NATIONAL INSTITUTE OF PUBLIC HEALTH AND THE ENVIRONMENT
BILTHOVEN, THE NETHERLANDS

Report no. 733 008 004

# Source apportionment and quantification of nitrogen transport and retention in the River Rhine

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April, 1997

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This project has been carried out on behalf of the
Directorate General for Sciences, Research and Development of the
European Community,
Brussels, Belgium
and the
Directorate-General for Environmental Protection
Directorate of Drinking Water, Water and Agriculture of the
Ministry of Housing, Spatial Planning and Environment
The Hague, The Netherlands

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TOTAL NUMBER OF PAGES: 106

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## PREFACE

This report has been written within the scope of a Master of Science (MSc) programme, University of Greenwich, Department of Environmental Research, with the Rijkshogeschool IJselland, Department of Environmental Chemistry in the Netherlands acting as programme coordinator.

The project was carried out on commission of the National Institute of Public Health and the Environment (RIVM), the Netherlands during the period September 1995 – March 1997. It constitutes a part of another project "An East-West perspective on riverine load of nutrients into the Baltic Sea" commissioned and financially supported by the European Union.

Dr. Ir. G.M. van Dijk (Head of the Department of Aquatic Ecology, Laboratory for Water and Drinking Water Research) and Ir. J. Knoop (Department of Modeling and Statistics), also of the Laboratory for Water and Drinking Water Research) are responsible for the RIVM contribution to the "East- West" project, while Ing. S. van Dijk's task is to carry out the present project under supervision of G.M. van Dijk and J. Knoop. Drs. M.W.J. Flooren from Rijkshogeschool IJselland is supervising the progress of this research and the remaining (theoretical) part of the MSc programme.

Participants in the Project "An East-West perspective on riverine load of nutrients into the Baltic Sea":

- Linköping University, Sweden (Coordinator)
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- National Institute of Public Health and the Environment (RIVM), Bilthoven, The Netherlands
- Institute of Meteorology and Water Management, Wroclaw, Poland
- Tallinn Technical University, Estonia

***Acknowledgements***

First of all, I would like to acknowledge all those supplying data to this project:
Dr. I.A. Bach, Bayerisches Landesamt für Wasserwirtschaft; Dr. H.D. Hartmann, Umweltministerium Hessen; Dr. K. Vogt, Landesamt für Wasser und Abfall Nordrhein-Westfalen; Dr. Rocker, Ministerium für Umwelt, Raumordnung und Landwirtschaft NRWF; Dr. P. Diehl, Rheingütestation Worms Landesamt für Wasserwirtschaft Rheinland - Pfalz; Dr. Wendler, Landesamt für Umweltschutz; Dr. Koch, Landeshydrologie- und geologie; Dr. M. Keller, Bundesanstalt für Gewässerkunde; Drs. R. Wortelboer and Drs. P. Puijenbroek, National Institute of Public Health and the Environment (RIVM).

Secondly, I would like to thank all the participants of the project group and especially Dr. Horst Behrendt, Professor Anders Grimvall and Dr. Anatoly Vasiljev for their kind assistance and substantial contribution to my work. In addition thanks goes out to Gerda van Dijk for her supervision, Carol Bartels for her work on the cartography and to Michiel Flooren (RHIJ) for his initiation and supervision of the complete MSc programme for which I am very grateful. I am sincerely grateful to Rick Wortelboer for his useful comments on the manuscript and his enormous help by teaching me the ins and outs of the Access program. Besides he assisted, together with Peter van Puijenbroek and Pepijn Abbink Spaink, by gathering data. My special personal thanks goes out to Joost Knoop and Marcel de Wit for their co-operation in improving the manuscript, their large contribution to the work and their particularly good company.

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## SUMMARY

To allow efficient measures to bring about a reduction of the riverine input of nutrients to surface water and the sea, apportionment of the total load to its origin (either diffuse or point sources) is needed as a first step.

The objective of the present project was to carry out a source apportionment of the observed nitrogen load (to the source, either point or diffuse) and to quantify nitrogen transport, emission and retention in the supranational River Rhine and its main tributaries. This overall objective comprised investigating the differences between 30 sub-catchments for the contribution of diffuse or point sources of nutrients, and the (area-specific) emission of these sources and nutrient retention. Furthermore, two fundamentally different types of approaches - a riverine and an input—output approach - of source apportionment and nutrient load analysis were investigated with respect to their concept, results and applicability. A qualitative source apportionment and a retention calculation based on mass balances were also carried out. The time period considered was 1990—1995.

The riverine method is based on both concentration—discharge, and load—discharge, relationships using the observed water quality at the river mouth. Relationships between temperature and concentration are used to estimate the emissions or gross loads. The so called input—output approach is likewise an empirical method of source apportionment of riverine loads. Nutrient loss and source strength are estimated simultaneously by using non-linear regression techniques. Source strength and nutrient loss are estimated on the basis of information on different pathways of input and input—output balances, respectively.

By applying the riverine approach, the emission of dissolved inorganic nitrogen (DIN) within the total area upstream of Lobith was estimated to be 361 $kt \cdot y^{-1}$ (unit area emission of 23 $kg \cdot ha^{-1} \cdot y^{-1}$), of which 47% originates from diffuse sources. The retention within the entire catchment upstream of Lobith was 32% of the total DIN emission. The highest DIN retention was observed in the area upstream of the sampling points along the mainstream of the Rhine and the most upstream sub-basins of the Moselle (30% - 45%). The more downstream basins of the Moselle and most of the basins of the Main had a retention of dissolved inorganic nitrogen of less than 20%.

By employing the input—output approach the estimate of total nitrogen emission upstream of Lobith was found to be 344 $kt \cdot y^{-1}$ (which implies an unit area emission of 22 $kg \cdot ha^{-1} \cdot y^{-1}$). The diffuse contribution to the emission of total nitrogen within the entire catchment upstream of Lobith was estimated to be 48%. The diffuse contribution to the total load for each sub-basin individually (defined as the catchment area between two adjacent sampling sites) ranges from about 20% (Wupper Opladen, Emscher Mündung, Rhine Bad-Honnef) to 90% (Rhine Dipoldsau, Aare Brugg and Rhine Oeningen).

The results of source strength, emission and retention estimation of both approaches show that the origin of the total load (from either point or diffuse sources), the unit area emission and the percentage of the total emission retained, differ between the various sub-catchments.

Despite local differences, the results obtained with both approaches applied are generally in good agreement with each other. The input—output approach is data intensive and has stringent requirements for the study area. An advantage of this method is the high spatial detail and possibility to employ user-defined modelling concepts. The riverine approach is more generally applicable and less data intensive. The method is very convenient to quick source apportionment and emission estimates with a relatively course resolution

## SAMENVATTING

Voor het opstellen van effectieve maatregelen ter reductie van de toevoer van nutriënten naar zee middels rivieren, is een brontoebedeling van de nutriëntvracht naar zijn oorsprong (van diffuse of puntbronnen) benodigd.

Het doel van onderhavige studie was, het toebedelen van de stikstofvracht naar zijn oorsprong van punt- en diffuse bronnen en het quantificeren van de stiksofvracht, emissie en retentie in de supranationale rivier de Rijn en zijn voornaamste zijrivieren. Deze overkoepelende doelstelling houdt onderzoek in naar de verschillen tussen 30 sub-stroomgebieden met betrekking tot de bijdrage van punt en diffuse bronnen van stikstof, oppervlakspecifieke emissie en retentie. Daarbij is een vergelijk gemaakt tussen twee methoden van brontoebedeling en vrachtanalyse. Het onderzoek richt zich op de periode 1990-1995.

Toegepast is een zogenaamde "riverine" (afvoer en waterkwaliteit gerelateerd) en een input—output benadering. Additioneel is een kwalitatieve brontoebedeling en een retentie berekening gebaseerd op massa balansen uitgevoerd. De "riverine" benadering is gebaseerd op analyse van concentratie—afvoer en vracht—afvoer relaties. Relaties tussen temperatuur en concentratie zijn gebruikt voor de emissie schattingen. De input—output benadering is eveneens empirisch van aard. Retentie en bronsterkte worden simultaan geschat door gebruikmaking van niet lineaire regressietechnieken. Schattingen van bronsterkte en retentie zijn respectievelijk gebaseerd op informatie omtrent de verschillende potentiële bronnen en invoer—uitvoer balansen van stikstof voor de verschillende sub-stroomgebieden.

De met de riverine benadering geschatte emissie van opgelost anorganisch stikstof (DIN) in het totale gebied bovenstrooms van Lobith bedraagt 361 $kt \cdot jr^{-1}$ (oppervlak specifieke emissie van 23 $kg \cdot ha^{-1} \cdot jr^{-1}$), waarvan 47% afkomstig is van diffuse bronnen. De retentie is geschat op 32% van de totale DIN emissie. De hoogste retentie is berekend voor de gebieden bovenstrooms van monsterpunten in de hoofdstroom van de Rijn en de meest bovenstroomse delen van het intrek gebied van de Moezel. De meer stroomafwaarts gelegen sub-stroomgebieden van de Moezel en de meeste deelstroomgebieden binnen het intrekgebied van de Main hebben een lage retentie van opgelost anorganisch stikstof (minder dan 20%).

De emissie van totaal stikstof in het gebied bovenstrooms van Lobith is met de input—output benadering geschat op 344 $kt \cdot jr^{-1}$ (dit houdt een oppervlak-specifieke emissie van 22 $kg \cdot ha^{-1} \cdot jr^{-1}$ in). De bijdrage van diffuse bronnen aan deze totale emissie is geschat op 48%. Voor de sub-stroomgebieden (gedefinieerd als het oppervlak tussen twee opvolgende monsterpunten) varieert de diffuse bijdrage van 20% (Wupper Opladen, Emscher Mündung, Rijn Bad-Honnef) tot 90% (Rijn Dipoldsau, Aare Brugg en Rijn Oeningen).

Uit de resultaten van beide schattingsmethoden blijkt de oorsprong van de stikstofvracht (van diffuse of puntbronnen), de oppervlak-specifieke emissie en de retentie verschillend voor de onderscheidde sub-stroombegieden.

Ondanks lokale verschillen stemmen de resultaten van de beide toegepaste methoden over het algemeen goed overeen. De input—output methode is ten opzichte van de riverine benadering data-intensief gebleken en stelt meer voorwaarden aan het stroomgebied. Een voordeel van de methode is de hoge ruimtelijke resolutie en de mogelijkheid tot aanpassingen binnen het algemene modelconcept. De riverine benadering is zeer geschikt gebleken voor een relatief snelle brontoebedeling en emissieschatting met grote ruimtelijke resolutie.

# 1. INTRODUCTION

Rivers contribute to a great extent to the total input of nutrients to the sea (Brockmann *et al.*, 1988; Isermann, 1990; Stålnacke, 1996). In the 1980s convincing evidence was presented that large water bodies, such as the North Sea, can be threatened by nitrogen enrichment (eutrophication). In recent years extensive algal blooms in estuaries demonstrate the effect of nutrient enrichment. Many scientists (e.g. Isermann, 1990; Fleckseder, 1995) have expressed the need to quantify nutrient emission (to water), transport and retention within river catchments. On the occasion of the 2nd International Conference on Environmental Protection of the North Sea (March 1987) the environmental ministers of the EC countries agreed on the goal of reducing the nitrogen and phosphate emissions into surface waters by 50% by the mid-1990s.

To enable efficient measures to reduce the riverine input of nutrients to surface water and the sea apportionment of the total load to its origin, of either diffuse or point sources, is needed as a first step. Source apportionment of pollutants has two main objectives: 1) to identify the sources responsible for observed pollutants in a river system; 2) to apportion the responsibility of observed pollution levels among the identified sources.

The two major sources of nutrient loads were found to be the leaching and runoff of nutrients from agricultural soil (diffuse source) and wastewater discharge (point source) (Jolankai *et al.*, 1992; Hamm *et al.*, 1995; Stålnacke, 1996). However, because of the combined uncertainty on emission of nutrients to the water and the retention within the water course, it is difficult to quantify the impact of different sources on the nutrient transport recorded at the river mouth (Jolankai *et al.*, 1992; Sundblad *et al.*, 1994; Stålnacke, 1996).

The main processes that affect in-stream retention of riverine loads have already been ascertained. Experimental studies have provided hectare-scale data on emission of nutrients from soil to water (Foster, 1981; Gronvang, 1992; Linden *et al.*, 1993; Dorioz & Ferhi, 1994). The remaining uncertainty about riverine loads of nutrients is related to the extent to which the various identified processes actually occur on the spatial scale of large river basins and their sub-basins (Grimvall *et al.*, 1994).

***Objective***

The objective of the present project was to carry out a source apportionment of the observed nitrogen load (to the origin of either point or diffuse sources) and to quantify nitrogen transport, emission* and retention in the supranational River Rhine and its main tributaries. The time period considered was 1990–1995.

Within this overall objective several subjects for investigation can be distinguished.

*Differences between the various sub-basins of the River Rhine*

- the sources of nutrients (either point or diffuse)
- the (area-specific) emission of nutrients
- the retention of nutrients

*Comparison of two approaches of source apportionment and nutrient load analysis*

- results with regard to the sources of nutrients
- results with regard to retention estimates
- concept, potentials, spatial scale, sensitivity, data requirement

***Methods***

Two fundamentally different types of approaches of source apportionment and retention estimation are used. A riverine approach and an input—output approach. A qualitative source apportionment and a retention calculation based on mass balances were also carried out. The riverine and input—output approach together cover a wide range of possibilities with respect to data requirements, model concept and spatial detail. Due to their differences in concept and data requirements, the results obtained with the different approaches can be compared as independent modelling attempts. Uncertainties in the source apportionment's and retention estimates of both methods depend on the quality of the input data available. A qualitative source apportionment was carried out preliminary to the input—output approach. An additional retention analysis was carried out on the basis of mass balances.

*Riverine approach*

Source apportionment and estimation of nutrient emission to the surface water are based on concentration—discharge and load—discharge relationships, using the observed water quality at the river mouth only. Observed load can be apportioned to its origin of either diffuse or point sources, without any further subdivision. Apportionment is based on the differences in flow dependency of both source types. All flow-dependent input is assigned to the category of diffuse sources. In consequence the point source contribution to the total load consists of all flow-independent input. The analysis comprises an individual basin (determined by the total catchment upstream of a sampling point) without the possibility of considering more basins and their dependency simultaneously. The riverine model has the advantage of being less data intensive and generally applicable, presuming the availability of water quality data. Relations between temperature and concentration are used to estimate the emissions or gross loads.

* Emission is defined as the actual input of nitrogen into the river system.

*Input—output approach*

As preliminary exercise to the input—output approach, a qualitative method of source apportionment is carried out by grouping individual sub-basins into categories. The categorisation is based on those characteristics of the sub-basins which are assumed to reflect their potential nutrient emission. This provides an impression of the contribution of different sources to the nitrogen emission. The input—output approach applied is an empirical method of source apportionment of riverine loads in which retention and source strength are estimated simultaneously by using non-linear regression techniques. Source strength and nutrient losses are estimated on the basis of information on different pathways of input and input—output balances, respectively. Input is represented by parameters based on the basin characteristics: area of different landuse types, specific runoff and point-source emission estimations. Output is the observed riverine transport at the mouth of the river basin. Retention can be described as a function of any basin characteristic or equation. Observed load can be apportioned to its origin of either point or diffuse sources and any subdivisions within these two fundamental types of sources. In contrast to the riverine approach, apportionment is based on the estimated source strengths. The sources considered within the category of point or diffuse sources are thus defined by the parameters used to represent the input of nutrients to the river. In the estimation of load and source strength, dependency on upstream basins is considered.

*Additional analysis*

Mass balances are used as independent retention estimation to calculate the in-stream retention of nutrients in the mainstream of the Main and Moselle.

## 2. THE STUDY AREA

In terms of discharge the River Rhine is one of the most important rivers of Europe and one of the most densely used shipping routes of the world. Besides navigation, it is of great economic importance because it constitutes the water supply for industrial, domestic and agricultural purposes. With a total length of about 1320 km the Rhine is the largest river in Western Europe. The catchment of about 190 000 $km^2$ is shared by several countries. Germany covers 100 000 $km^2$. Switzerland, France and the Netherlands each cover 20 000-30 000 $km^2$. Austria and Luxembourg occupy about 2500 $km^2$. The other countries (Belgium, Italy and Liechtenstein) contribute much less. On the basis of the relief map the basin can be divided into the mountain area (Alps) upstream of Basel (Switzerland) and a middle and lowland part downstream of Basel UBA, 1993; Kwadijk, 1991). According to Jolankai *et al.* (1992) it is evident that the River Rhine is one of the major contributors to the nutrient load to the North Sea: 28% of the total direct input of 1.5 million tonnes of nitrogen goes into the North sea and 37% of the sewage sludge (total input 0.1 million tonnes of nitrogen) originate from the inputs of the River Rhine.

In the present research, the catchment of the River Rhine upstream of Lobith is divided into 30 sub-basins for which catchment characteristics and water quality data have been gathered (Figure 2.1.). The division into sub-basins is based on the natural ramification of the drainage network and the location of existing sampling sites. The separate sub-basins and river stretches are named after their most downstream sampling site. Some catchments are omitted in the calculation of net characteristics for the different sub-basins. The ratio between their own area and the area upstream of the most upstream sampling site is too narrow; this introduces large errors in mass balance calculations. The basins omitted are: Main Schwurbitz, Rhine Koblenz, Rhine Seltz. The sub-catchments distinguished are shown in Figure 2.2. The branching of the Rhine and the artificial channelling in the Netherlands makes the application of catchment and discharge-based modelling extremely difficult (though not impossible). For this reason Lobith is the most downstream sampling site included in the analysis.

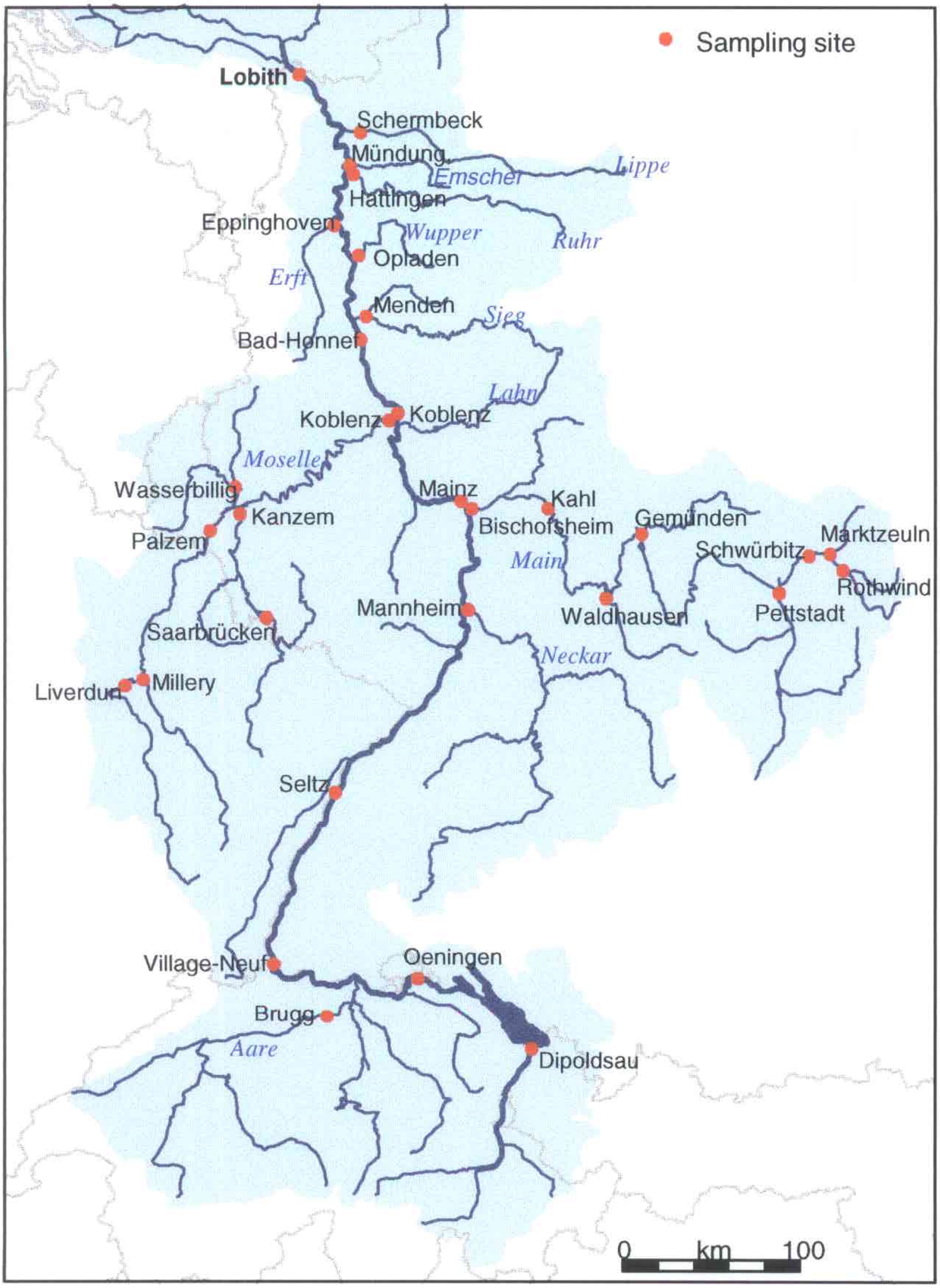



**Figure 2.1**
**Sampling sites within the River Rhine**

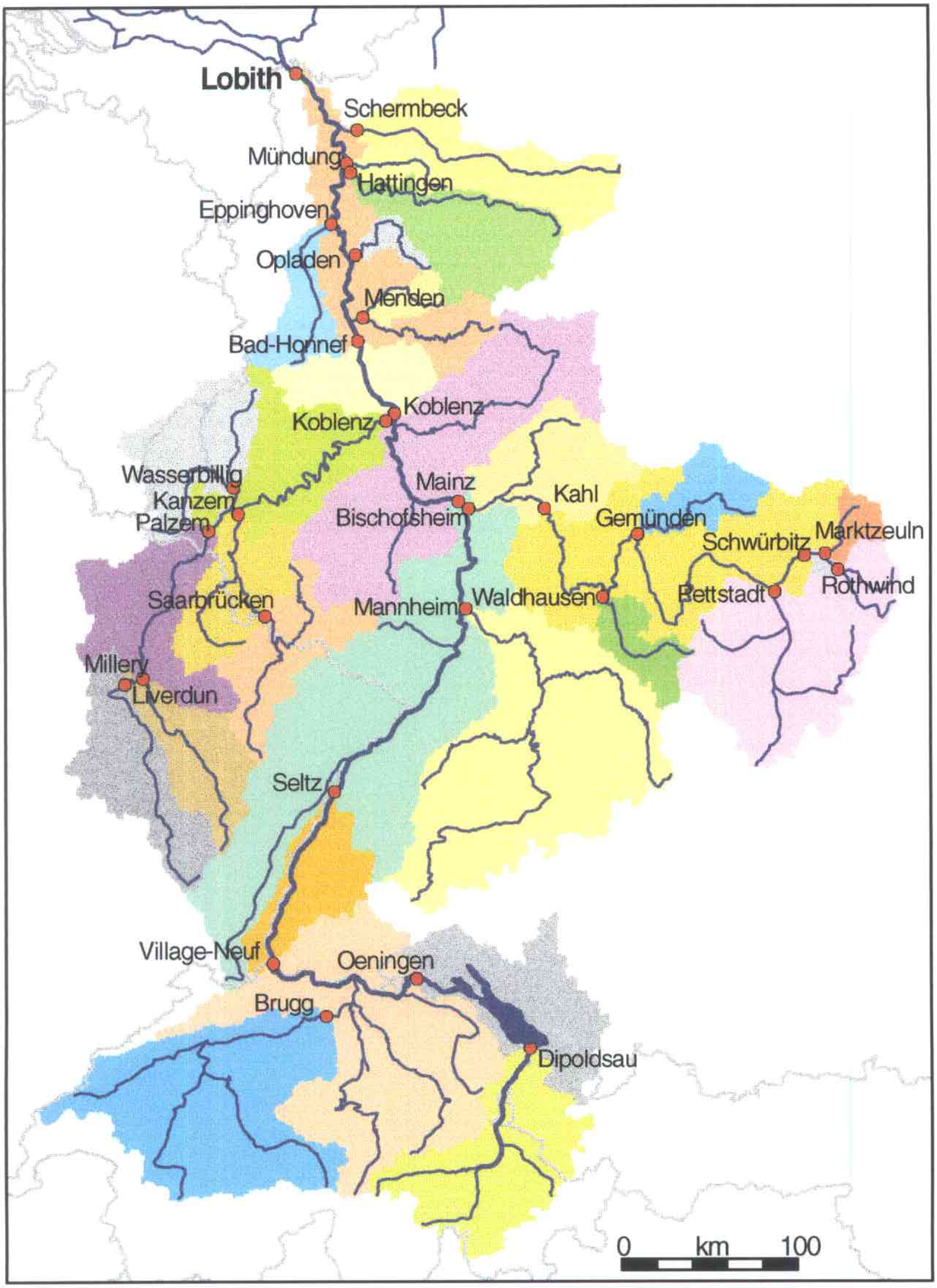



**Figure 2.2**
**Sub-catchments within the Rhine basin**

To verify the water balance of the different sub-basins, the specific runoff (unit area discharge) is calculated for each basin individually (defined as the sub-catchment between two adjacent sampling sites). The specific runoff of the different catchments is presented in Figure 2.3. There are big differences between the sub-basins with respect to the specific runoff. The mountainous upstream areas (including the Alps) can clearly be distinguished by their high specific runoff. These basins upstream of Village-Neuf have a specific runoff of about 30 $l^{-1} \cdot s^{-1} \cdot km^{-2}$. The Catchments situated along the mainstream of the Rhine have a specific runoff of less than 10 $l^{-1} \cdot s^{-1} \cdot km^{-2}$. The negative water balance for the catchment upstream of Lobith (around the mainstream) is most likely due to the withdrawal of water by the industries situated in the catchments of the rivers in the Ruhr area. The Rivers Ruhr, Sieg, Wupper and Emscher have a high specific runoff of about 13 $l^{-1} \cdot s^{-1} \cdot km^{-2}$. The specific runoff of most sub-basins within the catchment of the Moselle is slightly higher than the sub-basins of the Main.

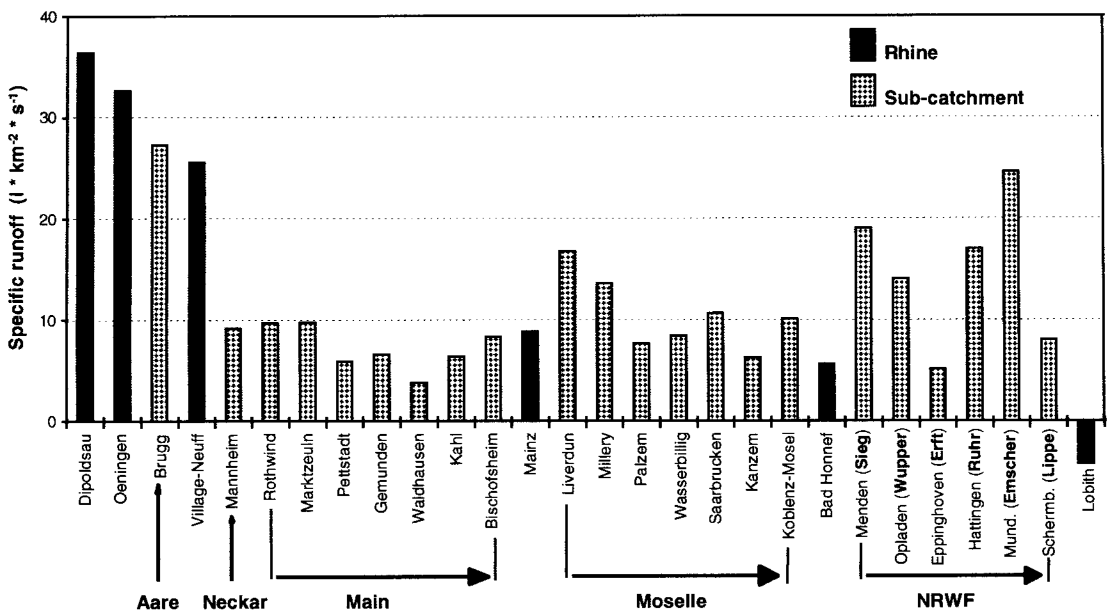



**Figure 2.3.**
**Average net specific runoff, period 1990-1994 within each sub-basin (defined as the area between two adjacent sampling sites)**

The population density of the different sub-basins of the River Rhine is presented in Figure 2.4. There are big differences in population densities between the different basins, ranging from 69 inhabitants per $km^2$ in the area upstream of Dipoldsau up to 2330 inhabitants per $km^2$ in the catchment of the Emscher (Mündung). All catchments within the North-Rhine Westphalian (NRWF) district (most downstream part of the Rhine basin) are densely populated. Most of the sub-basins of the Main and the Moselle are sparsely populated (about 125 inhabitants per $km^2$), except the moderately populated catchments upstream of Kanzem and Saarbrücken (Moselle) and the sub-basins of the Main upstream of Pettstad and Bischofsheim, which are moderately populated.

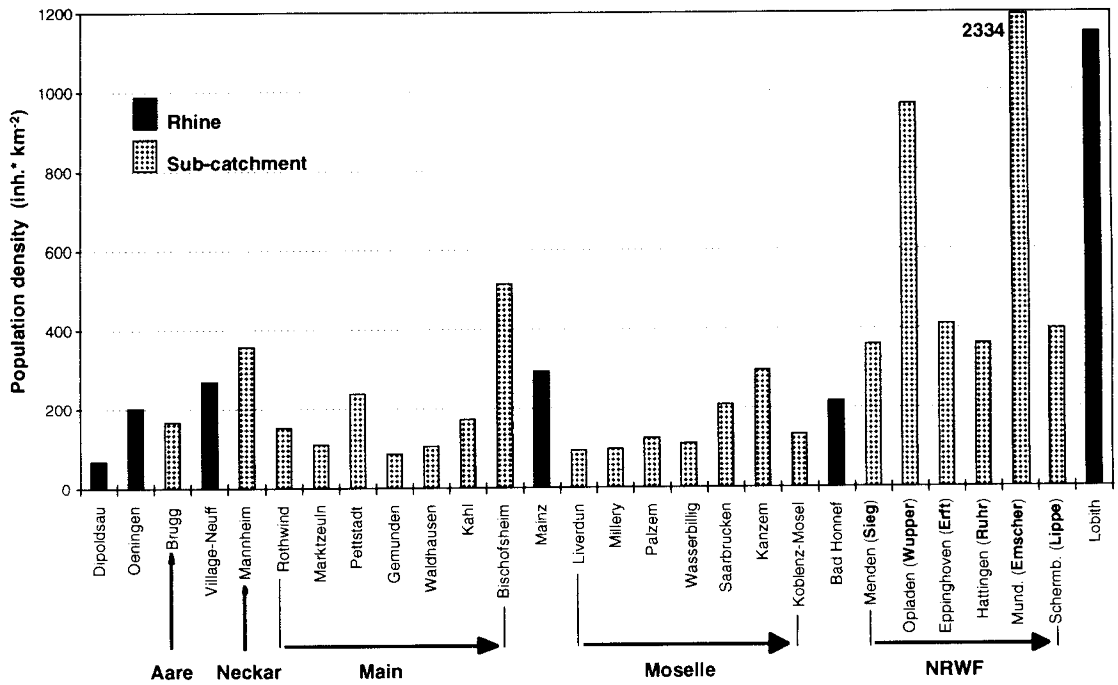



**Figure 2.4.**
**Average net population density within the period 1990-1994 within each sub-basin (defined as the area between two adjacent sampling sites)**

Different types of land cover, found within different catchments, are presented as portions of the total area of the sub-basins in Table 2.1. This table also gives the exact figures of specific runoff, population density and unit area load within the various sub-basins.

