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PREFACE

The research described in this working paper 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 for Public Health and Environmental Protection (RIVM). The goal of the study is to determine, by mass balance analysis, the inputs and outputs to the Rhine Basin over the time period from 1950 to 2010. Particular attention is being 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 working paper 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 senior author of this paper. 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 of the major goals of the study.

Point and diffuse loads of selected pollutants in the river Rhine and its main tributaries

by Horst Behrendt & Michael Böhme

1. Introduction

The analysis presented 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 based on a collaborative agreement between the National Institute of Public Health and Environment Hygiene (RIVM) of the Netherlands and the International Institute of Applied System 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 a high spatial, temporal, and structural resolution, which would be necessary for generating scenarios as part of a decision support system.

This paper describes an alternative method for estimating the amount and fractions of pollutant loads from point and nonpoint sources. The method, developed by BEHRENDT (1991), 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 to calibrate 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/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 summarized overview on 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 river Rhine and its main tributaries.

2. Data base

The data base 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:

Rivers:	**Rhine**	**Moselle**	**Main**	**Neckar**
Stations:	Rekingen	Koblenz	Kostheim	Mannheim
	Village-Neuf	(ICPR)	(DKSR)	(DKSR)
	Seltz			
	Koblenz			
	Bimmen/Lobith			
	(all ICPR)			

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 station Lobith)

1973 - 1987 all other substances

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

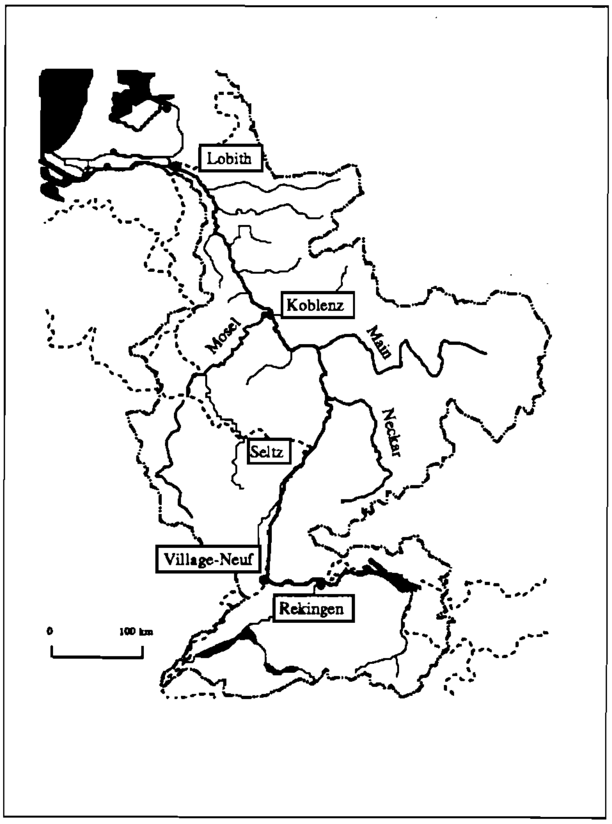

Fig. 1: Map of the Rhine basin with the location of river monitoring stations.

3. Method

According to NOVOTNY & 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 or not related to meteorological factors. Sources are identifiable points.

- **Diffuse sources** are mostly highly dynamic in 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. Sources often 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 to the river. For example, wash off of road dust from an urban area during a storm is a diffuse or source independent of whether this load reaches the river mainly through canalization and effluent discharge from sewage treatment plants. Instead, point and diffuse sources are differentiated by the relationship between the concentration/load of pollutants and the runoff or discharge.

It is further assumed that the load of a pollutant at a given time and point (e.g. monitoring station) is the result of a linear combination of the loads caused by different hydrological components and the point load. According to DYCK (1985) surface runoff (Q_S) and subsurface runoff (Q_I; sum of interflow and basic flow) are considered as the main hydrological components of river flow.

From these assumptions, the model given in equations (1) to (3) was applied for each pollutant investigated:

$$K = (K_I \bullet Q_I + K_S \bullet Q_S + K_P \bullet Q_P) / Q \qquad (1)$$

$$L = K \bullet Q = K_I \bullet Q_I + K_S \bullet Q_S + K_P \bullet Q_P \qquad (2)$$

$$Q = Q_I + Q_S + Q_P \qquad (3)$$

where:

Q = measured discharge at the monitoring station;

Q_I = sum of interflow or subsurface flow of water within the watershed;

Q_S = sum of surface flow of water within the watershed;

Q_P = sum of water flow caused by all point sources within the watershed;

K = measured concentration of pollutant at the monitoring station

K_I = weighted mean of the concentration of pollutant caused by interflow or subsurface flow;

K_S = weighted mean of the concentration of pollutant caused by surface flow;

K_P = weighted mean of the concentration of pollutant of all point sources within the watershed;

L = estimated load of pollutant at the monitoring station.

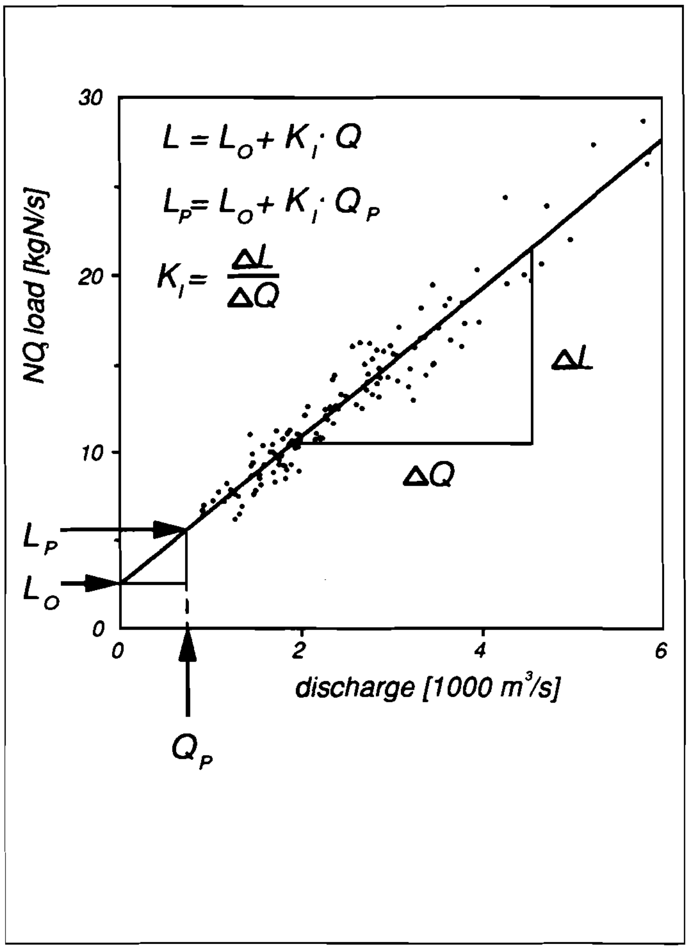

Fig. 2: Dependence of nitrate load on the discharge for the Rhine at the Lobith station for the period 1983-87 as an example for the load-discharge relationship (simple case and graphical presentation of model parameters.

A more detailed description of the model is referred to in BEHRENDT (1991 a).
By conversion of equations (1) to (3) we get the following basic equations for the statistical analysis:

Case A: The total flow is greater than the subsurface flow ($Q>Q_I$)

$$K = K_S + (Q_I \bullet (K_I - K_S) + Q_P \bullet (K_P - K_S)) / Q \qquad (4) \text{ or}$$

$$L = K \bullet Q = K_S \bullet Q + (Q_I \bullet (K_I - K_S) + Q_P \bullet (K_P - K_S)) = K_S \bullet Q + L_{S0} \qquad (5).$$

Case B: The surface flow is negligible (Q_S=0)

$$K = K_I + (Q_P \bullet (K_P - K_I)) / Q \qquad (6) \text{ or}$$

$$L = K \bullet Q = K_I \bullet Q + Q_P \bullet (K_P - K_I) = K_I \bullet Q + L_0 \qquad (7).$$

The concentration of pollutants during times where subsurface or surface flow dominates the total flow can be estimated by means of regression between concentration or load and discharge considering equations (4) and (5), or (6) and (7), respectively.

If the concentration of subsurface and surface flow is approximately the same then the equations (4) and (5) are identical to equations (6) and (7). The representation of different parameters used in the model is illustrated for a simple case in Figure 2. In such a case two kinds of behavior of the concentration or load-flow relationship must be considered, depending on the magnitude of the point and diffuse concentrations (Fig. 3a and 3b). Fig. 3b (case $K_P > K_I = K_S$) shows the common dilution effect of a point load with increasing discharge.

But Fig. 3a (case $K_P < K_I = K_S$) shows a nonlinear increase of measured concentration with increasing discharge. In contrast to previous investigations which attribute this behavior to an increase of the diffuse concentration (K_I), the actual reason is that the mean concentration of the diffuse sources is higher than the mean concentration of the point sources ($K_P<K_I$).

Fig. 3c (case $K_P < K_I < K_S$) illustrates one case, where the concentration of surface flow (K_S) is higher than the concentration of subsurface flow (K_I) and of point sources (K_P). These examples show that the model describes qualitatively the different possible concentration or load-flow relationships.

If the water flow from point sources is known, the regression according to case B (see eq. (6) and (7)) allows one to estimate the point load of the river. The total diffuse load is calculated as the difference between the total load (L) and the estimated point load. Furthermore, the regressions based on the equations (4) or (5) and (6) or (7), respectively, are used to estimate the mean weighted concentrations of the pollutant for the different hydrological conditions. All estimated concentrations and loads are net values corresponding to weighted means for the whole watershed at the monitoring station during the considered time period. In general the gross concentrations and loads are higher due to losses (e.g. sedimentation, treatment of used water, denitrification) which can occur within the river and the catchment area.In this context two assumptions are important for the application of the model as described above:

1. For a given pollutant, the sources and sinks within the river are the same for point and diffuse loads. Thus, the processes within the river depend only on the substance, and not on its sources.

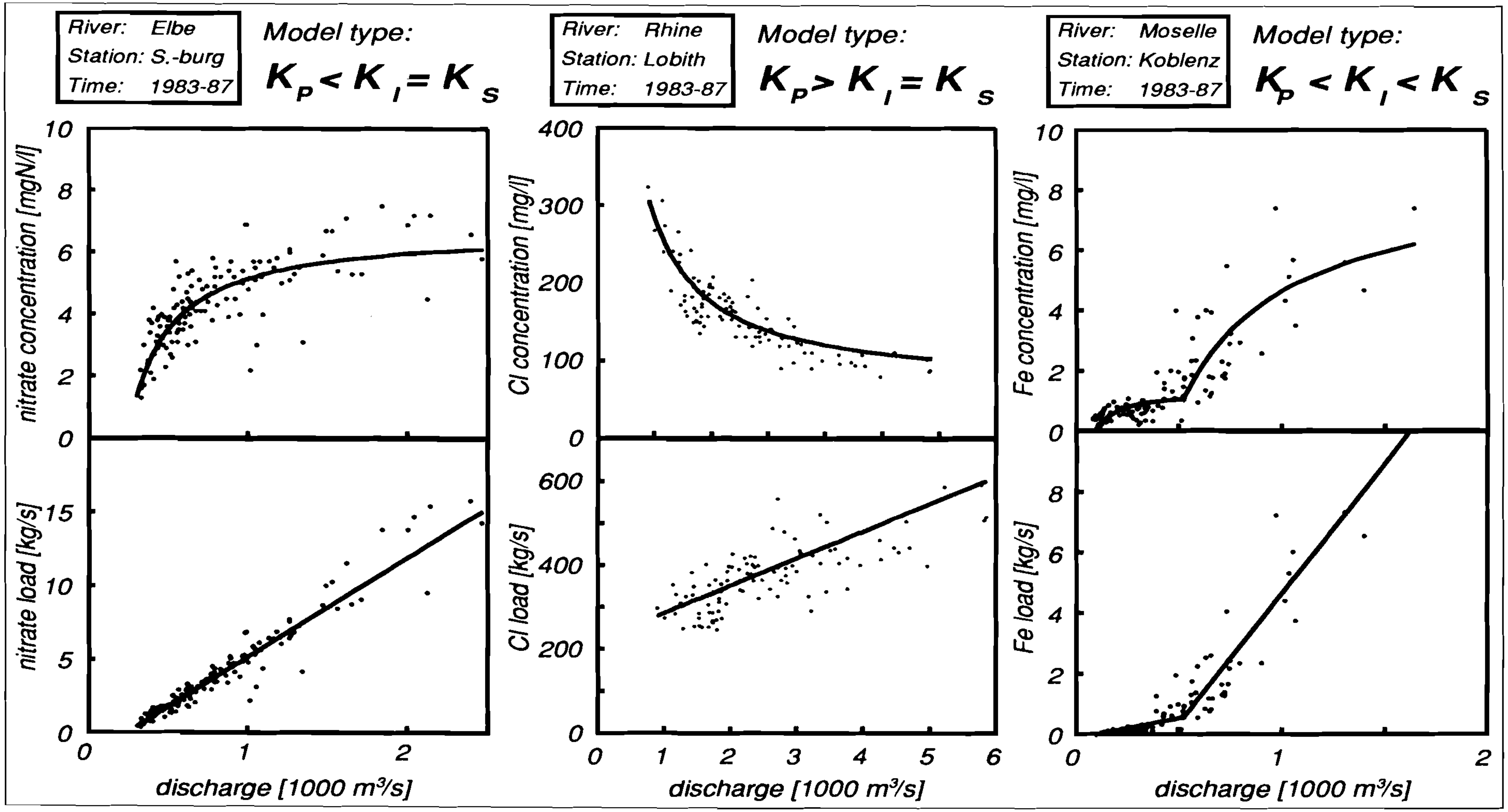

Fig. 3: Examples for different dependencies of pollutant concentration and load on the discharge and results of the presented model.

