorus is assumed to be the governing parameter responsible for the export of P from soils • In a GIS phosphorus sorption capacity, depth of the groundwater table and the annual P balance are used to calculate the time span that is needed for the soil to be P saturated.	Simple calculations	Only susceptibility for P leaching, but not likelihood of P reaching the streams taken into consideration	Estimation of P leaching	Germany
	Localization of critical sampling points Strobl et al., 2006	• Method to detect best suitable sampling points in order to monitor pollution load by ranking the stream cells according to their predicted potential pollution • Logistic and financial restrictions are incorporated	• Low data requirements, but at the same time many parameters included • Inclusion of logistic and financial restrictions	Complicated calculations	Ranking of sampling points	USA (Pennsylvania), Ecuador (Amazon basin), Central Chile

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