The unit area transport of total nitrogen is presented by sub-basin in Figure 2.5. The transport per unit area differs substantially between the different catchments. It ranges from about 8 kg·ha$^{-1}$ ·y$^{-1}$, within the catchment of the Erft (Eppinghoven), up to 250 kg·ha$^{-1}$ ·y$^{-1}$ within the Emscher basin (Mündung). The river basins of the Ruhr (Hattingen), Sieg (Menden), Wupper (Opladen) Erft (Eppinghoven) and Lippe (Schermbeck) have a high unit area load of about 30 kg·ha$^{-1}$ ·y$^{-1}$ . The basins Village-Neuf and Brugg have a unit area transport higher than 20 kg·ha$^{-1}$ ·y$^{-1}$. The two most upstream catchments of the River Rhine, Oeningen and Dipoldsau, have low unit area transport of about 10 kg·ha$^{-1}$ ·y$^{-1}$.

**Table 2.1**
**Percentage of different landuse types, specific runoff and population density within each sub-basin (defined as the area between two adjacent sampling sites)**

| Sub-catchment | Forest | Arable | Grass | Agric. total | Specific runoff | Population | Unit area load |
|---|---|---|---|---|---|---|---|
| | % | % | % | % | $l \cdot km^{-2} \cdot s^{-1}$ | $inh \cdot km^{-2}$ | $kg \cdot ha^{-1} \cdot y^{-1}$ |
| Dipoldsau | 27 | 1 | 31 | 33 | 36 | 69 | 11 |
| Oeningen | 27 | 13 | 32 | 47 | 33 | 202 | 15 |
| Brugg (Aare) | 31 | 14 | 33 | 47 | 27 | 168 | 22 |
| Village-Neuff | 34 | 11 | 31 | 42 | 26 | 269 | 27 |
| Mannheim | 36 | 25 | 15 | 41 | 9 | 358 | 18 |
| Rothwind | 38 | 29 | 17 | 46 | 10 | 153 | 19 |
| Marktzeuln | 48 | 24 | 14 | 38 | 10 | 111 | 13 |
| Pettstadt | 36 | 32 | 13 | 45 | 6 | 238 | 14 |
| Gemünden | 40 | 29 | 9 | 38 | 7 | 87 | 12 |
| Waldhausen | 28 | 46 | 9 | 56 | 4 | 106 | 10 |
| Kahl | 38 | 35 | 7 | 43 | 6 | 174 | 11 |
| Bischofsheim | 37 | 23 | 10 | 34 | 8 | 515 | 32 |
| Mainz | 39 | 24 | 9 | 36 | 9 | 294 | 14 |
| Liverdun | 41 | 21 | 25 | 46 | 17 | 95 | 19 |
| Millery | 41 | 22 | 24 | 46 | 14 | 98 | 19 |
| Palzem | 32 | 31 | 21 | 53 | 8 | 125 | 15 |
| Wasserbillig | 37 | 18 | 28 | 46 | 8 | 112 | 18 |
| Saarbrücken | 35 | 25 | 17 | 42 | 11 | 209 | 18 |
| Kanzem | 33 | 22 | 16 | 38 | 6 | 295 | 13 |
| Koblenz-Mosel | 44 | 19 | 13 | 35 | 10 | 133 | 22 |
| Bad-Honnef | 40 | 22 | 10 | 34 | 6 | 217 | 10 |
| Menden (Sieg) | 44 | 9 | 19 | 29 | 19 | 360 | 26 |
| Opladen (Wup.) | 33 | 5 | 22 | 28 | 14 | 965 | 41 |
| Eppinghoven (Erft) | 21 | 38 | 9 | 48 | 5 | 410 | 7 |
| Hattingen (Ruhr) | 48 | 13 | 17 | 31 | 17 | 360 | 34 |
| Mündung (Emscher) | 11 | 15 | 4 | 19 | 25 | 2334 | 243 |
| Schermbeck (Lippe) | 20 | 43 | 11 | 54 | 8 | 397 | 26 |
| Lobith | 19 | 25 | 11 | 36 | -4 | 1147 | 54 |

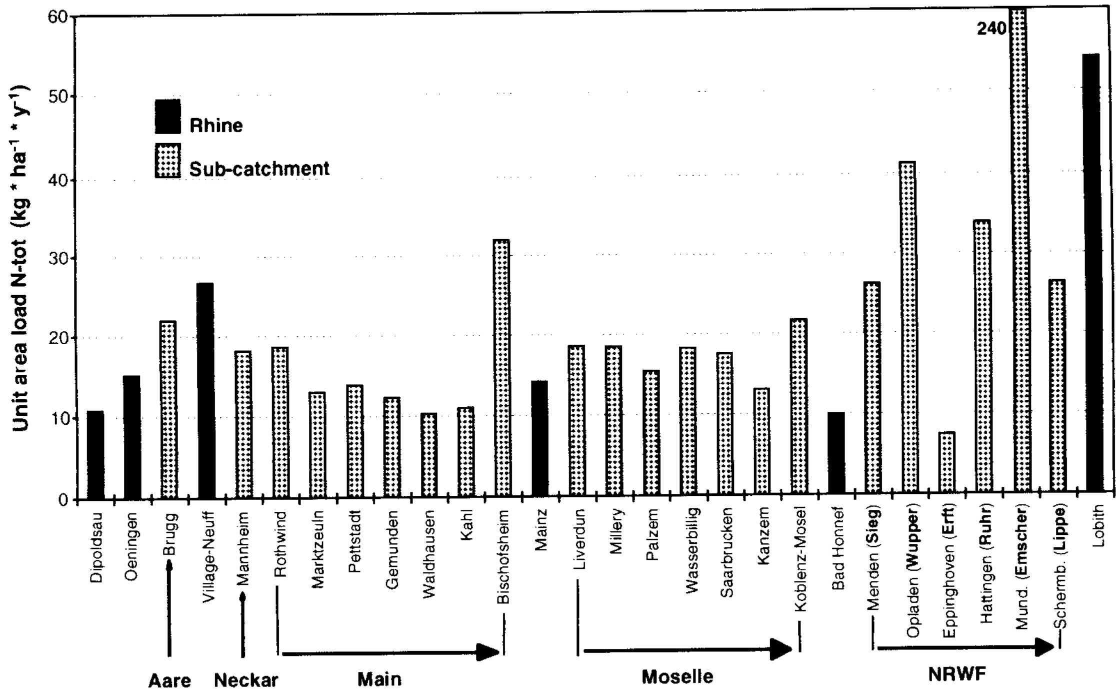



**Figure 2.5**
**Average net unit area load within the period 1990-1994 within each sub-basin (defined as the area between two adjacent sampling sites)**

# 3. DATA PROCESSING AND ORIGIN

***water quality data***

Water quality data are mainly obtained from monitoring programmes of local water boards. Most of the sites of the IRC (International Rhine Commission) and DKRR (Deutsche Kommission zur Reinhaltung des Rheins) are available in the database.

Data were gathered for the period 1990-1995. The parameters searched were nitrate, nitrite, ammonium, Kjehldal nitrate, total nitrogen, chloride, discharge and temperature. For the period 1990-1995 a thorough set of data could only be constructed for the parameters: discharge (>27700 records), temperature (>7600 records), nitrate (>7100 records) and ammonium (>7000 records) only.

The DIN parameter (dissolved inorganic nitrogen) is calculated by adding up nitrate and ammonium only. Few measurements present concentration values less than the detection limit. In this case the detection limits are assumed to represent the concentration values. Almost only point samples are included in the analysis (mainly biweekly measurements), the cases indicated in which blended samples were used. In the case of three small tributaries within the Ruhr area (Lippe, Erft and Ruhr), the discharge data were obtained from sampling sites situated slightly upstream from the concentration gauging stations (20, 7, and 20 km, respectively). The effect of this discrepancy is assumed to be negligible. Load calculations were performed according to the "direct method", used by the ICPR (International Commission for Protection of the Rhine) and described in ICPR (1993). The direct method is recommended by Klavers & Vries (1993) when monitoring "Rhine-like" rivers without the availability of daily discharge data. According to the direct method calculation of average load within a certain time period, averaging calculated daily loads is applied. Daily load is calculated on the basis of concentration and discharge data of the same date. The equation of the direct-load calculation method is:

$$\text{Average Load} = K * \frac{\left(\sum_{i=1}^{n} C_i Q_i\right)}{dt}$$

| | |
|---|---|
| K | = factor for unit conversion |
| $C_i$ | = concentration on day i |
| $Q_i$ | = discharge on day i |
| n | = number of measurements available |
| dt | = number of days for which concentration and discharge values are available |

On occasion data is available from different authorities at the same sampling site and period. In such cases consistency between the two available data sets is checked using several methods of one-way analysis of variance (for instance, least-significant difference with Bonferroni correction, Student-Newman-Keuls and Scheffé). Appendix 3.1. presents the possible references and origin of all data considered in the annual average loads. If significant discrepancies between two data sets are found, only the most complete set of data is used.

***Catchment characteristics***

Landuse, wastewater and population data for the different countries situated in the catchment of the River Rhine are available from administrative unit. Detailed maps of 1: 200 000 are used to define in which sub-basin the administrative units are situated. A database is constructed filing the statistics based on administrative units. The data sources and level of aggregation vary by topic and country. For a detailed description of the data base the reader is referred to de Wit *et al.* (1997a). For the main topics data sources and aggregation levels are listed by country in Appendix 3.2. The variation in land use, population density and connection rate to wastewater treatment plants within the whole basin of the Rhine is illustrated in Appendix 3.3.

# 4. SOURCE ANALYSIS BASED ON A RIVERINE APPROACH

## 4.1 Theoretical background

***Origin of the method***

One way to conduct a source apportionment analysis is to employ a runoff model by which the transport of selected substances to the river is calculated as a function of the concentration of the deposited substances on the land, type of land use, various hydrological flow parameters, and a loading factor which defines, for a given deposition concentration, the fraction of the substance mobilised from the land during runoff. In addition, data are required on the outflow of sewage treatment plants and direct industrial disposal of waterborne wastes.

Hellmann (1989), Gronvang (1992) and Behrendt (1993 a) were some of the researchers describing alternative methods for estimating pollutant loads from point and non-point sources based on water-quality data. The method described by Behrendt (1993a) is based on the analysis of concentration—discharge and load—discharge relationships, respectively, using the monitoring data of a river system and its main tributaries. This method was developed within the scope of the "East-West" project to which also present study is a contribution. To allow comparison between the results obtained for different river basins this riverine method described by Behrendt (1993a) is used in present project as well. A summarised overview and some modifications of this method are given in Appendix 4.1. For argumentation and an elaborate description the reader is referred to the original paper. The following section provides a simple overview of the method.

***Calculation method***

According to Novotny & Chesters (1981) and Novotny (1988) the sources of chemical loads to a river may be differentiated as follows:

- **Diffuse sources** are mostly highly dynamic but occur at random, intermittent intervals (within the temporal scale of years). The variability ranges are often more than several orders of magnitude. The amount of pollution is closely related to the meteorological variable precipitation. Often sources cannot be identified or defined.

- **Point sources** are fairly steady in flow and quality (within the temporal scale of years); variability ranges are less than one order of magnitude. The magnitude of pollution is less than the magnitude of meteorological factors or not related to them. Sources are identifiable points.

According to this classification there are two main types of *concentration—discharge relationships* (Figure 4.1. ): type A in which the total concentration is dominated by the discharge of the substance originating from diffuse sources and type B in which the total concentration is dominated by point discharge. The shape of the type A curve is explained by the increase in the concentration when river flow (precipitation determines the amount of pollution from diffuse sources) is increased up to a certain saturation concentration.

If point sources dominate the total load (type B) the curve has the shape of a typical dilution curve (the amount of pollution of point sources is less related or not at all to precipitation).

*The load—discharge relationships* of both types of concentration-discharge curves are nearly linear (Figure 4.1.). But the imaginable intercept of the curve with the load axis is positive for the case in which point load dominates and negative in the case of a total load dominated by contributions from diffuse sources.

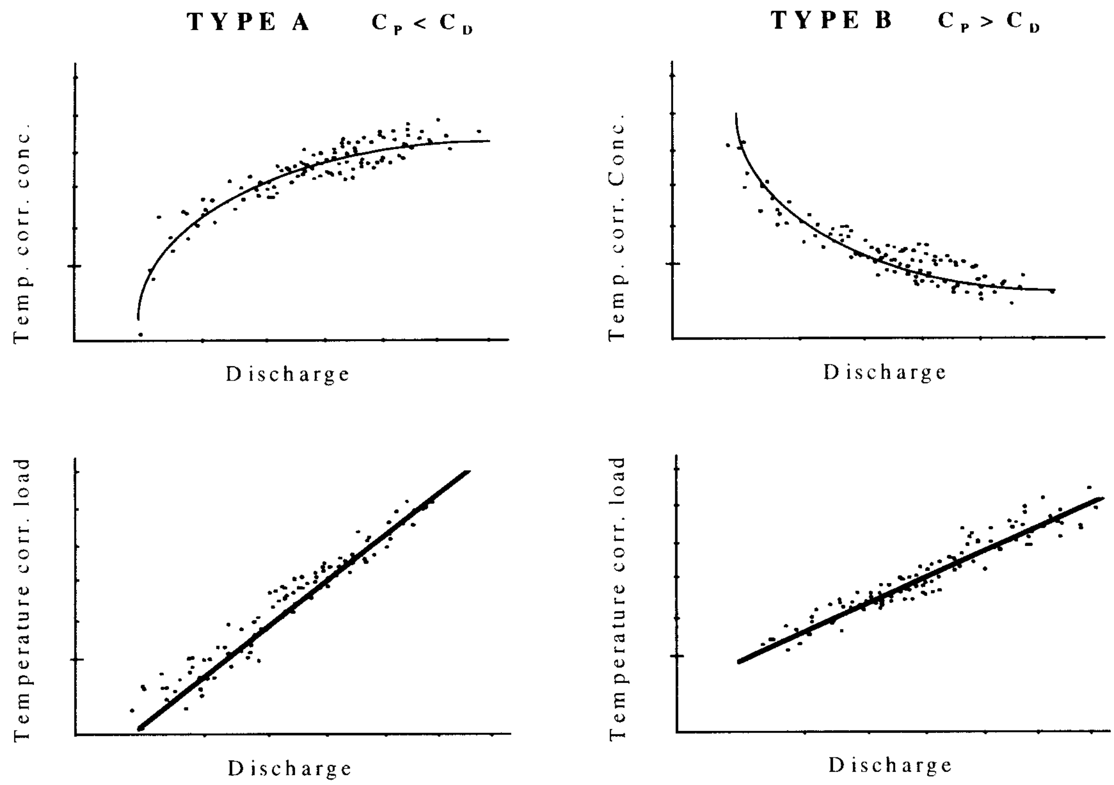



**Figure 4.1.**
**Two main types of concentration—discharge and load—discharge relationships**

All measured concentrations and calculated loads are temperature corrected to 0 °C. Retention is assumed to be absent at this temperature level.

If different data sets of net pollutant concentrations ($C_t$) and discharge ($Q_t$) exist for a given time period at a monitoring station, the means of net diffuse concentration of pollutant ($C_D$) and parameter $L_0$ can be estimated using the linear regression between the measured load ($L_m$) and the discharge ($Q_m$) as shown in Figure 4.2.

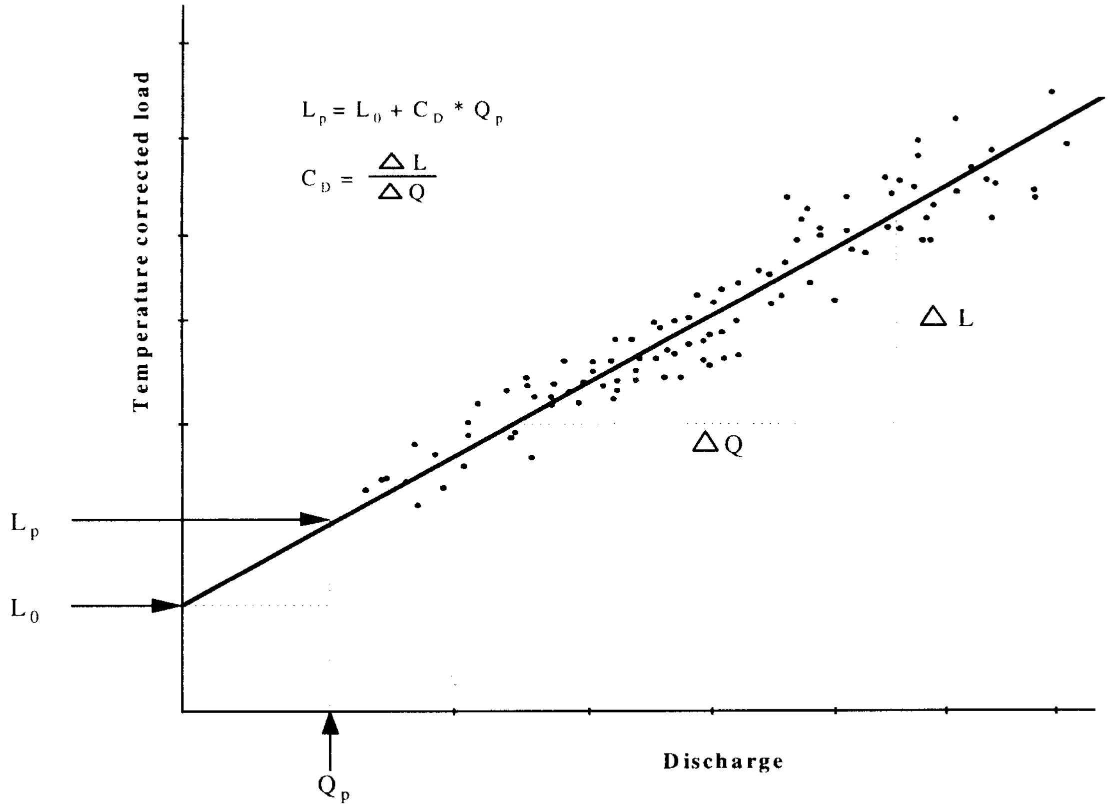



**Figure 4.2.**
**Linear regression between the measured load and the discharge**

If the mean part of the *discharge caused by point sources ($Q_P$ ) is known*, the mean point load of the pollutant is carried out using equation 4.1 and the parameter $C_D$ which was calculated by the regression of Q versus temperature-corrected load.

(4.1) $L_0 = Q_P (C_P - C_D)$

The diffuse net load ($L_D$ ) can be estimated from the difference between the total net load ($L_{Tot}$) and the estimated point net load $L_P$

(4.2) $L_D = L_{Tot} - L_P$

The quality of the results depends mainly on the scattering of the concentration— and load—discharge relationship and the uncertainty in the estimate of the discharge caused by point sources. To analyse the uncertainty in the calculated point and diffuse load, minimum and maximum point, and diffuse loads are calculated. If the minimum diffuse or point load is estimated as negative, it is forced to be at least 0. The minimum point and diffuse loads are presented as the calculated load because these loads are at least present. The uncertainty in the estimate is presented as the sum of maximum minus mean and mean minus minimum load. In the equation:

(4.3) $\text{Uncertainty} = (L_{Max} - L_{Mean}) + (L_{Mean} - L_{Min})$

$L_{Max}$ = maximum calculated load

$L_{Mean}$ = mean calculated load

$L_{Min}$ = minimum calculated load

## 4.2 Input and data availability

### *4.2.1 Water quality data*

As stated in § 4.1, m different data sets of concentration measurements ($C_t$ ) and discharge ($Q_t$) are needed at a monitoring station for a given time period. To apply the temperature correction to the concentration data, temperature data ($T_t$) is also needed for all samples. Mainly point samples (biweekly measurements) for which all three parameters are present on a similar date (point samples) are included in the analysis. Only for the locations Dipoldsau (Rhine), Oeningen (Rhine) and Brugg (Aare) are blended samples (biweekly) used. Analysis is performed for the period 1990-1995. Appendix 4.2. presents an overview of the included sampling sites, average concentrations, discharges and temperatures.

### *4.2.2 Estimation of point discharge*

As stated in § 4.1. the discharge originating from point sources is needed to employ the riverine method of source apportionment and emission estimation. How to determine the point discharge is a matter of discussion. Stålnacke & Grimvall (1996b) propose the option of estimating the runoff corresponding to 100% waste water in the river. Behrendt (1993a) estimates point discharges from population densities and wastewater statistics. In the present study two other methods are used. The first is based on calculation of the total wastewater discharge from data provided by statistical agencies. The second is based on the observed wastewater discharges of the river. Cooling water is included in the estimation of point wastewater flow because transformation, elimination, or increase of the pollutant load can occur from the cooling process itself, additives and zones of reduced flow velocity.

***Estimation of point discharge based on wastewater statistics***

Calculation of the discharge originating from point sources ($Q_p$) is mainly based on data published by the Statistisches Bundesamt Deutschland. The total amount of point discharges within a basin consists of the directly discharged industrial contribution, added to the total discharge of wastewater treatment plants.

In SBU (1991 Reihe 2.1.) the total amount of waste water discharged by wastewater treatment plants (WWTP) is presented together with the number of inhabitants connected to the wastewater treatment plants. Wastewater data and population numbers only account for the German part of a given sub-basin defined by the SBU ("SBU-basin"). The connection rate of inhabitants to wastewater treatment plants (WWTPs) by total sub-basins, including non-German parts, is estimated on the basis of wastewater statistics per administrative unit of different countries. Data sources and calculation methods used to calculate the connection rate have already been described in chapter 3. The connection rate to WWTPs and the point discharge per inhabitant, are assumed to be equal for the different countries within a sub-basin. Furthermore, the amount of waste water discharged by point sources is assumed proportional to population numbers. Apportionment of the point discharge (given per "SBU basin") to the partitioning of sub-basins used, can thus be based on population numbers. Point discharge per inhabitant (of the SBU-defined basins) are calculated. To estimate the total discharge of WWTPs per basin (situated in any hierarchy of basins), the population numbers of these basins are multiplied by the point discharge per inhabitant of the SBU basin in which the present sub-basin is situated.

In SBU (1991 Reihe 2.2.) the total amount of waste water discharged by industries is given for different branches. The total discharge is divided into direct and indirect discharge. Only the direct discharge of all types of industry is included in the calculation of industrial point discharge. The indirect discharge is routed to WWTPs or industrial treatment plants, and thus is already taken into account. Although cooling water is mainly taken from the river and discharged again, cooling water is also taken into account in the calculation. The percentage of cooling water in the discharge originating from point sources is highly variable, and depends on the type of industrial practices within a catchment. Compilations to calculate the industrial discharge by sub-basin are similar to the procedure used to calculate the discharge from WWTPs.

***Estimation of point discharge based on flow data***

As stated in Brinkman (1983) and Behrendt (1993a), for example, the principal sources of discharge during low water periods are base flow and wastewater discharges. To estimate the amount of water originating from point sources, the lowest discharge measured (within the five-year period of investigation) is assumed to represent the point source derived discharge of the river. After assuring the measurement to be no outlier (manual check). The confidence intervals of the estimated point discharge are determined empirically for the sampling sites along the mainstream. The lowest discharge measured in the biweekly samples (during the five-year period) is compared with the minimum discharge observed in daily discharge measurements for the same period. The estimated point discharge based on biweekly measurements is found to be at most 5% higher than the daily estimates. The estimated point discharge based on biweekly measurements can only be too high and not too low; therefore a one-way uncertainty range is used. The uncertainty of the point discharge estimates at sites along the mainstream is set at 5%. The estimated point discharge of the tributaries could not be validated. Due to levelling-out effects, variations in the observed discharge are smoothed as the catchment area increases, allowing a higher uncertainty of 10% to be assumed in the case of all tributaries of the River Rhine.

## 4.3 Results

Heads of the source apportionment and emission estimation, employed by the riverine approach, are the estimation of discharge originating from point sources and the temperature correction of the concentration data. In the following sections the results of both heads will be described previous to the results of the source apportionment and emission estimation.

### *4.3.1 Retention estimates*

A significant correlation between nitrate concentration and temperature is found in most tributaries investigated (Table 4.1.). Also within the time periods 1954-1988 and 1975-1984, Hellmann (1989) and van der Weijden & Middelburg (1989) described a pronounced relationship between the respective nitrate concentration and temperature in the Rhine River. The observed negative relationship between nitrate and temperature indicates retention due to microbiological activity (Hellmann, 1989). The dependency on temperature is less pronounced for ammonium. This is caused by temporary ammonium depletion, When without reaching the retention capacity of the river during summer all available ammonium is transformed. Since the contribution of ammonium to the total nitrogen transport is almost negligible (Appendix 5.2. and Von Malle, 1988) discussion with regard to retention will be concentrated on nitrogen.

The amount of nitrogen retained presumably increases for the more downstream river basins because of the increasing catchment area and thus increasing residence time. This general presumption only holds if the input of nutrients is distributed homogeneously within the catchment area. A very significant correlation exists between catchment area and total amount of retained inorganic nitrogen and nitrate ($R^2 = 0.966$ and $R^2 = 0.9494$ respectively). Minor discrepancies in the relation of retention versus area are most likely due to inhomogenity of input.

There are obvious differences between the sub-basins with regard to the amount of nitrate retained per unit area (Table 4.1.). These differences can be partly due to the differences in the specific runoff of the basins (Berendt, 1997; de Wit et al., 1997b). Runoff represents residence time and nutrient leaching from soils. Inhomogenity in specific runoff can thus cause inhomogenity in the distribution of input. Regarding the relative retention within the different basins (by considering the retained fraction of the total load), there are still obvious differences between the sub-basins (Table 4.1). The correlation between the percentage of nitrogen retained and the area of catchment is apparently not significant. This absence of correlation implies that the differences in retention, standardised for differences in specific runoff, cannot be explained by differences in catchment area of the basins. Within the Moselle and the main-stream of the Rhine, the percentage of nitrogen retained is lower for the catchment area of more downstream sampling sites. Going more downstream there is an increase in input which exceeds the increase in retention and thus obscures the correlation between retention and area. Although the impact of the densely populated Frankfurt area can be clearly distinguished by the decrease in retention between Kahl and Bischofsheim (Table 4.1.), the sources within the rest of the Main basin seem to be distributed more homogeneously (with the exception of one small densely populated catchment).

The calculated retention of dissolved inorganic nitrogen (DIN) within the total Rhine basin (upstream of the sampling site Lobith) is 32 % of the total emission of 361 kt·y$^{-1}$. Nitrate is retained by 28%. The highest nitrate and DIN retention is observed in the area upstream of the sampling points along the mainstream of the Rhine and the most upstream sub-basins of the Moselle (30% - 45%). The more downstream basins of the Moselle and most of the basins of the Main have a nitrate retention of less than 20% (Table 4.1.).

**Table 4.1**
**Retention estimates of nitrate ($NO_3$) by emploiment of the riverine approach**

| Basin | Corr. coeff. Conc. $NO_3$ versus Temp | Retention kt·y$^{-1}$ | unit area retention kg·ha$^{-1}$·y$^{-1}$ | % Retention of total emission % |
|---|---|---|---|---|
| Dipoldsau | 0.16 | 1.89 | 3.10 | 30 |
| Oeningen | 0.87 | 5.77 | 5.80 | 38 |
| Brugg (Aare) | 0.61 | 13.30 | 11.76 | 42 |
| Village-Neuff | 0.86 | 40.42 | 11.47 | 44 |
| Seltz | 0.91 | 37.42 | 7.71 | 36 |
| Mannheim | 0.53 | 6.86 | 4.78 | 21 |
| Schwürbitz | 0.17 | 0.24 | 0.96 | 6 |
| Rothwind | 0.45 | 0.20 | 1.61 | 9 |
| Marktzeuln | 0.06 | 0.03 | 0.24 | 2 |
| Pettstadt | 0.37 | 2.55 | 3.62 | 22 |
| Gemünden | 0.40 | 0.23 | 1.03 | 8 |
| Waldhausen | 0.64 | 0.30 | 1.83 | 19 |
| Kahl | 0.74 | 6.97 | 3.10 | 20 |
| Bischofsheim | 0.57 | 4.53 | 1.68 | 12 |
| Mainz | 0.81 | 80.37 | 8.24 | 43 |
| Liverdun | 0.74 | 3.07 | 9.95 | 44 |
| Millery | 0.74 | 3.15 | 4.89 | 28 |
| Palzem | 0.84 | 7.84 | 7.20 | 43 |
| Wasserbillig | 0.77 | 1.82 | 3.98 | 21 |
| Saarbrücken | 0.51 | 0.46 | 1.27 | 10 |
| Kanzem | 0.50 | 1.19 | 1.48 | 12 |
| Koblenz-Mosel | 0.61 | 7.76 | 2.70 | 16 |
| Koblenz-Rhine | 0.65 | 73.51 | 6.72 | 32 |
| Bad-Honnef | 0.85 | 104.92 | 7.47 | 36 |
| Menden (Sieg) | 0.03 | 0.05 | 0.21 | 1 |
| Opladen (Wupper) | 0.33 | -0.80 | -7.39 | -27 |
| Eppinghoven (Erft) | 0.56 | 1.11 | 5.22 | 51 |
| Hattingen (Ruhr) | 0.58 | 2.22 | 5.19 | 17 |
| Mündung (Emscher) | 0.04 | 0.02 | 0.29 | 8 |
| Schermbeck (Lippe) | 0.43 | 1.65 | 3.50 | 15 |
| Lobith | 0.75 | 91.59 | 5.72 | 28 |

### *4.3.2 Discharges originating from point sources*

The results of the two methods used to estimate the discharge originating from point sources (the first one based on wastewater statistics and a second on water-quality data) are presented in Table 4.2. There are relatively large discrepancies between the results obtained with the two different estimation methods. All point discharge estimates in the North-Rhine Westphalian district (NRWF) based on wastewater statistics are much higher than the riverine estimates. This is most likely due to the extensive use of cooling water in this highly industrialised region. The same bias can be observed for some other areas in which point-source discharge is a substantial part of the total discharge e.g. Kanzem (Moselle), Mannheim (Neckar), Pettstadt (Main). The high estimates of point discharge, applying the riverine assessment, within the upstream part of the Rhine basin are possibly caused by a considerable base flow, mostly supported by water from snowmelt during the low flow conditions during summer (van der Weijden & Middelburg, 1989).

