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POINT AND DIFFUSE LOADS OF SELECTED POLLUTANTS IN THE RIVER RHINE AND ITS MAIN TRIBUTARIES

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Foreword

The research described in this report was conducted for the study "Sources of Chemical Pollution in the Rhine Basin." The study is a collaborative effort between IIASA and the Netherlands National Institute of Public Health and Environmental Protection (RIVM). The goal of the study is to determine, by mass balance analysis, the inputs and outputs of selected chemicals to the Rhine Basin over the time period from 1950 to 2010. Particular attention is given to "cradle-to-grave" analysis in which the pollutants are traced from their pathways through the industrial economy and into the environment. For the historical analysis, it is necessary to estimate emissions from various industrial sectors (*point sources*) and runoff from urban, agricultural, and forested lands (*diffuse sources*). The analysis is hindered, however, by the scarcity of historical data on sources of emission. On the other hand, the Rhine River has been intensively monitored for heavy metals since the early 1970s, and for nutrients and other hydrological parameters since the 1950s. These data provide a basis for making reasonable estimates of inputs to the river in previous decades. Prior to the analysis presented herein, no comprehensive investigation of the long-term time series of chemical loads to the river had been undertaken. This report not only quantifies the total loads of the various chemicals over time. It also subdivides the loads into the *point source* and *diffuse* fractions, applying a new methodology developed by the author of this report. With the estimates provided here, it is possible to calibrate the emission factors assumed for industrial and diffuse sources. The paper thus makes an invaluable contribution to a major goal of the study.

William Stigliani
Leader
Rhine Basin Study

1 Introduction

The analysis in this report was conducted within the framework of the study of the "Sources of Pollution of Selected Chemicals in the Basins of the Rhine, Meuse, and Scheldt Rivers." The study is part of a collaborative agreement between the National Institute of Public Health and Environmental Protection (RIVM) of the Netherlands and the International Institute for Applied Systems Analysis (IIASA).

One aim of the IIASA/RIVM study is to determine the linkages between sources of selected pollutants in the basins and the pathways by which they are transported to the river. Such pathways may include runoff from land to river of pollutants from non-point (diffuse) sources, as well as direct aqueous discharges to the river from point sources. Another aim of the study is to determine how the sources of pollution may have changed over time.

One way to conduct the analysis is to employ a runoff model, by which the transport of selected chemicals to the river is calculated as a function of the concentration of the deposited chemicals 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 chemical mobilized from the land during runoff. In addition, data are required on the outflow of sewage treatment plants and direct industrial disposal of waterborne wastes. The model is developed in several consecutive steps. It consists of different *constants* and variables, each of which is associated with a substantial error. The advantage of such a model is the possibility of high spatial, temporal, and structural resolutions, which would be necessary for generating scenarios as part of a decision support system.

The paper describes an alternative method for estimating the amount and fractions of pollutant loads from point and non-point sources. The method presented relies on the analysis of concentration–discharge and load–discharge relationships respectively, using the extensive monitoring data on the Rhine River and its tributaries given in water quality monitoring reports by the International Commission for Protection of the Rhine (ICPR) and the national Deutsche Kommission zum Schutz des Rheins vor Verunreinigung (DKSR). The results are suitable for calibrating the runoff/chemical mobilization model, because they are obtained independently of the above-mentioned method. This method is relatively simple to apply. The quality of the results depends mainly on the scattering of the concentration–discharge/load–discharge relationship, and on the detection limits for some pollutants, e.g., cadmium. The spatial resolution depends on the density of monitoring stations within the catchment area, and the temporal resolution depends on the frequency of single measurements and the scattering of the relationship.

This report gives a detailed description of the method used and a summarized overview of the results regarding the estimation of point and non-point net loads of zinc, lead, cadmium, phosphorus, and nitrogen for different monitoring stations of the catchment area of the river Rhine and its main tributaries.

2 Database

The database consists of more than 31,000 concentration and discharge values. The sources of data were the annual reports of the ICPR and the DKSR. Data were analyzed from the following monitoring stations at the rivers Rhine, Neckar, Main, and Mosel:

River	Rhine	Mosel	Main	Neckar
Station	Rekingen Village-Neuf Seltz Koblenz Bimmen/Lobith (all ICPR)	Koblenz (ICPR)	Kostheim (DKSR)	Mannheim (DKSR)

Investigated pollutants	Dissolved inorganic nitrogen (DIN) Total phosphorus (TP) Lead (Pb) Zinc (Zn) Cadmium (Cd)
Investigated time periods	1953–1987: NH_4, NO_3, and DIN at the Lobith station 1973–1987: All other substances

A map of the entire catchment area of the Rhine River and the locations of monitoring stations is given in *Figure 1*.

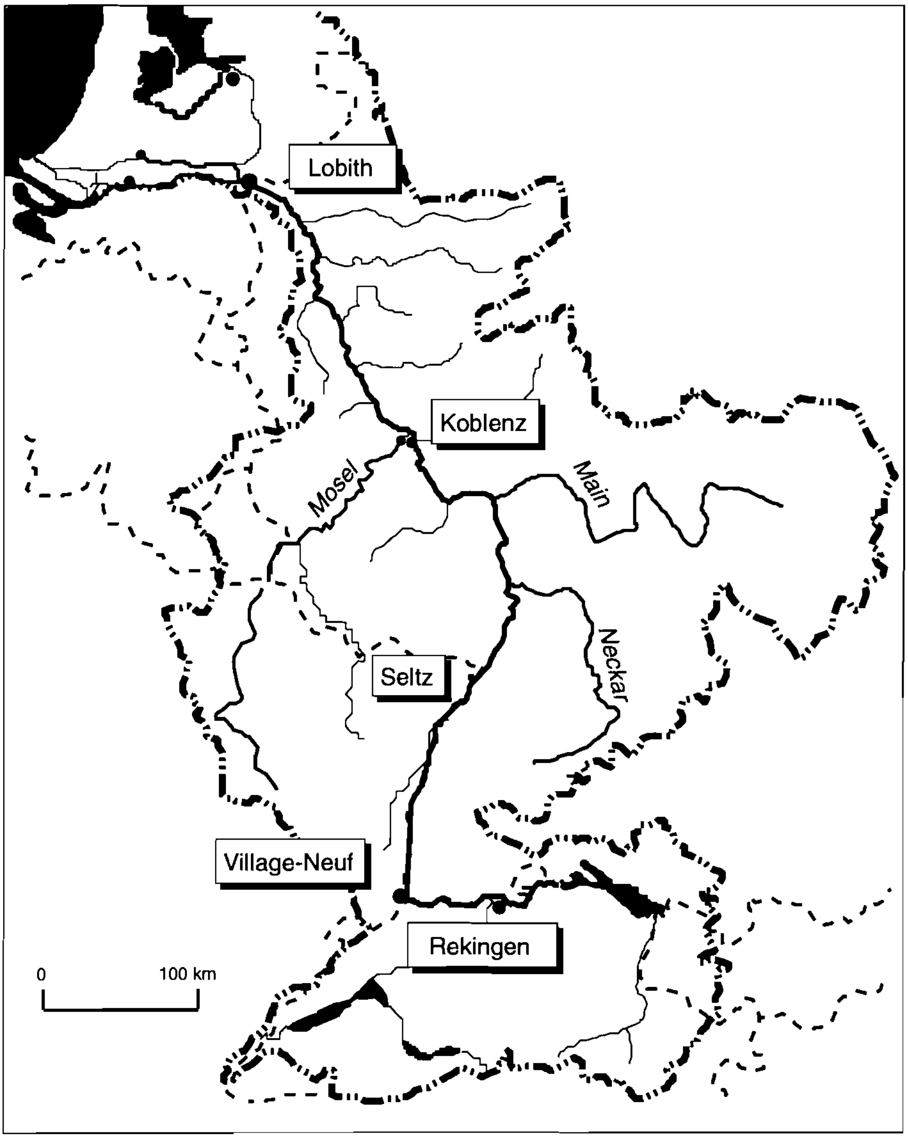

Figure 1. Map of the Rhine basin with the location of the monitoring stations.

3 Method

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

- *Point sources* are fairly steady in flow and quality, variability ranges are less than one order of magnitude. The magnitude of pollution is less than or not related to the magnitude of meteorological factors. Sources are identifiable points.
- *Diffuse sources* are mostly highly dynamic but occur at random, intermittent intervals. The variability ranges are often more than several orders of magnitude. The amount of pollution is closely related to meteorological variables such as precipitation. Often sources cannot be identified or defined.

According to this classification the characterization of a pollutant source does not depend on the pathway by which a pollutant arrives in the river. For example, wash off of road dust from an urban area during a storm is a diffuse source, independent of whether this load reaches the river mainly through canalization and effluent discharge from sewage treatment plants. To estimate the pollutant load of the different sources (point and diffuse) the different hydrological components within the watershed have to be considered.

An overview of the hydrological cycle within a given area is shown in *Figure 2*. In general, the runoff generated by rain and snow can be divided into the following three natural components (Novotny and Chesters, 1981; Dyck, 1985):

- *Surface runoff* is the result of precipitation if all losses of water within the area have been satisfied. Evaporation, infiltration, depression storage, ponding, and interception by vegetation are the losses which are taken into account in the water balance.
- *Interflow* is the result of infiltration diminished by groundwater recharge, storage of soil moisture, and evapotranspiration of the topsoil. The interflow is a subsurface flow where the water uses lower permeability zones of the subsoil.
- *Base flow* or groundwater flow is the difference between groundwater recharge and geological water losses and groundwater storage. The origins of base flow are mainly springs and wells.

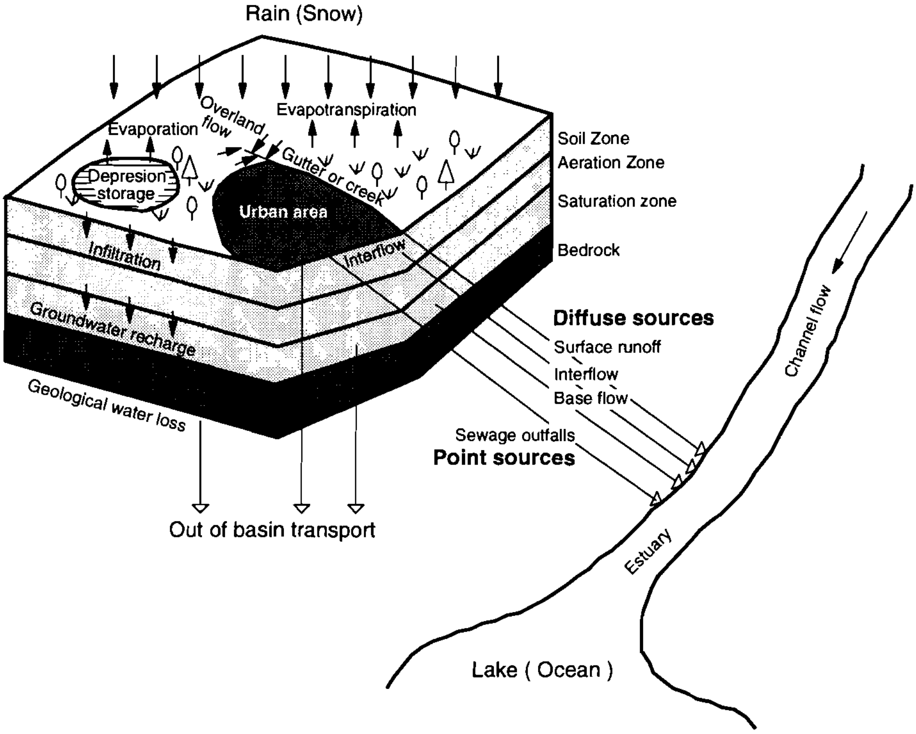

Figure 2. Schematic representation of the hydrologic situation and the runoff components within a part of a river basin (after Novotny and Chesters, 1981).

Interflow and base flow together form the subsurface components of the runoff. Depending on the different retention times of water, the whole subsurface flow can also be separated into a fast and a slow part, where the fast part is equal to the interflow and the slow part is mainly caused by base flow.

In the following discussion the objective is to develop an approach which gives us the possibility of separating the total pollutant load caused by point and diffuse sources using the monitored data of a river. One set of data characterizes the hydrological (measured discharge) and the load (measured concentration) conditions within the river basin above the monitoring station at a given time t. Because the spatial distribution of the different sources of pollution has to be taken into account, the watershed of the river is divided into n different parts.

In addition to the natural components of runoff, the flow caused by point sources (e.g., sewage treatment plants, industrial sewage) have to be regarded as a further component if part of a watershed includes urban and/or industrial areas. In this case the natural components of runoff, mainly base flow and interflow, are diminished by the amount of human water use. In general, the total discharge of part i of the whole watershed at a given time is defined as

$$Q_{i,t} = Q_{B_{i,t}} + Q_{I_{i,t}} + Q_{R_{i,t}} + Q_{P_{i,t}} \quad , \tag{3.1}$$

where $Q_{i,t}$ is the total discharge of part i of the watershed at a given time t, $Q_{B_{i,t}}$ is the base flow within part i of the watershed at time t, $Q_{I_{i,t}}$ is the interflow within part i of the watershed at time t, $Q_{R_{i,t}}$ is the surface runoff of part i of the watershed at time t, and $Q_{P_{i,t}}$ is the point discharge of part i of the watershed at time t.

With regard to the load of a pollutant, the different runoff components transport different amounts of mass. The total mass transport of a pollutant into the surface water of part i of a watershed is the sum of the gross loads caused by the different components of runoff. Additionally, losses of the pollutant due to sedimentation, transformation, and water use occur in the surface water. Therefore, the pollutant net load of the surface water at the end of part i of a watershed equals

$$L_{i,t} = L^g_{B_{i,t}} + L^g_{I_{i,t}} + L^g_{R_{i,t}} + L^g_{P_{i,t}} - LOSS_{i,t} \quad , \tag{3.2}$$

where $L_{i,t}$ is the pollutant net load of part i of the watershed at time t, $L^g_{B_{i,t}}$ is the pollutant gross load of part i of the watershed caused by base flow at time t, $L^g_{I_{i,t}}$ is the pollutant gross load of part i of the watershed caused by interflow at time t, $L^g_{R_{i,t}}$ is the pollutant gross load of part i of the watershed caused by surface runoff at time t, $L^g_{P_{i,t}}$ is the pollutant gross load of part i of the watershed caused by point sources at time t, $LOSS_{i,t}$, are the pollutant losses within the surface water of part i of the watershed at time t.

In general the gross concentrations and loads are high due to losses (e.g., sedimentation, denitrification) which can occur within the surface water of the different parts of the catchment area. In this context two assumptions are important:

- For a given pollutant, the sources and sinks within the surface water of a given area are the same for point and diffuse loads. Thus, the processes within the surface water depend only on the substance and not on its sources.
- For the correctness of the equation (3.3) it has to be assumed that the order of magnitude of the loss processes within the surface water of a given part of the watershed is independent of the source pollution (load from runoff or point load). Because the magnitude of the losses depends on the retention time of water in the surface water this assumption is true only if the point sources within the area are distributed equally and/or possess, on average, the same magnitude of losses as the diffuse sources. This means that the partition of the whole watershed cannot be too small.

The different gross loads within part i of a watershed at a given time can be described by the product of the different runoff components with a specific pollutant concentration (gross):

$$\begin{aligned} L_{i,t} &= K^g_{B_{i,t}} \cdot Q_{B_{i,t}} + K^g_{I_{i,t}} \cdot Q_{I_{i,t}} + K^g_{R_{i,t}} \cdot Q_{R_{i,t}} \\ &\quad + K^g_{P_{i,t}} \cdot Q_{P_{i,t}} - LOSS_{i,t} \ , \end{aligned} \tag{3.3}$$

where $K^g_{B_{i,t}}$ is the pollutant gross concentration of the base flow for part i of watershed at time t, $K^g_{I_{i,t}}$ is the pollutant gross concentration of the interflow for part i of watershed at time t, $K^g_{R_{i,t}}$ is the pollutant gross concentration of the surface runoff for part i of watershed at time t, and $K^g_{P_{i,t}}$ is the pollutant gross concentration of the point load for part i of watershed at time t.

Consequently, the net concentration of a pollutant ($K_{i,t}$) at the end of the surface water of part i of a watershed is

$$\begin{aligned} K_{i,t} &= \left(\frac{K^g_{B_{i,t}} \cdot Q_{B_{i,t}} + K^g_{I_{i,t}} \cdot Q_{I_{i,t}} + K^g_{R_{i,t}} \cdot Q_{R_{i,t}}}{Q_{i,t}} \right) \\ &\quad + \left(\frac{K^g_{P_{i,t}} \cdot Q_{P_{i,t}} - LOSS_{i,t}}{Q_{i,t}} \right) \ . \end{aligned} \tag{3.4}$$

For the whole watershed of a river the total discharge and the total net load of a pollutant equal the sum over all n parts of the watershed. The discharge, the pollutant net load, and the pollutant net concentration at a given point of the stream can be calculated using equations (3.1) to (3.4) as

$$Q_t = \sum_{i=1}^{n} Q_{i,t} = \sum_{i=1}^{n} Q_{B_{i,t}} + \sum_{i=1}^{n} Q_{I_{i,t}} + \sum_{i=1}^{n} Q_{R_{i,t}} + \sum_{i=1}^{n} Q_{P_{i,t}} \ , \qquad (3.5)$$

$$\begin{aligned} L_t &= \sum_{i=1}^{n} L_{i,t} \qquad (3.6) \\ &= \sum_{i=1}^{n} L^g_{B_{i,t}} + \sum_{i=1}^{n} L^g_{I_{i,t}} + \sum_{i=1}^{n} L^g_{R_{i,t}} + \sum_{i=1}^{n} L^g_{P_{i,t}} - LOSS_{tot,t} \end{aligned}$$

or

$$\begin{aligned} L_t &= \sum_{i=1}^{n} K^g_{B_{i,t}} \cdot Q_{B_{i,t}} + \sum_{i=1}^{n} K^g_{I_{i,t}} \cdot Q_{I_{i,t}} + \sum_{i=1}^{n} K^g_{R_{i,t}} \cdot Q_{R_{i,t}} \qquad (3.7) \\ &\quad + \sum_{i=1}^{n} K^g_{P_{i,t}} \cdot Q_{P_{i,t}} - LOSS_{tot,t} \ , \end{aligned}$$

and

$$\begin{aligned} K_t &= \left(\frac{\sum_{i=1}^{n} K^g_{B_{i,t}} \cdot Q_{B_{i,t}} + \sum_{i=1}^{n} K^g_{I_{i,t}} \cdot Q_{I_{i,t}} + \sum_{i=1}^{n} K^g_{R_{i,t}} \cdot Q_{R_{i,t}}}{\sum_{i=1}^{n} Q_{i,t}} \right) \qquad (3.8) \\ &\quad + \left(\frac{\sum_{i=1}^{n} K^g_{P_{i,t}} \cdot Q_{P_{i,t}} - LOSS_{tot,t}}{\sum_{i=1}^{n} Q_{i,t}} \right) \ , \end{aligned}$$

where L_t is the total net load of the pollutant at time t, K_t is the pollutant net concentration of the river at time t, Q_t is the total discharge of the river at time t, and $LOSS_{tot,t}$ are total losses of the pollutant within the surface water of the basin at time t.

Total losses within the surface waters of the whole watershed are greater than the total sum of the losses in all parts i, because pollutant losses within the main river must be taken into account.