2. The processes within the river are small compared to the load or do not depend on discharge. Loss processes independent of discharge are i.e. nitrification and denitrification (only in the case of nitrogen) and the 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 depending on discharge are, for example, increasing sedimentation with decreasing flow, or resuspension of sediments with increasing flow, respectively. In the following it is assumed that processes which depend on flow can be neglected in the case of the river Rhine and the investigated tributaries.

Values of the rates of interflow and surface flow into the river for each measured discharge were not available. Therefore the total range of observed flow was divided in to a lower and an upper range. Most of the load-discharge relationships of the Rhine and its tributaries show a significant break (Fig.3c). The break marks a flow, above which the surface flow begins to dominate the total flow. Below the break, total flow is dominated by base flow, interflow, and point waste water flow by point sources.
To find a reasonable breakpoint, which marks the upper limit of the low flow range, a procedure was derived including 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 some cases, especially for substances like nitrate which are transported in the dissolved phase, it was impossible to detect a break. Then the results were based on the regression line of the entire flow range. Otherwise, only the regression over the low flow range was used to estimate the point load.
For chemicals derived mainly from point sources, it was possible to do the analysis with nonlinear concentration-discharge regressions, for instance, ammonia, dissolved inorganic phosphorus (DIP) and chloride. The results of both the concentration and load-based regressions were often similar. The concentration results are not shown separately, but are taken into consideration in the final summary shown in Tables 2 to 4.

4. Results and Discussion

4.1. Estimation of point flow

To estimate the mean point waste water flow within the whole catchment area at each monitoring station, various sources of information were used.
For the German part of the Rhine River basin the data on municipal and industrial waste water and cooling water effluents were taken from publications of Statistisches Bundesamt (STATISTISCHES BUNDESAMT, 1979, 1981). The French and Swiss contribution to the point waste water flow was estimated by means of the comparison between the population living in the German, French and Swiss part of the catchment area of Rhine given by ICPR (1987, 1989).
Ranges of point waste water flow were used, because the calculated values are only raw estimations. Tab.1 shows the estimated values of point source flows. For comparison the lowest discharge of the rivers within a 14 year time span are given.

Table 1: Estimated waste water discharges of point sources to the River Rhine and tributaries [m^3/s]

Profile	point waste water flow	lowest river discharge		
		73-77	78-82	83-87
Seltz/Maxau	300 - 400	620	619	546
Koblenz	550 - 650	670	800	679
Bimmen/Lobith	850 - 950	880	1010	912
Neckar	80 - 100			36
Main	80 - 100			74
Moselle	50 - 100	12	74	77

4.2. Testing of model results

Regarding the loads and their sources, Tab.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 on the heavy metal balances of the Rhine (Waterloopkundig laboratorium, 1989). For the comparison it should be noted that the time periods are different for the different studies. Especially in the year 1985 (the basic year for the German and French inventory of pollutant sources), there was a significantly lower discharge and pollutant loads for the different monitoring stations compared with the average discharge of the five year period 1983-1987.

In contrast to our results, the given amounts of point and diffuse loads cited in the other studies have to be understood 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 Tab.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 ktN/a. Considering the loss of nitrogen by denitrification (see section 4.4.1) the gross point load of dissolved inorganic nitrogen was estimated between 230 and 260 ktN/a. On the basis of data from 1985 the magnitude of the gross point load of total nitrogen was estimated at 297 ktN/a by ICPR (1990) for the whole Rhine River basin (including the load from the Netherlands). A point load of approximately 260 ktN/a can be assumed from ICPR estimation for the Rhine River basin at 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 particulate 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 ktN/a for the whole catchment area. This magnitude seems to be underestimated in comparison with our results (see Table 4) and also with the calculations given by other authors (see i.e. AUERSWALD et al., 1990; FIRK & GEGENMANTEL, 1986; WOLF et al., 1989), too.

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

On the other hand, in the case of cadmium, lead and zinc the point loads estimated by the inventory of ICPR is very close by 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 (1983-87 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 estimated gross point loads are within the range of our results.

In all cases of Tab.2 the gross loads are close by 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 are possible to explain these differences:

1. The assumption of the model, that flow dependent processes in the river can be neglected, is not strictly correct.

Tab. 2: Comparison between estimated net load (point and diffuse) at different monitoring stations of the river Rhine for the time period 1983-87 and estimated gross load (point and diffuse) of 1985 for the German parts of the watershed. All values in t/a.

		Rhine Lobith	Rhine Koblenz	Rhine Seltz	Mosel Koblenz
Zn	point load (mean)(a)	2134	595	180*	164
	range	1753-2548	400-814	57-326	0-391
	point load(b)	2010	616	216	158
	point load(c)	2635			
	diffuse load	2812	2114	1028*	932
	(mean)(a)	2397-3192	1895-2309	893-1161	705-1096
	range				
	diffuse load(b)	1249			
	diffuse load(c)				
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	465	248	134	138
	(mean)(a)	410-515	234-261	115-150	111-158
	range	149	86	53	38
	diffuse load(b)	284			
	diffuse load(c)				
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	15.3		5.9	3.9
	(mean)(a)	14.4-16.4		4.8-6.8	2.8-4.6
	range	2.2	1.3	0.2	0.2
	diffuse load(b)	8			
	diffuse load(c)				
TP	point load (mean)(a)	22500	13800	3400	1800
	range	20500-24700	12800-15000	2900-3900	500-2100
	point load(b)	32000	19300	6400	3675
		(28000)	(17000)	(5600)	(3200)
	diffuse load	12900	10700	5700	3500
	(mean)(a)	10700-14900	9500-11700	5200-6200	3200-3800
	range	8600	5200	900	1450
	diffuse load(b)	(12600)	(7500)	(1700)	(1925)

(a) calculation from this study. Data in brackets are corrected values of the model considering rain water overruns of combined sewage systems (see text).
(b) data based on the inventory of priority substances 1985 (ICPR, 1989; DKSR, 1989; Agence de l'eau Rhin-Meuse, 1988).
(c) mean values for the time period 1984-1986. Source:"Zware metalen balans Rijn. Project Onderzoek Rijn, fase 2", Waterloopkundig laboratorium (1989).
* estimates based on data from 1984-87 only.

For example, the comparison between our net point loads and the gross point load of the inventories for the Mosel area shows that phosphorus and lead are eliminated more by sedimentation during times of lower discharge than zinc.
Referred to HELLMANN (1987), the annual rate of sedimentation in the watercourses of the F.R. Germany is relatively small. It ranges from 2 % to a maximum of 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 Tab.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 definition given above, the pollutant load caused by washoff from urban areas (e.g. dust load from streets and roofs) is a diffuse source. That means the real gross point load of the inventory is smaller than the total point load given by ICPR inventory. Especially for lead, where the load from urban areas dominates, the diffuse load can be an important part of the total load from sewage plants. In the referred Dutch study (WATERLOOPKUNDIG LABORATORIUM, 1989) it is pointed out that the load from streets and the deposition in urban areas which goes via canalization into sewage plants is assumed as a point source.

4. The estimated diffuse load based on our model includes, depending on the substance, a fraction of point sources, which enters the river system at high discharges through rainwater overflows. This occur because the combined sewage systems can not transport all of the entire water volume to the sewage treatment plant during storm events. The proportion of storm water overruns compared to the total load of sewage treatment plants was estimated by SPERLING (1986) at 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 the Rhine stations Lobith and Koblenz are higher by 3 and 2 ktP/a, respectively, and the diffuse loads are reduced by these magnitudes. The corrected values of the point and diffuse load of phosphorus are given in brackets in the Tab.2.
Considering this change from diffuse to point load of phosphorus our estimated values are between 80 and 85 % of the gross point loads estimated by ICPR (1989), and the studies of the diffuse load of phosphorus in West Germany (see section 4.4.2; AUERSWALD et al., 1990; FIRK & GEGENMANTEL, 1986) .

5. In the case of phosphorus, one must consider that input by point sources is reduced within the time period 1983-1987. HAMM (1989) states that the total phosphorus point

load in the F.R. Germany is reduced from 56.3 ktP/a in 1985 to 47.6 ktP/a 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. The numerous possibilities for the explanations of the differences between our results and the others do not clearly allow for an unambiguous explanation.
Therefore, it will be assumed that the model results with regard to the amount of net point load are approximately correct with exception of the river Mosel, where sedimentation at low discharges and resuspension during floods cannot be excluded.

Several authors (see e.g. HAMM, 1989; FIRK & GEGENMANTEL, 1986; AUERSWALD et al., 1990) have recently published detailed balances of phosphorus and nitrogen for West Germany (old FRG). The results of these investigations can be also used to test the estimations based on our model. The most detailed analysis of the diffuse sources of nitrogen and phosphorus is given by AUERSWALD et al. (1990).
The portion of the diffuse load compared to 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 to the total load is 50-60 % for dissolved inorganic nitrogen (NH_4+NO_3) and 30-35 % for total phosphorus. Both relations are in a good agreement with the results of AUERSWALD et al. (1990), 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 (see section 4.4.2).
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/load-flow relationship from the one shown in Fig.3a (K_P<K_I) to the one shown in Fig.3b (K_P>K_I). An example of such a change is presented in Fig.4.

Tab.3: Results of the model for nitrate at the Rhine station Lobith for different time periods.

	time period 1953-57	time period 1983-87
results of regression $y = a \cdot x + b$:		
$a = K_I$ [mgN/l]	2.09	3.50
$b = Q_P(K_P-K_I)$ [kgN/s]	-0.745	1.29
r	0.895	0.909
n	112	131
estimated net point load (Q_P=700-900 m^3/s) [ktN/a]	18-40	110-147
estimated net diffuse load [ktN/a]	74-96	170-207

This Figure shows the dependence of nitrate concentration and load on the discharge at the Rhine station at Lobith for the time periods 1953-1957 and 1983-1987. Additionally the Figure includes the estimations calculated 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 reproduce the changes over time realistically. 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 installation of industrial and municipal sewage treatment plants with biological nitrification capabilities.That is reflected in the model by the fact that the constant parameter (b) of the regression is changed from b<0 to b>0 (Table 3).