**Table 4.2.**
**Comparison of estimates of point discharges obtained with different estimation methods (riverine and statistics) and the literature (Behrendt 1993)**

| Basin | Riverine<br>$m^3 \cdot s^{-1}$ | Statistics<br>$m^3 \cdot s^{-1}$ | Behrendt<br>$m^3 \cdot s^{-1}$ | Riverine from total Q<br>% |
|---|---|---|---|---|
| Dipoldsau | 91 | 20 | | 41 |
| Oeningen | 186 | 58 | | 53 |
| Brugg (Aare) | 133 | 164 | | 43 |
| Village-Neuff | 405 | 363 | | 40 |
| Seltz | 589 | 472 | 300-400 | 50 |
| Mannheim | 40 | 71 | 80-100 | 30 |
| Schwürbitz | 4 | 4 | | 18 |
| Rothwind | 3 | 3 | | 21 |
| Marktzeuln | 1 | 2 | | 8 |
| Pettstadt | 19 | 22 | | 46 |
| Gemünden | 3 | 3 | | 17 |
| Waldhausen | 2 | 2 | | 25 |
| Kahl | 39 | 52 | | 27 |
| Bischofsheim | 36 | 83 | 80-100 | 20 |
| Mainz | 780 | 471 | | 52 |
| Liverdun | 4 | 3 | | 8 |
| Millery | 11 | 5 | | 12 |
| Palzem | 15 | 10 | | 11 |
| Wasserbillig | 8 | 5 | | 22 |
| Saarbrücken | 9 | 3 | | 22 |
| Kanzem | 16 | 18 | | 24 |
| Koblenz-Mosel | 40 | 39 | 50-100 | 14 |
| Koblenz-Rhine | 713 | 521 | 550-650 | 45 |
| Bad-Honnef | 852 | 616 | | 45 |
| Menden (Sieg) | 9 | 9 | | 20 |
| Opladen (Wupper.) | 6 | 12 | | 41 |
| Eppingh. (Erft) | 7 | 10 | | 68 |
| Hattingen (Ruhr) | 21 | 19 | | 29 |
| Mündung (Emscher) | 10 | 21 | | 53 |
| Schermbeck (Lippe) | 16 | 23 | | 41 |
| Lobith | 903 | 864 | 850-950 | 44 |

Despite the local differences between the results obtained with both methods, the estimates of point discharge within the total area upstream of Lobith match fairly well. The riverine method has the advantage of being less data intensive and is based on measured water quality data instead of national wastewater statistics. For data provided by statistical agencies different sources of waste water are often not defined similarly for different countries. Besides, the riverine method already includes the water originating from base flow. The point discharge estimates of the riverine method are used in all calculations.

For the upstream parts of the Rhine basin (upstream of Dipoldsau, Oeningen) the discharge originating from point sources is approximately 20% of the total discharge (of about 300 $m^3/s$, Table 4.2.). The point source contribution to the total discharge increases up to 30-40% (of a total discharge of 1500-2050 m3 s-1) for the area covered by the more downstream sampling sites along the mainstream of the River Rhine. The estimate of the point source discharge for the area upstream of Mainz (Rhine) is too high compared to the same estimates for the direct upstream and downstream sampling sites. The contribution of point sources to the total discharge is high (40%-70%) for all rivers situated in the North-Rhine Westphalian (NRWF) area (including the Ruhr area).

The point source contribution to the total water discharge is very low in the Moselle basins and moderate for the upstream sub-basins of the Main. The location of Frankfurt in the downstream part of the Main basin (between the sampling sites Kahl and Bischofsheim) apparently elevates the portion of discharge originating from point sources (Table 4.2.). Within the catchment area of the River Regnitz (represented by the sampling site Pettstadt) there is also a high portion of the discharge originating from point sources.

The estimated point source discharges for the different basins approximately match with the estimates of point source discharges stated by Behrendt (1993a) (Table 4.2.).

### *4.3.3 Emission estimates and source apportionments*

#### 4.3.3.1 Emissions

The total emission (into the water) increases from 16 kilotons per year upstream of Oeningen to 361 kilotons per year upstream of Lobith (Table 4.3.). The total emission of dissolved inorganic nitrogen to the catchment of the Main (sampling site Bischofsheim) is estimated to be 42 kt per year. The Neckar (sampling site Mannheim) and Moselle (Koblenz) contribute 35 kt and 50 kt per year, respectively.

**Table 4.3**
**Emission estimates and uncertainties**

| Basin | Emis. DIN | Unc.DIN | Emis. $NO_3$ | Unc.$NO_3$ | Emis. $NH_4$ | Unc.$NH_4$ |
|---|---|---|---|---|---|---|
| | $kt \cdot y^{-1}$ | % | $kt \cdot y^{-1}$ | % | $kt \cdot y^{-1}$ | % |
| Dipoldsau | 9 | 53 | 6 | 30 | * | * |
| Oeningen | 16 | 11 | 15 | 12 | 1.1 | 3 |
| Brugg (Aare) | 39 | 14 | 32 | 8 | * | * |
| Village-Neuff | 97 | 7 | 91 | 6 | 6.2 | 10 |
| Seltz | 108 | 6 | 103 | 6 | 5.4 | 11 |
| Mannheim | 35 | 9 | 33 | 8 | 1.3 | 28 |
| Schwürbitz | 4 | 9 | 4 | 8 | 0.3 | 22 |
| Rothwind | 3 | 7 | 2 | 6 | 0.2 | 19 |
| Marktzeuln | 1 | 8 | 1 | 7 | 0.1 | 18 |
| Pettstadt | 13 | 9 | 12 | 7 | 1.3 | 24 |
| Gemünden | 3 | 6 | 3 | 5 | 0.1 | 36 |
| Waldhausen | 2 | 11 | 2 | 10 | 0.0 | 30 |
| Kahl | 36 | 6 | 35 | 6 | 1.4 | 15 |
| Bischofsheim | 42 | 7 | 39 | 6 | 2.9 | 18 |
| Mainz | 208 | 13 | 185 | 12 | 22.9 | 16 |
| Liverdun | 7 | 17 | 7 | 16 | 0.2 | 38 |
| Millery | 13 | 11 | 11 | 10 | 1.3 | 26 |
| Palzem | 20 | 11 | 18 | 11 | 1.5 | 17 |
| Wasserbillig | 9 | 11 | 8 | 9 | 0.6 | 36 |
| Saarbrücken | 5 | 10 | 5 | 7 | 0.9 | 29 |
| Kanzem | 12 | 11 | 10 | 8 | 2.1 | 27 |
| Koblenz-Mosel | 50 | 7 | 48 | 6 | 2.6 | 19 |
| Koblenz-Rhine | 247 | 8 | 227 | 7 | 20.6 | 10 |
| Bad-Honnef | 305 | 8 | 289 | 7 | 16.1 | 16 |
| Menden (Sieg) | 6 | 9 | 5 | 8 | 0.4 | 26 |
| Opladen (Wupper) | 5 | 18 | 3 | 7 | 1.9 | 35 |
| Eppinghoven (Erft) | 3 | 22 | 2 | 21 | 0.5 | 29 |
| Hattingen (Ruhr) | 15 | 11 | 13 | 8 | 2.5 | 30 |
| Mündung (Emscher) | 8 | 15 | 0.3 | 69 | 7.5 | 13 |
| Schermbeck (Lippe) | 12 | 9 | 11 | 8 | 1.4 | 15 |
| Lobith | 361 | 6 | 323 | 6 | 38.1 | 10 |

(* no analysis)

The estimated unit area emissions of dissolved inorganic nitrogen are different for the various sub-basins (Table 4.4.). A high unit area emission is found for the areas upstream of the sampling points along the mainstream and the catchments within the North-Rhine Westphalian (NRWF) district. The unit area emission of dissolved inorganic nitrogen ranges from approximately 22 kg·ha$^{-1}$ ·y$^{-1}$ upstream of the mainstream stations, to more than 35 kg·ha$^{-1}$ ·y$^{-1}$ within the North-Rhine Westphalian district. Lower emissions per unit area are found in most sub-basins of the Main and the Moselle. The unit area emissions within the catchment of the River Main are about 10 to 18 kg·ha$^{-1}$ ·y$^{-1}$. The sub-basins of the Moselle have an unit area emission of 15 to 20 kg·ha$^{-1}$ ·y$^{-1}$. The unit area emissions within the entire catchment upstream of Lobith is 23 kg·ha$^{-1}$ ·y$^{-1}$ (which implies an absolute emission of 361 kt·y$^{-1}$).

**Table 4.4**
**Unit area emissions**

| **Basin** | **DIN** kg·ha$^{-1}$·y$^{-1}$ | **$NO_3$** kg·ha$^{-1}$·y$^{-1}$ | **$NH_4$** kg·ha$^{-1}$·y$^{-1}$ |
|---|---|---|---|
| Dipoldsau | 15 | 10 | * |
| Oeningen | 16 | 15 | 1.1 |
| Brugg (Aare) | 35 | 28 | * |
| Village-Neuff | 28 | 26 | 1.7 |
| Seltz | 22 | 21 | 1.1 |
| Mannheim | 24 | 23 | 0.9 |
| Schwürbitz | 16 | 15 | 1.4 |
| Rothwind | 20 | 19 | 1.7 |
| Marktzeuln | 13 | 11 | 1.2 |
| Pettstadt | 19 | 17 | 1.9 |
| Gemünden | 13 | 13 | 0.6 |
| Waldhausen | 10 | 9 | 0.2 |
| Kahl | 16 | 16 | 0.6 |
| Bischofsheim | 16 | 15 | 1.1 |
| Mainz | 21 | 19 | 2.3 |
| Liverdun | 23 | 22 | 0.5 |
| Millery | 19 | 17 | 2.0 |
| Palzem | 18 | 17 | 1.4 |
| Wasserbillig | 20 | 19 | 1.2 |
| Saarbrücken | 15 | 12 | 2.4 |
| Kanzem | 15 | 12 | 2.6 |
| Koblenz-Mosel | 17 | 17 | 0.9 |
| Koblenz-Rhine | 23 | 21 | 1.9 |
| Bad-Honnef | 22 | 21 | 1.1 |
| Menden (Sieg) | 24 | 22 | 1.7 |
| Opladen (Wupper) | 45 | 27 | 18.0 |
| Eppinghoven (Erft) | 13 | 10 | 2.5 |
| Hattingen (Ruhr) | 36 | 30 | 5.9 |
| Mündung (Emscher) | 103 | 4 | 99.9 |
| Schermbeck (Lippe) | 26 | 23 | 3.0 |
| Lobith | 23 | 20 | 2.4 |

(* no analyse)

*4.3.3.2* Contribution of different sources to the total load

The results of the apportionment of DIN to diffuse and point sources is approximately the same for the areas upstream of all sampling points along the mainstream (Figure 4.3.).Within these "mainstream basins" both sources (diffuse and point) contribute about 50% to the total emission. Within the entire catchment upstream of Lobith diffuse sources contribute 47% to the total load of DIN.

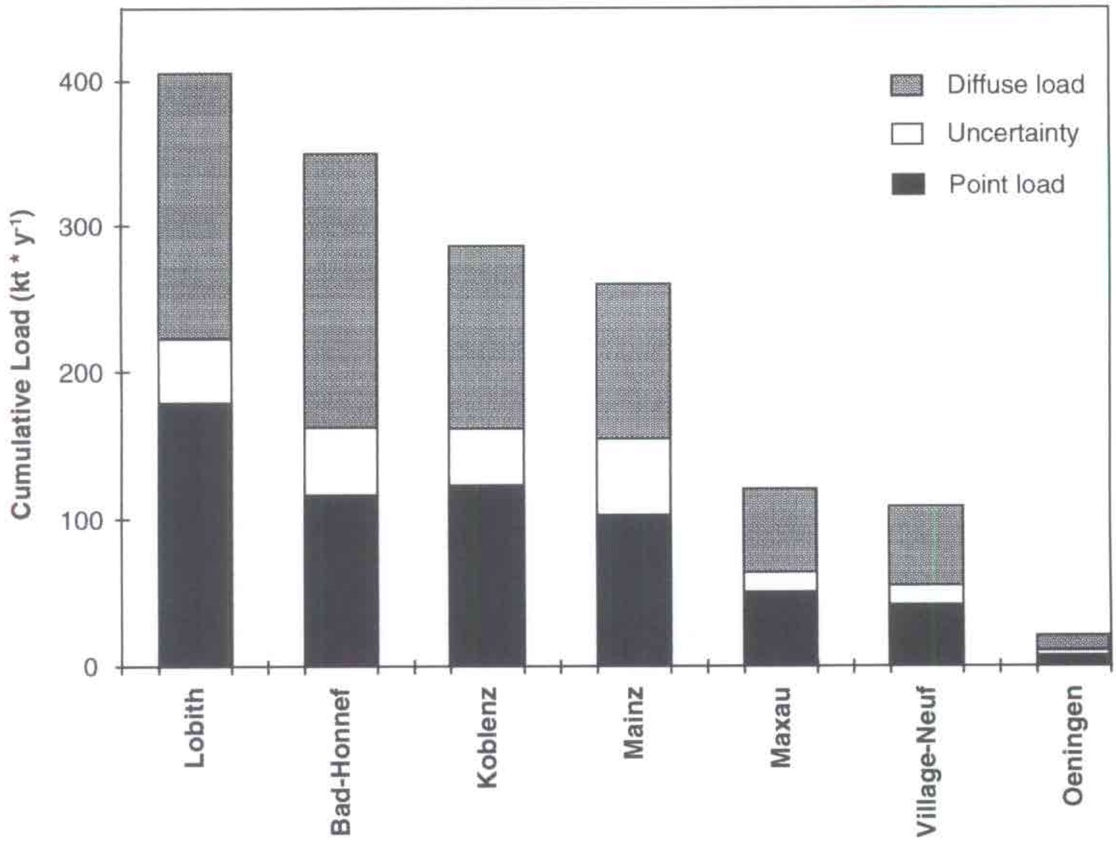



**Figure 4.3**
**Source apportionment of the "mainstream basins" (basin devined as the entire area upstream of a sampling site)**

The dissolved inorganic nitrogen (DIN) load of river basins situated in North-Rhine Westphalian (including the Ruhr area) seems to originate mainly from diffuse sources, despite the amount of industry situated in this region (Figure 4.4.). Only the DIN emission into the Wupper and the Emscher originates for more than 50% from point sources.

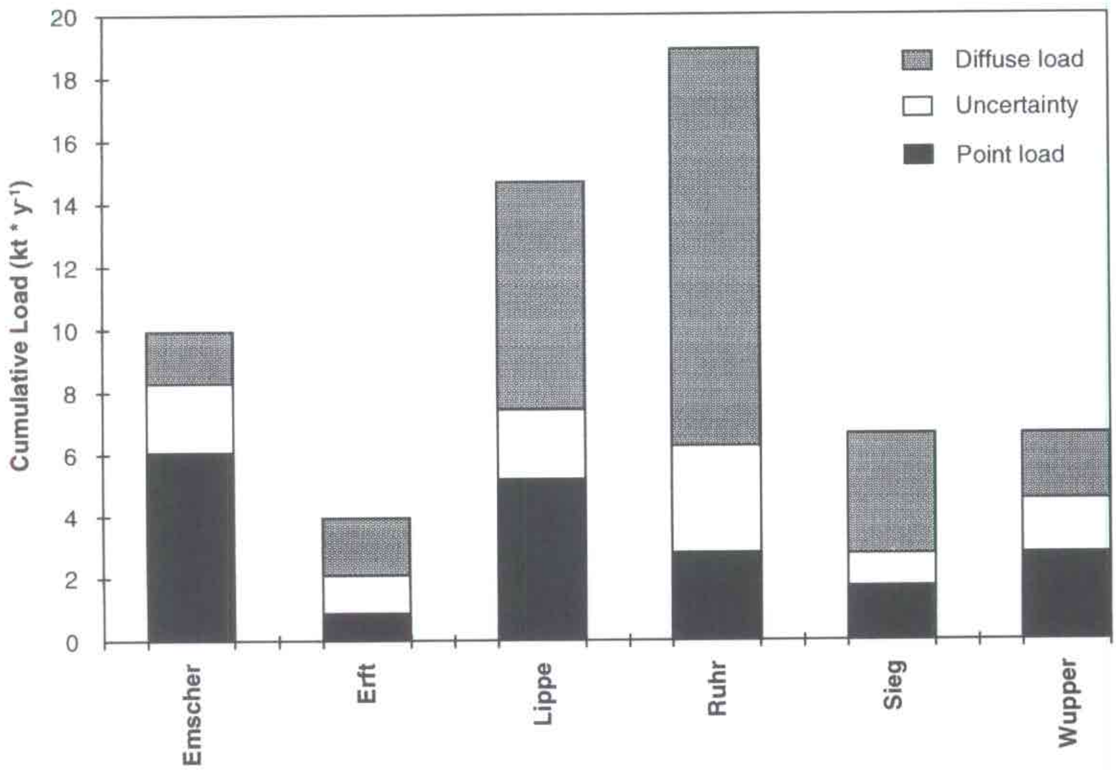



**Figure 4.4.**
**Source apportionment of the basins situated in North-Rhine Westphalian (basin devined as the entire area upstream of a sampling site)**

Diffuse emission dominates the load of DIN in all sub-basins of the River Main; it accounts for about 65% of the total input (Figure 4.5.). Except for the catchment of the River Saar (upstream of Kanzem and Saarbrücken), the emission into the Moselle is to a great extent dominated by diffuse sources (Figure 4.6.). The emission estimates of dissolved inorganic nitrogen show a big non-point source contribution in the area between Palzem and Koblenz.

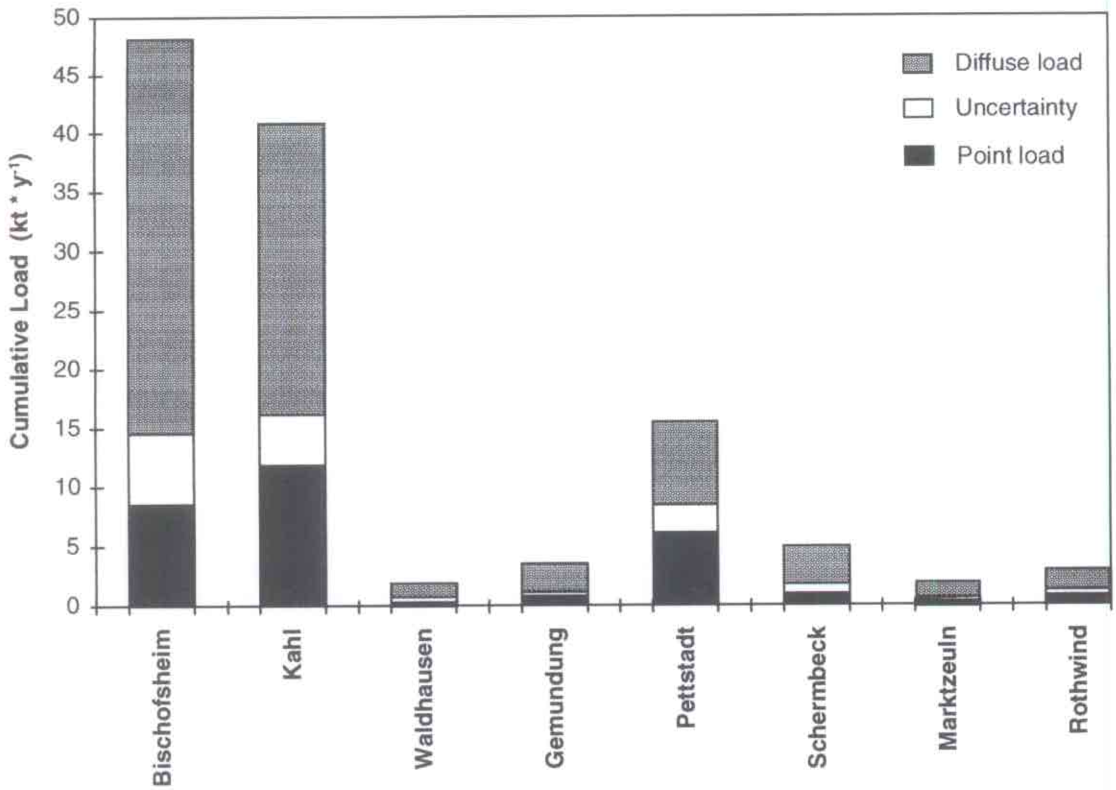



**Figure 4.5**
**Source apportionment of the Main basins (basin devined as the entire area upstream of a sampling site)**

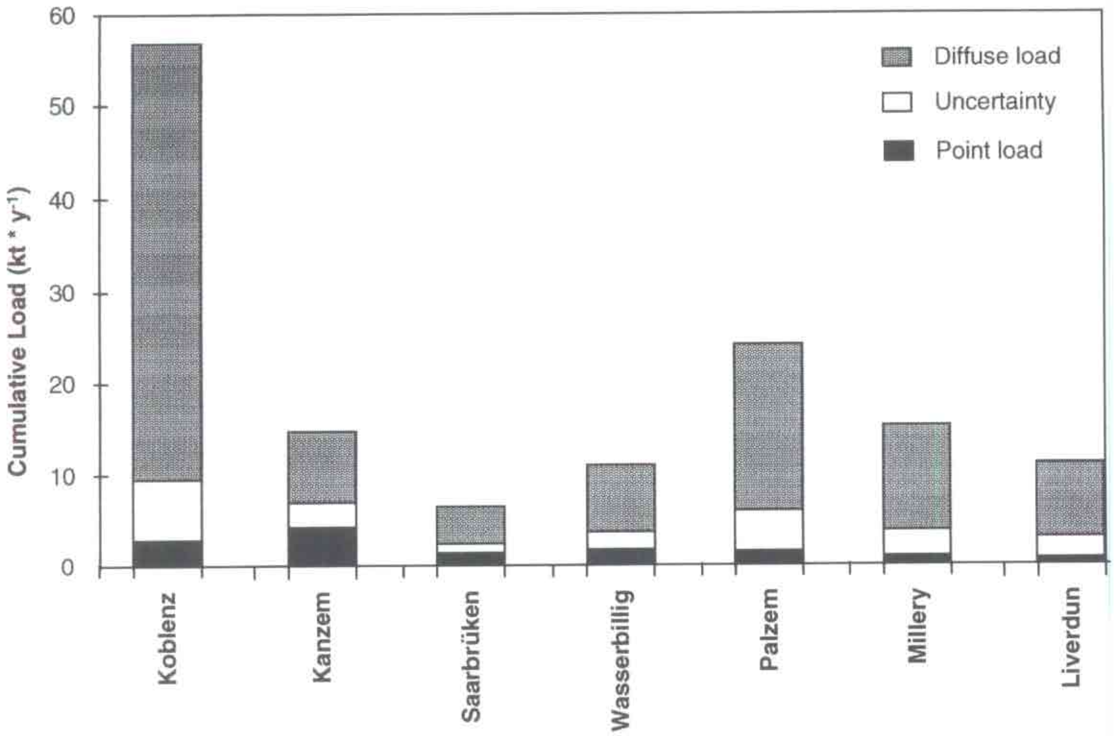



**Figure 4.6**
**Source apportionment of the Moselle basins (basin devined as the entire area upstream of a sampling site)**

4.3.3.3 Uncertainty of emission estimates

Almost all emission estimates of dissolved inorganic nitrogen (DIN) have a total uncertainty of less than 10% (Table 4.3.). However, the emission estimates of DIN upstream of Dipoldsau (upper Rhine) are unreliable. In addition, the emission estimates for the basins upstream of Eppinghoven (Erft) and Opladen (Wupper) have an uncertainty of about 20%. The uncertainty of the total inorganic nitrogen emission of the total area upstream of Lobith is calculated to be 6%. Nitrate emission estimates are less uncertain than those of DIN (Table 4.3.). The emission estimates of the big tributaries Main, Moselle and Neckar have an uncertainty of 7 %, 6% and 9%, respectively. The ammonium emissions are much more uncertain (Table 4.3.). Only the estimates upstream of the sampling points situated in the Main have an uncertainty of less than 15 %. All other emission estimates of ammonium are less accurate. The small contribution of ammonium to the total emission of DIN justifies the consideration of DIN in the analysis.

#### 4.3.3.4 Source apportionments of the riverine load in the periods before 1990

Source apportionment estimates and average discharge during different time periods are charted in Figure 4.7. for some of the most important sampling sites.

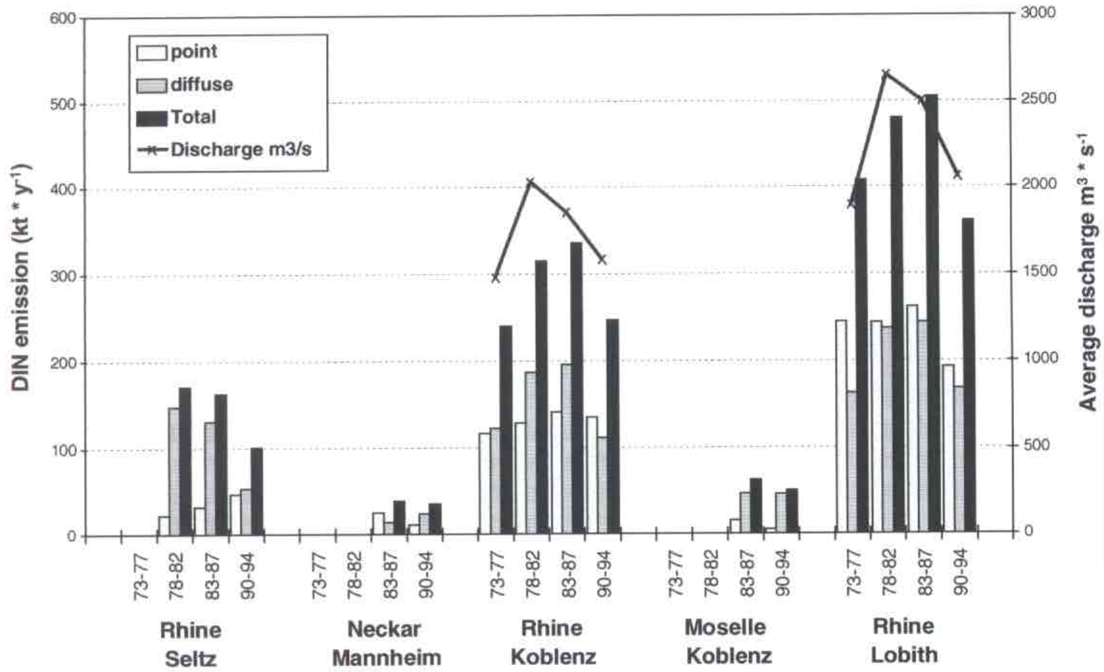



**Figure 4.7**
**Source apportionment estimates of dissolved inorganic nitrogen (DIN) together with average discharge during different time periods**

The results of the source apportionment estimates for the areas downstream of Koblenz and Lobith both present the same temporal changes. The temporal variation in the total transport at Koblenz and Lobith seems to be mainly dependant on water discharge in different time periods. The changes in the relative importance of diffuse sources compared to the total load is obscured by the differences in discharge between different time periods. The nutrient concentration of the discharge originating from diffuse sources in general represents the contribution of diffuse sources to the total emission at standardised hydrological circumstances (Haith & Tubbs, 1981). Therefore the regression of temperature-corrected unit-area transport versus specific runoff can be used to examine the relative contribution of diffuse emission within the different time periods, exclusive of the direct effect of various hydrological circumstances within the different years (As stated in § 4.1. and by Hellmann (1989) and Gronvang (1992).

The regression of the temperature-corrected (unit area) load of nitrate versus specific runoff, for the different time periods investigated, is shown in Figure 4.8. The differences in point source contribution between the time periods can be seen from the horizontal position of the regression line. An increase in point source contribution (as also found in chart Figure 4.7.) in the period 1973-1987 is indicated in Figure 4.8. by the horizontal shift of the regression lines towards higher unit area loads. In the period 1990-1995 the contribution of point sources to the total emission is not significantly different from the point source contribution during the period 1983-1987. There are only slight differences in the importance of diffuse sources between the different periods. A little higher non-point source contribution is found within the period 1983-1987 compared to the period 1978-1982 (as also stated in Hellmann, 1989). The contribution of diffuse sources in the period 1990-1995 is slightly higher than that in the period 1983-1987.

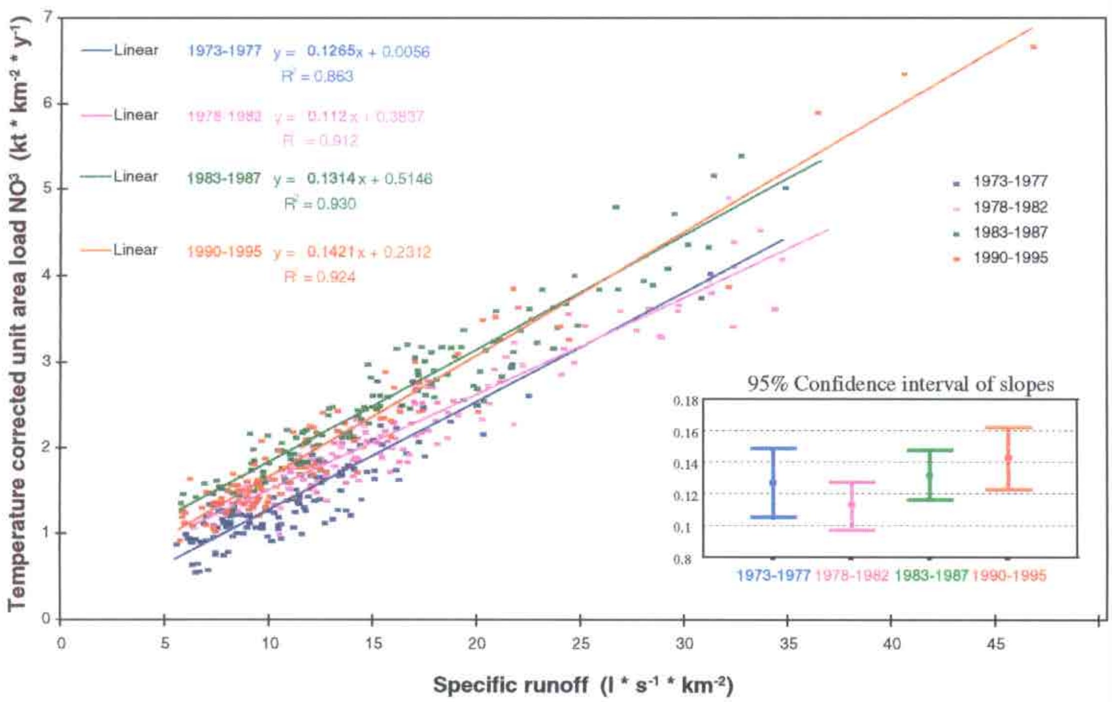



**Figure 4.8**
**The regression of the temperature-corrected (unit area) load of nitrate versus specific runoff, for different time periods**

# 5. SOURCE ANALYSIS BASED ON ASSIGNED RETENTION AND SOURCE STRENGTH PARAMETERS

## 5.1 Preliminary analysis: A qualitative source apportionment

As preliminary analysis to the input—output approach, a qualitative source apportionment was carried out to get a first impression of the sub-catchments and their characteristics. Division of sub-basins into categories is carried out on the basis of the observed basin characteristics: population density and specific runoff. Population density is a relatively certain Figure and is assumed to represent the emission originating from point sources (Stålnacke & Grimvall, 1996a). Distinction with respect to specific runoff is made because large differences between the sub-basins are observed and specific runoff is assumed to affect the amount of diffuse emission (Tonderski *et al.*, 1994; Probst, 1985; Van Dijk *et al.*, 1996; Stålnacke, 1996). Based on population density and specific runoff, four categories of sub-basins can be distinguished in the catchment of the River Rhine:

L Sparsely populated catchments
ML Moderately populated catchments with moderate specific runoff
MH Moderately populated catchments with high specific runoff
H Densely populated catchments

The division is presented on a river map in Figure 5.1.

The sparsely populated areas are all situated the farthest upstream of the defined river network. The moderately populated areas with high specific runoff are situated in the upstream part of the mainstream, covering the alpine area of Switzerland. The densely populated regions are situated along the downstream part of the mainstream including the Ruhr area. Population numbers, specific runoff, estimated emission from point sources, transport and percentage of different land-use types are all calculated as net contributions from the individual sub-basins and added up for the sub-catchments within the different categories.