To simplify these equations the following abbreviations are used:

$$K^g_{B_t} = \frac{\sum_{i=1}^{n} K^g_{B_{i,t}} \cdot Q_{B_{i,t}}}{Q_{B_t}} \ , \quad K^g_{I_t} = \frac{\sum_{i=1}^{n} K^g_{I_{i,t}} \cdot Q_{I_{i,t}}}{Q_{I_t}} \ ,$$

$$K_{R_t}^g = \frac{\sum_{i=1}^{n} K_{R_{i,t}}^g \cdot Q_{R_{i,t}}}{Q_{R_t}} \ , \ K_{P_t}^g = \frac{\sum_{i=1}^{n} K_{P_{i,t}}^g \cdot Q_{P_{i,t}}}{Q_{P_t}} \ ;$$

$$L_{B_t}^g = \sum_{i=1}^{n} L_{B_{i,t}}^g \ , \ L_{I_t}^g = \sum_{i=1}^{n} L_{I_{i,t}}^g \ ,$$

$$L_{R_t}^g = \sum_{i=1}^{n} L_{R_{i,t}}^g \ , \ L_{P_t}^g = \sum_{i=1}^{n} L_{P_{i,t}}^g \ ;$$

$$Q_{B_t} = \sum_{i=1}^{n} Q_{B_{i,t}} \ , \ Q_{I_t} = \sum_{i=1}^{n} Q_{I_{i,t}} \ ,$$

$$Q_{R_t} = \sum_{i=1}^{n} Q_{R_{i,t}} \ , \ Q_{P_t} = \sum_{i=1}^{n} Q_{P_{i,t}} \ ;$$

where $K_{(B,I,R,P)_t}^g$ are the flow weighted means of pollutant gross concentration, $L_{(B,I,R,P)_t}^g$ are the total gross loads, and $Q_{(B,I,R,P)_t}$ are the total discharges caused by the different runoff components at time t. Equations (3.5) to (3.8) can be transformed now to

$$\begin{aligned}
Q_t &= Q_{B_t} + Q_{I_t} + Q_{R_t} + Q_{P_t} && (3.9)\\
L_t &= L_{B_t}^g + L_{I_t}^g + L_{R_t}^g + L_{P_t}^g - LOSS_{tot,t} && (3.10)\\
L_t &= K_{B_t}^g \cdot Q_{B_t} + K_{I_t}^g \cdot Q_{I_t} + K_{R_t}^g \cdot Q_{R_t} && (3.11)\\
&\quad + K_{P_t}^g \cdot Q_{P_t} - LOSS_{tot,t}\\
K_t &= \left(\frac{K_{B_t}^g \cdot Q_{B_t} + K_{I_t}^g \cdot Q_{I_t} + K_{R_t}^g \cdot Q_{R_t}}{Q}\right) && (3.12)\\
&\quad + \left(\frac{K_{P_t}^g \cdot Q_{P_t} - LOSS_{tot,t}}{Q}\right) \ .
\end{aligned}$$

Using the parameter N_t, which is defined as the ratio between the total net load and the total gross load at the monitoring station at time t

$$N_t = \frac{K_{B_t}^g \cdot Q_{B_t} + K_{I_t}^g \cdot Q_{I_t} + K_{R_t}^g \cdot Q_{R_t} + K_{P_t}^g \cdot Q_{P_t} - LOSS_{tot,t}}{K_{B_t}^g \cdot Q_{B_t} + K_{I_t}^g \cdot Q_{I_t} + K_{R_t}^g \cdot Q_{R_t} + K_{P_t}^g \cdot Q_{P_t}} \qquad (3.13)$$

equations (3.10) to (3.12) can be rewritten as

$$L_t = N_t(L_{B_t}^g + L_{I_t}^g + L_{R_t}^g + L_{P_t}^g) \qquad (3.14)$$

$$L_t = N_t(K^g_{B_t} \cdot Q_{B_t} + K^g_{I_t} \cdot Q_{I_t} + K^g_{R_t} \cdot Q_{R_t} + K^g_{P_t} \cdot Q_{P_t}) \tag{3.15}$$

$$K_t = \frac{N_t \cdot (K^g_{B_t} \cdot Q_{B_t} + K^g_{I_t} \cdot Q_{I_t} + K^g_{R_t} \cdot Q_{R_t} + K^g_{P_t} \cdot Q_{P_t})}{Q} \; . \tag{3.16}$$

If the new parameters $K_{(B,I,R,P)_t}$ and $L_{(B,I,R,P)_t}$ are introduced as

$$K_{B,I,R,P_t} = N_t \cdot K^g_{B,I,R,P_t}$$

and

$$L_{B,I,R,P_t} = N_t \cdot L^g_{B,I,R,P_t} \; ,$$

the net concentration and the total net load caused by the different runoff components, the result of equations (3.14) to (3.16) is

$$L_t = L_{B_t} + L_{I_t} + L_{R_t} + L_{P_t} \tag{3.17}$$

$$L_t = K_{B_t} \cdot Q_{B_t} + K_{I_t} \cdot Q_{I_t} + K_{R_t} \cdot Q_{R_t} + K_{P_t} \cdot Q_{P_t} \tag{3.18}$$

$$K_t = \frac{K_{B_t} \cdot Q_{B_t} + K_{I_t} \cdot Q_{I_t} + K_{R_t} \cdot Q_{R_t} + K_{P_t} \cdot Q_{P_t}}{Q_t} \; . \tag{3.19}$$

In general, the assumption that the ratio N_t is the same over the whole range of discharge can be used only if the loss processes within the river are small compared with the load or do not depend on discharge. Loss processes independent of discharge are, e.g., nitrification and denitrification (only in the case of nitrogen) and water use. Pollutant losses from water use play an especially important role in the Rhine area between Koblenz and Lobith, where the water balance can be negative at low discharges. Processes which seem to depend on discharge are, for example, increasing sedimentation with decreasing flow or resuspension of sediments with increasing flow. But sedimentation and resuspension do not depend directly on flow. The driving forces of these processes are the transport capacity of water, the flow velocity, and its changes. Sedimentation occurs during periods of low discharge if the discharge is decreased during high discharges or if the flow velocity is reduced due to an increasing cross section area during floods. On the other hand, resuspension of material from the river bed can also occur during phases of low discharges if the discharge increases due to increasing transport capacity. Because the dynamics of the transport and of fine suspended particulate material and its transformation within the river is still uncertain, in the following discussion it is assumed as a first approximation that processes which depend on flow can be neglected in the case of big rivers such as the river Rhine and the tributaries investigated.

Equations (3.18) and (3.19) provide the possibility of carrying out the estimation of the different net loads and concentrations of a pollutant from upstream, if the different components of discharge [equation (3.9)] are known at time t. But the magnitude of the discharge and its three natural components is highly stochastic. Therefore the magnitude of the different natural runoff components cannot be estimated at a given time. Furthermore, the concentrations of the different discharge components are also stochastic.

It is not enough to estimate the pollutant loads of all different hydrological components. It would be sufficient if the pollutant net point load could be separated. Then the pollutant net diffuse load could be estimated from the difference between the measured total load per year and the estimated net point load.

Therefore, a separation of diffuse and point loads seems to be possible in some special cases.

3.1 Case A

In this case weighted means of the pollutant net concentrations of the three runoff components of the diffuse load are about the same or do not differ very much. This means

$$K_{D_t} = K_{B_t} \simeq K_{I_t} \simeq K_{R_t} \ .$$

In this case equations (3.9), (3.18), and (3.19) can be transformed to

$$Q_t = Q_{D_t} + Q_{P_t} \ , \tag{3.20}$$

$$L_t = K_{D_t} \cdot Q_{D_t} + K_{P_t} \cdot Q_{P_t} \ , \tag{3.21}$$

$$K_t = \frac{K_{D_t} \cdot Q_{D_t} + K_{P_t} \cdot Q_{P_t}}{Q_t} \ , \tag{3.22}$$

where K_{D_t} is the pollutant net concentration of the diffuse sources within the watershed at time t and Q_{D_t} is the total discharge of all diffuse components at time t.

If Q_{D_t} in equations (3.21) and (3.22) is replaced by $(Q_t - Q_{P_t})$ the result is

$$L_t = K_{D_t} \cdot Q_t + Q_{P_t}(K_{P_t} - K_{D_t}) \tag{3.23}$$

$$K_t = K_{D_t} + \frac{Q_{P_t}(K_{P_t} - K_{D_t})}{Q_t} \ . \tag{3.24}$$

In general, the two parameters in equations (3.23) and (3.24) which characterize the pollutant point load are nearly time independent (see definition of point source on page 4).

As a first approximation it is assumed that the diffuse net concentration of a pollutant K_{D_t} is nearly time independent. This assumption can be tested by a qualitative discussion of the load–discharge and concentration–discharge relationships given in equations (3.23) and (3.24). According to these equations two cases must be distinguished: $K_{P_t} > K_{D_t}$ and $K_{P_t} < K_{D_t}$.

If our assumption is correct, then the load–discharge relationship has to be nearly linear in both cases. But the imaginable intercept of the curve with the load axis is positive for $K_{P_t} > K_{D_t}$ and negative for $K_{P_t} < K_{D_t}$. The behavior of the concentration–discharge relationship is quite different for both cases. If $K_{P_t} > K_{D_t}$, the relationship is characterized by a typical dilution curve. In the other case an increase of the concentration can be observed up to a certain saturation concentration. A special case of equations (3.23) and (3.24) is a zero point load; then the imaginable intercept of the load–discharge relationship is zero. The concentration–discharge relationship would present a nearly constant magnitude over the whole range of the discharge. As shown in *Figure 3*, both cases can be observed. Especially for substances which are transported in dissolved forms (e.g., nitrate, ammonium, chloride, sulfate, calcium, magnesium, potassium), such types of load–discharge and concentration–discharge relationships can often be observed.

If m different data sets of K_t and Q_t exist for a given time period (e.g., a year) at a monitoring station, equations (3.20), (3.21), and (3.22) can be used to estimate the means of net diffuse concentration of pollutant K_D and parameter $L_0 = Q_P(K_P - K_D)$. In this case we have three systems of m equations:

$$\begin{aligned} Q_1 &= Q_{D_1} + Q_{P_1} \\ Q_2 &= Q_{D_2} + Q_{P_2} \\ &\vdots \\ Q_m &= Q_{D_m} + Q_{P_m} \end{aligned} \tag{3.25}$$

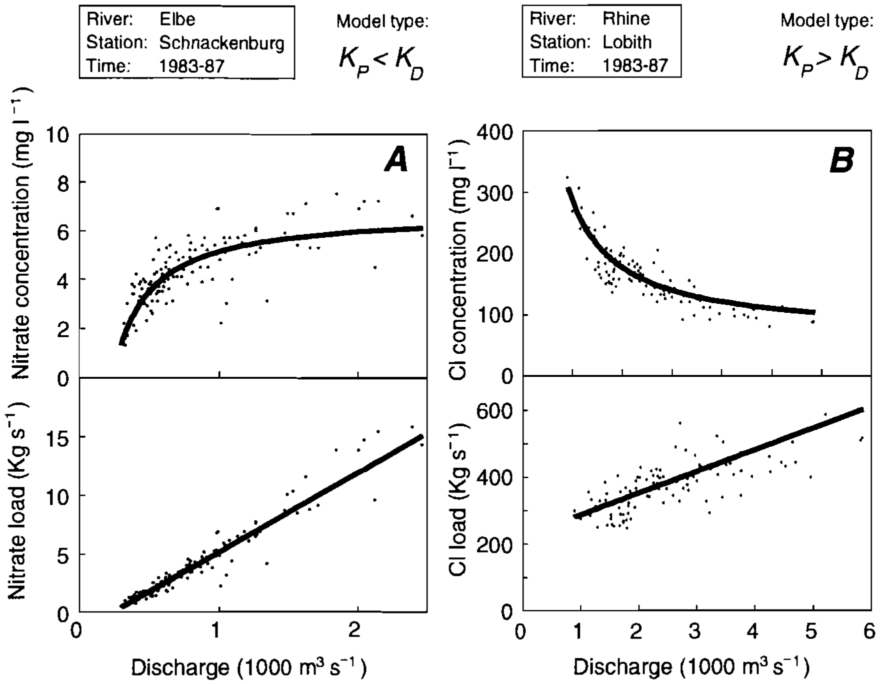

Figure 3. Dependencies of concentration and load on the discharge of nitrate in the river Elbe (A) and chloride in the river Rhine (B).

$$\begin{aligned} L_1 &= K_{D_1} \cdot Q_{D_1} + K_{P_1} \cdot Q_{P_1} \\ L_2 &= K_{D_2} \cdot Q_{D_2} + K_{P_2} \cdot Q_{P_2} \\ &\vdots \\ L_m &= K_{D_m} \cdot Q_{D_m} + K_{P_m} \cdot Q_{P_m} \end{aligned} \tag{3.26}$$

$$\begin{aligned} K_1 &= \frac{K_{D_1} \cdot Q_{D_1} + K_{P_1} \cdot Q_{P_1}}{Q_1} \\ K_2 &= \frac{K_{D_2} \cdot Q_{D_2} + K_{P_2} \cdot Q_{P_2}}{Q_2} \\ &\vdots \\ K_m &= \frac{K_{D_m} \cdot Q_{D_m} + K_{P_m} \cdot Q_{P_m}}{Q_m} \ . \end{aligned} \tag{3.27}$$

Using the same procedure as shown above the three systems of equations (3.25), (3.26), and (3.27) can be transformed to following two systems of equation:

$$\begin{array}{rcl} L_1 & = & K_{D_1} \cdot Q_1 + L_{0_1} \\ L_2 & = & K_{D_2} \cdot Q_{D_2} + L_{0_2} \\ & \vdots & \\ L_m & = & K_{D_m} \cdot Q_{D_m} + L_{0_m} \end{array} \tag{3.28}$$

$$\begin{array}{rcl} K_1 & = & K_{D_1} + \dfrac{L_{0_1}}{Q_1} \\ K_2 & = & K_{D_2} + \dfrac{L_{0_1}}{Q_2} \\ & \vdots & \\ K_m & = & K_{D_m} + \dfrac{L_{0_1}}{Q_m} \ , \end{array} \tag{3.29}$$

where

$$L_{0_m} = Q_{P_m}(K_{P_m} - K_{D_m}) \ . \tag{3.30}$$

Either of these two systems can be used for the estimation of the average values of K_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 system (3.28). In the case of system (3.29) a linear regression is also possible, if the transformation $X_t = 1/Q_t$ is introduced in system (3.29).

With regard to system (3.28) reflecting the load–discharge relationship the results are:

$$\begin{array}{l} K_D = \dfrac{\sum\limits_{j=1}^{m} K_{D_j}}{m} = \dfrac{m \cdot \sum\limits_{j=1}^{m} Q_j \cdot L_j - \sum\limits_{j=1}^{m} Q_j \cdot \sum\limits_{j=1}^{m} L_j}{m \cdot \sum\limits_{j=1}^{m} Q_j^2 - \sum\limits_{j=1}^{m} Q_j \cdot \sum\limits_{j=1}^{m} Q_j} \\ L_0 = \dfrac{\sum\limits_{j=1}^{m} L_{0_j}}{m} = \dfrac{1}{m} \left(\sum\limits_{j=1}^{m} L_j - K_D \cdot \sum\limits_{j=1}^{m} Q_j \right) \ . \end{array} \tag{3.31a}$$

For system (3.29) which represents the concentration–discharge relationship we find

$$L_0 = \frac{\sum_{j=1}^{m} L_{0_j}}{m} = \frac{m \cdot \sum_{j=1}^{m} X_j \cdot K_j - \sum_{j=1}^{m} X_j \cdot \sum_{j=1}^{m} K_j}{m \cdot \sum_{j=1}^{m} X_j^2 - \sum_{j=1}^{m} X_j \cdot \sum_{j=1}^{m} X_j}$$

$$K_D = \frac{\sum_{j=1}^{m} K_{D_j}}{m} = \frac{1}{m}\left(\sum_{j=1}^{m} K_j - L_0 \cdot \sum_{j=1}^{m} X_j\right) \tag{3.31b}$$

where the variable X_j is the transformed variable $1/Q_j$.

According to equation (3.30) the parameter L_0 is defined as

$$L_0 = Q_P(K_P - K_D) \ . \tag{3.32}$$

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 (3.32) and the parameter K_D which was calculated by the regression (3.31):

$$L_P = Q_P \cdot K_P = L_0 + K_D \cdot Q_P \ . \tag{3.33}$$

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

$$L_{tot} = \frac{\sum_{j=1}^{n} K_j \cdot Q_j}{m} \ . \tag{3.34}$$

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

$$L_D = L_{tot} - L_P \ . \tag{3.35}$$

The different parameters of equation (3.23) are shown in *Figure 4*.

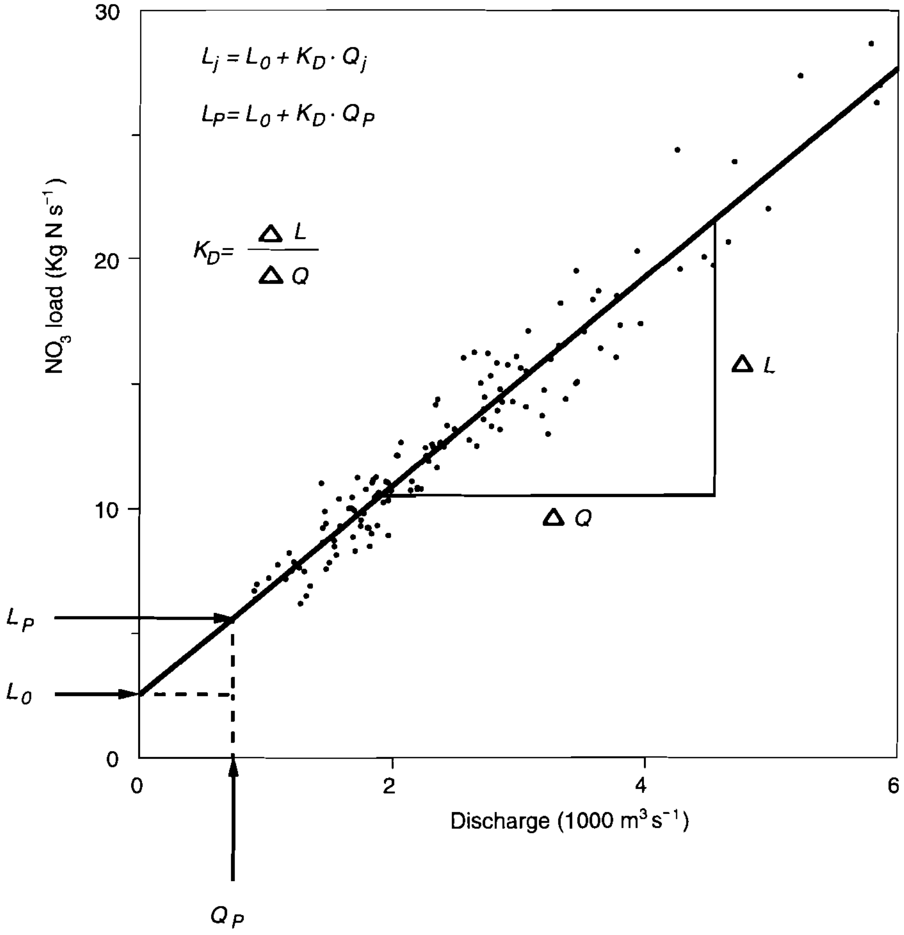

Figure 4. Dependencies of nitrate load on the discharge as an example of the load–discharge relationship of case A and model parameters.

3.2 Case B

Because not all concentration–discharge and load–discharge relationships can be described on the basis of case A, in the following discussion we try to describe equations (3.9), (3.18), and (3.19) in more detail. An example of other concentration–discharge and load–discharge relationships is shown in *Figure 5*. The figure shows that the relationship between load and discharge is not linear as in case A. Curves of the type

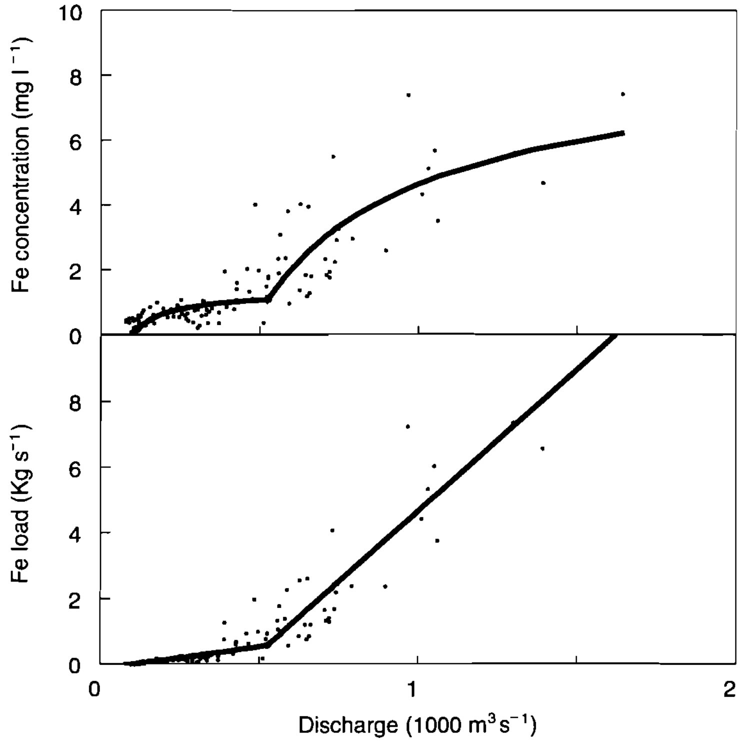

Figure 5. Dependencies of iron concentration and load on the discharge (river Mosel; Koblenz station; time period 1983–1987).

in *Figure 5* can sometimes be found for pollutants which are mainly transported as particulate material. In *Figure 5* the load is increasing linearly in the range of lower discharge. But above a certain discharge the load increases faster than in the lower ranges of discharge. To describe such behavior and to separate point and diffuse load of a pollutant in such a case the assumption is made that the pollutant net concentrations of the interflow and the base flow (K_{I_t}) and (K_{B_t}) are about the same or do not differ very much:

$$K_{S_t} = K_{I_t} \simeq K_{B_t} \tag{3.36}$$

where K_{S_t} is the assumed net concentration of the pollutant caused by the sum of both subsurface flows ($Q_{S_t} = Q_{I_t} + Q_{B_t}$).

Using the summarizing parameters K_{S_t} and Q_{S_t}, equations (3.9), (3.18), and (3.19) can be transformed to

$$Q_t = Q_{S_t} + Q_{R_t} + Q_{P_t} \tag{3.37}$$

$$L_t = K_{S_t} \cdot Q_{S_t} + K_{R_t} \cdot Q_{R_t} + K_{P_t} \cdot Q_{P_t} \tag{3.38}$$

$$K_t = \frac{K_{S_t} \cdot Q_{S_t} + K_{R_t} \cdot Q_{R_t} + K_{P_t} \cdot Q_{P_t}}{Q_t} \quad . \tag{3.39}$$

For a qualitative discussion of equations (3.38) and (3.39) a model river was simulated, where the components of the discharge do not possess a stochastic nature and the pollutant concentrations of the discharge components are time independent. With regard to the different component of discharge a constant flow was assumed, caused by point sources, a subsurface flow increasing nonlinearly to a saturation value, and a surface flow increasing exponentially. As shown in *Figure 6* six different types of concentration–discharge/load–discharge relationships are possible in such a case. Types A and D in *Figure 6* are identical to the types presented in case A.

The observed concentration–discharge and load–discharge relationships in *Figure 5* correspond to type F given in *Figure 6*. The shapes of the curves of *Figure 5* are explained in the following discussion. The point load of iron in this river is low. The increase of load and concentration is slow during the phase when the total discharge is dominated by the subsurface flow. If the discharge is dominated by surface runoff the load and the concentration of iron increases, due to a higher specific concentration of the surface runoff (e.g., caused by erosion).

From the viewpoint of modeling it would be interesting if examples of the other types of curves in *Figure 6* due to the different kinds of loads were observed. On the basis of the original data sets this is difficult, because the values of the observed concentrations within a certain time period vary in a relatively wide range. Therefore, the use of estimated concentrations and loads for classes of different discharges can be helpful. *Figure 7* shows the results of such a procedure for different heavy metals at the Lobith monitoring station of the river Rhine.

It is obvious that the types of dependencies of concentration and load on the discharge presented in *Figure 7* are the same as those shown for type B in *Figure 6*. For these heavy metals the relationships between concentration or load and discharge for the river Rhine at Lobith can be interpreted.