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

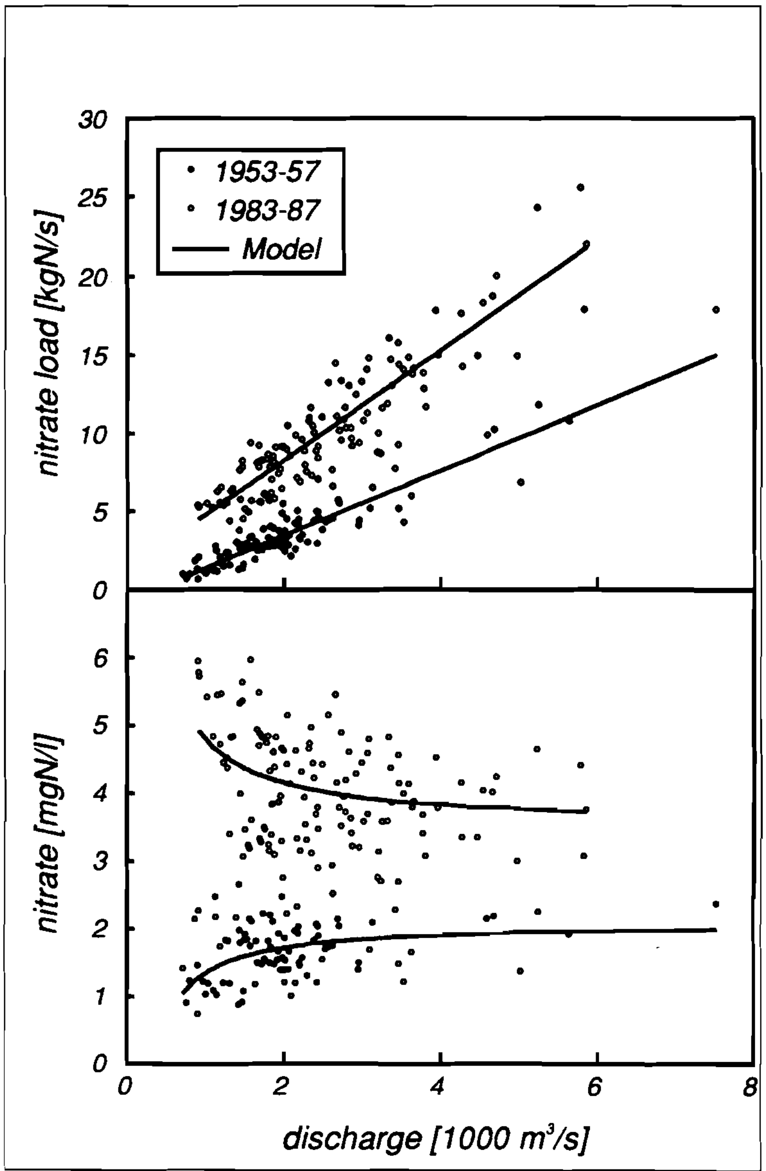

Fig. 4: Changes in the nitrate concentration and load-discharge relationship at the Rhine station at Lobith for the time periods 1953-57 and 1983-87.

Detailed phosphorus balances are available for West Germany for the years 1975, 1985

and 1987 (BERNHARDT et al., 1978; FIRK & 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 %.
All these comparisons demonstrate that the proposed model can approximately simulate the amounts of different sources of pollutants within a river and its changes with time.

4.3. Analysis of point and diffuse loads of pollutants within the catchment area of the river Rhine over the period 1973 - 1987.

An overview of the diffuse, point, and total net loads into the river Rhine and the tributaries Mosel, Main and Neckar is given in Table 4.

The analysis includes the changes in point and diffuse loads at the Rhine stations Lobith, Koblenz and Seltz for the various time periods since the mid 1970's with additional estimate for the period 1983-87 at the Neckar, Main and Mosel stations.
These results are also shown graphically for each of investigated pollutant at the Rhine stations Koblenz and Lobith in the Figure 5 through 9.
With exception of DIN the total load for all investigated pollutants has been reduced since 1973, especially in the case of the heavy metals (Table 4 and 5). With regard to the diffuse load, the changes are less certain and not uniform for all chemicals.

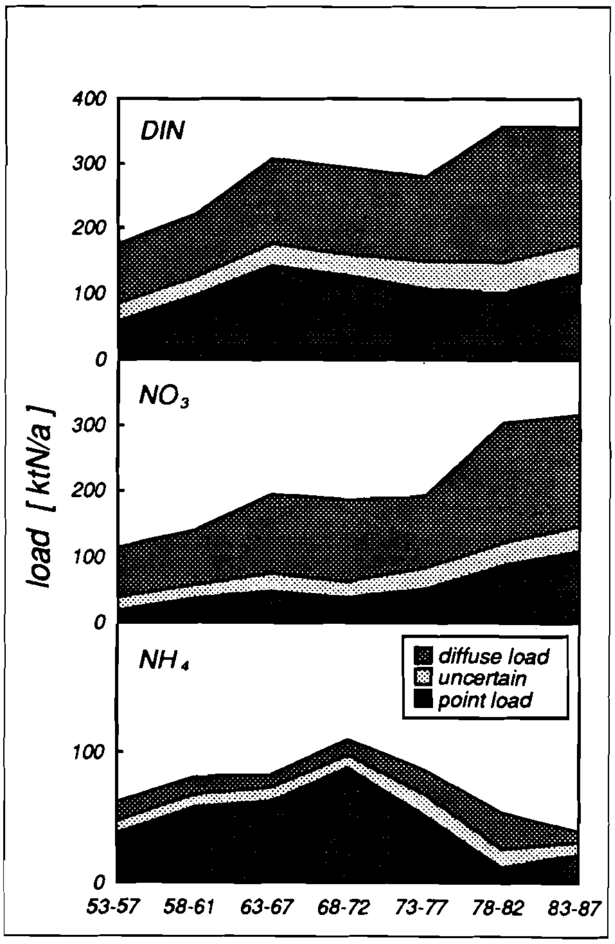

Fig. 5: Changes of estimated point and nonpoint load of ammonia, nitrate and dissolved inorganic nitrogen (DIN) at the rhine station Lobith since the mid of 1950s.

As shown in Table 5 the decrease of the diffuse load of cadmium was most highest with an average reduction of 42 % over the whole time period. Also in the case of zinc a reduce of 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 %.

Tab. 4: Estimated total, point and diffuse loads of nitrogen, phosphorus, zinc, lead and cadmium at different monitoring stations of Rhine and its main tributaries Neckar, Main an Mosel.

river station period		TP [kt/a]			N [kt/a]			N_{corr} [kt/a]		
		min	max	min	min	mean	max	min	mean	max
Rhine Lobith 1983-87	total load		35.4			356			505	
	point	20.5	22.5	24.7	156	167	179	252	262	273
	point [%]	58		70	44		50	50		54
	diffuse	10.7	12.9	14.9	178	189	200	232	243	253
	diffuse [%]	30		42	50		56	46		50
Rhine Lobith 1978-82	total load		41.4			359			480	
	point	24.2	26.5	29.0	126	137	149	233	243	254
	point [%]	58		70	35		42	48		53
	diffuse	12.5	15.0	17.3	210	221	232	226	237	247
	diffuse [%]	30		42	58		65	47		52
Rhine Lobith 1973-77	total load		50.3			284			407	
	point	31.6	34.6	37.8	133	146	159	232	245	258
	point [%]	63		75	47		56	57		63
	diffuse	12.6	15.8	18.7	124	138	151	149	163	176
	diffuse [%]	25		37	44		53	37		43
Rhine Koblenz 1983-87	total load		24.5			216			336	
	point	12.8	13.8	15.0	83	91	99	131	141	151
	point [%]	52		61	38		46	39		45
	diffuse	9.5	10.7	11.7	117	126	133	184	195	204
	diffuse	39		48	54		62	55		61
Rhine Koblenz 1978-82	total load		32.5			213			315	
	point	15.5	16.5	17.7	50	58	67	119	128	138
	point [%]	48		55	23		31	38		44
	diffuse	14.7	15.9	17	146	155	163	177	187	196
	diffuse [%]	45		52	69		77	56		62

* - based on data 1984-87 only.

Tab. 4: (continued)

river station period		TP [kt/a] min	 max	 min	N [kt/a] min	 mean	 max	N_{corr} [kt/a] min	 mean	 max
Rhine	total load		30.5			138			240	
Koblenz	point	15.9	17.1	18.3	51	59	68	106	117	128
1973-77	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	
Seltz	point	2.9	3.4	3.9	25	32	40	23	32	42
1983-87	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	
Seltz	point	11.2	13.4	16.3	6	16	28	8	23	40
1978-82	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
1983-87	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
1983-87	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
1983-87	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

Tab.4: (continued)

river station period		Zn [t/a]			Pb [t/a]			Cd [t/a]		
		min	max	min	min	mean	max	min	mean	max
Rhine Lobith 1983-87	total load		4946			704			25.9	
	point	1753	2134	2548	189	240	294	9.5	10.6	11.5
	point [%]	35		52	23		42	37		45
	diffuse	2397	2812	3192	410	465	515	14.4	15.3	16.4
	diffuse [%]	48		65	58		73	55		63
Rhine Lobith 1978-82	total load		9562			805			96.1	
	point	4978	6070	7286	212	265	323	68.9	76.5	84.8
	point [%]	52		76	26		40	72		88
	diffuse	2276	3491	4584	482	540	593	11.2	19.6	27.1
	diffuse [%]	24		48	60		74	12		28
Rhine Lobith 1973-77	total load		10164			1502			145.1	
	point	4324	6165	8013	168	872	1502	106.6	118.9	132.4
	point [%]	43		79	11		100	73		91
	diffuse	2420	3999	5840	0	630	1333	12.7	26.2	38.5
	diffuse [%]	21		57	0		89	9		27
Rhine Koblenz 1983-87	total load		2709			329				
	point	400	595	814	68	81	95			
	point [%]	15		30	21		29			
	diffuse	1895	2114	2309	234	248	261			
	diffuse	70		85	71		79			
Rhine Koblenz 1978-82	total load		3431			402			22.5	
	point	1111	1480	1912	73	102	134	8.4	9.9	11.7
	point [%]	32		56	18		33	37		52
	diffuse	1519	1951	2320	268	300	329	10.8	12.6	14.1
	diffuse [%]	44		68	67		82	48		63

* - based on data 1984-87 only.

Tab.4: (continued)

river station period		Zn [t/a]			Pb [t/a]			Cd [t/a]		
		min	max	min	min	mean	max	min	mean	max
Rhine	total load		3661			307			24.6	
Koblenz	point	839	1241	1700	158	191	230	1.9	5.6	10.0
1973-77	point [%]	23		46	51		75	8		40
	diffuse	1962	2420	2822	77	117	150	14.7	19.0	22.7
	diffuse [%]	54		77	25		49	60		92
Rhine	total load		1218			161			7.5	
Seltz	point	57	180	326	12	27	46	0.7	1.6	2.7
1983-87	point [%]	5		27	7		29	9		36
	diffuse	893	1028	1161	115	134	150	4.8	5.9	6.8
	diffuse [%]	73		95	71		93	64		91
Rhine	total load		3456			482			44.9	
Seltz	point	1217	1554	1986	348	395	456	27.5	31.3	36.2
1978-82	point [%]	34		57	72		95	61		81
	diffuse	1470	1901	2239	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						
1983-87	point [%]	53		82						
	diffuse	46	85	120						
	diffuse [%]	18		47						
Main	total load		1189			64			2.5	
Kostheim	point	398	510	638	2	7	13	0.8	1.0	1.2
1983-87	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		1096			169			4.7	
Koblenz	point	0	164	391	11	31	58	0.1	0.7	1.9
1983-87	point [%]	0		36	7		34	2		40
	diffuse	705	932	1096	111	138	158	2.8	3.9	4.6
	diffuse [%]	64		100	66		93	60		98

The rate of decrease of the diffuse load of zinc and cadmium from 1978-82 to 1983-87 was higher compared to the change from 1973-77 to 1978-82.This behavior can be explained by the higher proportion of high discharges related to the total discharge during 1978-82 (see Table 7). An increase of diffuse load by erosion and storm runoff from urban areas can be expected, especially at high discharge 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 is estimated to have occurred between 1973-77 and 1983-87 for West Germany (STAT.YEARBOOKS of FRG).

Tab.5: Changes of loads into the river Rhine at the station Lobith since 1973. All values in percent; loads from the time period 1973-77 are expressed as 100 %.

