

**Part B      PRESENT AND FUTURE QUALITY OF SEDIMENTS IN THE RHINE  
CATCHMENT AREA – HEAVY METALS**

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## 1 Introduction

For many years, the Rhine was Europe's prime example of a polluted river. Water quality deteriorated particularly sharply in the post-war era, when the Rhine basin was the scene of extensive reconstruction and industrial development. Between 1960 and 1975 the Rhine became seriously polluted. Thereafter, concentrations of heavy metals decreased sharply until 1985. Since then, they have been more or less stable. Heavy metal concentrations in the Rhine are now more or less stable, albeit at levels in excess of the long-term targets.

Heavy metal pollution is still a problem in the sediments of the riverbed and especially in ports. The current Dutch chemical criteria for relocation of dredged material in the North Sea (table D 5.2) include besides heavy metals a number of organic substances: polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), several pesticides and hexachlorobenzene. With regard to the present regulation, several heavy metals are of concern, i.e. that concentrations of these substances frequently exceeded the Sea/Slufter limits (for relocation in the North Sea) in dredged material from the eastern parts of the port of Rotterdam.

For that reason, five heavy metals were selected for the following investigation of point and diffuse sources in the Rhine catchment area, focussing on the relevant pathways with the aim to estimate their contribution to the contamination of the sediments in the port of Rotterdam. The methodology generally is comparable to the one applied to PAHs and PCBs (in section C): (i) immission analysis, (ii) emission analysis with MONERIS, (iii) scenarios.

The quality of dredged material is determined by the input of substances from both point and diffuse sources. These sources contribute to the natural background level (e.g. erosion for nutrients and heavy metals) and elevated levels for organic chemicals, nutrients and heavy metals. The definitions are:

**Point sources** are *identifiable points* and are (fairly) *steady in flow and quality* (within the temporal scale of years). The magnitude of pollution is not influenced by the magnitude of meteorological factors. Major point sources under this definition included: municipal wastewater effluents; industrial wastewater effluents.

**Diffuse sources** are *highly dynamic spreaded pollution sources* and their magnitude is *closely related to meteorological factors* such as precipitation. Major diffuse sources under this definition include: surface runoff (load from atmospheric deposition), groundwater, erosion (load from eroded material), diffuse loads of paved urban areas (atmospheric deposition, traffic, corrosion), including combined sewer overflows since these events occur discontinuous in time and are closely related to precipitation.

Figure 1-1 presents the various diffuse and point sources contributing to the input of substances in a river system.

Both point and diffuse sources contribute to the total contaminant load of rivers. A distinction between them is necessary for future restoration actions and determining the effect of past control measures at industrial sources.

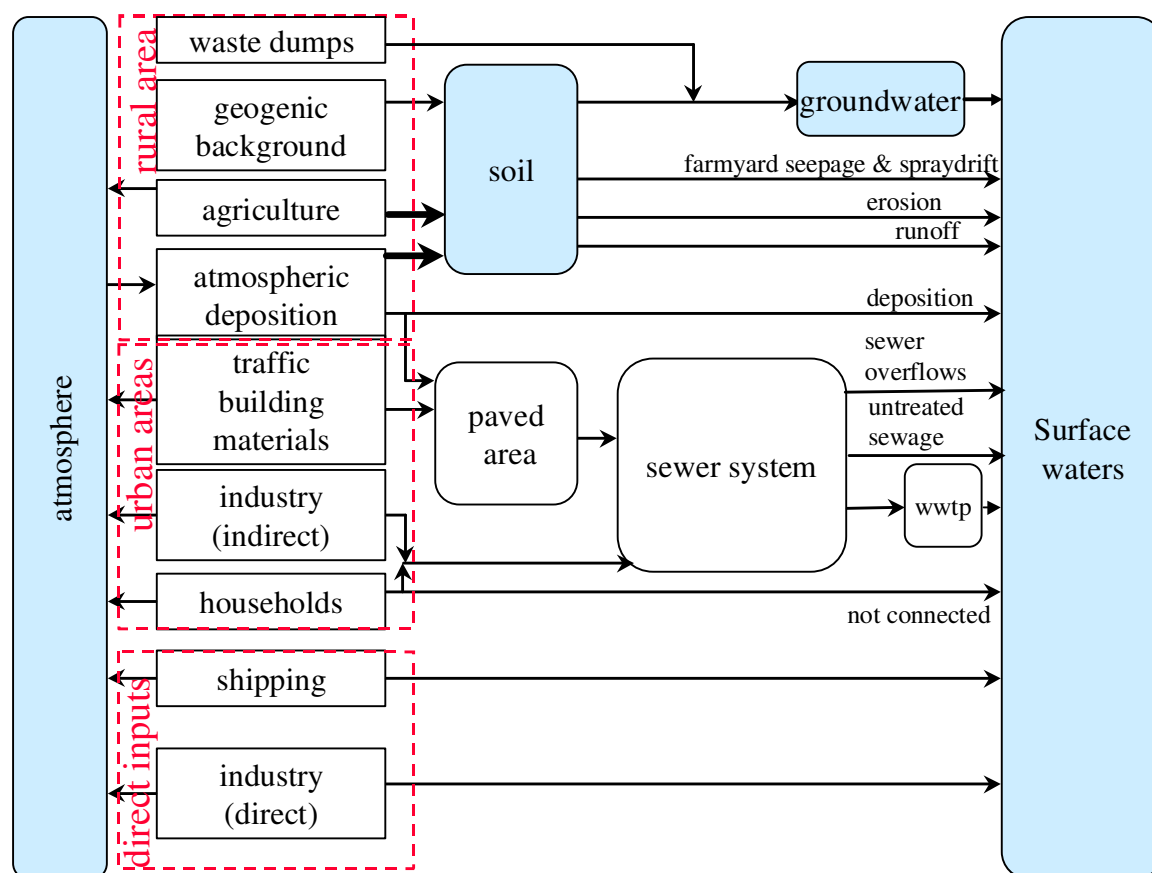


Figure 1-1: Flow of materials considered in the Rhine river basin.

Several studies focused on estimating the emissions and pathways of contaminants for large river basins or catchments (Behrendt, 1993; Behrendt, 1994; Behrendt, 1996; Behrendt, 1997; de Wit 1999). But many researchers (Olendrzynski et al., 1995; Hahn and Xanthopoulos, 1994) only investigated one particular emission source at a certain specific location (e.g. canalisation in urban areas). Whereas other studies focused on estimating riverine transported loads (Grimvall & Stalnacke, 1996; Tonderski et al., 1994) by looking at discharge-concentration relationships. These discharge-concentration relationships have been used for comparisons between both estimated emissions and transported riverine loads of nutrients (van Dijk et al., 1997; Behrendt, 1993). Most studies estimating point and diffuse emissions as well as source apportionment focus on nutrients (Behrendt, 1996; Behrendt, 1997; Behrendt & Bachor, 1998; Behrendt et al., 1999). Similar studies on heavy metals have been carried out for the Rhine (Behrendt, 1993) and Elbe catchment (Vink et al. 1999; Vink et al., 2000). Both methods are complementary. The emission method can be validated against the total amounts transported by the river (as measured for instance at measuring stations like Lobith) and its distinction of point and diffuse sources can be validated against the immission method. The immission method only gives the total of all point and all diffuse sources and does not allow for a distinction of individual sources.

Therefore, it is important to do an analysis of the source apportionment study with two different methods (emission and immission analysis) on the contribution of point and diffuse sources in drainage basins. Both methods were tested and applied to several river basins in Europe (Behrendt et al., 1993; Behrendt et al., 1999; Vink et al., 1999; Vink et al., 2000).

The modelling approach in the next chapters comprises basically the following steps:

1. Immission analysis: estimation of point and diffuse loads (chapter 2)
2. Emission analysis (MONERIS) for source apportionment (chapter 3)
3. Trends in dredged material quality of the port of Rotterdam and link with the suspended particulate matter quality of the Rhine (chapter 4)
4. Scenarios modelled with MONERIS and driven by reduction coefficients for the individual pathways (chapter 5)

All four steps of the modelling approach were carried out for the Rhine catchment area upstream Bimmen/Lobith, the Dutch/German border. Subsequently the results of the scenario analysis were used to forecast the future quality of sediments in the eastern parts of the port of Rotterdam.

## 2 Immission analysis

In this chapter a source apportionment (immission) study will be made with water quality data from several monitoring stations in the Rhine catchment. The theoretical background of the immission analysis is first discussed (chapter 2.1) and then the results from several monitoring stations for the two selected time periods (1983-1987 and 1993-1997) are shown and compared to other studies as well.

### 2.1 Theoretical background

One way for estimating the pressures caused by pollution is to quantify all the emissions by point and diffuse sources for the several pathways. These estimations of the emissions are considered as gross inputs into the river because these estimates, especially for diffuse sources, are based on a three or four year average and therefore rather give an emission potential than a real emission. These emission estimates will be presented in chapter 3. Another method, presented in this chapter, is to separate the fractions of point and diffuse loads by analysing the concentration - discharge and load - discharge relationships using data sets from monitoring stations of the main river and its tributaries. The observed, realised load of a particular substance at a particular monitoring station is called immission. The difference between immission and emission lies in the fact that immission is the in reality occurring substance input, including losses caused by e.g. transformation whereas emission is a potential. This is already described in detail by Behrendt (1993, 1994 & 1996), where this method was applied to the Rhine and some parts of the Elbe for nutrients and phosphorous. A short overview will be given here.

The method is based on difference in definition between the point and diffuse sources and their different relationship to meteorological factors such as precipitation, whereas point sources are relatively constant in magnitude, identifiable and not or less dependant on meteorological factors. The inputs by diffuse sources are highly variable and correlated to meteorological factors. An overview of the main components of the hydrological cycle is given in figure 2-1. According to Dyck and Peschke (1995) the discharge of a catchment can be divided into three main components:

1. Surface runoff, which is the net result of the overall water balance on the surface between rainfall and water losses by evaporation, infiltration, interception and depression storage.
2. Interflow, which is the result of the water balance in the aeration zone. This is the result of infiltration diminished by groundwater recharge, storage of soil moisture and evapotranspiration of the topsoil.
3. Groundwater flow, which is the difference between groundwater recharge and geological water losses and groundwater storage.

Interflow and groundwater flow are the two subsurface flow components, where interflow is equal to the fast component and groundwater flow is equal to the slow component.

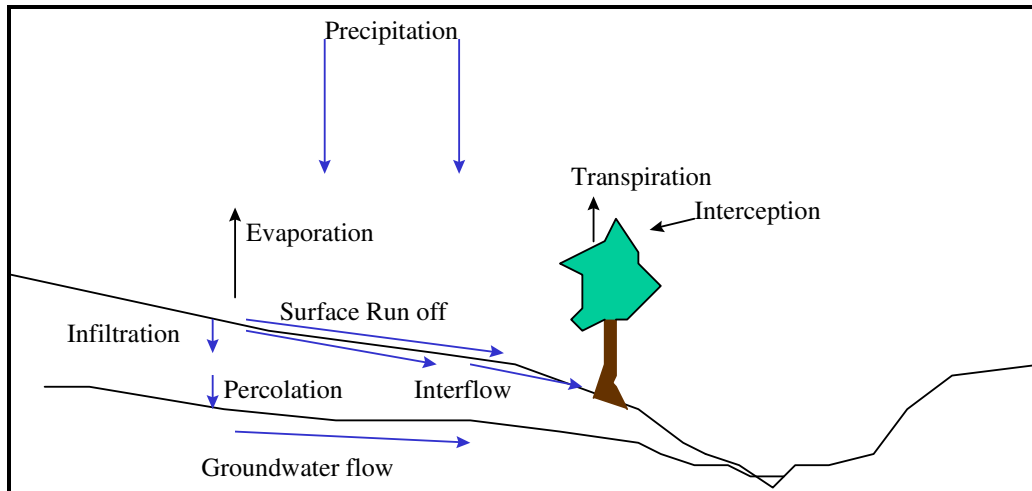


Figure 2-1: Overview of the hydrological cycle

It is assumed that the catchment lying upstream from the monitoring station can be divided into several sub-catchments  $i$ . In these sub-catchments the following water balance can be performed:

$$Q_{i,t} = Q_{B,i,t} + Q_{R,i,t} + Q_{I,i,t} + Q_{P,i,t}, \quad 2.1$$

where  $Q_{i,t}$  is the total discharge of the sub-catchment  $i$  at a given time  $t$ ,  $Q_{B,i,t}$  is the base flow within this sub-catchment  $i$  at time  $t$ ,  $Q_{R,i,t}$  is the surface runoff of this sub-catchment  $i$  at time  $t$ ,  $Q_{I,i,t}$  is the interflow of this sub-catchment  $i$  at time  $t$  and  $Q_{P,i,t}$  is the point discharge of the sub-catchment  $i$  at time  $t$ .

Assuming the load of a pollutant can be described by the sum of all mass carried by the different runoff components (gross load) minus the losses occurring through e.g. sedimentation :

$$L_{i,t} = L_{B,i,t}^g + L_{R,i,t}^g + L_{I,i,t}^g + L_{P,i,t}^g - Losses_{i,t}, \quad 2.2$$

where  $L_{i,t}$  is the net pollutant load of the sub-catchment  $i$  at a given time  $t$ ,  $L_{B,i,t}^g$  is the pollutant gross load in the sub-catchment  $i$  caused by baseflow at time  $t$ ,  $L_{R,i,t}^g$  is the pollutant gross load in the sub-catchment  $i$  caused by surface runoff at time  $t$ ,  $L_{I,i,t}^g$  is the pollutant gross load in the sub-catchment  $i$  caused by interflow at time  $t$ ,  $L_{P,i,t}^g$  is the pollutant gross load in the sub-catchment  $i$  caused by point sources at time  $t$  and  $Losses_{i,t}$  are the pollutant losses in sub-catchment  $i$  within the surface water at time  $t$ .

With this equation it is assumed that the so-called losses and their magnitude are only dependant on the processes in the surface water, groundwater and interflow and not on the type of source of the pollutant. With equation 2.2 it is possible to estimate both point and diffuse load for a particular sub-catchment and the whole catchment, where diffuse load is the difference in the mean load over a particular time period and the estimated point load.

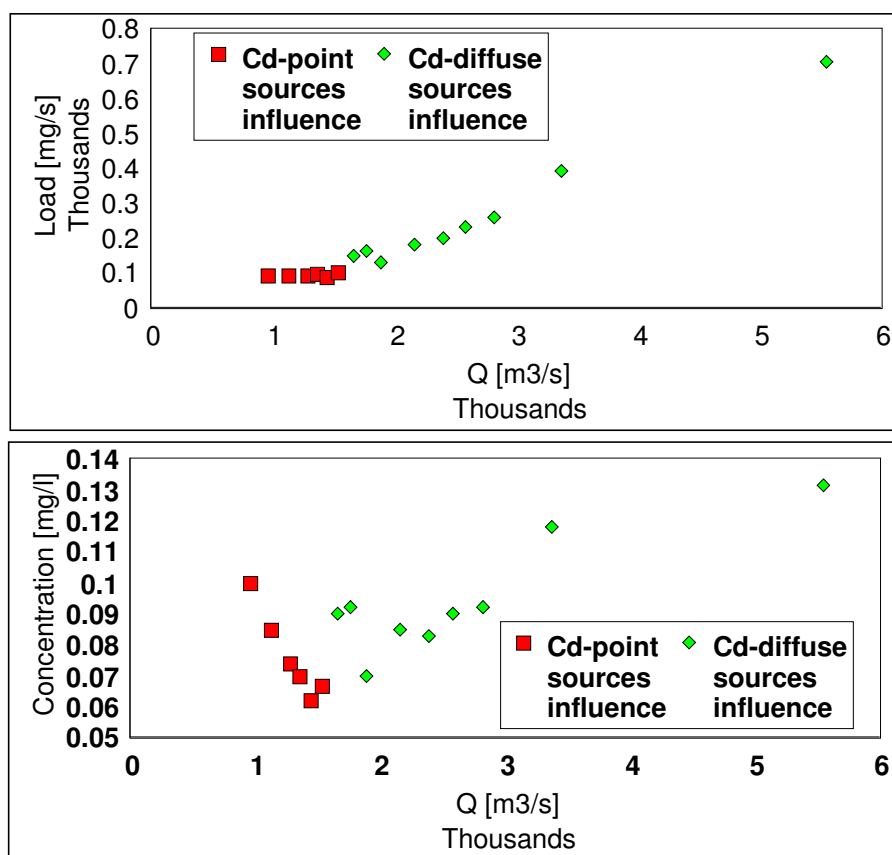


Figure 2-2: Example of a non-linear load-discharge relationship (Based on Cd data from Bad Honnef 1993-1997)

Further mathematical background of the immission method and examples of possible relationships for load-discharge and concentration-discharge are given in Behrendt (1993). Behrendt describes several possible relationships of the different substances. In some cases there was not a linear relationship between load and discharge, as shown in figure 2-2. It can be explained by a high input of point load with high concentrations of heavy metals at low discharge periods. With increasing discharge the concentration decrease by dilution with more unpolluted subsurface flow, which is defined as the sum of the base flow component and the inter flow component. After reaching a minimum heavy metal concentration the concentration of heavy metals increases again because of the growing contribution of surface runoff from e.g. urban areas to the discharge. For this situation load-discharge relationships are established. In the lower reaches of the discharge regime it is assumed that the contribution of surface runoff equals about zero and that this lower range is representative for the influence of continuous point source discharges (see figure 2-2; green squares).

This method for estimating point and diffuse portions also includes errors and uncertainties because of the uncertainties in concentration measurements. The results from the model therefore should be considered as averages. Based on the uncertainties in the estimated point wastewater flow and on the errors in the regression equations ranges for point load and diffuse load are given.

It is also interesting to compare sum of the calculated point and diffuse loads of those sub-catchments to the result of the whole catchment. This also gives some indication of relative



importance of particular sub-catchments and also the importance of point versus diffuse sources.

## 2.2 Results of immission analysis

Data from monitoring stations from the River Rhine and its tributaries were analysed over the period 1983-1987 and 1993-1997 (see appendix 2.2a). These data sets were obtained from the ICPR, DKSR, IKSM, IKSS, BfG, Bayerisches Landesamt für Wasserwirtschaft, Landesumweltamt Nordrhein-Westfalen. Data was gathered for the period 1983-1998, but some data sets were incomplete so that not for all monitoring stations or all parameters average loads could be estimated over the whole period.

The application of this method on the monitoring stations strongly depends on the quality of the used data set. When measurements were below the detection limits the concentration was considered to be half the detection limit concentration.

The calculated average discharges and average loads for the periods 1983-1987 and 1993-1997 for all monitoring stations are shown in appendices 2.2b-c. The calculated average discharges and average loads of main monitoring stations along the river Rhine over the periods 1983-1987 and 1993-1997 are shown in table 2-1. The average five-year heavy metal load was calculated according to OSPAR (1996).

In general, the discharge for all drainage areas is lower in the period 1993-1997 when compared to the period of 1983-1987. From the comparison of the average heavy metal loads in table 2-1, it is clear that for all heavy metals the loads measured at all monitoring stations have decreased over the period 1983-1987 to 1993-1997. In general, all heavy metal loads tend to increase in a downstream direction. For some stations inconsistencies exist when analysing the loads at downstream and upstream stations. The main observed inconsistencies for the heavy metal loads are shortly discussed in the next section.

### *Cadmium*

For the period 1983-1987 the cadmium load measured at Lobith/Bimmen seems to be over-estimated in comparison to the load measured at the downstream station of Duesseldorf and taking into account the contribution of several smaller tributaries. For the period 1993-1997 the measured loads at the stations Mainz and Karlsruhe seem to be over-estimated. At the station Mainz even a higher cadmium load is observed than at the catchment outlet at Lobith/Bimmen.

### *Copper*

For the period 1983-1987 the copper load measured at Duesseldorf seems to be slightly over-estimated when compared to the stations of Lobith, Bad Honnef and taking into account the contribution to the load by several smaller tributaries. The copper load at Seltz-Lauterbourg also seems to be over-estimated. For the period 1993-1997 the measured loads all stations seem to be consistent.

