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Emissions of Heavy Metals and Lindane into River Basins of Germany

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16. **Abstract**

According to international agreements, encouraging all partners to diminish the emission of priority pollutants into North- and Baltic Sea significantly within a time period of 1985 to 2000, the aim of this project was to quantify the changes in the emission situation for both heavy metals and lindane within the mentioned period
To reach this aim the total emissions of heavy metals (As, Cd, Cr, Cu, Hg, Ni, Pb, Zn) and the pesticide lindane (γ-HCH) into German river systems were quantified for the periods of 1983-1985, 1993-1995 and 1999/2000.
For the quantification of the emissions via point sources a nation-wide survey on heavy metal data of municipal wastewater treatment plants and industrial direct discharges was carried out. The input via diffuse pathways was calculated using an adapted version of the model MONERIS. This model accounts for the significant transport processes, and it includes a Geographical Information System (GIS) that provides digital maps as well as extensive statistical information.
For a comparison of the calculated heavy metal emission with the measured heavy metal load at monitoring stations the losses of heavy metals due to retention processes within the river systems have to be considered. Therefore heavy metal retention was calculated according to the retention function given by Vink/Behrendt (2002). For the large river basins a good correspondence could be found between estimated and measured heavy metal loads in rivers.
The total emission into the German river basins decreased for each metal during the period of 1985 to 2000. The reduction varies between 36 and 85 % mainly caused by the decline of emissions via point sources. Today's emissions of heavy metals into river basins of Germany are dominated by the input via diffuse pathways. The most important diffuse pathways are paved urban areas (Cd, Cu, Hg, Pb, Zn), erosion (Pb, Cr) and groundwater (As, Ni).
Since the application of the pesticide lindane is illegal today a reduction of lindane input of 67 % was achieved for Germany within the period of 1985-1999/2000. Nevertheless there are significant emissions of lindane via diffuse pathways into German river systems due to the persistence of lindane in the environment.

17. **Keywords**
Heavy metals, Arsenic, Cadmium, Chromium, Copper; Mercury, Lead, Nickel, Zinc, lindane, diffuse emissions, tile drainage, erosion, groundwater, surface runoff, atmospheric deposition, MWWTP, industrial direct discharges, river basins

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GLOSSARY

AbfKlärV: Ordinance on Sewage Sludge

AbwAG : Wastewater Levy Act

ATV:	German Association for the Water, Wastewater and Waste
BBA:	Federal Biological Research Centre for Agriculture and Forestry of Germany
BBodSchV:	Federal Soil Protection Act
BGR:	Federal Institute for Geosciences and Natural Resources of Germany
BMU:	Federal Environmental Ministry
DM:	Dry mass
EMEP:	Co-operative Programme for Monitoring and Evaluation of the Long Range Transmission of Air Pollutants in Europe
ER:	Enrichment ratio
HELCOM:	Baltic Marine Environment Protection Commission
I:	Inhabitants
ICPD:	International Commission for the Protection of the Danube
ICPE:	International Commission for the Protection of the Elbe
ICPO:	International Commission for the Protection of the Odra
ICPR:	International Commission for the Protection of the Rhine
INC:	North Sea Conference
LABO:	Working Group of the Federal States on soil problems
LAWA:	Working Group of the Federal States on water problems
MSC-East:	Meteorological Synthesizing Centre East, Moscow
NFS:	New Federal States of Germany, equivalent to the area of the former German Democratic Republic (GDR)
OFS:	Old Federal States of Germany, equivalent to the area of the Federal Republic of Germany (FRG) before 1990
OSPAR:	Commission for the Protection of the Marine Environment of the North East Atlantic
PE:	Population equivalents
PT:	Total number of inhabitants and population equivalents
QL:	Quantification limit
StaBu:	Federal Statistical Office of Germany
TNO:	Netherlands Organisation for Applied Scientific Research
UBA:	Federal Environmental Agency of Germany
WHG:	Water Resources Policy Act

Summary

With the completion of this project a quantification of heavy metal and lindane emissions into surface waters is provided for the first time for Germany and for the years 1985, 1995 and 2000. Using the statistical and geographical basic data integrated in the MONERIS model system (**Mo**delling **N**utrient **E**missions in **R**iver **S**ystems), substance inputs were calculated by methods analogous to those used for the balancing of the nutrients. They were differentiated according to their sources and pathways and documented for the specific pathways. For this purpose, extensive studies and model adaptations were required to provide a most realistic representation of substance specific transport and retention processes. All quantification approaches as well as the applied basic data were thoroughly documented. As a result an accessible overall model, always open to new perceptions, is now available.

As was to be expected, heavy metal inputs largely decreased in Germany. Depending on the metal observed, emission reductions amount to between 36 and 85 % within 1985 - 2000. The measures taken by industry and implemented within the scope of a more rigorous water legislation but most of all the massive decrease of industrial activities in the New Federal States (NFS former GDR) since 1990, have decisively contributed to an improvement of environmental conditions. Direct industrial discharges only play a secondary role in the year 2000. Municipal wastewater treatment plants remain important now as before. It can be observed, however, that in the year 2000 the water pollution load was mainly caused by diffuse inputs. The major pathways are sewer systems, erosion and groundwater inflow. Combined sewer systems and storm water runoff from separate systems cause, for instance, between 10 and 40 % of the total emissions. Especially high shares are reached for the metals zinc, lead and copper. Due to the fact that in combined systems a considerable share of the storm water runoff is transferred to wastewater treatment plants, the pollution load in regard to heavy metals is lower than in separate sewer systems. Erosion is the main cause for chromium and lead inputs into the surface waters. Arsenic and nickel are mainly emitted by groundwater impact. Significant load diversities resulting from both landuse and meteorological factors exist between the various river basins. In the year 2000 for instance, the highest specific loads were identified in the Rhine catchment. This is directly related to a more than average urbanisation intensity in this area. The comparison of the calculated inputs reduced by the retention in surface waters with the loads obtained by means of monitoring data, altogether shows good correspondence. The best results were obtained for metals featuring a good data base for emissions and immissions (e.g. copper, zinc and nickel) and for large catchment area units. For copper, zinc and nickel the total deviation for Germany was of < 30 %, for all further metals it was of < 50 %. In smaller subcatchments, regional and local

peculiarities may lead to inputs ranging distinctly beyond or below the surface water loads.

Lindane emissions as well could be distinctly reduced between 1985 and 2000. This is due to the fact that lindane applications have been drastically limited in Germany since the mid-eighties and that they were prohibited in 1999. Despite of its production and application prohibition, lindane is still found in the atmosphere, the soil and the water as a result of its persistency. It is thus still emitted into surface waters in 2000. Inputs from urban sources represent the major share. Figure 1 shows the importance of the pathways for heavy metals and lindane in the years 1985, 1995 and 2000, as well as the loads discharged into the surface waters.

The results obtained prove that the model approaches and the data base used allow a plausible evaluation of inputs from point and diffuse sources in the large river basins of Germany. The model provides an instrument allowing to identify the major sources and impact regions and provide the basis for further analysis aiming at the formulation of successful pollution reducing measures.