		1973-77	1978-82	1983-87
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

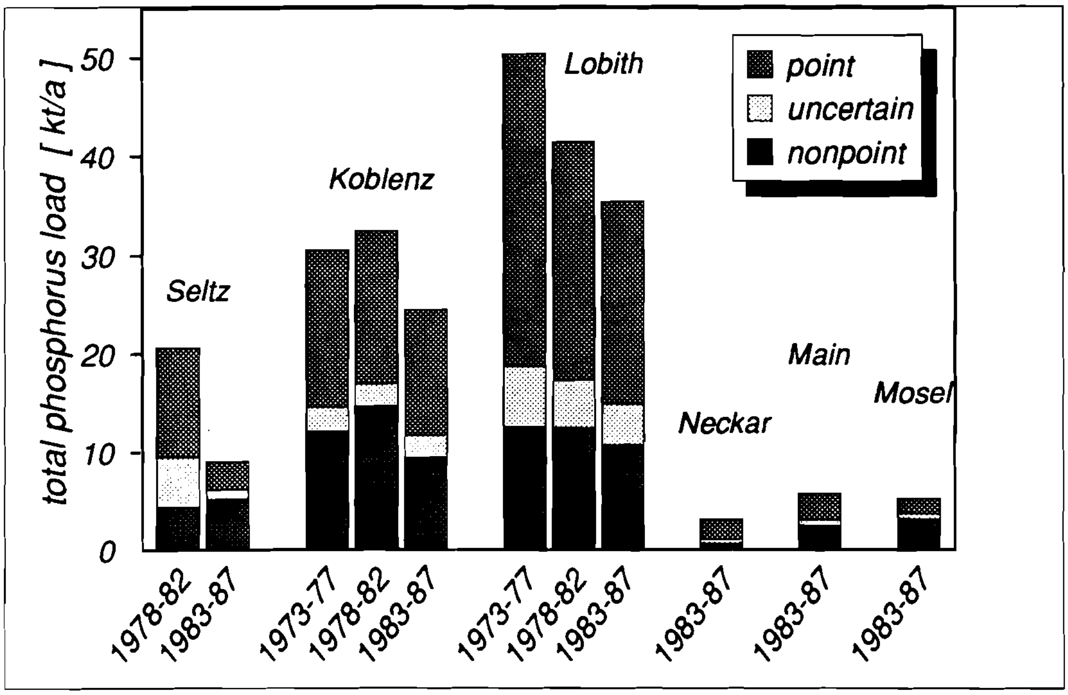

Fig. 6: Estimated point and diffuse load of total phosphorus (TP) at the Rhine station Koblenz and Lobith since the mid 1970s and for later time periods for the Rhine station Seltz and the main tributaries Neckar, Main and Mosel.

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 since the beginning of the 1970s, and decreased rates of zinc corrosion caused by the reduction of SO_2 deposition since the mid of 1960s.
For phosphorus, the estimated mean diffuse load in 1973-77 was a little higher than the load in the period 1978-82 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 load and their changes over time. Such an analysis is given for the heavy metals in section 4.4.3.
In general, it must be pointed out that the estimated trends in the diffuse load of heavy metals are rather uncertain particularly for the first two time periods analyzed, because application of our method was limited by the low number of measurements compared with the time period 1983-1987.
A small decline of the diffuse load was estimated over the whole time period for phosphorus. In contrast, there was a large reduction of point phosphorus load caused by the increasing elimination of phosphorus in detergents.
The causes are not sure for the reduction of the diffuse P-load. Three reasons are possible:

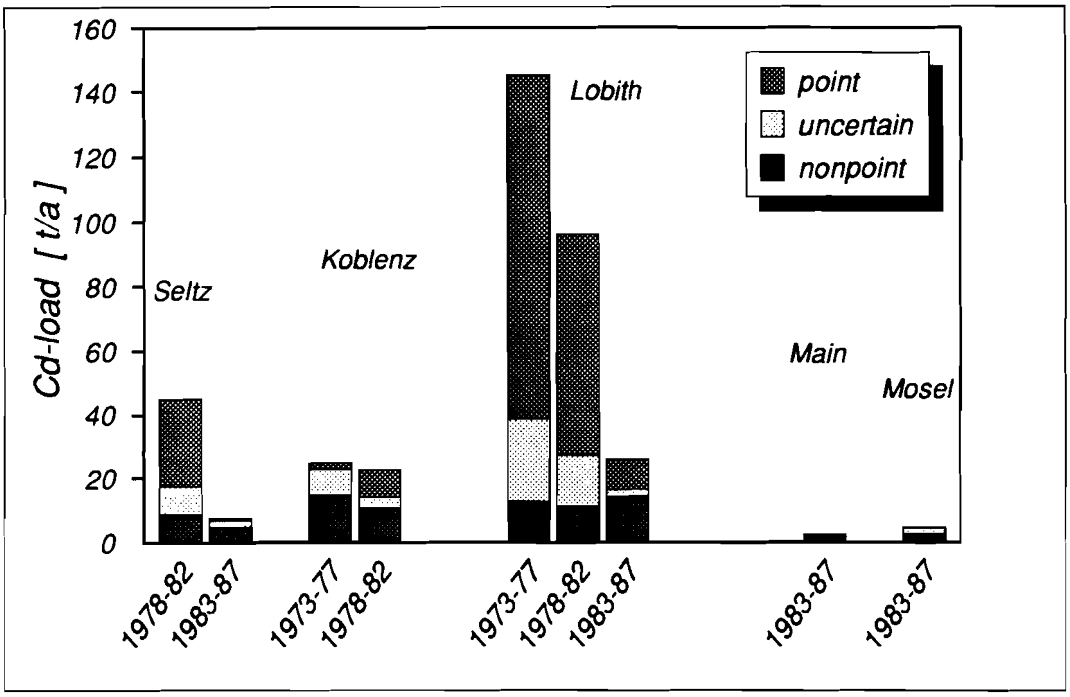

Fig. 7: Estimated point and diffuse load of cadmium at the Rhine stations Koblenz and Lobith since the mid 1970s and for later periods for the Rhine station Seltz and the main tributaries Neckar, Main and Mosel.

1. According to BERNHARDT et al. (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 of 1970s must have result in a reduction in phosphorus deposition, especially in urban and industrial areas where local fallout of particulate matter is expected to be most significant. But as shown in section 4.4.2, the contribution of atmospheric deposition and direct surface flow of rain water into the river is small compared with the other sources of the diffuse phosphorus load.

2. The load of urban areas is not taken into account as a diffuse source of pollutant load in the most studies on the phosphorus balance. As noted by BEHRENDT (1991 b) the proportion of the diffuse urban load of phosphorus is approximately 20 % of the total diffuse phosphorus load in East Germany (former G.D.R.). Compared with the situation in the Rhine River basin, the proportion of urban area on the total area is much higher than in East 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 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 waste water to the municipal sewage treatment plants. A part of the waste water overflows the sewage treatment plant and directly enters the river or flows to special rain water reservoirs. According to SPERLING (1986) the magnitude of the phosphorus load in

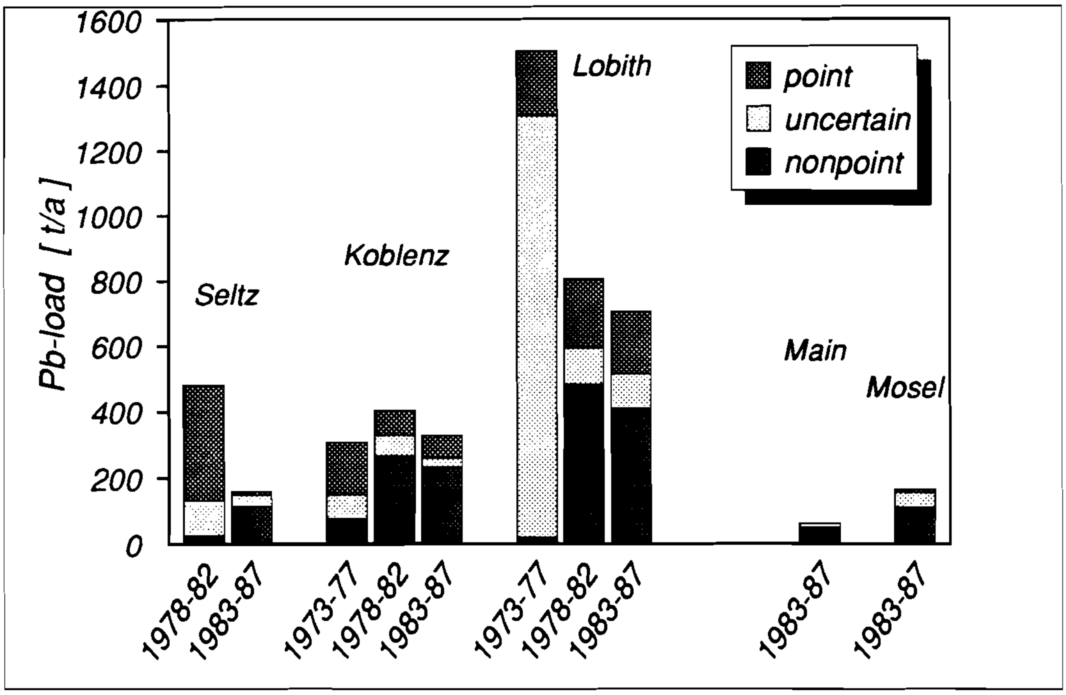

Fig. 8: Estimated point and diffuse load of lead at the Rhine station Koblenz and Lobith since the mid 19702 and for later periods for the Rhine station Seltz and the main tributaries Neckar, Main and Mosel.

rain water 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 waste water 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.

According to our model, both cases, rain water 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 also with a smaller extent to a decrease of the total diffuse load.

As shown in Table 5 and Figure 5, the dissolved inorganic nitrogen is the only substance where the total as well as the diffuse load increased over the three time periods. The increase of diffuse DIN-load was about 50 % between 1973-77 and 1983-87. This phenomenon can be explained by the 30 % lower average discharge at the Lobith station in the time period 1973-77 compared to the later periods. On the other hand, the estimated concentration of diffuse DIN-load is more than 25 % higher during the periods 1978-82 and 1983-87 respectively, compared with the time period 1973-77.

Figure 5 shows the changes in the load of nitrate, ammonia and dissolved inorganic nitrogen over the 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

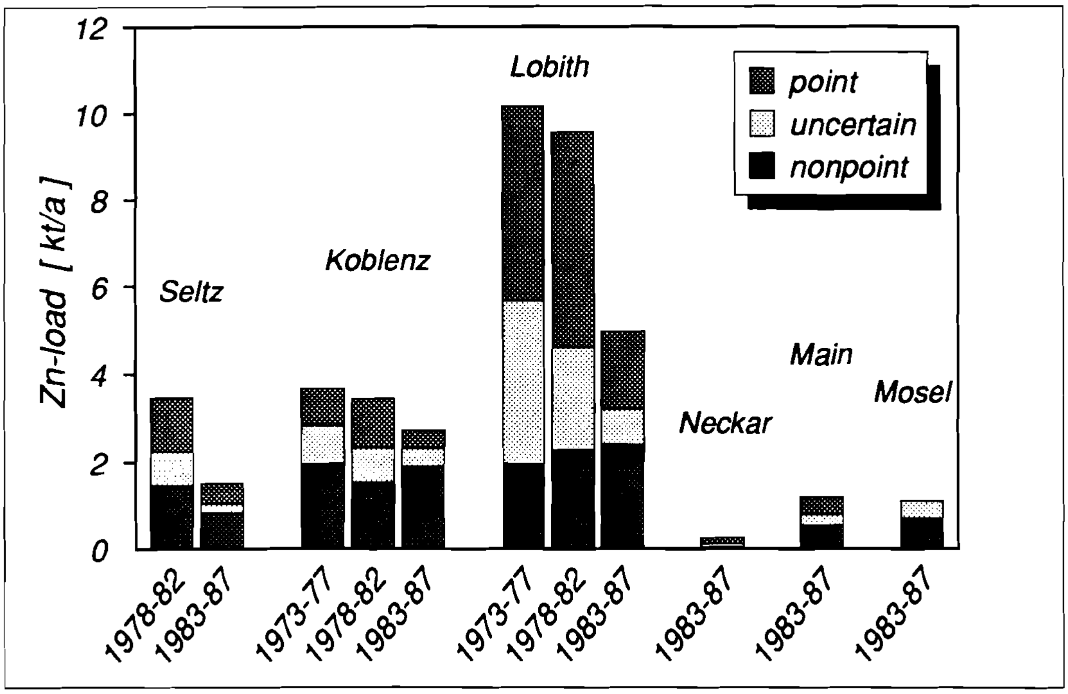

Fig. 9: Estimated point and diffuse load zinc at the Rhine station Koblenz and Lobith since the mid of 1970s and for later time periods for the Rhine station Seltz and the main tributaries Neckar, Main and Mosel.

ammonia, however, did not change significantly over time. The point load of ammonia increased from the beginning of the 1950s to the end of 1960s. This trend was the result of growing industrial production (especially for the chemical industry) and the increased deployment of sewer systems and waste water treatment plants without nitrification. Since the end of the 1960s the magnitude of ammonia point load has decreased to values lower than at the beginning of the 1950s. The point load of ammonia seems to be constant in the last ten years. The decline in the ammonia point load resulted from the introduction of a nitrification process in the most of the municipal and industrial sewage treatment plants since the 1970s. In contrast, the point load of nitrate is increasing particular since the end of the 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 second half of 1970s. The main reason is the large unbalance between inputs of nitrogen fertilizer and manure and crops uptake of nitrogen within the Rhine River basin (see e.g. ISERMANN, 1990; BEHRENDT, 1988, ETCHANCHU & SOUCHU, 1988).