Table 2-1: Overview of average discharge and heavy metal loads in the periods 1983-1987 and 1993-1997 for selected monitoring stations along the river Rhine

River	Station	Discharge [m <sup>3</sup> /s]		Load									
				Cd [t/a]	Cd [t/a]	Cu [t/a]	Cu [t/a]	Hg [t/a]	Hg [t/a]	Pb [t/a]	Pb [t/a]	Zn [t/a]	Zn [t/a]
		1983- 1987	1993- 1997	1983- 1987	1993- 1997	1983- 1987	1993- 1997	1983- 1987	1993- 1997	1983- 1987	1993- 1997	1983- 1987	1993- 1997
Rhein	Weisweil	1051	1082	0.9	0.7	97	51	1.5	0.5	46	35	947	275
Rhein	Seltz Lauterbourg	1295	1269	6.5	6.2	477	255	2.6	2.8	150	90	1667	850
Neckar	Mannheim	177	155	1.2	0.6	41	24	0.3	0.1	21	9	182	79
Main	Kahl a. Main	184	177	1.4	0.5	50	56	0.9	0.3	11	13	190	215
Rhein	Mainz	1734	1629	9.4	7.6	400	237	3.4	3.1	138	89	1754	877
Mosel	Koblenz	394	328	2.1	1.1	68	54	1.4	0.6	129	50	901	389
Rhein	Koblenz	1860	1735	8.8	5.2	387	266	7.4	2.5	218	181	2710	1290
Rhein	Duesseldorf	2449	2263	12.8	6.2	905	422	12.8	0.8	508	194	4177	1696
Rhein	Lobith Bimmen	2504	2201	22.2	6.4	874	458	7.9	2.2	652	269	4911	2069

### Mercury

For the period 1983-1987 the mercury load measured at Duesseldorf seems to be too high. For Mainz the calculated mercury load seems to be slightly under-estimated. For the period 1993-1997 the mercury load measured at Duesseldorf seems to be under-estimated. For Seltz, Mainz and Karlsruhe the calculated mercury load seems to be slightly over-estimated.

### Lead

For the period 1983-1987 the lead load estimated for the station Seltz/Lauterbourg is over-estimated. For the period 1993-1997 the lead load estimated at Duesseldorf and Mainz seems to be slightly under-estimated.

### Zinc

For the period 1983-1987 the zinc load seems to be consistent. For the period 1993-1997 the zinc load estimated at Duesseldorf and Mainz seems to be slightly under-estimated.

A comparison of heavy metal loads stemming from main tributaries shows the importance of the River Mosel and River Main nowadays (see table 2-1 and appendices 2.2b-c). The River Mosel's contribution to the measured transport at Lobith Bimmen ranges from 12% for copper to 27% for mercury. The contribution of the river Main to the measured transport at Lobith Bimmen ranges from 10% for zinc to 27 % for mercury.

The estimates of the point source wastewater flow within a particular catchment area were gathered from the German Statistical Yearbooks (1984, 1989 & 1994) and Schmoll (1998).

The volumes of point wastewater flow have an uncertainty of 30%. The average point flow estimates used are shown in appendix 2.2d.

In appendices 2.2e-f, the results of the immission analysis of heavy metals are shown. From a comparison between 2.2e and 2.2f the following can be stated:

- In general we can conclude that the contribution of diffuse sources to the heavy metal load in the Rhine for the period 1983-1987 as well as 1993-1997 dominates.
- The average discharge for almost all stations is in 1983-1987 about 20% lower as for the period 1993-1997.
- For some tributaries (Neckar and Mosel) and along the main stream of the Rhine a slight increase of the contribution of diffuse sources can be observed for cadmium, and lead.
- For the other substances the contribution of the diffuse sources remains approximately the same or even slightly decreases. This decrease could be caused by the fact that the discharge in the period of 1993-1997 is lower and therefore related to this less diffuse input from rainfall-dependant diffuse sources (e.g. urban runoff, surface runoff etc.) is expected.
- The results show that in the period 1983-1987 (see appendix 2.2e) a large amount of heavy metals are originating from emissions of diffuse sources. Only the Neckar has a significant higher contribution of point sources than other stations in Rhine drainage area.
- The average contribution of diffuse sources in the Rhine drainage area varies between 74% for cadmium to 85% for copper.
- The highest specific diffuse cadmium, copper, mercury and lead load is derived from the Wupper and the highest specific zinc load from the Sieg.

In appendix 2.2f, the results are given for the period 1993-1997. From appendix 2.2f it is clear that:

- high contributions to the total loads result from inputs from diffuse sources.
- The average contribution of diffuse sources in the Rhine drainage area varies between 84% for lead and mercury to 86% for copper.
- The highest specific diffuse cadmium, copper load is originating from the Emscher. The highest diffuse mercury and lead load from the Wupper and the highest specific zinc load from the Sieg.

Since the immission analysis is applied to two periods, we can compare the absolute and relative changes in heavy metal load. The absolute amounts of point discharges are reduced from 1983-1987 to 1993-1997. The comparison of the average contribution of diffuse sources in both periods shows that little has changed in general, but for individual stations changes can be bigger. In figure 2-3 the results of the source apportionment analysis are shown for both periods. The highest increases of diffuse load are observed in the Neckar and in the Mosel for cadmium. For all stations a slight increase in the contribution of diffuse sources can be observed. Only at the station Lobith we observe a significant decrease in diffuse mercury load. A clear explanation for this increase of the contribution of point sources could not be found.

## Part B: Present and future quality of sediments – heavy metals

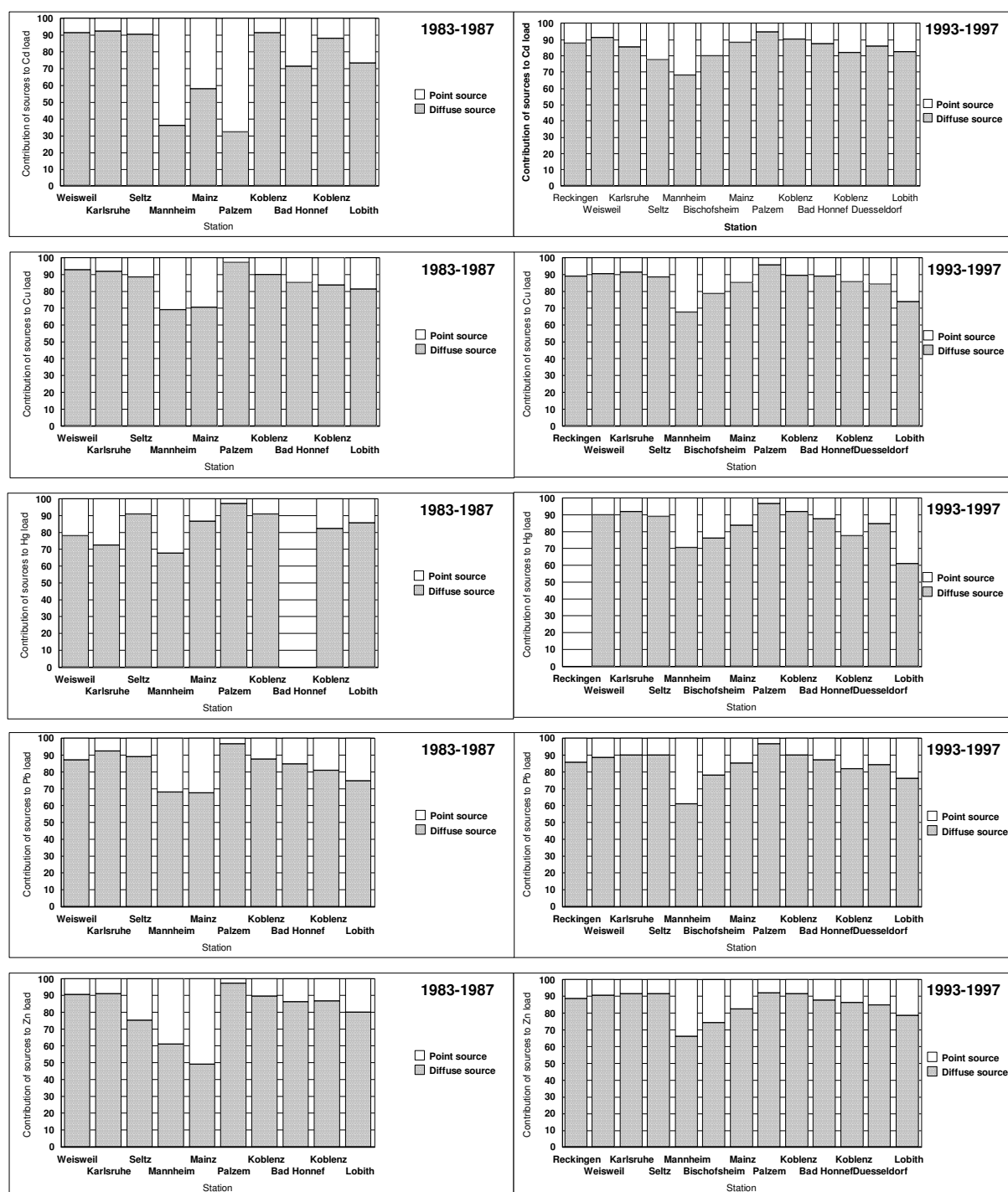


Figure 2-3: Results from source apportionment analysis for 1983-1987 and 1993-1997

### 2.3 Summary and conclusions

The use of the immission method provides insight and information on the development of the contribution of the point and diffuse sources and their distribution within the Rhine catchment. Data from the several monitoring stations in the Rhine catchment was analysed over the period 1983-1987 and 1993-1997.

In general, the discharge for all drainage areas is lower in the period 1993-1997 when compared to the period of 1983-1987. The measured heavy metal loads for the Rhine

drainage area decreased for all heavy metals over the period 1983-1987 to 1993-1997. The highest decrease in heavy metal loads occurred in the Ruhr and the Wupper.

In general about 80% of the total load can be explained by inputs from diffuse sources. Only the Neckar has a significant higher contribution of point sources than other stations in Rhine drainage area. This might be caused by industrial sources or wastewater treatment plants. In 1983-1987 the average contribution of diffuse sources in the Rhine drainage area varies between 74% for cadmium to 85% for copper. A comparison of the point and diffuse contributions of cadmium, lead and zinc in the River Rhine for the period 1983-1987 (see appendix 2.3), showed main differences for the station Lobith. In general, Behrendt (1993) estimated slightly higher point source contributions, which were caused by the difference in the volume of the point source discharges. The highest specific diffuse cadmium, copper, mercury and lead load is derived from the Wupper and the highest specific zinc load from the Sieg in 1983-1987.

In 1993-1997 the average contribution of diffuse sources in the Rhine drainage area varies between 84% for lead and mercury to 86% for copper. The highest specific diffuse cadmium, copper load is originating from the Emscher. The highest diffuse mercury and lead load from the Wupper and the highest specific zinc load from the Sieg.

In general the diffuse contributions (in %) to the total heavy metal loads of the period 1993-1997 remained on the same levels as those of 1983-1987 or only slightly increased. The only changes that have occurred are in the Neckar and Mosel where point source loads have decreased. No clear indication of point source reductions could be found in the inventory of industrial sources and therefore remains unexplained. Because the total heavy metal loads decreased, both point and diffuse loads also decreased.

Since about 20% of the observed transports in the Rhine basin nowadays originates from point sources (industry and wastewater treatment plants), measures taken to prevent emissions from these point sources will not drastically decrease the heavy metal transports in the Rhine basin. Therefore, more effort should be put in the prevention of emissions from the diffuse sources whose contribution nowadays is about 80%.

### **3 Modelling of point and diffuse sources in the Rhine catchment area**

In this chapter all emissions of heavy metals in the Rhine basin are quantified with a model called MONERIS. First the modelling approach to estimate all emissions is explained. Then, the emissions from all point and diffuse sources are discussed. Further, emissions from the Netherlands contributing to the heavy metal emissions upstream of Rotterdam are assessed. Finally, these emission estimates are compared to other studies.

#### **3.1 Emission analysis (MONERIS) – Rhine basin upstream Bimmen/Lobith**

MONERIS (**MO**deling **N**utrient **E**missions in **R**iver **S**ystems) is a tool for quantifying nutrient emissions along the various hydrological pathways in river basin. The Institute of Freshwater Ecology and Inland Fisheries developed this model (Behrendt et al., 1999). Their main aim was to quantify the nutrient emissions of whole Germany, Switzerland, Poland and the Czech Republic for the period 1983-1997 and development of scenarios for reducing nutrient inputs in the German catchments, partly in view of international regulations on reducing inputs into the North Sea and Baltic Sea. In this study the model was adapted for the simulation of heavy metals in the Rhine catchment.

The GIS-oriented Model MONERIS was adapted for the estimation of heavy metal inputs by various point and diffuse sources into the Rhine basin for the periods 1983 to 1987 and 1993 to 1997. The basic input into the model is data on discharges, data on water quality of the investigated river basins and a Geographical Information System integrating digital maps as well as statistical information for different land use types, wastewater treatment, soil types, geology etc.

Whereas the inputs of municipal waste water treatment plants and direct industrial discharges enter the river system directly, the sum of the diffuse heavy metal inputs into the surface waters is the result of different pathways realised by several runoff components (see figure 3-1).

The distinction between the inputs from the different runoff components is necessary, because the concentrations of substances within the runoff components and the processes within these runoff components are very different. Therefore the MONERIS model takes seven pathways into account:

- discharges from point sources
- inputs into surface waters by atmospheric deposition
- inputs into surface waters from groundwater
- inputs into surface waters from tile drainage
- inputs into surface waters from paved urban areas
- inputs into surface waters by erosion
- inputs into surface waters by surface runoff (only dissolved heavy metals)

Within the diffuse pathways, various transformation-, loss and retention processes are identified. To quantify and forecast the heavy metal inputs in relation to their cause requires knowledge of these transformation and retention processes. This is not yet possible through detailed dynamic process models because the current state of knowledge and existing databases is limited for medium and large river basins. Therefore, existing approaches of macro-scale modelling should be complemented and modified and if necessary attempts will be made to derive new applicable conceptual models for the estimation of heavy metal inputs via the individual diffuse pathways to enable sound modelling of large river basins.

Use of a Geographical Information System gives the possibility for a regionalized estimation of heavy metal inputs in large river basins. The calculation was done for two time periods 1983 to 1987 and 1993 to 1997. The results of both periods were compared with estimations of other authors and analysed for changes of heavy metal inputs. These changes were estimated based on the different hydrological conditions as well as the same hydrological conditions in the two time periods. The assumption of unique hydrological conditions for both time periods can be used to identify the changes caused by anthropogenic activities. The heavy metal inputs from different pathways were estimated as described in the next chapters. For all sources emission factors from various studies were evaluated and averages were used to describe the magnitude of the heavy metal emission in this study. The used emission factors are highlighted in the different tables in the appendices.

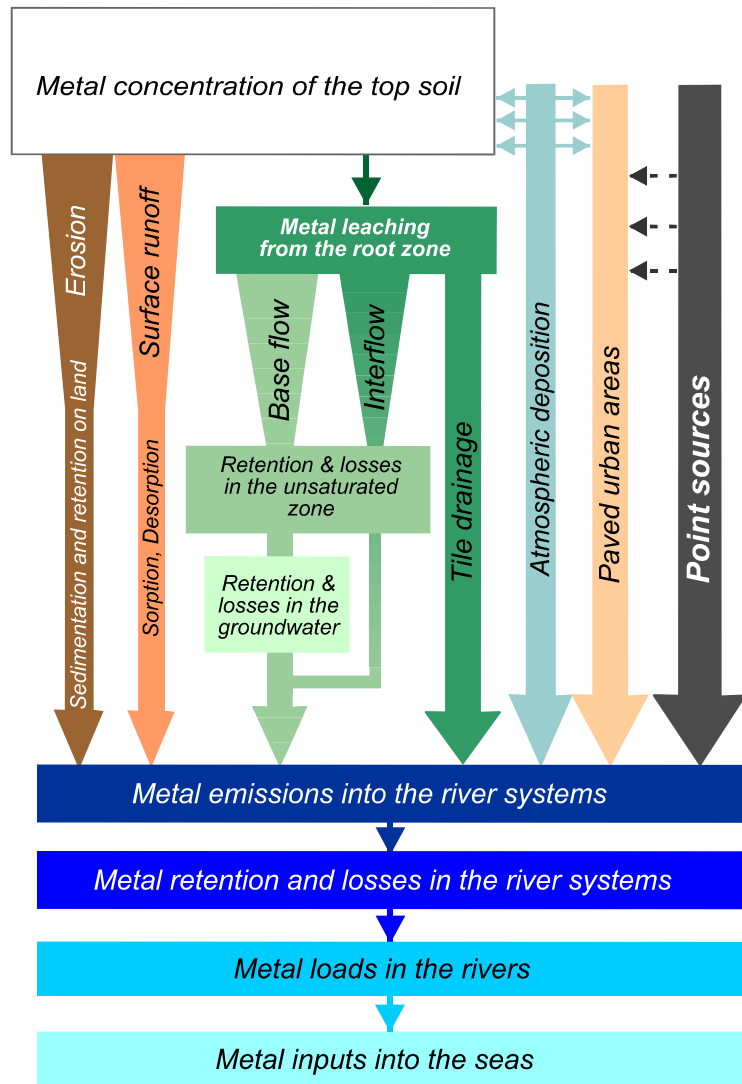


Figure 3-1: Pathways and processes in MONERIS (adapted from Behrendt et al., 2000)

### 3.1.1 Industry

The International Commission for Protection of the River Rhine (ICPR, 1989, 1994 & 1999) reports the heavy metal emissions from industrial sources for the years 1985, 1992 and 1996. The major industrial sources of heavy metals in Rhine drainage area are covered in these databases, still not all emissions are listed. These emission inventories were used estimate the

emissions for the periods 1983-1987 and 1993-1997. When the location of the industrial emission was known, the specific industrial emission was attributed to the location in the particular sub-catchment. For the rest of the emissions of which the location was unknown, the emissions were attributed proportionately to the urban areas. It is assumed that with increasing urban areas, the amount of industrial activities also increase (Behrendt, pers. comm.).

### 3.1.2 Wastewater treatment plants

The population, which is connected to a wastewater treatment plant (WWTP), was estimated depending on the size of the WWTP according to the sewage statistics for all medium and large German rivers. The emissions from municipal discharges into the surface waters are substantial (RIZA, 1999). The sewer system is the central collector of heavy metals in urban areas. Since heavy metals are not degraded in wastewater treatment systems, sewage sludge withdrawal is the only means of loss from an urban sewer system.

The regionalized estimation of heavy metal inputs from municipal WWTPs is based on a country wide GIS-supported inventory (Schmoll, 1998; Behrendt et al, 1999). This inventory includes more than 8000 WWTPs (80% of all WWTPs and 99% of treated wastewater) for both time periods. It comprises the following information: rate of utilisation, treated population equivalents, treated population equivalents (inhabitants), treated population equivalents (indirect industrial discharges). The yearly quantity of treated water is separated into domestic wastewater, industrial and commercial wastewater, external water, urban wastewater, storm wastewater and total wastewater. The heavy metal emissions of a WWTP were estimated based on the basis of an inhabitant specific heavy metal emission and the treatment efficiency for different types of wastewater treatment (see appendix 3.1.2). The inhabitant specific heavy metal emission are estimated and based on available data published by Peek (1993), De Waal and Maalefijt (1982), StBa (1986, 1992 & 1996), Hahn & Xanthopoulos (1994), Firk (1993), Ried (1992), Fuchs & Hahn (1999) and RIZA (1999). The emissions factors per inhabitant were generally based on the data of Zessner (1999), but in the case of Pb an average was used of the RIZA (1999) and Zessner (1999) values. There is not sufficient literature available to derive two different emission factors for both periods. The emissions from wastewater treatment plants ( $WWTP_M$ ) are estimated by multiplication of the specific emission per inhabitant ( $M_{POP}$ ), amount of inhabitants connected to the wastewater treatment plant ( $POP_{WWTP}$ ) and the efficiency of wastewater treatment plants for the elimination of phosphorous ( $WWTP_{eff}$ ), assuming that heavy metals behave the same as phosphorous.

$$WWTP_M [g a^{-1}] = POP_{WWTP} [-] * M_{POP} [g inhabitant^{-1} a^{-1}] * WWTP_{eff} \quad (3.1)$$

### 3.1.3 Atmospheric deposition

Emissions into the air by coal plants, industries, traffic and transboundary air pollution from neighbouring countries result in atmospheric deposition. Firstly, pollutants in the atmosphere can be deposited directly on surface waters. Secondly, pollutants can be deposited on other land use types (e.g. on agricultural soil or on urban areas), and can reach the surface waters through e.g. surface runoff and erosion.