Further improvements may be realised rather in the field of available and adequate basis data than in the field of calculation approaches. Both for heavy metals and for lindane it may be stated that in almost all environmental compartments valid measured data are only available to a limited extent. In the areas of municipal wastewater treatment plants, water quality and groundwater monitoring, i.e. in areas where many measurements have been taken, the quality of the measured values is affected by frequently implausible quantification limits. As a result, the major part of the data collected and filed with a great deal of energy, may not be used for quantification purposes. Both, an improved analytical technology and data base management may contribute to the solution of this problem in the future. A higher spatial resolution of quantification results may be obtained when regionally differentiated input data become available. First promising approaches are now available for atmospheric deposition from simulation results obtained by EMEP (Co-operative Programme for Monitoring and Evaluation of the Long Range Transmission of Air Pollutants in Europe) and for input into the groundwater from the New Geochemical Atlas (Federal Institute for Geosciences and Natural Resources of Germany). However, for inputs originating from sewer systems, a regionalisation of the basic data for Germany is not possible in the light of present scientific knowledge. This, however, reveals to be urgently required given the importance of this pathway. Moreover, it turned out within the scope of this project that emissions via historic mining activities cause load shares that are not to be neglected. So far, merely inputs originating from point sources may be registered to some extent. On top of this, increased diffuse inputs for which no data is available so far, are to be expected from these areas.

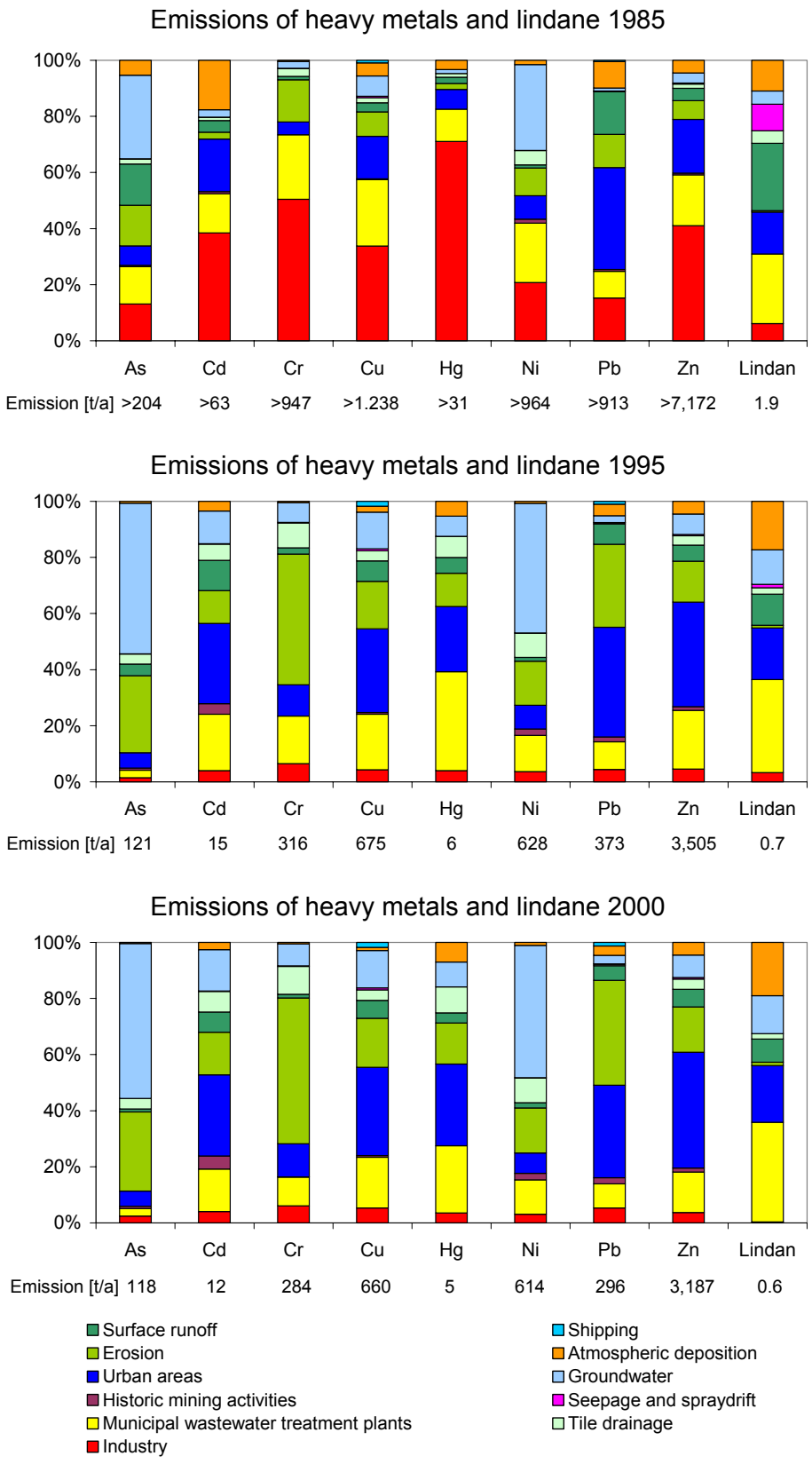

Figure 1 Emissions from point and diffuse sources into German river catchments in t/a.

PART I INTRODUCTION

1 Motive and objective of the project

The input of heavy metals and pesticides into surface waters represents a serious impairment of the aquatic environment. The reduction of the pollutant input into inland waters and seas is thus an ecological necessity. In view of a reduced pollutant input, the Federal Republic of Germany agreed on volume reduction targets for priority hazardous substances within the frame of international treaties on river catchments and treaties on the protection of the seas. The most essential among these are the North Sea Conference (INC), the OSPAR Commission for the Protection of the Marine Environment of the North-East Atlantic (OSPAR) and the Helsinki Convention on the Protection of the Marine Environment of the Baltic Sea Area (HELCOM) as well as the international river basin commissions for the protection of the Rhine (ICPR), of the Elbe (ICPE), the Danube (ICPD) and the Odra (ICPO). A number of report commitments arise from these agreements, e.g. regarding the quantification of the pollutant input and the implementation of reduction goals. The reduction goals listed in Table 1-1 apply to the metals arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), lead (Pb) and zinc (Zn) as well as to the pesticide lindane (γ-HCH).

Table 1-1 Reduction targets for heavy metals and lindane resulting from international protection agreements (UBA, 1999a).

	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn	Lindane
North Sea[1)]	50%	70%	50%	50%	70%	50%	70%	50%	50%
Baltic Sea[2)]	50%	50%	50%	50%	50%	50%	50%	50%	50%
Rhine[3)]	50%	70%	50%	50%	70%	50%	70%	50%	50%

[1)] North Sea (4. INC) reduction of emissions 1985-2000; [2)] Baltic Sea (HELCOM) reduction of emissions 1987-1995; [3)] Rhine (ICPR) reduction of emissions 1985-1995.

On the level of the European Union, the new EU-Water Framework Directive became effective in 2000 (EU, 2000). One goal of this directive is to constantly reduce water pollution and provide "good ecological conditions" for the surface water bodies. The member states are bound to gather data on anthropogenic influences and significant water pollution loads caused by point and diffuse sources. Up to now, 11 priority hazardous substances among which cadmium (Cd), mercury (Hg) and lindane (γ-HCH) have been identified. They are monitored on a European level to prevent their emission into the environment in the medium term. Lead (Pb) counts among a list of 14 further substances discussed to be specified among the priority hazardous substances.

Moreover, quality targets for heavy metals were established by the Working Group of the Federal States on Water Problems (LAWA) to protect surface inland waters. They list concentration data for water, suspended solids and sediments. If these concentrations are not exceeded, the subjects of protection under consideration are not threatened in the light of present scientific knowledge. Since 1990, the compliance with the set targets has been regularly controlled by the Federal Environment Agency (UBA). The target is reached, if the 90 % percentile of the measured heavy metal concentration in the total water sample does not exceed the set target for the subject to be protected. As for pesticides, set targets were merely defined for 'drinking water supply' (LAWA, 1998).