4.4. Estimation of the sources of diffuse load within the river Rhine

Based on the model approaches of equations (4) or (5) and (6) or (7), mean weighted net concentrations of the diffuse load at low and high flow rates can be estimated for each investigated pollutant.

An overview on 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.

Especially at the Mosel station Koblenz the concentration of iron during high discharges is more than tenfold higher than during lower discharges. Also for lead the difference 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 Lobith and Koblenz, but are nevertheless still large (factors of 4.3 and 6, respectively).

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

In general the concentrations of elements during high discharges are higher within the Mosel watershed than at the Rhine stations Koblenz and Lobtih. With regard to the concentrations of pollutants during periods of lower discharges, it can be observed that the differences for different stations are smaller than in cases with high discharges.

In contrast to the results for the monitoring stations, the picture is an other for the watershed between Koblenz and Lobith (excluding the Mosel River basin). In this area industrial and urban influences dominate the diffuse loads. Especially 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.

The estimated TP-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 2 to 3 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 Rhine basin between Koblenz and Lobith these estimated concentrations are comparable with the concentrations of separate sewer systems.

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. AUERSWALD et al. (1990) and HELLMANN (1986) assumed that approximately 10 % of the total runoff is caused by floods. That means that approximately $7.9 \cdot 10^9$ m^3/a of the discharge at the Rhine station Lobith are caused by floods.

Tab.6: Estimated concentrations of interflow (K_I) and surface flow (K_S) at different monitoring stations of the Rhine River basin (data base: Zahlentafeln 1983-1987, Internationale Kommission zum Schutze des Rheins gegen Verunreinigung). All values in mg/m³.

		Rhine Lobith	Rhine Koblenz	Mosel Koblenz	Rhine between Koblenz-Lobith
Zn	K_I	54	49	48	53
	K_S	99	111	155	376
Pb	K_I	8.2	5.6*	5.8*	10.9
	K_S	21.5	11.7	27.3	68.2
Cd	K_I	0.31	0.16		0.2
	K_S	0.36	0.37		1.3
Fe	K_I	1540	810	860	3230
	K_S	6640	4850	9950	7160
TP	K_I	127	185	310	263
	K_S	532	421	660	917

* most of values represent the limit of measurement of 5 µg/l. Therefore, the estimated K_I is probably too high.

Table 7 presents an overview of the ratio of high discharges on the total discharge at the Rhine stations Lobith and Koblenz for the investigated three time periods. It is shown that this ratio varies between 0 (Koblenz station, 1973-77) and 13 % (both stations, 1978-82). The estimated ratios agree on average with the magnitude of floods given by AUERSWALD et al. (1990).

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 with 10 % of the water flow during floods.

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

Tab.7: Ratio of the sum of high discharge (Q_H) to the sum of total discharge at the Rhine stations Lobith and Koblenz for different time periods. High discharges are defined as Q>5000 m^3/s at the Lobith station and Q>3500 m^3/s at the Koblenz station, respectively.

	1973-77	1978-82	1983-87
Koblenz sum(Q_H)/sum(Q) [%]	0	13	8
Lobith sum(Q_H)/sum(Q) [%]	3	13	7

Tab.8: Estimated means of diffuse loads caused by low and high discharges at Rhine stations Lobith in the period 1983-87 (based on the assumption that 10 % of the total discharge is caused by floods).

	Zn [t/a]	Pb [t/a]	Cd [t/a]	Fe [kt/a]	TP [kt/a]
$load_{high\ flow}$	780	170	2,8	52	4,2
$load_{low\ flow}$	2220	323	9,7	49	8,8
$load_{high\ flow}$ / total diffuse load	26%	31%	23%	51%	32%

In the following section we attempt to identify and quantify more precisely the sources of the total diffuse loads of each of the pollutants using known information on land use, deposition and soil contents of pollutants. All of these analyses must be viewed as rough estimates.

4.4.1. Nitrogen

AUERSWALD et al. (1990) have conducted a detailed study on the sources of the diffuse load of nitrogen in West Germany . Furthermore, FIRK & GEGENMANTEL (1986) give an overview of the main sources of the nitrogen load into the surface waters of West Germany. As a first approximation 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 the comparison between the total diffuse loads at the Lobith station and for West Germany as a whole.

Tab.9: Sources of diffuse nitrogen load within the catchment area of the river Rhine.

source	diffuse nitrogen load [ktN/a] 1983-87	
	AUERSWALD et al. (1990)	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)	189 (221)
estimated diffuse load at Lobith (see Tab.4)	178 - 214	

The bracket values of the first column in Table 9 present the results of AUERSWALD et al. (1990) for watersheds with an area greater than 1000 km^2. In this case the load of particulate nitrogen caused by erosion is lower than for small watersheds, because additional sinks of particulate material have to be considered. The bracket values of the second column show
As shown in Table 9 the sum of all diffuse sources estimated on the basis of the data of AUERSWALD et al. (1990) is approximately one third higher than our values. The major

reason for this discrepancy is the occurrence of nitrogen-loss processes to the atmosphere (mainly denitrification of nitrate) that reduce the actual nitrogen load entering the river. Furthermore, our estimates do not include the fraction of particulate nitrogen, because the total nitrogen was not measured. AUERSWALD et al. (1990), however, do not include the load from urban areas as a separate diffuse source, although, based on the estimates of FIRK & 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 & GEGENMANTEL (1986) are within the range of our estimates. But it must be noted that the assumption of these authors for wet deposition of nitrogen (8 kgN/(ha·a)) is low compared with the estimates of other authors. According to NLW (1985) the wet deposition of nitrogen is between 10 - 22 kgN/(ha·a) in rural areas of "Niedersachsen". The arithmetic mean was estimated to be 17 kgN/(ha·a). BRECHTEL (1989) gives a range of the wet deposition of dissolved inorganic nitrogen between 6.6-31.3 kg/(ha·a) (arithmetic mean 15.7 kg/(ha·a)). If it is assumed that the wet deposition of nitrogen (NO_3 + NH_4) is 17 kgN/(ha·a), than the load from atmosphere is about 53 ktN/a (bracket value in the column FIRK & GEGENMANTEL of Table 9). If this change is considered, the total diffuse load estimated on the basis of results of FIRK & GEGENMANTEL (1986) is about 217 ktN/a.

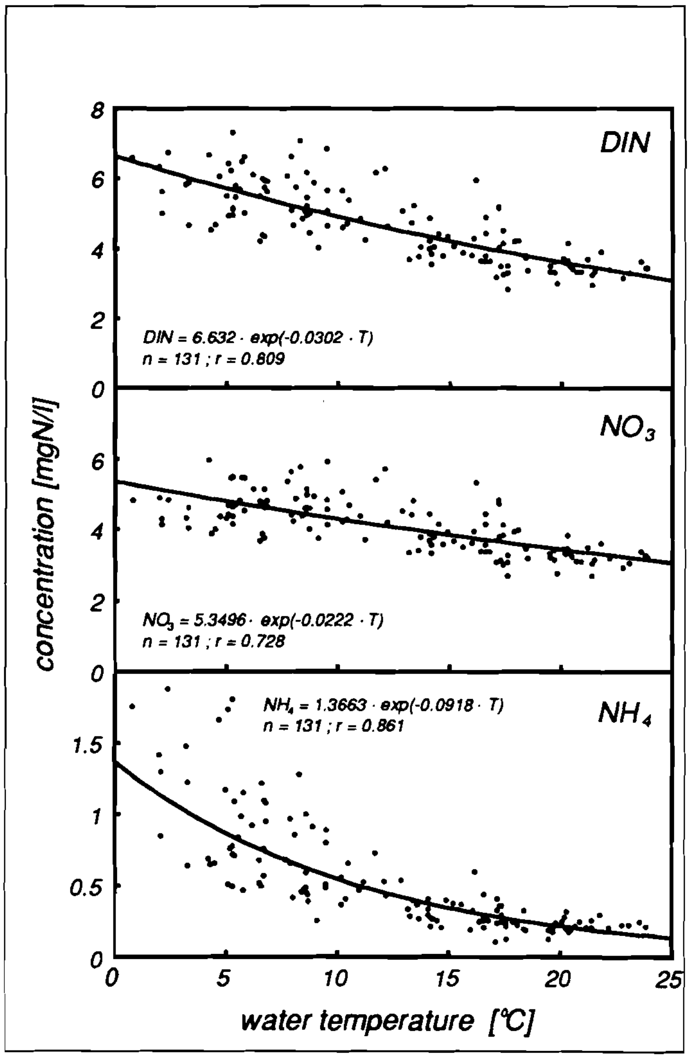

Fig.10: Dependencies of ammonia, nitrate and dissolved inorganic nitrogen (DIN) on the water temperature at the Rhine station Lobith (time period: 1983-87).

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 10), 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 11).

The influence of oxygen concentration on denitrification was not considered because in this case the O_2-concentration near the sediment is important but was not observed.

If we take the temperature-correction into account with regard to our calculated range for the diffuse nitrogen load, then the corrected range amounts to 237 - 275 kt/a. This value is directly comparable with the total gross load value estimated by AUERSWALD et al. (1990). The corrected total load of dissolved inorganic nitrogen at the Lobith station (505 kt/a, see Table 4) agrees with the magnitude estimated by WOLF et al. (1989) (total nitrogen load within the Rhine River basin 505 ktN/a).

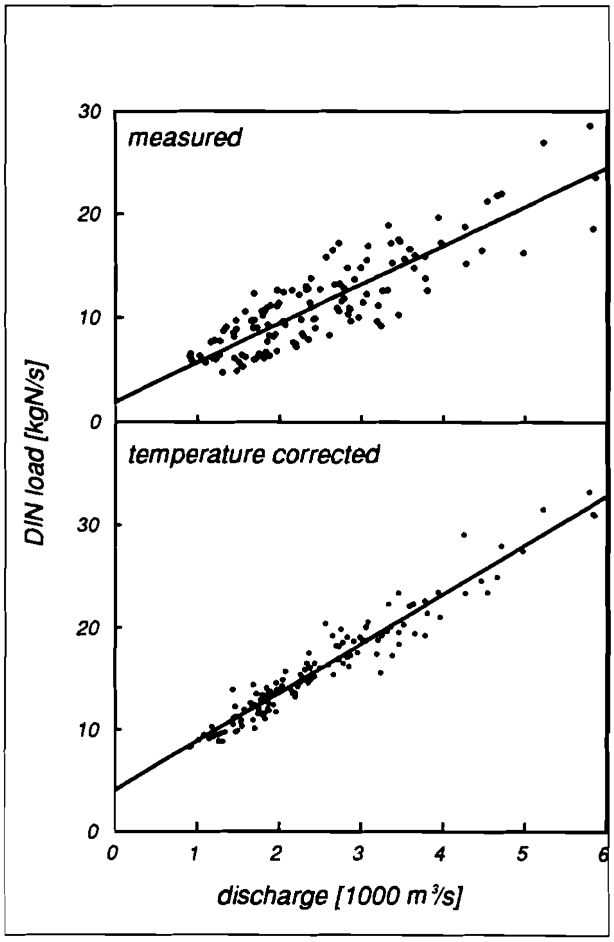

Fig.11: Dependence of measured and temperature corrected dissolved inorganic nitrogen load on the discharge of the river Rhine at the Lobith station (time period: 1983-87)

The difference between the estimated net load and 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 river station Lobith was estimated to be approximately 150 ktN/a. The proportion of denitrification, transport and transformation of particulate nitrogen, respectively, on the total gross load is 30 %. WOLF et al. (1989) assumed that the losses of dissolved inorganic nitrogen are 34 % in the surface waters of

West Germany.
ADMIRAAL & van der VLUGT (1988) estimated high denitrification rates of between 15-49 gNO_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 gN/m^3 in 1985. Then the mean load of particulate nitrogen at Lobith is approximately 63 ktN/a (mean discharge: 2500 m^3/s). WOLF et al. (1989) assume 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 80-90 ktN/a in the Rhine and its main tributaries.
According to Table 9 the load of nitrate via groundwater caused by leaching of nitrate from agricultural areas is the major source of the diffuse nitrogen load (66 %). The contributions of the other sources to the diffuse load are not so certain, 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 of lower than 10 % of the total diffuse load.