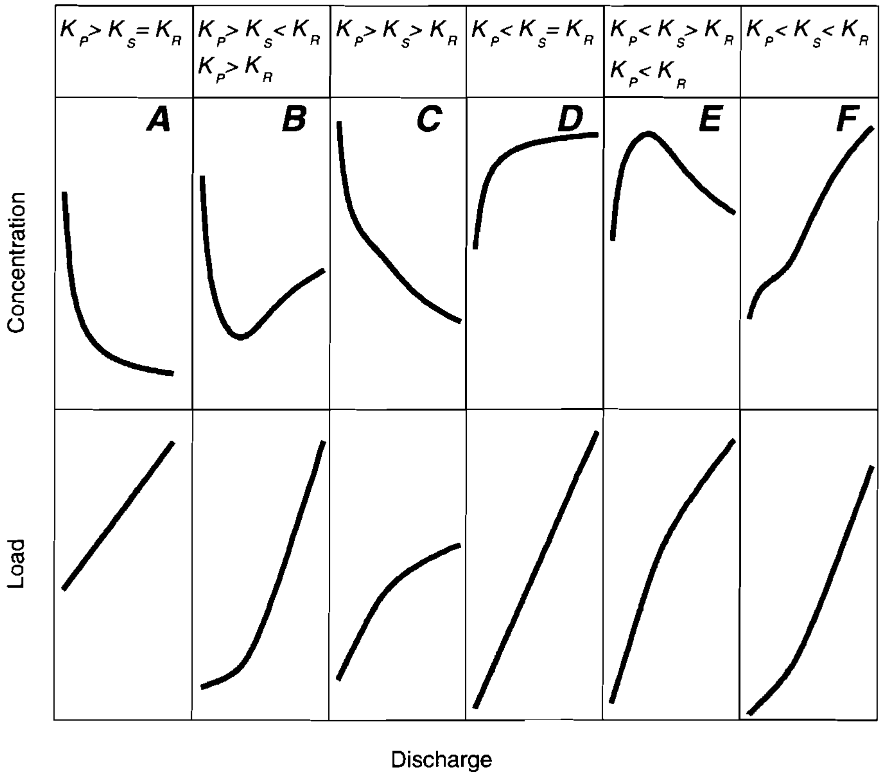

Figure 6. Possible dependencies of pollutant concentration and load on the discharge of a model river with the following hydrological components: subsurface flow, surface runoff, and point wastewater flow.

A relatively high point load which causes a high concentration of heavy metals seems to exist during phases of low discharges. With increasing discharge the concentration decreases due to dilution of point load by subsurface flow with a lower concentration of heavy metals. During this phase the increase of heavy metal load is relatively low. Above a certain discharge, where the concentration reaches a minimum, the concentration of heavy metals increases once more and the load grows rapidly, due to a higher concentration of heavy metals in surface runoff compared with the concentration of subsurface flow.

Dependencies of the concentration and load on the discharge of types *C* and *E* in *Figure 6* can sometimes be determined in a river, but only

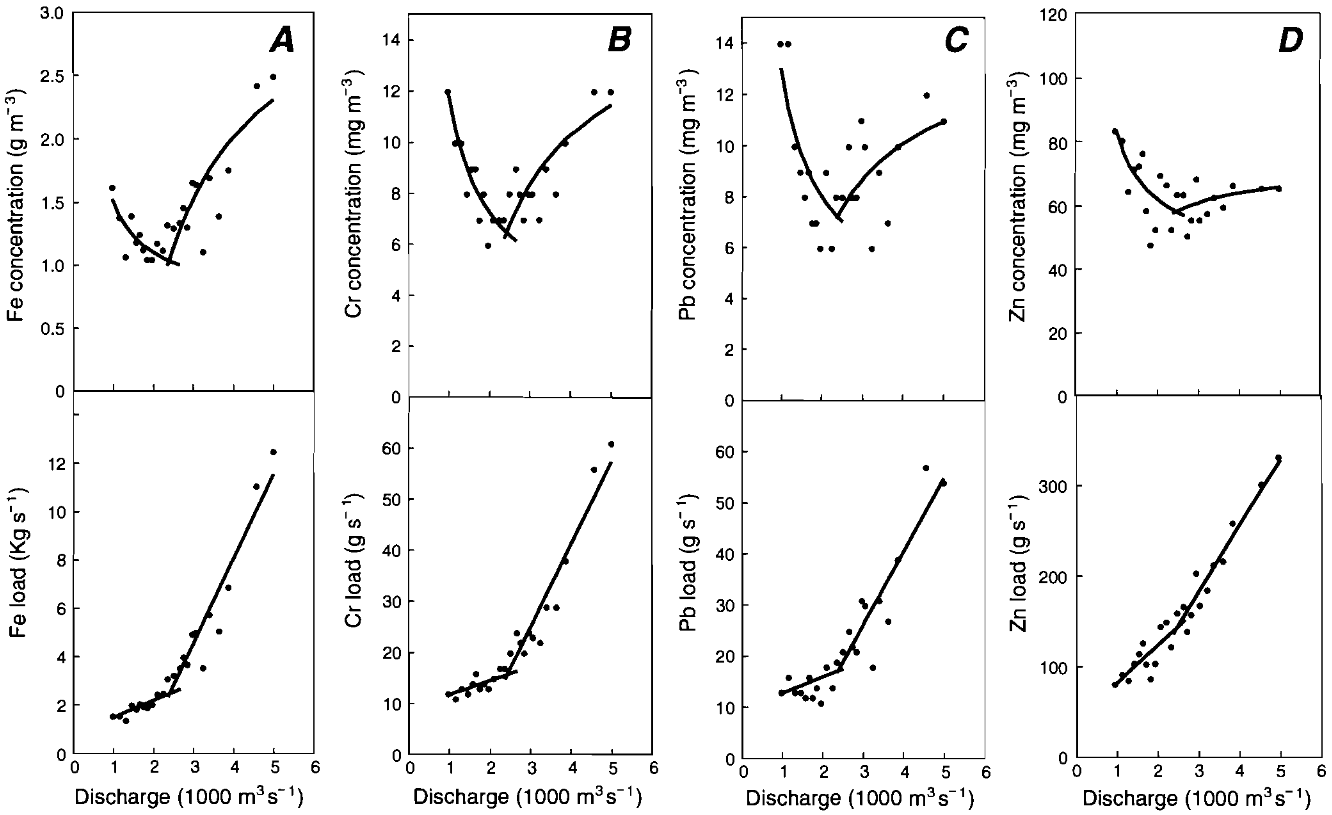

Figure 7. Dependencies of the concentration and load on means of discharge classes for heavy metals (iron, chromium, zinc, and lead) at the Lobith station of the Rhine, 1983–1987.

for substances which are dissolved during transport. According to the model, types C and E in *Figure 6* can be explained by a lower pollutant concentration of surface runoff compared with the concentration of subsurface flow. Types C and E in *Figure 6* differ with regard to the magnitude of the concentration of point load. *Figure 6C* presents a type of model where the concentration of point load is higher than the concentration of subsurface flow, but the concentration of point load is smaller than the concentration of subsurface flow in *Figure 6E.*

The discussion of the qualitative behavior of the model presented in equations (3.37), (3.38), and (3.39) shows that such a model can describe a very large range of possible observed concentration–discharge and load–discharge relationships. But can the parameters of equations (3.38) and (3.39) be estimated quantitatively, too?

To do this the procedure is about the same as the procedure for case A, but one substantial difference exists. The whole range of observed dependencies of concentration and load on the discharge has to be divided into two parts: one part where the discharge is low and mainly influenced by the point and subsurface flows and another part where the discharge is dominated by surface runoff.

It is assumed that the surface runoff is zero or can be disregarded within the lower range of discharge: $Q_{R_t} \simeq 0$. If this condition is taken into account, then the concentration–discharge and load–discharge relationships is characterized by the following equations:

$$Q_t = Q_{S_t} + Q_{P_t} \tag{3.40}$$

$$L_t = K_{S_t} \cdot Q_{S_t} + K_{P_t} \cdot Q_{P_t} \tag{3.41}$$

$$K_t = \frac{K_{S_t} \cdot Q_{S_t} + K_{P_t} \cdot Q_{P_t}}{Q_t} \quad . \tag{3.42}$$

Equations (3.40), (3.41), and (3.42) correspond to equations (3.20), (3.21), and (3.22) in case A. Therefore, the procedure used in case A can be applied to estimate the means of the parameter K_{S_t} and L_{0_t} for the time period investigated. The important difference is that now only the lower part of the dependencies of concentration and load on discharge is involved into the regression. As a result of this procedure, parameters K_S and L_0 can be calculated from the load–discharge relationship in the following:

$$K_S = \frac{\sum_{j=1}^{m} K_{S_j}}{m} = \frac{m \cdot \sum_{j=1}^{m} Q_j \cdot L_j - \sum_{j=1}^{m} Q_j \cdot \sum_{j=1}^{m} L_j}{m \cdot \sum_{j=1}^{m} Q_j^2 - \sum_{j=1}^{m} Q_j \cdot \sum_{j=1}^{m} Q_j}$$

$$L_0 = \frac{\sum_{j=1}^{m} L_{0_j}}{m} = \frac{1}{m} \left(\sum_{j=1}^{m} L_j - K_S \cdot \sum_{j=1}^{m} Q_j \right) \, . \tag{3.43a}$$

According to the solution of the system representing the concentration–discharge relationship the results are

$$L_0 = \frac{\sum_{j=1}^{m} L_{0_j}}{m} = \frac{m \cdot \sum_{j=1}^{m} X_j \cdot K_j - \sum_{j=1}^{m} X_j \cdot \sum_{j=1}^{m} K_j}{m \cdot \sum_{j=1}^{m} X_j^2 - \sum_{j=1}^{m} X_j \cdot \sum_{j=1}^{m} X_j}$$

$$K_S = \frac{\sum_{j=1}^{m} K_{S_j}}{m} = \frac{1}{m} \left(\sum_{j=1}^{m} K_j - L_0 \cdot \sum_{j=1}^{m} X_j \right) \, , \tag{3.43b}$$

where the variable X_j is again the transformed variable $1/Q_j$. But in this case L_0 is defined as

$$L_0 = Q_P(K_P - K_S) \tag{3.44}$$

because only the range of low discharge is taken into account.

Based on these parameters the point load of the pollutant is estimated as in case A. The total diffuse load is estimated again from the difference between the estimated total load [see equation (3.34)] and the point load according to equation (3.33) using the parameters L_0 and K_S. This means that the lower range of discharge is sufficient for the separation of the point and the diffuse loads of a pollutant.

Equations (3.37), (3.38), and (3.39) have to be used if the range of concentration–discharge and load–discharge relationships is taken into account, where the discharge is high.

If the substitution

$$Q_{R_t} = Q_t - Q_{S_t} - Q_{P_t} \tag{3.45}$$

is introduced equations (3.38) and (3.39) can be transformed to

$$L_t = K_{R_t} \cdot Q_t + L_{R0_t} \tag{3.46}$$

$$K_t = K_{R_t} + \frac{L_{R0_t}}{Q_t} \ , \tag{3.47}$$

where

$$L_{R0_t} = Q_{S_t}(K_{S_t} - K_{R_t}) + Q_{P_t}(K_{P_t} - K_{R_t}) \ . \tag{3.48}$$

For a given time period with a data set of m measurements of concentration and discharge we get systems of equations that are similar to those in equations (3.28) and (3.29).

The mean K_R and L_{R0} of the parameter K_{R_t} and L_{R0_t}, respectively, can be estimated by the solution of the system of the load–discharge relationship

$$\begin{aligned} L_1 &= K_{R_1} \cdot Q_1 + L_{R0_1} \\ L_2 &= K_{R_2} \cdot Q_2 + L_{R0_2} \\ &\vdots \\ L_m &= K_{R_m} \cdot Q_m + L_{R0_1} \end{aligned} \tag{3.49}$$

or of the system of the dependencies of concentration on discharge

$$\begin{aligned} K_1 &= K_{R_1} + \frac{L_{R0_1}}{Q_1} \\ K_2 &= K_{R_2} + \frac{L_{R0_1}}{Q_2} \\ &\vdots \\ K_m &= K_{R_m} + \frac{L_{R0_1}}{Q_m} \end{aligned} \tag{3.50}$$

$$\begin{aligned} K_R &= \frac{\sum_{j=1}^{m} K_{R_j}}{m} = \frac{m \cdot \sum_{j=1}^{m} Q_j \cdot L_j - \sum_{j=1}^{m} Q_j \cdot \sum_{j=1}^{m} L_j}{m \cdot \sum_{j=1}^{m} Q_j^2 - \sum_{j=1}^{m} Q_j \cdot \sum_{j=1}^{m} Q_j} \\ L_{R0} &= \frac{\sum_{j=1}^{m} L_{R0_j}}{m} = \frac{1}{m} \left(\sum_{j=1}^{m} L_j - K_R \cdot \sum_{j=1}^{m} Q_j \right) \end{aligned} \tag{3.51a}$$

$$L_{R0} = \frac{\sum_{j=1}^{m} L_{R0_j}}{m} = \frac{m \cdot \sum_{j=1}^{m} X_j \cdot K_j - \sum_{j=1}^{m} X_j \cdot \sum_{j=1}^{m} K_j}{m \cdot \sum_{j=1}^{m} X_j^2 - \sum_{j=1}^{m} X_j \cdot \sum_{j=1}^{m} X_j}$$

$$K_R = \frac{\sum_{j=1}^{m} K_{R_j}}{m} = \frac{1}{m}\left(\sum_{j=1}^{m} K_j - L_{R0} \cdot \sum_{j=1}^{m} X_j\right) \quad . \qquad (3.51b)$$

Here it is taken into account that the procedure is used only for the data sets within the range of a high discharge above an observed break within the measured load–discharge relationship. How can the ranges of low and high discharges be separated? Such a separation can be done graphically using a plot as shown in *Figures 3, 5*, and *7*. If a break within the load–discharge relationship is visible, the parameter estimation of case B has to be used. For the estimation of the point load and the concentration of subsurface flow, the range of discharge lower than the discharge where the break was observed is used. The concentration of surface runoff can be estimated using the range of curve where the discharge is higher than the break point observed.

A reasonable break point, which marks the upper limit of the low flow range, can be found by using a procedure which includes the following features:

- Interactive selection of a pollutant load data set.
- Sorting by flow.
- Step-by-step linear regression in an ascending and descending order, each step including one additional data set.
- Graphic representation of the load–flow relationship, the slopes, and correlation coefficients of all regression lines.
- Interactive selection and storage of results.

In the next section we apply this method to the river Rhine and its main tributaries and compare the results with independent investigations of the point and diffuse loads of phosphorus, nitrogen, and heavy metals (zinc, lead, and cadmium). In general, the results of both the concentration and load-based regressions were similar. But usually the results of load-based regressions were used, because a transformation of the variable Q_t was not necessary in this case. The concentration results

Table 1. Estimated wastewater discharges of point sources to the river Rhine and its tributaries, in cubic meters per second.

Profile	Point wastewater flow	Lowest river discharge 1973–1977	1978–1982	1983–1987
Seltz/Maxau	300–400	620	619	546
Koblenz	550–650	670	800	679
Bimmen/Lobith	850–950	880	1,010	912
Neckar	80–100			36
Main	80–100			74
Mosel	50–100	12	74	77

are not shown separately, but are taken into consideration in the cases were the result of load-based regressions alone was not sufficient.

The estimation of the point and diffuse loads of the pollutants based on the method presented includes errors and uncertainties depending mainly on the fluctuations of the concentration measured and the model approach. Therefore a possible range of point and diffuse loads is given besides the averages. These ranges were estimated using the minimum and maximum of point wastewater flows (see *Table 1*) and the standard error of the concentrations (K_D or K_S) estimated by regression. Based on this standard error a possible minimum and maximum of these concentrations were calculated. These maximal and minimal concentrations and point wastewater flows were used to estimate minimal and maximal point and diffuse loads according to equations (3.33) and (3.35), respectively. Ranges of uncertainty given in the following figures were estimated by the difference between the maximum and the minimum. If the different sources of error considered (standard error of calculated concentrations and range of wastewater point flow) are compared, then the standard error of concentration has a much higher influence on the range of uncertainty.

4 Results and Discussion

4.1 Estimating the point flow

Various sources of information were used to estimate the mean point wastewater flow within the whole catchment area at each monitoring station.

For the German part of the Rhine River basin the data on municipal and industrial wastewater and cooling water effluent were taken from the *Statistisches Bundesamt* (1979, 1981). The French and Swiss contribution to the point wastewater flow was estimated by a comparison between the populations living in the German, French, and Swiss part of the catchment area of Rhine given by ICPR (1987, 1989). Cooling water has to be included in the estimation of point wastewater flow because a transformation, elimination, or increase of the pollutant load can occur from the cooling process itself, additives, and zones of reduced flow velocity.

Ranges of point wastewater flow were used because the values calculated are only estimations. *Table 1* shows the estimated values of point source flows. For a comparison the lowest discharge of the rivers over a 14-year time span are given.

4.2 Testing model results

Regarding the loads and their sources, *Table 2* shows a comparison between the results of this study, the inventories of pollutant sources of German, French, and Swiss parts of the Rhine catchment area for 1985 (ICPR, 1989; DKSR, 1989; Agence de l'eau Rhin-Meuse, 1988), and the results of a Dutch study of the heavy metal balances of the Rhine (Waterloopkundig Laboratorium, 1989). It should be noted that the time periods are different for the different studies. Especially in the year 1985 (the base year for the German and French inventory of pollutant sources), there were significantly lower discharge and pollutant loads measured at the different monitoring stations compared with the average discharge over the five-year period 1983–1987.

In contrast to our results, the amount of points and diffuse loads cited in the other studies have to be taken as gross loads into the river. If loss processes occur in the river, then these gross loads have to be higher than our estimated net loads. The comparisons given in *Table 2* are not entirely consistent.

For dissolved inorganic nitrogen the net point load estimated by our model at the Lobith station was between 140 and 170 kilotons of nitrogen per year (kt N a^{-1}). Considering the loss of nitrogen by denitrification (see Section 4.4) the gross point load of dissolved inorganic nitrogen was estimated between 230 and 260 kt N a^{-1}. On the basis of data from 1985 the magnitude of the gross point load of total nitrogen

Table 2. Comparison between estimated net load (point and diffuse) at different monitoring stations of the river Rhine for the time period 1983–1987 and estimated gross load (point and diffuse) in 1985 for the German parts of the watershed. All values are in tons per year.

	Rhine Lobith	Rhine Koblenz	Rhine Seltz	Mosel Koblenz
Zn				
Point load (mean)[a]	2,134	595	180[d]	164
Range	1,753-2,548	400-814	57-326	0-391
Point load[b]	2,010	616	216	158
Point load[c]	2,635			
Diffuse load (mean)[a]	2,812	2,114	1,028[d]	932
Range	2,397-3,192	1,895–2,309	893–1,161	705-1,096
Diffuse load[c]	1,249			
Pb				
Point load (mean)[a]	240	81	27	31
Range	189-294	68–95	12–46	11-58
Point load[b]	240	61	19	29
Point load[c]	200			
Diffuse load (mean)[a]	465	248	134	138
Range	410-515	234–261	115-150	111–158
Diffuse load[b]	149	86	53	38
Diffuse load[c]	284			
Cd				
Point load (mean)[a]	10.6		1.6	0.7
Range	9.5–11.5		0.7–2.7	0.1–1.9
Point load[b]	6.0	2.6	1.1	0.8
Point load[c]	7			
Diffuse load (mean)[a]	15.3		5.9	3.9
Range	14.4–16.4		4.8–6.8	2.8–4.6
Diffuse load[b]	2.2	1.3	0.2	0.2
Diffuse load[c]	8			
TP				
Point load (mean)[a]	22,500 (28,000)	13,800 (17,000)	3,400 (5,600)	1,800 (3,200)
Range	20,500-24,700	12,800–15,000	2,900-3,900	500-2,100
Point load[b]	32,000	19,300	6,400	3,675
Diffuse load (mean)[a]	12,900 (12,600)	10,700 (7,500)	5,700 (1,700)	3,500 (1,925)
Range	10,700-14,900	9,500-11,700	5,200-6,200	3,200-3,800
Diffuse load[b]	8,600	5,200	900	1,450

[a] Calculation from this study. Data in parenthese are corrected values of the model considering rainwater overruns of combined sewage systems (see text).

[b] Data based on the inventory of priority substances in 1985 (ICPR, 1989; DKSR, 1989; Agence de l'eau Rhin-Meuse, 1988).

[c] Mean values for the time period 1984–1986.

[d] Estimates based on data from 1984–1987 only.

Source: Waterloopkundig Laboratorium 1989.

was estimated at 297 kt N a^{-1} by ICPR (1990) for the whole Rhine River basin (including the load from the Netherlands). A point load of approximately 260 kt N a^{-1} can be assumed from the ICPR estimation for the Rhine River basin at the Lobith station. Both estimations of the point load of nitrogen agree if it is taken into account that the results of the model does not include the particular nitrogen which is approximately 13% of the total nitrogen load (Wolf *et al.*, 1989). The diffuse load of nitrogen was estimated by ICPR (1990) at 140 kt N a^{-1} for the whole catchment area. This magnitude seems to be underestimated in comparison with our results (see *Table 4* in Section 4.3) and also with the calculations given by other authors (i.e., Werner *et al.*, 1991; Firk and Gegenmantel, 1986; Wolf *et al.*, 1989).

In general, the diffuse loads estimated are smaller in the ICPR inventory and the Dutch study than the diffuse loads calculated by our method. The Dutch estimates, however, are very crude, and in the case of the ICPR inventory some diffuse loads of pollutants are not even considered.

Nevertheless, in the case of cadmium, lead, and zinc the point loads estimated by the ICPR inventory are very close to the results of our analysis of net point loads. One exception is the point load of cadmium at the Lobith station where our estimated load is higher than the load given by the ICPR inventory. One reason for this discrepancy may be the different time periods estimated (1983–1987, on the one hand, and only 1985, on the other). The comparison with the Dutch study shows a higher point load only for zinc at the Lobith station. In the other cases, the gross point loads estimated are within the range of our results.