The heavy metal pollution of most German rivers has considerably decreased over the last years. The reduction of the emissions mainly results from a thorough application of the state of the art in both sewage purification and avoidance. However, presently the set targets of LAWA (Working Group of Federal States on Water Problems) are still exceeded for Cd, but also for Cu, Ni, Zn, Hg and Pb (LAWA, 1998). Given this, input via diffuse sources increasingly becomes the focus of interest.

The estimation of the input of these substances from relevant point sources and along diffuse pathways on the level of large river basins mainly serves the identification of major sources of input. Based on major impact regions reported in large-scale studies, further studies may be conducted to define successful measures to reduce pollution.

Emission evaluations for heavy metals in large river basins have been published by Behrendt (1993) and the ICPR (1999) for the Rhine as well as by Vink/Behrendt (2002) for Rhine and Elbe. The Fraunhofer Institute Systems and Innovation Research, Karlsruhe, in co-operation with the Institute for Aquatic Environmental Engineering, University of Karlsruhe, was entrusted on behalf of the Federal Environment Agency (UBA) to quantify the heavy metal inputs into all large German river basins for the period 1995-1997 according to a unified method (Böhm et al., 2001). This project concentrated on the identification of all point sources originating from industry and municipal wastewater treatment plants. Moreover, a first evaluation of the diffuse inputs was conducted.

Diffuse inputs of pesticides into surface waters were compiled for the first time by Huber (1998) for all of Germany. However, the insecticide lindane had not been considered, as in 1993/1994 the use of lindane had ceased almost entirely.

Given the report commitment for the 5th North Sea Conference (INC) in 2002, the Institute for Aquatic Environmental Engineering, University of Karlsruhe, in co-operation with the Fraunhofer Institute Systems and Innovation Research Karlsruhe and the Institute for Freshwater Ecology and Inland Fisheries, Berlin, was entrusted

by the Federal Environment Agency (UBA) to gather data on changes of heavy metal and lindane inputs for the period 1985-2000.

The project had to quantify the point and diffuse heavy metal emissions for cadmium (Cd), chromium (Cr), copper (Cu), mercury (Hg), nickel (Ni), lead (Pb) and zinc (Zn) for the years 1985, 1995 and 2000 on the basis of a unified method for the large river basins of Germany. The already finished research project of Böhm et al. (2001) served as a methodical framework.

For arsenic (As), only direct industrial discharges had been published so far (Böhm et al., 2001). Inputs originating from municipal wastewater treatment plants and diffuse sources were to be complemented within the scope of this project. It turned out that the semi-metal As is not routinely analysed in the list of heavy metals. This is why the data base, particularly in the municipal domain, is considerably smaller as compared to the other heavy metals.

An additional task was to develop a methodology for the quantification of point and diffuse inputs of the pesticide lindane and to conduct an evaluation of the emissions for 1985, 1995 and 2000.

On the basis of these results it had to be evaluated whether Germany had fulfilled the international agreements on a 50-70 % reduction of heavy metals and lindane input (see table 1-1).

The loads determined at river discharge gauging stations were used to prove the plausibility of emission estimates.

The presentation of the very different substance groups considered in this research project was organised in the present report as follows:

Chapter 2 describes the emission method and the respective formulas. The data underlying the emission estimation as well as their changes occurring during the period 1985-2000 are separately represented in chapter 3 for heavy metals and in chapter 4 for lindane, given their differing origins and characteristics.

Subsequently, chapter 5 comprises a description of the approaches to estimate immission and retention. Again, the results were presented separately for heavy metals and lindane in chapters 6 and 7. The presentation of the emissions occurred according to their origins for the large river basins of the Danube, Rhine, Ems, Weser, Elbe, Odra as well as for the coastal areas of the North and Baltic Sea (figure 1-1). The input into the German part of the Maas catchment area was added to that of the Rhine.

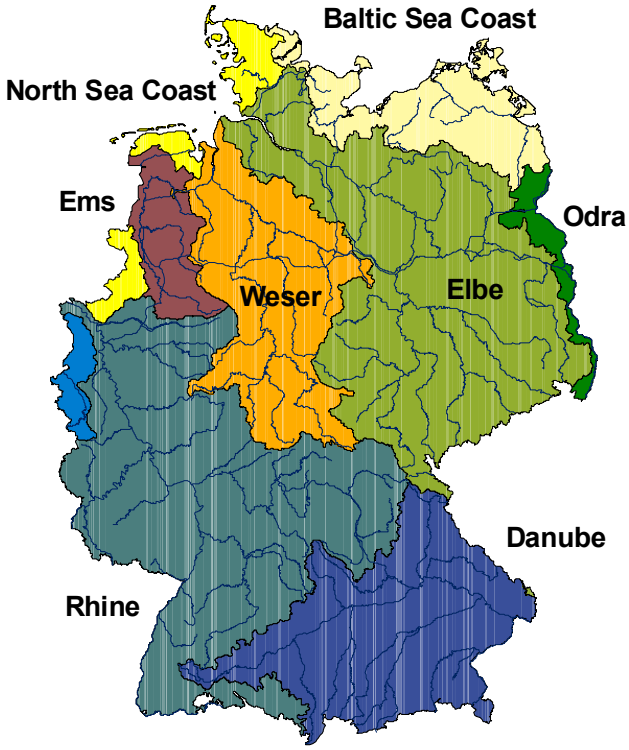

Figure 1-1 Large river basins of Germany following the classification of the Federal Environment Agency (UBA)

PART II MATERIAL AND METHODS

2 Calculation approaches for the emission method

To quantify the emissions, point and diffuse pathways had to be distinguished. Point sources are defined by discrete, clearly located and almost continuous inputs such as e.g. the effluents from municipal wastewater treatment plants and industrial plants. Emissions from diffuse sources travel along various pathways that are tied to different discharge components (see figure 2-1). A differentiation of the discharge components is necessary, as both the concentrations and the processes they are based on usually differ considerably from one another (Behrendt et al., 1999). Besides anthropogenic sources that usually represent the major load, diffuse heavy metal inputs may also result from natural geogenous sources (Novotny/Olem, 1994). The sources and pathways considered as well as their interconnections are schematically represented in figure 2-1.