The direct input of heavy metals into the river by atmospheric deposition is estimated by multiplication of the deposition rate of heavy metals and the total area of surface water in a specific region. The atmospheric deposition rate is derived from measurements of a nation wide monitoring programme or modelling results as shown in appendix 3.1.3. Appendix 3.1.3 shows that there was a decline in atmospheric deposition of all heavy metals which of course is related to the decline in emissions within the Rhine basin as well as other countries in Europe.

The basis for estimating direct atmospheric inputs into freshwaters by atmospheric deposition is the knowledge of the area of all surface waters within a basin, which is connected to the river system. The land use map according to CORINE-landcover was used for the estimation of larger lakes and rivers. Additionally, the area of the river system itself has to be taken into account. This was estimated according to Behrendt and Opitz (1999), where it is assumed that the area of a river system is dependent on the size of the catchment. The indirect atmospheric input of heavy metals to urban areas and agricultural soils is considered in the emissions from urban areas and erosion.

### 3.1.4 Surface runoff

The input by surface runoff is defined as the input of dissolved heavy metals during high rainfall events, which cause surface runoff from unpaved areas. The specific surface runoff itself was calculated according to the approach of Liebscher & Keller (1979). In this method the mean summer and winter precipitation are the main variables controlling the volume of this flow component. Further, it was assumed that surface runoff of unpaved areas does not occur. This means forest, wetlands, surface waters and mining areas are not included. The input of particle bound heavy metals during these high rainfall events will be considered in the erosion pathway. The dissolved heavy metals, prevailing in the surface runoff, are mainly originating from deposition. The heavy metal emissions along this pathway are derived from the product of an average heavy metal concentration in the surface runoff (as shown in appendix 3.1.4) and the volume of surface runoff. The heavy metal concentration in the surface runoff was slightly assumed to change over this relatively small time period.

The method to calculate the emissions from surface runoff is:

$$E_S = F_S * C_{M,S} \quad (3.2)$$

in which,

$E_S$  =Emission from surface runoff [ $t a^{-1}$ ],

$F_S$  =Surface runoff flux [ $m^3 a^{-1}$ ],

$C_{M,S}$  =Heavy metal concentration in the surface runoff [ $t m^{-3}$ ].

### 3.1.5 Erosion

Behrendt et al. (1999) developed a method to derive the nutrient emissions via erosion, which was adapted for heavy metals. Figure 3-2 shows the procedure for estimating heavy metal inputs by erosion, based on the soil loss rate, the sediment delivery ratio and the enrichment ratio of heavy metals. To calculate soil loss in the river basins, the digital erosion potential map for Germany was modified to adapt for different land use types (C-factor), which was calculated according to the modified USLE (Universel Soil Loss Equation) from the *Fraunhofer Institute of*

*Ecotoxicology* (Klein, personal communication). The attribution of the C-factor follows Deumlich & Frielinghaus (1994). Additionally, soil loss data estimated for administrative units by Deumlich & Frielinghaus (1994) for the new German states and by Gündra et al. (1995) for Baden-Württemberg was used for validation.

For the estimation of the sediment delivery ratio a new GIS-supported method is proposed through a separation of areas which contribute to soil loss into the river systems. Because the GIS-supported method needs digital records (water networks, land use-, soil- and elevation information) with a high resolution, the application of this method is now limited up to 30 river basins. On the basis of a digital relief analysis, grids are selected, which possess a distance of 30 m from a water-body, an agricultural usage and a slope greater than 1%. For these areas, their watersheds or source areas are estimated with the GIS-function WATERSHED. It is assumed that in the case of erosion events in these areas, the possibility exists of movement of eroded soil material into the neighboring water body. The sediment area ratio ( $SAR_{GIS}$ ), which is related to the sediment delivery ratio, is defined as the sum of the "source areas" divided by the area of the catchment. For a transfer to other river basins, a modification of this method is necessary. For that, relationships between the  $SAR_{GIS}$  and easily determined characteristics of basins or parameters, which are available for all Germany were investigated. Through regression analysis, the mean slope of a basin and the share of the arable land are identified as the parameters, which explain the greatest part of the variance.

The  $SAR_{GIS}$  model was in the next step validated using the long term records of daily measurements of suspended solids for 23 river basins located in Bavaria and Baden-Wuerttemberg. For the validation only loads of suspended solids above a critical discharge were used to prevent that particles caused by point sources and autochthonous growth processes influence the relationship. To adapt the estimations for differences in hydrological conditions between the time periods a weighting factor, which considers the number of days with high flow rates, was introduced according to Rogler & Schwerdtmann (1981).

Data on heavy metal contents of the agricultural soils in the different regions was gathered as shown appendix 3.1.5 (ICPR, 1999, LABO 1998). For the whole period of 1983-1997 we assumed constant topsoil concentrations, because it is likely that over this relatively small time scale the topsoil concentrations only have slightly increased.

The method to calculate the erosion pathway is:

$$E_E = L_E * C_{M-Soil} * ER * 10^{-9} \quad (3.3)$$

in which,

$E_E$  =Emission from erosion [ $t a^{-1}$ ],

$L_E$  =Erosion flux from agricultural areas [ $kg a^{-1}$ ],

$C_{M-Soil}$  =heavy metal concentration in the top soil [ $mg kg^{-1}$ ]

ER =enrichment ratio [-].

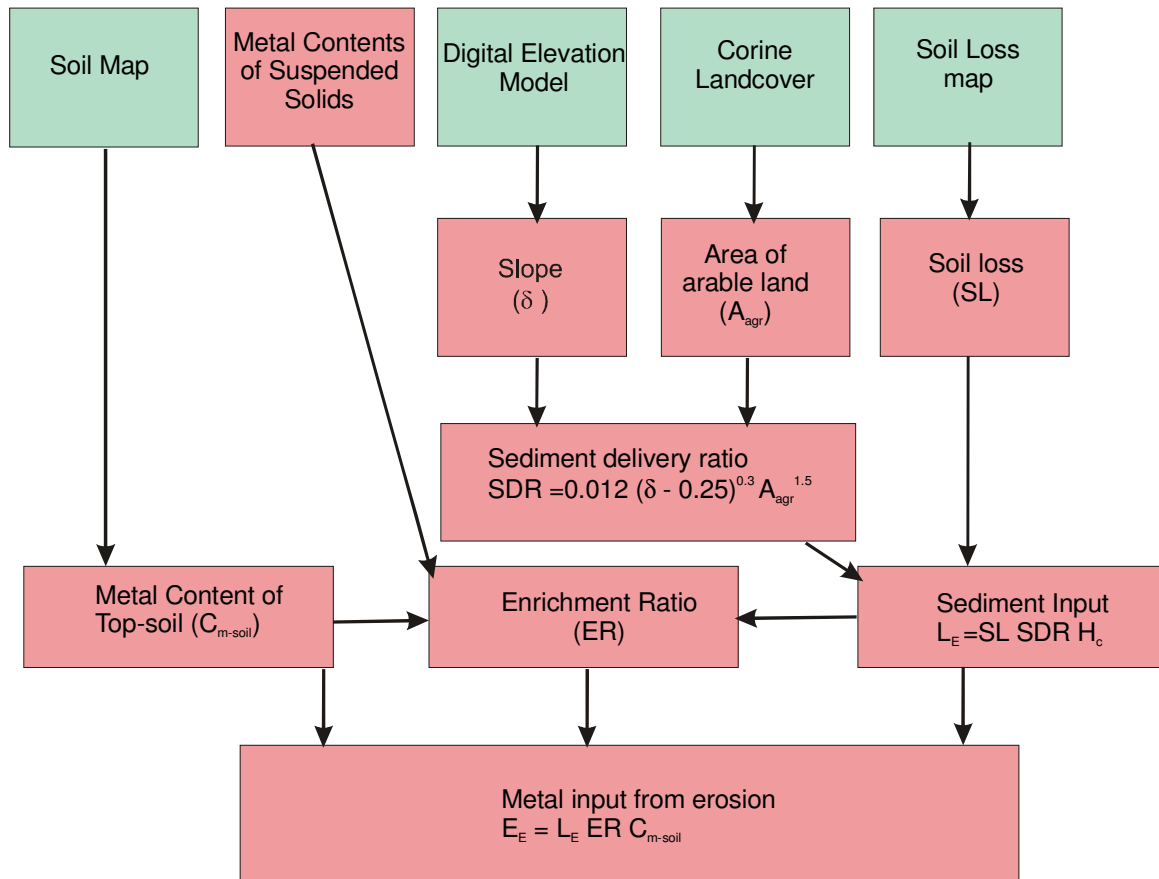


Figure 3-2: Scheme for the estimation of heavy metal inputs by erosion (adapted from: Behrendt et al., 2000)

Heavy metal concentrations in suspended material tend to be higher than in the upper soil (Hahn et al., 1992) because of the enrichment of smaller particles during the process of erosion and the preference of smaller particles transported from the soil to the river. Therefore, the amount of heavy metals transported along the erosion pathway ( $M_E$ ) can not be calculated directly from upper soil concentrations ( $C_{M-Soil}$ ) and soil losses ( $L_E$ ). Erosion is characterised by the enrichment of heavy metals in the smaller sized particles and the enrichment of smaller sized particles during transport downstream. Enrichment is defined as:

$$ER = C_{M,SPM} / C_{M-Soil} \quad (3.4)$$

where  $C_{S,SPM}$  is the heavy metal concentration in the suspended particulate matter [ $\text{mg kg}^{-1}$ ].

Several authors (Auerswald 1989a & 1989b) developed empirical equations to estimate the enrichment. Auerswald and Haider (1992) estimated enrichment for copper about 2.1. Isermann (1992) used an enrichment of 1.6 for cadmium. Behrendt et al.(1999) found that the enrichment ratio for phosphorous is reverse proportional to the square root of the specific sediment input.

For each heavy metal data was gathered on average heavy metal concentrations of suspended particulate matter from several smaller sized rivers with negligible influence of point sources (Donau, Rhine, and rivers in Mecklenburg-Vorpommern). Average heavy metal concentrations of the top-soil in these small catchments were calculated. From these data, enrichment ratios were calculated (see equation 3.4) for each of the monitoring stations where data on heavy metal contents of suspended particulate matter was available. Assuming that heavy metals are

similar as P bound to suspended particulate matter, the enrichment ratios for all heavy metals were plotted versus the specific sediment yield of the catchment. In figure 3-2 the relation between the enrichment ratio and the specific sediment yield of a catchment for each heavy metal is shown. Non linear regression delivered for each heavy metal an individual enrichment model.

The heavy metal inputs by erosion are finally calculated as the product of the heavy metal content of soil, the specific enrichment ratio model, the sediment delivery ratio, the weighting factor and the soil loss.

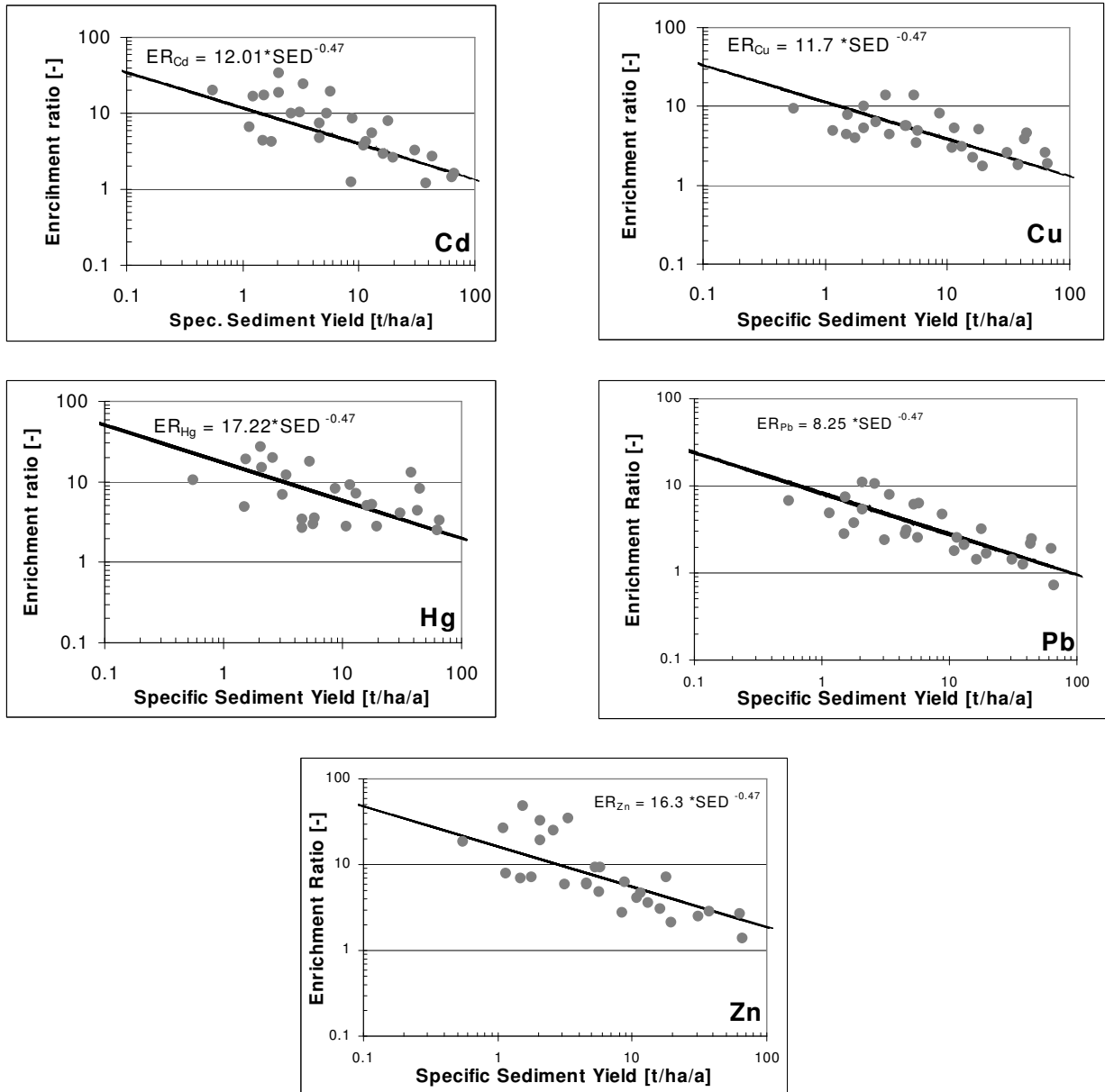


Figure 3-2: Relationship between enrichment ratio of heavy metals (as calculated according to equation 3.4) and the specific sediment yield

### 3.1.6 Drainage

The quantification of heavy metal inputs through drainage is based on the size of the drained area, the amount of drainage water and the average heavy metal concentrations in the drainage water. For the estimation of the size of drained areas within a basin, the survey of Bach et al. (1998) on agricultural administrations concerning the drained area of arable land and pasture is used. From these survey results, the proportion of drained land for the German states was estimated. The drainage water volume is calculated according to Kretzschmar (1977) under the assumption that the drained water is the sum of 50% of winter and 10% of summer precipitation.

The heavy metal concentrations in drainage water are uncertain since not much literature is available on heavy metals in drainage water. In appendix 3.1.6, an overview is given of the data on heavy metal concentrations in drainage water and the values used in this study. For both time periods the same heavy metal concentrations are used since there was not enough literature available to derive different emission factors for both periods.

Equation 3.5 shows the method to calculate the flux of heavy metals along the drainage pathway (Behrendt et al., 1999):

$$E_D = q_D * A_{\text{drainage}} * C_{M,D} \quad (3.5)$$

in which

$E_D$  =Emission from drainage [ $t a^{-1}$ ],

$q_D$  =Specific drainage flux [ $m^3 ha^{-1} a^{-1}$ ] as calculated from Kretzschmar (1977),

$A_{\text{drainage}}$  =Drained area [ha]

$C_{M,D}$  =Heavy metal concentration in the drainage water [ $t m^{-3}$ ].

### 3.1.7 Groundwater

When water infiltrates into the soil and reaches the groundwater also dissolved substances are transported. Most of the groundwater flows into the river and then is transported downstream. The emissions along the groundwater pathway are estimated by multiplying the volume of groundwater draining to the river and measured concentrations in the groundwater, as shown in equation 3.6.

$$E_G = F_G * C_{M,G} \quad (3.6)$$

In which,

$E_G$  =Emission from groundwater [ $t a^{-1}$ ],

$F_G$  =Groundwater flux [ $m^3 a^{-1}$ ],

$C_{M,G}$  =heavy metal concentration in the groundwater [ $t m^{-3}$ ].

The absence of methods for the estimating natural interflow causes that this pathway includes both the base flow and the natural interflow. The groundwater flow was calculated for each basin from the difference of the observed runoff at a monitoring station and the estimated sum of the other water balance components (drain flow, surface runoff, storm water runoff from

paved urban areas and the amount of water directly deposited on surface waters).

In appendix 3.1.7, an overview is given of (background) concentrations measured in the upper aquifers in the Rhine basin. Data from the German States (Bayern, Hessen, Nordrhein-Westfalen) was gathered. Since residence times of heavy metal in the groundwater for Germany are unknown and changes in concentrations could not be detected over the period 1983-1997, the same heavy metal concentrations in the groundwater were used for both periods. If the groundwater measurements lie below the detection limit, the measured values was set to half of the detection limit value. For comparison to other data, ranges of measurements in the different States and data from the ICPR are listed as well.

### 3.1.8 Urban areas

Major inputs of heavy metals in urban areas into the river is via precipitation, following surface runoff which partly enters the urban sewer system. Heavy metals, which are anthropogenic in urban sewer systems, can be found in high concentrations in surface and storm water runoff (Xanthopoulos & Hahn, 1994). These high heavy metal concentrations are caused by various sources (e.g. traffic, corrosion of building materials and atmospheric deposition) which are more concentrated in urban areas. The runoff from urban areas can follow different routes when it reaches the paved surface. Unpaved urban areas are already accounted for in the total emissions to the soil compartment. Possible routes in urban drainage areas are (see figure 3-3): (1) inputs from paved urban areas connected to separate sewer systems (SSS), (2) inputs from paved urban areas by combined sewer overflows (CSS), (3) inputs from households and paved urban areas connected to sewers without WWTPs and (4) inputs from households and paved urban areas which are not connected to sewer systems.

The paved urban area is calculated from the CORINE-landcover map but takes additional into account the population density according to the approach of Heaney *et al.* (1976). The total paved urban area is split into the different sewer systems according to the length of the different sewer systems in the river basins. The total discharge from the different sewer systems was estimated from the mean precipitation and the sewer system's specific share of paved urban area in a river catchment (Heaney *et al.*, 1976). A schematic overview of the applied method is given in figure 3-3.

The estimation of the heavy metal inputs from CSS is based on the approaches of Mohaupt *et al.* (1998) and Brombach & Michelbach (1998). The quantity of water discharged during storm water events from combined sewer overflows is dependent on the specific runoff from the paved urban areas, the number of people connected to CSS, the inhabitant specific water discharge (130 l/(inh. d), the share of industrial areas at the total paved urban area (0,8%), the area specific runoff from these industrial areas (432m<sup>3</sup>/(ha d) and the number of the days on which storm water events occur (50). The discharge rate of a CSS was estimated according to a method developed by Meissner (1991) and is dependent on the storage volume of the CSS as well as the annual precipitation. Data on the storage volume of the CSS was taken from the sewage water statistics of the German countries. The heavy metal concentration in a CSS can be calculated from the area specific emission rate of the paved urban area, the inhabitant specific heavy metal emissions and the concentration of indirect industrial effluents (see appendix 3.1.8a). The heavy metal discharge into each river system is then calculated from the

product of the quantity of water discharged by the overflow and the mean heavy metal concentration during such events.