In all cases in *Table 2* the gross loads are close to our averages or within the upper range of our net loads with the exception of phosphorus. Our estimated point loads of phosphorus, based on average values, are only about 70% to 90% of the values given by the inventory of ICPR. The following reasons may help to explain these differences:

1. The assumption of the model, that flow dependent processes in the river can be disregarded, is not completely correct. For example, the comparison between our net point loads and the gross point loads of the inventories for the Mosel area shows that during times of lower discharge sedimentation eliminates more phosphorus and lead than zinc. The annual rate of sedimentation in the watercourses of

Germany is relatively small. It ranges between 2% and 10% of the total quantity of solids transported. Hellmann (1987) points out, however, that deposits of suspended solids may occur in very slow-flowing waters with regulated flow, e.g., in the Mosel, the Main, and the Neckar.

2. The point source flows at the different monitoring stations (see *Table 1*) are underestimated especially for the catchment area of the river Mosel.
3. The inventory of aqueous emissions from all municipal sewage plants includes not only point sources. According to the definition given in Section 3, the pollutant load caused by wash off from urban areas (e.g., dust load from streets and roofs) is a diffuse source. This means that the real gross point load of the inventory is smaller than the total point load given by the ICPR inventory. For lead, which is a major pollutant in urban areas, the diffuse load can be an important part of the total load from sewage plants. The Dutch study (Waterloopkundig Laboratorium, 1989) points out that the load from streets and the deposition in urban areas which travels through canals to sewage plants are considered point sources.
4. The estimated diffuse load based on our model includes, depending on the substance, a small number of the point sources which enter the river system at high discharges through rainwater overflows. This occurs because the combined sewage systems cannot transport all of the water volume to the sewage treatment plant during a storm. The proportion of storm water overruns compared to the total load of sewage treatment plants was estimated by Sperling (1986) to be 12% and 14% for phosphorus and nitrogen, respectively. If one assumes, as a maximum estimation, that all of the phosphorus load from storm water overflows is not influenced by diffuse urban sources, then the point loads of phosphorus at Lobith and Koblenz stations are higher by 3 and 2 kt P a^{-1}, respectively, and the diffuse loads are reduced by these magnitudes. The corrected values of the point and diffuse loads of phosphorus are given in parentheses in *Table 2*. Considering this change from diffuse load to point load of phosphorus our estimates are between 80% and 85% of the gross point loads estimated by ICPR (1989) and the studies of the diffuse load of phosphorus in the former West Germany (see Section 4.4; Werner *et al.*, 1990; Firk and Gegenmantel, 1986).

5. In the case of phosphorus, one must consider that input from point sources is reduced within the time period 1983–1987. Hamm (1989) states that the total phosphorus point load in West Germany was reduced from 56.3 kt P a^{-1} in 1985 to 47.6 kt P a^{-1} in 1987.

In general, the error in the estimation of point loads is at least 10% or more as demonstrated by the comparison between the Dutch estimations of point loads (Waterloopkundig Laboratorium, 1989) and the ICPR inventory for the Lobith station. There are numerous possible explanations for the differences between our results and the others, and no unambiguous explanation can be given.

Therefore, it will be assumed that the model results with regard to the amount of net point load are approximately correct with the exception of the river Mosel, where sedimentation at low discharges and resuspension during floods cannot be excluded.

Several authors (Hamm, 1989; Firk and Gegenmantel, 1986; Werner *et al.*, 1991) have recently published detailed balances of phosphorus and nitrogen for the former West Germany. The results of these investigations can also be used to test the estimations based on our model. The most detailed analysis of the diffuse sources of nitrogen and phosphorus is given by Werner *et al.* (1991).

The portion of the diffuse load in the total load was estimated to be 57% and 42% for nitrogen and phosphorus, respectively. We found that for the catchment area of the Rhine (Lobith station) the portion of the diffuse load in the total load is 50% to 60% for dissolved inorganic nitrogen (NH_4+NO_3) and 30% to 35% for total phosphorus. Both relations are in a good agreement with the results of Werner *et al.* (1991), considering that the German part dominates the total catchment area of the river Rhine at Lobith, and that phosphorus load by erosion is smaller for big catchment areas.

An important test for the results of the model is its capability of detecting large changes in the diffuse and point loads over time by observing a change in the type of concentration–flow/load–flow relationships from the one shown in *Figure 3A* ($K_P < K_D$) to the one shown in *Figure 3B* ($K_P > K_D$). An example of such a change is presented in *Figure 8*.

The figure shows the dependence of nitrate concentration and load on the discharge at the Lobith station for the 1953–1957 and 1983–1987 time periods. Additionally the figure includes the estimations calculated

Table 3. Results of the model for nitrate concentration at the Lobith station.

	1953–1957	1983–1987
Results of regression $L_t = K_D \cdot Q_t + L_0$		
K_D (mg N l^{-1})	2.090	3.500
$L_0 = Q_P(K_P - K_D)$ (kg N s^{-1})	-0.745	1.290
r	0.895	0.909
n	112	131
Estimated net point load		
($Q_P = 850 - 950$ m^3 s^{-1}) (kt N a^{-1})	18–40	110–147
Estimated net diffuse load (kt N a^{-1})	74–96	170–207

by the model for these two different time periods. The model coefficients based on these data are given in *Table 3*. The coefficients were estimated on the basis of the load–discharge relationships for each time period, and applied without changes to either of these concentration–discharge relationships.

The results of the model can be used to reproduce the changes over time. In the 1950s the concentration of the diffuse load of nitrate was only about 60% of the concentration in the 1980s. But the point load of nitrate also changed over time due to the installation of industrial and municipal sewage treatment plants with biological nitrification capabilities. This change is reflected in the model by a change in the parameter (L_0) of the regression from $L_0 < 0$ to $L_0 > 0$ (*Table 3*).

The reason for this behavior is that in the 1950s the mean nitrate concentration from point sources was smaller than the concentration from diffuse sources, but in the 1980s the opposite was true. If we assume that the water flow of all point sources was approximately the same in the 1950s and 1980s then the nitrate load from point sources increased fourfold to fivefold in the last 40 years.

Detailed phosphorus balances are available for West Germany for the years 1975, 1985, and 1987 (Bernhardt, 1978; Firk and Gegenmantel, 1986; Hamm, 1989). It can be inferred from these studies that the phosphorus point load was reduced by approximately 70% from the 1970s to the 1980s. According to our model the reduction of the phosphorus point load is calculated to be about 68%.

These comparisons demonstrate that the model proposed can approximately simulate the amounts from different sources of pollutants within a river and its changes with time.

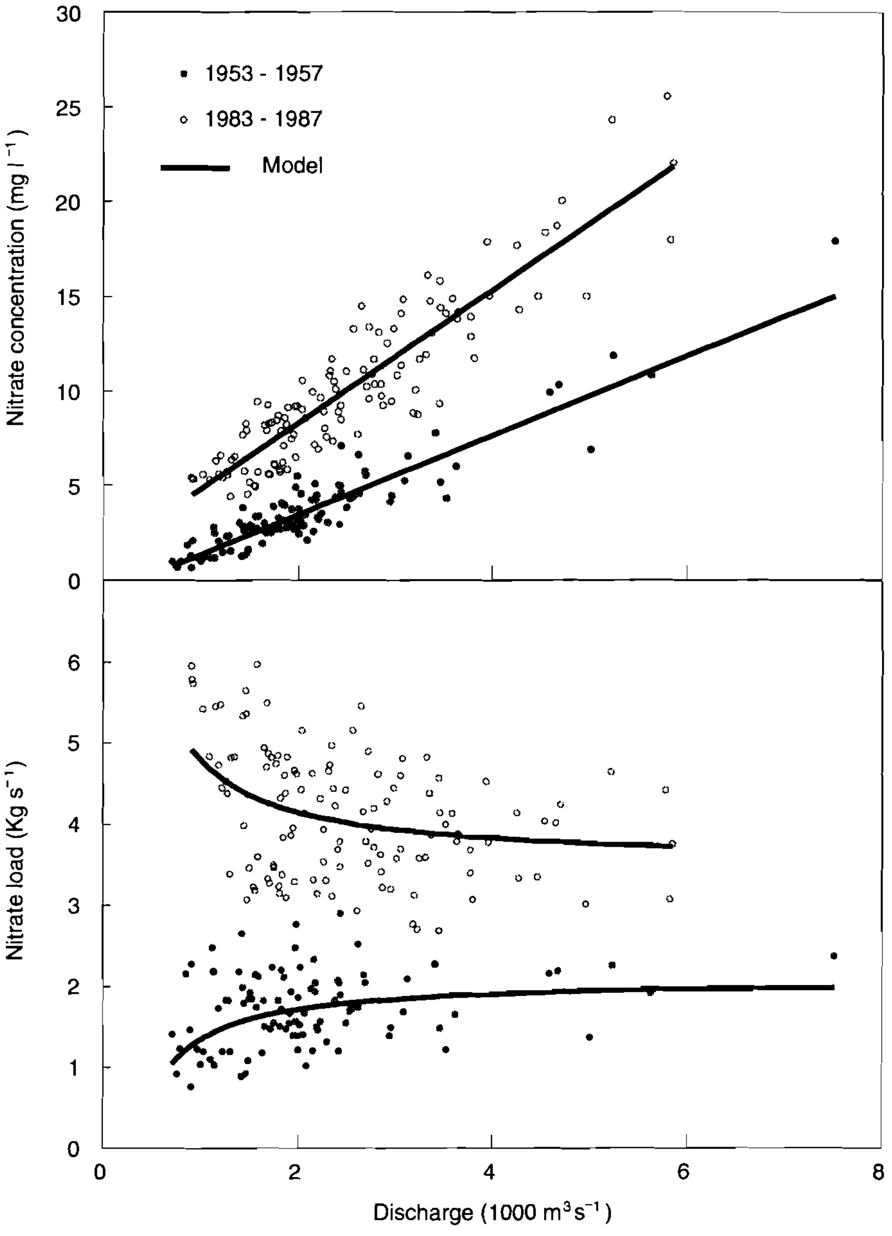

Figure 8. Changes in the nitrate concentration–discharge/load–discharge relationships at the Lobith station for the time periods 1953–1957 and 1983–1987. See *Table 3* for results of regression.

4.3 Analysis of point and diffuse loads of pollutants within the catchment area of the Rhine: 1973–1987

An overview of the diffuse, point, and total net loads into the river Rhine and its tributaries (Mosel, Main, and Neckar) is given in *Table 4*. The analysis includes the changes in point and diffuse loads at the Rhine monitoring stations in Lobith, Koblenz, and Seltz for various time periods beginning in the mid-1970s with additional estimate for the period 1983–1987 at the Neckar, Main, and Mosel stations. These results are also shown for each pollutant investigated at the Rhine stations in Koblenz and Lobith in the *Figures 9* through *13*.

With the exception of DIN the total load for all pollutants investigated has been reduced since 1973, especially in the case of the heavy metals (*Tables 4* and *5*). With regard to the diffuse load, the changes are less certain and not uniform for all chemicals.

As shown in *Table 5* the decrease of the diffuse load of cadmium was highest with an average reduction of 42% over the whole time period. Also in the case of zinc a reduction in the diffuse load can be detected from 1973 to 1987 based on the averages for the different time periods. The mean decrease of diffuse zinc load was estimated at 30%.

The rate of decrease of the diffuse load of zinc and cadmium from 1978–1982 to 1983–1987 was higher than the change from 1973–1977 to 1978–1982. This can be explained by the higher proportion of high discharges in the total discharge during 1978–1982 (see *Table 7* in Section 4.4).

An increase of diffuse load by erosion and storm runoff from urban areas can be expected, especially at high-discharge areas where surface flow dominates.

The changes in the loads of diffuse cadmium, lead, and zinc since 1973 are most likely caused by the reduction of dust emissions from industrial and urban point sources, i.e., localized dry deposition from atmospheric emissions. A 50% reduction of dust emissions has been estimated to have occurred between 1973–1977 and 1983–1987 in West Germany (statistical yearbooks of the FRG).

With regard to the diffuse urban load, further reasons for the reductions are the enhanced elimination of heavy metals from urban storm water by the rapid increase in the installation of secondary sewage treatment plants in the early 1970s and decreased rates of zinc corrosion caused by the reduction of SO_2 deposition since the mid-1960s. For

Table 4. Estimated total, point, and diffuse loads of nitrogen, phosphorus, zinc, lead, and cadmium at different monitoring stations along the Rhine and its main tributaries (Neckar, Main, and Mosel).

River										
Station		TP (kt a^{-1})			N (kt a^{-1})			N_{corr} (kt a^{-1})		
Period		Min.	Mean	Max.	Min.	Mean	Max.	Min.	Mean	Max.
Rhine	Total load		35.4			356			505	
Lobith	Point	20.5	22.5	24.7	156	167	179	252	262	273
1983–1987	Point (%)	58.0		70.0	44		50	50		54
	Diffuse	10.7	12.9	14.9	178	189	200	232	243	253
	Diffuse (%)	30.0		42.0	50		56	46		50
Rhine	Total load		41.4			359			480	
Lobith	Point	24.2	26.5	29.0	126	137	149	233	243	254
1978–1982	Point (%)	58.0		70.0	35		42	48		53
	Diffuse	12.5	15.0	17.3	210	221	232	226	237	247
	Diffuse (%)	30.0		42.0	58		65	47		52
Rhine	Total load		50.3			284			407	
Lobith	Point	31.6	34.6	37.8	133	146	159	232	245	258
1973–1977	Point (%)	63.0		75.0	47		56	57		63
	Diffuse	12.6	15.8	18.7	124	138	151	149	163	176
	Diffuse (%)	25.0		37.0	44		53	37		43
Rhine	Total load		24.5			216			336	
Koblenz	Point	12.8	13.8	15.0	83	91	99	131	141	151
1983–1987	Point (%)	52.0		61.0	38		46	39		45
	Diffuse	9.5	10.7	11.7	117	126	133	184	195	204
	Diffuse (%)	39.0		48.0	54		62	55		61
Rhine	Total load		32.5			213			315	
Koblenz	Point	15.5	16.5	17.7	50	58	67	119	128	138
1978–1982	Point (%)	48.0		55.0	23		31	38		44
	Diffuse	14.7	15.9	17.0	146	155	163	177	187	196
	Diffuse (%)	45.0		52.0	69		77	56		62

Table 4. Continued.

River Station Period		TP (kt a^{-1})			N (kt a^{-1})			N_{corr} (kt a^{-1})		
		Min.	Mean	Max.	Min.	Mean	Max.	Min.	Mean	Max.
Rhine	Total load		30.5			138			240	
Koblenz	Point	15.9	17.1	18.3	51	59	68	106	117	128
1973–1977	Point (%)	52		60	37		49	44		53
	Diffuse	12.1	13.4	14.6	71	79	88	112	123	134
	Diffuse (%)	40		48	51		63	47		56
Rhine	Total load		9.1			118			163	
Selz	Point	2.9	3.4	3.9	25	32	40	23	32	42
1983–1987	Point (%)	32		43	21		34	14		26
	Diffuse	5.2	5.7	6.2	78	86	93	121	131	140
	Diffuse (%)	57		68	66		79	74		86
Rhine	Total load		20.7			119			171	
Selz	Point	11.2	13.4	16.3	6	16	28	8	23	40
1978–1982	Point (%)	54		79	5		23	5		23
	Diffuse	4.3	7.2	9.5	91	102	112	132	148	163
	Diffuse (%)	21		46	77		95	77		95
Neckar	Total load		3.1			34			40	
Mannheim	Point	2.1	2.3	2.5	18	21	24	22	25	28
1983–1987	Point (%)	66		80	54		70	56		72
	Diffuse	0.6	0.9	1.1	10	13	16	11	14	17
	Diffuse (%)	20		34	30		46	28		44
Main	Total load		5.8			54			57	
Kostheim	Point	2.7	3.0	3.3	24	26	29	28	30	33
1983–1987	Point (%)	47		57	45		53	49		58
	Diffuse	2.5	2.8	3.1	26	28	30	24	27	29
	Diffuse (%)	43		53	47		55	42		51
Mosel	Total load		5.3			56			63	
Koblenz	Point	1.5	1.8	2.1	8	12	16	13	16	21
1983–1987	Point (%)	29		40	15		28	20		32
	Diffuse	3.2	3.5	3.8	40	44	48	43	47	51
	Diffuse (%)	60		71	72		85	68		80

Table 4. Continued.

River Station Period		Zn (t a^{-1})			Pb (t a^{-1})			Cd (t a^{-1})		
		Min.	Mean	Max.	Min.	Mean	Max.	Min.	Mean	Max.
Rhine	Total load		4,946			704			25.9	
Lobith	Point	1,753	2,134	2,548	189	240	294	9.5	10.6	11.5
1983–1987	Point (%)	35		52	23		42	37		45
	Diffuse	2,397	2,812	3,192	410	465	515	14.4	15.3	16.4
	Diffuse (%)	48		65	58		73	55		63
Rhine	Total load		9,562			805			96.1	
Lobith	Point	4,978	6,070	7,286	212	265	323	68.9	76.5	84.8
1978–1982	Point (%)	52		76	26		40	72		88
	Diffuse	2,276	3,491	4,584	482	540	593	11.2	19.6	27.1
	Diffuse (%)	24		48	60		74	12		28
Rhine	Total load		10,164			1,502			145.1	
Lobith	Point	4,324	6165	8,013	168	872	1,502	106.6	118.9	132.4
1973–1977	Point (%)	43		79	11		100	73		91
	Diffuse	2,420	3,999	5,840	0	630	1,333	12.7	26.2	38.5
	Diffuse (%)	21		57	0		89	9		27
Rhine	Total load		2,709			329				
Koblenz	Point	400	595	814	68	81	95			
1983–1987	Point (%)	15		30	21		29			
	Diffuse	1,895	2,114	2,309	234	248	261			
	Diffuse (%)	70		85	71		79			
Rhine	Total load		3,431			402			22.5	
Koblenz	Point	1,111	1,480	1,912	73	102	134	8.4	9.9	11.7
1978–1982	Point (%)	32		56	18		33	37		52
	Diffuse	1,519	1,951	2,320	268	300	329	10.8	12.6	14.1
	Diffuse (%)	44		68	67		82	48		63

Table 4. Continued.

River Station Period		Zn (t a^{-1})			Pb (t a^{-1})			Cd (t a^{-1})		
		Min.	Mean	Max.	Min.	Mean	Max.	Min.	Mean	Max.
Rhine	Total load		3,661			307			24.6	
Koblenz	Point	839	1,241	1,700	158	191	230	1.9	5.6	10.0
1973–1977	Point (%)	23		46	51		75	8		40
	Diffuse	1,962	2,420	2,822	77	117	150	14.7	19.0	22.7
	Diffuse (%)	54		77	25		49	60		92
Rhine	Total load		1,218[a]			161			7.5	
Selz	Point	57	180	326	12	27	46	0.7	1.6	2.7
1983–1987	Point (%)	5		27	7		29	9		36
	Diffuse	893	1,028	1,161	115	134	150	4.8	5.9	6.8
	Diffuse (%)	73		95	71		93	64		91
Rhine	Total load		3,456			482			44.9	
Selz	Point	1,217	1,554	1,968	348	395	456	27.5	31.3	36.2
1978–1982	Point (%)	34		57	72		95	61		81
	Diffuse	1,470	1,901	2,239	25	102	134	8.7	13.6	17.3
	Diffuse (%)	43		65	5		28	19		39
Neckar	Total load		254							
Mannheim	Point	134	169	208						
1983–1987	Point (%)	53		82						
	Diffuse	46	85	120						
	Diffuse (%)	18		47						
Main	Total load		1,189			64			2.5	
Kostheim	Point	398	510	638	2	7	13	0.8	1.0	1.2
1983–1987	Point (%)	33		54	3		20	32		47
	Diffuse	551	679	791	52	57	62	1.3	1.5	1.7
	Diffuse (%)	46		67	80		97	53		68
Mosel	Total load		1,096			169			4.7	
Koblenz	Point	0	164	391	11	31	58	0.1	0.7	1.9
1983–1987	Point (%)	0		436	7		34	2		40
	Diffuse	705	932	1,096	111	138	158	2.8	3.9	4.6
	Diffuse (%)	64		100	66		93	60		98

[a] Based on 1984–1987 data.

Table 5. Changes of loads into the river Rhine at the Lobith station from 1973 to 1987. All values are in percent; loads from the 1973–1977 time period are expressed as 100%.

		1973–1977	1978–1982	1983–1987
DIN	Total load	100	126	125
	Point load	100	94	114
			86–102	107–123
	Diffuse load	100	160	137
			152–168	129–145
TP	Total load	100	82	70
	Point load	100	77	65
			70–84	59–71
	Diffuse load	100	95	82
			79–109	68–95
Cd	Total load	100	66	18
	Point load	100	64	9
			58–71	8–10
	Diffuse load	100	75	58
			43–103	54–63
Pb	Total load	100	54	47
	Point load	100	34	28
			14–30	22–34
	Diffuse load	100	81	74
			54–108	65–82
Zn	Total load	100	94	49
	Point load	100	98	35
			81–118	85–41
	Diffuse load	100	87	70
			57–115	60–80

phosphorus, the estimated mean diffuse load in 1973–1977 was a little higher than the load in the 1978–1982 period, the likely reason being the installation of secondary sewage treatment plants.