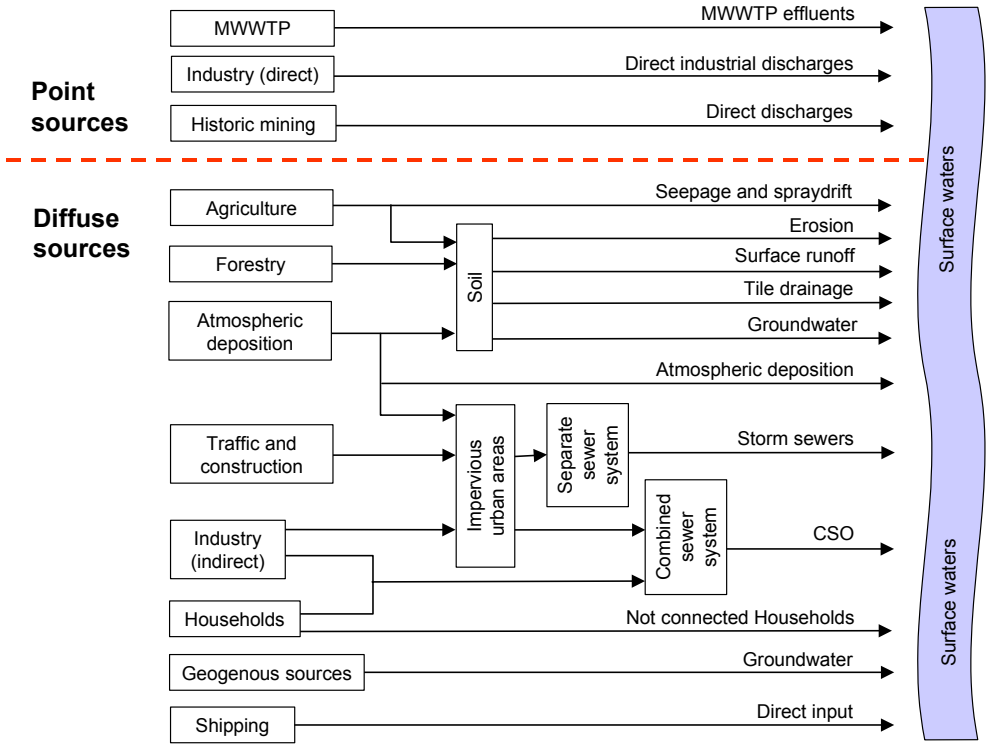

Figure 2-1 Sources and pathways of substances in river basins.

Within the scope of the balancing of nutrient emissions into German river systems, the MONERIS model (**MO**delling **N**utrient **E**missions in **RI**ver **S**ystems) was developed at the Institute for Freshwater Ecology and Inland Fisheries (IGB, Berlin) (Behrendt et al., 1999). This model is based on a Geographic Information System (GIS), which includes both, digital maps and extensive physiogeographical and statistic data. The calculation basis of MONERIS consists of about 300 river systems of an average catchment area of 1000 km^2 (see figure 2-2). In order to use the same basic data as for the calculation of nutrient emissions, MONERIS was adapted for heavy metals and lindane within the scope of this project.

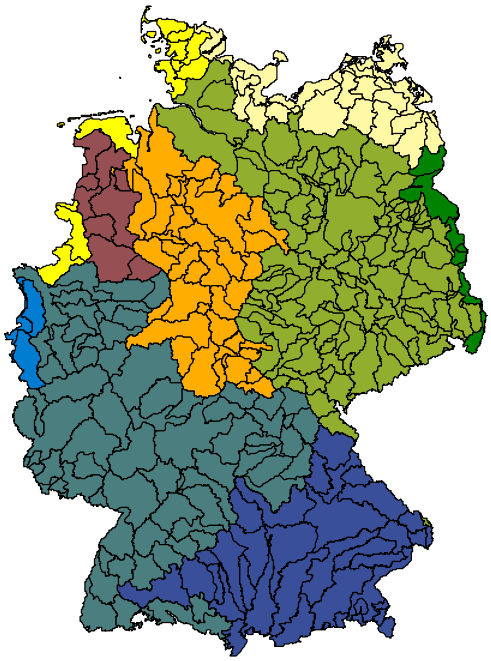

Figure 2-2 River systems in the MONERIS model (Behrendt et al., 1999).

MONERIS allows a pathway-specific calculation of emissions originating from municipal wastewater treatment plants as well as the calculation of all diffuse pathways relevant to nutrient transport. Given the present state of knowledge, the available data base and the size of the areas to be studied, a detailed, dynamic process-oriented modelling of large river systems is not possible. This is why, for MONERIS, existing approaches for a large-scale modelling of substance input were used and modified and new models, applicable on all of Germany, were derived. River discharge gauge data was used to calibrate the water volumes from the different pathways calculated in the model (Behrendt et al., 1999).

To adapt the model, all specific concentration and load data as well as the main transport and retention factors for heavy metals and lindane for the years 1985,

1995 and 2000 had to be gathered, respectively derived. Moreover, additional pathways had to be considered.

Besides the concentrations, meteorological and hydraulical factors have a considerable impact on the emission rate. This is why periods of several years have been analysed for each reference year, as trends can only be derived on the basis of average conditions. Considering the periodicity of meteorological and hydrological quantities a five-year period was chosen. This is why for the years 1985 and 1995, data of the periods 1983-1987 and 1993-1997 were gathered. For the year 2000, however, only data of the period 1999/2000 could be considered so far.

For the majority of the pathways the quantification of the two substance groups and of all reference years could be conducted using the same method. However, different sources of heavy metals and lindane as well as the considerably smaller amount of data available for the mid-eighties sometimes required different proceedings.

2.1 Point sources

Among the point sources are:

- *municipal wastewater treatment plants (MWWTP)*,
- *direct industrial discharges* and
- *direct discharges caused by historic mining activities*.

As extensive monitoring data is available for these pathways, a data collection has been conducted from the respective authorities of all Federal States in Germany.

2.1.1 Municipal wastewater treatment plants

The input via municipal wastewater treatment plants was quantified following two different proceedings. The preferred method was to calculate the loads based on measured concentrations at the treatment plant effluent and the total sewage flow treated (Böhm et al., 2001):

$$E_{KA} = C_{KA} \cdot Q_{KA} \qquad \textbf{Equation 2-1}$$

E_{KA} = substance input via municipal wastewater treatment plants [kg/a]
C_{KA} = concentrations in the MWWTP effluent [µg/l]
Q_{KA} = total treated sewage flow [Mio. m^3/a]

If no measured values were available for the effluent of municipal wastewater treatment plants, the calculation was conducted by means of the wastewater treatment plant module of the MONERIS model. For this purpose the inflow load of the substance in the sewage works had to be determined. Following the efficiency of wastewater treatment it was then converted into an effluent load:

$$E_{KA} = F_{ZU} \cdot (1 - W_{KA}) \qquad \textbf{Equation 2-2}$$

E_{KA} = substance input via municipal wastewater treatment plants [kg/a]
F_{ZU} = influent load [kg/a]
W_{KA} = efficiency of wastewater treatment

2.1.2 Direct industrial discharges

With regard to the methodological procedure and the problems arising when calculating the heavy metal and lindane inputs of direct industrial discharges, the following points have to be considered:

- The type of data provided by the Federal States was very heterogeneous. It partly consisted of pollution loads, partly of individual concentration measurements combined with data of measured respectively authorised sewage flows.

- Some values of the concentration data provided lay below the quantification limit. In these cases the concentration used was set to 50 % of the quantification limit. If, however, all measurements of a parameter lay below the quantification limit, it was assumed that the concentration equals 0.

- As the actual load of a respective year had to be determined, higher loads caused by an irregular incident were included.

- The basis for the load calculations consisted in the measured concentrations and the sewage flow obtained by monitoring. In a few cases these were not available and authorised values have thus been used to complete them.

- Given that different data sources have been considered, various and partly diverging data was available for some dischargers (e.g. official monitoring data and data originating from environmental agreements/self-monitoring). Generally, the monitoring data was assigned a higher priority. It has to be considered, however, that these monitoring data usually originate from very few measured values (frequently only 1 to 5 samples/year are analysed even for major discharger). Inaccuracies and high fluctuations between the differ-

ent years are thus inevitable. Given the higher temporal density of the measured values, self-monitoring data has thus also been included in justified cases.

2.1.3 Historic mining activities

While working on this project it became clear that input from former ore productions cannot be neglected. This is why the relevant Federal States were asked to provide data on this type of emissions. The water authorities partly disposed of information characterised by the mentioned methodological limitations for the direct industrial discharges. In most cases no data was available on the discharged heavy metal loads.

2.2 Diffuse pathways

The MONERIS system allows the quantification of six diffuse pathways:

- *Direct input on the water surface by atmospheric deposition*,
- *Input via runoff from unpaved areas*,
- *Input via erosion*,
- *Input via drainages,*
- *Input via groundwater* and
- *Diffuse input from urban areas (sewer systems and not connected inhabitants)*.