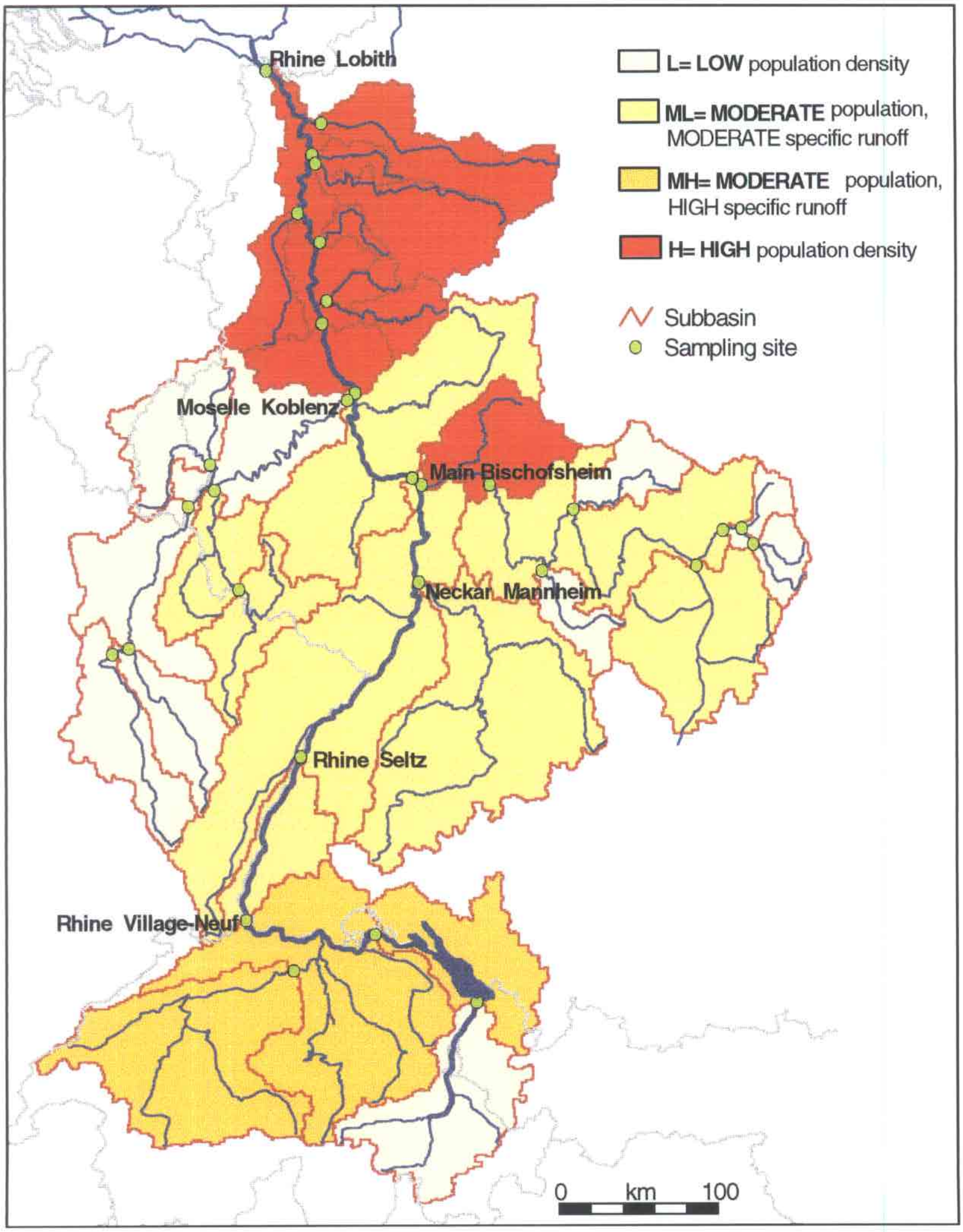



**Figure 5.1**
**Division of sub-basins into categories based on the basin characteristics: population density and specific runoff**

## 5.2 Theoretical background

***Origin of the method***

Grimvall *et al.* (1994), Wittgren & Arheimer (1996) and Jones (1996) describe basically similar statistical source apportionment methods. The method described by Grimvall *et al.* (1994) combines information about riverine loads at different sites in a study area with data on the spatial distribution of sources and selected river basin characteristics. This was to carry out a statistical source apportionment of the riverine load at the outlet of an arbitrary sub-basin. This method was developed within the scope of the "East-West" project to which also the present study is a contribution. To allow comparison between the results obtained for different river basins this input—output method described by Grimvall *et al.* (1994) is used in the present project aswell. A summarised overview and some modifications of this method are given in Appendix 5.1. For argumentation and an elaborate description the reader is referred to the original paper. The following section provides a simple overview of the method. A summarised overview of this method is given in the following paragraph; for argumentation and an elaborate description the reader is referred to the original paper.

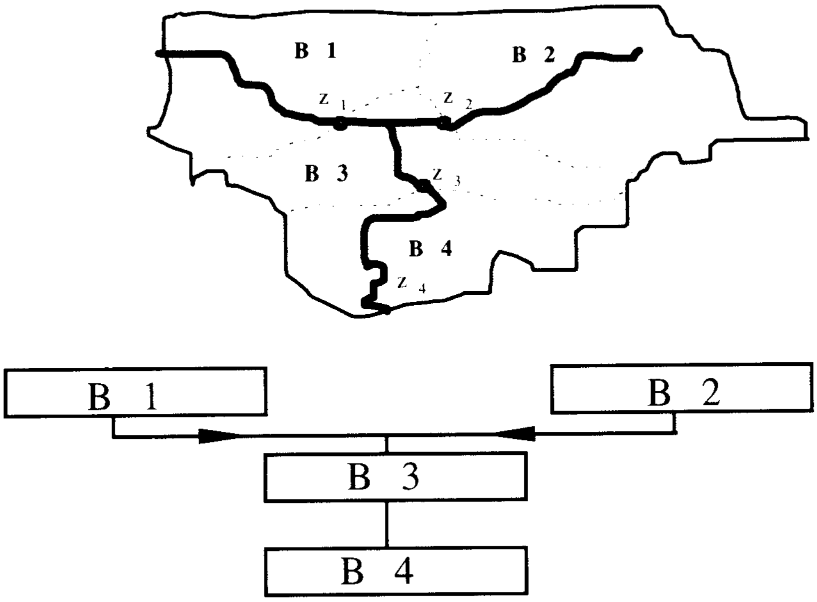
***Calculation***

The source apportionment approach of Grimvall *et al.* (1994) is based on the following:
1) a partitioning of the study area into mutually independent (disjoint) sub-basins partially ordered by their upstream—downstream relations; 2) matrix equations for the transport and retention of an arbitrary substance in such a system of sub-basins; 3) matrix equations for the source apportionment of the output from an arbitrary sub-basin; 4) general principles for the parameterisation of losses of substances from soil and retention of substances in lakes and watercourses.

*Partitioning of the study area*

Let $z_1$, $z_2$ ..., $z_N$ be N arbitrary sampling sites along the watercourses of a river basin. The upstream—downstream relationships between these sites can then be summarised in an NxN matrix. A partitioning of the river basin into a set of disjoint, partially ordered sub-basins is also defined in Figure 5.2.

To describe the flow of substances through $B_1$, $B_2$, ... , $B_N$, two matrices are needed.
One presenting the output from each of the sub-basins, another which denotes the fraction of the riverine input which is retained in the sub-basin. The output from an arbitrary sub-basin can then be decomposed into contribution from sources in sub-basins further upstream and the contribution from sources within the sub-basin under consideration.




$$H = \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 \end{pmatrix}$$

**Figure 5.2.**
**Partitioning of the river basin into sub-basins**

*Source apportionment*

To apportion the responsibility for the observed riverine load at the outlet of an arbitrary sub-basin, the retention of the studied substance between the outlets of any two sub-basins in the study area is computed by matrix calculation.

The simplest way of modelling the distribution of the diffuse sources in the study area is to classify the entire land area into different categories and assign a so-called export coefficient to each land category. Land use normally plays a key role in the classification of land.

Information about point sources is normally more accurate than that on diffuse sources. Therefore point emissions can often be treated as constants. If a point source of unknown magnitude is located in a sub-basin it may be necessary to introduce an unknown parameter.

*Retention*

If lakes are present in the study area retention can be denoted as a function of the hydrolic residence time of the lakes, irrespective of the exact retention mechanism. If no lakes are present in the study area, or the factors influencing the retention are unknown, we can use sub-basin area as an explanatory variable.

## 5.3 Input and data availability

Input of nutrients to the surface water is represented by parameters based on the sub-basin characteristics: area of different land-use types, specific runoff and point source emission estimations. Output is the observed riverine transport at the mouth of the river basin. Calculation methods of the data used to represent the input from different sources is described in the following.

***Water-quality data***

Average annual loads are calculated as described in chapter 3. In order to enable the use of a consistent hierarchy of sub-basins for all analyses, missing water quality data are filled in by interpolation. The few missing discharge numbers are interpolated in time, based on the assumption of a constant ratio of discharge between adjacent sampling sites. Since ammonium mainly originates from point sources, of which the load is fairly constant over time, a constant load is used for interpolation of ammonium data in time. Nitrate concentrations proved to depend mainly on input from diffuse sources, of which the concentration is more-or-less constant over time. The interpolation of nitrate data in time is based on a constant flow-weighted concentration between adjacent sampling sites. Nitrate and ammonium loads are added up to calculate the amount of dissolved inorganic nitrogen (DIN). At most sampling sites at least a small number of total nitrogen samples are available. The organic nitrogen comprises only a minor part of the total load and has a fairly constant concentration over time. The same interpolation procedures as for nitrate are used. In Appendix 5.2. annual loads of nitrate, ammonium and organic nitrogen, as well as their origin (of either measured or extrapolated), are presented.

***Point emission estimation***

As stated by de Wit (1997) the emission originating from point sources is not easily located and quantified in the case of a large supranational river basin. The most important point sources of nitrogen in Germany are by far communal and industrial waste water (Gleisberg *et al.*, 1991). Two sets of point emission estimates are used, both taking into account the contribution of N from communal and industrial waste water.

The communal contribution to point sources, in the *first set* of point emission estimates, is based on population and wastewater treatment data. The influent per inhabitant and the efficiencies of different treatment types are taken into account. Industrial contributions are estimated on the basis of data reported by IKSR (Internationale Kommission zum schutze des Rheins). For calculation schemes and data sources the reader is referred to de Wit (1997).

*The second method* of point emission calculation is based on data published by IKSR (1992). By IKSR (1992) the point emission is summed up for the countries Germany, France and Switzerland. The point emission is presented separately for two sources. 1) emission originating from main industries; 2) other point emissions. The IKSR data used are shown in Appendix 5.3.

From the database described in chapter 3 population numbers per country are used to calculate the point emissions per capita (for the different countries). Luxembourg and Belgium are (based on their adjacent situation but furthermore arbitrarily) assumed to have the same emission per inhabitant as

Germany. Even so, the emission per inhabitant in Austria is assumed to equal the emission per inhabitant of Switzerland. The number of inhabitants living in France, Germany, Luxembourg, Belgium, Switzerland and Austria is calculated from the database for each watershed.

Multiplying these population numbers with the calculated emission per inhabitant (for the different countries) results in the amount of substance emitted within the watersheds upstream of the sampling points. Apportionment of the point emission to separate sub-basins depends on the upstream—downstream relations defined in the present analysis. The emission rate of point sources is assumed to be constant for the years within the period 1990-1995.

## 5.4 Results

### *5.4.1 Qualitative source apportionment*

The assignment of the different sub-basins to the four categories defined in § 5.1. is given in Appendix 5.4. together with some important basin characteristics. The total population density and specific runoff are presented by category in Figure 5.3. and Figure 5.4., respectively. The average population density within the category containing low populated catchments (category L) is 106 inhabitants per square kilometre. The average population density of the catchments within the group of high populated areas (category H) is 585 inhabitants per km$^2$. Both categories of moderately populated areas (categories ML and MH) have an average population density of about 250 inhabitants per km$^2$.

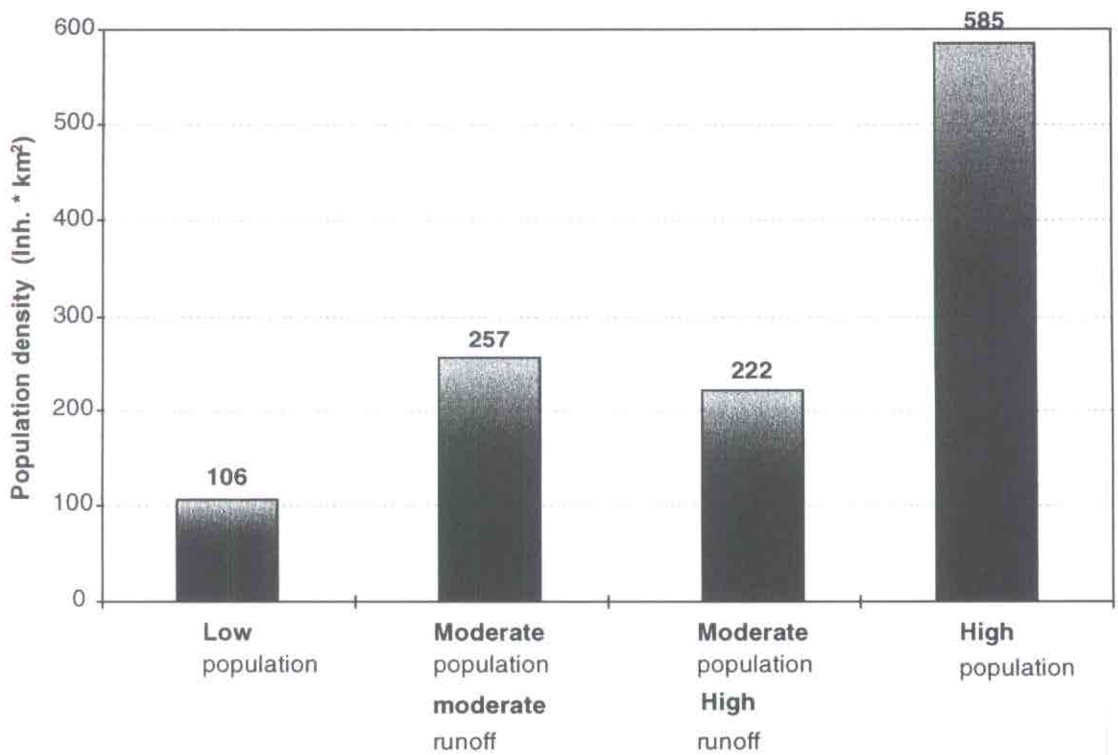



**Figure 5.3**
**Population density by different categories of sub-basins**

There are big differences between the four categories with respect to the average specific runoff observed within one category of sub-basins. The specific runoff of about 15 litres per square kilometre per year within category L is fairly high. The category of moderately populated areas with low specific runoff (category ML) has a runoff of about 9 $l^{-1} \cdot s^{-1} \cdot km^{-2}$. The average specific runoff of category H equals this runoff of category HL. The specific runoff within category MH (containing moderately populated areas with high specific runoff) is about 27 $l^{-1} \cdot s^{-1} \cdot km^{-2}$. The estimated point emission per unit area is ranges from 0.4 $t \cdot km^{-2} \cdot y^{-1}$ within category L, to 2.5 $t \cdot km^{-2} \cdot y^{-1}$ within category H.

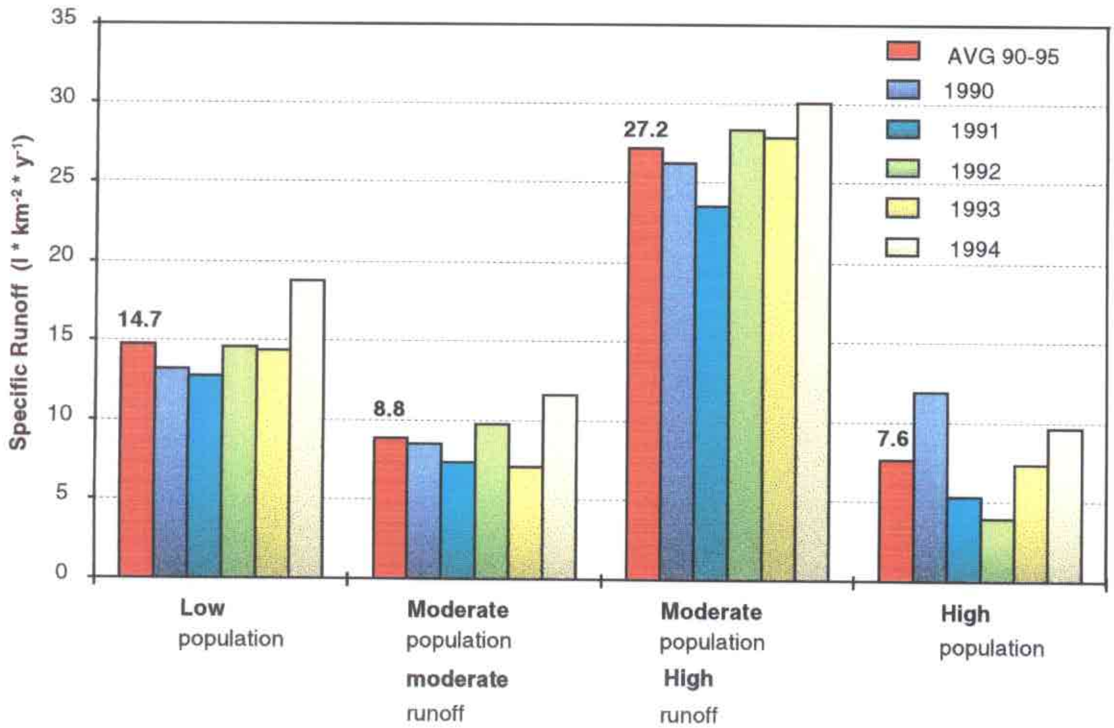



**Figure 5.4**

**Specific runoff by different categories of sub-basins**

The percentage of total agricultural land, differs only slightly between the four categories of basins. Figure 5.5. presents a subdivision of the total land use into: forested land, grassland, arable land and other land. The percentage of arable land, which is assumed to be an important factor with respect to the leaching of nutrients to the surface water (Wittgren & Arheimer, 1996), varies between 12 and 27 % for the categories ML and MH, respectively. The percentage of arable land in the catchments with high population densities is high.

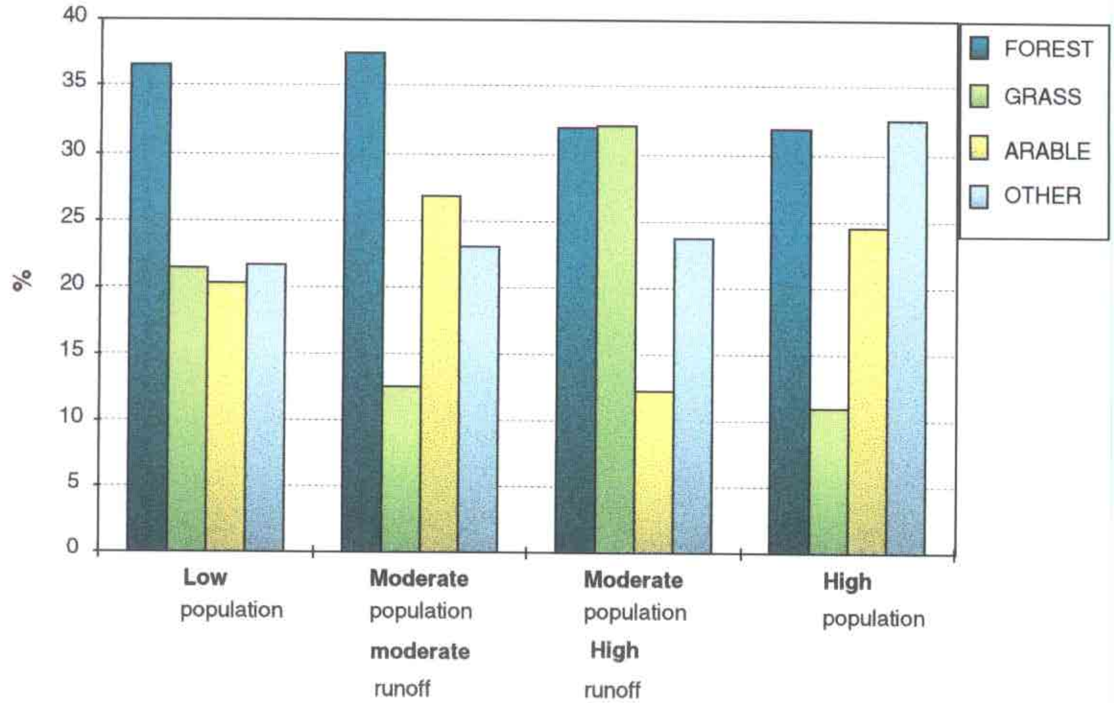



**Figure 5.5.**

**Land use by different categories of sub-basins**

All nitrogen emissions or emission potencies described result in a measured unit area load of nitrogen as presented in Figure 5.6. The smallest unit area load, 1.3 tonnes of nitrogen per square kilometre per year, is found for category ML. The basins within the category of high populated catchments (H) have the biggest unit area load (3.6 $t{\cdot}km^{-2}{\cdot}y^{-1}$). The unit area load of category L is larger than the unit area load of the moderate populated areas with low specific runoff (ML). This happens despite the fact that the areas with low population densities have a much smaller point emission (per unit area) and less arable land compared to the basins with moderate population densities and low specific runoff. The high unit area load of category L compared to category ML can only be explained by the high specific runoff of the basins within the category of sparsely populated areas. This emphasises the importance of diffuse sources within these sparsely populated sub-basins.

Comparison of the categories ML and MH also shows the importance of specific runoff to the nitrogen load. Despite the smaller point emission and smaller portion of arable land, the nitrogen load of category MH is higher. It can be concluded that the variation in unit area transport between the basins depends mainly on specific runoff in the case of the sparsely and moderately populated catchments. The nitrogen transport of these basins originates mainly from diffuse sources. The nitrogen transport of densely populated areas originates mostly from diffuse sources also. The estimated point source emission within this group of basins is 2.5 of the total measured load of 3.6 $t{\cdot}km^{-2}{\cdot}y^{-1}$. This implies a diffuse contribution of about one-third of the total emission.

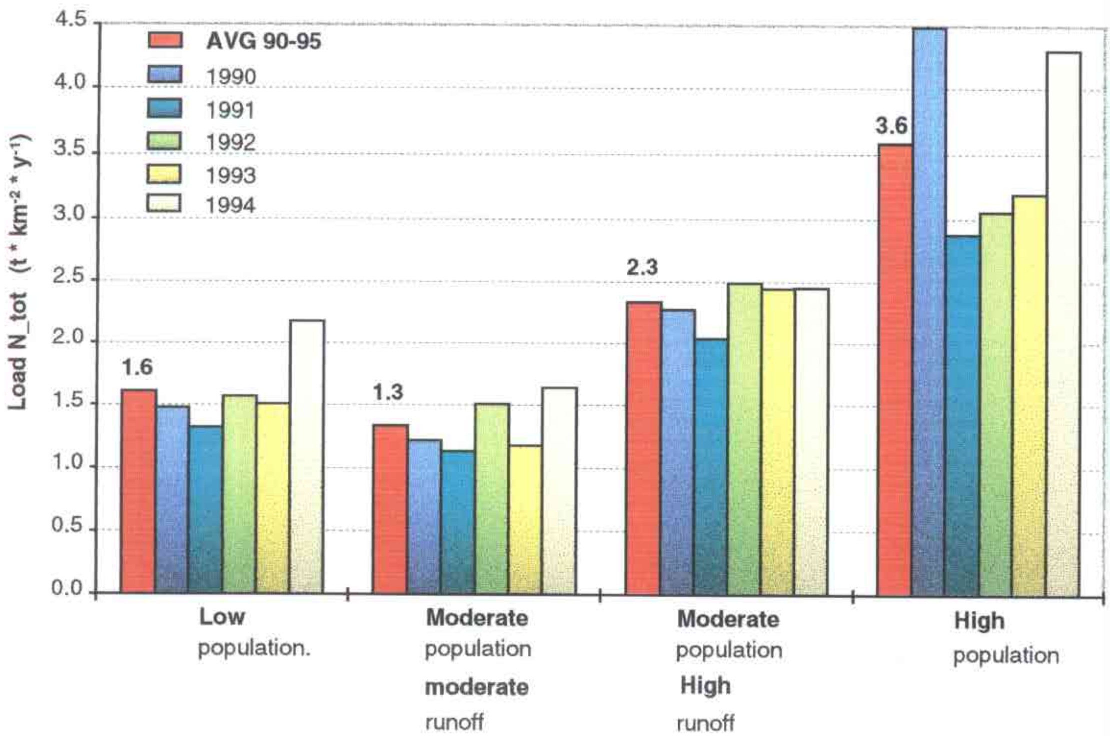



**Figure 5.6**
**Unit area load by different categories of sub-basins**

The nutrient concentration of the discharge originating from diffuse sources in general represents the contribution of diffuse sources to the total emission at standardised hydrological circumstances (Haith & Tubbs, 1981). Therefore the regression of temperature-corrected unit-area transport versus specific runoff can be used to examine the relative contribution of diffuse emission within the different categories of basins, exclusive of the direct effect of various hydrological circumstances within the different years (As stated in chapter 4 and by Hellmann (1989) and Gronvang, 1992).

To enable temperature correction to the original transport data, only data of upstream catchments can be used. Temperature correction is applied to exclude possible differences in retention between the different categories of basins. Because of their strong dependency on discharge, nitrate data are used to investigate the differences in importance of diffuse sources between the categories of basins. The regression of the temperature corrected (unit area)load of nitrate versus specific runoff for the different categories of basins is shown in Figure 5.7. There is no significant difference between the slopes (representing the concentration of nitrate originating from diffuse sources) of category H and ML. Both categories have the largest slope (highest concentration of nitrate originating from diffuse sources) of the four categories defined. The lowest concentration of nitrate originating from diffuse sources is found for the moderately populated catchments with high specific runoff. The differences in the concentration of diffuse nitrogen between the categories represents the percentage of arable land in the different basin categories (Appendix 5.4.) if the difference between the percentage of arable land of category H and ML is assumed to be negligible (25% and 27%, respectively).

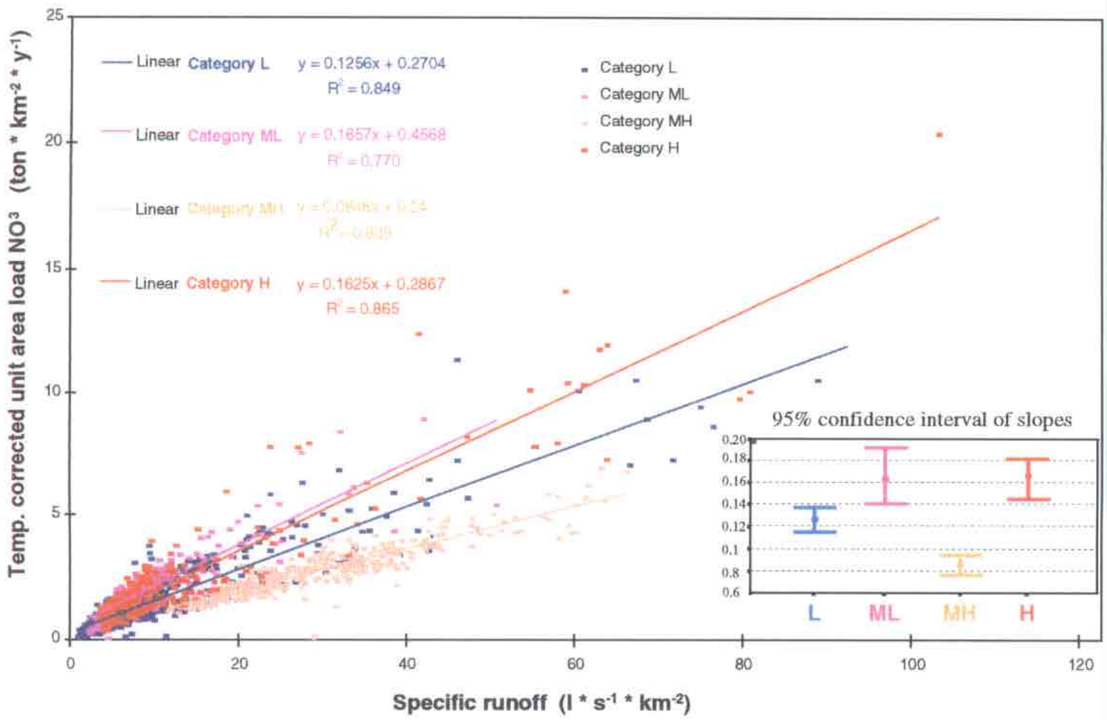



**Figure 5.7.**

**Regression of temperature-corrected unit-area transport versus specific runoff by different categories of basins**

### *5.4.2 Evaluation and selection of the input to the model*

With the applied method, source strength and nutrient loss are estimated based on information on different pathways of input and input—output balances, respectively. Apportionment is based on the estimated source strengths. The sources considered, within the category of point or diffuse sources, are thus defined by the parameters used to represent the input of nutrients to the river. The previous statement implies that the usage of different input (drainage network, parameters to describe the input of nitrogen and different retention formulas) provide a variety of different modelling attempts. A simple strategy with respect to the selection of the input of the model is followed. The model requires a drainage network containing a minimum of sub-basins (depending on the number of free parameters). The accuracy of the modelling results improves as the number of sub-basins included increases. Hence the differences between the characteristics of the basins included increases; this provides better possibilities for parameter estimation. Thus the aim is to use the most extensive drainage network. The number of parameters should be limited as much as possible (without the loss of information on sources) to prevent the use of correlated parameters and to keep the model simple. The next section describes the selection of the final input to the model.

***Drainage network***

The most extensive hierarchy of sub-basins used in the present analysis comprises all sub-basins as shown in Figure 2.2. The use of lumped drainage networks did not improve (or even diminish) the load prediction and source apportionment. This certifies that possible discrepancies between predicted and measured load, of basins which are not so-called first order catchments (basins which are not the most upstream basin of a branch of the drainage network), are not due to faulty water-quality data of certain sampling sites. The inaccuracy in the load predictions of first-order basins are not due to too small catchment areas either. In these cases discrepancies would be withdrawn by the exclusion of the faulty water-quality data or the enlargement of the small catchments. The extensive drainage network provides a maximum of information with respect to source strengths, and retention, and meets the statistical requirement of the number of sub-catchments.

***Diffuse emission***

Input from diffuse sources is represented by nutrient leaching from soils with different types of land use. The areas of different types of land use are calculated as described in chapter 3. The main land-use types distinguished are: built-up areas, forest, open water, agricultural land, arable land, grassland and other land. Land use is assumed to be constant within the period 1990-1995. To describe the export of nutrients from different land-use types the so-called unit area approach or concentration approach can be applied. The concentration approach uses estimated or measured concentrations of the discharge originating from different land-use types to predict the nutrient emission (Haith & Tubbs, 1981; Haith & Shoemaker, 1987). The unit area approach presumes the area of a certain land-use type to represent the nutrient emissions (Jones, 1996; Wittgren & Arheimer, 1996). The easily applicable unit area approach is used in the present analysis and also because the concentration of the discharge to the surface water is not necessarily the same as the concentration of the water leaching directly from the soil. Moreover, concentrations of the percolation water and runoff entering the surface water are probably hardly available.