A more detailed analysis of the causes of observed trends in diffuse loads can be given only on the basis of studies of the different sources of diffuse loads and their changes over time. Such an analysis is given for heavy metals in Section 4.4. In general, the trends estimated in the diffuse load of heavy metals are rather uncertain particularly for the first two time periods analyzed, because application of our method was

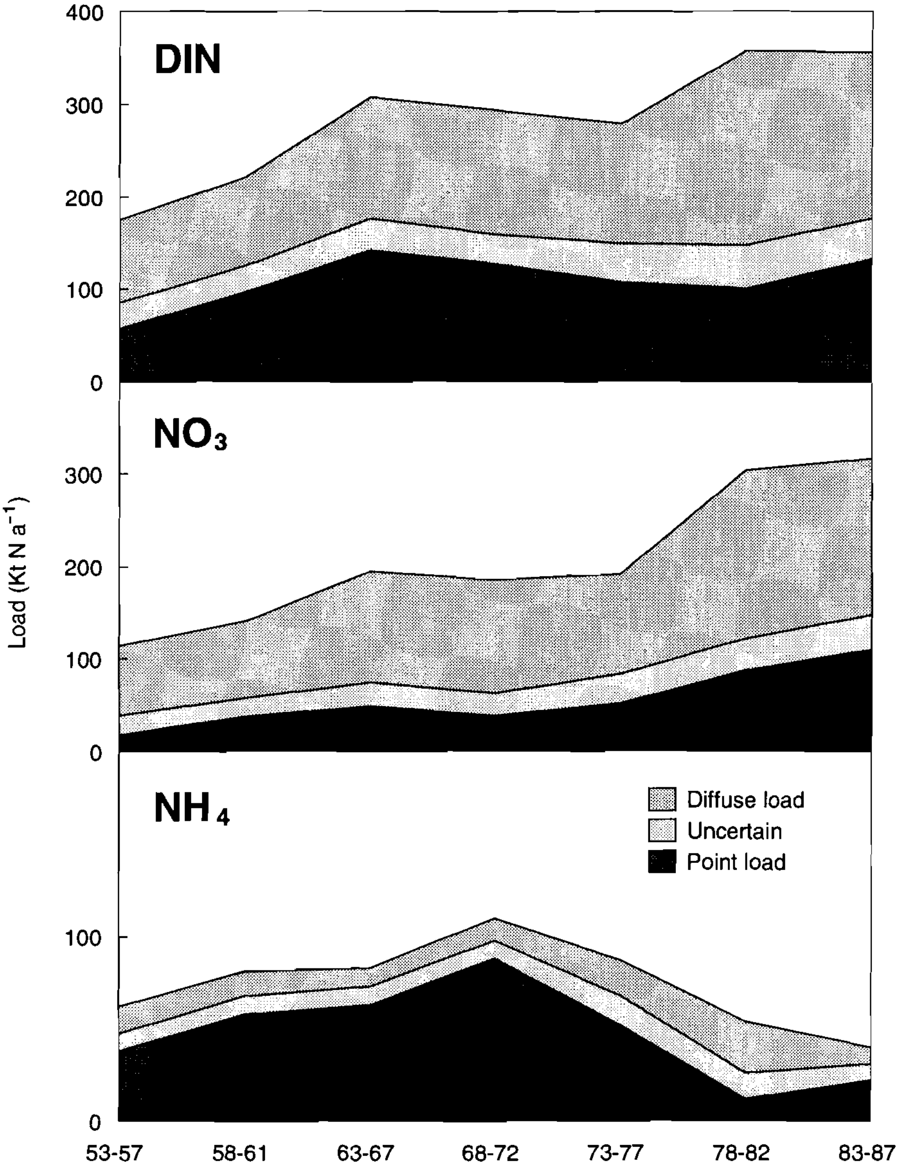

Figure 9. Changes of estimated point and non-point loads of ammonia, nitrate, and dissolved inorganic nitrogen (DIN) at the Rhine monitoring station in Lobith since the mid-1950s.

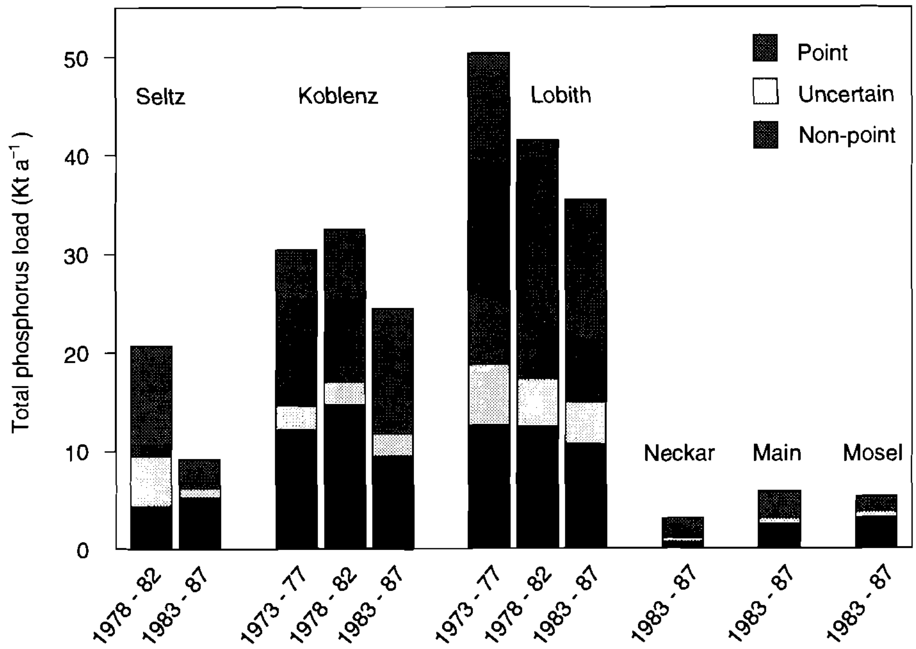

Figure 10. Estimated point and diffuse loads of total phosphorus (TP) at the Rhine monitoring station in Koblenz and Lobith since the mid-1970s and for later time periods at the Rhine monitoring stations in Seltz and along the Neckar, Main, and Mosel tributaries.

limited by the low number of measurements compared with the 1983–1987 time period.

A small decline of the diffuse load was estimated over the whole time period for phosphorus. In contrast, there was a large reduction of the point load of phosphorus caused by the increasing elimination of phosphorus in detergents.

The causes for the reduction of the diffuse phosphorus load are not certain. Three reasons are possible:

1. According to Bernhardt (1978), combustion of coal generates particles and dust with a phosphorus content of about 1%. Therefore a reduction in dust emissions as occurred in the Rhine basin since the mid-1970s must result in a reduction in phosphorus deposition,

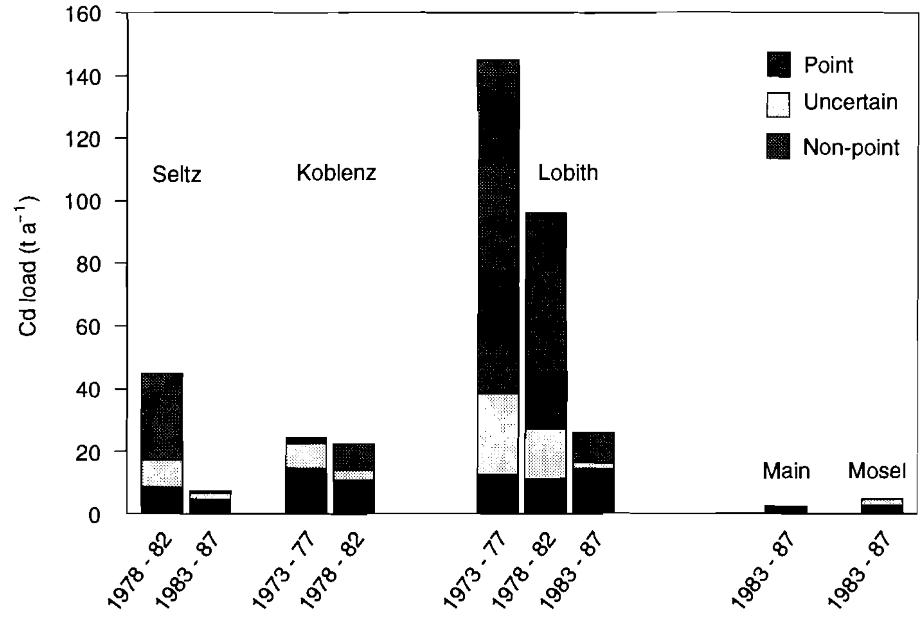

Figure 11. Estimated point and diffuse loads of cadmium at the Rhine monitoring stations in Koblenz and Lobith since the mid-1970s and for later periods at the Rhine monitoring stations in Seltz and along the Neckar, Main, and Mosel tributaries.

especially in urban and industrial areas where local fallout of particulate matter is expected to be most significant. But as shown in Section 4.4, the contribution of atmospheric deposition and direct surface flow of rainwater into the river is smaller than the contribution of other sources to the diffuse load of phosphorus.

2. The load from urban areas is not taken into account as a diffuse source of the pollutant load in most studies on the phosphorus balance. As noted by Behrendt (1991) the proportion of the urban diffuse load of phosphorus is approximately 20% of the total diffuse load of phosphorus in eastern Germany. The proportion of urban area in the total area is much higher in the Rhine River basin than in eastern Germany. Therefore as a first crude estimate, it can be assumed that the proportion of the urban diffuse load to the total load is at least 20% in the Rhine watershed, too. In this case a

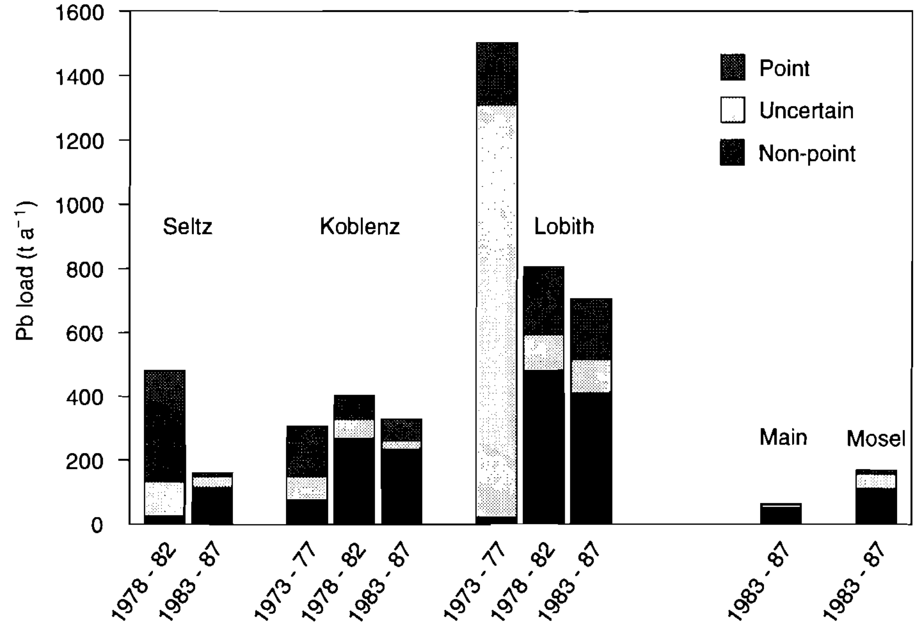

Figure 12. Estimated point and diffuse loads of lead at the Rhine monitoring stations in Koblenz and Lobith since the mid-1970s and for later periods at the Rhine monitoring stations in Seltz and along the Neckar, Main, and Mosel tributaries.

reduction of dust emission of 50% can contribute to a decrease of about 10% of the total diffuse load of phosphorus.

3. During storm events combined urban sewer systems do not transport all of the wastewater to the municipal sewage treatment plants. Part of the wastewater overflows the sewage treatment plant and directly enters the river or flows to special rainwater reservoirs. According to Sperling (1986) the magnitude of the phosphorus load in rainwater overruns is approximately 12% of the total load of municipal sewage treatment plants. Furthermore, in the case of phosphorus the efficiency of a sewage treatment plant in removing phosphorus from the wastewater is reduced by approximately 10% during storm periods. This phenomenon further contributes to an increase in the total phosphorus load during periods of high discharge.

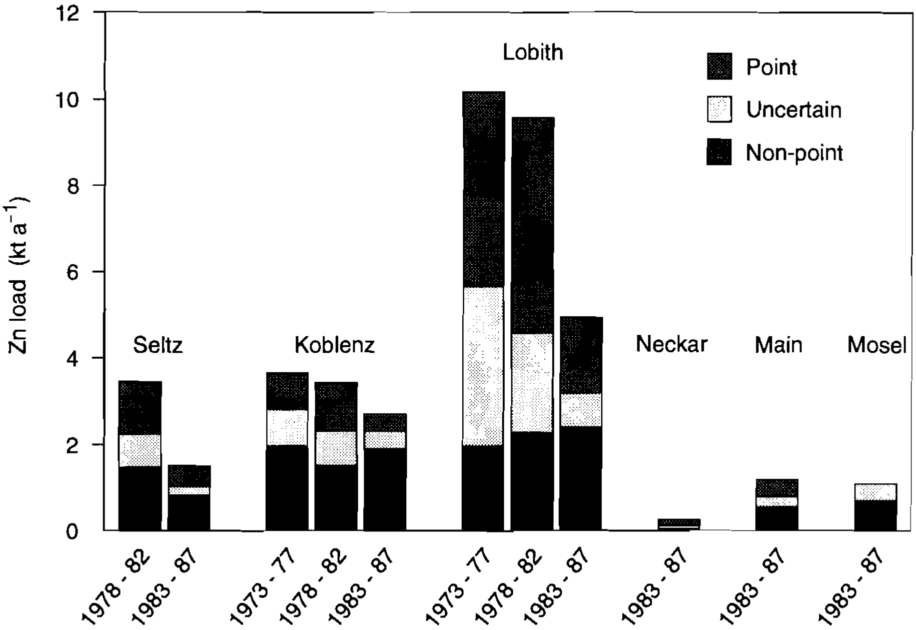

Figure 13. Estimated point and diffuse loads of zinc at the Rhine monitoring stations in Koblenz and Lobith since the mid-1970s and for later time periods at the Rhine monitoring stations in Seltz and along the Neckar, Main, and Mosel tributaries.

> According to our model, both cases – rainwater overruns and decreased efficiency of sewage treatment plants during a storm event – are categorized as diffuse sources. Therefore, a decrease in the point load of municipal sewage treatment plants leads, to a small extent, to a decrease of the total diffuse load.

As shown in *Table 5* and *Figure 9*, only dissolved inorganic nitrogen shows an increase in the total load as well as the diffuse load over the three time periods. The increase of the diffuse DIN load was about 50% between 1973–1977 and 1983–1987. This phenomenon can be explained by the 30% lower average discharge at the Lobith station in the 1973–1977 time period compared with the later periods. On the other hand, the estimated concentration of diffuse DIN load is more than 25% higher during the 1978–1982 and 1983–1987 periods than during 1973–1977.

Figure 9 shows the changes in the load of nitrate, ammonia, and dissolved inorganic nitrogen over time since 1953 as estimated by our model. As shown in this figure the proportion of the diffuse load of ammonia is low compared with the total load except for the last two time periods. The magnitude of the diffuse load of ammonia, however, did not change significantly over time. The point load of ammonia increased from the early 1950s to the late 1960s. This trend was the result of growing industrial production (especially for the chemical industry) and the increased deployment of sewer systems and wastewater treatment plants without nitrification. Since the late 1960s the magnitude of ammonia point load has decreased to values lower than those of the early 1950s. The point load of ammonia seems to be constant in the last 10 years. The decline in the ammonia point load resulted from the introduction of a nitrification process in most of the municipal and industrial sewage treatment plants since the 1970s.

In contrast, the point load of nitrate is increasing, particularly since the late 1960s. The estimated total point load of dissolved inorganic nitrogen seems to be nearly constant since the 1960s. But the total load of dissolved inorganic nitrogen has increased over the entire time period because of the increase in the diffuse load of nitrate. This increase is particular noticeable in the last two time periods. This trend is in accordance with the growing number of nitrate problems in drinking water caused by groundwater pollution since the late 1970s. The main reason for these problems is the large imbalance between inputs of nitrogen fertilizer and manure and crop uptake of nitrogen within the Rhine River basin (see, e.g., Isermann, 1990; Behrendt, 1988; Souchu and Etchanchu, 1988).

4.4 Estimation of the sources of diffuse load within the Rhine

Based on the model approaches of case B (see Section 3), mean weighted net concentrations of the diffuse load at low and high flow rates can be estimated for each pollutant investigated. An overview of the estimated mean concentrations of substances related to interflow and surface flow for the different catchment areas of the river Rhine is given in *Table 6*. The table shows strong differences between the mean concentration of pollutants at low (interflow-dominated) and high (surface-flow-dominated) discharges.

Table 6. Estimated concentrations of subsurface flow (K_S) and surface runoff (K_R) at different monitoring stations of the Rhine River basin. All values are in milligrams per cubic meter.

		Rhine Lobith	Rhine Koblenz	Mosel Koblenz	Rhine between Koblenz and Lobith
Zn	K_S	54.00	49.00	48.0	53.0
	K_R	99.00	111.00	155.0	376.0
Pb	K_S	8.20	5.60[a]	5.8[a]	10.9
	K_R	21.50	11.70	27.3	68.2
Cd	K_S	0.31	0.16		0.2
	K_R	0.36	0.37		1.3
Fe	K_S	1,540.00	810.00	860.0	3,230.0
	K_R	6,640.00	4,850.00	9,950.0	7,160.0
TP	K_S	127.00	185.00	310.0	263.0
	K_R	532.00	421.00	660.0	917.0

[a] Most values represent the limit of measurement of 5 micrograms per liter. Therefore, the estimated K_S is probably too high. Database: Zahlentafeln 1983–1987, Internationale Kommission zum Schutze des Rheins gegen Verunreinigung.

At the Mosel station in Koblenz the concentration of iron during high discharges is more than tenfold higher than during low discharges. For lead the difference also is high (by a factor of 4.7) at this station. The ratio of concentrations of iron at high and low discharges are smaller at the Rhine stations in Lobith and Koblenz, but they are nevertheless still large (by factors of 4.3 and 6, respectively).

The ratio of concentration differences for zinc, lead, and phosphorus are approximately the same, varying from a factor of 1.8 (zinc at the Rhine monitoring station in Koblenz) to a factor of 3.2 (zinc at the Mosel monitoring station in Koblenz).

In general the concentrations of elements during high discharges are higher within the Mosel watershed than at the Rhine monitoring stations in Koblenz and Lobith. With regard to the concentrations of pollutants during periods of low discharges, the differences observed for different stations are smaller than during periods with high discharges.

The picture is different for the watershed between Koblenz and Lobith (excluding the Mosel River basin). In this area industrial and urban influences dominate the diffuse loads. For zinc, lead, and cadmium the estimated ratio between the concentration at high and low discharges is 7.1, 6.7, and 6.5, respectively.

Table 7. Ratio of the sum of high discharge (Q_H) to the sum of total discharge at the Rhine stations in Lobith and Koblenz, for different time periods. High discharges are defined as $Q < 5{,}000$ cubic meters per second at the Lobith station and $Q > 3{,}500$ cubic meters per second at the Koblenz station.

	1973–1977	1978–1982	1983–1987
Koblenz			
$\sum(Q_H)/\sum(Q)$	0%	13%	8%
Lobith			
$\sum(Q_H)/\sum(Q)$	3%	13%	7%

The estimated total phosphorus concentration at high discharges is also higher than the estimated values for the monitoring station. For iron the concentration at high discharges does not differ appreciably from the monitoring station, but the mean concentration of diffuse load at low discharges is two to three times higher in the area between Koblenz and Lobith.

These estimated high concentrations of diffuse load during periods with high discharges indicate the extreme importance of river pollution from urban areas during storm events. For the part of the Rhine basin between Koblenz and Lobith these estimated concentrations are comparable with the concentrations from separate sewer systems and combined sewer overflows (NWRW, 1989; Ellis, 1988).

If the portion of high flows and floods is known then the load from diffuse sources at low and high discharges can be calculated from the total estimated diffuse load. Werner *et al.* (1991) and Hellmann (1987) have assumed that approximately 10% of the total runoff is caused by floods. This means that approximately 7.9 billion cubic meters per year of the discharge at the Rhine station in Lobith are caused by floods.

Table 7 presents an overview of the ratio between high discharge and the total discharge at the Rhine stations in Lobith and Koblenz for the three time periods investigated. It is shown that this ratio ranges between 0% (Koblenz station, 1973–1977) and 13% (both stations, 1978–1982). The estimated ratios agree, on average, with the magnitude of floods given by Werner *et al.* (1991).

The estimated contribution of these floods to the total diffuse load of the pollutants is given in *Table 8*. According to *Table 8* approximately 23% to 51% of the total diffuse load of pollutants are transported by

Table 8. Estimated means of diffuse loads caused by low and high discharges at the Rhine monitoring station in Lobith in the 1983–1987 period (based on the assumption that 10% of the total discharge is caused by floods).

	Zn ($t\ a^{-1}$)	Pb ($t\ a^{-1}$)	Cd ($t\ a^{-1}$)	Fe ($kt\ a^{-1}$)	TP ($kt\ a^{-1}$)
$\mathrm{Load}_{\mathrm{highflow}}$	780	170	2.8	52	4.2
$\mathrm{Load}_{\mathrm{lowflow}}$	2,220	323	9.7	49	8.8
$\frac{\mathrm{Load}_{\mathrm{highflow}}}{\mathrm{Total\ diffuse\ load}}$	26%	31%	23%	51%	32%

10% of the water flow during floods. This means that the transport of pollutants during high flow periods is important to the total diffuse load. The sources of this load are mainly the erosion of particulate material from land, the direct flow from rainwater into the rivers, and the direct runoff from urban areas during storm events by the overflow of sewage systems. It is not possible to use our method to distinguish further between the various sources of pollutant loads without additional information.

In the following sections we attempt to identify and quantify more precisely the sources of the total diffuse loads of each pollutant using information on land use, deposition, and soil content. These analyses must be viewed as rough estimates.

Nitrogen

Werner *et al.* (1991) have conducted a detailed study of the sources of the diffuse load of nitrogen in West Germany. In addition, Firk and Gegenmantel (1986) give an overview of the main sources of the nitrogen load into the surface waters of West Germany. The results of these studies can be applied to the total catchment area of the river Rhine (*Table 9*). The conversion based on the different areas was made by comparing the total diffuse loads at the Lobith station with the total loads for West Germany.

The values in parentheses in the first column in *Table 9* present the results of Werner *et al.* (1991) for watersheds with an area greater than 1,000 km^2. In this case the load of particulate nitrogen caused by erosion is lower for large watersheds than for small watersheds, because additional sinks of particulate material have to be considered. The values in

Table 9. Sources and pathways of diffuse nitrogen load within the catchment area of the river Rhine.