All input data, independent from substances, such as landuse, volume flows and statistical data (e.g. number of inhabitants) were directly taken over from MONERIS.

The inputs via the pathways

- *seepage on farmyards and spraydrift* and
- *shipping*

were quantified according to the methods proposed by the ICPR (1999).

2.2.1 Direct input on the water surface by atmospheric deposition

The direct input into the surface waters via atmospheric deposition was calculated on the basis of the area of water surface of a river system and the deposition rate of the studied substance. Therefore, the deposition rates for heavy metals and lindane had to be determined (→ chapters 3.2.1 and 4.2.2.1).

$$E_D = \frac{A_{GEW} \cdot D}{1.000}$$ **Equation 2-3**

E_D = input via atmospheric deposition [kg/a]
A_{GEW} = total area of surface waters [ha]
D = deposition rate of the studied substance [g/(ha·a)]

2.2.2 Seepage on farmyards and spraydrift

This pathway comprises any inputs that enter surface waters directly from the farmyards, due to farm management and farming practices. Given the different substance specific sources, heavy metals and lindane had to be differentiated. The input data and emission factors to be considered are explained in chapters 3.2.2 and 4.2.2.2.

Heavy metals:

$$E_{HA} = A_D \cdot C_D \cdot a$$ **Equation 2-4**

E_{HA} = inputs via seepage on farmyards and spraydrift [kg/a]
A_D = fertiliser masses[kg/a]
C_D = heavy metal content in the fertiliser (separately for organic manure and mineral fertilisers) [mg/kgDM]
a = share of fertiliser mass arriving directly in the surface waters

Lindane:

$$E_{HA} = A_{Pf} \cdot a$$ **Equation 2-5**

E_{HA} = input via seepage on farmyards and spraydrift [kg/a]
A_{Pf} = fertiliser mass (lindane) [kg/a]
a = share of fertiliser mass arriving directly in the surface waters

2.2.3 Runoff from unpaved areas

The surface runoff from unpaved areas consists of both, **runoff**, i.e. the dissolved load, and the particle input caused by **erosion**. The mainly dissolved load originating from unpaved areas such as arable land, grassland and mountain areas arriving in surface waters after heavy storm events is comprised in this pathway. The input via erosion will be examined separately in chapter 2.2.4.

The surface runoff load from unpaved areas results from the volume of and concentration in the rainfall runoff. The share of the surface runoff in the total runoff was calculated in the MONERIS model on the basis of a simplified approach according to Liebscher/Keller (1979). The substantial concentrations in the rainfall runoff are specified in chapters 3.2.3 and 4.2.2.3.

Moreover, the load from surface runoff arriving in surface waters has to be supplemented by the washoff of fertilisers (heavy metals) or pesticides (lindane). The additional load E_{AD} is calculated following the method used in chapter 2.2.2

$$E_{OA} = \frac{Q_{OA} \cdot C_{OA}}{1.000.000} + E_{AD}$$ **Equation 2-6**

E_{OA} = input via runoff from unpaved areas [kg/a]
Q_{OA} = surface runoff from unpaved areas [m^3/a]
C_{OA} = concentrations in precipitation [µg/l]

Heavy metals:

E_{AD} = heavy metal load caused by manure, mineral fertiliser and sewage sludge washoff from agricultural areas [kg/a] (calculation according to equation 2-4)

Lindane:

E_{AD} = lindane load washed off from agricultural and forested areas [kg/a] (calculation according to equation 2-5)

2.2.4 Erosion

Input via erosion is determined by the concentrations in the topsoil, the sediment input into surface waters and an enrichment factor due to the preferential transport of fine particles (Enrichment ratio, ER).

$$E_{ER} = C_B \cdot SED \cdot ER \cdot 1.000$$ **Equation 2-7**

E_{ER} =input via erosion [kg/a]
C_B = concentrations in the topsoil [mg/kg]
SED = sediment input [t/a]
ER = enrichment ratio

Given the preferential transport of fine particles, the eroded sediment shows an enrichment of fine grain classes during the erosion process. As pollutants are mainly bound to fine particles due to their higher specific surface, the erosion process also causes pollutant enrichment. The enrichment of a substance in the erosion load is described by the enrichment factor ER in comparison to the initial load of the substance in the topsoil:

$$ER = \frac{C_{SED}}{C_B}$$ **Equation 2-8**

C_{SED} = concentration in eroded sediments [mg/kg]
C_B = concentration in agricultural topsoil[mg/kg]

For heavy metals and lindane, the topsoil concentrations, their temporal changes as well as the enrichment factor due to the preferential transport of fine particles had to be determined respectively derived (→ chapter 3.2.4 and 4.2.2.4).

2.2.5 Drainages

The quantification of the input via drainage water was calculated as the product of the drained area, the drain rate and concentrations in the drainage water:

$$E_{DR} = \frac{Q_{DR} \cdot A_{DR} \cdot C_{DR}}{1.000.000}$$ **Equation 2-9**

E_{DR} = input via drainages [kg/a]
Q_{DR} = drain rate [m³/m²·a]
A_{DR} = size of the drained area [m²]
C_{DR} = concentrations in the drainage water [µg/l]

Almost no data was available on heavy metal and lindane concentrations in drainage water, which is why seepage water concentrations were used. For lindane, the applied masses were considered additionally (→ chapters 3.2.5 and 4.2.2.5).

2.2.6 Groundwater

To calculate the input via groundwater flux, the respective concentrations had to be collected (→ chapter 3.2.6 and 4.2.2.6). The dissolved load was then calculated by means of the following equation:

$$E_{GW} = \frac{Q_{GW} \cdot C_{GW}}{1.000.000}$$ **Equation 2-10**

E_{GW} = input via groundwater [kg/a]
Q_{Gw} = groundwater flux [m³/a]
C_{GW} = concentrations in the groundwater flux [µg/l]

In the MONERIS model, the groundwater flux is calculated from the difference between total average runoff surface runoff from paved and unpaved areas, drainage flow and precipitation.

2.2.7 Urban areas: Sewer systems and not connected inhabitants

The diffuse inputs via urban areas are quantified as the sum of inputs originating from storm sewers of the separate sewer system, combined sewer systems and households that are not connected to a wastewater treatment plant (with or without connection to a sewer). The substance specific emission factors for heavy metals and lindane are derived in chapters 3.2.7 and 4.2.2.7.

2.2.7.1 Separate sewer systems

In the case of separate sewers, the wastewater flow is routed into the wastewater treatment plant separately from the storm water. Storm water is generally directly conducted into the surface waters. The quantification of heavy metal inputs from storm sewers occurs on the basis of substance specific heavy metal inputs from impervious urban areas that are connected to separate sewers:

$$E_{UT} = AS_{URB} \cdot A_{URBVT} \cdot 100$$ **Equation 2-11**

E_{UT} = input via storm sewers of separate sewer systems [kg/a]
AS_{URB} = substance specific heavy metal input from impervious urban areas [kg/(ha·a)]
A_{URBVT} = paved urban area connected to storm sewers [km²]

2.2.7.2 Combined sewer systems

Combined sewer systems collect both the domestic input, the indirect industrial input and the surface runoff in one sewer. During storm events the system is only able to retain a fraction of the total water volume. The water quantity exceeding the storage volume is discharged into surface waters by means of **combined sewer overflows**.