4.4.2. Phosphorus

Detailed studies of the sources of diffuse loads of phosphorus are also available for West Germany (AUERSWALD et al.1990, FIRK & GEGENMANTEL, 1986, HAMM, 1989).
The procedure for separation of different sources of the diffuse phosphorus load is similar to that for nitrogen. The results are shown in Tab.10. The major sources of the diffuse P-load are erosion, and the direct or indirect loading of phosphorus from applications of animal-waste and other agricultural sewage. AUERSWALD et al. (1990) estimated that about 2 ktP/a enter the surface waters of West Germany from application of excessive amounts of animal-waste slurries to agricultural lands.
The comparison of the results of these authors shows the highest differences for erosion. The estimates of FIRK& GEGENMANTEL (1986) and HAMM (1989), however, are based on crude assumptions, while the estimation of AUERSWALD et al. (1990) 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 for the whole Rhine area is larger than the amount that actually reaches the Rhine and its major 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 brackets of Table 10 is applicable to catchment areas greater than 1000 km2, 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 estimated approximately the same amounts.

AUERSWALD et al. (1990) as well as HAMM (1989) 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.

Table 10: Sources of diffuse phosphorus load within the catchment area of the river Rhine.

source	diffuse phosphorus load [ktP/a] 1983-87		
	AUERSWALD et al.(1990)	FIRK & 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		

The diffuse urban P-load estimated by FIRK & GEGENMANTEL (1986) seems to be underestimated, because the assumed stormwater runoff of the paved area (2800 $m^3/(ha \cdot a)$) is smaller compared with the value estimated according to the formula of FALK (1987) (4000 - 5000 m^3/s).

The change of P-load over time is mainly dependent on the balance of phosphorus in the agricultural soils. At the present level of application of P-fertilizer and manure, this balance is positive for West Germany (BEHRENDT, 1988; AUERSWALD et al., 1990, ISERMANN, 1990). According to these authors the annual increase of P-content in agricultural soils is about 1-2 %. The situation in France and Switzerland is comparable to West Germany. Based on the increase of P-content in agricultural soils, the erosion of phosphorus is estimated to have increased about 10 - 20 % from the mid 1970s to the mid

1980s in the Rhine basin. But the P-concentration in drainage depends also on the total P-content of soils. Therefore the P-load from drainage has also increased since the mid 1970s. On the other hand the P-load by surface runoff and from paved urban areas has decreased in the last two decades (see chapter 4.3).

4.4.3. The sources of diffuse heavy metal loads

To estimate the load of heavy metals within the Rhine Basin a similar procedure was applied as for nitrogen and phosphorus. Generally, four sources of heavy metal load have to be distinguished from the point of view of hydrological origin. These sources are surface runoff (load of deposited material), erosion (load of eroded material), groundwater, and the load of paved urban area. The load form urban areas is considered separately because quite different hydrological and geochemical conditions prevail. All of the following estimations were done for the catchment area as a whole. Therefore the results should be considered as very crude, and only as a first approximation.
According to WATERLOOPKUNDIG LABORATORIUM (1986), the catchment area of the Rhine upstream from the Lobith station is divided into a part of low contamination (11.4 10^6 ha), an area of higher contamination (3.5 10^6 ha) and a total paved urban area of approximately 0.6 10^6 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 10^6 ha and a mean portion of paved area to the total urban area of one third.

4.4.3.1. Groundwater

The mean water transport from ground water to surface water (basic flow) in the Rhine area is assumed to 254 mm/(m^2 a) or about 39 10^9 m^3/a (AUERSWALD et al., 1990). 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 10^9 m^3/a and 9 10^9 m^3/a, 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 waters 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 & NEUMANN (1981) 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 between

9 and 50 mg/m^3. In the case of lead the concentrations varied between 1 and 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), in which maps are presented of heavy metal concentrations in springs. If it is assumed that the source of the springs is mainly groundwater, then these maps can be used as a rough estimation of heavy metal concentration. Ranges and mean concentrations of the low and high contaminated areas are presented in Table 11 for cadmium, lead and zinc.

Tab. 11: Concentrations of cadmium, lead and zinc in brooks and springs (source: Geochemical Atlas of Germany, FAUTH et al., 1985). All concentrations are given in mg/m^3 for the time period 1983-87.

	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

Tab. 12: Estimated load of cadmium, lead and zinc in the surface waters of the Rhine basin transported by groundwater. All values are given in t/a for the time period 1983-87.

	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

The load of heavy metals in surface waters of the Rhine Basin from transport by groundwater may be calculated by multiplying these assumed concentrations by the estimated basic flow of low and high contaminated areas. The loads of different areas and the total load are shown for the 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 top soil to groundwater was neglected.

4.4.3.2. Surface runoff

The load of heavy metals caused by surface runoff was estimated using the same procedure as for nitrogen and phosphorus described by AUERSWALD et al. (1990) and FIRK & GEGENMANTEL (1987). According to these authors about 10 % of the annual flow enters directly into the River Rhine via surface runoff in the catchment area, with exception of paved urban areas. The results of the measured wet deposition of Cd, Pb and Zn are summarized in Table 13. According to the ranges of wet deposition on rural areas the ranges of heavy metal loads were calculated. A mean wet deposition in the lower contaminated areas was assumed to be 2 g/(ha·a) for cadmium, 80 g/(ha·a) for lead and 150 g/(ha·a) for zinc. In the case of higher contaminated non urban 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 caused by surface runoff. These values have approximately the same order of magnitude as the estimated loads 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.
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) the total dust emissions were reduced from $1.3 \cdot 10^6$ t in 1970 to $0.55 \cdot 10^6$ t in 1986. The reduction of atmospheric emissions related to industrial point sources of heavy metals was estimated by ANDERBERG (pers. comm.) According to his results the emissions were in the period 1983-87 relative to the early 1970s were 72 % for Cd, 76 % for Pb and 78 % for Zn. 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 major 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.

Table 13: Results of different measurements of wet deposition of cadmium, lead and zinc.

Location	Cd	Pb	Zn	Source
Type of area	[g/(ha·a)]			
West Germany				
rural area	1 - 3	29 - 125	75 - 620	NGUYEN et al.
urban area	2 - 9	124 - 550	170 - 1810	(1990)
ind. area	6 - 85	255 - 2354	270 - 8800	
rural area		80 - 220	130 - 480	NLW (1987)
mean		140	250	
range	2 - 33	50 - 640	90 - 4900	BRECHTEL (1989)
mean	6	190	540	
rural area	2.7	110	150	LINKERSDÖRFER
ind. area	9.1	370 - 730	730	& BENECKE(1987)
rural area	1 - 4	85 - 140	90 - 280	NÜRNBERG et al.
urban area	3 - 9	100 - 420	185 - 830	(1982)
ind. area	6 - 25	320 - 330	270 - 1900	
München / urban	6	138	545	THOMAS (1981)
Nürnberg / urban	4	130	437	(total deposition)
Moosburg/suburb.	3	108	378	
Grassau / rural	5	150	275	
all stations	4 - 14	140 - 580		ROHBOCK et al. (1981)
urban area	11	440		(total deposition)
Stuttgart / traffic	12	432	1320	IFS (1980)
Switzerland				
not specified	4 - 8	500 - 2900	1700 - 3700	IMBODEN et al. (1975)
urban / traffic	3.4	760	680	DAUBER et al. (1978)
Denmark				HOVMAND (1977, 1978)
rural areas	2	93	150	
Copenhagen/urban		700	1100	
Yerseke, NL				
rural area	1 - 2	54 - 103	88 - 152	NGUYEN et al., (1990)
Walsall, UK				
rural area	4 - 11	73 - 243		SIMMONS &
ind. area	6 - 18	121 - 1220		POCOCK (1987)
mean	6	168	3250	
Birmingham,UK				
rural area	4 - 20	275 - 500	225 - 650	HEDGES & WREN (1987)

LIEDHOLM et al. (1981) reported that the contribution of vehicle exhausts to the total lead emissions to the atmosphere was about 74 % in Sweden in 1977/78. 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 period 1978-1982 and 49 % in the period 1983-87.

Tab.14: Estimated loads of cadmium, lead and zinc via surface runoff in the river Rhine and its main tributaries. All values given in t/a for the time period 1983-87.

	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

4.4.3.3. Erosion

The estimation of heavy metal load by erosion was conducted by comparison with the phosphorus erosion calculated by AUERSWALD et al. (1990). The condition for the validity of such a comparison is that the heavy metals and phosphorus are bound approximately to the same size fractions of soil particles. The data summarized by NOVOTNY & CHESTERS (1981) show that most phosphorus and heavy metals are bound to the smallest soil particles.
Since direct, detailed measurements of the contents of heavy metals in soils over wide spatial areas in the Rhine Basin are not available, the heavy metal contents in the sediments of springs in West Germany (FAUTH et al. 1985) provided a basis for estimating their contents in soils. The mean content of cadmium in the top soil layers of West Germany was estimated at approximately 660 g/ha (0.22mg/kg assuming a bulk density of 1.5 and a soil layer of 20 cm) in the mid 1970s (UBA, 1981). Compared to the cadmium content in the spring sediments (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 because cadmium is bound to smaller soil particles possessing a higher erodibility factor. But on the other hand heavy metals are particularly concentrated at the soil surface.
For soils in the U.S. WIGINGTON (1981) estimated a typical range for Cd between 0.01 and 0.7 ppm. The ranges for Pb and Zn are estimated between 2-200 ppm and 10-300 ppm, respectively. The cadmium content in the soils varies between 0.05 and 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 sediments (Table 15).

In the following analysis, the heavy metal contents in the spring sediments were

applied for estimating the load by erosion, because investigations similar to cadmium do not exist for lead and zinc in the Rhine catchment area, and the discrepancy in the case of cadmium can not be explained quantitatively. In any case, the calculated estimates based on this assumption probably represent an overestimation of the actual load from erosion.
The load by erosion is calculated from the metal contents of Table 15 assuming proportionality to phosphorus erosion. For a mean phosphorus content in the top soil of about 700 mg/kg (AUERSWALD et al., 1990), the total erosion load of phosphorus into the Rhine was 2.2 kt/a (Table 10). The potential ranges and the mean total loads of cadmium, lead and zinc are given in Table 16. Considering the Cd-content of soil according to UBA (1981) the cadmium load into the Rhine would be about 0.7 t/a or one third of the estimated load of 2.3 t/a according to Table 16. All of 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 about 4. In contrast to phosphorus, the dissolved load caused by erosion was neglected, because it seems to be questionable that a transfer from the particular to the dissolved fraction plays an important role for the investigated heavy metals. The erosion loads estimated in the comparison with phosphorus pertain mainly to the loads from agricultural lands and arable areas.

Tab. 15: Contents of cadmium, lead and zinc in sediments of springs (source: Geochemical Atlas of Germany, FAUTH et al., 1985). All values are given in mg/kg.

	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

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 a first approximation of the trends in loads from erosion in the last two decades.
The balance of cadmium in agricultural areas in the mid of the 1970s is given by UBA (1981). The major inputs were the atmospheric deposition (3.5 g/(ha·a)) and cadmium in phosphorus fertilizers (5.4 g/(ha·a)). The inputs caused by sewage sludge and other sources were assumed to be 2.0 g/(ha·a). Compared with these total inputs of 10.9 g/(ha·a) the loss of 1.1 g/(ha·a) mainly to the water (1.0 g/(ha·a) is only 10 %.
The enrichment of cadmium in the soil by about 10 g/(ha·a) 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 compared to the 1970s.

In the case of lead, the only important input to the agricultural areas is via 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 is given by ISERMANN (1990) to 1.25 kgP/(ha·a), based on the results of AUERSWALD et al. (1990) for agricultural areas. If we compare the phosphorus and lead content in the top soil, the specific loss of lead caused by erosion is estimated at about 40 - 100 g/(ha·a). 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 - 15 years.

Tab.16: Estimated loads of cadmium, lead and zinc in the surface waters of the Rhine basin caused by erosion. All values in t/a for the time period 1983-87.