The differences in observed nitrogen transport between the sub-basins can obviously not be explained by the differences in area of arable land or other land-use types only. The variation in runoff between the different sub-basins must be considered to contribute to a significant prediction of the observed load. The impact of specific runoff on the transport of nutrients was already found in the additional analysis, in which a qualitative source apportionment was employed. Also Haith & Tubbs (19810 and Haith & Schoemaker (1987) mentioned the effect of runoff on diffuse pollution. Specific runoff is included in the analysis as a five-year mean value normalised to a flow-weighted mean. Inclusion of only two land-use types, arable land and other land, yielded the best prediction of the amount of diffuse emission. Usage of more land-use types as explanatory variables did not improve or even diminish the accuracy of the nitrogen leaching factors from the different land-use types, as well as the predicted nitrogen transport. Moreover, the importance of the percentage of arable land (besides the impact of specific runoff) to the amount of diffuse load was found within the preliminary analysis. In addition, Prasuhn & Braun (1995) stressed the major importance of arable land to the diffuse emission of nitrogen within the Swiss part of the Rhine basin. Gronvang (1992) relates the same importance of arable land to the diffuse part of the nitrogen emission for a small catchment in Denmark. Table 2.1.

presents a list of the various sub-basins and their percentages of different land-use types. From this Table it can be inferred that there is enough variation in percentage of the various land-use types between the sub-catchments to carry out a statistical source apportionment.

***Point emission***

Figure 5.8. presents the results of point source emission estimations carried out with the two different estimation methods described. The emission estimates based on statistics provided by the IKSR are about 15% higher in almost all cases. Large discrepancies (about 50%) are found for the basins upstream of Brugg (Aare) and Village-Neuf (Rhine). The emission estimates based on the "IKSR statistics" are lower only within the area around the mainstream upstream of Lobith if compared to the estimates described in De Wit (1997). The emission estimates of De Wit (1997) are based on more data with more spatial detail. Assuming these estimates to be correct and more detailed (as also stated in De Wit (1997), they will be used in all calculations.

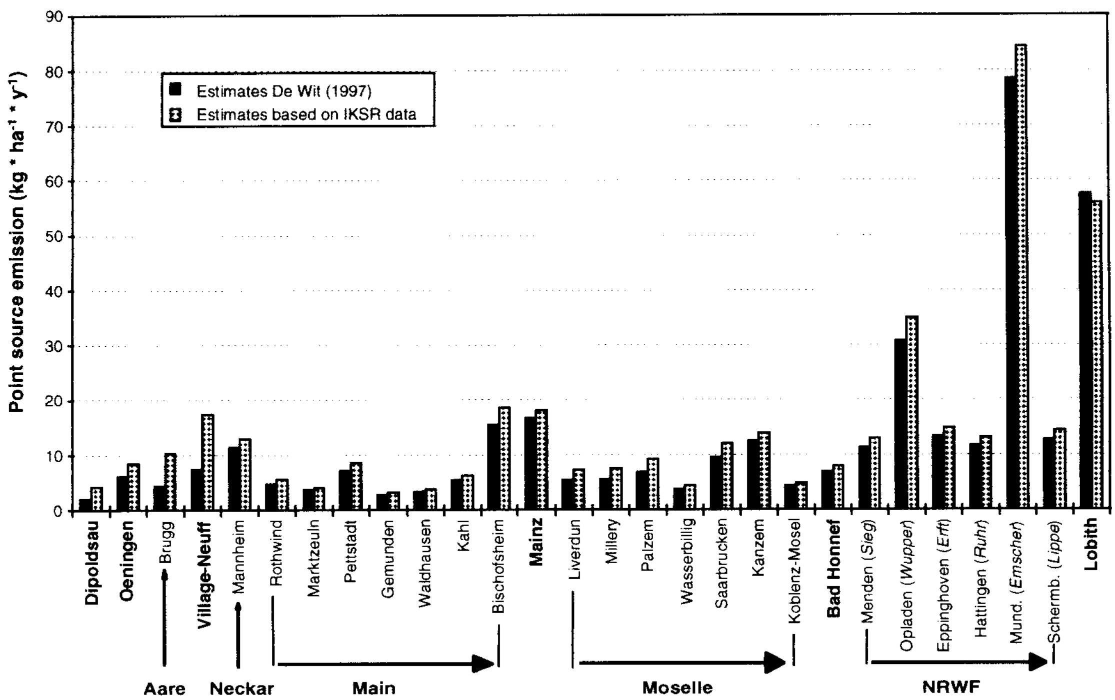
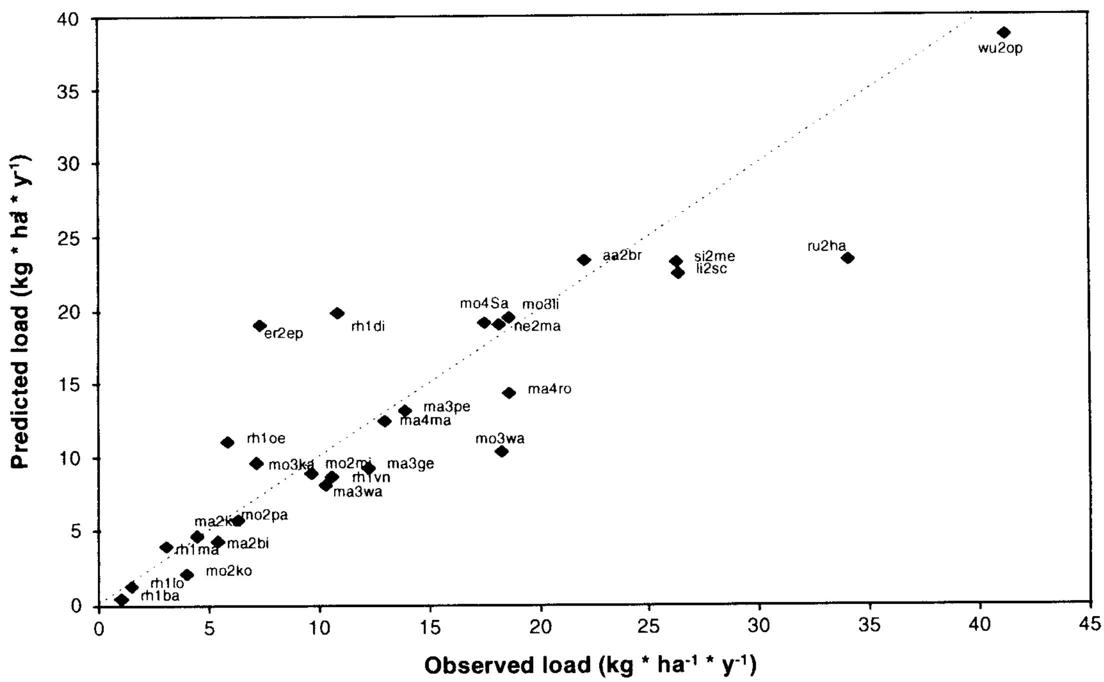



**Figure 5.8.**
**Point source emission estimations carried out with two different estimation methods**

### 5.4.3 *Final results obtained with the input—output model*

***Prediction of the measured transport***

Predicted versus measured load (area weighted) is plotted in Figure 5.9. The measured transport of the Emscher exceeds by far the predicted transport. As stated before, the Emscher is a very exceptional basin because of its large point source contribution and deviant water management. Within the basins of Dipoldsau and Oeningen (Rhine) the predicted load is too high when compared to the measured load. The discrepancy between the measured and predicted load of the basin of Oeningen is most likely due to the situation of the Bodensee within this catchment. The discrepancies of Dipoldsau as well as Erft (Eppinghoven), Ruhr (Mündung) and Wasserbillig (Moselle) do not have apparent causes. As presented in Appendix 5.5. the predicted loads (exclusive of the Emscher) are accurate within the 95% confidence interval (P-value 0.524 > 0.001). From this Appendix it can also be concluded that the unit area transport differs significantly between the various sub-catchments (P-value 0.000 < 0.001).




| Code | Name | Code | Name |
|---|---|---|---|
| rh1di | Dipoldsau | mo2mi | Millery |
| rh1oe | Oeningen | mo2pa | Palzem |
| aa2br | Brugg (Aare) | mo3wa | Wasserbillig |
| rh1vn | Village-Neuff | mo4sa | Saarbrücken |
| ne2ma | Mannheim | mo3ka | Kanzem |
| ma4ro | Rothwind | mo2ko | Koblenz-Mosel |
| ma4ma | Marktzeuln | rh1ba | Bad-Honnef |
| ma3pe | Pettstadt | si2me | Menden (Sieg) |
| ma3ge | Gemünden | wu2op | Opladen (Wupper) |
| ma3wa | Waldhausen | er2ep | Eppinghoven (Erft) |
| ma2ka | Kahl | ru2ha | Hattingen (Ruhr) |
| ma2bi | Bischofsheim | em2mu* | Mündung (Emscher) |
| rh1ma | Mainz | li2sc | Schermbeck (Lippe) |
| mo3li | Liverdun | rh1lo | Lobith |

* omitted from chart measured load = 243 predicted load = 97

**Figure 5.9**
**Measured versus predicted unit area load**

***Emission and source apportionment***

The total emission within the entire catchment upstream of Lobith is estimated to be 344 $kt{\cdot}y^{-1}$, (which implies a unit area load of 22 $kg{\cdot}ha^{-1}{\cdot}y^{-1}$), of which 48% originates from diffuse sources. The apportionment of the total load to the different sources within the various basins (defined as the total area upstream of a sampling site) is presented in Table 5.1. The apportionment of the total load to the different sources within each sub-basin individually (defined as the catchment area between two adjacent sampling sites) is also presented in Table 5.1. The diffuse contribution to the total load ranges from about 20% (Wupper Opladen, Emscher Mündung, Rhine Bad-Honnef) to 80-90% (Rhine Dipoldsau, Aare Brugg and Rhine Oeningen). Clear point-source contributions can be distinguished within the catchments of Saarbrücken (Moselle), Kanzem (Moselle) and Bischofsheim (Main). An apparent diffuse contribution can be distinguished between Palzem and Koblenz (Moselle).

**Table 5.1**
**Estimates of the contribution from different sources to the emission by application of different approaches (riverine and input-output)**

| Basin | Net diffuse Inp—outp % | Point Inp—outp % | Arable land Inp—outp % | Other land Inp—outp % | Total diffuse Inp—outp % | Total diffuse Riverine % |
|---|---|---|---|---|---|---|
| Dipoldsau | 90 | 10 | 5 | 85 | 90 | 52 |
| Oeningen | 79 | 15 | 18 | 67 | 85 | 53 |
| Brugg (Aare) | 82 | 18 | 35 | 46 | 82 | 53 |
| Village-Neuff | 69 | 22 | 27 | 51 | 78 | 52 |
| Seltz | * | * | * | * | * | 48 |
| Mannheim | 43 | 57 | 26 | 17 | 43 | 69 |
| Schwurbitz | * | * | * | * | * | 72 |
| Rothwind | 68 | 32 | 45 | 23 | 68 | 62 |
| Marktzeuln | 71 | 29 | 42 | 28 | 71 | 85 |
| Pettstadt | 46 | 54 | 32 | 14 | 46 | 48 |
| Gemunden | 70 | 30 | 47 | 24 | 70 | 74 |
| Waldhausen | 59 | 41 | 47 | 12 | 59 | 76 |
| Kahl | 57 | 44 | 39 | 17 | 56 | 64 |
| Bischofsheim | 42 | 49 | 34 | 17 | 51 | 75 |
| Mainz | 24 | 44 | 26 | 30 | 56 | 43 |
| Liverdun | 73 | 27 | 41 | 32 | 73 | 106 |
| Millery | 68 | 29 | 40 | 31 | 71 | 85 |
| Palzem | 54 | 35 | 39 | 26 | 65 | 86 |
| Wasserbillig | 64 | 36 | 33 | 31 | 64 | 75 |
| Saarbrucken | 50 | 50 | 31 | 20 | 50 | 69 |
| Kanzem | 30 | 60 | 24 | 16 | 40 | 59 |
| Koblenz-Mosel | 66 | 44 | 32 | 24 | 56 | 91 |
| Koblenz-Rhine | * | * | * | * | * | 45 |
| Bad Honnef | 18 | 45 | 27 | 28 | 55 | 57 |
| Menden (Sieg) | 52 | 48 | 17 | 35 | 52 | 64 |
| Opladen (Wup.) | 21 | 79 | 4 | 16 | 21 | 33 |
| Eppingh. (Erft) | 31 | 69 | 23 | 8 | 31 | 51 |
| Hattingen (Ruhr) | 51 | 49 | 21 | 30 | 51 | 75 |
| Mündung (Ems.) | 19 | 81 | 9 | 10 | 19 | 12 |
| Schermb.(Lippe) | 44 | 56 | 34 | 10 | 44 | 52 |
| Lobith | -16 | 52 | 24 | 24 | 48 | 47 |

(* no analysis)

*Leaching factors from different land-use types*

The estimated nitrogen leaching factors are 29 and 6 kg·ha$^{-1}$ ·y$^{-1}$ for arable land and other land respectively. The standard error of the estimated leaching factor is 14 kg·ha$^{-1}$ ·y$^{-1}$ for arable land and 2 kg·ha$^{-1}$ ·y$^{-1}$ for other land. This implies a moderate but significant regression within the 95% confidence interval in both cases. The predicted leaching factors are in good agreement with the factors cited in the literature. Jolankai *et al.* (1992) estimated the leaching factor from agricultural land within the Rhine basin to be in the range of 10-100 kg·ha$^{-1}$ ·y$^{-1}$. Werner *et al.* (1991) estimated the nitrogen emission to be about 21 kg·ha$^{-1}$ ·y$^{-1}$ from agricultural land in total and about 4 kg·ha$^{-1}$ ·y$^{-1}$ from forested and fallow land together. Werner & Wodsak (1991) stated that 77% of the total diffuse nitrogen input into surface waters of the "former" Federal Republic of Germany (mainly the catchment of the Rhine River) are due to leaching processes of nitrogen from the upper soil layers. The nitrogen input into surface waters in combination with erosion processes is estimated using a share of about 5% of the total diffuse inputs. This confirms the substantial contribution of leaching of nitrogen from agricultural areas. The nitrogen leaching is estimated to be 17 kg·ha$^{-1}$ ·y$^{-1}$ and 35.6 kg·ha$^{-1}$ ·y$^{-1}$ for all land and agricultural land, respectively. There are differences in intensity of agricultural practice between the various catchments. The agricultural practice within the more upstream catchments e.g. Rhine Dipoldsau and Liverdun (Moselle), is less intensive compared to more downstream catchments e.g. Ruhr, Sieg and Petstadt (Main). This might be a reason for the moderate significance of the explanation of diffuse load by area of arable land. In the case of the Dipoldsau and Liverdun basins the predicted load was indeed higher than the observed load, in contrast to the transport estimates for the Ruhr, Sieg and Petstadt for which the measured load exceeded the predicted loads. The lower emission of nitrogen from agricultural areas within the upstream areas of the Rhine basin are confirmed by Prasuhn & Braun (1995), who estimated the emission from diffuse sources to be 9, 14, 16 and 27 kg·ha$^{-1}$ ·y$^{-1}$ only within the regions of the Alps, Pre-Alps, Jura and Mittelland, respectively. Even though nutrient load from rural areas is often considered uniform with respect to soil type (Haith & Shoemaker, 1985), differences in bio-physical characteristics and drainage between the sub-basins might also affect the nutrient leaching. Natural geochemical conditions of different sub-catchments are presumably of minor importance to the total load. Prasuhn & Braun (1995) estimated a relative contribution of natural background loads from non-point sources to the total diffuse load of nitrogen of about 20 % within the Swiss part of the catchment of the River Rhine. The contribution of natural background loads can be inferred to be much lower within the rest of the Rhine basin because of the lower runoff within this area.

*Point emission estimation*

If a free coefficient is assigned to the point-source emission estimates, the model estimates the coefficient to be 1.0004. This implies that the model would predict the average point source contribution as it is provided from the original estimates.

***Retention***

Retention is assumed to be a power function of the total area of the watershed. A power of 1.2 is found to yield the most likely load prediction and source strength estimation. However, consideration of retention in the model does not significantly improve the prediction of the measured transport (P-value 0.499 > 0.001, Appendix 5.6.).

The retention within the total area upstream of Lobith is calculated to be only 8%. The retention within the various basins individually (defined as the catchment area between two adjacent sampling sites) ranges from less than 1% to 7% (Appendix 5.7). The estimated total retention of nitrogen of each individual basin to the outlet of the system at Lobith is also presented in Appendix 5.7. The total retention during the transport to the outlet of the system at Lobith is calculated to be up to 15% in the case of substances originating from most sub-basins of the mainstream and the basins upstream of Village-Neuf.

# 6. ADDITIONAL ANALYSIS

## 6.1 Retention calculation using mass balances

Mass balances based on water quality data can be used to calculate the in-stream retention of nutrients. The riverine input of all tributaries of a river stretch (mainstream) is compared to the output of the stretch. A part of the mainstream of the River Main serves as an example. The sub-basins and sampling sites are shown in Figure 6.1. The emission from sources situated in the area directly around the mainstream (which is not covered by the catchment of the tributaries) must be considered to enable the calculation of in-stream retention only. Possible time lags in water discharge must be considered as well. The possible input of local sources or time lag in the water discharge is settled on the basis of the surplus or depletion of water in the water balance. The mass balance is corrected by assuming the water needed to neutralise the water balance to have a concentration equal to the average (flow weighted) concentration of all tributaries.

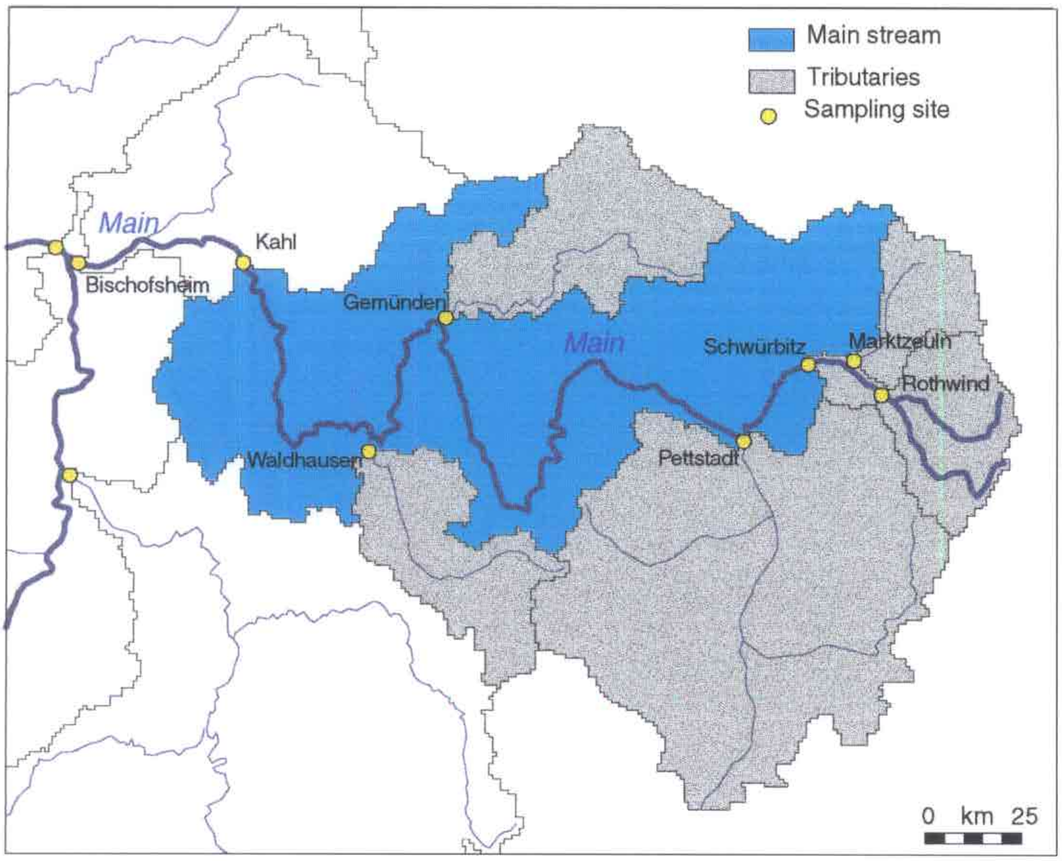



**Figure 6.1**
**Sub-basins and sampling sites of the Main upstream of Kahl**

In the equation the mass balance calculation can be described as follows:

$$R = L_{loc} + \sum L_i - L_{out}$$

$$L_{loc} = C_{loc} * Q_{loc}$$

$$C_{loc} = \frac{\sum C_i * Q_i}{\sum Q_i} = \frac{\sum L_i}{\sum Q_i}$$

$$Q_{loc} = Q_{out} - \sum Q_i$$

$$L_i = C_i * Q_i$$

$R$ = instream retention of the present rivers stretch

$L_{loc}$ = local load (load from the area directly around the mainstream)

$L_{out}$ = measured load at the outlet of the entire drainage network considered

$Q_{loc}$ = local discharge (discharge from the area directly around the mainstream)

$C_{loc}$ = concentration of local discharge (discharge from the area directly around the mainstream)

$Q_{out}$ = measured discharge at the outlet of the entire drainage network considered

$Q_i$ = measured discharge at i upstream sampling sites

$C_i$ = measured concentration at i upstream sampling sites

$L_i$ = measured load at i upstream sampling sites

Monthly average water quality data are used to enable mass balance calculation.

## 6.2 Results

As described in the last section a stretch of the mainstream of the River Main (Figure 6.1.) is used for mass balance calculation The emission of nitrogen per unit discharge is about equal for the area around the mainstream and the catchment of the tributaries. Figure 6.2. presents the discharge of the mainstream in comparison with the discharge of all tributaries. There is an obvious need to correct for the amount of water (and nitrogen) originating from local sources. In some cases, correction of time lag in the discharge is also needed.

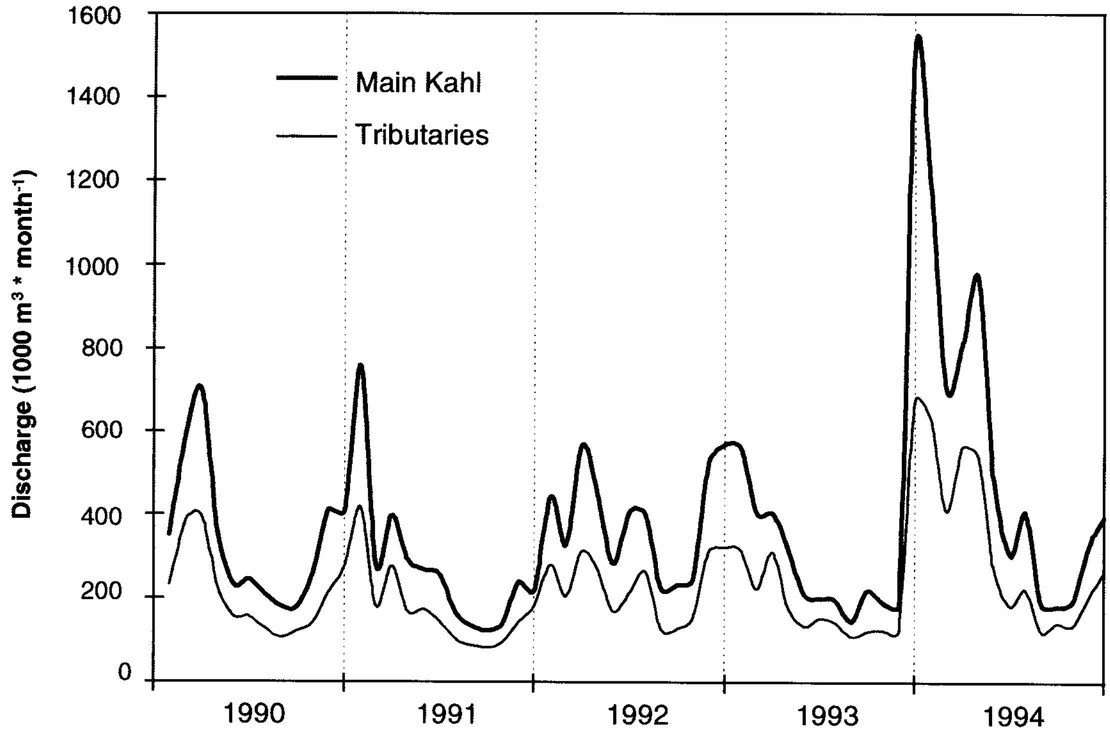



**Figure 6.2**
**Discharge of the mainstream in comparison with the discharge of all tributaries**

The calculated retention of dissolved inorganic nitrogen, nitrate and ammonium is shown in Figure 6.3., Appendixes 6.1. and 6.2. respectively. The retention of dissolved inorganic nitrogen within the mainstream of the Main upstream of Kahl is estimated to be up to 26% of the total transport (August). Although the retention of ammonium is calculated to be up to 47% (April), the transformation of ammonium into nitrate does not really affect the amount of transported nitrogen because of the small amount of ammonium transported in comparison to the nitrate transport. The retention of the dissolved inorganic nitrogen is mainly due to denitrification of nitrate (as also found by Wittgren & Arheimer, 1996). The ammonium retention appears earlier in the year than the nitrate retention. The lack of ammonium retention during the summer months (after June) is due to the depletion of ammonium in this period (The depletion can be seen from the annual concentration patterns of ammonium.) Most emitted ammonium is transformed before reaching the sampling site of the mainstream.

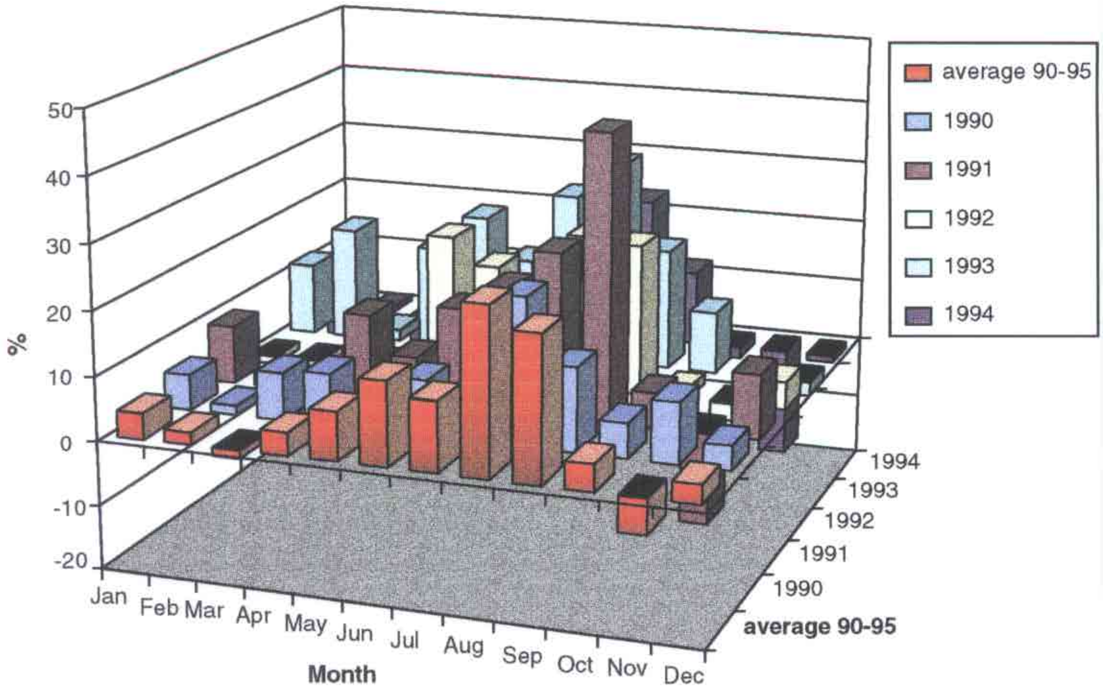



**Figure 6.3**
**Retention of dissolved inorganic nitrogen within the mainstream of the Main**

Within the period 1990-1994 the annual average percentage of the total nitrate transport retained in the mainstream is estimated to be 7%. The retention of ammonium is estimated to be 11% of the total ammonium transport, although the retention of ammonium does not affect the amount of retained dissolved inorganic nitrogen substantially. The resulting retention of the total dissolved inorganic nitrogen is 7%. The estimated annual retention for the different substances and years is presented in Appendix 6.3.

For the Moselle basin, the input potency (e.g. area of arable land, and agricultural land and population numbers) of nitrogen per unit of discharge around the mainstream is higher than the average input potency of the tributaries. The much lower average input from the catchment areas of the tributaries (per unit discharge) is also reflected in the observed nitrate concentrations. This difference in input, between the area around the mainstream and the tributaries, implies inhomogenity in the distribution of sources within the area and prohibits the correction for local sources based on the water balance. Thus retention calculation, with the employed model of mass balance calculation, is impossible for the Moselle basin. If regardless this knowledge retention calculations are carried out it is apparent that the input exceeds the retention as going downstream.

# 7. COMPARISON OF THE RESULTS OBTAINED WITH DIFFERENT MODELLING CONCEPTS

## 7.1 Emission and source apportionment: riverine compared to input—output approach

The estimates of emitted nitrogen into the surface water within the entire area upstream of Lobith by applying the riverine and input—output approach match fairly well (361 and 344 kt·y$^{-1}$, respectively). The discrepancy between the results of both methods are most likely due to the low retention estimates by applying the input—output model. According to Jolankai *et al.* (1992) the total emission falls in the range of 400-500 kt·y$^{-1}$ for the mid-eighties.

The apportionment by employing the input—output model and the riverine method for the entire area upstream of Lobith are in fairly good agreement with each other (Table 5.1.) and the values cited in the literature. This is certainly true if considering the remarks of Jolankai *et al.* 1992, in which it is stated that it is fairly obvious from the reported source apportionment attempts in literature that neither the absolute magnitude nor the percentage of contribution of the various sources can be reliably determined at the present level of knowledge up to 1992. The estimated diffuse contribution within the Rhine basin upstream of Lobith as mentioned in Jolankai *et al.* (1992) ranges from 30% (Iternationale Kommission fur Hydrology des Rheingebietes, 1990) to about 50% (Behrendt & Böhme, 1992. Werner & Wodsak (1991) estimated the diffuse source contribution within the former Federal Republic of Germany to be 56%.

There are some discrepancies in the estimated source strength for the various sub-catchments (defined as the area upstream of a sampling site) by the application of the riverine and input—output approach. Except for the upstream basins, the riverine method provides higher estimates of diffuse source contributions compared to the input—output approach. There are two plausible explanations for the local differences between the results of the two methods.

First, the sources considered in the definition of point and diffuse sources are not exactly the same for the both approaches of source apportionment applied (riverine and input—output). Within the riverine method the overflow of treatment plants during storm events is, for instance, considered as a diffuse source. On the other hand, nitrogen transported by base flow is considered as input from point sources, although this emission is negligible according to Werner *et al. (1991)*. The riverine method requires a natural hydrology of the river system to which point sources are ceaselessly draining. Lakes, reservoirs and wires thus also affect the source apportionment. Deviant discharges due to wires or discontinued drainage from industries possibly elevate the estimated contribution of diffuse sources to the total load.

Secondly, source apportionment with the input—output approach is carried out for the load of total nitrate in contrast to the apportionment of the load of dissolved inorganic nitrogen by using the riverine approach. The difference in apportioned substances with both approaches is due to differences in data availability. The differences in the source apportionment are possibly due to the difference in apportioned substance. Within the basin with high specific runoff (upstream basins) the portion of diffuse load is high for total nitrogen. Within this basin particulate nitrogen, transported by the high specific runoff, elevates the diffuse nitrogen load. Within the other basins the particulate fraction of nitrogen, originating from diffuse sources, is of minor importance compared to that originating from point sources. The high portion of particulate nitrogen of the total diffuse load of nitrogen in the the Alps region is also described by Prasuhn & Braun (1995).