The extent of the pollution load discharged depends on the effective annual overflow duration of combined sewer overflows. This duration varies in relation to the retention volume and operation mode of the sewer system. The processes to be considered are very complex and show a high temporal and spatial variability. Simplifying the real processes the load emitted via this pathway could be estimated calculating an overflow rate according to Meißner (1991):

$$RE = \frac{\frac{4000 + 25 \cdot q_R}{0{,}551 + q_R}}{V_S + \frac{36{,}8 + 13{,}5 \cdot q_R}{0{,}5 + q_R}} - 6 + \frac{N_J - 800}{40} \qquad \textbf{Equation 2-12}$$

RE = overflow rate of the combined sewer [%]
q_R = runoff rate [l/(ha·s)]
V_S = storage volume [m^3/ha]
N_J = annual precipitation [l/(m^2·a)]

The share of discharged combined sewage that may thus be calculated comprises, besides the load runoff from paved areas, also a wastewater share. Behrendt et al. (1999) estimated the share of nutrients originating from the wastewater fraction depending on the number of effective annual heavy rainfall events. For heavy metals and lindane, another calculation method was chosen based on the effective overflow duration of combined sewers. According to Brombach/Wöhrle (1997) it is of 230 hours per year. The total load discharged into surface waters was calculated using the following equation:

$$E_{UM} = (AG_E \cdot E_{KA} + C_{GEW} \cdot Q_{GEWM}) \cdot TE + (AS \cdot A_{URBVM} \cdot 100) \cdot \frac{RE}{100} \qquad \textbf{Equation 2-13}$$

E_{UM} = input via combined sewage overflow [kg/a]
AG_E = inhabitant specific metal load [mg/(I·h)]
E_{KA} = inhabitants connected to wastewater treatment plants
C_{GEW} = concentrations in commercial sewage[µg/l]
Q_{GEWM} = runoff from commercial areas with combined sewer connection [l/h]
TE = annual discharge duration [h]
AS = substance specific heavy metal input from impervious urban areas [g/(ha·a)]
A_{URBVM} = impervious urban areas connected to a combined sewer system [km^2]

2.2.7.3 Sewers not connected to wastewater treatment plants

This pathway considers inputs from urban areas, households and commercial businesses connected to a sewer but not to a wastewater treatment plant:

$$E_{UK} = E_{UAK} + E_{EWK} \cdot AG_{EG} \cdot 365 + E_{GEWK} \qquad \textbf{Equation 2-14}$$

E_{UK} = input from urban areas and inhabitants only connected to sewers [kg/a]
E_{UAK} = input from paved areas only connected to sewers [kg/a]
E_{EWK} = inhabitants connected only to sewers
AG_{EG} = inhabitant specific load of dissolved heavy metals [kg/I·d]
E_{GEWK} = input from industrial-commercial wastewater [kg/a]

The calculation of the industrial-commercial input corresponds to the method described for combined sewer systems. However, for this pathway the duration of the industrial-commercial wastewater flow has to be considered as well. It was estimated by 10 h/day according to Mohaupt et al. (1998).

2.2.7.4 Not connected households

For households connected neither to sewers nor to a wastewater treatment plant it was assumed that only the dissolved share of pollutants enters the waters bodies after percolation of the sewage through the soil. Industrial-commercial input is not to be expected for this pathway and has not been considered:

$$E_{UN} = (E_{AUN} + E_{EWN} \cdot AG_{EG} \cdot 365) \cdot a \qquad \textbf{Equation 2-15}$$

E_{UN} = input via households and urban areas neither connected to sewers nor to wastewater treatment plants [kg/a]
E_{AUN} = input from urban areas connected neither to sewers nor to wastewater treatment plants [kg/a]
AG_{EG} = inhabitant specific load of dissolved heavy metals [kg/I·d]
E_{EWN} = inhabitants connected neither to sewers nor to wastewater treatment plants
a = load share entering the surface water bodies after percolation through the soil

2.2.8 Shipping

Direct inputs entering the surface waters via direct uses for shipping are only relevant for heavy metals. The estimation of the loads was based on the number of business ships respectively sporting boats and the registered heavy metal load per ship:

$$E_{SCHIP} = A_{SCHIP} \cdot F_{SCHIP}$$ **Equation 2-16**

E_{SHIP} = input of heavy metals due to direct uses for shipping [kg/a]
A_{SHIP} = number of business ships/sporting boats in the catchment area
F_{SHIP} = heavy metal input per business ship/sporting boat [kg/a]

3 Heavy metals

The following chapter illustrates the data that were taken as a basis for the quantification of heavy metal emissions via point and diffuse sources into surface waters.

3.1 Heavy metal inputs via point sources

3.1.1 Municipal wastewater treatment plants

The preferred method to quantify heavy metal inputs via municipal wastewater treatment plants (MWWTP) is based on the multiplication of heavy metal concentrations in the sewage works effluent and the treated sewage volume (→ equation 2-1). For the period 1993-1997, heavy metal emission data have already been collected from the respective authorities in 1999 (Böhm et al., 2001). In early 2001, the studies for 1983-1987 and 1999/2000 were reiterated and the Federal State Authorities were asked to control the data obtained for 1995. Table 3-1 lists the number of measured values obtained for the periods 1983-1987, 1993-1997 and 1999/2000.

Table 3-1 Number of measured values for heavy metal concentrations in the sewage works effluent for 1985, 1995 and 2000.

	Year	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
Number of data	1985	-	70	-	-	70	-	-	-
	1995	144	9,241	9,402	10,260	7,886	11,596	7,990	5,304
	2000	-	6,089	7,056	8,038	6,123	7,544	6,559	2,272

As follows from table 3-1, poor respectively no data are available for the mid-eighties. This is why the 1985 input data was balanced according to equation 2-2. Given that As is not comprised in the Wastewater Levy Act (Appendix 1, § 3 AbwAG) it is usually not analysed in the effluent of MWWTP. As-emissions from wastewater treatment plants could thus only be estimated approximately.

Heavy metal inputs via municipal wastewater treatment plants for 1995 and 2000

The quantity and quality of the data available on heavy metal concentrations in the effluent of municipal wastewater treatment plants varied considerably for the different Federal States. The number and share of measured values exceeding the quantification limits and the average heavy metal concentrations in the effluent are listed in Appendix 1 for the different Federal States. Given that the period was shorter, less data was available for 1999/2000 than for 1993-1997 (see table 3-1).

A percental distribution of the plants classified by their design capacity for which data on heavy metal emissions are available, is shown in figure 3-1. The Federal States affected are Baden-Wuerttemberg, Bavaria, Mecklenburg-Western Pomerania, Rhineland-Palatinate, Schleswig-Holstein and Thuringia, given that the respective data was only available for these states. To draw the comparison, the repartition of the total number of inhabitants and population equivalents (PT) on design capacity classes was complemented with the data of the Federal Statistical Office (StaBu, 1998b) in figure 3-1.

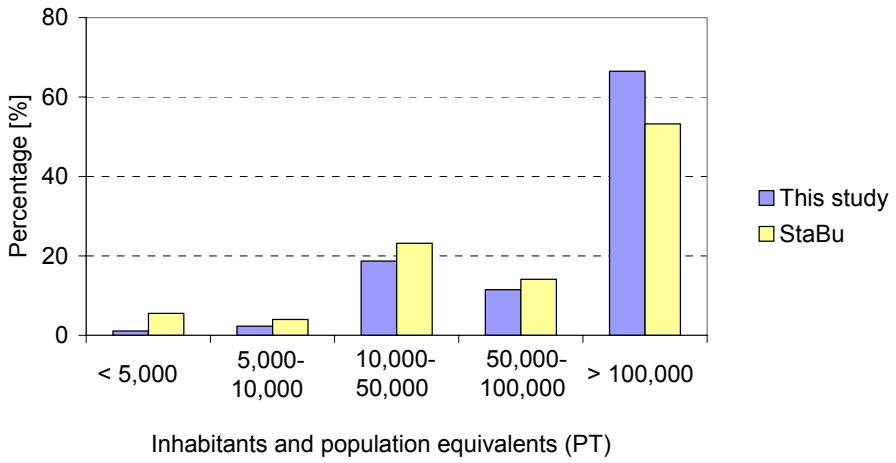

Figure 3-1 Distribution of design capacity classes of wastewater treatment plants in Germany (StaBu, 1998b) as compared to the plants considered in the study (in %).