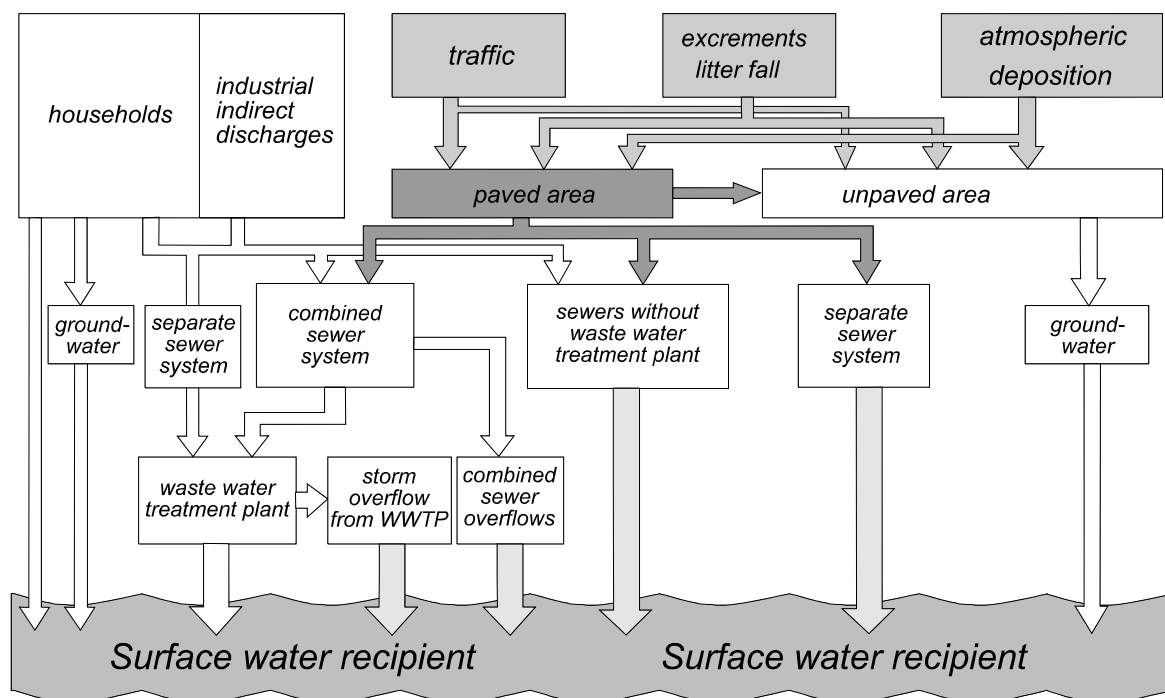


Figure 3-3: Scheme for the estimation of heavy metal inputs from paved urban areas (from Behrendt, 1993)

Additionally to the inputs from SSS and CSS, the heavy metal emission into the river systems from paved urban areas and people have to be considered, which are not connected to a sewer system. Whereas the calculation procedure for paved urban areas is similar to the described method for SSS, we used only the dissolved portion of the inhabitant specific heavy metal emissions (80% for heavy metals), because the particulate fraction will generally be transported to a wastewater treatment plant.

Area specific emission rates of paved urban areas are estimated as the sum of several pathways and sources occurring within an urban area. There are several sources: traffic, atmospheric deposition and corrosion of building materials. The emissions from the various sources are individually estimated with pollutant specific emission factors and regional statistics (e.g. amount of houses, traffic, people etc.).

#### *Traffic emissions in urban areas*

Traffic emissions originate from various sources like wear of tires and combustion of automotive fuel. These emissions partially deposit on the road surface from which the deposited substances can be windblown or flushed off with rainwater. The emissions can be discharged directly into surface waters as well as indirectly (via sewer system and wastewater treatment plants). The emission sources are tyre abrasion; wear of road surfaces, leakage of oil and exhaust gases. These sources cause an extra input of Pb, Cd, Cu and Zn into the environment (Behrendt, 1993; Feenstra & van der Most, 1986; Wyers et al., 1991). The emissions in appendix 3.1.8b are given as emissions per inhabitant.

The emissions from traffic are calculated according to equation:

$$E_T = e_t * PD_u \quad (3.7)$$

$E_t$  = emissions from traffic

$e_t$  = traffic emission per inhabitant per year

$PD_u$  = population density in paved urban areas [-]

#### *Corrosion of building materials in urban areas*

Heavy metals used as building materials will (if exposed to atmospheric influences) corrode over time, which means that the surface will be affected by chemical influences. Paint application and application of metallic alloys (both contain heavy metals) are also subject to these corrosion processes. Several commonly used building materials release heavy metals in the environment (van Bentum, 1996). Well-known examples are sheet lead and zinc gutters and roofs. The emissions from building materials can also be the result of abrasion of heavy metal surfaces. The total emission is calculated by multiplying the total exposed metal surface with a mean annual corrosion rate. This results in a yearly total emission which is divided over the different pathways e.g. separate sewer system, combined sewer system, not connected sewer systems and not connected households using the wastewater statistics.

Zinc emissions from gutters and roofs can be estimated according to the method described by Coppoolse et al. (1993) from the estimated exposed surface area of zinc gutters and roofs. This total exposed surface area is based on an estimate of the total amount of houses. Zinc contains trace amounts of cadmium and hence corrosion of gutters and roofs causes cadmium to be released into the environment.

The corrosion rate is influenced by several factors of which  $SO_2$  concentration in the air, temperature, amount of rainfall, pH and humidity are the most important ones. Hrehoruk (1991) estimated corrosion rates for several West German cities, based on  $SO_2$  concentrations in air. This resulted in mean yearly zinc corrosion rates in urban areas of  $15-30 \text{ g m}^{-2} \text{ a}^{-1}$  in the middle of 1980s. According to Coppoolse et al. (1993) the corrosion rates in the Netherlands ranged between  $20-40 \text{ g m}^{-2} \text{ a}^{-1}$  in 1985, and a mean of  $28 \text{ g m}^{-2} \text{ a}^{-1}$ . Using the relationship between  $SO_2$  concentrations in the air and the corrosion rate, given by the ECE (1984) we can estimate the corrosion rates for urban areas over the time period 1985-1995:

$$Y = 0.45 * [SO_2] + 0.7 \quad (3.8)$$

where Y is the average yearly corrosion rate of one square meter of galvanised steel.

$SO_2$  is the mean annual concentration of sulphur dioxide in the air.

The average yearly atmospheric concentrations of  $SO_2$  have been measured by the meteorological services in all countries (Umweltbundesamt, 1986-1999). The measured  $SO_2$  concentrations are shown in figure 3-4.

Estimations on the total exposed area of galvanised material are quite inaccurate. Annema et al. (1993) calculated an average galvanised (zinc) surface of  $3 \text{ m}^2$  per house and an average galvanised (zinc) surface of  $0.08 \text{ m}^2$  per  $\text{m}^2$  utility surface area in the Netherlands. The zinc emissions are distributed over the (paved) urban areas.



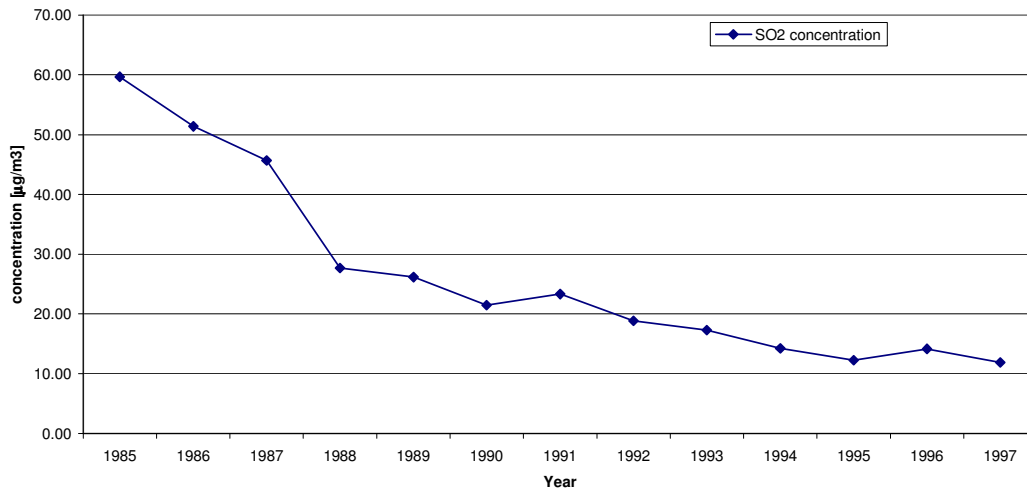


Figure 3-4: Average SO<sub>2</sub> concentration in the Rhine catchment

Behrendt (1993) developed an equation to estimate the area of galvanised steel per ha urban area.

$$a_{\text{steel}} = 47.2 + 1.77 * PD_u \quad (3.9)$$

$a_{\text{steel}}$  = galvanised steel surface [m<sup>2</sup>/ha paved urban area]

$PD_u$  = population density in paved urban areas [-]

Basically the total emission caused by corrosion is estimated from the product of the total area of galvanised material subjected to air and the mean corrosion rate per year according to equation:

$$E_{\text{cor}} = Y * a_{\text{steel}} \quad (3.10)$$

$E_{\text{cor}}$  = emission from corrosion [t/a]

$a_{\text{steel}}$  = galvanised steel surface [m<sup>2</sup>/ha paved urban area]

Zinc materials contain cadmium as an impurity (0.3 % according to Raad et al., 1993), that is emitted as a result of zinc corrosion.

The total amount of heavy metals released through corrosion is depicted in appendix 3.1.8c. Appendix 3.1.8c shows that emissions from corrosion in urban areas have decreased dramatically over the last 20 years. This is mainly caused by the improved air quality.

#### Atmospheric deposition in urban areas

Generally atmospheric deposition in urban areas is higher than in the rest of the surrounding rural areas. This is caused by the concentration of industrial areas around urban areas and their influence on the local surroundings. In appendix 3.1.8d the atmospheric deposition rates in urban areas are shown. For urban atmospheric deposition we assumed the deposition rate to be twice as high as the deposition rates discussed in appendix 3.1.3 (see Behrendt, 1993). Appendix 3.1.8d shows that the atmospheric deposition has decreased over the last 15 years. The phase out of lead in leaded petrol and air pollution control measures taken, are the main reasons for this decline.

*Total deposition rates in urban areas*

The total urban deposition into urban areas is calculated from the sum of contributions of corrosion of building materials, urban atmospheric deposition and emissions from traffic:

$$E_U = E_{cor} + E_A + E_T \quad (3.11)$$

- $E_U$  = emission to urban areas [g/(ha/a)]
- $E_{cor}$  = corrosion emission [g/(ha/a)]
- $E_A$  = urban atmospheric deposition load [g/(ha/a)]
- $E_T$  = urban traffic emission [g/(ha/a)]

In appendix 3.1.8e, an overview is given of the specific heavy metal loads to urban areas over time. In case of cadmium all sources contribute evenly to the total load over time. For lead traffic and atmospheric deposition were the dominating sources in the 1980's, but nowadays these have declined because of the phase out policy of lead from petrol. Traffic causes the main copper input into urban areas. Corrosion and traffic are the main source of zinc deposition in urban areas.

### 3.2 Results of the emission analysis – Rhine basin upstream Lobith/Bimmen

First the results are given for all the individual pathways in chapters 3.2.1-3.2.8. In chapter 3.2.9 an overview is given of the total emissions in the Rhine basin.

#### 3.2.1 Industry

In tables 3-1 and 3-2 an overview is given of the industrial heavy metal emissions into the Rhine river system over the period 1983-1987 and 1993-1997 (ICPR, 1999). The industrial emissions have decreased by 73 - 83 %. The comparison of both tables shows that over the period 1985-1996 industrial emissions have decreased in all countries of the Rhine catchment. This is mainly caused by the policy targets to minimise industrial emissions directly into the rivers. Germany has the highest contribution to the total industrial emissions upstream of Lobith, ranging from 48 % for cadmium to 82 % for lead.

*Table 3-1: Industrial emissions in the Rhine drainage area in 1983-1987*

Substance	Total	Switzerland	France	Germany
Cd [kg/a]	2705	220	710	1775
Cu [kg/a]	145685	11685	48000	86000
Hg [kg/a]	972	177	70	725
Pb [kg/a]	96230	2330	11500	82400
Zn [kg/a]	620310	17310	102000	501000

Table 3-2: Industrial emissions in the Rhine drainage area in 1993-1997

Substance	Total	Switzerland	France	Germany
Cd [kg/a]	<700	<95	242	336
Cu [kg/a]	38673	800	11190	26683
Hg [kg/a]	239	13	74	152
Pb [kg/a]	19113	<400	3120	15593
Zn [kg/a]	126885	7430	41100	78355

### 3.2.2 Wastewater treatment plants

The development of the emissions from wastewater treatment plants over the time periods is given in tables 3-3 and 3-4. The emissions from wastewater treatment plants have decreased by 42 - 65%. This is caused by the decrease in specific heavy metal emissions per inhabitant, the higher connectivity of inhabitants to sewer systems and wastewater treatment plants and the upgrading of wastewater treatment plants with further P-removal steps. The contribution of heavy metal emissions to the total emissions range from 17 % for cadmium to 23% for mercury in 1993-1997.

Table 3-3: Emissions from wastewater treatment plants in the Rhine drainage area in 1983-1987

Substance	Total	Switzerland	France	Germany
Cd [kg/a]	2403	231	534	1638
Cu [kg/a]	186956	17998	41533	127425
Hg [kg/a]	2195	211	488	1496
Pb [kg/a]	164638	15849	36575	112214
Zn [kg/a]	1468943	141411	326333	1001198

Table 3-4: Emissions from wastewater treatment plants in the Rhine drainage area in 1993-1997

Substance	Total	Switzerland	France	Germany
Cd [kg/a]	1355	90	290	975
Cu [kg/a]	105356	7000	22540	75816
Hg [kg/a]	928	62	198	668
Pb [kg/a]	59365	5479	17644	36241
Zn [kg/a]	514635	47500	152967	314168

### 3.2.3 Atmospheric deposition

The direct atmospheric deposition of heavy metal on inland waters only contributes small amounts in comparison to other sources. The contribution to the total emissions range on average between about 2% for copper to about 7% for cadmium (see chapter 3.3). From the comparison of tables 3-5 and 3-6 it is clear that atmospheric deposition emissions have

decreased over the period 1983-1997.

*Table 3-5: Emissions from direct atmospheric deposition in the Rhine drainage area in 1983-1987*

Substance	Total	Switzerland	France	Germany
Cd [kg/a]	1042	451	168	423
Cu [kg/a]	13400	5800	2200	5400
Hg [kg/a]	120	50	20	50
Pb [kg/a]	29766	12882	4793	12091
Zn [kg/a]	148830	64408	23966	60456

*Table 3-6: Emissions from atmospheric deposition in the Rhine drainage area in 1993-1997*

Substance	Total	Switzerland	France	Germany
Cd [kg/a]	601	258	96	247
Cu [kg/a]	9015	3865	1440	3710
Hg [kg/a]	60	26	10	25
Pb [kg/a]	12020	5153	1920	4946
Zn [kg/a]	75123	32206	12002	30915

The relatively large contribution of Switzerland to the total atmospheric emissions (about 43%) can be explained by the large influence of the Lake of Constance on the total area of receiving waters.

### 3.2.4 Surface runoff

The emissions from surface runoff are defined as the dissolved heavy metal inputs from unpaved areas. Therefore, these emissions from surface runoff are influenced by anthropogenic activities and change over time. The decline of emissions from surface runoff is mainly caused by the decrease of the heavy metal concentrations in the surface runoff and the change in the volume of surface runoff between the two time periods.

There were insufficient data to regionalize the heavy metal concentrations in the surface runoff. Therefore, tables 3-7 and 3-8 show areas with high rates of surface runoff (e.g. Switzerland) also have a higher contribution to the total emission.

Table 3-7: Emissions from surface runoff in the Rhine drainage area in 1983-1987

Substance	Total	Switzerland	France	Germany
Cd [kg/a]	915	416	279	220
Cu [kg/a]	60080	17955	14528	27597
Hg [kg/a]	327	109	76	142
Pb [kg/a]	12419	3874	2959	5586
Zn [kg/a]	148696	41401	36777	70519

Table 3-8: Emissions from surface runoff in the Rhine drainage area in 1993-1997

Substance	Total	Switzerland	France	Germany
Cd [kg/a]	690	240	140	310
Cu [kg/a]	53850	18622	11320	23909
Hg [kg/a]	345	119	73	153
Pb [kg/a]	10356	3581	2177	4598
Zn [kg/a]	151302	42308	33961	75034

### 3.2.5 Erosion

The estimates of heavy metal emissions from erosion are shown in tables 3-9 and 3-10. The regional differences in emissions are caused by differences in erosion estimates on the one hand and differences in heavy metal contents of soils on the other hand. Changes in heavy metal contents of the upper soil are not considered in this study, since Behrendt (1993) showed that heavy metal balances of agricultural soils over a period of 10 years only show a slight increase of 1%. Heavy metal inputs by the atmosphere and fertilisers into the agricultural soils also have rapidly declined, which means that given the uncertainty in the erosion estimates, this increase or decrease in heavy metal content of the top soil caused by heavy metal inputs from atmosphere or fertiliser can be neglected.

Table 3-9: Emissions from erosion in the Rhine drainage area in 1983-1987

Substance	Total	Switzerland	France	Germany
Cd [kg/a]	1304	394	215	695
Cu [kg/a]	82205	22702	13621	45882
Hg [kg/a]	675	197	116	362
Pb [kg/a]	102881	32289	16029	54563
Zn [kg/a]	482006	155900	77398	248709

*Table 3-10: Emissions from erosion in the Rhine drainage area in 1993-1997*

Substance	Total	Switzerland	France	Germany
Cd [kg/a]	1299	410	201	688
Cu [kg/a]	76726	17593	13456	45677
Hg [kg/a]	667	194	112	361
Pb [kg/a]	92830	24457	14818	53555
Zn [kg/a]	462157	153564	66502	242091

The relatively steep areas in the South of Germany (Main and Mosel) and Switzerland cause high contributions to the emissions. The differences in emissions between the two periods are only caused by the differences in discharge between both periods. The contribution of the emissions from erosion to the total emissions in the Rhine basin ranged from 9% for cadmium and 17% for lead in 1983-1987. Nowadays, erosion contributes relatively higher amounts to the total emission, ranging from 15% for cadmium to 35% for lead.

### 3.2.6 Drainage

The emissions from drainage water are related to the drained area and the heavy metal concentration of the drained water. The results (tables 3-11 and 3-12) show that drainage is more important for the German part than for the other parts of the Rhine basin. This is caused by the higher amount of drained area in Germany. Contributions to the total emissions in the Rhine basin range between 2% - 4%.

*Table 3-11: Emissions from drainage in the Rhine drainage area in 1983-1987*

Substance	Total	Switzerland	France	Germany
Cd [kg/a]	345	58	76	211
Cu [kg/a]	12243	2044	2710	7489
Hg [kg/a]	86	14	19	53
Pb [kg/a]	3405	570	753	2082
Zn [kg/a]	44807	7486	9923	27398

*Table 3-12: Emissions from drainage in the Rhine drainage area in 1993-1997*

Substance	Total	Switzerland	France	Germany
Cd [kg/a]	334	48	71	215
Cu [kg/a]	11840	1692	2510	7638
Hg [kg/a]	84	12	18	54
Pb [kg/a]	3285	469	696	2119
Zn [kg/a]	45163	6196	11022	27946

### 3.2.7 Groundwater

Heavy metal emissions from groundwater transport are related to the amount of baseflow from an area and the heavy metal concentration in the groundwater. Heavy metal concentrations in the groundwater are often below the detection limit and therefore the estimates as shown in tables 3-13 and 3-14 should (in case of cadmium and mercury) be considered as maximum emissions. The contribution of groundwater emissions to the total emissions in the Rhine basin ranges from 9% (for lead) to 21% (for copper).