## 7.2 Source apportionment: quantitative analysis compared to the input—output approach

Source apportionment by employing the input—output approach of assigned retention and source strength estimation results in estimates of the contribution of diffuse sources to the total load as expected according to the categorisation of sub-basins based on population density and specific runoff (as described in chapter 6.). The diffuse contribution to the total load is presented for the various individual sub-catchments within the different categories of basins in Figure 7.1. Within the category of sparsely populated basins (category L), the contribution of diffuse sources to the total load is large (about 65%), despite the moderate nitrate concentration of the discharge originating from diffuse sources (as stated in the description of the results from the qualitative source apportionment). This confirms the presumption about the importance of specific runoff for the diffuse load (also stated in the results of the qualitative source apportionment). The estimates of the diffuse contribution to the load, resulting from the input—output analysis, are also high for the basins within the category of moderately populated sub-catchments with high specific runoff (category MH). Although the basins within the category of moderately populated areas with low specific runoff (category ML) have a relative high nitrate concentration of the discharge originating from diffuse sources, the percentage of the load originating from diffuse sources is moderate (about 50%). The basins with high population densities have the lowest contribution of diffuse sources to the total load, nevertheless the percentage of the load originating from diffuse sources within this category is still substantial (30% on the average). Obvious differences between the importance of diffuse sources within different sub-basins of the Swiss part of the Rhine basin are mentioned by Prasuhn & Braun (1995).

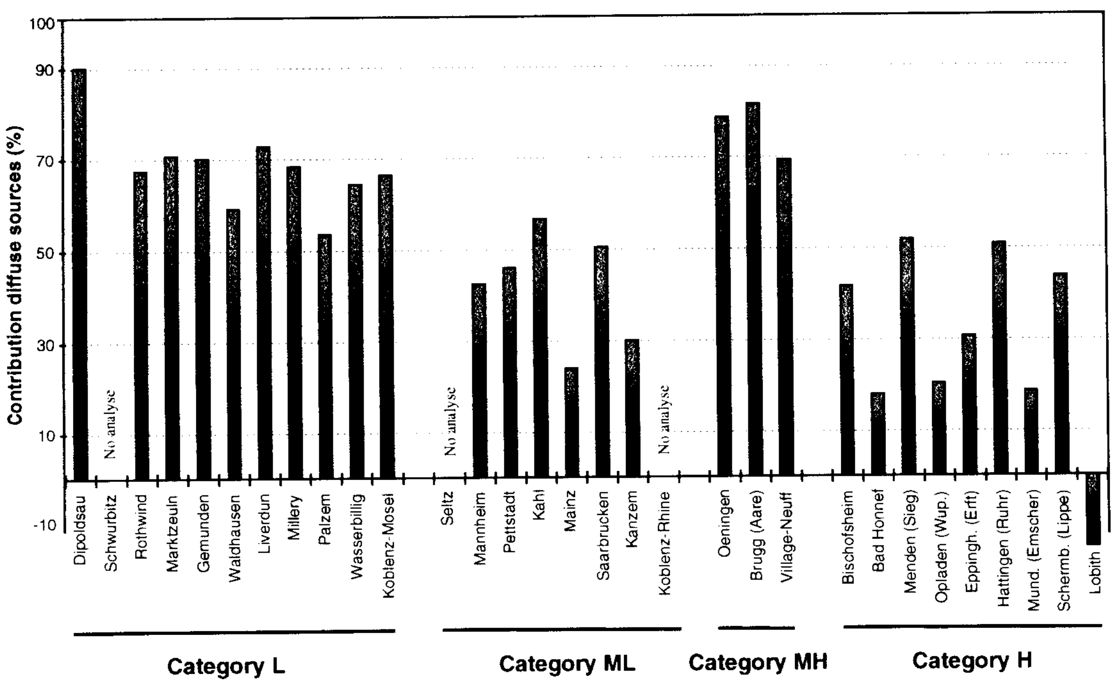



**Figure 7.1**
**Contribution of diffuse sources to the total emission by different categories of basins**

Summing up, it is apparent that the results of the input—output approach certify the possibility to classify all sub-catchments into four categories of basins with respect to the catchment characteristics for population density and specific runoff, representing the emission potency from point and diffuse sources, respectively.

As previously stated, the results of source apportionment carried out with the input—output and riverine approaches (thus comprising the total area upstream of all sapling points) match fairly well. Although the results of the riverine load cannot be presented as net contributions of each individual sub-basin (between two adjacent sampling sites), it can thus be inferred that the source apportionment based on riverine load also results in estimates of the contribution of diffuse sources to the total load, as expected according to the categorisation of sub-basins.

## 7.3 Retention estimates by riverine, input—output and mass balance approach

Based on the riverine approach, the retention of dissolved inorganic nitrogen within the entire catchment upstream of Lobith is estimated to be 32%. The estimates of the riverine approach are in agreement with the estimates made by Behrendt (1996) (about 38 % of total nitrogen) and De Wit *et al.* (1997b). Consideration of retention in the input—output model does not improve the prediction of the measured transport significantly. This implies that the estimated retention of 8% within the area upstream of Lobith is invalid.

According to the difference in retention estimates for the total area upstream of Kahl (20%, input—output approach) and the retention in the mainstream of this river stretch only (8%, mass balance calculation), the retention within the tributaries of the mainstream of the Main is 12% of the total transport of dissolved inorganic nitrogen, presuming the riverine method and the mass balance calculation to be reliable. By application of the riverine, as well as the mass balance method of retention calculation, inhomogenity in the distribution of sources within the Moselle basin was noticed.

# 8. CONCLUSIONS

***Emissions***

It can be concluded that the area specific transport and emission of nutrients differs substantially between the various sub-catchments.

From a qualitative source apportionment it can be concluded that for sparsely and moderately populated catchments, the variation in unit area transport between the various basins depends mainly on specific runoff.

By applying the *input—output approach* the emission estimate of total nitrogen upstream of Lobith is found to be 344 $kt \cdot y^{-1}$. The predicted loads (exclusive of the Emscher one) are accurate within the 95% confidence interval (P-value 0.524 > 0.001). By applying the *riverine approach* the dissolved inorganic nitrogen emission within the total area upstream of Lobith is estimated to be 361 $kt \cdot y^{-1}$ with an uncertainty of 6%.

The estimates of unit area emissions of dissolved inorganic nitrogen, by applying the riverine approach, range from approximately 22 $kg \cdot ha^{-1} \cdot y^{-1}$ within the entire area upstream of the sampling sites along the mainstream to more than 35 $kg \cdot ha^{-1} \cdot y^{-1}$ within the North-Rhine Westphalian district (NRWF). Lower emissions per unit area are found in most sub-basins of the Main (10 to 18 $kg \cdot ha^{-1} \cdot y^{-1}$) and the Mosel (15 to 20 $kg \cdot ha^{-1} \cdot y^{-1}$).

***Source apportionment***

The results of source strength estimation of both approaches (riverine and input—output) show that the origin of the total load (from either point or diffuse sources) differs between the various sub-catchments.

The results of all emission and source apportionment estimates confirm the possibility of classifying all sub-catchments into four categories of basins according to the catchment characteristics population density and specific runoff, representing the emission potency from point and diffuse sources respectively.

Compared to the period 1978–1982 there is an increase in emission, of DIN at Koblenz and Lobith, despite the decrease in discharge, which is due to an increase in the emission from point sources as well as diffuse sources. The point source contribution in the period 1990—1994 is lower compared to that between 1983 and 1987, in contrast to a slightly higher concentration of the discharge originating from diffuse sources.

By employing the *riverine approach* the contribution from diffuse sources to the total load of dissolved inorganic nitrogen (DIN) upstream of Lobith is calculated to be 47%. From source apportionment's, for the various sub-catchments (defined as the total area upstream of a sampling site), it is concluded that the dissolved inorganic nitrogen load of river basins situated in North-Rhine Westphalian (NRWF) originates from diffuse sources mainly. Only the DIN emission into the Wupper and the Emscher originates from point sources for more than 50%. Diffuse emission dominates the load of DIN in all sub-catchments of the River Main (about 65%). Except for the catchment of the River Saar (upstream of Kanzem and Saarbrücken), the emission into the Moselle is to a great extent dominated by diffuse sources.

The *input—output approach* provides estimates of 48% for the diffuse contribution to the load of total nitrogen within the entire catchment upstream of Lobith. The estimated nitrogen leaching factors are 29 and 6 $kg \cdot ha^{-1} \cdot y^{-1}$ for arable land and other land respectively. The standard error of the estimated leaching factor is 14 $kg \cdot ha^{-1} \cdot y^{-1}$ for arable land and 2 $kg \cdot ha^{-1} \cdot y^{-1}$ for other land. The apportionment of the total load to the different sources is carried out for each sub-basin individually (defined as the catchment area between two adjacent sampling sites) The diffuse contribution to the total load ranges from about 20% (Wupper Opladen, Emscher Mündung, Rhine Bad-Honnef) up to 90% (Rhine Dipoldsau, Aare Brugg and Rhine Oeningen).

***Retention***

Although the transformation rate of ammonium (into nitrate) is much higher than that of nitrate (into volatile nitrogen gas), the transformation of ammonium into nitrate does not really affect the amount of transported nitrogen. The amount of ammonium transported compared to that of nitrate is too small to have a considerable impact on the transport of total nitrogen. The retention of dissolved inorganic nitrogen is mainly due to the denitrification of nitrate.

By comparison of retention estimates for the mainstream only to retention estimates for the total area downstream of Kahl (including the tributaries), the retention within the total area can be stated to take place in the tributaries (12%) and the mainstream (7%).

*Riverine approach*

The calculated retention of dissolved inorganic nitrogen (DIN) within the total Rhine basin (sampling site Lobith) is 32 % of the total emission. Nitrate and ammonium are retained by 28% and 60% respectively. The retention of DIN ranges from 20% (within the catchment of the Main) to 45% (area upsteam of sampling sites Mains and Village-Neuf).

*Input—output approach*

Consideration of retention in the input—output model does not improve the prediction of the measured transport significantly. This implies that the estimated retention (8% within the area upstream of Lobith) is invalid.

*Mass balances*

Mass balance calculations for the mainstream of the Main upstream of Kahl provide estimates of instream retention of dissolved inorganic nitrogen of 7% on an annual basis. The DIN retention on monthly basis is estimated to be up to 26% of the total transport within this stretch of the mainstream (August). Monthly annual retention of ammonium up to 47% is found (April).

***Comparing the results of the riverine and input—output approach***

*Source apportionment*

The source apportionment by employing the input—output model as well as the riverine method for the entire area upstream of Lobith are in good agreement with each other and the values cited in literature. Despite the correspondence in predicted contribution from different sources, there are some discrepancies in the estimated source strengths for the various sub-catchments. Except for the upstream basins of the Rhine, the riverine method provides higher estimates of diffuse source contributions compared to the input—output approach. These discrepancies are presumably due to the different definitions of point and diffuse sources within the two approaches of source apportionment. Deviant discharges due to wires or discontinue drainage from industries possibly elevate the estimated contribution of diffuse sources in case diffuse sources are defined as in the riverine method. Moreover source apportionment with the input—output approach is carried out for the load of total nitrate. In contrast to the apportionment of the load of dissolved inorganic nitrogen by using the riverine approach.

*Retention*

With respect to retention, comparison between the input—output and the riverine method is impossible because of the inaccurate retention estimate of the input—output approach.

*Methods*

If good data sets of water quality and different potential sources of nutrients are available, the input—output method can be used for source strength and retention estimation with high spatial detail. Consequently, this implies the extensive data requirement of the method. The study area is presumed to consist of about 25 sub-catchment with a certain variation with respect to the basin characteristics which represent potential sources of nutrients. In addition the unit area emission of a certain source is presumed to be equal for the different sub-basins. If the variation between the sub-catchments is too little or the variation in unit area retention or immission from a certain source is too big, the benefit of considering the entire basin as a hierarchy of individual sub-basins, considering their mutual dependency, is lost. An apparent advantage of the input—output approach is the possibility to apportion the observed load to distinct sources within the basic subdivision of point and diffuse sources. Another convenience is the possibility to examine different, user defined, emission and retention models.

The riverine approach is relatively simple applicable and less data intensively compared to the input output approach, presuming the availability of reliable water quality data. The hydrology of the study area is required to be dependent on meteorological circumstances and not determined by wires, reservoirs, artificial drainage or big lakes. Point sources are presumed to drain ceaselessly with constant discharges.

Resuming, both approaches of source apportionment and retention estimation amplify each other in stead of one being superior.

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# APPENDIX

*Appendices chapter 3*



*Appendices chapter 4*



*Appendices chapter 5*



*Appendices chapter 6*

**APPENDIX 3.1.**
**Sources of water quality data**

| Basin Name | Year | Ref. $NO_3$ | Ref. $P_{tot}$ | Ref. $N_{tot}$ | Ref. $NH_4$ | Method N | Method P |
|---|---|---|---|---|---|---|---|
| Aare upstream Brugg | 1990 | 11 | 11 | 11 | | Blended | Blended |
| Aare upstream Brugg | 1991 | 11 | 11 | 11 | | Blended | Blended |
| Aare upstream Brugg | 1992 | 11 | 11 | 11 | | Blended | Blended |
| Aare upstream Brugg | 1993 | 11 | 11 | 11 | | Blended | Blended |
| Aare upstream Brugg | 1994 | 11 | 11 | 11 | | Blended | Blended |
| Emscher mündung | 1990 | 10 | 10 | | 10 | Point | Point |
| Emscher mündung | 1991 | 10 | 10 | | 10 | Point | Point |
| Emscher mündung | 1992 | 10 | 10 | 10 | 10 | Point | Point |
| Emscher mündung | 1993 | 10 | 10 | 10 | 10 | Point | Point |
| Emscher mündung | 1994 | 10 | 10 | 10 | 10 | Point | Point |
| Erft up Eppinghoven | 1990 | 10 | 10 | 10 | 10 | Point | Point |
| Erft up Eppinghoven | 1991 | 10 | 10 | 10 | 10 | Point | Point |
| Erft up Eppinghoven | 1992 | 10 | 10 | 10 | 10 | Point | Point |
| Erft up Eppinghoven | 1993 | 10 | 10 | 10 | 10 | Point | Point |
| Erft up Eppinghoven | 1994 | 10 | 10 | 10 | 10 | Point | Point |
| Lippe up Schermbeck | 1990 | 10 | 10 | 10 | 10 | Point | Point |
| Lippe up Schermbeck | 1991 | 10 | 10 | 10 | 10 | Point | Point |
| Lippe up Schermbeck | 1992 | 10 | 10 | 10 | 10 | Point | Point |
| Lippe up Schermbeck | 1993 | 10 | 10 | 10 | 10 | Point | Point |
| Lippe up Schermbeck | 1994 | 10 | 10 | 10 | 10 | Point | Point |
| Main up Bischofsheim | 1990 | 8,13 | 13 | | 8,13 | Point | Blended |
| Main up Bischofsheim | 1990 | 13 | 13 | | 13 | Point | Blended |
| Main up Bischofsheim | 1991 | 13 | | | 13 | Point | |
| Main up Bischofsheim | 1992 | 8,13 | 8,13 | 13 | 8,13 | Point | Point |
| Main up Bischofsheim | 1993 | 8,13 | | 13 | 8,13 | Point | |
| Main up Kahl | 1990 | 8,12,13 | 12 | | 8,12,13 | Point | Point |
| Main up Kahl | 1991 | 12,13 | 12 | | 12,13 | Point | Point |
| Main up Kahl | 1992 | 8,12,13 | 8,12,13 | 13 | 8,12,13 | Point | Point |
| Main up Kahl | 1993 | 8,12,13 | 8,12,13 | 13 | 8,12,13 | Point | Point |
| Main up Kahl | 1994 | 12,13 | 12,13 | 13 | 12,13 | Point | Point |
| Main up Kahl | 1995 | 12 | 12 | | 12 | Point | Point |
| Frankische Saale up Gemünden | 1990 | 12 | 12 | | 12 | Point | Point |
| Frankische Saale up Gemünden | 1991 | 12 | 12 | | 12 | Point | Point |
| Frankische Saale up Gemünden | 1992 | 12 | 12 | | 12 | Point | Point |
| Frankische Saale up Gemünden | 1993 | 12 | 12 | | 12 | Point | Point |
| Frankische Saale up Gemünden | 1994 | 12 | 12 | | 12 | Point | Point |
| Frankische Saale up Gemünden | 1995 | 12 | 12 | | 12 | Point | Point |
| Regnitz up Pettstadt | 1990 | 12 | 12 | | 12 | Point | Point |
| Regnitz up Pettstadt | 1991 | 12 | 12 | | 12 | Point | Point |
| Regnitz up Pettstadt | 1992 | 12 | 12 | | 12 | Point | Point |
| Regnitz up Pettstadt | 1993 | 12 | 12 | | 12 | Point | Point |
| Regnitz up Pettstadt | 1994 | 12 | 12 | | 12 | Point | Point |
| Regnitz up Pettstadt | 1995 | 12 | 12 | | 12 | Point | Point |
| Main up Schwürbitz | 1990 | 12 | 12 | | 12 | Point | Point |
| Main up Schwürbitz | 1991 | 12 | 12 | | 12 | Point | Point |
| Main up Schwürbitz | 1992 | 12 | 12 | | 12 | Point | Point |
| Main up Schwürbitz | 1993 | 12 | 12 | | 12 | Point | Point |
| Main up Schwürbitz | 1994 | 12 | 12 | | 12 | Point | Point |
| Main up Schwürbitz | 1995 | 12 | 12 | | 12 | Point | Point |

# APPENDIX

| Basin Name | Year | Ref. $NO_3$ | Ref. $P_{tot}$ | Ref. $N_{tot}$ | Ref. $NH_4$ | Method N | Method P |
|---|---|---|---|---|---|---|---|
| Tauber up Waldhausen | 1990 | 12 | 12 | | 12 | Point | Point |
| Tauber up Waldhausen | 1991 | 12 | 12 | | 12 | Point | Point |
| Tauber up Waldhausen | 1992 | 12 | 12 | | 12 | Point | Point |
| Tauber up Waldhausen | 1993 | 12 | 12 | | 12 | Point | Point |
| Tauber up Waldhausen | 1994 | 12 | 12 | | 12 | Point | Point |
| Tauber up Waldhausen | 1995 | 12 | 12 | | 12 | Point | Point |
| Rodach up Marktzeuln | 1990 | 12 | 12 | | 12 | Point | Point |
| Rodach up Marktzeuln | 1991 | 12 | 12 | | 12 | Point | Point |
| Rodach up Marktzeuln | 1992 | 12 | 12 | | 12 | Point | Point |
| Rodach up Marktzeuln | 1993 | 12 | 12 | | 12 | Point | Point |
| Rodach up Marktzeuln | 1994 | 12 | 12 | | 12 | Point | Point |
| Rodach up Marktzeuln | 1995 | 12 | 12 | | 12 | Point | Point |
| RoterMain up Rothwind | 1990 | 12 | 12 | | 12 | Point | Point |
| RoterMain up Rothwind | 1991 | 12 | 12 | | 12 | Point | Point |
| RoterMain up Rothwind | 1992 | 12 | 12 | | 12 | Point | Point |
| RoterMain up Rothwind | 1993 | 12 | 12 | | 12 | Point | Point |
| RoterMain up Rothwind | 1994 | 12 | 12 | | 12 | Point | Point |
| RoterMain up Rothwind | 1995 | 12 | 12 | | 12 | Point | Point |
| Moselle up Koblenz | 1990 | 1,8 | | | 1,8 | Point | |
| Moselle up Koblenz | 1990 | 13 | | | 1,8 | Point | |
| Moselle up Koblenz | 1991 | 1 | 8 | 8 | 1,8,13 | Point | Point |
| Moselle up Koblenz | 1991 | 13 | 8 | 8 | 1,8,13 | Point | Point |
| Moselle up Koblenz | 1992 | 8 | 8,13 | 13 | 1,8,13 | Point | Point |
| Moselle up Koblenz | 1992 | 1 | 8,13 | 13 | 1,8,13 | Point | Point |
| Moselle up Koblenz | 1992 | 8,13 | 8,13 | 13 | 1,8,13 | Point | Point |
| Moselle up Koblenz | 1992 | 8 | 8,13 | 13 | 1,8,13 | Point | Point |
| Moselle up Koblenz | 1993 | 8 | 8,13 | 13 | 8,13 | Point | Point |
| Moselle up Koblenz | 1993 | 8,13 | 8,13 | 8,13 | 8,13 | Point | Point |
| Moselle up Koblenz | 1993 | 8 | 8,13 | 8,13 | 8,13 | Point | Point |
| Moselle up Koblenz | 1994 | 13 | 13 | 13 | 13 | Point | Point |
| Moselle Fr up Millery | 1990 | 8 | 8 | 8 | 8 | Point | Point |
| Moselle Fr up Millery | 1991 | 8 | 8 | 8 | 8 | Point | Point |
| Moselle Fr up Millery | 1992 | 8 | 8 | 8 | 8 | Point | Point |
| Moselle up Palzem | 1990 | 8 | 8 | | 8,13 | Point | Point |
| Moselle up Palzem | 1990 | 13 | 8 | | 8,13 | Point | Point |
| Moselle up Palzem | 1991 | 8 | 8 | | 8,13 | Point | Point |
| Moselle up Palzem | 1991 | 13 | 8 | | 8,13 | Point | Point |
| Moselle up Palzem | 1992 | 8,13 | 8,13 | 13 | 8,13 | Point | Point |
| Moselle up Palzem | 1992 | 8 | 8,13 | 13 | 8,13 | Point | Point |
| Moselle up Palzem | 1992 | 8 | 8,13 | 13 | 8,13 | Point | Point |
| Moselle up Palzem | 1993 | 8,13 | 8,13 | 13 | 8,13 | Point | Point |
| Moselle up Palzem | 1993 | 8 | 8,13 | 13 | 8,13 | Point | Point |
| Moselle up Palzem | 1994 | 13 | 13 | 13 | 13 | Point | Point |
| Saar up Kanzem | 1990 | 13 | 13 | | 13 | Point | Blended |
| Saar up Kanzem | 1991 | 13 | 13 | | 13 | Point | Blended |
| Saar up Kanzem | 1992 | 13 | 13 | 13 | 13 | Point | Point |
| Saar up Kanzem | 1993 | 13 | 13 | 13 | 13 | Point | Point |
| Saar up Kanzem | 1994 | 13 | 13 | 13 | 13 | Point | Point |
| Moselle up Liverdun | 1990 | 8 | 8 | 8 | 8 | Point | Point |
| Moselle up Liverdun | 1991 | 8 | 8 | 8 | 8 | Point | Point |
| Moselle up Liverdun | 1992 | 8 | 8 | 8 | 8 | Point | Point |

# APPENDIX

| Basin Name | Year | Ref. $NO_3$ | Ref. $P_{tot}$ | Ref. $N_{tot}$ | Ref. $NH_4$ | Method N | Method P |
|---|---|---|---|---|---|---|---|
| Sure up Wasserbillig | 1990 | 8 | 8 | | 8 | Point | Point |
| Sure up Wasserbillig | 1991 | 8 | 8 | | 8 | Point | Point |
| Sure up Wasserbillig | 1992 | 8 | 8 | | 8 | Point | Point |
| Saar up Saarbrücken | 1990 | 13 | 13 | | 13 | Point | Blended |
| Saar up Saarbrücken | 1991 | 13 | 13 | | 13 | Point | Blended |
| Saar up Saarbrücken | 1992 | 13 | 13 | 13 | 13 | Point | Point |
| Saar up Saarbrücken | 1993 | 13 | 13 | 13 | 13 | Point | Point |
| Saar up Saarbrücken | 1994 | 13 | 13 | 13 | 13 | Point | Point |
| Neckar up Mannheim | 1990 | 1,8,13 | 13 | | 1,8,13 | Point | Blended |
| Neckar up Mannheim | 1991 | 1,13 | 13 | | 1,13 | Point | Blended |
| Neckar up Mannheim | 1992 | 1,8,13 | 8,13 | 13 | 1,8,13 | Point | Point |
| Neckar up Mannheim | 1993 | 8,13 | | | 8,13 | Point | |
| Neckar up Mannheim | 1994 | 13 | | | 13 | Point | |
| Rhine up Bad-Honnef | 1990 | 8,13 | 13 | | 8,13 | Point | Blended |
| Rhine up Bad-Honnef | 1991 | 13 | 13 | | 13 | Point | Blended |
| Rhine up Bad-Honnef | 1992 | 8,13 | 8,13 | | 8,13 | Point | Point |
| Rhine up Bad-Honnef | 1993 | 8,13 | 8,13 | 13 | 8,13 | Point | Point |
| Rhine up Bad-Honnef | 1994 | 13 | 13 | 13 | 13 | Point | Point |
| Rhine up Dipoldsau | 1990 | 11 | 11 | 11 | | Blended | Blended |
| Rhine up Dipoldsau | 1991 | 11 | 11 | 11 | | Blended | Blended |
| Rhine up Dipoldsau | 1992 | 11 | 11 | 11 | | Blended | Blended |
| Rhine up Dipoldsau | 1993 | 11 | 11 | 11 | | Blended | Blended |
| Rhine up Dipoldsau | 1994 | 11 | 11 | 11 | | Blended | Blended |
| Rhine up Koblenz | 1990 | 1,8 | 8 | 8 | 1,8,13 | Point | Point |
| Rhine up Koblenz | 1990 | 13 | 13 | 8 | 1,8,13 | Point | Blended |
| Rhine up Koblenz | 1991 | 1,8 | | 8 | 1,8,13 | Point | |
| Rhine up Koblenz | 1991 | 13 | 13 | 8 | 1,8,13 | Point | Blended |
| Rhine up Koblenz | 1992 | 8 | 8,13 | 13 | 1,8,13 | Point | Point |
| Rhine up Koblenz | 1992 | 1 | 8,13 | 13 | 1,8,13 | Point | Point |
| Rhine up Koblenz | 1992 | 8,13 | 8,13 | 13 | 1,8,13 | Point | Point |
| Rhine up Koblenz | 1992 | 8 | 8,13 | 13 | 1,8,13 | Point | Point |
| Rhine up Koblenz | 1993 | 8 | 8,13 | 8,13 | 8,13 | Point | Point |
| Rhine up Koblenz | 1993 | 8,13 | 8,13 | 8,13 | 8,13 | Point | Point |
| Rhine up Koblenz | 1993 | 8 | 8,13 | 8,13 | 8,13 | Point | Point |
| Rhine up Koblenz | 1994 | 13 | 13 | 13 | 13 | Point | Point |
| Rhine up Lobith | 1990 | 8 | | | 8,13 | Point | |
| Rhine up Lobith | 1990 | 13 | | | 8,13 | Point | |
| Rhine up Lobith | 1990 | 13 | | | 13 | Point | |
| Rhine up Lobith | 1991 | 8 | 8 | 8 | 8,13 | Point | Point |
| Rhine up Lobith | 1991 | 13 | 8 | 8 | 13 | Point | Point |
| Rhine up Lobith | 1991 | 8 | 8 | 8 | 8,13 | Point | Point |
| Rhine up Lobith | 1991 | 8 | 8,13 | 8 | 8,13 | Point | Point |
| Rhine up Lobith | 1992 | 8 | 8,13 | 13 | 8,13 | Point | Point |
| Rhine up Lobith | 1992 | 8 | 8,13 | 13 | 8,13 | Point | Point |
| Rhine up Lobith | 1992 | 8 | 8,13 | 13 | 8,13 | Point | Point |
| Rhine up Lobith | 1992 | 13 | 8,13 | 13 | 8,13 | Point | Point |
| Rhine up Lobith | 1993 | 8 | 8,13 | 13 | 8,13 | Point | Point |
| Rhine up Lobith | 1993 | 8 | 8,13 | 13 | 8,13 | Point | Point |
| Rhine up Lobith | 1993 | 8 | 8,13 | 13 | 8,13 | Point | Point |
| Rhine up Lobith | 1993 | 8 | 8,13 | 8 | 8,13 | Point | Point |
| Rhine up Lobith | 1994 | 13 | 13 | 13 | 13 | Point | Point |

| Basin Name | Year | Ref. $NO_3$ | Ref. $P_{tot}$ | Ref. $N_{tot}$ | Ref. $NH_4$ | Method N | Method P |
|---|---|---|---|---|---|---|---|
| Rhine up Mainz | 1990 | 8,13 | 13 | | 8,13 | Point | Blended |
| Rhine up Mainz | 1991 | 13 | 13 | | 13 | Point | Blended |
| Rhine up Mainz | 1992 | 8,13 | 8,13 | 13 | 8,13 | Point | Point |
| Rhine up Mainz | 1992 | 8 | 8,13 | 13 | 8,13 | Point | Point |
| Rhine up Mainz | 1993 | 8,13 | 8,13 | 13 | 8,13 | Point | Point |
| Rhine up Mainz | 1993 | 8 | 8,13 | 13 | 8,13 | Point | Point |
| Rhine up Mainz | 1994 | 13 | 13 | 13 | 13 | Point | Point |
| Rhine up Oeningen | 1990 | 8,13 | 11 | | | Point | Blended |
| Rhine up Oeningen | 1992 | 8,13 | 8,13 | | 8 | Point | Point |
| Rhine up Oeningen | 1992 | 8 | 8,13 | | 8 | Point | Point |
| Rhine up Oeningen | 1993 | 8,13 | 8 | | 8 | Point | Point |
| Rhine up Oeningen | 1993 | 8 | 8 | | 8 | Point | Point |
| Rhine Seltz | 1990 | 13 | 8 | | 1,8,13 | Point | Point |
| Rhine Seltz | 1990 | 1 | 8 | | 1,8,13 | Point | Point |
| Rhine Seltz | 1991 | 13 | 8 | 8 | 1,8,13 | Point | Point |
| Rhine Seltz | 1991 | 1,8 | 8 | 8 | 1,8,13 | Point | Point |
| Rhine Seltz | 1992 | 13 | 8 | 8 | 1 | Point | Point |
| Rhine Seltz | 1992 | 13 | 8,13 | 8,13 | 1,8,13 | Point | Point |
| Rhine Seltz | 1992 | 1,8 | 8,13 | 8,13 | 1,8,13 | Point | Point |
| Rhine Seltz | 1993 | 13 | | | 13 | Point | |
| Rhine Seltz | 1994 | 13 | | | 13 | Point | |
| Rhine upstream Village-Neuf | 1990 | 8,13 | | 11 | 8,13 | Blended | Blended |
| Rhine upstream Village-Neuf | 1991 | 13 | | 11 | 8,13 | Blended | Blended |
| Rhine upstream Village-Neuf | 1992 | 8,13 | 8,13 | | 8,13 | Blended | Point |
| Rhine upstream Village-Neuf | 1993 | 8,13 | | 11 | 8,13 | Blended | Blended |
| Rhine upstream Village-Neuf | 1994 | 13 | | 11 | 13 | Blended | Blended |
| Ruhr up Hattingen | 1990 | 10 | 10 | | 10 | Point | Point |
| Ruhr up Hattingen | 1991 | 10 | 10 | | 10 | Point | Point |
| Ruhr up Hattingen | 1992 | 10 | 10 | | 10 | Point | Point |
| Ruhr up Hattingen | 1993 | 10 | 10 | 10 | 10 | Point | Point |
| Ruhr up Hattingen | 1994 | 10 | 10 | 10 | 10 | Point | Point |
| Sieg up Menden | 1990 | 10 | 10 | 10 | 10 | Point | Point |
| Sieg up Menden | 1991 | 10 | 10 | 10 | 10 | Point | Point |
| Sieg up Menden | 1992 | 10 | 10 | 10 | 10 | Point | Point |
| Sieg up Menden | 1993 | 10 | 10 | 10 | 10 | Point | Point |
| Sieg up Menden | 1994 | 10 | 10 | 10 | 10 | Point | Point |
| Wupper up Opladen | 1990 | 10 | 10 | 10 | 10 | Point | Point |
| Wupper up Opladen | 1991 | 10 | 10 | 10 | 10 | Point | Point |
| Wupper up Opladen | 1992 | 10 | 10 | 10 | 10 | Point | Point |
| Wupper up Opladen | 1993 | 10 | 10 | 10 | 10 | Point | Point |
| Wupper up Opladen | 1994 | 10 | 10 | 10 | 10 | Point | Point |

| Reference no. | Reference |
|---|---|
| 1 | Institut für Gewaserökologie und Binnenfischerei (IGB), Berlin, H.Behrendt |
| 8 | National Institute of Public Health and the Environment (RIVM), P.Puijenbroek |
| 10 | Landesamt für Wasser und Abfall Nordrhein-Westfalen, K. Vogt |
| 11 | Landeshydrologie und geologie, Switserland, C. Koch |
| 12 | Bayerisches Landesamt für Wasserwirtschaft, Dr. I. A. Bach |
| 13 | Bundesanstalt für Gewasserkunde, Koblenz, M. Keller |