Figure 3-1 shows that mainly larger plants have been studied as for their heavy metal emission. For smaller plants, particularly < 5,000 PT, almost no data on heavy metal concentrations in the effluent is available. Further evaluations on the dependency of heavy metal concentrations in the effluent from the design capacity class or the share of industrial wastewater showed, however, that there is no correlation between heavy metal emissions and these parameters (s. Böhm et al.,

2001). It is thus assumed, that the bias of the distribution does not represent a major source of error and that the available data are representative for Germany.

When calculating the load, the high fluctuation rate of the quantification limits (QL) causes most considerable uncertainties, as the values below QL are considered with a 50 % QL concentration. It was thus necessary to assure the data quality of the effluent concentrations used. “Analytically meaningful” quantification limits were derived on the basis of actually measured values (all values exceeding QL) and “analytically unjustified” limits were excluded from the calculation. The method is described in detail by Böhm et al. (2001).

An additional quality criterion to be determined was that the data of a Federal State should only be used for metals the measured values of which exceed the quantification limits by at least 10 %. If less than 10 % of the measured values exceed the quantification limit, the resulting average value depends almost exclusively from the level of the respective quantification limits. For data sets of a metal that did not meet this criterion, an average value was generated from the data of Federal States that showed a sufficiently high number of measured values exceeding the quantification limits, involving weightening by the total number of inhabitants and population equivalents (PT) of the Federal States. The period 1993-1997 showed considerable differences as for the effluent concentrations in the New and Old Federal States[1]. This is attributed to the formerly lower technical standard of sanitary engineering in the NFS. The OFS and NFS were thus considered separately for the calculation of the average value. The average effluent concentrations are listed in table 3-2.

Table 3-2 Average values for heavy metal concentrations in the Old (OFS) and New Federal States (NFS) in the reference year 1995 and for Germany in the year 2000 in µg/l.

	Year	**Cd**	**Cr**	**Cu**	**Hg**	**Ni**	**Pb**	**Zn**
Old German States	1995	0.25	5.09	13.2	0.19	7.86	3.29	70.5
New German States	1995	0.76	8.78	15.5	0.37	13.1	7.64	93.7
Germany	2000	0.18	2.99	12.4	0.12	7.82	2.64	46.7

Based on the effluent concentrations of the Federal States, average effluent concentrations were calculated for the river basins. Here again the weightening by

[1] New Federal State NFS → former GDR

Old Federal States OFS → area of FRG before 1990

the total number of inhabitants and population equivalents (PT) was applied. The resulting concentrations are shown in table 3-3.

Table 3-3 Average heavy metal concentrations in municipal wastewater treatment plants for large river basins in µg/l.

River basin	Year	Cd	Cr	Cu	Hg	Ni	Pb	Zn
Danube	1995	0.17	4.53	13.4	0.16	6.36	4.69	94.9
	2000	0.12	3.14	12.0	0.10	4.38	2.31	63.0
Rhine	1995	0.28	5.17	14.0	0.20	7.68	3.34	73.2
	2000	0.19	3.20	12.6	0.12	8.24	2.70	49.4
Ems	1995	0.24	5.47	11.1	0.19	7.33	3.06	70.6
	2000	0.18	2.99	14.0	0.12	10.63	3.03	43.2
Weser	1995	0.23	5.26	10.1	0.23	6.01	2.42	61.7
	2000	0.21	3.12	11.6	0.13	8.03	3.34	35.5
Elbe	1995	0.55	8.13	14.4	0.29	14.68	5.33	76.7
	2000	0.22	2.66	12.3	0.13	8.62	2.48	41.3
Odra	1995	0.74	6.66	14.2	0.16	11.58	5.71	71.1
	2000	0.18	2.99	12.4	0.12	7.82	2.64	46.7
North Sea Coast	1995	0.19	4.38	12.8	0.16	6.10	2.63	55.8
	2000	0.15	2.36	13.4	0.09	8.72	2.50	35.1
Baltic Sea Coast	1995	0.52	2.66	17.2	0.15	7.83	6.95	32.5
	2000	0.06	0.63	11.7	0.03	4.65	0.55	24.3

The load calculation was conducted on the basis of the total treated sewage flow in the river basins (StaBu, 1998, 2001a). Uncertainties arise for metals for which some data sets did not reach the “10 % criterion”. In 1995, only Hg was affected, in 2000, however, Cd, Cr and Pb also showed numerous values of smaller quantification limits (see appendix 1).

Heavy metal inputs via municipal wastewater treatment plants in 1985

For 1985, the heavy metal inputs via municipal wastewater treatment plant were quantified by means of the MONERIS wastewater treatment plant module (→ equation 2-2). The MONERIS data base is based on a classification of statistical data on wastewater treatment plants in Germany and their sites. The collection of the data was conducted separately for 1985 and 1995. Table 3-4 compares the inhabitants connected to municipal wastewater treatment plants to population equivalents (PE) for 1985 and 1995.

Table 3-4 Comparison between inhabitants connected to municipal wastewater treatment plants and population equivalents (PE) for 1985 and 1995 (from MONERIS).

River basin	Inhabitants [1000]			Population equivalents (PE) [1000]		
	1985	**1995**	**Change**	**1985**	**1995**	**Change**
Danube	6,734	8,096	+ 20 %	5,767	5,653	- 2.0 %
Rhine	32,005	35,023	+ 9.4 %	22,674	21,797	- 3.9 %
Ems	1,906	2,405	+ 26 %	2,023	2,129	+ 5.2 %
Weser	7,076	8,217	+ 16 %	5,013	4,723	- 5.8 %
Elbe	13,199	14,241	+ 7.9 %	9,719	6,377	- 34 %
Odra	481	477	- 1 %	710	205	- 71 %
North Sea	1,074	1,233	+ 15 %	1,283	1,352	+ 5.4 %
Baltic Sea	1,965	2,153	+ 9.6 %	1,816	1,278	- 30 %
Germany	64,442	71,846	+ 11.5 %	49,005	43,515	- 11 %

To estimate the loads in the effluent of the wastewater treatment plants it is necessary to determine the inhabitant specific load in domestic wastewater, the specific load in industrial-commercial wastewater as well as the heavy metal concentration in storm water runoff and infiltration/inflow (Behrendt et al., 1999). In combination with the efficiency of the techniques applied in the plants, the emitted heavy metal load may be calculated subsequently.

Literature provides data on heavy metal contents in domestic wastewater and in runoff. It is not possible, however, to generalise the industrial-commercial input as it fluctuates considerably and depends very much on the local situation. On top of that, even more than for domestic wastewater and runoff, adequate data are completely lacking.