*Table 3-13: Emissions from groundwater in the Rhine drainage area in 1983-1987*

Substance	Total	Switzerland	France	Germany
Cd [kg/a]	1334	192	342	800
Cu [kg/a]	109361	18894	24843	65623
Hg [kg/a]	534	91	123	320
Pb [kg/a]	29327	5262	6449	17616
Zn [kg/a]	496096	86101	112270	297725

*Table 3-14: Emissions from groundwater in the Rhine drainage area in 1993-1997*

Substance	Total	Switzerland	France	Germany
Cd [kg/a]	1237	205	264	768
Cu [kg/a]	101999	17160	21735	63104
Hg [kg/a]	497	82	107	307
Pb [kg/a]	24838	4109	5360	15370
Zn [kg/a]	462961	78305	98252	286405

### 3.2.8 Urban areas

Paved urban areas are particularly important contributors to the total emissions in the Rhine basin (see tables 3-15 and 3-16). The main inputs of heavy metals occur along the pathways of traffic, atmospheric deposition and corrosion of building materials. The final emissions into the surface waters not only depend on the contribution of these urban pathways but also on the connection of people to the different types of sewer systems (separate sewer system (SSS) or combined sewer system (CSS)) and wastewater treatment plants. Emissions from urban areas have declined with 56%-74% (e.g. 56% for Cu to 74% for Pb and Hg) between 1983-1987 and 1993-1997.

The decline in urban Cd and Hg emissions is mainly caused by a decline in atmospheric deposition rates. For Hg the decline in Hg discharges from dentist practices also plays an important role. A decline in atmospheric deposition rates and a decline in traffic emissions mainly cause the decline in urban Cu and Pb emissions. The decline in urban Zn emissions is mainly caused by the decrease of SO<sub>2</sub> concentrations and consequently emissions from the corrosion of building materials.

Table 3-15: Emissions from urban areas in the Rhine basin in 1983-1987

Substance	Total	Switzerland	France	Germany
Cd [kg/a]	7742	99	1723	5921
Cu [kg/a]	193869	2484	46830	144555
Hg [kg/a]	4327	51	1013	3263
Pb [kg/a]	183419	2576	49726	131117
Zn [kg/a]	1605648	16570	302628	1286450

Table 3-16: Emissions from urban areas in the Rhine basin in 1993-1997

Substance	Total	Switzerland	France	Germany
Cd [kg/a]	2177	41	461	1674
Cu [kg/a]	85438	1684	17519	66234
Hg [kg/a]	1078	21	227	831
Pb [kg/a]	47414	944	9155	37315
Zn [kg/a]	522343	10608	108901	402834

Especially the Emscher and Wupper in the Ruhr-area have high specific urban loads because of the relatively large paved urban areas in these catchments. Figures 3-5 and 3-6 show the high contribution of emissions from the CSS. The rest term is the sum of emissions from inhabitants not connected to a sewer system and emissions from sewers, which are not connected to a wastewater treatment plant. In the Rhine basin about 77% of the people are connected to a CSS and 16 % are connected to a SSS. This high connectivity to a CSS causes high amounts of heavy metal inputs into the surface waters during high rainfall events.

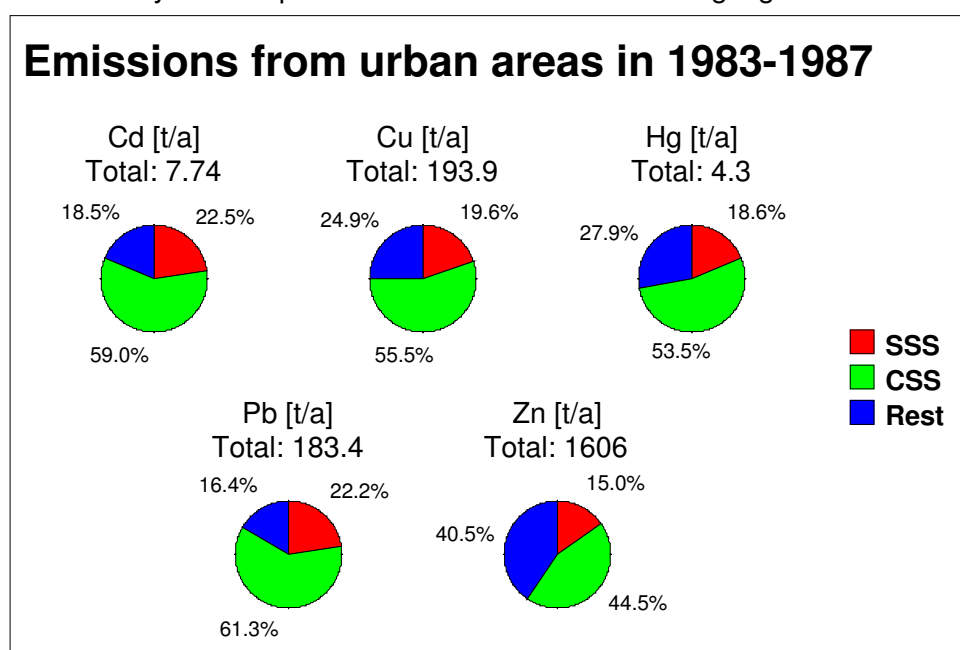


Figure 3-5: The relative contribution of the different pathways in urban areas upstream of Lobith in 1983-1987 (SSS means separate sewer system and CSS means combined sewer system)



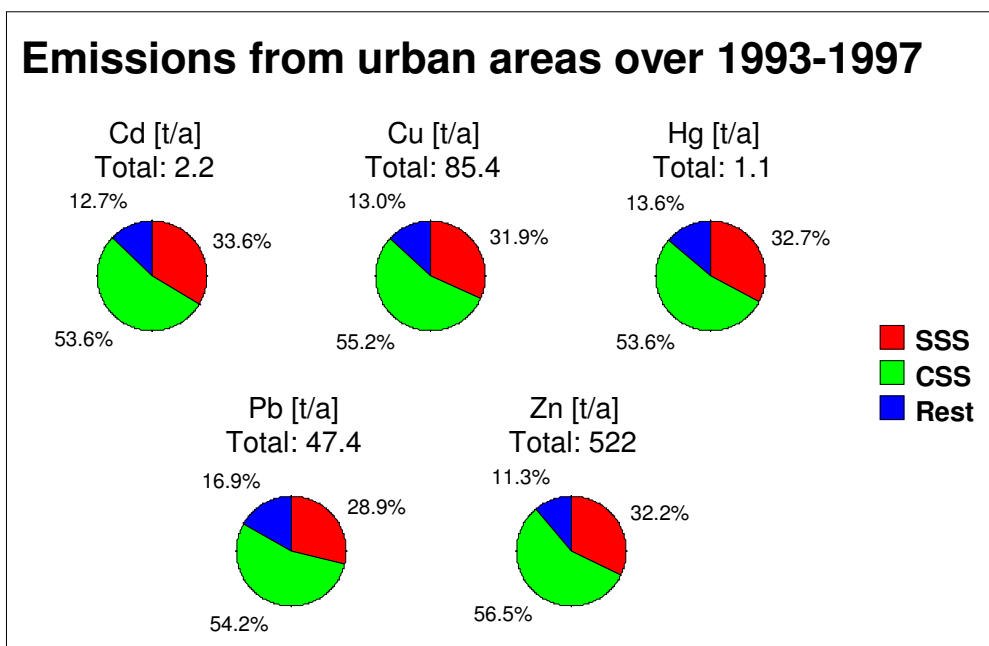


Figure 3-6: The relative contribution of the different pathways in urban areas upstream of Lobith in 1993-1997 (SSS means separate sewer system and CSS means combined sewer system)

### 3.2.9 Total heavy metal emissions in the Rhine basin upstream of Lobith/Bimmen

Tables 3-17 and 3-18 summarise the overall results of the emission analysis from different point and diffuse pathways in the Rhine basin. The total emissions upstream of Lobith decreased with 40% (for copper) - 58% (for mercury) over the period 1983-1997. This decrease in total emissions is mainly caused by a decline in emissions from wastewater treatment plants, industry and urban areas over the period 1983-1987 to 1993-1997.

Table 3-17: Overview of the total emissions in the Rhine basin in 1983-1987

Source	Cd [t/a]	Cu [t/a]	Hg [t/a]	Pb [t/a]	Zn [t/a]
Industry	2.7	145.7	1.0	96.2	766.0
Wastewater treatment plant	2.4	187.0	2.2	164.6	1468.9
Atmospheric deposition	1.0	13.4	0.1	29.8	148.8
Surface Runoff	0.9	60.1	0.3	12.4	148.7
Erosion	1.3	82.2	0.7	102.9	482.0
Drainage	0.3	12.2	0.1	3.4	44.8
Groundwater	1.3	109.4	0.5	29.3	496.1
Urban areas	7.7	193.9	4.3	183.4	1605.6
Total emissions (excl. Netherlands)	17.6	803.8	9.2	622.1	5161.0

Table3-18: Overview of the total emissions in the Rhine basin in 1993-1997

Source	Cd [t/a]	Cu [t/a]	Hg [t/a]	Pb [t/a]	Zn [t/a]
Industry	0.7	39	0.2	19	127
Wastewater treatment plant	1.4	105	0.9	59	515
Atmospheric deposition	0.6	9	0.1	12	75
Surface Runoff	0.7	54	0.3	10	151
Erosion	1.3	77	0.7	93	462
Drainage	0.3	12	0.1	3	45
Groundwater	1.2	102	0.5	25	463
Urban areas	2.2	85	1.1	47	522
Total emissions (excl. Netherlands)	8.4	483	3.9	269	2361

Inputs from wastewater treatment plants rather than emissions from industries nowadays dominate the emissions from point sources. The emissions from urban areas have decreased because the deposition rates of heavy metals in urban areas have declined and the percentage of urban areas connected to sewer systems and wastewater treatment plants also have increased. The diffuse sources are mainly dominated by inputs from urban areas, erosion and groundwater.

From the figures 3-7 and 3-8 it is clear that for all heavy metals the reductions of point sources like industries and wastewater treatment plants were successful. However, nowadays a relatively high portion of the heavy metal emissions is caused by erosion, surface runoff and groundwater. This is caused by the fact that point source emissions and emissions from urban areas have decreased and therefore the other sources will have a higher contribution to the total emission. Following, more reduction of heavy metal emissions in the Rhine basin will mean tackling of sources with a more diffuse character like urban areas, drainage or surface runoff.

Appendices 3.2.9a-b summarise the contribution of diffuse sources to the total emissions for the several sub-catchments as calculated with MONERIS. Regional differences in the contribution of point sources are hardly noticeable. This is caused by the fact that all large point sources (industries) already apply BAT (Best Available Techniques) and the contribution of diffuse sources is dominating. Only in the Mosel area we find a higher contribution of point sources. The comparison of the appendices 3.2.9a and 3.2.9b shows that the contribution of diffuse sources has increased over the period 1983-1997 with approximately 5-10%.

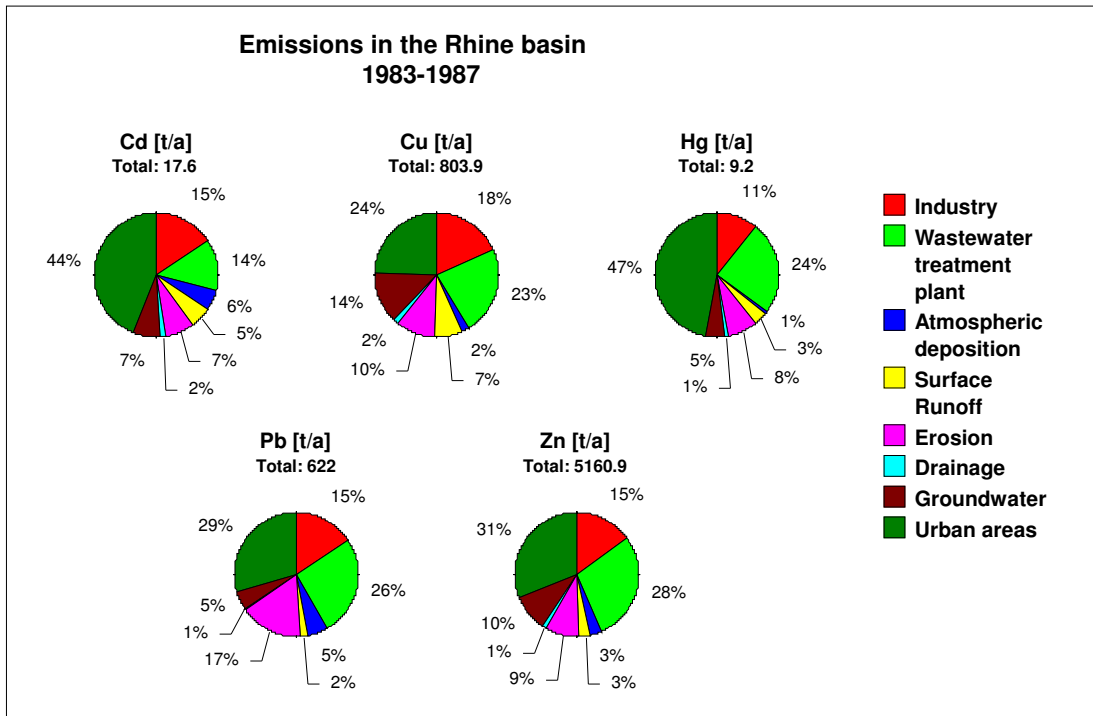


Figure 3-7: Overview of the sources contributing to the total emissions at Lobith in 1983-1987

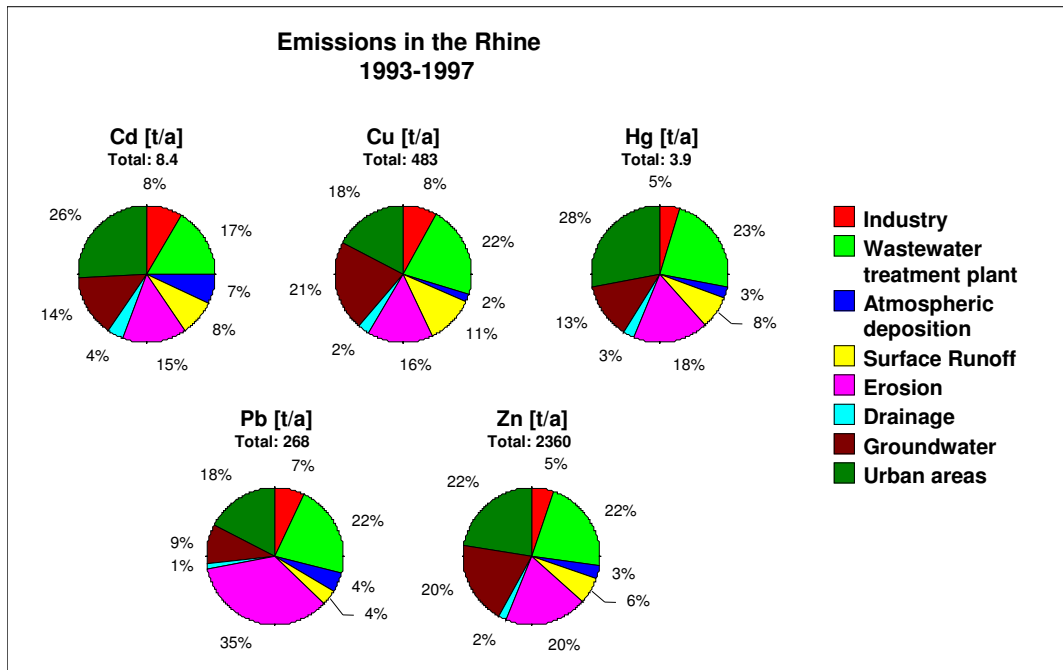


Figure 3-8: Overview of the sources contributing to the total emissions at Lobith in 1993-1997

### 3.3 Emissions in the Netherlands

The emissions in the Netherlands were based on the estimates given by the ICPR (1999). These emission estimates were calculated with the support of an expert team of the German Rhine Protection Commission as well as other Dutch, French and German experts, by carrying out an intensive literature study about diffuse heavy metal pathways, their rates and concentrations (Mohaupt et al., 1998). Data on heavy metal emissions from groundwater in the Netherlands are missing since the ICPR did not consider these emissions in their approach. The emission estimates for the Netherlands were recalculated with heavy metal concentrations in the drainage water as listed in appendix 3.1.6. A comparison from this table 3-19 to the emission estimates of the Rhine basin upstream of Lobith (table 3-18) shows that the emissions in the Netherlands only contribute about 12% of the total emissions in the Rhine basin. Only for Cadmium and Lead the Dutch emissions contribute 17% of the total emissions in the Rhine basin.

Table 3-19: Emissions in the Dutch Part of the Rhine basin for the period 1993-1997

Sources	Cd [t/a]	Cu [t/a]	Hg [t/a]	Pb [t/a]	Zn [t/a]
Industry	0.41	7.07	0.21	3.78	14.91
Wastewater treatment plant	0.29	9.37	0.09	5.3	66.8
Atmospheric deposition	0.6	9.05	0.06	12.1	75.4
Surface Runoff	0	0.74	0	0.1	1.6
Erosion	0	0.25	0	0.3	0.8
Drainage*	0.17	6.1	0.04	16.8	22.2
Groundwater	-	-	-	-	-
Urban areas	0.43	13.42	0.09	12.4	59.2
Total emissions	1.9	46	0.49	50.78	240.91

\* Drainage emissions were calculated with heavy metal concentrations from appendix 3.1.6

These emissions in the Netherlands also include the heavy metal emission inside of the port of Rotterdam. This was analysed with data supplied by Ministry of Transport, Public Works and Water Management, directorate South Holland (van der Meulen, pers. comment). The contribution of the industrial sources inside of Rotterdam to the total emissions in the Netherlands range from about 63% for Zn to 100% for Cd and Hg. This implies that these industrial emissions within the Rotterdam port area, locally (in individual port segments) might strongly influence the local dredged material quality. The emissions from wastewater treatment plants inside of the area of Rotterdam could not be analysed since there were no estimates on heavy metal emissions available (van der Meulen, pers. comment). Nowadays, the chemical industry (producing artificial manure, fertilizer) no longer emits into the port of Rotterdam. This type of industry used to account for 70% of the total Cd emissions in the port of Rotterdam.

### 3.4 Summary and conclusions

The results from MONERIS show that the developed calculation method also is applicable for the estimation of heavy metal fluxes in large river basins as the Rhine. The regional differences in various sub-catchments (e.g. differences in connectivity to wastewater treatment plants and volumes of retention basins) can be visualised. The total emissions upstream of Lobith decreased with 40% (for copper) - 58% (for mercury) over the period 1983-1997. This decrease in total emissions is mainly caused by a decline in emissions from wastewater treatment plants, industry and urban areas over the period 1983-1987 to 1993-1997. This confirms the effectivity of the policy to reduce pollution from point sources. Inputs from wastewater treatment plants rather than emissions from industries nowadays dominate the emissions from point sources. The emissions from urban areas have decreased because the deposition rates of heavy metals in urban areas have declined and the percentage of urban areas connected to sewer systems and wastewater treatment plants also have increased. The diffuse sources are mainly dominated by inputs from urban areas, erosion and groundwater. A relatively high portion of the heavy metal emissions is caused by 'semi-natural' sources. About 50% of the heavy metal emissions in the period 1993-1997 are stemming from erosion, surface runoff and groundwater. A comparison from current heavy metal emissions in the Netherlands (downstream of Lobith) with the emission estimates of the Rhine basin upstream of Lobith showed that the emissions in the Netherlands only contribute about 12% of the total emissions in the Rhine basin. Only for cadmium and lead the Dutch emissions contribute 17% of the total emissions in the Rhine basin upstream of Rotterdam. The emission upstream of Lobith are dominated by emissions from Germany (about 60%) and France contributes about 20%.

A comparison with emission estimates from other studies (see appendices 3.4a-c) showed that for the period 1983-1987 the emissions are relatively similar to the results from Behrendt (1993). For the period 1993-1997, large deviations exist between the emission estimates from MONERIS and the emission estimates as given by the ICPR (1999). A comparison for the German part of the Rhine basin with Fuchs and Scherer (1999) showed similar results for all heavy metals.