	Diffuse nitrogen load in 1983–1987 (kt N a^{-1})	
Source	Werner *et al.* (1991)	Firk & Gegenmantel (1986)
Atmosphere	6	25 (53)
Surface runoff	7	
Erosion		7
Dissolved	9	
Particular	21 (5)	
Groundwater	169	104
Drainage	25	14
Agriculture	18	26
Urban area		2 (4)
Other		8
Sum	255 (239)	186 (217)
Estimated diffuse load at Lobith (see *Table 4*)		178 - 214

parentheses in the second column show the magnitude of nitrogen load caused by surface runoff and urban areas, if the ammonia deposition is included.

As shown in *Table 9* the sum of all diffuse sources estimated on the basis of the data in Werner *et al.* (1991) is approximately one-third higher than our values. The main reason for this discrepancy is the occurrence of the nitrogen-loss process to the atmosphere (mainly denitrification of nitrate) that reduces the actual nitrogen load entering the river. Furthermore, our estimates do not include the small amount of particulate nitrogen, because the total nitrogen was not measured. Werner *et al.* (1991), however, do not include the load from urban areas as a separate diffuse source, although, based on the estimates of Firk and Gegenmantel (1986), this load seems to be low.

The sum of the different sources of diffuse load based on conversion of the results of Firk and Gegenmantel (1986) is within the range of our estimates. But it must be noted that the assumption of these authors for wet deposition of nitrogen (8 kg N ha^{-1} a^{-1}) is low compared with the estimates of other authors. According to NLW (1986) the wet deposition of nitrogen is between 10 and 22 kg N ha^{-1} a^{-1} in rural areas of Niedersachsen. The arithmetic mean was estimated to be 17 kg N ha^{-1}

a^{-1}. Brechtel (1989) gives a range of the wet deposition of dissolved inorganic nitrogen between 6.6 and 31.3 kg N ha^{-1} a^{-1} (arithmetic mean 15.7 kg N ha^{-1} a^{-1}). If it is assumed that the wet deposition of nitrogen (NO_3 + NH_4) is 17 kg N ha^{-1} a^{-1}, then the load from the atmosphere is about 53 kt N a^{-1} (values in parentheses in the Firk and Gegenmantel column of *Table 9*). If this change is considered the total diffuse load estimated on the basis of results of Firk and Gegenmantel (1986) is about 217 kt N a^{-1}.

For nitrogen, it is also necessary to correct the measured concentrations as a function of temperature, because nitrogen compounds in water are strongly influenced by temperature-dependent processes like nitrification and denitrification (Hellmann, 1987). The result, obtained by applying an exponential relationship (see *Figure 14*), is the hypothetical nitrogen concentration (N-corr) which would occur at 0° C, a temperature at which none of these processes are important. After eliminating the temperature-dependent effects, a significant increase in the correlation coefficient was obtained for the DIN load–discharge relationship (see *Figure 15*).

The influence of oxygen concentration on denitrification was not considered. Although the O_2 concentration near the sediment is important, it was not monitored.

If we take the temperature correction into account with regard to our calculated range for the diffuse nitrogen load, then the corrected range amounts from 237 to 275 kt a^{-1}. This value is directly comparable with the total gross load value estimated by Werner *et al.* (1991). The corrected total load of dissolved inorganic nitrogen at the Lobith station (505 kt a^{-1}, see *Table 4*) agrees with the magnitude estimated by Wolf *et al.* (1989).

The difference between the estimated net load and the gross load of dissolved inorganic nitrogen can be explained mainly by denitrification in the water of the Rhine River. But algal growth during spring and summer also leads to a reduction of dissolved inorganic nitrogen. Both processes reduce the DIN concentration and are strongly dependent on temperature. Furthermore, the load of particulate organic nitrogen from sewage treatment plants and various diffuse sources must be considered.

The magnitude of DIN load losses at the station in Lobith was estimated to be approximately 150 kt N a^{-1}. The proportion of denitrification, transport, and transformation of particulate nitrogen in the

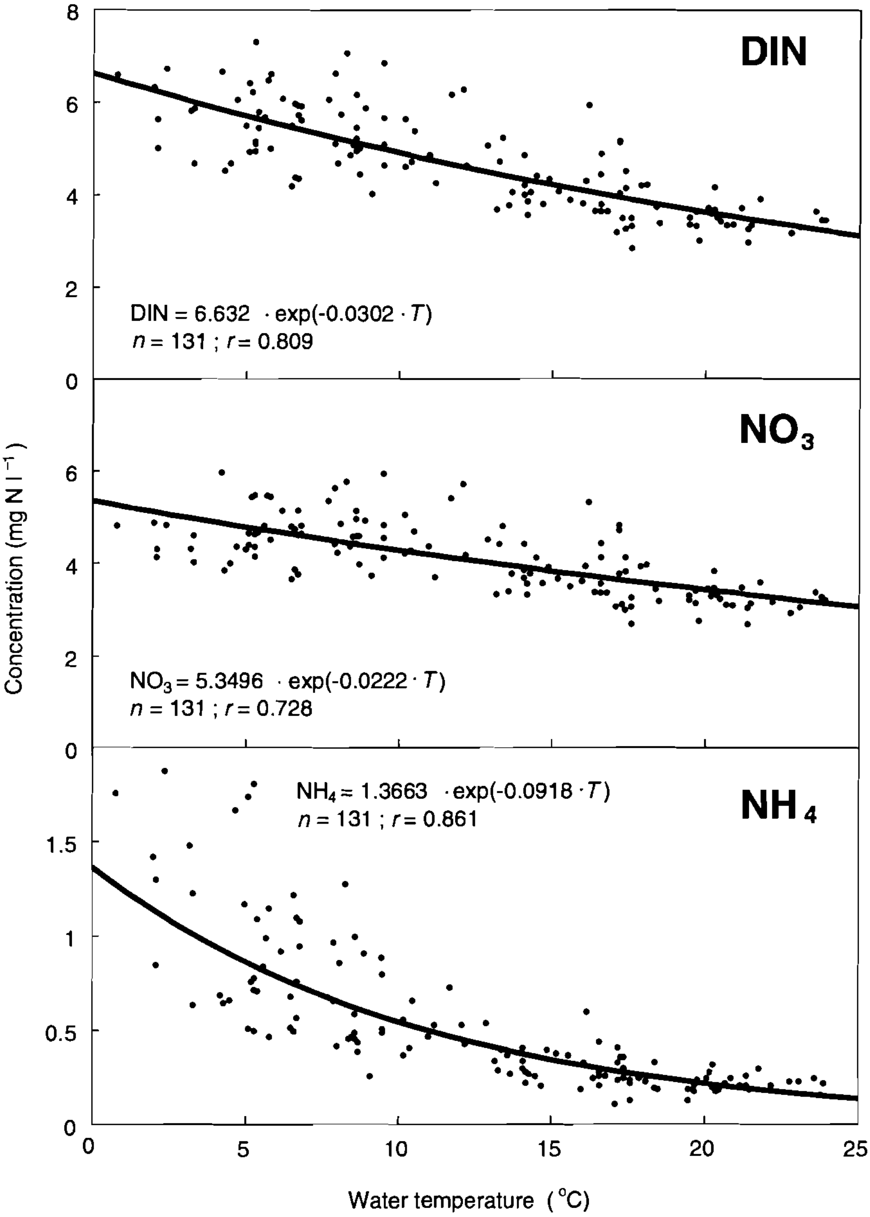

Figure 14. Dependencies of ammonia, nitrate, and dissolved inorganic nitrogen (DIN) on the water temperature at the Rhine monitoring station in Lobith, 1983–1987.

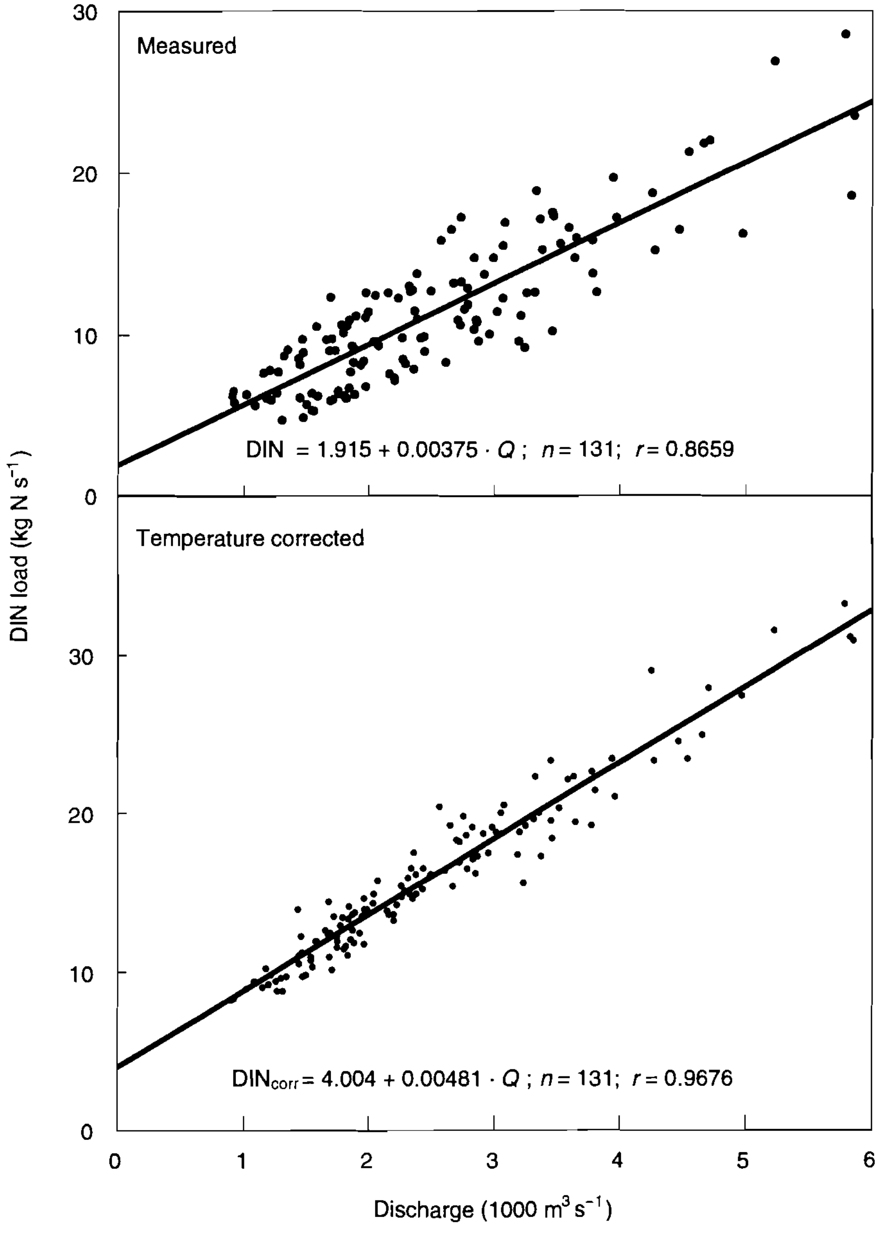

Figure 15. Dependencies of measured and temperature-corrected dissolved inorganic nitrogen (DIN) load on the discharge of the river Rhine at the Lobith station, 1983–1987.

total gross load is 30%. Wolf *et al.* (1989) have assumed that the losses of dissolved inorganic nitrogen are 34% in the surface waters of West Germany.

Admiraal and van der Vlugt (1988) have estimated high denitrification rates of between 15 and 49 g NO_3-N m^{-2} a^{-1} in a storage reservoir supplied by Rhine water. According to these authors the concentration of particulate nitrogen in the Rhine at the Lobith station was about 0.8 g N m^{-3} in 1985. Then the mean load of particulate nitrogen at Lobith is approximately 63 kt N a^{-1} (mean discharge: 2,500 m^3 s^{-1}). Wolf *et al.* (1989) have assumed that the proportion of particulate transported nitrogen is approximately 13% of the total nitrogen.

Based on the this calculation the loss of dissolved inorganic nitrogen caused by denitrification is on the order of magnitude of about 80 to 90 kt N a^{-1} in the Rhine and its main tributaries.

According to *Table 9* the load of nitrate caused by leaching of nitrate from groundwater in agricultural areas is a major source of the diffuse nitrogen load (66%). The contributions of the other sources to the diffuse load are not clear, but it seems that the loads from erosion, drainage, surface runoff, and the direct load by other agricultural activities have approximately the same order of magnitude (lower than 10%) of the total diffuse load.

Phosphorus

Detailed studies of the sources of diffuse loads of phosphorus are also available for West Germany (Werner *et al.*, 1991; Firk and Gegenmantel, 1986; Hamm, 1989).

The procedure for separating different sources of the diffuse phosphorus load is similar to that for nitrogen. The results are shown in *Table 10*. The main sources of the diffuse phosphorus load are erosion and the direct or indirect loading of phosphorus from applications of animal waste and other agricultural sewage. Werner *et al.* (1991) have estimated that about 2 kt P a^{-1} enter the surface waters of West Germany from the application of excessive amounts of animal waste slurries to agricultural lands.

A comparison of the results of these authors shows the highest differences for erosion. The estimates of Firk and Gegenmantel (1986) and Hamm (1989) are based on crude assumptions, while the estimation of

Table 10. Sources and pathways of diffuse phosphorus load within the catchment area of the river Rhine in 1983–1987, in kilotons per year.

Source	Werner *et al.* (1990)	Firk and Gegenmantel (1986)	Hamm (1989)
Atmosphere	0.1	1.2	1.1
Surface runoff	1.7		
Erosion		3.5	3.7
Dissolved	4.0		
Particular	8.6 (2.2)		
Groundwater	0.4		0.1
Drainage	1.3	1.3	1.3
Agriculture	2.8	4.5	3.0
Urban area		0.9	
Other		0.3	0.4
Sum	18.9 (12.5)	11.7	9.6
Estimated range of diffuse load at Lobith		10.7–14.9	

Werner *et al.* (1991) is based on a detailed study of eroded soil material in watersheds of different sizes. On the other hand, the estimated amount of eroded phosphorus of 8.6 kt a^{-1} for the whole Rhine area is larger than the amount that actually reaches the Rhine and its main tributaries. This value represents the loss of phosphorus from agricultural areas estimated for watersheds smaller than 18 km^2. The value of eroded particulate phosphorus given in the parentheses in *Table 10* is applicable to catchment areas greater than 1,000 km^2, because only this amount of phosphorus is loaded and transported to the river.

With regard to the phosphorus load caused by surface runoff and groundwater (including drainage) the different authors have estimated approximately the same amounts. Werner *et al.* (1991) as well as Hamm (1989) have assumed that the load from urban areas is included in the load from sewage treatment plants. Therefore these authors did not consider diffuse urban loads separately.

The diffuse urban phosphorus load estimated by Firk and Gegenmantel (1986) seems to be underestimated, because the assumed storm water runoff of the paved area (2,800 m^3 ha^{-1} a^{-1}) is smaller than the value estimated according to the formula of Falk (1987) (4,000–5,000 m^3 s^{-1}).

The change of phosphorus load over time is mainly dependent on the balance of phosphorus in agricultural soils. At the present level of application of phosphorus fertilizer and manure, this balance is positive for western Germany (Behrendt, 1988; Werner *et al.*, 1991; Isermann, 1990). According to these authors the annual increase of phosphorus content in agricultural soils is about 1% to 2%. The situation in France and Switzerland is comparable to the western German situation. Based on the increase of phosphorus content in agricultural soils, the erosion of phosphorus is estimated to have increased about 10% to 20% from the mid-1970s to the mid-1980s in the Rhine basin. But the phosphorus concentration in drainage also depends on the total phosphorus content of soils. Therefore the phosphorus load from drainage has also increased since the mid-1970s. On the other hand, the phosphorus load from surface runoff and from paved urban areas has decreased in the last two decades (see Section 4.3).

Sources of Diffuse Heavy Metal Loads

To estimate the load of heavy metals within the Rhine basin a procedure similar to the one applied to nitrogen and phosphorus was used. Four sources of heavy metal loads from a hydrological origin have to be distinguished. These sources are surface runoff (load from deposited material), erosion (load from eroded material), groundwater, and the load of paved urban area. The load from urban areas is considered separately because quite different hydrological and geochemical conditions prevail. The following estimations were done for the catchment area as a whole. Therefore the results should be considered very crude, and only a first approximation.

According to Waterloopkundig Laboratorium (1986), the catchment area of the Rhine upstream from the Lobith station is divided into an area of low contamination (11.4 million ha), an area of high contamination (3.5 million ha), and a total paved urban area (approximately 0.6 million ha). The size of paved urban area was estimated based on a total urban area in the Rhine basin upstream from the Lobith station of 1.8 million ha and a mean portion of paved area to the total urban area of one-third.

Groundwater. The mean water transport from groundwater to surface water (basic flow) in the Rhine area is assumed to be 254 mm m^{-2} a^{-1}

Table 11. Concentrations of cadmium, lead, and zinc in brooks and springs. All concentrations are in milligrams per cubic meter for the 1983–1987 time period.

	Cd	Pb	Zn
Range	<0.06–1.2	<1–16	< 9–140
Low-contaminated area	0.06	1	10
High-contaminated area	0.15	3	25

Source: Fauth *et al.*, 1987.

or about 39 billion m^3 a^{-1} (Werner *et al.*, 1991). This basic flow is relatively constant over time but fluctuates spatially in a wide range depending on the geographical and hydrological conditions in different parts of the basin. If it is assumed that the areas of low and high contamination possess the same basic flow per unit area, then the total flow from these areas is about 30 billion m^3 a^{-1} and 9 billion m^3 a^{-1}, respectively.

Measurements of cadmium concentration in groundwater or well water were published by Imhoff *et al.* (1984). According to these authors the median value of cadmium in well water is 0.4 mg m^{-3}, mostly caused by natural sources of geochemical origin. The aqueous cadmium standard of the European Commission (1 mg m^{-3}) is exceeded in some parts of the Ruhr area. Foerster and Neumann (1981) have published results on the concentration of lead and zinc in small brooks in mainly agricultural areas of Lower Saxony. Depending on the type of brook and hydrological conditions, the measured zinc concentration varied from 9 to 50 mg m^{-3}. In the case of lead the concentrations varied from 1 to 4.2 mg m^{-3}.

A more general view of the heavy metal concentrations in groundwater is provided by the *Geochemical Atlas of Germany* (Fauth *et al.*, 1985), which presents maps indicating the springs with heavy metal concentrations. If it is assumed that the source of the springs is mainly groundwater, then these maps can be used to estimate heavy metal concentrations. Ranges and mean concentrations of the low- and high-contaminated areas are presented in *Table 11* for cadmium, lead, and zinc.

The load of heavy metals in surface waters of the Rhine basin from groundwater transport may be calculated by multiplying these

Table 12. Estimated load of cadmium, lead, and zinc in the surface waters of the Rhine basin from groundwater. All values are in tons per year for the 1983–1987 time period.

	Cd	Pb	Zn
Range	1.6–8.0	40–200	350–1600
Low-contaminated area	1.8	30	300
High-contaminated area	1.4	27	230
Mean total load	3.2	57	530

assumed concentrations by the estimated basic flow of low- and high-contaminated areas. The loads in different areas and the total load are shown for three heavy metals in *Table 12*. The heavy metal groundwater load to the river Rhine and its main tributaries is probably not affected by anthropogenic activities since the source of the metals is from natural geological deposits. In this estimation, however, the leaching of heavy metals from the topsoil to groundwater was neglected.

Surface runoff. The load of heavy metals caused by surface runoff was estimated using the procedure described by Werner *et al.* (1991) and Firk and Gegenmantel (1986). According to these authors about 10% of the annual flow enters directly into the river Rhine via surface runoff in the catchment area, with the exception of paved urban areas. Measurements of wet deposition of cadmium, phosphorus, and zinc are summarized in *Table 13*. Using the ranges of wet deposition in rural areas the ranges of heavy metal loads were calculated. A mean wet deposition in the low-contaminated areas was assumed to be 2 g ha^{-1} a^{-1} for cadmium, 80 g ha^{-1} a^{-1} for lead, and 150 g ha^{-1} a^{-1} for zinc. In the case of higher-contaminated nonurban areas, the values are assumed to be double those for lower-contaminated areas. *Table 14* shows the estimated ranges and mean values of the heavy metal load from surface runoff. These values have approximately the same order of magnitude as the loads estimated from groundwater flow.

In contrast to the heavy metal loads from groundwater, it is assumed that the load from surface runoff is influenced by anthropogenic activities and changes over time. The main sources of cadmium and zinc are from atmospheric emissions generated from combustion of fossil fuels and other thermal industrial processes.

Table 13. Measurements of wet deposition of cadmium, lead, and zinc in grams per hectare per year.

Type of area	Cd	Pb	Zn	Source
West Germany				
Rural	1–3	29–125	75–620	Nguyen *et al.*, 1990
Urban	2–9	124–550	170–1,810	
Industrial	6–85	255–2,354	270–8,800	
Rural		80–220	130–480	NLW, 1986
Mean		140	250	
Range	2–33	50–640	90–4,900	Brechtel, 1989
Mean	6	190	540	
Rural	2.7	110	150	Linkersdörfer &
Industrial	9.1	370–730	730	Benecke, 1987
Rural	1–4	85–140	90–280	Nürnberg *et al.*, 1982
Urban	3–9	100–420	185–930	
Industrial	6–25	320–330	270–1,900	
Munich/urban	6	138	545	Thomas, 1981
Nuremberg/urban	4	130	437	(total deposition)
Moosburg/suburban	3	108	378	
Grassau/rural	5	150	275	
All stations	4–14	140–580		Rohbock *et al.*, 1981
Urban	11	440		(total deposition)
Stuttgart/traffic	12	432	1,320	IFS, 1980
Switzerland				
Not specified	4–8	500–2,900	1,700–3,700	Imboden *et al.*, 1975
Urban/traffic	3.4	760	680	Dauber *et al.*, 1978
Denmark				
Rural	2	93	150	Houmand, 1977, 1978
Copenhagen/urban		700	1,100	
Netherlands				
Yerseke/rural	1–2	54–103	88–152	Nguyen *et al.*, 1990
UK				
Walshall/rural	4–11	73–243		Simmonds &
Walshall/industrial	6–18	121–1,220		Pocock, 1987
Mean	6	168	3,250	
Birmingham/rural	4–20	275–500	225–650	Hedges & Wren, 1987

Table 14. Estimated loads of cadmium, lead, and zinc by means of surface runoff in the river Rhine and its main tributaries. All values are given in tons per year for the 1983–1987 time period.