	Cd	Pb	Zn
range	0.9 - 11.3	60 - 1200	120 - 1500
low contaminated area	1.4	55	240
high contaminated area	0.9	35	180
mean total load	2.3	90	420

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

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

4.4.3.4. Other nonurban sources of diffuse load

In addition to the heavy metal load caused by groundwater, surface runoff, and erosion, a part of the agriculturally applied animal-waste slurries enters directly to the surface water. AUERSWALD et al. (1990) assumed that about 2 % of the liquid manure produced flows directly into the surface water. If a phosphorus content of farm slurry of 10 - 50 gP/kg dry weight is assumed, the total phosphorus in farm slurries is estimated to be about 100,000 tP/a for West Germany (AUERSWALD et al., 1990). With regard to heavy metals, the zinc content of farm slurry is between 0.2 to 1.5 g/kg dry weight (FEENSTRA & van BAAL, 1989). The Cd and Pb content in animal-waste slurries is negligible. The total amount of zinc in farm slurries in West Germany is estimated at 2000 - 3000 t/a. From this total amount 2 % or 40 - 60 t/a 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 - 35 t/a. This load is very low in comparison to the loads of zinc from the other sources.

4.4.3.5. Diffuse load of paved urban areas

With regard to the diffuse load, urban areas, and 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 non-urban areas;
- the deposition rates of pollutants in urban areas are higher;
- the pathways by which pollutants enter the river in urban areas are quite different from pathways in non-urban areas.

Although the portion of urban land to the total area is generally small, the contribution of the pollutant load of urban areas is high compared with the total load. WIGINGTON (1981) reported that the loads of Cd, Pb and Zn from the urban area in the Occoquan watershed (Northern Virginia, U.S.) are 47 %, 87 % and 33 %, respectively, of the total load , even though the urban area is only 6.2 % of the total area.

Figure 12 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 deposition, because aerosols, gasses and small dust particles emitted by traffic can be measured as a part of atmospheric deposition. Spills of oil and grease, tire wear and wear of road surfaces are additional sources of the heavy metal load and have to taken into account separately. In the following sections the components of the area specific loads of heavy metals as depicted in figure 12 are estimated. Because paved urban areas are particularly important contributors to the total load, the estimation focusses on atmospheric deposition, traffic and corrosion in the paved areas. Secondly, we track the fate of these loads as they move from the paved area to the river.

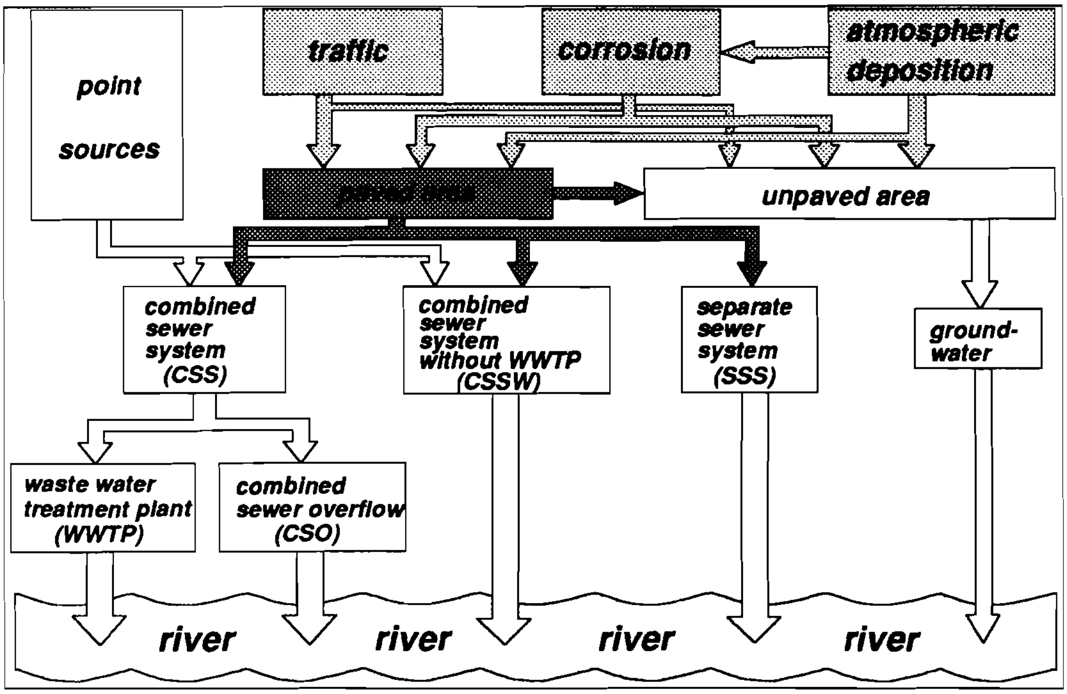

Fig.12: Sources and pathways of diffuse heavy metal loads in urban areas.

- **The sources of the heavy metal load 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 pollutant in the air and the deposition velocity. FEENSTRA & van BAAL (1989) and FEENSTRA & van der MOST (1986) assumed that the dry deposition of zinc and cadmium is approximately 10 - 20 % of the wet deposition. For lead the dry deposition amounts about 40 % of wet deposition. These assumptions agree qualitatively with the results of American investigations. RANDALL et al. (1981) pointed out that precipitation was a major source of heavy metals in urban runoff in a watershed of Virginia (U.S.). In addition they reported that dry deposition was the major 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 antecedent dry days did not correlate with stormwater zinc load (WILBER et al., 1980). ROHBOCK et al. (1981) reported dry deposition to be 17 and 18 % of the total deposition of lead and cadmium, respectively. The percentage of dry deposition of lead is only half of value given by FEENSTRA & van der MOST (1986). In general the study of ROHBOCK et al. (1981) shows that the portion of dry deposition to the total deposition is smaller in rural areas (4-8 %) than in urban areas (13-22 %). Using the results of Table 13, the mean wet deposition of Cd, Pb and Zn is assumed to be 6 g/(ha·a), 300 g/(ha·a) and 600 g/(ha·a) for the urban areas in the Rhine basin. Dry deposition is assumed to be about 20 % of the wet deposition for all three metals. These values are given in Table 17 together with the assumed specific wet deposition of heavy metals.

Traffic: The specific heavy metal load of urban lands is increased on the 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 Pb and Zn (FEENSTRA & van der MOST, 1986; WIRINGTON, 1981; NOVOTNY & CHESTERS, 1981). Although lead in leaded gasoline is certainly the largest source of lead in urban areas of the Rhine, only a part of it is included here since emissions to the atmosphere has already been taken into account in the specific estimates of wet and dry deposition. MALMQVIST (1983) reported that about 60-80 % of automobile-related lead emissions are released directly to the atmosphere. The remaining 20-40 % contribute directly to the load of lead as street dust. CHRISTENSEN & GUINN (1979) found that only 7.6 % of emitted lead is deposited on the street surface.
FEENSTRA & van BAAL (1989) 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 Cd, Pb and Zn. Zinc in motor oil also has comparably high concentrations.
Total rates of traffic related loads of 0.0157 g/(vehicle·km) for Pb (total emission of lead) and of 0.00196 g/(vehicle·km) for Zn are reported by SHAHEEN (1975). CHRISTENSEN & GUINN (1979) estimated a street-related load of 0.003 g/(vehicle·km) for zinc and 0.0049 g/(vehicle·km) for lead. HOFFMAN et al. (1985) published specific loading factors of 0.02 mg/(vehicle·km) for Cd, 0.0044 g/(vehicle·km) for lead and 0.022 g/(vehicle·km) for Zinc, respectively. MALMQVIST (1983) reported car specific emissions of lead and zinc of 0.034 g/(vehicle·km) and 0.004 g/(vehicle·km), respectively. Assuming a mean car density of 500 vehicles per 1000 inhabitants for 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), the total stock of cars of 23.5 million can be estimated. If we assume that each car travels about 15000 km/a, then, using the automobile-related emission factors for cadmium of HOFFMAN et al. (1985), for zinc of MALMQVIST (1983) and for lead of CHRISTENSEN & GUINN (1979 and HOFFMAN et al. (1985), the annual street related traffic emissions are about 7.1 t for cadmium, 1750 t for lead and 1400 t for zinc. DE WAAL MALEFIJT (1982) assumed that only 40 % of the traffic occurred in streets of urban areas. If a total paved urban area of about 600,000 ha is considered, then the area related loads can be estimated to be about 4.7 g/(ha·a) for cadmium, 1200 g/(ha·a) for lead and 950 g/(ha·a) for zinc. If the automobile-related lead emissions of CHRISTENSEN & GUINN (1979) and HOFFMAN et al. (1985) is used then we have to taken into account that the lead content of gasoline was different in the U.S. at the end 1970s and in the Rhine basin at the mid of 1980s. CHRISTENSEN & GUINN (1979) reported that the lead content of gasoline was in this time 0.37 g/l. PACYNA (1991) stated that the lead content of gasoline in Germany was 0.15 g/l since the end of 1970s. Based on this lead content of gasoline the street-related lead load is estimated to be about 490 g/(ha·a) in the mid 1980s.

Corrosion: The load caused by corrosion of galvanized surfaces has to be taken into account for zinc, and to less 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 Zn-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 concentration of SO_2 in the air, humidity, and temperature are the most important factor influencing the corrosion rate (BODEN, 1989; HAAGENRUD et al., 1983; HARTER, 1986; UNITED NATION ECONOMIC COMMISSION FOR EUROPE, 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) estimated the corrosion rates of different German cities within the Rhine basin based on the monitored SO_2-concentrations in air.

The equations given by HAAGENRUD et al. (1982) 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 galvanized surface in the mid of 1980s. DE WAAL MALEFIJT (1982) 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) measured a corrosion rate of 4.4 $mg/m^2/mm$ rainfall. If we assume a mean rainfall intensity of 700 $mm/(m^2 \cdot a)$, than the annual corrosion rate is about 30 g/m^2. Corrosion rates between 3 $g/(m^2 \cdot a)$ and 8 $g/(m^2 \cdot a)$ were published for Swedish cities by MALMQVIST (1983) and HOGLAND & 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) assumed a galvanized surface of a 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 paved urban area or 33 m^2/ha total urban area can be estimated. A zinc surface of 600 m^2/ha urban area and 900 m^2/ha paved urban area can be estimated from the data of van DAM et al. (1986) for Lelystad. MALMQVIST (1983) reported zinc surface areas between 67 and 490 m^2/ha paved urban area (13 - 292 m^2/ha total urban area) for four different locations in the city of Göteborg. A strong linear relation seems to exist for all of these data. If it is assumed that the area specific zinc surface is zero for a population density of zero, than the zinc surface per urban area can be estimated by multiplying the population density by a factor of about 1.2. For zinc surface per paved urban area this factor was found to be about 1.9. The mean population density of urban areas within the Rhine is about 30 inh./ha urban area. Assuming a mean annual corrosion rate of 23 g/m^2 the mean area specific zinc load caused by corrosion is about 1300 $g/(ha \cdot a)$ in the mid 1980s. This estimate of corrosion is used in the following analysis as a first approximation for estimating the urban heavy metal load in the Rhine basin.

In general, cadmium is an impurity of applied zinc materials. Its portion in zinc is assumed to 0.2 % (DE WAAL MALEFIJT, 1982). Therefore a Cd-corrosion rate of about 2.6 $g/(ha \cdot a)$ has been assumed.

Table 17 summarizes the total loads of cadmium, lead and zinc on the paved urban areas in the Rhine basin for the period 1983-87. They are about 13.3 $g/(ha \cdot a)$ for cadmium, 660 $g/(ha \cdot a)$ for lead and 2820 $g/(ha \cdot a)$ for zinc. With regard to the sources the situation is different for each of the investigated metals. In the case of cadmium atmospheric deposition (wet and dry) is the major source, contributing about 54 % of the total load. For lead the emissions caused by traffic dominate the load. The major source of the zinc load in the urban areas of the Rhine basin seems to be corrosion , accounting for 46 % of the total urban zinc load. The combination of traffic and corrosion contribute 75 % to the total zinc load. These estimates of lead and zinc loads correspond qualitatively and quantitatively with the results of different authors, who conducted empirical investigations of the loads of these metals in urban areas (DAUBER et al., 1978; IFS, 1980; KLEIN, 1982; MALMQVIST, 1983; LISPER, 1974).

Tab.17: Specific heavy metal loads of paved urban areas used for estimation of total loads of urban areas in the Rhine basin. All values are given in [g/(ha·a)] for the time period 1983-87.