## APPENDIX 3.2.
**Origin of the data concerning catchment characteristics**

**Land use and population data**

| Country | Data source (see list of references) | Aggregation level |
|---|---|---|
| Germany | SBU, 1995 | Nuts3, "Kreise" |
| France | SRSA, 1993 | Nuts3, "Kreise" |
| Switzerland | BFS, 1985; BFS, 1993; BFS, 1995 | "Bezirk" |
| Luxemburg | STATEC,1995 | Nuts3 |
| Belgium | OECD, 1991 | Nuts3 |
| Austria | STAT, 1995 | "Bundeslander" |

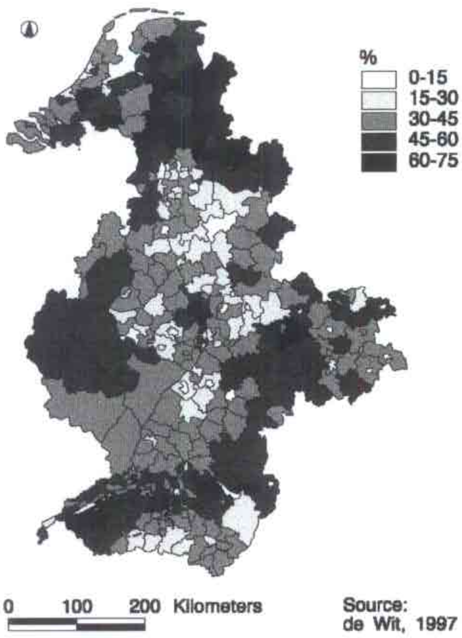
**Connection rate to waste water treatment plants**

| Country | Data source (see list of references) | Agregation level |
|---|---|---|
| Germany | SBU, 1995 | Nuts3, "Kreise" |
| France | WRI/UNEP/UNDP, 1994 | Nuts0 |
| Switzerland | BUWAL, 1993 | "Kanton" |
| Luxemburg | STATEC, 1995 | Nuts3 |
| Belgium | OECD, 1991 | Nuts3 |
| Austria | STAT, 1994 | "Bundeslander" |

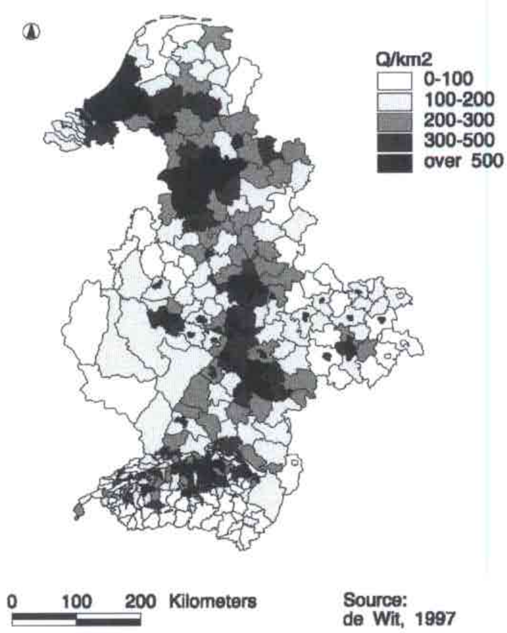
# APPENDIX

## APPENDIX 3.3.

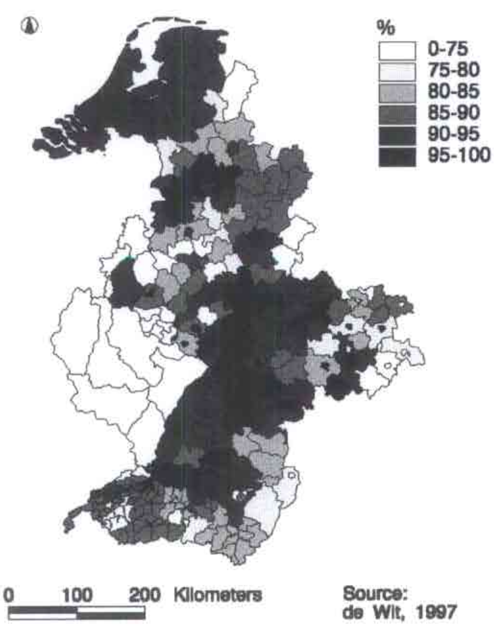
Percentage agricultural land (1990-1995)




Population density (1990-1995)




Population connected to waste water treatment plants (1990-1995)



**APPENDIX 4.1.**
**Summary of the riverine approach of source apporionment and emission estimation.**

All measured concentrations and calculated loads are temperature corrected to the inferred level in the case of a water temperature of 0 °C by the following functions:

$$\text{Corrected Concentration} = \frac{\text{Concentration}}{e^{b*T}}$$

b = slope of regression LnConcentration (y-axis) against Temperature (x-axis)
T = Temperature in degrees Celsius

$$\text{Corrected Load} = \frac{\text{Load}}{e^{b*T}}$$

b = slope of regression LnConc (y-axis) against Temperature (x-axis)
T = Temperature in degrees Celsius

If m different data sets of $C_t$ and $Q_t$ exist for a given time period at a monitoring station, the following equations can be used to estimate the means of net diffuse concentration of pollutant ($C_D$) and parameter $L_0 = Q_P (C_P - C_D)$

(X.1) $Q_t = Q_{Dt} + Q_{Pt}$

(X.2) $L_{Dt} = C_{Dt} * Q_{Dt} + C_{Pt} * Q_{Pt}$

(X.3) $C_t = \dfrac{C_{Dt} * Q_{Dt} + C_{Pt} * Q_{Pt}}{Q_t}$

| | | |
|---|---|---|
| $Q_t$ | = | total discharge at time t |
| $Q_{Dt}$ | = | discharge of all diffuse components at time t |
| $Q_{Pt}$ | = | discharge of all point sources at time t |
| $L_{Dt}$ | = | diffuse load at time t |
| $C_{Dt}$ | = | pollutant net concentration of the diffuse sources at time t |
| $C_{Pt}$ | = | pollutant net concentration of the point sources at time t |
| $C_t$ | = | pollutant net concentration at time t |

In this case we have three systems of m equations:

(X.4) $Q_m = Q_{Dm} + Q_{Pm}$

(X.5) $L_m = C_{Dm} * Q_{Dm} + C_{Pm} * Q_{Pm}$

(X.6) $$C_m = \frac{C_{Dm} * Q_{Dm} + C_{Pm} * Q_{Pm}}{Q_m}$$

The three systems of equations can be transformed to the following equation:

(X.7) $$L_m = C_{Dm} * Q_{Dm} + L_{0m}$$

This system can be used for the estimation of the average values of $C_D$ and $L_0$ within the time period investigated. The linear regression between the measured load ($L_m$) and the discharge ($Q_m$) is applied as a method for the solution of this system (equation X.7). The parameters of this equation are shown in a load—discharge relationship in Figure 4.2.

With regard to this system reflecting the load—discharge relationship the result is:

(X.8) $$C_D = \frac{\sum_{j=1}^{m} C_{Dj}}{m} = \frac{m * \sum_{j=1}^{m} Q_j * L_j - \sum_{j=1}^{m} Q_j * \sum_{j=1}^{m} L_j}{m * \sum_{j=1}^{m} Q_j^2 - \sum_{j=1}^{m} Q_j * \sum_{j=1}^{m} Q_j}$$

$$L_0 = \frac{\sum_{j=1}^{m} L_{0j}}{m} = \frac{1}{m}\left(\sum_{j=1}^{m} L_j - C_D * \sum_{j=1}^{m} Q_j\right)$$

(X.9) $$L_0 = Q_P (C_P - C_D)$$

If the mean part of the *discharge caused by point sources is known*, the mean point load of the pollutant is carried out using equation X.9 and the parameter $C_D$ which was calculated by the regression (equation X.8) of Q versus temperature-corrected load according to:

(X.10) $$L_p = Q_p * C_p = L_0 + C_D * Q_P$$

The total pollutant net load at the monitoring station for the time period investigated is defined as:

(X.11) $$L_{Tot} = \frac{\sum_{j=1}^{m} C_j * Q_j}{m}$$

The diffuse net load can be estimated from the difference between the total net load (Ltot) and the estimated point net load Lp

(X.12) $$L_D = L_{Tot} - L_P$$

# APPENDIX

### *Uncertainty*

The quality of the results depends mainly on the scattering of the concentration— and load—discharge relationship and the uncertainty in the estimate of the discharge caused by point sources. To analyse the uncertainty in the calculated point and diffuse load, minimum and maximum point, and diffuse loads are calculated using the equations:

(X.13) $L_{P\text{-}Max} = (L_0 + \varepsilon L_0) + (C_D - \varepsilon C_D) * Q_{P\text{-}Max}$

| | | |
|---|---|---|
| $L_{P\text{-}Max}$ | = | maximum point load |
| $Q_{P\text{-}Max}$ | = | highest estimated point discharge |
| $L_0$ | = | intercept regression of discharge (x-axis) versus (temperature-corrected) load (y-axis) |
| $C_D = b$ | = | slope regression discharge (x-axis) versus (temperature-corrected) load (y-axis) |
| $\varepsilon L_0$ | = | standard error of $L_0$ |
| $\varepsilon C_D$ | = | standard error of $C_d$ |

(X.14) $L_{D\text{-}max} = L_{Tot\_Avg} - L_{P\text{-}Min}$

| | | |
|---|---|---|
| $L_{D\text{-}max}$ | = | maximum diffuse load |
| $L_{Tot\_Avg}$ | = | average of all (temperature-corrected) load measurements |
| $L_{P\text{-}Min}$ | = | lowest calculated point load |

(X.15) $L_{P\text{-}Min} = (L_0 + \varepsilon L_0) + (C_D + \varepsilon C_D) * Q_{P\text{-}Min}$

| | | |
|---|---|---|
| $L_{P\text{-}Min}$ | = | minimum point load |
| $Q_{P\text{-}Min}$ | = | lowest estimated point discharge |

(X.16) $L_{D\text{-}min} = L_{Tot\_Avg} - L_{P\text{-}Max}$

| | | |
|---|---|---|
| $L_{D\text{-}Min}$ | = | minimum diffuse load |
| $L_{Tot\_Avg}$ | = | average of all (temperature-corrected) load measurements |
| $L_{P\text{-}Max}$ | = | highest calculated point load |

If the Minimum diffuse or point load is estimated as negative, it is forced to be at least 0.

The minimum point and diffuse loads are presented as the calculated load because these loads are at least present. The uncertainty in the estimate is presented as the sum of maximum minus mean and mean minus minimum load. In the equation:

(X.17) $\text{Uncertainty} = (L_{Max} - L_{Min}) + (L_{Mean} - L_{Min})$

| | | |
|---|---|---|
| $L_{Max}$ | = | maximum calculated load |
| $L_{Mean}$ | = | mean calculated load |
| $L_{Min}$ | = | minimum calculated load |

**APPENDIX 4.2.**
**Waterquality data used with the riverine approach**

| Basin | No. of samples | Discharge | Temperature | Concentration | Concentration |
|---|---|---|---|---|---|
| | | $m^3 \cdot s$ | deg. C | $NO_3$ $gN \cdot m^{-3}$ | $NH_4$ $gN \cdot m^{-3}$ |
| Dipoldsau* | 131 | 225 | 8 | 0.67 | · |
| Oeningen | 45 | 362 | 12 | 0.84 | 0.10 |
| Brugg (Aare)* | 130 | 308 | 12 | 1.99 | · |
| Village-Neuff* | 131 | 1010 | 12 | 1.76 | · |
| Seltz | 188 | 1141 | 14 | 3.19 | 0.10 |
| Mannheim | 80 | 146 | 15 | 5.73 | 0.16 |
| Schwürbitz | 151 | 26 | 10 | 4.34 | 0.30 |
| Rothwind | 134 | 13 | 11 | 5.20 | 0.61 |
| Marktzeuln | 152 | 13 | 10 | 3.36 | 0.27 |
| Pettstadt | 155 | 45 | 12 | 6.56 | 0.26 |
| Gemünden | 154 | 16 | 11 | 5.22 | 0.10 |
| Waldhausen | 51 | 5 | 11 | 7.62 | 0.07 |
| Kahl | 134 | 159 | 13 | 5.44 | 0.16 |
| Bischofsheim | 102 | 163 | 13 | 6.70 | 0.32 |
| Mainz | 39 | 1461 | 15 | 2.26 | 0.24 |
| Liverdun | 36 | 49 | 12 | 1.82 | 0.14 |
| Millery | 46 | 97 | 13 | 2.22 | 0.38 |
| Palzem | 63 | 107 | 14 | 2.62 | 0.35 |
| Wasserbillig | 36 | 36 | 11 | 5.27 | 0.24 |
| Saarbrücken | 72 | 39 | 12 | 3.40 | 0.62 |
| Kanzem | 124 | 66 | 12 | 4.03 | 0.89 |
| Koblenz-Mosel | 207 | 280 | 13 | 4.11 | 0.16 |
| Koblenz-Rhine | 206 | 1531 | 14 | 3.19 | 0.18 |
| Bad Honnef | 56 | 1942 | 15 | 2.85 | 0.08 |
| Menden (Sieg) | 53 | 45 | 12 | 4.11 | 0.18 |
| Opladen (Wupper) | 55 | 15 | 14 | 9.26 | 0.65 |
| Eppinghoven (Erft) | 63 | 11 | 15 | 2.94 | 0.37 |
| Hattingen (Ruhr) | 62 | 75 | 13 | 4.38 | 0.73 |
| Mündung (Emscher) | 46 | 16 | 15 | 0.37 | 31.99 |
| Schermbeck (Lippe) | 59 | 39 | 13 | 7.48 | 0.67 |
| Lobith | 105 | 2015 | 14 | 3.63 | 0.24 |

(* = blended samples, · = no data)

## APPENDIX 5.1.
**Summary of the input—output approach of source apportionment and emission estimation**

The source apportionment approach of Grimvall *et al.* (1994) is based on the following:
1) a partitioning of the study area into mutually independent (disjoint) sub-basins partially ordered by their upstream—downstream relations; 2) matrix equations for the transport and retention of an arbitrary substance in such a system of sub-basins; 3) matrix equations for the source apportionment of the output from an arbitrary sub-basin; 4) general principles for the parameterisation of losses of substances from soil and retention of substances in lakes and watercourses.

*Hierarchy matrix, input—output equations and retention of partially ordered sub-basins*
Let $z_1$, $z_2$ ..., $z_N$ be N arbitrary sampling sites along the watercourses of a river basin. The upstream—downstream relationships between these sites can then be summarised in an NxN matrix H, where

H(i,j)=

$$\begin{cases} 1, \text{if } z_j \text{ is the nearest site downstream from } z_i \\ 0, \text{otherwise} \end{cases}$$

If $C_j$ denotes the entire area upstream from $z_j$ and let

$$B_j = \bigcap_{\{j\,;\,H(ij)=1\}} (C_j \setminus C_i \qquad j=1, \dots, N,$$

a partitioning of the river basin into a set of disjoint, partially ordered sub-basins is also defined in Figure 5.2.

To describe the flow of substances through $B_1$, $B_2$, ... , $B_N$, two matrices are needed.
One presents the output from each of the sub-basins:

an Nx1 matrix $E = (e_1, e_2, \dots, e_N)^T$

Another is one in which the j:th diagonal element $r_j$ denotes the fraction of the riverine input to $B_j$ which is retained in the sub-basin:

$$R = \begin{pmatrix} r_1 & 0 & . & 0 \\ 0 & r_2 & . & 0 \\ . & . & . & . \\ 0 & 0 & . & r_N \end{pmatrix}$$

The output $e_j$ from an arbitrary sub-basin $B_j$ can then be decomposed into contribution $i_j$ from sources in sub-basins further upstream and the contribution $l_j = e_j - u_j$ from sources within $B_j$.

Output vector $E = (e_1, e_2, \dots, e_N)^T$ in this case is decomposed into a vector:

(X.1) $$U = (I - R)\, H^T E$$

of contributions from sources located in sub-basins further upstream and a vector:

(X.2) $$L = ( I - (I - R)\, H^T)\, E$$

of contributions from sources within the sub-basins under consideration.

The expression for L is derived from L = E - U. The inverse of expression L (equation X.3) provides a link between the sources and the retention in the disjoint sub-basins $B_1, B_2, \dots, B_N$, and observed riverine loads $e_1, e_2, \dots, e_N$ at the outlets of the same basins.

(X.3) $$E = (I - (I - R)\, H^T)^{-1} L$$

Furthermore, the difference $D_{out\text{-}in}$ between the output and input for each of the sub-basins can be written as:

(X.4) $$D_{out\text{-}in} = (I - H^T)\,(I - R)\, H^T)^{-1} L$$

If there is no retention, the vectors $D_{out\text{-}in}$ and L in equation X.4 will be identical.

To apportion the responsibility for the observed riverine load at the outlet of an arbitrary sub-basin, the retention of the studied substance between the outlets of any two sub-basins in the study area must be computed. This can be accomplished by matrix calculations using the matrices defined so far.

*Apportionment of riverine loads among sub-basins and sources*

If it is assumed that the vector L of contributions from sources in the different sub-basins to the outputs from the same sub-basins can be written as a sum, where $R_1$, $R_2$ and $R_3$ are retention matrices of the same type as R, S, P and D, then Nx1 matrices representing losses from soil (S), point discharges (P) and atmospheric deposition on lakes (D). In this case the load vector can be written as:

(X.5) $$L = (I - R_1)\, S + (I - R_2)\, P + (I - R_3)\, D$$

The contributions from the different sub-basins to the output from an arbitrary sub-basin $B_k$ are given by:

(X.6) $$[(I - R_1)\, S + (I - R_2)\, P + (I - R_3)\, D] * [\tilde{H}_k\, (I - R)]^n\, V_k$$

* = element-wise multiplication
n = the longest branch in the hierarchy of sub-basins

The total contribution from leaching processes in soil to the output from $B_k$ is given by

(X.7) $$S_T (1 - R_1) [\tilde{H}_k (I - R)]^n V_k$$

The contributions from other sources are computed analogously.

*Parameterisation of source apportionment models*

*Retention*

Irrespective of the exact retention mechanism, it is assumed that the retention in the different sub-basins is of the form:

(X.8) $$R_j = 1 - \frac{1}{1+\lambda x_j} \qquad j = 1, 2, \dots , N$$

$S_j$ is a suitable covariate. In case of retention in lakes, $x_j$ can be denoted as V/Q i.e. the hydraulic residence time of the lake. Since Q is approximately proportional to the drainage area of the lake, the retention is also a function of the lake area to its drainage area. If no lakes are present in the study area, or the factors influencing the retention are unknown, we can use sub-basin area as an explanatory variable.

In equation X.5, different sources were assigned different retention matrices. This is normally not necessary. If partitioning of the study area is carried out in such a way that the outlets of major lakes coincide with outlets of sub-basins, and if the qualitative differences between sources are moderate, it can be assumed that the retention is the same for all sources.

## Losses from soil

The contribution of substances from leaching processes in soil is a function of land use, soil type, topography, climate and other factors. The simplest way of modelling the distribution of this diffuse source in the study area is to classify the entire land area into different categories and assign a so-called export coefficient to each land category. This results in models of the form:

(X.9) $$S = A\,F = \begin{pmatrix} a_{11} & a_{12} & \cdot & a_{1m} \\ a_{21} & a_{22} & \cdot & a_{2m} \\ \cdot & \cdot & \cdot & \cdot \\ a_{N1} & a_{N2} & \cdot & a_{Nm} \end{pmatrix} \begin{pmatrix} f_1 \\ f_2 \\ \cdot \\ f_m \end{pmatrix}$$

where $a_{jk}$ is the area of the k:th land category in the j:th sub-basin and $f_1, f_2, \dots , f_m$ are the export coefficients for the different land categories. Land use normally plays a key role in the classification of land.

When export coefficients $f_1$, $f_2$, ... , $f_m$ in equation X.9 are to be estimated from observed data, they can be treated as unknown parameters

$$f_j = \theta_j \qquad j = 1, 2, \ldots, m$$

or as functions of unknown parameters and covariates, whereas the coefficients $a_{jk}$ are invariably assumed to be known constants.

$$f_j = f(\theta_1, \theta_2, \ldots, \theta_p; x_1, x_2, \ldots, m \qquad j = 1, 2, \ldots, m$$

## Point sources

Information about point sources is normally more accurate than that on diffuse sources. Therefore point emissions can often be treated as constants. If a point source of unknown magnitude is located in a sub-basin it may be necessary to introduce an unknown parameter.

*Choice of dependent variable and method of parameter estimation*

The final model relating sources to observed riverine loads has the general form:

(X.10) $$E = [(I - R)^{-1} - H^T]^{-1} (GAF + P + D) + \varepsilon$$

$\varepsilon$ = vector of independent $N(0;\sigma)$ error terms
I,A,H = known matrices
R,G,F,P = known matrices or functions of covariates and unknown parameters

Similarly, the difference $D_{out\text{-}in}$ between the output and input of the different sub-basins can be written

(X.11) $$D_{out\text{-}in} = (I - H^T)E = (I - H^T) [(I - R)^{-1} - H^T]^{-1} (GAF + P + D) + \varepsilon$$

In both cases, the unknown parameters can be estimated using Stat-Graphics or other non-linear regression programs that permit matrices in function expressions.

**APPENDIX 5.2.**
**Origin of the water-quality data used for the input—output approach**

| Basin | Year | No. samp. $NO_3$ | No. samp. $NH_4$ | No. samp. N-org | Ref $NH_4$ | Ref $NO_3$ | Ref $N_{-org}$ | Dis-charge ($m^3 \cdot s^{-1}$) | Load $NO_3$ ($kg \cdot s^{-1}$) | Load $NH_4$ ($kg \cdot s^{-1}$) | Load $N_{-org}$ ($kg \cdot s^{-1}$) | Load $N_{-tot}$ ($kg \cdot s^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Dipoldsau | 1990 | | | | 3 | 3 | 2 | 188 | 0.11 | | | 0.18 |
| Dipoldsau | 1991 | | | | 3 | 3 | 2 | 199 | 0.12 | | | 0.22 |
| Dipoldsau | 1992 | | | | 3 | 3 | 2 | 227 | 0.14 | | | 0.25 |
| Dipoldsau | 1993 | | | | 3 | 3 | 2 | 240 | 0.13 | | | 0.20 |
| Dipoldsau | 1994 | | | | 3 | 3 | 2 | 254 | 0.12 | | | 0.19 |
| Oeningen | 1990 | | | | 4 | 4 | 4 | 327 | 0.26 | 0.036 | 0.069 | 0.37 |
| Oeningen | 1991 | | | | 4 | 4 | 4 | 304 | 0.24 | 0.036 | 0.064 | 0.34 |
| Oeningen | 1992 | 21 | 21 | 11 | 1 | 1 | 1 | 360 | 0.29 | 0.036 | 0.084 | 0.41 |
| Oeningen | 1993 | 25 | 25 | | 1 | 1 | 2 | 360 | 0.30 | 0.036 | 0.076 | 0.41 |
| Oeningen | 1994 | | | | 4 | 4 | 4 | 388 | 0.32 | 0.036 | 0.082 | 0.44 |
| Brugg (Aare) | 1990 | | | | 3 | 3 | 2 | 312 | 0.62 | | | 0.84 |
| Brugg (Aare) | 1991 | | | | 3 | 3 | 2 | 263 | 0.53 | | | 0.70 |
| Brugg (Aare) | 1992 | | | | 3 | 3 | 2 | 321 | 0.63 | | | 0.84 |
| Brugg (Aare) | 1993 | | | | 3 | 3 | 2 | 295 | 0.57 | | | 0.72 |
| Brugg (Aare) | 1994 | | | | 3 | 3 | 2 | 352 | 0.64 | | | 0.86 |
| Village-Neuff | 1990 | | | | 3 | 3 | 2 | 952 | 1.69 | | | 2.29 |
| Village-Neuff | 1991 | | | | 3 | 3 | 2 | 885 | 1.51 | | | 2.10 |
| Village-Neuff | 1992 | | | | 3 | 3 | 2 | 1053 | 1.90 | | | 2.55 |
| Village-Neuff | 1993 | | | | 3 | 3 | 2 | 1053 | 1.77 | | | 2.46 |
| Village-Neuff | 1994 | | | | 3 | 3 | 2 | 1129 | 1.80 | | | 2.45 |
| Seltz | 1990 | 25 | 25 | | 1 | 1 | 1 | 1130 | 1.94 | 0.138 | | 2.64 |
| Seltz | 1991 | 24 | 24 | | 1 | 1 | 1 | 1037 | 1.80 | 0.124 | | 2.50 |
| Seltz | 1992 | 26 | 26 | | 1 | 1 | 1 | 1229 | 2.12 | 0.152 | | 2.89 |
| Seltz | 1993 | 25 | 25 | | 1 | 1 | 1 | 1138 | 1.84 | 0.125 | | 2.58 |
| Seltz | 1994 | 25 | 26 | | 1 | 1 | 1 | 1345 | 2.24 | 0.135 | | 3.01 |
| Mannheim | 1990 | 48 | 48 | | 1 | 1 | 2 | 118 | 0.72 | 0.031 | 0.018 | 0.77 |
| Mannheim | 1991 | 50 | 50 | | 1 | 1 | 2 | 100 | 0.65 | 0.024 | 0.015 | 0.69 |
| Mannheim | 1992 | 52 | 52 | 10 | 1 | 1 | 1 | 162 | 1.03 | 0.032 | 0.022 | 1.08 |
| Mannheim | 1993 | 26 | 26 | | 1 | 1 | 2 | 119 | 0.75 | 0.021 | 0.018 | 0.79 |
| Mannheim | 1994 | 26 | 26 | | 1 | 1 | 2 | 160 | 0.77 | 0.024 | 0.025 | 0.82 |
| Schwürbitz | 1990 | 27 | 27 | | 1 | 1 | 2 | 23 | 0.10 | 0.008 | 0.011 | 0.12 |
| Schwürbitz | 1991 | 20 | 20 | | 1 | 1 | 2 | 15 | 0.07 | 0.011 | 0.007 | 0.08 |
| Schwürbitz | 1992 | 26 | 26 | | 1 | 1 | 2 | 26 | 0.10 | 0.009 | 0.013 | 0.12 |
| Schwürbitz | 1993 | 26 | 26 | | 1 | 1 | 2 | 23 | 0.12 | 0.006 | 0.011 | 0.13 |
| Schwürbitz | 1994 | 26 | 26 | | 1 | 1 | 2 | 34 | 0.14 | 0.006 | 0.017 | 0.17 |
| Rothwind | 1990 | 25 | 25 | | 1 | 1 | 2 | 10 | 0.05 | 0.007 | 0.005 | 0.07 |
| Rothwind | 1991 | 26 | 26 | | 1 | 1 | 2 | 8 | 0.04 | 0.008 | 0.004 | 0.05 |
| Rothwind | 1992 | 26 | 26 | | 1 | 1 | 2 | 13 | 0.07 | 0.007 | 0.006 | 0.08 |
| Rothwind | 1993 | 24 | 24 | | 1 | 1 | 2 | 9 | 0.05 | 0.004 | 0.005 | 0.06 |
| Rothwind | 1994 | 22 | 22 | | 1 | 1 | 2 | 21 | 0.10 | 0.004 | 0.011 | 0.12 |
| Marktzeuln | 1990 | 26 | 26 | | 1 | 1 | 2 | 11 | 0.04 | 0.003 | 0.005 | 0.05 |
| Marktzeuln | 1991 | 24 | 24 | | 1 | 1 | 2 | 8 | 0.02 | 0.003 | 0.004 | 0.03 |
| Marktzeuln | 1992 | 26 | 26 | | 1 | 1 | 2 | 13 | 0.04 | 0.003 | 0.006 | 0.05 |
| Marktzeuln | 1993 | 25 | 25 | | 1 | 1 | 2 | 11 | 0.04 | 0.002 | 0.005 | 0.05 |
| Marktzeuln | 1994 | 26 | 26 | | 1 | 1 | 2 | 15 | 0.05 | 0.003 | 0.008 | 0.06 |