	Cd	Pb	Zn
Range	1.5–6.0	50–700	100–900
Low-contaminated area	2.3	90	230
High-contaminated area	1.4	50	140
Mean total load	3.7	140	370

Therefore the trends in atmospheric emissions are assumed to be proportional to the change of load by surface runoff since 1970. According to the *Statistical Yearbook of Germany* (1989) total dust emissions were reduced from 1.3 million tons in 1970 to 0.55 million tons in 1986. The reduction of atmospheric emissions from industrial point sources of heavy metals was estimated by Anderberg (pers. comm.) According to his results the emissions in the period 1983–1987 were relative to the early 1970s: 72% for cadmium, 76% for lead, and 78% for zinc.

We assumed that the atmospheric deposition is reduced by the same factors as the emissions for cadmium and zinc (see *Table 19*), because the industrial point sources of atmospheric emissions are the main sources of cadmium and zinc in the atmosphere. In the case of lead the traffic-related atmospheric emissions must be taken into account also, because their portion of the total emissions is relatively high.

Liedholm *et al.* (1981) have reported that the contribution of vehicle exhausts to the total lead emissions to the atmosphere was about 74% in Sweden in 1977–1978. If the time trend in traffic-related air emissions are considered, then the reduction of atmospheric lead emissions relative to the mid-1970s was 53% in the 1978–1982 period and 49% in the 1983–1987 period.

Erosion. The estimation of heavy metal loads from erosion was determined by a comparison with the phosphorus erosion calculated by Werner *et al.* (1991). The condition for the validity of such a comparison is that the heavy metals and phosphorus are bound approximately to the same size soil particles. The data summarized by Novotny and Chesters (1981) show that most phosphorus and heavy metals are bound to the smallest soil particles.

Table 15. Cadmium, lead, and zinc content in spring sediment. All values are in milligrams per kilogram.

	Cd	Pb	Zn
Range	<0.6–3.6	<25–380	< 55–470
Low-contaminated area	0.6	25	100
High-contaminated area	1.2	50	250

Source: Fauth *et al.*, 1985.

Since direct, detailed measurements of the content of heavy metals in soils over wide spatial areas in the Rhine basin are not available, the heavy metal contents in the sediment of springs in West Germany (Fauth *et al.*, 1985) provided a basis for estimating the contents of heavy metals in soils. The mean content of cadmium in the topsoil layers of West Germany was estimated at approximately 660 g ha^{-1} (0.22 mg kg^{-1} assuming a bulk density of 1.5 and a soil layer of 20 cm) in the mid-1970s (UBA, 1981). Compared with the cadmium content in spring sediment (*Table 15*) this value is very low. This discrepancy can be explained in part by a higher sorption capacity in the aqueous environment, and in part by the fact that cadmium is bound to smaller soil particles possessing a higher erodibility factor. On the other hand, heavy metals are particularly concentrated in the soil surface.

For soils in the USA Wigington (1981) has estimated a typical range for cadmium between 0.01 and 0.7 ppm. The ranges for phosphorus and zinc are estimated to be between 2 and 200 ppm and 10 and 300 ppm, respectively. The cadmium content in the soils varies from 0.05 to 0.74 ppm for sand and clay in the Netherlands (Langeweg, 1989). The values from Wigington (1981) and Langeweg (1989) correspond to the lower range of concentrations of these metals in West German spring sediment (*Table 15*).

In the following analysis, the heavy metal content in spring sediment was used to estimate the load by erosion, because investigations like those done for cadmium do not exist for lead and zinc in the Rhine catchment area, and the discrepancy in the case of cadmium cannot be explained quantitatively. In any case, the estimates calculated probably represent an overestimation of the actual load from erosion.

The load from erosion is calculated from the metal content listed in *Table 15* assuming proportionality to phosphorus erosion. For a mean phosphorus content in the topsoil of about 700 mg kg^{-1} (Werner *et al.*,

Table 16. Estimated loads of cadmium, lead, and zinc in the surface waters of the Rhine basin caused by erosion. All values are in tons per year for the 1983–1987 time period.

	Cd	Pb	Zn
Range	0.9–11.3	60–1,200	120–1,500
Low-contaminated area	1.4	55	240
High-contaminated area	0.9	35	180
Mean total load	2.3	90	420

1991), the total erosion load of phosphorus into the Rhine was 2.2 kt a^{-1} (*Table 10*). The potential ranges and the mean total loads of cadmium, lead, and zinc are given in *Table 16*. Considering the cadmium content of soil according to UBA (1981) the cadmium load into the Rhine would be about 0.7 t a^{-1} or one-third of the estimated load of 2.3 t a^{-1} according to *Table 16*. The values in *Table 16* represent only the part of eroded material which reaches the larger tributaries in the Rhine watershed. For river watersheds with a smaller area this load may increase by a factor of four. In contrast to phosphorus, the dissolved load caused by erosion was disregarded, because it seems to be questionable that a transfer from the particulate to the dissolved fraction plays an important role in the heavy metals investigated. The erosion loads estimated in the comparison with phosphorus pertain mainly to the loads from agricultural lands and arable areas.

With regard to the change in the erosion load over time, the annual and long-term balance of cadmium, lead, and zinc in the agricultural areas has to be considered. Such a detailed balance is not the subject of this paper, but it is possible to make an approximation of the trends in loads from erosion in the last two decades.

The balance of cadmium in agricultural areas in the mid-1970s is given by UBA (1981). The main inputs were atmospheric depositions (3.5 g ha^{-1} a^{-1}) and cadmium in phosphorus fertilizers (5.4 g ha^{-1} a^{-1}). The inputs caused by sewage sludge and other sources were assumed to be 2.0 g ha^{-1} a^{-1}. Compared with these total inputs of 10.9 g ha^{-1} a^{-1} the loss of 1.1 g ha^{-1} a^{-1} mainly to the water (1.0 g ha^{-1} a^{-1}) is only 10%.

The enrichment of cadmium in the soil by about 10 g ha^{-1} a^{-1} is very substantial, causing an increase of the total cadmium content in the soil of about 1% to 1.5% per year. With regard to the cadmium lost by erosion an increase of 1% per year can be assumed, because the present situation has not changed significantly since to the 1970s.

In the case of lead, the only important input to the agricultural areas is by means of long-range atmospheric deposition. The leaching of lead to groundwater is negligible. The outputs of lead are uptake by crops and vegetation and losses to surface waters caused by erosion and surface runoff of deposited material. We assumed that 10% of deposited lead goes directly into the surface water. The area-specific erosion loss of phosphorus given by Isermann (1990) is 1.25 kg P ha^{-1} a^{-1}, based on the results of Werner *et al.* (1991) for agricultural areas. If we compare the phosphorus and lead content in the topsoil, the specific loss of lead caused by erosion is estimated to be about 40 to 100 g ha^{-1} a^{-1}. This range agrees quite well with the atmospheric deposition of lead in rural areas (*Table 13*). Therefore it seems plausible that inputs and outputs of lead in agricultural soils are equal, and a change in lead erosion is not detectable in the last 10 to 15 years.

For zinc, a rough estimation of its soil balance in agricultural areas can be made based on the investigations of Feenstra and van Baal (1989) for the EC countries. According to this study, the main inputs to the agricultural area are deposition (100–200 g ha^{-1} a^{-1}, see *Table 13*) and farm slurries (150–250 g ha^{-1} a^{-1}). Furthermore zinc in phosphorus fertilizers (40–60 g ha^{-1} a^{-1}) and sewage sludge (10–30 g ha^{-1} a^{-1}) must be taken into account. The total losses of zinc (erosion, surface runoff, direct load of slurry) amount to an output of only 80 to 160 g ha^{-1} a^{-1}. The total mass balance of zinc is positive, with an annual enrichment in agricultural soils of between 220 and 380 g ha^{-1} a^{-1}. This value, however, is low compared with the total zinc content of soil. Compared with information on the zinc content in spring sediment, the increase of zinc in soils is probably lower than 0.5% per year.

Summarizing the results of the cadmium, lead, and zinc balance of agricultural soils, it is assumed that only in the case of cadmium is there a significant increase of about 10% in the cadmium load by erosion from the mid-1970s to the mid-1980s.

Other nonurban sources of diffuse load. In addition to the heavy metal load caused by groundwater, surface runoff, and erosion, part of the agriculturally applied animal waste slurries directly enters the surface water. Werner *et al.* (1991) have assumed that about 2% of the liquid manure produced flows directly into the surface water. If a phosphorus content of farm slurry of 10 to 50 g P kg^{-1} dry weight is assumed, the total phosphorus in farm slurries is estimated to be about 100,000 t P a^{-1} for West Germany (Werner *et al.*, 1991). With regard to heavy metals, the zinc content of farm slurry is between 0.2 and 1.5 g kg^{-1} dry weight (Feenstra and van Baal, 1989). The cadmium and lead content in animal waste slurries is negligible. The total amount of zinc in farm slurries in West Germany is estimated at 2,000 to 3,000 t a^{-1}. From this total 2% or 40 to 60 t a^{-1} directly enter the surface waters of West Germany. Comparing the agricultural area of the Rhine basin upstream from Lobith with that of West Germany, the total zinc load caused by farm slurries is estimated to be about 25 to 35 t a^{-1}. This load is very low in comparison with the loads of zinc from the other sources.

Diffuse load of paved urban areas. With regard to the diffuse load, urban areas – particularly paved urban areas – are considered separately, because:

- The portion of precipitation which is discharged directly from the surface is high compared with unpaved urban areas and nonurban areas.
- The deposition rates of pollutants in urban areas are higher than the rates in nonurban areas.
- The pathways by which pollutants enter the river in urban areas are quite different from pathways in nonurban areas.

Although the portion of urban land in the total area is generally small, the contribution of the pollutant load of urban areas is high. Wigington (1981) reported that the loads of cadmium, phosphorus, and zinc from the urban area in the Occoquan watershed (Virginia, USA) are 47%, 87%, and 33%, respectively, of the total load, even though the urban area is only 6.2% of the total area.

Figure 16 shows an overview of the sources and the pathways of heavy metals in urban areas. Atmospheric deposition includes long- and short-range deposition as well as wet and dry deposition.

There is not always a clear distinction between traffic and atmospheric depositions, because aerosols, gases, and small dust particles emitted by traffic can be measured as part of the atmospheric deposition. Spills of oil and grease, tire wear, and wear of road surfaces

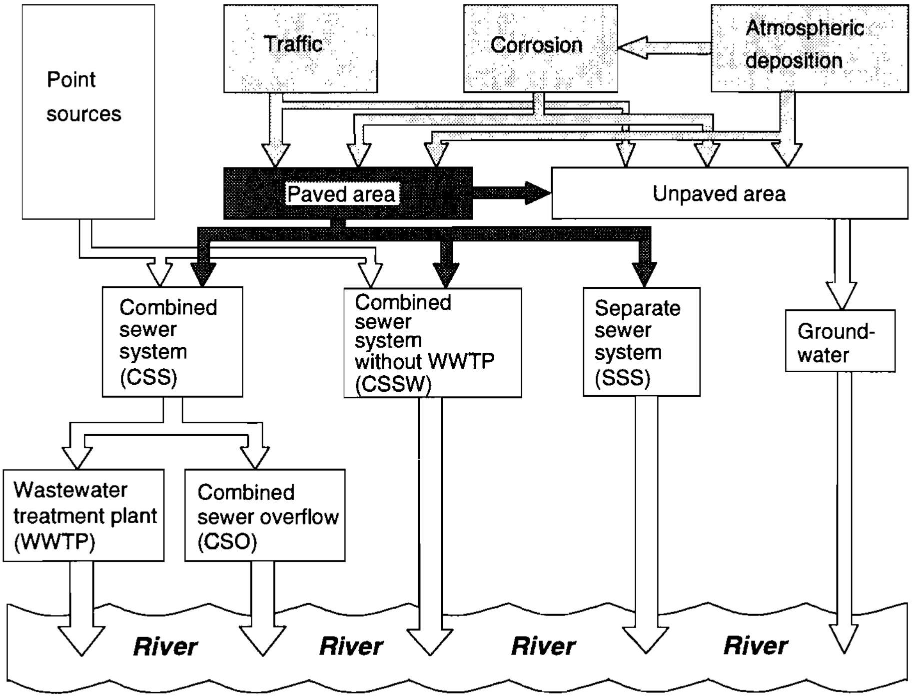

Figure 16. Sources and pathways of diffuse heavy metal loads in urban areas.

are additional sources of the heavy metal load and have to be taken into account separately. In the following sections the components of the area-specific loads of heavy metals in *Figure 16* are estimated. Because paved urban areas are particularly important contributors to the total load, the estimation focuses on atmospheric deposition, traffic, and corrosion in the paved areas. We then track the course of these loads as they move from the paved area to the river.

Sources of the Heavy Metal Loads in Urban Areas

Atmospheric deposition. Results of wet deposition measurements in urban and industrial areas are given in *Table 13*. Data on dry deposition are scarce. Dry deposition may be calculated using the concentration of pollutants in the air and the deposition velocity. Feenstra and van Baal (1989) and Feenstra and van der Most (1986) have assumed that

Table 17. Specific heavy metal loads of paved urban areas used to estimate total loads in urban areas in the Rhine basin. All values are in grams per hectare per year for the 1983–1987 time period.

	Cd	Pb	Zn
Wet deposition	6.0	300	600
Dry deposition	2.4	150	180
Traffic	5.3	530	790
Corrosion	3.5	0	1,750
Total load	17.2	980	3,320

dry deposition of zinc and cadmium is approximately 10 to 20% of wet deposition. For lead the dry deposition amounts to about 40% of wet deposition. These assumptions agree qualitatively with the results of US investigations. Randall *et al.* (1981) point out that precipitation was a major source of heavy metals in urban runoff in a watershed in Virginia (USA). In addition they report that dry deposition was the main source of lead. Furthermore, the lead concentration in urban runoff was positively correlated with the number of dry days before a runoff event. In contrast the number of previous dry days did not correlate with storm water zinc load (Wilber *et al.*, 1980). Rohbock *et al.* (1981) have reported dry deposition to be 17% and 18% of total deposition of lead and cadmium, respectively. The percentage of dry deposition of lead is only half the value given by Feenstra and van der Most (1986). In general the study by Rohbock *et al.* (1981) shows that the portion of dry deposition to total deposition is smaller in rural areas (4% to 8%) than in urban areas (13% to 22%). Ammema (pers. comm.) have estimated, on the basis on measurements in the Netherlands, that dry deposition is about 61% for cadmium, 64% for lead, and 28% for zinc. Using the results of *Table 13*, the mean wet deposition of cadmium, lead, and zinc is assumed to be 6 g ha^{-1} a^{-1}, 300 g ha^{-1} a^{-1}, and 600 g ha^{-1} a^{-1} for the urban areas in the Rhine basin. According to the results of Rohbock *et al.* (1981) and Annema (pers. comm.), dry deposition is assumed to be about 40% of wet deposition for cadmium, 50% for lead, and 30% for zinc. These values are given in *Table 17* together with the assumed specific wet deposition of heavy metals.

Traffic. The specific heavy metal load from urban lands increases as it makes its way to the river by emissions from traffic areas, caused by engine exhausts, wear of tires and road surfaces, and so on. These traffic-related loads are particularly relevant for lead and zinc (Feenstra and van der Most, 1986; Wigington, 1981; Novotny and Chesters, 1981). Although leaded gasoline is certainly the largest source of lead in urban areas of the Rhine, only part of it is included here since emissions into the atmosphere have already been taken into account in the specific estimates of wet and dry deposition. Malmqvist (1983) has reported that about 60% to 80% of automobile-related lead emissions are released directly to the atmosphere. The remaining 20% to 40% contribute directly to the load of lead as road dust. Christensen and Guinn (1979) have found that only 7.6% of emitted lead is deposited on the street surface.

Feenstra and van Baal (1989) have stated that the wear of tires is the most important source of the traffic-related heavy metal load, because rubber includes the highest amounts of cadmium, lead, and zinc. Zinc in motor oil also has comparably high concentrations.

Total rates of traffic-related loads of 0.0157 grams per vehicle per kilometer for lead (total emission of lead) and 0.00196 grams per vehicle per kilometer for zinc are reported by Shaheen (1975). Annema (pers. comm.) has estimated a traffic-related emission of lead of about 0.002 grams per vehicle per kilometer for the Netherlands. Christensen and Guinn (1979) have estimated a street-related load of 0.003 grams per vehicle per kilometer for zinc and 0.0049 grams per vehicle per kilometer for lead. Hoffman *et al.* (1985) have published specific loading factors of 0.02 milligrams per vehicle per kilometer for cadmium, 0.0044 grams per vehicle per kilometer for lead, and 0.022 grams per vehicle per kilometer for zinc. Malmqvist (1983) report car-specific emissions of lead and zinc of 0.034 grams per vehicle per kilometer and 0.004 grams per vehicle per kilometer, respectively. Assuming a mean car density of 500 vehicles per 1,000 inhabitants in the Rhine basin in the mid-1980s, with a total population in the Rhine area of about 47 million (statistical yearbooks of Germany and France), a total stock of 23.5 million cars can be estimated. If we assume that each car travels about 15,000 km a^{-1}, then, using the automobile-related emission factors for cadmium of Hoffman *et al.* (1985), for zinc of Christensen and Guinn (1979), and for lead of Christensen and Guinn (1979) and Hoffman *et al.* (1985), the annual street-related traffic emissions are about 7.1 tons for cadmium, 1,750 tons for lead, and 1,050 tons for zinc. De Waal Malefijt (1982) has assumed that only 40% of the traffic occurred in urban streets. The proportion of urban streets in the total length of streets is about 45% for West Germany (statistical yearbooks). If a total paved urban area of about 600,000 is considered, then the area-related loads can be estimated at about 5.3 g ha^{-1} a^{-1} for cadmium, 1,300 g ha^{-1} a^{-1} for lead, and 790 g ha^{-1} a^{-1} for zinc. If the automobile-related lead emission measurements of Christensen and Guinn (1979) and Hoffman *et al.* (1985) are used then we have to take into account that the lead content of gasoline was different in the USA in the late 1970s and in the Rhine basin in the mid-1980s. Christensen and Guinn (1979) report that the lead content of gasoline at this time was 0.37 g l^{-1}. Pacyna (1991) has stated that the lead content of gasoline in Germany has been 0.15 g l^{-1} since the late 1970s. Based on this lead content of gasoline the street-related lead load was estimated to be about 530 g ha^{-1} a^{-1} in the mid-1980s.

Corrosion. The load caused by corrosion of galvanized surfaces has to be taken into account for zinc and to a lesser extent for cadmium. The amounts of corroded zinc and cadmium depend on two factors. One is the total surface area of galvanized materials. The other is the specific corrosion rate (per zinc surface or per galvanized area), which is strongly dependent on the level of air pollution. Different studies of the corrosion process have concluded that the concentrations of SO_2 in the air, humidity, and temperature are the most important factors influencing the corrosion rate (Boden, 1989; Haagenrud *et al.*, 1983; Harter, 1986; ECE, 1984).

Within the framework of the IIASA/RIVM study of the "Sources of Pollution of Selected Chemicals in the Basins of the Rhine, Meuse, and Scheldt Rivers," Hrehoruk (1991) has estimated the corrosion rates of different German cities within the Rhine basin based on the SO_2 concentrations monitored in air.

The equations given by Haagenrud *et al.* (1983) were used for this estimation. According to the results of Hrehoruk (1991), it can be assumed that the mean corrosion rates of zinc in the urban areas of the Rhine basin were between 15 and 30 g m^{-2} of galvanized surface in the mid-1980s. De Waal Malefijt (1982) has assumed a mean zinc corrosion rate of 27 g m^{-2} for the Netherlands. For the small Dutch city Lelystad, van Dam *et al.* (1986) have measured a corrosion rate of 4.4 mg m^{-2} mm^{-1} of rainfall. If we assume a mean rainfall intensity of 700 mm m^{-2} a^{-1}, then the annual corrosion rate is about 30 g m^{-2}.

Corrosion rates between 3 g m^{-2} a^{-1} and 8 g m^{-2} a^{-1} for Swedish cities were published by Malmqvist (1983) and Hogland and Niemczynowicz (1980). These lower rates can be explained by the lower SO_2 concentration in these areas (Malmqvist, 1983).

Assumptions about the total area of exposed galvanized surfaces are more uncertain. De Waal Malefijt (1982) has assumed a galvanized surface of one-half square meter per inhabitant for the Netherlands. Using his assumption and the population density in urban areas, an area-specific zinc surface of 100 m^2 ha^{-1} of paved urban area can be estimated. A zinc surface of 900 m^2 ha^{-1} of paved urban area can be estimated from the data of van Dam *et al.* (1986) for Lelystad. Malmqvist (1983) has reported zinc surface areas between 67 and 490 m^2 ha^{-1} of paved urban area for four different locations in the city of Göteborg. A strong linear relation seems to exist for all of these data. The data on the surface of paved urban area with zinc concentrations were summarized. The result is a relatively strong relationship between the surface of paved urban area with zinc concentration and the population density of the urban area. This relationship can be described by the following regression:

$$\mathrm{Zn}_S = 47.24 + 1.773 \cdot \mathrm{PD}; n = 6; r^2 = 0.9844 \quad ,$$

where is Zn_S is the unpainted zinc surface of paved urban area in m^2 ha^{-1} and PD is the population density of the urban area given in inhabitants per hectare.