Of course further research in several individual pathways is necessary. This can be seen from the differences in the emission estimates from a comparison of various studies (appendices 3.4a-c). The influence of the size and treatment type of a wastewater treatment plant on the efficiency of heavy metals removal should be further investigated. An international comparison of the emission factors for heavy metals per inhabitant could reduce the errors made in estimates of wastewater treatment plants and urban areas. The diffuse pathways of surface runoff and drainage should be more investigated and also focus on possible changes over time caused by decreasing heavy metal loads from the atmosphere and decreased fertiliser and manure inputs.

Future policy options should focus more on the reduction of emissions from diffuse sources, since the contribution of these diffuse sources is in general more than 70%. Therefore, further efforts to reduce emissions from industries would only reduce the total emissions with less than 30%, which probably will not be cost-effective, since the cheap reduction possibilities already have been applied. Of the emissions from point sources about 20% is caused by inputs from wastewater treatment plants, which could be reduced by implementing further treatment.

## **4 Trends in the quality of suspended particulate matter in the Rhine and link to the quality of dredged material in Rotterdam**

In this chapter an analysis of the present quality of dredged material (in the Eastern part of the port so-called Region 3) and the present quality of suspended particulate matter of several monitoring stations along the river Rhine is given. Further a comparison of the point and diffuse contributions in the immission approach (chapter 2) and emission approach (chapter 3) in the Rhine basin is made to validate both methods. Then, retention functions are developed for modelling heavy metal loads in the Rhine basin using the estimated emissions. Since the eastern part of the Rotterdam port is (almost) completely under the influence of the River Rhine and a relative time-delay between Lobith and Rotterdam is not observed in the present quality of dredged material and suspended particulate matter (at Lobith), it was assumed that an improvement in heavy metal loads at Lobith will almost directly influence the dredged material quality in Rotterdam (so-called 'link').

### **4.1 Trends in the quality of dredged material**

In three areas of the port of Rotterdam dredged material quality is analysed. Standardised and unstandardised quality data of the dredged material of the port of Rotterdam were provided from the Rotterdam Municipal Port Management (RMPM, 1998) over the period 1977-1998 for heavy metals. The quality of sediments/dredged material in/from the western parts of the port of Rotterdam is mainly influenced by suspended particulate matter (SPM), settling in these areas, stemming from the North Sea. The following comparison of the quality of dredged material from the port of Rotterdam and SPM of the Rhine focuses on the eastern parts of the port, mainly influenced by SPM-bound heavy metals originating from the Rhine catchment area.

With regard to the Sea/Slufter limits for relocation of dredged material in the North Sea, as well concerning other classification systems for dredged material quality, concentrations of heavy metals are normalised (standardised) towards the content of organic matter and clay in the sediments/dredged material (RMPM, 2000). Evaluating trends in the quality of sediments/dredged material in/from the port of Rotterdam, heavy metal concentrations are standardised and are corrected (weighted) towards average dredged volumes of the specific port areas (RMPM, 1998).

The yearly average of 'corrected' standardised dredged material concentrations of cadmium, copper, mercury, lead and zinc for the eastern ports is shown in figure 4-1. When measurements were below the detection limits the concentration was considered to be half the detection limit concentration. From this figure we observe a decline in heavy metal contents in the late eighties and early nineties. Nowadays only a slow decline or even stagnation of heavy metal contents is observed.

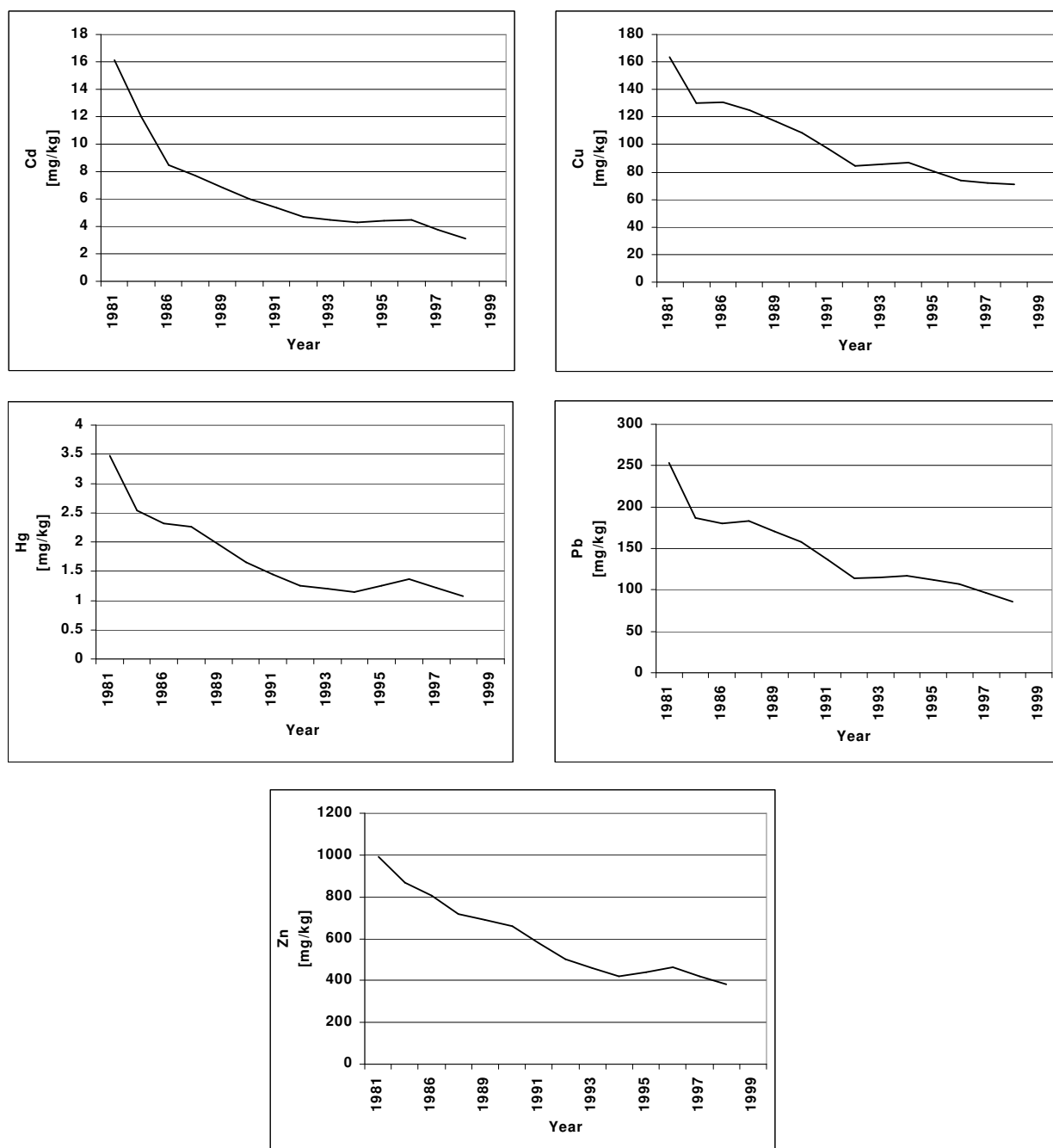


Figure 4-1: 'Corrected' standardised average heavy metal contents of dredged material in the eastern parts of the port of Rotterdam (RMPM, 1998)

## 4.2 Trends in quality of suspended particulate matter in the Rhine

The amount of suspended particulate matter increases downstream with increasing discharge (see figure 4-2). The calculated suspended particulate matter load at Koblenz seems to be underestimated for the period 1993-1997. A possible explanation is the underestimation of the suspended particulate matter load for the high discharge year 1995. The suspended particulate matter load at Lobith can for about 85 % be explained from the contributions of the suspended particulate matter load at Mainz and the contributions of tributaries (Mosel, Neckar and Main).

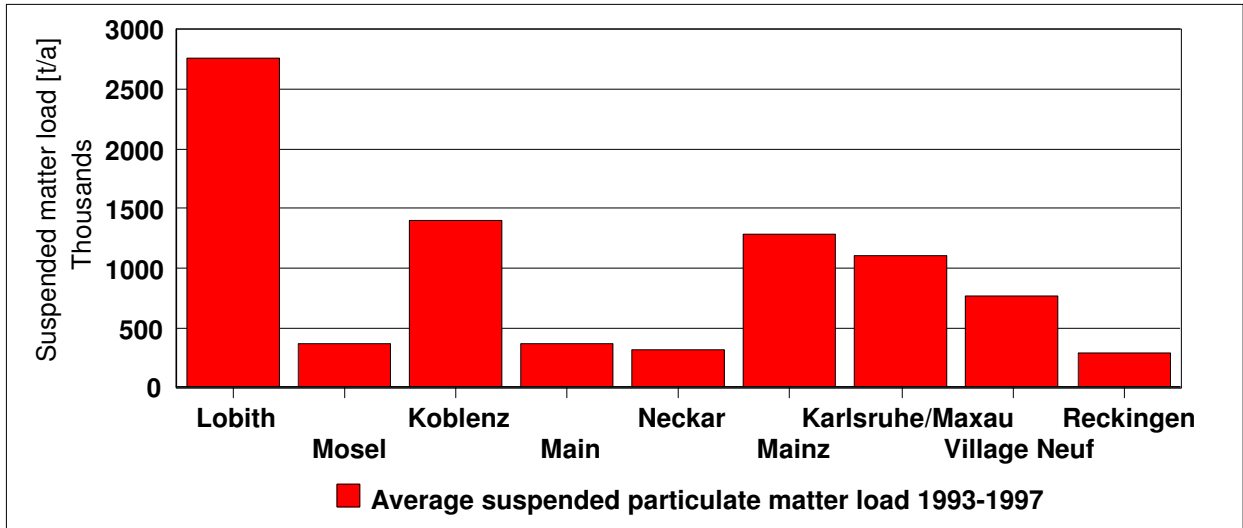


Figure 4-2: Annual average suspended particulate matter load as a function of Rhine kilometres

Averaged annual heavy metal concentrations for several monitoring stations along the Rhine were calculated. The quality of the suspended particulate matter has been measured at several water quality stations over the period 1990-1998. The period is relatively short for a detection of a real trend in the heavy metal contents of the suspended particulate matter.

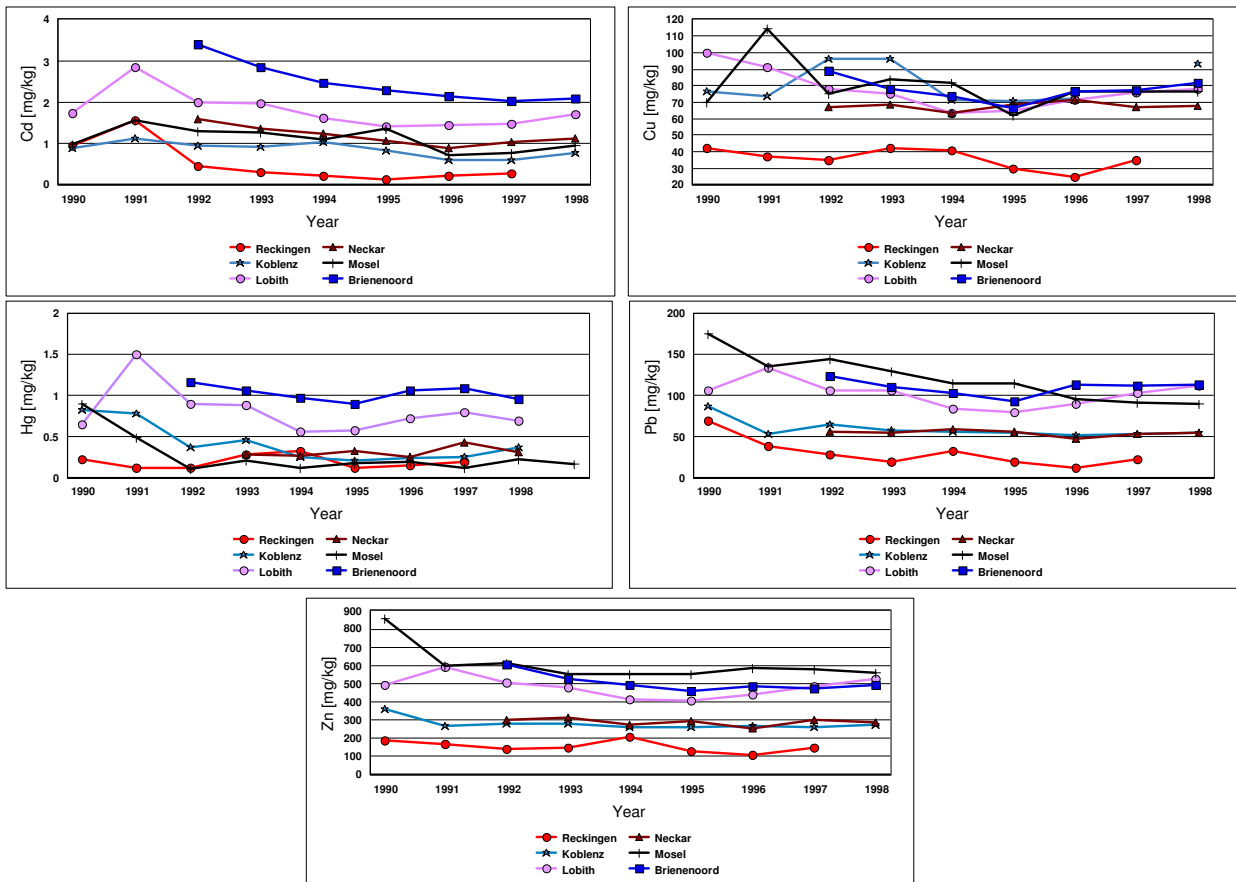


Figure 4-3: Average annual heavy metal concentrations in suspended particulate matter at several monitoring stations along the river Rhine



From figure 4-3 a general trend of increase in heavy metal content from upstream to downstream stations can be observed. This could be caused by enrichment of heavy metals in the finer fraction of the transported suspended particulate matter. The lead and zinc concentrations in the suspended particulate matter of the River Mosel is even higher than for Lobith. An explanation could be found in higher inputs by point and diffuse sources into the rivers or higher background concentrations of these elements in the soils of these catchments. ICWS (1994b) already reported that the average measured particle bound heavy metal load contributes more than half of the total measured heavy metal load as shown in table 4-1. From this table it is very clear that the majority of the heavy metals studied here are transported with the suspended particulate matter load. Only copper and cadmium are transported more in a dissolved phase than the other heavy metals. Especially lead is highly bound to SPM (93%).

*Table 4-1: Overview of the contribution of particle bound heavy metal load measured over time period 1984-1992 at Lobith (ICWSb, 1994)*

	Discharge [m <sup>3</sup> /s]	Deviation n [%]	Suspended particulate matter load [Mton/y]	Deviation [%]	Partition coefficients [m <sup>3</sup> /kg]	Deviation [%]	Dissolved heavy metal load [%]	Deviation [%]
Cd	2223	19	2.79	33	66.2	34	30.3	34
Cu	2223	19	2.79	33	27.7	19	48.8	12
Hg	2223	19	2.79	33	136.6	37	17.2	24
Pb	2223	19	2.79	33	446.9	47	7	64
Zn	2223	19	2.79	33	88.3	30	24	28

These contributions clearly show the variability and uncertainty of the measurements in the suspended particulate matter load (as shown in figure 4-2). In general, no downward trend of the heavy metal concentrations in the SPM could be detected. This could indicate and confirm the assumption that the quality of the SPM and the heavy metal loads in the Rhine are not significantly decreasing anymore. This might also indicate that the decrease in the point and diffuse emissions in the Rhine catchment has come to a standstill.

### 4.3 Comparison of suspended particulate matter and dredged material

Measurements of RIZA during the period 1988-1992 showed that the composition of the suspended particulate matter measured at Lobith (28.9% clay and 11.1% total organic matter) is approximately similar to the composition of a standard soil (25% clay and 10% total organic matter). Based on these results ICWS (1994a) concluded that a comparison of heavy metal concentrations in suspended particulate matter at Lobith and standardised heavy metal concentrations of the sediment of Rotterdam is possible. The composition of suspended particulate matter at Brienoord (over 1992-1999) was estimated at 30.2% clay and 16% total organic matter and also shown in figure 4-4. Figure 4-4 shows that the concentrations of most heavy metals in suspended particulate matter nowadays are within the same range as those measured in the standardised sediment. Only, cadmium and mercury show already lower concentrations in suspended particulate matter than the standardised sediment concentrations.

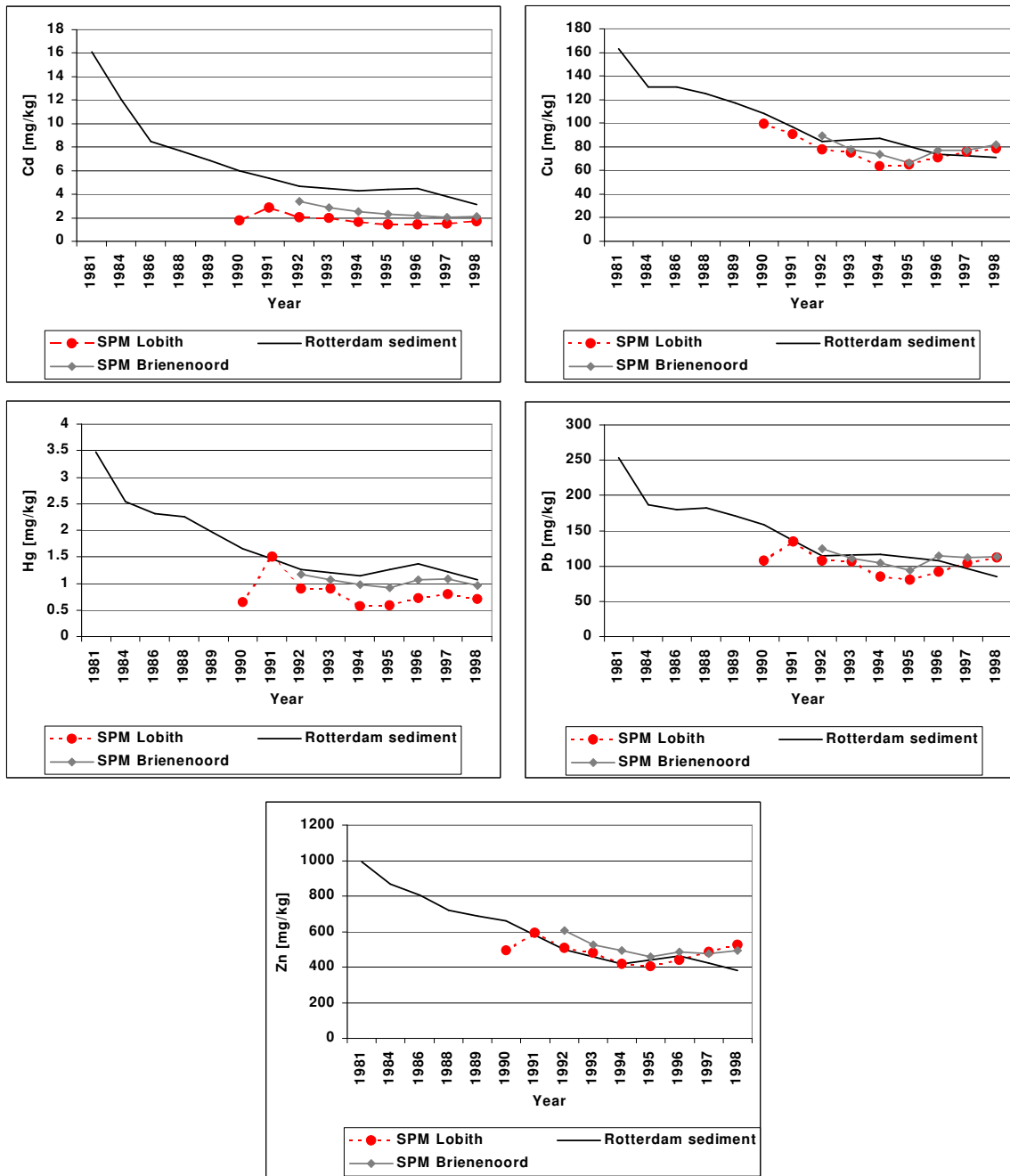


Figure 4-4: Comparison of heavy metal content in standardised dredged material at Rotterdam and suspended particulate matter at Lobith and Brienoord

This could indicate that relatively cleaner suspended particulate matter is nowadays flowing into the port of Rotterdam. This so-called time delay can be explained by the fact that the dredged material quality is lagging behind the fresh suspended particulate matter quality, because not all deposited sediment is removed every year (RIKZ, 1995). For the other heavy metals extra measures (upstream of Lobith) should be taken to reduce the heavy metal concentrations in the suspended particulate matter, since they appear to be within the same range of heavy metal concentrations in the standardised port sediments.