# APPENDIX

| Basin | Year | No. samp. NO3 | No. samp. NH4 | No. samp. N-org | Ref NH4 | Ref NO3 | Ref N-org | Discharge ($m^3 \cdot s^{-1}$) | Load $NO_3$ ($kg \cdot s^{-1}$) | Load $NH_4$ ($kg \cdot s^{-1}$) | Load $N_{-org}$ ($kg \cdot s^{-1}$) | Load $N_{-tot}$ ($kg \cdot s^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Pettstadt | 1990 | 26 | 26 | | 1 | 1 | 2 | 40 | 0.27 | 0.017 | 0.020 | 0.31 |
| Pettstadt | 1991 | 26 | 26 | | 1 | 1 | 2 | 34 | 0.25 | 0.015 | 0.017 | 0.28 |
| Pettstadt | 1992 | 26 | 26 | | 1 | 1 | 2 | 42 | 0.27 | 0.012 | 0.021 | 0.30 |
| Pettstadt | 1993 | 26 | 26 | | 1 | 1 | 2 | 37 | 0.26 | 0.008 | 0.019 | 0.29 |
| Pettstadt | 1994 | 26 | 26 | | 1 | 1 | 2 | 54 | 0.33 | 0.011 | 0.027 | 0.37 |
| Gemünden | 1990 | 26 | 26 | | 1 | 1 | 2 | 15 | 0.08 | 0.002 | 0.007 | 0.08 |
| Gemünden | 1991 | 25 | 25 | | 1 | 1 | 2 | 10 | 0.05 | 0.001 | 0.005 | 0.06 |
| Gemünden | 1992 | 26 | 26 | | 1 | 1 | 2 | 14 | 0.08 | 0.002 | 0.007 | 0.09 |
| Gemünden | 1993 | 26 | 26 | | 1 | 1 | 2 | 16 | 0.08 | 0.002 | 0.008 | 0.09 |
| Gemünden | 1994 | 26 | 26 | | 1 | 1 | 2 | 19 | 0.11 | 0.003 | 0.010 | 0.12 |
| Waldhausen | 1990 | 26 | 26 | | 1 | 1 | 2 | 5 | 0.04 | 0.000 | 0.003 | 0.05 |
| Waldhausen | 1991 | 25 | 25 | | 1 | 1 | 2 | 4 | 0.04 | 0.000 | 0.002 | 0.04 |
| Waldhausen | 1992 | | | | 4 | 4 | 4 | 6 | 0.05 | 0.000 | 0.003 | 0.06 |
| Waldhausen | 1993 | | | | 4 | 4 | 4 | 6 | 0.05 | 0.000 | 0.003 | 0.05 |
| Waldhausen | 1994 | | | | 4 | 4 | 4 | 9 | 0.07 | 0.000 | 0.004 | 0.07 |
| Kahl | 1990 | 36 | 36 | | 1 | 1 | 2 | 123 | 0.68 | 0.024 | 0.056 | 0.77 |
| Kahl | 1991 | 26 | 26 | | 1 | 1 | 2 | 102 | 0.59 | 0.021 | 0.046 | 0.65 |
| Kahl | 1992 | 26 | 26 | 17 | 1 | 1 | 1 | 148 | 0.86 | 0.020 | 0.058 | 0.94 |
| Kahl | 1993 | 26 | 26 | 23 | 1 | 1 | 1 | 142 | 0.78 | 0.023 | 0.057 | 0.86 |
| Kahl | 1994 | 24 | 24 | 23 | 1 | 1 | 1 | 202 | 1.16 | 0.025 | 0.057 | 1.24 |
| Bischofsheim | 1990 | 24 | 24 | | 1 | 1 | 2 | 161 | 1.05 | 0.075 | 0.061 | 1.18 |
| Bischofsheim | 1991 | 26 | 26 | | 1 | 1 | 2 | 144 | 0.99 | 0.061 | 0.061 | 1.11 |
| Bischofsheim | 1992 | 26 | 26 | 22 | 1 | 1 | 1 | 178 | 1.17 | 0.039 | 0.061 | 1.28 |
| Bischofsheim | 1993 | 26 | 26 | 24 | 1 | 1 | 1 | 169 | 1.20 | 0.030 | 0.062 | 1.29 |
| Bischofsheim | 1994 | | | | 4 | 4 | 4 | 255 | 1.82 | 0.030 | 0.062 | 1.91 |
| Mainz | 1990 | 26 | 26 | | 1 | 1 | 2 | 1491 | 4.64 | 0.371 | 1.012 | 6.02 |
| Mainz | 1991 | 26 | 26 | | 1 | 1 | 2 | 1308 | 3.73 | 0.285 | 0.888 | 4.90 |
| Mainz | 1992 | 26 | 26 | 25 | 1 | 1 | 1 | 1499 | 3.93 | 0.319 | 1.024 | 5.27 |
| Mainz | 1993 | 25 | 25 | 25 | 1 | 1 | 1 | 1470 | 3.52 | 0.274 | 0.935 | 4.73 |
| Mainz | 1994 | 26 | 26 | 25 | 1 | 1 | 1 | 1789 | 5.04 | 0.248 | 1.246 | 6.53 |
| Liverdun | 1990 | 12 | 12 | 12 | 1 | 1 | 1 | 45 | 0.10 | 0.006 | 0.031 | 0.14 |
| Liverdun | 1991 | 12 | 12 | 12 | 1 | 1 | 1 | 37 | 0.08 | 0.005 | 0.028 | 0.11 |
| Liverdun | 1992 | 12 | 12 | 12 | 1 | 1 | 1 | 64 | 0.19 | 0.005 | 0.046 | 0.24 |
| Liverdun | 1993 | | | | 4 | 4 | 4 | 44 | 0.13 | 0.005 | 0.032 | 0.17 |
| Liverdun | 1994 | | | | 4 | 4 | 4 | 70 | 0.20 | 0.005 | 0.050 | 0.26 |
| Millery | 1990 | 12 | 12 | 11 | 1 | 1 | 1 | 71 | 0.17 | 0.030 | 0.066 | 0.27 |
| Millery | 1991 | 12 | 12 | 12 | 1 | 1 | 1 | 84 | 0.20 | 0.033 | 0.065 | 0.30 |
| Millery | 1992 | 22 | 22 | 22 | 1 | 1 | 1 | 119 | 0.33 | 0.024 | 0.117 | 0.47 |
| Millery | 1993 | | | | 4 | 4 | 4 | 83 | 0.23 | 0.024 | 0.081 | 0.34 |
| Millery | 1994 | | | | 4 | 4 | 4 | 131 | 0.37 | 0.024 | 0.128 | 0.52 |
| Palzem | 1990 | 27 | 27 | | 1 | 1 | 2 | 118 | 0.35 | 0.037 | 0.089 | 0.48 |
| Palzem | 1991 | 27 | 27 | | 1 | 1 | 2 | 117 | 0.38 | 0.031 | 0.088 | 0.50 |
| Palzem | 1992 | 26 | 26 | 24 | 1 | 1 | 1 | 134 | 0.45 | 0.036 | 0.103 | 0.59 |
| Palzem | 1993 | 24 | 24 | 24 | 1 | 1 | 1 | 111 | 0.40 | 0.028 | 0.221 | 0.65 |
| Palzem | 1994 | 26 | 26 | 26 | 1 | 1 | 1 | 177 | 0.59 | 0.029 | 0.148 | 0.77 |

# APPENDIX

| Basin | Year | No. samp. $NO_3$ | No. samp. $NH_4$ | No. samp. N-org | Ref $NH_4$ | Ref $NO_3$ | Ref $N_{-org}$ | Dis-charge ($m^3 \cdot s^{-1}$) | Load $NO_3$ ($kg \cdot s^{-1}$) | Load $NH_4$ ($kg \cdot s^{-1}$) | Load $N_{-org}$ ($kg \cdot s^{-1}$) | Load $N_{-tot}$ ($kg \cdot s^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Wasserbillig | 1990 | 12 | 12 | | 1 | 1 | 1 | 34 | 0.20 | 0.007 | 0.024 | 0.24 |
| Wasserbillig | 1991 | 12 | 12 | | 1 | 1 | 1 | 25 | 0.13 | 0.012 | 0.019 | 0.16 |
| Wasserbillig | 1992 | 12 | 12 | | 1 | 1 | 1 | 49 | 0.30 | 0.007 | 0.035 | 0.34 |
| Wasserbillig | 1993 | | | | 4 | 4 | 4 | 33 | 0.20 | 0.007 | 0.023 | 0.23 |
| Wasserbillig | 1994 | | | | 4 | 4 | 4 | 52 | 0.32 | 0.007 | 0.037 | 0.36 |
| Saarbrücken | 1990 | 22 | 22 | | 1 | 1 | 2 | 29 | 0.10 | 0.019 | 0.136 | 0.25 |
| Saarbrücken | 1991 | 25 | 25 | | 1 | 1 | 2 | 24 | 0.09 | 0.020 | 0.066 | 0.18 |
| Saarbrücken | 1992 | 26 | 26 | 26 | 1 | 1 | 1 | 36 | 0.13 | 0.019 | 0.019 | 0.17 |
| Saarbrücken | 1993 | 26 | 26 | 26 | 1 | 1 | 1 | 50 | 0.15 | 0.018 | 0.034 | 0.20 |
| Saarbrücken | 1994 | 26 | 26 | 26 | 1 | 1 | 1 | 54 | 0.17 | 0.031 | 0.022 | 0.22 |
| Kanzem | 1990 | 22 | 22 | | 1 | 1 | 2 | 66 | 0.25 | 0.052 | 0.060 | 0.36 |
| Kanzem | 1991 | 26 | 26 | | 1 | 1 | 2 | 52 | 0.21 | 0.044 | 0.047 | 0.30 |
| Kanzem | 1992 | 26 | 26 | 25 | 1 | 1 | 1 | 66 | 0.28 | 0.043 | 0.060 | 0.38 |
| Kanzem | 1993 | 24 | 24 | 24 | 1 | 1 | 1 | 63 | 0.26 | 0.037 | 0.156 | 0.45 |
| Kanzem | 1994 | 26 | 26 | 26 | 1 | 1 | 1 | 84 | 0.31 | 0.035 | 0.092 | 0.44 |
| Koblenz-Moselle | 1990 | 51 | 51 | | 1 | 1 | 2 | 274 | 1.19 | 0.062 | 0.237 | 1.49 |
| Koblenz-Moselle | 1991 | 52 | 52 | 26 | 1 | 1 | 1 | 247 | 1.04 | 0.052 | 0.202 | 1.29 |
| Koblenz-Moselle | 1992 | 52 | 52 | 25 | 1 | 1 | 1 | 277 | 1.21 | 0.052 | 0.255 | 1.52 |
| Koblenz-Moselle | 1993 | 26 | 26 | 26 | 1 | 1 | 1 | 255 | 1.35 | 0.033 | 0.178 | 1.56 |
| Koblenz-Moselle | 1994 | 26 | 26 | 26 | 1 | 1 | 1 | 391 | 1.86 | 0.062 | 0.263 | 2.19 |
| Koblenz-Rhine | 1990 | 52 | 52 | 26 | 1 | 1 | 1 | 1457 | 5.01 | 0.335 | 1.142 | 6.48 |
| Koblenz-Rhine | 1991 | 52 | 52 | 26 | 1 | 1 | 1 | 1352 | 4.24 | 0.277 | 1.063 | 5.58 |
| Koblenz-Rhine | 1992 | 52 | 52 | 26 | 1 | 1 | 1 | 1631 | 4.70 | 0.264 | 0.959 | 5.92 |
| Koblenz-Rhine | 1993 | 26 | 26 | 26 | 1 | 1 | 1 | 1547 | 4.32 | 0.195 | 0.827 | 5.34 |
| Koblenz-Rhine | 1994 | 26 | 26 | 26 | 1 | 1 | 1 | 1940 | 7.26 | 0.262 | 1.067 | 8.59 |
| Bad-Honnef | 1990 | 26 | 26 | | 1 | 1 | 2 | 1748 | 5.49 | 0.344 | 1.518 | 7.35 |
| Bad-Honnef | 1991 | 26 | 26 | | 1 | 1 | 2 | 1625 | 5.06 | 0.330 | 1.410 | 6.81 |
| Bad-Honnef | 1992 | 26 | 26 | | 1 | 1 | 2 | 1870 | 5.85 | 0.258 | 1.623 | 7.73 |
| Bad-Honnef | 1993 | 25 | 25 | 12 | 1 | 1 | 1 | 1798 | 5.36 | 0.180 | 1.604 | 7.14 |
| Bad-Honnef | 1994 | 26 | 26 | 22 | 1 | 1 | 1 | 2360 | 7.38 | 0.218 | 1.112 | 8.71 |

# APPENDIX

| Basin | Year | No. samp. $NO_3$ | No. samp. $NH_4$ | No. samp. N-org | Ref $NH_4$ | Ref $NO_3$ | Ref $N_{-org}$ | Dis-charge ($m^3 \cdot s^{-1}$) | Load $NO_3$ ($kg \cdot s^{-1}$) | Load $NH_4$ ($kg \cdot s^{-1}$) | Load $N_{-org}$ ($kg \cdot s^{-1}$) | Load $N_{-tot}$ ($kg \cdot s^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Menden (Sieg) | 1990 | 13 | 13 | | 1 | 1 | 2 | 25 | 0.10 | 0.007 | 0.015 | 0.13 |
| Menden (Sieg) | 1991 | 13 | 13 | | 1 | 1 | 2 | 36 | 0.15 | 0.007 | 0.022 | 0.18 |
| Menden (Sieg) | 1992 | 13 | 13 | | 1 | 1 | 2 | 40 | 0.15 | 0.010 | 0.024 | 0.19 |
| Menden (Sieg) | 1993 | 13 | 13 | 13 | 1 | 1 | 1 | 49 | 0.17 | 0.007 | 0.030 | 0.20 |
| Menden (Sieg) | 1994 | 13 | 13 | 11 | 1 | 1 | 1 | 71 | 0.23 | 0.006 | 0.038 | 0.27 |
| Opladen (Wupper) | 1990 | 13 | 13 | | 1 | 1 | 2 | 10 | 0.09 | 0.006 | 0.011 | 0.10 |
| Opladen (Wupper) | 1991 | 13 | 13 | | 1 | 1 | 2 | 13 | 0.11 | 0.013 | 0.015 | 0.14 |
| Opladen (Wupper) | 1992 | 13 | 13 | | 1 | 1 | 2 | 15 | 0.11 | 0.013 | 0.017 | 0.13 |
| Opladen (Wupper) | 1993 | 13 | 13 | 13 | 1 | 1 | 1 | 17 | 0.12 | 0.007 | 0.019 | 0.15 |
| Opladen (Wupper) | 1994 | 12 | 12 | 8 | 1 | 1 | 1 | 22 | 0.15 | 0.011 | 0.014 | 0.18 |
| Eppinghoven (Erft) | 1990 | 13 | 13 | | 1 | 1 | 2 | 10 | 0.03 | 0.005 | 0.013 | 0.04 |
| Eppinghoven (Erft) | 1991 | 13 | 13 | | 1 | 1 | 2 | 11 | 0.03 | 0.006 | 0.013 | 0.05 |
| Eppinghoven (Erft) | 1992 | 13 | 13 | | 1 | 1 | 2 | 10 | 0.03 | 0.003 | 0.013 | 0.05 |
| Eppinghoven (Erft) | 1993 | 13 | 13 | 11 | 1 | 1 | 1 | 11 | 0.04 | 0.003 | 0.013 | 0.06 |
| Eppinghoven (Erft) | 1994 | 13 | 13 | 10 | 1 | 1 | 1 | 11 | 0.04 | 0.005 | 0.004 | 0.05 |
| Hattingen (Ruhr) | 1990 | 13 | 13 | | 1 | 1 | 2 | 54 | 0.23 | 0.026 | 0.073 | 0.33 |
| Hattingen (Ruhr) | 1991 | 13 | 13 | | 1 | 1 | 2 | 56 | 0.28 | 0.059 | 0.075 | 0.41 |
| Hattingen (Ruhr) | 1992 | 13 | 13 | | 1 | 1 | 2 | 72 | 0.32 | 0.064 | 0.096 | 0.48 |
| Hattingen (Ruhr) | 1993 | 13 | 13 | 13 | 1 | 1 | 1 | 82 | 0.39 | 0.043 | 0.110 | 0.55 |
| Hattingen (Ruhr) | 1994 | 13 | 13 | 12 | 1 | 1 | 1 | 100 | 0.44 | 0.061 | 0.037 | 0.54 |

# APPENDIX

| Basin | Year | No. samp. $NO_3$ | No. samp. $NH_4$ | No. samp. N-org | Ref $NH_4$ | Ref $NO_3$ | Ref $N_{-org}$ | Dis-charge ($m^3 \cdot s^{-1}$) | Load $NO_3$ ($kg \cdot s^{-1}$) | Load $NH_4$ ($kg \cdot s^{-1}$) | Load $N_{-org}$ ($kg \cdot s^{-1}$) | Load $N_{-tot}$ ($kg \cdot s^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Mündung (Emscher) | 1990 | 13 | 13 | | 1 | 1 | 2 | 15 | 0.01 | 0.508 | 0.160 | 0.67 |
| Mündung (Emscher) | 1991 | 13 | 13 | | 1 | 1 | 2 | 15 | 0.00 | 0.471 | 0.160 | 0.64 |
| Mündung (Emscher) | 1992 | 13 | 13 | 1 | 1 | 1 | | 15 | 0.00 | 0.456 | 0.160 | 0.62 |
| Mündung (Emscher) | 1993 | 5 | 5 | 5 | 1 | 1 | 1 | 21 | 0.01 | 0.337 | 0.201 | 0.54 |
| Mündung (Emscher) | 1994 | 2 | 2 | 1 | 1 | 1 | 1 | 26 | 0.06 | 0.263 | 0.072 | 0.40 |
| Schermbeck (Lippe) | 1990 | 13 | 13 | | 1 | 1 | 2 | 29 | 0.23 | 0.024 | 0.085 | 0.34 |
| Schermbeck (Lippe) | 1991 | 13 | 13 | | 1 | 1 | 2 | 29 | 0.24 | 0.026 | 0.085 | 0.35 |
| Schermbeck (Lippe) | 1992 | 10 | 10 | | 1 | 1 | 2 | 28 | 0.21 | 0.015 | 0.085 | 0.31 |
| Schermbeck (Lippe) | 1993 | 12 | 12 | 12 | 1 | 1 | 1 | 41 | 0.31 | 0.025 | 0.085 | 0.42 |
| Schermbeck (Lippe) | 1994 | 13 | 13 | 12 | 1 | 1 | 1 | 63 | 0.47 | 0.028 | 0.052 | 0.55 |
| Lobith | 1990 | 25 | 25 | | 1 | 1 | 2 | 2005 | 7.65 | 0.569 | 1.815 | 10.03 |
| Lobith | 1991 | 28 | 28 | 28 | 1 | 1 | 1 | 1724 | 6.52 | 0.562 | 1.551 | 8.64 |
| Lobith | 1992 | 26 | 26 | 26 | 1 | 1 | 1 | 2034 | 7.66 | 0.490 | 2.282 | 10.43 |
| Lobith | 1993 | 25 | 25 | 25 | 1 | 1 | 1 | 1960 | 6.64 | 0.378 | 2.841 | 9.86 |
| Lobith | 1994 | 26 | 26 | 16 | 1 | 1 | 1 | 2585 | 8.92 | 0.456 | 2.206 | 11.58 |

1 = point samples
2 = calculated
3 = blended samples
4 = interpolated

## APPENDIX 5.3.

**Point source nitrogen emission period 1990-1995 as stated by the IKSR (Internationale Kommission zum schutze des Rheins)**

**Population-related immissions**

| Country | Population | Emission kg·y$^{-1}$ | Emission per capita kg·inh.$^{-1}$·y$^{-1}$ |
|---|---|---|---|
| Germany | 32500000 | 117312569 | 3.61 |
| France | 3700000 | 28200000 | 7.62 |
| Switzerland | 3000000 | 18500000 | 6.17 |

**Main industries (IRC reports)**

| Location | Emission kg·y$^{-1}$ |
|---|---|
| Basf AG, Ludwigshafen | 11831600 |
| Koln-Stammheim | 2100000 |
| Bayer AG, Leverkusen | 4200000 |
| Bayer AG, Dormagen | 2600000 |

**APPENDIX 5.4.**
**Assignment of sub-catchments to the four different categories of basins**

| Basin | Cate-gory | Pop. density | Spec. runoff | Point emis. | Load $N_{\_tot}$ | Forest | Grass | Arable | Other |
|---|---|---|---|---|---|---|---|---|---|
| | | $inh.\cdot km^{-2}$ | $l\cdot s^{-1}\cdot km^{-2}$ | $t\cdot km^{-2}\cdot y^{-1}$ | $t\cdot km^{-2}\cdot y^{-1}$ | % | % | % | % |
| Palzem | L | 1.3 | 7.6 | 0.7 | 1.5 | 32 | 21 | 31 | 16 |
| Rothwind | L | 1.5 | 9.7 | 0.5 | 1.9 | 38 | 17 | 29 | 16 |
| Marktzeuln | L | 1.1 | 9.8 | 0.4 | 1.3 | 48 | 14 | 24 | 15 |
| Gemünden | L | 0.9 | 6.5 | 0.3 | 1.2 | 40 | 9 | 29 | 22 |
| Waldhausen | L | 1.1 | 3.7 | 0.3 | 1.0 | 28 | 9 | 46 | 18 |
| Dipoldsau | L | 0.7 | 36.4 | 0.2 | 1.1 | 27 | 31 | 1 | 40 |
| Millery | L | 1.0 | 13.6 | 0.5 | 1.9 | 41 | 24 | 22 | 13 |
| Wasserbillig | L | 1.1 | 8.4 | 0.4 | 1.8 | 37 | 28 | 18 | 17 |
| Koblenz-Mosel | L | 1.3 | 10.0 | 0.4 | 2.2 | 44 | 13 | 19 | 24 |
| Schwürbitz | L | 1.3 | 3.3 | 0.4 | 0.7 | 37 | 13 | 33 | 17 |
| Liverdun | L | 1.0 | 16.8 | 0.5 | 1.9 | 41 | 25 | 21 | 13 |
| Kahl | ML | 1.7 | 6.4 | 0.5 | 1.1 | 38 | 7 | 35 | 20 |
| Kanzem | ML | 3.0 | 6.2 | 1.2 | 1.3 | 33 | 16 | 22 | 29 |
| Saarbrücken | ML | 2.1 | 10.6 | 1.0 | 1.8 | 35 | 17 | 25 | 23 |
| Seltz | ML | 2.1 | 12.1 | 0.9 | 0.8 | 42 | 12 | 23 | 24 |
| Mannheim | ML | 3.6 | 9.2 | 1.1 | 1.8 | 36 | 15 | 25 | 24 |
| Koblenz-Rhine | ML | 2.2 | 6.2 | 0.7 | 2.4 | 40 | 10 | 23 | 27 |
| Mainz | ML | 4.4 | 3.0 | 3.0 | 2.4 | 35 | 5 | 25 | 35 |
| Pettstadt | ML | 2.4 | 5.9 | 0.7 | 1.4 | 36 | 13 | 32 | 19 |
| Oeningen | MH | 2.0 | 32.7 | 0.6 | 1.5 | 27 | 32 | 13 | 28 |
| Brugg (Aare) | MH | 1.7 | 27.3 | 0.4 | 2.2 | 31 | 33 | 14 | 22 |
| Village-Neuff | MH | 2.7 | 25.6 | 0.7 | 2.7 | 34 | 31 | 11 | 24 |
| Schermb. (Lippe) | H | 4.0 | 8.0 | 1.3 | 2.6 | 20 | 11 | 43 | 26 |
| Menden (Sieg) | H | 3.6 | 19.1 | 1.1 | 2.6 | 44 | 19 | 9 | 28 |
| Bischofsheim | H | 5.2 | 8.3 | 1.5 | 3.2 | 37 | 10 | 23 | 29 |
| Münd. (Emscher) | H | 23.3 | 24.6 | 7.8 | 24.3 | 11 | 4 | 15 | 69 |
| Hattingen (Ruhr) | H | 3.6 | 17.0 | 1.2 | 3.4 | 48 | 17 | 13 | 22 |
| Eppingh. (Erft) | H | 4.1 | 5.1 | 1.3 | 0.7 | 21 | 9 | 38 | 31 |
| Opladen (Wup.) | H | 9.7 | 14.0 | 3.1 | 4.1 | 33 | 22 | 5 | 39 |
| Bad-Honnef | H | 2.0 | 2.6 | 0.7 | -5.9 | 42 | 13 | 16 | 29 |
| Lobith | H | 11.5 | -4.2 | 5.7 | 5.4 | 19 | 11 | 25 | 45 |

**L** = Low population density
**ML** = Moderate population density, moderate specific runoff
**MH** = Moderate population density, high specific runoff
**H** = High specific runoff

**APPENDIX 5.5.**
**Analysis of variance of measured versus predicted unit area load, considering retention**

| Source of Variation | Sum of Squares | DF | Mean Square | F | Sig of F |
|---|---|---|---|---|---|
| Main Effects | 7564.374 | 27 | 280.16 | 4.498 | 0.000 |
| Predict | 25.456 | 1 | 25.46 | 0.409 | 0.524 |
| Locat | 7538.919 | 26 | 289.96 | 4.656 | 0.000 |
| | | | | | |
| 2-Way Interactions | 759.469 | 26 | 29.21 | 0.469 | 0.986 |
| Predict Locat | 759.469 | 26 | 29.21 | 0.469 | 0.986 |
| | | | | | |
| Explained | 16555.610 | 53 | 312.37 | 5.016 | 0.000 |
| | | | | | |
| Residual | 6726.324 | 108 | 62.28 | | |
| | | | | | |
| Total | 23281.930 | 161 | 144.61 | | |

All analysis exclusive of Emscher mündung
Locat = variation between sampling sites
Predict = Predicted versus measured load

**APPENDIX 5.6.**
**Analysis of variance of measured versus predicted unit area load, with and without considering retention**

| Source of Variation | Sum of Squares | DF | Mean Square | F | Sig of F |
|---|---|---|---|---|---|
| Main Effects | 13944.96 | 28 | 498.03 | 7.997 | 0.000 |
| Locat | 13736.75 | 26 | 528.34 | 8.483 | 0.000 |
| Retention | 35.90 | 1 | 35.90 | 0.576 | 0.449 |
| Predict | 172.31 | 1 | 172.31 | 2.767 | 0.098 |
| 2-Way Interactions | 1709.86 | 53 | 32.26 | 0.518 | 0.997 |
| LOCAT RET | 62.93 | 26 | 2.42 | 0.039 | 1.000 |
| LOCAT PREDICT | 1611.04 | 26 | 61.96 | 0.995 | 0.476 |
| RET PREDICT | 35.90 | 1 | 35.90 | 0.576 | 0.449 |
| 3-Way Interactions | 62.93 | 26 | 2.42 | 0.039 | 1.000 |
| LOCAT RET PREDICT | 62.93 | 26 | 2.42 | 0.039 | 1.000 |
| Explained | 32601.81 | 107 | 304.69 | 4.892 | 0.000 |
| Residual | 13452.65 | 216 | 62.28 | | |
| Total | 46054.46 | 323 | 142.58 | | |

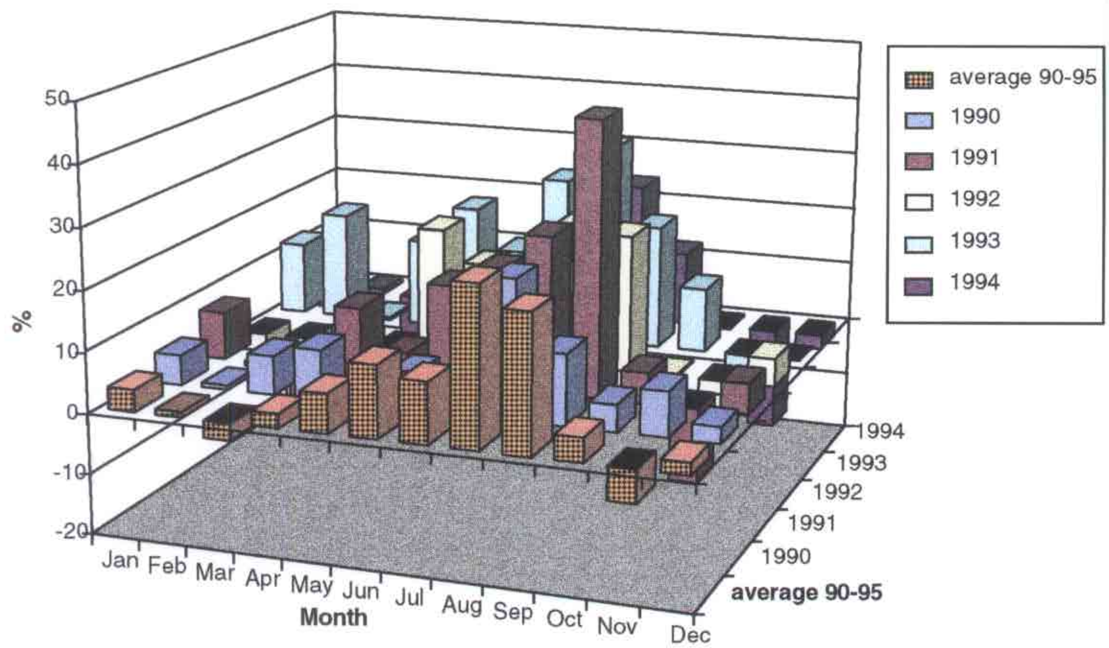
All analysis exclusive of Emscher mündung
Locat = Different sampling sites
Ret = Concideration of retention
Predict = Predicted versus measured load

## APPENDIX 5.7.

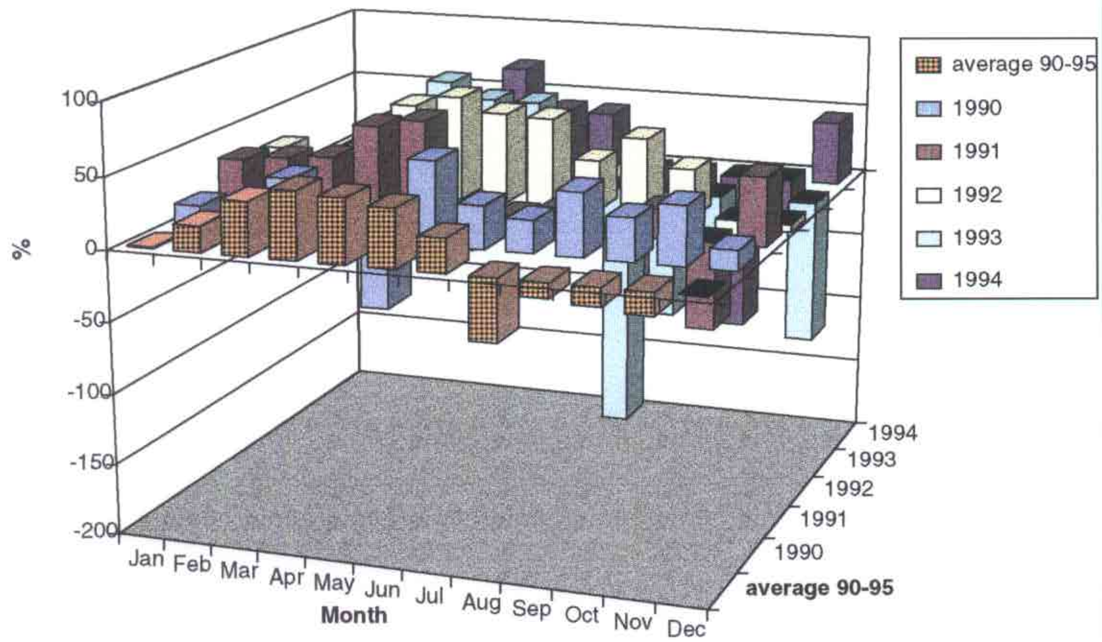
**Percentage of retained nitrogen within the idividual basins and during the transport to the outlet of the entire system at Lobith**

| Basin | Retention within sub-basin % | Retention to outlet % |
|---|---|---|
| Dipoldsau | 1.6 | 16 |
| Oeningen | 0.9 | 15 |
| Brugg (Aare) | 3.3 | 15 |
| Village-Neuff | 4.2 | 12 |
| Mannheim | 4.3 | 12 |
| Rothwind | 0.2 | 15 |
| Marktzeuln | 0.2 | 15 |
| Pettstadt | 1.9 | 15 |
| Gemunden | 0.5 | 15 |
| Waldhausen | 0.3 | 15 |
| Kahl | 2.5 | 13 |
| Bischofsheim | 1.1 | 12 |
| Mainz | 6.6 | 5 |
| Liverdun | 0.7 | 8 |
| Millery | 0.8 | 8 |
| Palzem | 1.1 | 7 |
| Wasserbillig | 1.1 | 7 |
| Saarbrucken | 0.9 | 8 |
| Kanzem | 1.1 | 7 |
| Koblenz-Mosel | 1.3 | 5 |
| Bad Honnef | 4.3 | 1 |
| Menden (Sieg) | 0.5 | 1 |
| Opladen (Wupper) | 0.2 | 1 |
| Eppinghoven (Erft) | 0.5 | 1 |
| Hattingen (Ruhr) | 1.0 | 1 |
| Mundung (Emscher) | 0.1 | 1 |
| Schermbeck (Lippe) | 1.2 | 1 |
| Lobith | 1.1 | 0 |

**APPENDIX 6.1.**
**$NO_3$ retention within the mainstream of the Main upstream of Kahl**



## APPENDIX 6.2.
**$NH_4$ Retention within the mainstream of the Main upstream of Kahl**



**APPENDIX 6.3.**
**Annual average retention within the mainstream of the Main upstream of Kahl**

| Period | Retention. $NO_3$ kg·month$^{-1}$ | Ret. $NH_4$ kg·month$^{-1}$ | Ret. DIN kg·month$^{-1}$ | Ret. $NO_3$ % | Ret. $NH_4$ % | Ret. DIN % |
|---|---|---|---|---|---|---|
| 1990 | 111557 | 23375 | 134932 | 6 | 22 | 7 |
| 1991 | 112887 | 30926 | 143813 | 10 | 21 | 11 |
| 1992 | 112887 | 30926 | 143813 | 10 | 21 | 11 |
| 1993 | 32297 | 26136 | 58433 | 4 | 37 | 5 |
| 1994 | 221630 | 11816 | 209814 | 14 | 17 | 14 |
| Average 1990-1994 | 77646 | 14442 | 92087 | 7 | 11 | 7 |