	Cd	Pb	Zn
wet deposition	6	300	600
dry deposition	1.2	60	120
traffic	4.7	490	950
corrosion	2.6	0	1300
total load	14.5	850	2970

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, a total paved urban area is estimated at about 600,000 ha based on the crude assumption that the paved area is approximately one third of the total urban area. By multiplication of the total loads of Table 17 by this area, the load for each metal which could potentially enter the Rhine river or its tributaries in the period 1983-87 can be estimated. The potential annual load from paved urban areas is about 8.7 t for cadmium, 510 t for lead 1780 t 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 small or large 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 are currently connected to sewer systems. Sewage systems for collecting street runoff are either connected to municipal sewage treatment plants, or they are connected to a separate stormwater system in which the runoff is not treated. It is assumed in our analysis that 90 % of the stormwater 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.

With regard to the two sewer systems it was assumed that about 54 % of the paved area are connected to combined sewer systems, and 36 % area are connected to a separate sewer system. Furthermore, it is assumed that 50 % of the runoff and the load, respectively, from paved urban areas which are not connected to a sewer system (about 10 % of the area) enters the waterbodies. With regard to combined sewer systems, during storm events the capacity of these systems is usually not sufficient to treat the entire volume of stormwater runoff, and overflows are installed. It is important to estimate how much of the loading of urban areas enters the river system via combined sewer overflows? FALK (1987) stated that in Sweden the yearly overflow volumes 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 quantity of stormwater overflows from paved areas is in the range between 74 and 120 mm/a (ONDERDELINDEN & TIMMER, 1986). In comparison with the possible range of total runoff from paved areas of about 300 - 600 mm reported by FALK (1987), these quantities appear to be relatively high. But in this context, FALK (1987) recommends against the use of flow or the input load from paved area to the sewer system when calculating the real load due to 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 stormwater runoff (HOGLAND et al. 1988).

According to SPERLING (1986) phosphorus and nitrogen entering the water through combined sewer overflows accounts for about 12 % of the total P-load and 14 % of the total N-load of municipal sewage treatment plants (54 % of the total load from paved areas are connected to combined sewers). That means about 6.5 % - 7.6 % of the potential heavy metal load of paved urban areas goes directly in to 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 of 44 % of the urban load connected to sewage treatment plants is treated. During treatment a part of the heavy metals is removed by sedimentation (mechanical or primary treatment), a part by sorption by organic material (secondary treatment), and, when tertiary treatment is available, a part is removed by flocculation. The rate of removal of heavy metals from waste water 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) stated that the percentage of dissolved loadings of zinc and lead is different. For different kinds of urban areas in the U.S.A., the percentage of the dissolved lead load varies between 5 and 15 %. In contrast to lead, the percentage of the dissolved zinc load is higher (31 - 70 %). The comparison between the particulate and dissolved concentrations of Cd, Pb and Zn upstream and downstream from urban areas shows that the most of the urban Zn and Cd load is in dissolved form (ELLIS, 1988). In contrast, for lead the particulate fraction contributes most of the total load.

If it is taken into account that the lead load is mainly particulate material, and the cadmium and zinc load is 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) reported 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 waste water 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 waste water treatment is about 8 % for the Rhine basin as a whole.

Table 18 summarizes the heavy metal loads from urban areas entering surface waters in the Rhine basin upstream from the Lobith station. All of the simulations pertain to the time period 1983 - 1987, during which the urban load of Cd, Pb and Zn entering the river system is estimated at about 6.6, 246 and 1250 t/a, respectively.

Tab.18: Estimated loads of cadmium, lead and zinc from paved urban areas in the Rhine basin (upstream from the Lobith station). All values in t/a for the period 1983-87.

	Cd	Pb	Zn
no sewer system	0.5	21	85
separate sewer system	3.4	155	645
combined sewer overflows	0.8	35	170
combined sewer systems	1.9	35	350
total load	6.6	246	1250

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 has been reduced significantly from the time period 1973-77 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 Cd, 76 % for Pb and 78 % for Zn. We assumed that the atmospheric deposition was reduced by the same percentages as the emissions for Cd an Zn. 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 so high as 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 % for the time period 1978-1982 and 49 % for the time period 1983-1987.

For the loads from traffic, the situation for Cd and Zn differs from that of Pb.

According to RAUTENGARTEN (pers. comm.) the traffic related loads of Cd an Zn were one third higher in 1985 than in 1975 because of the increase in the numbers of cars per inhabitant. Additionally, a reduction of the lead content of gasoline in the late 1970s had to be considered. Compared with the situation in 1985, the traffic related load of lead was 87 % in the period 1978-82 and 145 % in the period 1973-1977.
The specific corrosion rates have changed over this 10 year period, too. HREHORUK (1991) reported 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 with a sewer system was about 75 % in 1975. About 18 % of the population were connected to sewage systems with only primary (mechanical) treatment. With regard to the separate sewer systems for stormwater, it is assumed that this percentage was the same over the whole time period. Using all these assumptions, the estimated loads of Cd, Pb and Zn from paved urban areas since the mid 1970s are given in Table 19.

4.4.3.6. Total diffuse load of heavy metals and its change in time

Table 19 presents a survey of the results with regard to the loads of different diffuse sources. In the most recent time period (1983-1987) the load from paved urban areas is the main source, amounting to 41 %, 46 % and 48 % of the total diffuse load for Cd, Pb and Zn, respectively. The load of the other diffuse sources (groundwater, surface runoff, erosion) is similar in the last investigated period with exception of lead. In this case the surface runoff is the second dominant source with 26 %.
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 area was probably the major source of the diffuse Cd-load in the mid 1970s. In the case of lead, the load from paved urban areas, the source of which is mainly traffic, and load from surface runoff were the major sources over all three time periods. Both of these sources (surface runoff and paved urban areas) show approximately the same time trend because they are linked to change in atmospheric depositions.
The dominant 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 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.
For paved urban areas the decrease of heavy metal loads since the 1970s is not as large as for surface runoff, because the load caused by an increasing traffic intensity 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.
The 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 both methods agree for the time period 1983-87. The estimated loads of cadmium and zinc using the method of area specific loads

are relatively close to the averages of the diffuse load given in Table 4 for the Lobith station.

Tab.19: Estimated heavy metal loads of different diffuse sources and their change in time since the mid 1970s in the Rhine basin. The values in parentheses refer to consider the particular hydrological situation in the time period 1973-77. All values are given in t/a.

source	1973 -77	1978 - 82	1983 -87
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	12.9 (10.8)	8.0	6.6
total diffuse load	31.3 (25.0)	19.7	15.8
Pb			
groundwater	60	60	60
surface runoff	290 (210)	145	140
erosion	90 (65)	90	90
other sources			
paved urban area	486 (440)	273	246
total diffuse load	926 (775)	568	536
Zn			
groundwater	530	530	530
surface runoff	1700 (1230)	880	370
erosion	420 (300)	420	420
other sources	30	30	30
paved urban area	2230 (1830)	1710	1250
total diffuse load	4910 (3920)	3570	2600

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 given in Table 4. The reason for this discrepancy is that our estimation of the traffic related lead load does not consider that a small percentage of vehicles does not use leaded gasoline, which was introduced in the second half of this time period.
Also for the time period 1978-82 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 all within the ranges of loads estimated using the monitoring data at 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 number of data are low compared with the time period 1983-87.
In the time period 1973-77 some discrepancies exist for cadmium, zinc, and particularly for 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 estimated average values.
In this time period the available monitoring data was also small compared with the time period 1983-87. Furthermore, the range of uncertainty is extremely high, because the relationship between the lead load and the discharge at the Lobith station is unsure for the period 1973-77.
In contrast to the results based on the use of 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 investigated time periods. The mean discharge at the Lobith station was the highest in the period 1978-82 (about 2620 m^3/s). The mean discharge in the period of the mid 1980s was comparable to this with a value of about 2480 m^3/s. But in the first period (1973-77) the mean discharge at the Lobith station was only 1780 m^3/s or about 72 % of the discharge in the mid 1980s. Because most of the diffuse load depends on the runoff rate, one may assume also 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 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 load 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 period 1973-77. The values in parentheses given in Table 19 consider this effect. The comparison of the total diffuse loads which consider the hydrological situation in the period 1973-77, with the values of estimated diffuse loads on the basis of monitoring data shows that these values are similar close by the averages given in Table 4 than for the other two time periods.
If the mean concentrations of all diffuse loads of heavy metals are compared for the three time periods (Tab. 20) then their time trend is more similar with the trend of the area related load. This fact supports our assumption that the lower discharge in the time period 1973-77 is the major reason for the difference between the heavy metal loads estimated form the two used methods.
For cadmium and zinc, the decrease of the mean concentration is higher than the reduction of area specific loads. In contrast, the decline of the lead concentration is lower than the decrease in area related loads.

Tab. 20: Relation between the estimated mean concentration of all diffuse sources at the Lobith station for the time periods 1973-77 and 1983-87 and between the estimated total area related loads for these two time periods.

	Cadmium	Lead	Zinc
$L_{t(1973-77)}/L_{t(1983-87)}$	2.0	1.8	2.3
$K_{D(1973-77)}/K_{D(1983-87)}$	2.8	1.3	1.9

Based on this analysis one may assume that the losses of heavy metals from the different areas (potential or gross loads) were similar to our estimated area-related loads in the time period 1973-77. But the net loads measured at the Lobith station were lower than these gross loads because the potential loads are lower during periods of low discharge than in the time periods where the hydrological conditions were more close to the long term average.

5. Conclusions

A new method was presented 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 the heavy metals, cadmium, lead and zinc were compared with the loads of existing inventories (ICPR,1989). The diffuse loads these pollutants were compared with estimations calculated on the basis of 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 for the mid 1980s because there are no point source inventories or estimates of area-related diffuse loads prior to 1985. The river monitoring data, however, are available since the early 1970s for all of the investigated pollutants and since the early 1950s for nitrogen. Analyses of these data by the new method was 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 period 1983-87. 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 time periods 1973-77 and 1978-82. 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 exist only since the beginning of the 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 5) show dynamic changes dominated by two major developments. One is the evolution of wastewater treatment plants within the Rhine basin, 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 major 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 show a clear decreasing trend of point loads since the mid of 1970s mainly caused by the elimination of phosphorus in detergents. The reasons are unsure for the decrease of estimated diffuse load of phosphorus. 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 AUERSWALD (1991), FIRK & GEGENMANTEL (1986) and BERNHARDT et al. (1978). The order of magnitude of our estimated diffuse load of phosphorus agree with the results of these authors. It seems to be reasonable that the discrepancy is caused by the different definition of diffuse load.

Tab.21: Estimated point and diffuse loads of nitrogen, phosphorus, cadmium, lead and zinc to the Rhine river basin upstream from the Lobith station at different time periods since the mid 1970s. The values are given in kt/a for nitrogen and phosphorus and in t/a for the heavy metals.

Pollutant	**Source of load at the Lobith station**	**1973-77**	**1978-82**	**1983-87**
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	1500	800	700
	point load	730	260	240
	diffuse load	770	540	460
Zinc	total load	10100	9600	5000
	point load	6100	6100	2200
	diffuse load	4000	3100	2800

For phosphorus the analysis show a clearly decreasing trend in the point source loads since the mid of 1970s. This is the result of the elimination of phosphorus in detergents. The reason for the decrease of estimated diffuse load of phosphorus is unsure. 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 AUERSWALD (1991), FIRK & GEGENMANTEL (1986) and BERNHARDT et al. (1978). The order of magnitude of our estimated diffuse load of phosphorus agrees, however, with the results of these authors. It is reasonable to assume that the discrepancy is due to different definitions of diffuse load by the authors. The analyses of the phosphorus cycle in West Germany (AUERSWALD et al., 1991; FIRK & GEGENMANTEL, 1986; HAMM, 1989) do not consider the load from paved urban areas as a diffuse source. On the other hand, some of loads related to agricultural activities which were considered as diffuse loads in these studies are point source loads from the point of view of 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 of 1970s to the mid 1980s. For lead and cadmium the point load was reduced from the period 1973-77 to 1978-82. From 1978-82 to 1983-87 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 not before the period 1983-87. 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 of the total load have increased, the diffuse loads of the heavy metals have decreased since the mid of 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 decreased lead content of gasoline since 1976.
In the recent times the major 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 major sources of the diffuse lead load. But it can be assumed that the diffuse load of lead has decreased in the last ten years, because of reduction in the increasing use of lead-free gasoline in the Rhine basin.
The main source of the diffuse load of zinc is corrosion followed in importance 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 particularly on reduction of the load from the sources (e.g. further introduction of stormwater 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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