## 4.4 Link between emissions, immissions and dredged material quality

### 4.4.1 Retention of heavy metals in river systems

In chapter 3 the total inputs (emissions) of heavy metals from point and diffuse sources into the Rhine river basin have been estimated and in chapter 2 the measured transports of several monitoring stations are presented. A direct comparison of the heavy metal emissions and the observed heavy metal transports for all monitoring stations shows that the transport of heavy metals in general is lower than the total heavy metal emissions (see figure 4-5). This means that retention or loss processes can occur in rivers through e.g. sedimentation in areas of low streamflow velocity or sedimentation in lakes. Some stations (especially stations in smaller sized basins) have higher transports than estimated emissions, which also indicates errors in the measured heavy metal transports (as already observed in chapter 3) and errors in the estimated emissions. In general, there is a discrepancy between the sum of the loads along the different pathways (e.g. erosion, fast runoff and slow runoff) and measured loads at monitoring stations (Behrendt, 1996; de Wit, 1999; Vink et al., 1999), which is probably due to the retention of material in the river system and measurement errors. Heavy metals are to a great extent removed sedimentation in lakes and floodplains. Mueller et al. (1995) showed that in the Mulde sub-catchment 80- 90 % of the suspended particulate matter and 52 - 77% of the heavy metals are retained in the Bitterfelder Lake.

Behrendt (1997) and Behrendt and Opitz (1999) analysed the relation between the sum of all point and diffuse sources of emissions which represents the input into a catchment and the measured transport (immission or output) of nutrients at a monitoring station of a river. Behrendt and Opitz (1999) found that the loss of nutrients (both N and P) in a river system is related to the specific runoff (q) as illustrated in equation 4.1. When the specific runoff of a catchment is high the losses tend to be low and when specific runoff is low the losses tend to be high. Besides specific runoff, the occurrence of lakes and weirs, the river gradient and the distribution of the emissions will influence the loss of substances. In stretches of the river with a low gradient and large floodplains the losses or retention of material will be higher than in the upper steep river reaches.

$$\frac{L_{i,T}^M}{E_{i,T}^M} = \frac{1}{1 + a \cdot q_{i,T}^b} \quad (4.1)$$

$L_{i,T}^M$  = The total transport of a given substance M at monitoring station i over a certain time period T [t a<sup>-1</sup>]

$E_{i,T}^M$  = The total emissions of a given substance M at monitoring station i over a certain time period T [t a<sup>-1</sup>]

$q_{i,T}$  = The specific runoff of catchment over a certain time period T [l km<sup>-2</sup> s<sup>-1</sup>],

a, b= constants estimated by non-linear regression [-]

The parameters a, b are estimated by using a solver unit of a spreadsheet program. Behrendt & Opitz (1999) estimated the values at a = 26.6 and b = -1.71 for phosphorous, using 89 different river basins in Europe. The comparison of the simulated heavy metal transports (estimated by MONERIS minus the losses estimated by the retention function of equation 4.1)

with measured heavy metal transports (as estimated in chapter 2) for several stations in the Rhine drainage area was tested by least squares fit.

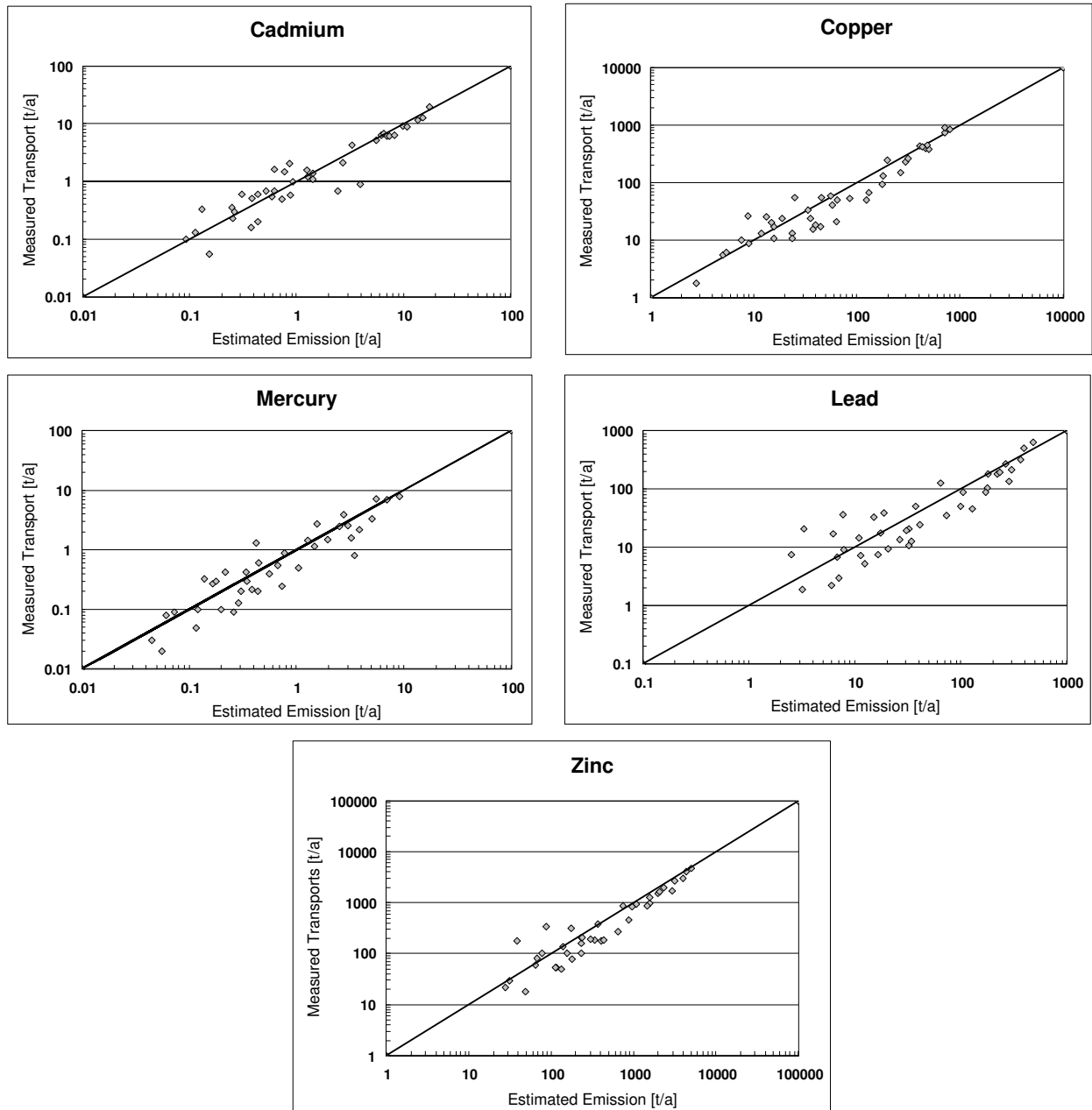


Figure 4-5: Relationship between observed heavy metal transports and the total emissions from point and diffuse sources for the investigated stations in the Rhine basin

For each heavy metal an individual statistical loss function was estimated with all data points of the period 1983-1997 since it was assumed that the natural processes influencing the losses did not change over this time period and that changes in transports are only influenced by the changes in emissions. The results of the statistical models related to specific runoff are presented for all river basins in table 4-2. About 91-98% of variance for the different heavy metals can be explained by the dependency on specific runoff. Change of the coefficient  $b$  did not bring a relevant improvement of the  $r^2$  and therefore the coefficient  $b$  remained  $-1.71$ .

Table 4-2: Results of regressions between heavy metal retention and the specific runoff for the Rhine basin

Parameters	Cadmium	Copper	Mercury	Lead	Zinc
$r^2$	0.97	0.97	0.91	0.93	0.98
n	40	40	40	40	40
a	16.23	16.91	12.58	28.96	21.48
b	-1.71	-1.71	-1.71	-1.71	-1.71

For the evaluation of the results of the statistical model, the calculated transports are compared with the measured transports of the Rhine as shown in chapter 2. The comparisons are shown in figure 4-6 using the specific statistical model with the highest  $r^2$  (as shown in table 4-2).

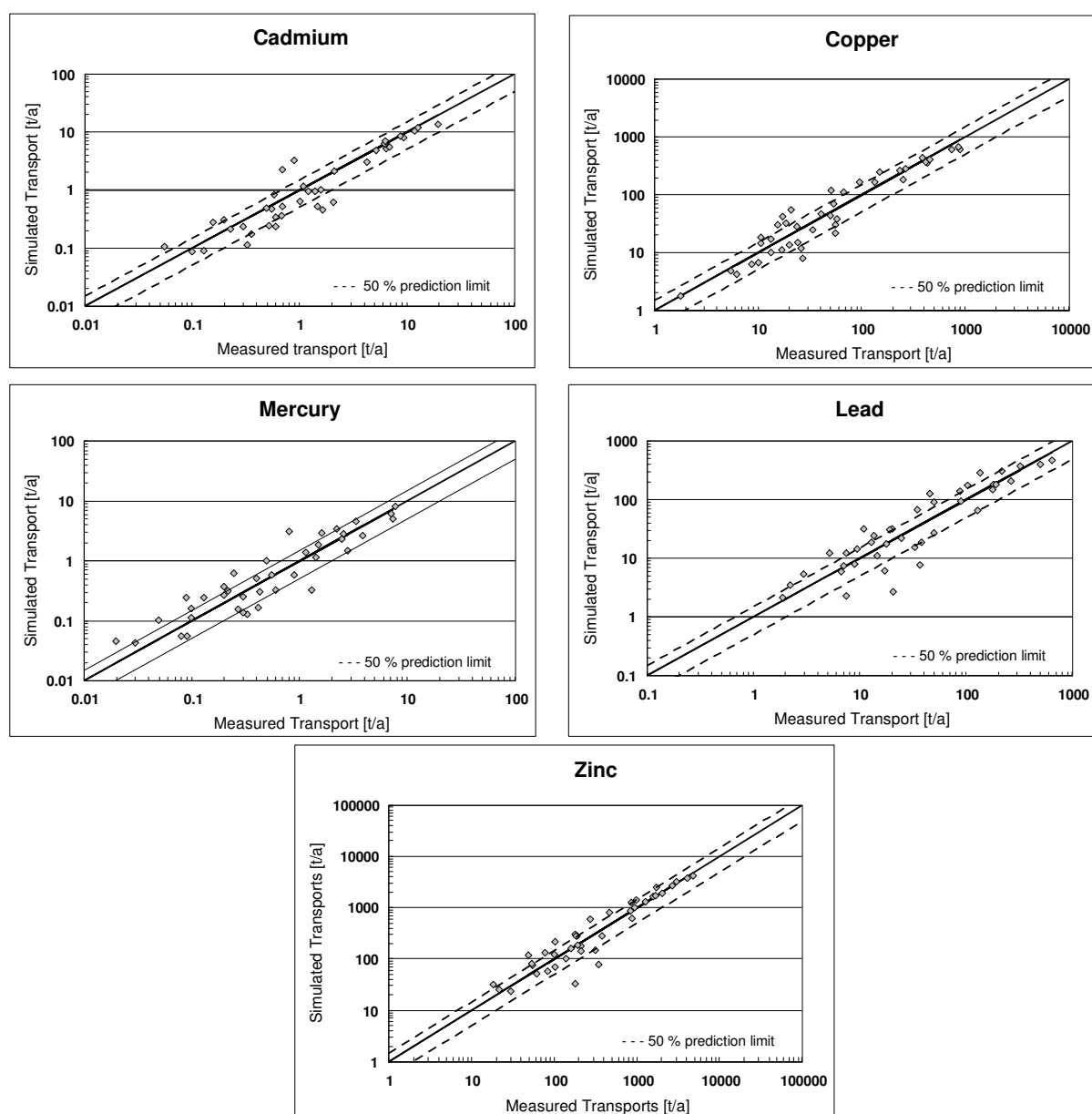


Figure 4-6: Relationship between the transport of heavy metals (as calculated in chapter 2) and the simulated transports (according to the retention model with the highest regression coefficient) for the investigated stations in the Rhine basin

The river systems with the highest deviation from the 1:1 line are the Wupper, Sieg and the monitoring stations in the upper part of Rhine basin (Reckingen, Seltz). This is caused by higher inputs from former mines in the case of Wupper and Sieg. For the stations located in the upper part of the Rhine basin, this deviation is caused by the influence of the Lake of Constance which is not represented in the retention function approach (Behrendt, pers.comment). Of course, the coefficients are only derived from the data set employed here and errors associated with the estimation of heavy metal transport and especially the heavy metal emission from point and diffuse sources have to be taken into account.

In table 4-3 the estimated losses in the River Rhine are given. For all heavy metals the maximum retention is reached in the Niers (1983-1987) and Nied (1993-1997) and the minimum retention is reached in the upstream parts of the Rhine basin, near Reckingen.

*Table 4-3: Percentage of heavy metal input to the surface water that is lost in the river system*

Retention	Cadmium		Copper		Mercury		Lead		Zinc	
	1983-1987	1993-1997	1983-1987	1993-1997	1983-1987	1993-1997	1983-1987	1993-1997	1983-1987	1993-1997
Average [%]	0.173	0.203	0.179	0.209	0.141	0.168	0.265	0.300	0.214	0.247
Minimum [%]	0.045	0.040	0.047	0.041	0.035	0.031	0.078	0.069	0.059	0.052
Maximum [%]	0.421	0.750	0.431	0.758	0.360	0.699	0.565	0.843	0.490	0.799

Nevertheless, a prediction of the total heavy metal emissions seems to be possible if the heavy metal load and the main characteristics of the basin such as basin size and specific runoff for a certain time period are known. The derived statistical model for each heavy metal allows the description of the retention behaviour of each heavy metal in river basins.

#### 4.4.2 Comparison of results from emission and immission analysis

The comparison of the results from the emission analysis (MONERIS, chapter 3) and the the results from the immission analysis (chapter 2) is possible for several stations in the Rhine basin. The diffuse contribution to the total load or to the total emission for both methods and both periods is shown in appendices 4.4.2a-b. The diffuse contribution to the measured load according to the immission method for the period 1983-1987 are higher than the diffuse estimates given by MONERIS. This observation was already made by Behrendt et al. (1999). Behrendt could show that this overestimation of diffuse sources were found especially in basins where combined sewers dominate. The reason is that in such basins the input of point sources includes also a part which is depending on precipitation (the material stored in the sewer during storm water events). This part is identified in the immission approach as a diffuse part but in the emission approach as a point source. For the period 1993-1997 the differences in the contribution of diffuse sources between both methods are relatively small. A comparison of appendices 4.4.2a and 4.4.2b shows that diffuse emissions have increased since the period 1983-1987. For the period 1993-1997 the results of both methods are more comparable than for the period 1983-1987. Only the Mosel gives relatively large errors but this could be caused by the fact the signal from the water quality data could be influenced by the locks and weirs in this

river. The same reason also counts for the river Neckar. Given the uncertainties in both source apportionment assessments, we can conclude that the results from the immission analysis supports the outcomes of the emission analysis. Furthermore, the contribution of diffuse sources estimated with the immission analysis is subjected to higher uncertainties since the occurrence of an error in one measurement can influence the results.

#### **4.5 Summary and conclusions**

The measured heavy metal concentrations in the dredged material of the eastern Rhine–influenced part of the port show a downward trend in the late eighties and early nineties. Nowadays only a slow decline or even a stagnation of the heavy metal contents of the dredged material in the eastern part of the port is observed.

The quality of the suspended particulate matter measured at several water quality stations over the period 1990-1998 was also analysed. Since the time period is relatively short, no real trend in the quality of SPM could be detected. But in general, no downward trend of the heavy metal concentrations in the SPM could be detected. This could indicate and confirm the assumption that the quality of the SPM and consequently the total heavy metal loads in the Rhine are not significantly decreasing anymore. This might also indicate that the decrease in the point and diffuse emissions in the Rhine catchment has come to a standstill. A general trend of increase in heavy metal contents from upstream to downstream stations was observed over this time period. This could be caused by the enrichment of heavy metals in the suspended particulate matter. Further, the suspended lead and zinc concentrations of the River Mosel are higher than for Lobith. This could indicate the presence of point sources of higher background levels in these catchments.

Nowadays, the concentrations of most heavy metals in the SPM are within the same range as those measured in the standardised sediment in the port of Rotterdam. Only for cadmium and mercury the concentrations in suspended particulate matter are already lower than the standardised sediment concentrations. This could indicate that relatively cleaner suspended particulate matter is nowadays flowing into the port of Rotterdam. This so-called time delay can be explained by the fact that the dredged material quality is lagging behind the fresh suspended particulate matter quality, because not all deposited sediment is removed every year (RIKZ, 1995). For the other heavy metals extra measures (upstream of Lobith) should be taken to reduce the heavy metal concentrations in the suspended particulate matter, since they appear to be within the same range of heavy metal concentrations as in the standardised port sediments.

A direct comparison of the heavy metal emissions (as estimated in chapter 3) and the observed heavy metal transports (as estimated in chapter 2) for all monitoring stations shows that the transport of heavy metals in general is lower than the total heavy metal emissions. This means that retention or loss processes can occur in rivers through e.g. sedimentation in areas of low streamflow velocity or sedimentation in lakes. The loss of heavy metals in a river system was found to be related to the specific runoff ( $q$ ) of the river. The highest retention of heavy metals in the Rhine occurred for Pb (27-30%) and lowest retention of heavy metals was reached for Hg (14-17%).

The comparison of the apportionment of point and diffuse sources in MONERIS (chapter 3) and

in the Immission method (chapter 2) is possible for several stations in the Rhine basin (see appendices 4.4.2a-b). This showed that given the uncertainties in both source apportionment assessments, we can conclude that the results from the immission analysis supports the outcomes of the emission analysis.



## **5 Scenarios of future development in the Rhine catchment area and impact on dredged material quality in Rotterdam**

In the previous chapters the historic and current situation of the heavy metal emissions and water quality in the river Rhine is investigated. Although in the past decades considerable reductions in emissions and improvement of water quality has been achieved, the amount of heavy metals in water, suspended particulate matter and sediments are usually still too high to achieve the targets set by the Dutch government. This means that a further reduction in future emissions is desirable as already described in the Fourth Policy Document on Water Management (Min. of Transport, Public Works and Water Management, 1999). The objective of this chapter is to indicate the effects of possible reductions in the emissions to the surface waters. The analysis has been made using two scenarios and uses the same MONERIS approach as already described in chapter 3.

The 'business as usual' (BAU) scenario is restricted to the current situation and only includes measures that have already been agreed on to be implemented within the next five years.

The 'Green Environment' scenario is the most environmental friendly scenario, which aims to reach water quality standards and emission reduction goals as soon as possible and to a maximum extent. This 'Green Environment' scenario assumes additional measures taken to prevent emissions at the source (e.g. industry) and infrastructural measures (e.g. level of sewer connections, upgrading of wastewater treatment).

The time horizon for all scenarios is considered to be 2015 and assumes that this situation will be reached by a linear change from 1998-2015. In the two scenarios the amount of wastewater, amount of people connected to sewers, treatment efficiencies of wastewater treatment and the distribution and size wastewater treatment plants have not changed in comparison to the results of MONERIS 1993-1997. The measures for reducing emissions can either influence the nature or size of the emission factor or the emission determining variable (e.g. amount of paved urban area). The implementation time of a measure before coming fully into effect, starting year of implementation, and the maximum effect of a measure are important aspects.