If we assume that the mean population density of urban areas along the Rhine is about 25 inhabitants per hectare, then the surface of the paved urban area with zinc concentration is about 92 m^2 ha^{-1} of paved urban area. The mean annual corrosion rate of the zinc concentration is estimated using the relationship between corrosion and SO_2 concentration in the air given by ECE (1984) for galvanized steel:

$$\mathrm{CORR} = 0.45 \cdot \mathrm{SO_2} + 0.7 \quad ,$$

where CORR is the annual corrosion of one square meter of galvanized steel and SO_2 is the mean concentration of sulfur dioxide in the air.

According to Hrehoruk (1991) a mean SO_2 concentration for the whole Rhine basin is estimated at about 40 μg m^{-3} during the period 1983–1987. A mean annual-specific zinc corrosion is calculated at about 19 g Zn m^{-2}. The annual-specific corrosion of zinc in paved urban area was about 1,750 g ha^{-1} within the Rhine basin in the mid-1980s. This estimate of corrosion is used in the following analysis as an approximation for estimating the urban heavy metal load in the Rhine basin.

In general, cadmium is an impurity of applied zinc materials. Its proportion in zinc is assumed to be 0.2% (De Waal Malefijt, 1982). Therefore a cadmium corrosion rate of about 3.5 g ha^{-1} a^{-1} has been assumed.

Table 17 summarizes the total loads of cadmium, lead, and zinc in the paved urban areas in the Rhine basin for the 1983–1987 period. They are about 17.2 g ha^{-1} a^{-1} for cadmium, 980 g ha^{-1} a^{-1} for lead, and 3,320 g ha^{-1} a^{-1} for zinc. A different source is responsible for each metal investigated. In the case of cadmium, atmospheric deposition (wet and dry) is the main source, contributing about 49% of the total load. For lead, the emissions from traffic dominate the load. The main source of the zinc load in the urban areas of the Rhine basin seems to be corrosion, accounting for 53% of the total urban zinc load. The combination of traffic and corrosion contribute 77% to the total zinc load. These estimates of lead and zinc loads correspond qualitatively and quantitatively with the results of different authors (Dauber *et al.*, 1978; IFS, 1980; Klein, 1982; Malmqvist, 1983; Lisper, 1974). In the case of cadmium such a comparison of results is not possible because most of the authors did not measure cadmium directly.

Pathways of Heavy Metal Loads in Urban Areas

For the Rhine basin upstream from the Lobith station, the total paved urban area is estimated at about 600,000 hectares based on the crude assumption that the paved area is approximately one-third of the total urban area. By multiplying the total loads in *Table 17* by this area, the load for each metal which could potentially enter the Rhine river or its tributaries in the period 1983–1987 can be estimated. The potential annual load from paved urban areas is about 10.3 tons for cadmium, 590 tons for lead, and 1,990 tons for zinc.

The pathways by which the heavy metal loads estimated from the specific loads in *Table 17* reach the river depend on the specific conditions in each community. Data are available at the national level on the percentage of the population connected to the sewer systems and municipal sewage treatment plants (statistical yearbooks of France, Germany, and Switzerland). These aggregated values were used in our calculation because data at the community level were not available.

According to national statistics, about 90% of the population living in the Rhine basin is currently connected to sewer systems. Sewage systems for collecting street runoff are either connected to municipal sewage treatment plants or connected to a separate storm water system in which the runoff is not treated. It is assumed in our analysis that 90% of the storm water runoff is connected to one or the other system. For storm waters channeled to separate sewer systems we assume that the sewage is not treated.

It was assumed that about 54% of the paved area is connected to combined sewer systems, and 36% of the area is connected to separate sewer systems. Furthermore, it is assumed that 50% of both the runoff and the load from paved urban areas which are not connected to a sewer system (about 10% of the area) enter the bodies of water. During storm events the capacity of the combined sewer systems is usually not sufficient to treat the entire volume of storm water runoff, so overflows have been installed. It is important to estimate how much of the load from urban areas enters the river system via combined sewer overflows. Falk (1987) states that in Sweden the yearly overflow volume varies from 0.1% to 10% of the volume going through the sewage treatment plant. In a study of two sewer systems in the Netherlands it is reported that the average amount of storm water overflow from paved areas ranges between 74 and 120 mm a^{-1} (Onderdelinden and Timmer, 1986). In comparison with the possible range of total runoff from paved areas of about 300 to 600 mm reported by Falk (1987), these amounts appear to be relatively high. But in this context, Falk (1987) argues against the use of flow or the input loads from paved area to the sewer system when calculating the real load from combined sewer overflows. Because sedimentation takes place in the sewer system during dry weather periods, the measured output of overflows can be two to five times higher than the inputs to the sewer system (point and diffuse load) during storm water runoff (Hogland *et al.* 1988).

According to Sperling (1986) phosphorus and nitrogen entering the water through combined sewer overflows account for about 12% of the total phosphorus load and 14% of the total nitrogen load of municipal sewage treatment plants (54% of the total load from paved areas are connected to combined sewers). Therefore, 6.5% to 7.6% of the potential heavy metal load of paved urban areas goes directly into the river system via combined sewer overflow. Considering the washout effect in the combined sewer system during storms (Hogland *et al.*, 1988), at least 10% of the total heavy metal load of paved urban areas is estimated to enter the river via combined sewer overflows. The remaining 44% of the urban load connected to sewage treatment plants is treated. During treatment part of the heavy metals is removed by sedimentation (mechanical or primary treatment), part is removed by sorption by organic material (secondary treatment), and, when tertiary treatment is available, part is removed by flocculation. The rate of removal of heavy metals from wastewater depends not only on the kind of treatment, but also on the specification of the load. Therefore, it is interesting to know the relation of the dissolved and particulate fractions of the total diffuse load. Wigington (1981) has stated that the percentage of dissolved loadings of zinc and lead is different. In different kinds of urban areas in the USA, the percentage of the dissolved lead load varies from 5% to 15%. In contrast to lead, the percentage of the dissolved zinc load is higher (31% to 70%). The comparison between the particulate and dissolved concentrations of cadmium, lead, and zinc upstream and downstream from urban areas shows that most of the urban zinc and cadmium loads are in dissolved form (Ellis, 1988). In contrast, for lead the particulate fraction contributes most of the total load.

If the lead load is mainly particulate material and the cadmium and zinc loads are mainly in the dissolved form, we can assume different elimination rates of these metals within the sewage treatment plant. For plants with primary and secondary treatment Imhoff *et al.* (1980) report a mean zinc reduction of 52%. For cadmium the same reduction rate as for zinc is assumed. A higher percentage of reduction is assumed in the case of lead. Because particulate material is removed more efficiently than dissolved material, a percentage of 80% is assumed for lead reduction. A reduction of cadmium and zinc of only 30% is assumed for wastewater treatment plants with primary treatment only. The reduction of lead is expected to be about 50% in these plants. Currently, paved urban areas which are connected to sewage plants with only primary wastewater treatment makeup about 8% of the Rhine basin as a whole.

Table 18. Estimated loads of cadmium, lead, and zinc from paved urban areas in the Rhine basin (upstream from the Lobith station). All values are in tons per year for the 1983–1987 period.

	Cd	Pb	Zn
No sewer system	0.6	24	95
Separate sewer system	4.0	180	720
Combined sewer overflows	0.9	40	190
Combined sewer systems	2.2	40	390
Total load	7.7	284	1,395

Table 18 summarizes the heavy metal loads from urban areas with surface waters in the Rhine basin upstream from the Lobith station. The simulations pertain to the 1983–1987 time period, during which the urban load of cadmium, lead, and zinc entering the river system is estimated at about 7.7, 284, and 1,395 t a^{-1}, respectively.

With regard to the time trends of loads from urban areas, it is necessary to estimate changes in the various sources (atmosphere, traffic, corrosion) as well as the evolution of sewage treatment. The atmospheric emissions of heavy metals have been reduced significantly from 1973–1977 to 1983–1987, particularly in urban and industrial areas.

The reductions of industrial point sources of atmospheric emissions estimated by Anderberg (pers. comm.) were about 72% for cadmium, 76% for lead, and 78% for zinc. We assume that the atmospheric deposition was reduced by the same percentages as the emissions for cadmium and zinc. For lead, the trends in traffic-related emissions must be taken into account in addition to the industrial sources of atmospheric emissions. Therefore, the trend in reduction of atmospheric deposition of lead since the mid-1970s is not as high as it is for cadmium and zinc. If we assume that the total atmospheric lead emissions are the sum of all industrial point source emissions and 70% of the automobile-related lead emissions, then the atmospheric deposition of lead compared with the mid-1970s was about 53% during the 1978–1982 time period and 49% during 1983–1987.

For the loads from traffic, the situation for cadmium and zinc differs from that of lead. According to Rautengarten (pers. comm.) the traffic-related loads of cadmium and zinc were one-third higher in 1985 than in 1975 because of the increase in the numbers of cars per inhabitants.

Additionally, the reduction in the lead content of gasoline in the late 1970s has to be considered. Compared with the situation in 1985, the traffic-related load of lead was 87% in 1978–1982 and 145% in 1973–1977.

The specific corrosion rates have changed over this 10-year period, too. Hrehoruk (1991) reports that the corrosion rates within the catchment area were about 50% higher in the mid-1970s compared with the situation in the mid-1980s. Changes in the unpainted galvanized surface area over the whole period have not been determined. As a first approximation, we assumed that these surface areas have not changed since 1975.

Furthermore the change in the pathways of the load caused by changes in the sewage treatment have to be taken into account. The percentage of population connected to a sewer system was about 75% in 1975. About 18% of the population was connected to sewage systems with only primary (mechanical) treatment. With regard to separate sewer systems for storm water, it is assumed that this percentage was the same over the whole time period.

Total Diffuse Load of Heavy Metals and Its Change over Time

Table 19 presents a survey of the results of the loads from different diffuse sources. In the most recent time period (1983–1987) the load from paved urban areas is the main source, amounting to 46%, 50%, and 51% of the total diffuse load for cadmium, lead, and zinc, respectively. The load from the other diffuse sources (groundwater, surface runoff, erosion) on the total load is similar for cadmium and zinc in the 1983–1987 period. For lead the surface runoff is the second important source, with 24%.

The calculated time trends of the diffuse load are mainly determined by the changes in the loads from surface runoff and paved urban areas. According to the estimations described previously surface runoff from rural and from paved urban areas was probably the main source of the diffuse cadmium load in the mid-1970s. In the case of lead, the load from paved urban areas, the source of which is mainly traffic, and the load from surface runoff were the main sources over all three time periods. Both sources (surface runoff and paved urban areas) show approximately the same time trend because they are linked to changes in atmospheric depositions.

The main sources of the zinc load from paved urban areas are corrosion and traffic. In the mid-1970s about a half of the zinc load from

Table 19. Estimated heavy metal loads from different diffuse sources and their change over time since the mid-1970s in the Rhine basin. The values in parentheses refer to the particular hydrological situation in the 1973–1977 time period. All values are in tons per year.

Source	1973–1977	1978–1982	1983–1987
Cd			
Groundwater	3.2	3.2	3.2
Surface runoff	13.1 (9.5)	6.3	3.7
Erosion	2.1 (1.5)	2.2	2.3
Other sources			
Paved urban area	15.2 (12.8)	9.4	7.7
Total diffuse load	33.6 (27.0)	21.1	16.9
Pb			
Groundwater	60	60	60
Surface runoff	290 (210)	145	140
Erosion	90 (65)	90	90
Other sources			
Paved urban area	560 (510)	320	285
Total diffuse load	1,000 (845)	615	575
Zn			
Groundwater	530	530	530
Surface runoff	1,700 (123)	880	370
Erosion	420 (300)	420	420
Other sources	30	30	30
Paved urban area	2,510 (2060)	1,900	1,395
Total diffuse load	5,190 (4150)	3,760	2,745

paved urban areas was caused by corrosion. Since that time, corrosion rates of zinc have decreased substantially because of large reductions in urban SO_2 concentrations.

The decrease of heavy metal loads since the 1970s from paved urban areas is not as large as from surface runoff, because the load caused by increasing traffic has tended to offset reductions in the loads from corrosion and atmosphere deposition. For lead large reductions can be expected in the future with the increasing use of lead-free gasoline.

A comparison of the results obtained by estimating the individual sources of the diffuse load with the results obtained from the analysis of river-monitoring data (see *Table 4*) is particularly interesting. Generally, the heavy metal loads estimated with these methods agree for the 1983–1987 time period. The estimated loads of cadmium and zinc using the method of area-specific loads are relatively close to the averages of the diffuse load in *Table 4* for the Lobith station. In the case of lead the diffuse load estimated on the basis of area-specific loads is higher than the highest value of the range of uncertainty in *Table 4*. The reason for this discrepancy is that our estimation of the traffic-related lead load does not take into account that a small percentage of vehicles do not use leaded gasoline, which was introduced in the second half of this time period.

Also for the 1978–1982 time period the diffuse loads estimated by the two methods are comparable. In this period the estimated area-related diffuse loads of cadmium, lead, and zinc fall within the ranges of loads estimated using the monitoring data from the Lobith station. In fact, the values calculated for the area-related loads are close to the average values calculated from the river-monitoring data. But the ranges of uncertainty are also higher in this time period, because the amount of data from this time period is low compared with the 1983–1987 time period. In the 1973–1977 time period some discrepancies exist for cadmium, zinc, and particularly lead. The total diffuse loads of these metals estimated from area-related loads are within the upper range of uncertainty estimated from monitoring data, but they are not so very close to the average values estimated.

In this time period the available monitoring data was also small compared with the 1983–1987 time period. Furthermore, the range of uncertainty is extremely high, because the relationship between the lead load and the discharge at the Lobith station is uncertain for the period 1973–1977. In contrast to the results based on the monitoring data for the estimation of diffuse load, the trends of diffuse cadmium, lead, and zinc loads are more heavy for the estimation using the area-related loads. With regard to this behavior it must be pointed out that the hydrological situation is different in the three time periods investigated. The mean discharge at the Lobith station was highest in the 1978–1982 period (about 2,620 m^3 s^{-1}). The mean discharge in the mid-1980s was comparable to this with a value of about 2,480 m^3 s^{-1}. But in the first period (1973–1977) the mean discharge at the Lobith station was only 1,780 m^3 s^{-1} or about 72% of the discharge in the mid-1980s. Because most of the diffuse load depends on the runoff rate, one may assume that the diffuse load of a pollutant into a river is influenced by the discharge. This behavior is taken into account for the loads estimated

Table 20. Relationship of the estimated mean loads (L_M) of all diffuse sources at the Lobith station for the 1973–1977 and 1983–1987 time periods, estimated by separating monitoring data, to the estimated diffuse loads for these two time periods, estimated on the basis of emission factors (L_E.)

	Cadmium	Lead	Zinc
$L_{E(1973-1977)}/L_{E(1983-1987)}$	1.6	1.5	1.5
$L_{M(1973-1977)}/L_{M(1983-1987)}$	1.7	1.7	1.4

on the basis of monitoring data. But the influence of runoff on the load-related processes was neglected in our analysis on the area-specific loads. Diffuse loads from paved urban area (particularly wet deposition and corrosion), surface runoff, and erosion are the sources of loads most dependent on runoff. If we assume that these loads depend linearly on the runoff, and the runoff is linearly correlated with the discharge at the Lobith station, then the actual load was only 72% of the potential load in the 1973–1977 period. The values in parentheses in *Table 19* take into account this effect. Comparison of the total diffuse loads which consider the hydrological situation in the 1973–1977 period with the values of diffuse loads estimated on the basis of monitoring data shows that these values are almost as close to the averages given in *Table 4* as to the other two time periods.

If the mean loads of all diffuse loads of heavy metals are compared for the different time periods (*Table 20*) then their time trend is more similar to the trend of the load estimated from emission factors, where the values of *Table 19* were taken into account which consider the special hydrological situation for 1973–1977. *Table 20* shows that the relationship between the loads of the two time periods is about the same independent of the way that was used for estimating the load. This fact supports our assumption that the lower discharge in the 1973–1977 time period is a major reason for lower total diffuse load as estimated without consideration of the special hydrological situation during the 1973–1977 time period. Furthermore, it can be concluded from *Table 20* that some of our approximations on the time trend of loads (e.g., zinc surface of paved area is not changed over the investigated period) do not seem to be false.

If the uncertainties of both methods are taken into account, then it must be point out that both methods for estimating diffuse load reflect the same time trend in the case of cadmium and zinc. The difference of the decline of the lead loads is a little bit higher. The reason for this could be the high range of uncertainty with regard to the diffuse load estimated using a limited amount of monitoring data.

5 Conclusions

This report presents a new method for estimating point and diffuse loads to the river Rhine from statistical analysis of river-monitoring data. The estimated point source loads of dissolved nitrogen, total phosphorus, and heavy metals (cadmium, lead, and zinc) are compared with the loads of existing inventories (ICPR,1989). The diffuse loads of these pollutants are compared with estimations calculated on the area-related loads of the main diffuse sources. Reasonable agreement was obtained in these comparisons, thus demonstrating the utility of the new method as a tool for analyzing point sources and diffuse loads of pollutants to river system from analysis of monitoring data.

The comparison could only be applied to the data from the mid-1980s because no point source inventories or estimates of area-related diffuse loads were taken prior to 1985. The river-monitoring data, however, have been available since the early 1970s for all of the pollutants investigated and since the early 1950s for nitrogen. Analyses of these data by the new method were employed for estimating historical trends in the point and diffuse loads.

The results of this historical reconstruction are shown in *Table 21*. The mean error for the given point and diffuse loads is approximately 10% for the 1983–1987 period. For dissolved inorganic nitrogen and total phosphorus it is also about 10% for the earlier periods. For the heavy metals a mean error of 20% must be assumed for the 1973–1977 and 1978–1982 time periods. The time period analyzed for the heavy metals and total phosphorus is limited to the period from the mid-1970s to the mid-1980s, because monitoring data have been available only since the early 1970s. In the case of dissolved nitrogen which represents about 90% of the total nitrogen, we could make estimations back to the 1950s, because of the availability of monitoring data.

The results of the analysis of dissolved inorganic nitrogen (*Figure 9*) show dynamic changes dominated by two developments. One is the evolution of wastewater treatment plants within the Rhine basin,

Table 21. Estimated point and diffuse loads of nitrogen, phosphorus, cadmium, lead, and zinc to the Rhine River basin upstream from the Lobith station since the mid-1970s. The values are in kilotons per year for nitrogen and phosphorus and in tons per year for the heavy metals.

Pollutant	Source of load at the Lobith station	1973–1977	1978–1982	1983–1987
Nitrogen	Total load	410	480	510
	Point load	245	245	260
	Diffuse load	165	235	250
Phosphorus	Total load	50	41	35
	Point load	34	26	22
	Diffuse load	16	15	13
Cadmium	Total load	145	96	26
	Point load	119	76	11
	Diffuse load	26	20	15
Lead	Total load	1,500	800	700
	Point load	730	260	240
	Diffuse load	770	540	460
Zinc	Total load	10,100	9,200	5,000
	Point load	6,100	6,100	2,200
	Diffuse load	4,000	3,100	2,800

particularly since the mid-1960s. This development is the reason for the decrease in the ammonia point load and the increase in the nitrate point load. The second development is the increase in the diffuse load of nitrate over the entire time period up to the mid-1980s due to the increasing using of nitrogen fertilizer and manure.

For phosphorus the analysis shows a clear decreasing trend of point loads since the mid-1970s mainly caused by the elimination of phosphorus in detergents. According to the main sources of diffuse phosphorus (erosion, surface runoff, and other agricultural activities) an increasing trend should exist based on the results of Werner (1991), Firk and Gegenmantel (1986), and Bernhardt (1978). The order of magnitude of our estimated diffuse load of phosphorus agrees with the results of these authors. It seems to be reasonable to assume that the discrepancy is caused by the different definition of diffuse load.

The analyses of the phosphorus cycle in West Germany (Werner *et al.*, 1991; Firk and Gegenmantel, 1986; Hamm, 1989) do not consider the load from paved urban areas as a diffuse source. On the other hand, some loads related to agricultural activities which were considered diffuse loads in these studies are point source loads according to our definition, because they do not really depend on meteorological or hydrological factors.

With regard to the heavy metals, a very large decreasing trend in the point sources was observed from the mid-1970s to the mid-1980s. For lead and cadmium the point load was reduced from 1973–1977 to 1978–1982. During this period the point load of lead was approximately the same, but the point load of cadmium was further reduced. Based on our results the point load of zinc was not significantly reduced before the 1983–1987 period.

Because of the decreases in the point loads of cadmium, lead, and zinc, the diffuse loads of these metals were higher than the point source loads by the mid-1980s. We estimate the diffuse load to be about 58% of the total load for cadmium, 66% for lead, and 56% for zinc. In contrast, in the mid-1970s the diffuse load was 18% of the total load for cadmium, 42% for lead, and 40% for zinc.

Although their percentages in the total load have increased, the diffuse loads of heavy metals have decreased since the mid-1970s. For cadmium and zinc this decrease is mainly due to large reductions of atmospheric emissions. In the case of zinc, reduction in rates of corrosion of zinc-galvanized material occurred because of large reduction in SO_2 concentration in urban areas. Additionally for lead, the decline in the diffuse load was realized by the decreased lead content in gasoline since 1976.

Recently the main source of the diffuse cadmium load in the Rhine basin is the surface runoff in rural and urban areas caused by atmospheric deposition. Surface runoff and traffic-related loads were the main sources of the diffuse lead load. But it can be assumed that the diffuse load of lead has decreased in the last 10 years because of reductions in the increasing use of lead-free gasoline in the Rhine basin.

The main source of the diffuse load of zinc is corrosion followed by the traffic-related diffuse load and the load from surface runoff in rural and urban areas.

With regard to the diffuse loads from paved urban areas, separate sewer systems are mainly responsible for their high contribution to the total diffuse load. Strategies for the reduction of urban diffuse loads should focus on reducing the load from the sources (e.g., further introduction of storm water reservoirs).

The results of this study are only the first step in the analysis of the pathways of selected pollutants in the Rhine basin. More detailed studies are necessary, particularly with a higher spatial resolution, to detect not only the values of point and diffuse loads for the whole basin but also the spatial allocation of these loads. Such an analysis will indicate areas of high accumulation of these pollutants, and would provide better guidance on measures for reducing the loads most efficiently.

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