Emissions are coupled to activities and physical units such as traffic and population density. In the future it is expected that an increase of several activities (e.g. traffic, paved urban areas) will occur. For the scenario analysis we used the same statistics on population, size of urban areas, amount of cars etc. as for the period 1993-1997. These statistics are likely to change slightly by the year 2015, but since no consensus could be reached on the growth numbers for Germany, it was decided to take the same statistics as for the period 1993-1997.

The scenario analysis for heavy metals, presented in this chapter, utilises the MONERIS approach as described in chapter 3. It is based on the current state (1993-1997) and estimates changes until 2015.

## 5.1 Assumptions for the scenario analysis

### 5.1.1 'Business as usual' scenario

This scenario serves as a reference scenario for comparison to other scenarios and for providing insights into problems and potentials of current regulation and policy. Current policy foresees measures being taken in several sectors.

- ◆ Industry

Although industrial emissions have strongly declined over the period 1985-1997, still a substantial share of emissions is caused by the industry. Industrial emissions continue on the same level as 1995, but in a situation of economic growth these emissions are likely to increase a little (RIZA, 1997a).

- ◆ Wastewater treatment plant

Municipal emissions are governed by the sewer policy. In Germany all wastewater treatment plants of category 3 should include a denitrification step and all wastewater treatment plants of category 4 have implemented a P-elimination step by the year 2005 (RIZA, 1999, Urban Waste Water Treatment Directive, 1991, IPC Directive, 1998, German Water Management Act (WHG), 1998). The amount of people connected to wastewater treatment plants remains equal to the level of 1995. Further efforts are taken to connect people, who were connected to a sewer system in 1995, to wastewater treatment plants.

- ◆ Direct atmospheric deposition

The goal of 50% emission reduction of atmospheric deposition of heavy metals in the year 1995 (compared 1985) was met for most countries. No further reductions are foreseen (RIZA, 1997b).

- ◆ Urban areas

Measures to reduce emissions from building materials and traffic until 2015 are not agreed upon (RIZA, 1996a & 1996b).

For the other sources groundwater, surface runoff, drainage and erosion, no extra measures are foreseen to reduce heavy metal emissions.

### 5.1.2 'Green environment' scenario

This scenario focuses on maximum feasible reduction of emissions. This requires fast implementation of emission reducing measures without considering costs. The measures are often a combination of prevention of emissions at the source (e.g. active replacement of building materials) and infrastructural measures (connection to sewer systems, high purification measures).

- ◆ Industry

Industrial emissions decrease by 10% compared to the level of 1995 (RIZA, 1997a). Measures taken to achieve this decrease are the use of cleaner raw materials, closure of the wastewater circuit, cleaner technology (BAT) and optimisation of wastewater treatment. Industrial cadmium, copper, mercury and lead emissions are likely to decline because of a decline in fertiliser production. Copper emissions could also decline substantially because the measures taken in

the usage of copper-free paint used for ships. Extra measures besides extra wastewater treatment and measures in galvanic departments can only slightly reduce zinc emissions further.

◆ Wastewater treatment plant

Municipal emissions are governed by the sewer policy (RIZA, 1999; Urban Waste Water Treatment Directive, 1991; IPC Directive, 1998; German Water Management Act (WHG), 1998). The same measures are taken as in the 'BAU' scenario. Extra measures are:

1. In all WWTPs of category 3 a P-elimination step will be implemented.
2. Microfiltration techniques in the largest wastewater treatment plants (Category 5) are taken in to reduce the amount of small sized particles in the effluent.

◆ Direct atmospheric deposition

The SO<sub>2</sub> emissions have already decreased considerably and are expected to decrease in the same rate as with the 'business as usual' scenario. The atmospheric deposition of heavy metals is not further reduced (RIZA, 1997b), since there is no international consensus on the further reduction of heavy metals.

◆ Urban areas

Diffuse emissions from building materials (e.g. corrosion of galvanised steel, sheet lead and water pipes) are expected to decrease for copper, lead and zinc. In this scenario old building materials that are subjected to corrosion are actively being replaced by more environmental friendly alternatives (e.g. coating of lead sheet and galvanised steel) (1996b). In new buildings alternative environmental friendly materials are used for water pipes, roof and gutters. The use of longer lasting car tyres and infiltration of run-off of roads will also reduce traffic emissions (1996a). These measures cause urban deposition rates to decrease with 10%. About 15 % of the paved urban areas are decoupled from the sewer system (RIZA, 1999; BBodSchG - German law of soil protection, 1999). In urban areas storage basins for rainwater are enlarged to 100% (23 m<sup>3</sup>/ha urban area) for both separate and combined sewer systems (Behrendt et al., 1999).

◆ Erosion

Diffuse emissions caused by erosion will be reduced by 25% through erosion reducing measures in the upstream parts of the Rhine basin with high erosion rates (BBodSchG - German law of soil protection, 1999).

For the other sources groundwater, drainage and surface runoff, no extra measures are foreseen to reduce heavy metal emissions.

## 5.2 Scenario results

In table 5-1 an overview is given of the two scenarios and their major measures for all the different sectors. The difference between both scenarios can be found in the sectors industry, wastewater treatment plant, urban areas and erosion. Whereas in the 'BAU' scenario only measures are taken in the treatment of wastewater, extra emission reduction measures are proposed in the 'Green Environment' scenario in industry, wastewater treatment, urban areas and erosion. Nowadays, the chemical industry (producing artificial manure, fertilizer) no longer

emits into the port of Rotterdam. This type of industry used to account for 70% of the total Cd emissions in the port of Rotterdam.

Table 5-1: Measures taken in the different scenarios

Source	'BAU' scenario	'Green environment' scenario
Industry	Same level as 1993-1997	BAT measures give 10% reduction
WWTP	All WWTPs of category 3 include a denitrification step and all WWTPs of category 4 have implemented a P-elimination step	Includes all measures in <i>BAU</i> , a P-elimination step in all WWTPs of category 3 and Microfiltration techniques in the largest WWTPs (category 5)
Direct atmospheric deposition	No reduction	No reduction
Urban areas	No reduction	Active replacement of building materials (e.g. coating of lead sheet and galvanised steel) Use of longer lasting car tyres and infiltration of run-off from roads Decoupling of paved urban areas from the sewer system Enlargement of rainwater storage basins in urban areas
Erosion	No reduction	Extra measures to reduce erosion in steep areas give 25% reduction
Groundwater	No reduction	No reduction
Drainage	No reduction	No reduction
Surface runoff	No reduction	No reduction

The results from the 'BAU' scenario are shown in table 5-2. The heavy metal emissions are reduced by 5.6-7.8% compared to the situation 1993-1997. This is caused by the implementation of the EU urban wastewater treatment directive in National German law (see chapter D.3.2.3), which upgrades wastewater treatment plants. The effect of a higher connectivity to wastewater treatment plants only has a minor effect on the emissions. The slight reduction in heavy metal emissions is caused by the fact many wastewater treatment plants in the Rhine basin already have biological treatment and therefore less additional measures are necessary.

The results from the 'Green Environment' scenario are shown in table 5-3. The measures taken in this scenario are relatively extreme for the urban areas. For example the decoupling of paved urban areas could be counteracted by the increase of paved urban areas over time. The 'Green Environment' scenario shows that measures in urban areas (decoupling of paved urban area, increase of retention capacity and decrease of urban deposition rates) cause a 55% reduction in the heavy metal emissions from urban areas. The extra microfiltration step in larger wastewater treatment plants also has a positive effect on the emissions from wastewater treatment plants. The total heavy metal emissions decline with about 30%.

Table 5-2: Results from the BAU scenario

Sources	Cd [t/a]	% change	Cu [t/a]	% change	Hg [t/a]	% change	Pb [t/a]	% change	Zn [t/a]	% change
Industry	0.7	0.0	39.0	0.0	0.2	0.0	19	0.0	127	0.0
Wastewater treatment plant	0.9	-33.6	69.7	-33.6	0.6	-33.6	39	-33.6	342	-33.6
Atmospheric deposition	0.6	0.0	9.0	0.0	0.1	0.0	12	0.0	75	0.0
Surface Runoff	0.7	0.0	54.0	0.0	0.3	0.0	10	0.0	151	0.0
Erosion	1.3	0.0	77.0	0.0	0.7	0.0	93	0.0	462	0.0
Drainage	0.3	0.0	12.0	0.0	0.1	0.0	3	0.0	45	0.0
Groundwater	1.2	0.0	102.0	0.0	0.5	0.0	25	0.0	463	0.0
Urban areas	2.2	0.0	85.0	0.0	1.1	0.0	47	0.0	522	0.0
Total emissions	7.9	-5.6	447.7	-7.3	3.6	-7.8	248	-7.7	2187	-7.4

Table 5-3: Results from the 'Green environment' scenario

Sources	Cd [t/a]	% change	Cu [t/a]	% change	Hg [t/a]	% change	Pb [t/a]	% change	Zn [t/a]	% change
Industry	0.6	-10	35	-10	0.2	-10	17	-10	114	-10
Wastewater treatment plant	0.6	-60	44	-58	0.4	-59	25	-58	214	-59
Atmospheric deposition	0.6	0	9	0	0.1	0	12	0	75	0
Surface Runoff	0.7	0	54	0	0.3	0	10	0	151	0
Erosion	1.0	-25	58	-25	0.5	-25	70	-25	347	-25
Drainage	0.3	0	12	0	0.1	0	3	0	45	0
Groundwater	1.2	0	102	0	0.5	0	25	0	463	0
Urban areas	0.9	-58	39	-55	0.5	-57	23	-51	234	-55
Total emissions	5.9	-30	351.6	-27	2.6	-34	184.5	-31	1642.4	-30

The long-term emission goal of 70-90% emission reduction set in the Third Policy Document on

Water Management (Min. of Transport, Public Works and Water Management, 1989) might be met for Hg and Pb, but not for the other heavy metals, when all the measures in the 'Green Environment' scenario are implemented.

*Forecast of dredged material quality in the eastern part of the port of Rotterdam*

In table 5-4 is shown what will happen if we linearly extrapolate the results of both scenarios directly to the suspended particulate matter concentrations at Lobith and standardised sediment concentrations in Rotterdam. The assumption is that suspended particulate matter concentrations, discharge and retention characteristics of the Rhine will not change over this time period. Of course, the influence of low discharge years and high discharge years on the heavy metal loads in the Rhine basin is excluded and in reality this 1:1 relation is more complicated.

The heavy metal concentrations (RMPM, 1999), describing the present state, were recalculated from the three sampling campaigns (315 samples) in the period 1994-1998. Mean individual heavy metal concentrations were derived after standardising to 10% organic matter and 25% lutite ('standard soil'), and weighting according to long-term mean dredged volumes at the individual sampling sites. For individual heavy metals, the quality of dredged material (present state, *BAU* and *GREEN*) is compared with the Dutch quality criteria for dredged materials (Sea/Slufter limits, target levels) in table 5-4.

Table 5-4 shows that the average heavy metal concentrations in the eastern part of port would decline below the Sea/Slufter limit in case all measures from the 'Green Environment' scenario are implemented and have reached their full effect. In the case of mercury and lead already with upgrading measures taken in WWTPs ('BAU' scenario) the Sea/Slufter limit can be reached. For cadmium, copper and zinc more measures from the 'Green Environment' scenario should be implemented for reaching the Sea/Slufter limit. For cadmium and mercury measures taken in the area of point source reduction (e.g. industrial reduction and implementation of further wastewater treatment) could already decrease the average heavy metal contents in the dredged material below the Sea/Slufter limit. For both zinc and copper extra measures in the sector of urban areas (as proposed in the 'Green Environment scenario') are necessary to decrease the concentrations below the Sea/Slufter limit. For all heavy metals, except for lead, the target levels will not even be reached in the Green Environment scenario.

In order to estimate future amounts of dredged material to be disposed in the Slufter, the variability of heavy metal concentrations in the eastern parts of the port of Rotterdam has to be taken into account. Assuming the same local variability of concentrations at the sampling sites and the same mean dredged volumes as they occur nowadays, the outcome of the BAU and the GREEN scenario were recalculated for each of the individual sampling sites in the eastern part of the port of Rotterdam including this local variability in the heavy metal concentration at the sampling site and the local variability in the mean dredged volume at the sampling site. The dredged volumes for each the individual sampling sites where the Sea/Slufter limits is not reached, are given as a percentage of the total dredged volume from the eastern part of the port of Rotterdam and shown in table 5-5. From table 5-5, it is clear that Cu and Zn are the main controlling parameters for the disposal of dredged material.

For all heavy metals the realisation of the reduction rate in the 'Green Environment' scenario is even uncertain since this scenario contains some very extreme measures (as the coating of building materials, decoupling of paved urban areas). Another point is that these measures are not implemented in future policy goals or regulations and therefore have voluntary character.

*Table 5-4: Average heavy metal content in the sediments of the eastern part of the Port of Rotterdam: Comparison of present state, BAU and GREEN scenarios with Sea/Slufter limit and target levels for heavy metals*

	Sea/Slufter limit	Target level	BAU reduction	Green reduction	Present 1994-1998	BAU 2015	Green 2015
	mg/kg dw <sup>1)</sup>	mg/kg dw <sup>1)</sup>	%	%	mg/kg dw <sup>2)</sup>	mg/kg dw <sup>2)</sup>	mg/kg dw <sup>2)</sup>
Cd	4	0.8	5.6	30	3.9	3.7	2.7
Cu	60	36	7.3	27	<b>77</b>	<b>71</b>	56
Hg	1.2	0.3	7.8	34	<b>1.2</b>	1.1	0.8
Pb	110	85	7.7	31	102	94	<u>71</u>
Zn	365	140	7.4	30	<b>419</b>	<b>388</b>	293

1) standardised to 10 % organic matter (bichromat method) and 25% lutite ('standard soil')

2) standardised to 10% organic matter (bichromat method), 25% lutite and corrected to dredged volumes

*Bold numbers indicate that the standardized dredged material concentrations are above Sea/Slufter limit*  
*Underlined numbers indicate that the standardized dredged material concentrations are below target levels*

*Table 5-5: Volumes of dredged material from the individual sampling sites in the eastern part of the port to be disposed in the Slufter according to present Dutch quality criteria (Sea/Slufter limit) for individual heavy metals (present state, BAU and GREEN scenario)*

	Volumes of dredged material exceeding Sea/Slufter limit for Heavy Metals		
	Present state 1994-1998	BAU 2015	GREEN 2015
	%	%	%
Cd	33	31	15
Cu	68	54	27
Hg	34	17	5
Pb	28	21	10
Zn	52	42	18
All Heavy Metals	74	60	31

### 5.3 Summary and conclusions

A further reduction of future emissions is desirable as already described in the Fourth Policy Document on Water Management (Min. of Transport, Public Works and Water Management, 1999), since for all heavy metals the concentrations are above the Sea/Slufter limit. Scenarios can indicate what reductions in the emissions to the surface waters would be feasible at various levels of environmental efforts. The 'business as usual' (BAU) is restricted to the current situation and only includes measures that have already been agreed on to be implemented within the next five years. The 'Green Environment' scenario is the most environmental friendly scenario, which aims to reach water quality standards and emission reduction goals as soon as possible and to a maximum extent. This 'Green Environment' scenario assumes additional measures taken to prevent emissions at the source (e.g. industry) and infrastructural measures (e.g. level of sewer connections, upgrading of wastewater treatment). The time horizon for all scenarios is considered to be 2015 and assumes that this situation will be reached by a linear change from 1998-2015. In the two scenarios the amount of wastewater, amount of people connected to sewers, treatment efficiencies of wastewater treatment and the distribution and size of wastewater treatment plants have not changed in comparison to the results of MONERIS 1993-1997 (as shown in chapter 3).

The heavy metal emissions in BAU scenario are reduced by 5.6-7.8% when compared to the situation 1993-1997. This is caused by the implementation of the EU urban wastewater treatment directive into National German law, which upgrades wastewater treatment plants of category 3 and 4.

The 'Green Environment' scenario shows that measures in urban areas (decoupling of paved urban area, increase of retention capacity and decrease of urban deposition rates) cause a 55% reduction in the heavy metal emissions from urban areas. The extra microfiltration step in larger wastewater treatment plants also has a positive effect on the emissions from wastewater treatment plants, but is a very costly operation. The total heavy metal emissions decline with about 30% when compared to the situation 1993-1997.

An overview of the results of both scenarios is shown in figure 5-1. It shows that even when all measures from the 'Green Environment' scenario are implemented and have reached their full effect, the concentrations of Cu (27% of dredged volume in eastern part to Slufter), Cd (15% of dredged volume in eastern part to Slufter) and Zn (18% of dredged volume in eastern part to Slufter) will cause that large amounts of dredged material will have to be disposed of in the Slufter (see table 5-5). In the case of mercury and lead already with upgrading measures taken in WWTPs ('BAU' scenario) the Sea/Slufter limit can be reached. For cadmium, copper and zinc more measures from the 'Green Environment' scenario should be implemented for reaching the Sea/Slufter limit. For cadmium and mercury measures taken in the area of point source reduction (e.g. industrial reduction and implementation of further wastewater treatment) could already decrease the heavy metal contents in the dredged material below the Sea/Slufter limit. For both zinc and copper extra measures in the sector of urban areas (as proposed in the 'Green Environment scenario') are necessary to decrease the concentrations below the Sea/Slufter limit. For all heavy metals, except for lead, the target levels are not reached.




























	<i>sea/sluffer limit values</i>			<i>target levels</i>	
	Present	BAU	Green	BAU	Green
Cd					
Cu					
Hg					
Pb					
Zn					

Figure 5-1: Present and estimated future quality of sediments in the eastern parts of the port of Rotterdam with regard to the current Dutch quality criteria. Dredged volumes exceeding Sea/Sluffer limits: “sad” > 25%, “happy” < 10%. Target levels: “sad” – mean concentrations exceed target levels.

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## List with abbreviations

$a_{\text{steel}}$	galvanised steel surface
BAT	Best Available Techniques
BfG	Federal Institute of Hydrology
Cd	Cadmium
$C_{M,D}$	heavy metal concentration in the drainage water
$C_{M,E}$	heavy metal concentration in the top soil
$C_{M,G}$	heavy metal concentration in the groundwater
$C_{M,S}$	heavy metal concentration in the surface runoff
Cu	Copper
DKSR	German Rhine Commission
$E_A$	atmospheric deposition load
$E_{\text{cor}}$	corrosion load
$E_{\text{cor}}$	emission from corrosion
$E_D$	Emission from drainage
$E_E$	Emission from erosion
$E_G$	Emission from groundwater
$E_S$	Emission from surface runoff
$E_t$	emissions from traffic
$e_t$	traffic emission per inhabitant per year
$E_T$	traffic load
$E_U$	load to urban areas
$F_D$	Drainage flux
$F_E$	Erosion flux
$F_G$	Groundwater flux
$F_S$	Surface runoff flux
ha	hectare
Hg	Mercury
i.e.	inhabitant equivalent
IKSM	International Mosel Commission
ICPR	International Commission for the Protection of the Rhine
IKSS	International Saar Commission
$M_{\text{POP}}$	Specific emission of heavy metals per inhabitant
Pb	Lead
$PD_u$	population density in paved urban areas



$POP_{\text{WWTP}}$	population connected to a wastewater treatment plant
$Q_{\text{point}}$	Discharge from point sources
$Q_{i,t}$	the total discharge of the sub-catchment i at a given time t,
$Q_{B,i,t}$	the base flow within this sub-catchment i at time t,
$Q_{R,i,t}$	the surface runoff of this sub-catchment i at time t,
$Q_{I,i,t}$	the interflow of this sub-catchment i at time t
$Q_{P,i,t}$	the point discharge of the sub-catchment i at time t.
$SO_2$	Sulphur dioxide
$SO_2$	the mean annual concentration of sulphur dioxide in the air.
SPM	Suspended particulate matter
$TE_i$	Traffic related emissions
WWTP	Wastewater treatment plant
$WWTP_{\text{eff}}$	efficiency of heavy metal removal for a certain wastewater treatment plants
$WWTP_M$	gross heavy metal emissions from a wastewater treatment plant
Y	the average yearly corrosion rate of one square meter of galvanised steel.
Zn	Zinc