Based on loads from municipal wastewater treatment plants derived for 1995 on the basis of heavy metal emissions (chapter 6.2.1), it was tried in a first step to determine the industrial-commercial input value as the difference between the load from households and rainfall runoff and the total load of the river basins. It became evident, however, that even the inhabitant specific share, usually supposed to be scarcely variable, had to be chosen differently for every river system to obtain a meaningful distribution of the loads from the major sources. For this purpose a number of assumptions that are not proven in literature would have had to be made.

Due to the described difficulties during the calibration of the various input parameters of the model, the 1985 influent load was determined following the procedure shown in figure 3-2.

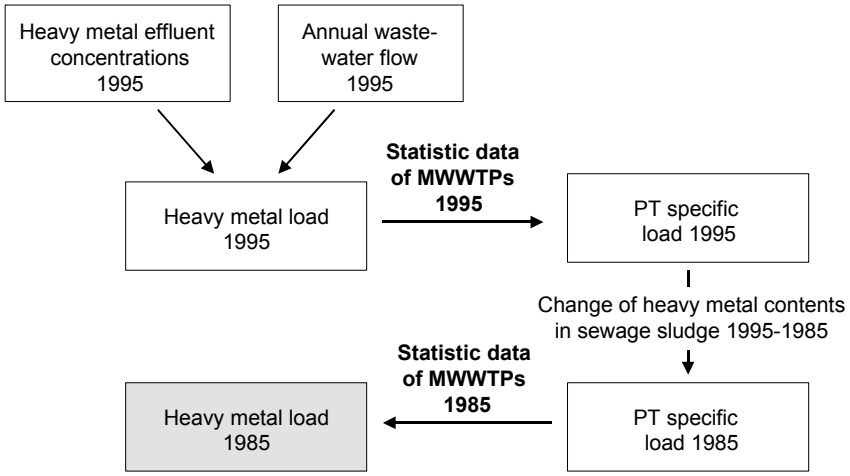

Figure 3-2 Schematic representation of the procedure for the determination of heavy metal input from municipal wastewater treatment plants in 1985.

In a first step, an „**inhabitant and population equivalent (PT) specific**“ input value was calculated for each river system by means of the model. The calculation was based on the emitted heavy metal load obtained for 1995 (chapter 6.2.1) and the efficiencies of the various wastewater techniques applied.

The average heavy metal separation rates were established on the basis of data reported in the literature as well as own evaluations of heavy metal data in the wastewater treatment plant effluent and the respective sewage sludges that were collected within the scope of the data research for 1995 and 2000. The data required to derive efficiencies were available for the Federal States of Schleswig-Holstein, Baden-Wuerttemberg and the Umlandverband Frankfurt (1996). The initial data as well as the average efficiencies underlying the major purification processes are listed in table 3-5.

Table 3-5 Efficiencies for the separation of heavy metals in wastewater treatment plants in % relative to the plant's influent load.

Reference	Cd	Cr	Cu	Hg	Ni	Pb	Zn
Mechanical treatment							
Mean	55	46	44	59	21	65	48
Firk (1986)	50	36	39	57	26	57	41
Oliver/Cosgrove (1974)	60	55	33	60	15	66	54
Schäfer/Hoffmann (1999)	-	-	61	-	-	73	-
Mechanical treatment + activated sludge treatment							
Mean	60	67	72	75	43	84	73
Switzerland (1983)[5)]	30-50	50-90	50-90	-	30-50	50-90	50-90
Firk (1986)	81	59	65	70	42	78	66
Oliver/Cosgrove (1974)	80	79	73	> 85	16	93	77
Jenkins/Russel (1994)	67	91	93	76	59	84	88
Klopp (1987)	-	83	80	-	61	90	83
Bode/Klopp (1997)	50	56	66	-	51	-	78
Koppe/Stozek (1998)	-	50	-	90	40	90	-
Zessner(1999)	42	53	58	55	38	84	47
Mechanical treatment + activated sludge treatment including P-elimination							
Mean	73	85	88	79[1)]	63	88	79
Umlandverband Frankfurt[2)]	-	81	88	-	57	-	79
Zessner (1999)	54	82	81	(> 48)	70	84	54
Schäfer/Hoffmann (1999)	-	-	94	-	-	91	-
Schleswig-Holstein[3)]	89	94	91	97	64	92	95
Baden-Württemberg[4)]	76	82	85	61	60	83	89

[1)] Values in brackets were not used to calculate mean heavy metal removal; [2)] mean heavy metal removal of 23 MWWTPs (Umlandverband Frankfurt. 1996); [3)] mean heavy metal removal determined from MWWTP data of Schleswig-Holstein 1999/2000; [4)] mean heavy metal removal determined from MWWTP data of Baden-Wuerttemberg; [5)] Federal office for environment protection of Switzerland (1983) cited in ATV (1984).

Table 3-6 shows the PT specific influent loads established for 1985 on the basis of the annual loads for 1995. These influent loads comprise the load shares from households, runoff, infiltration/inflow and industrial-commercial loads.

Table 3-6 PT specific input values for the MONERIS model in the influent of municipal wastewater treatment plants in mg/(PT·d) (generated from the 1995 emissions).

River basin	Cd	Cr	Cu	Hg	Ni	Pb	Zn
Danube	0.13	5.1	17.9	0.16	3.4	7.8	92
Rhine	0.25	7.1	23.1	0.23	4.9	6.6	86
Ems	0.12	4.4	10.7	0.13	2.6	3.4	47
Weser	0.13	4.7	10.6	0.18	2.5	3.1	46
Elbe	0.27	5.8	11.8	0.19	5.1	5.4	47
Odra	0.23	2.1	4.6	0.06	2.3	2.8	23
Coastal areas	0.14	1.9	10.3	0.07	1.8	3.9	20

The load reduction generated between 1985 and 1995 as a result of process engineering improvements (e.g. increased use of biological procedures and P-precipitation) as well as structural changes in the catchment area (inhabitants + population equivalents) was considered by the statistical data included in the MONERIS model. To quantify additionally the changes of the influent load resulting from measures taken in the catchment area of municipal wastewater treatment plants (e. g. monitoring of indirect discharges, reduction of atmospheric deposition etc.) between 1985 and 1995, heavy metal concentrations in sewage sludge were evaluated for the periods 1983-1987 and 1992-1997.

The data on heavy metal concentrations available from the literature are mainly data on agriculturally used sewage sludge. The total loads for sewage sludge polluted with heavy metals are thus underestimated, as higher polluted sewage sludges are not used in agriculture. However, the average relative change of heavy metal concentrations may also be derived from the data obtained for agriculturally used sludges. OFS and NFS have been considered separately.

For the OFS, the Federal Ministry for the Environment (BMU) listed the heavy metal contents in agriculturally used sewage sludges for the 1980ies and 90ies. Since 1991 this data has also been gathered for the NFS. No data on average heavy metal contents in agriculturally used sewage sludges in the former GDR is, however, available for the mid-eighties and does thus not allow to draw any comparison. Hornig/Lehmann (1994) published an entire inventory of sewage sludge concentrations covering the area of Dresden for the period 1987 to 1993. Assuming that the most dramatic changes of emissions from indirect dischargers occurred between 1987 and 1993, this period may be representative for the period 1985-1995. For the NFS the changes of heavy metal contents in sewage sludge were thus generated on the basis of the Dresden data. Heavy metal contents in sewage sludge and their relative changes are shown in table 3-7.

Table 3-7 Changes in the heavy metal content of sewage sludge between 1983-1987 and 1993-1997 (in %).

Area	Year	Cd	Cr	Cu	Hg	Ni	Pb	Zn
Old German States	1985 [mg/kgDM][1)]	3.3	71	346	2.3	41	152	1,263
	1995 [mg/kgDM][2)]	1.8	50	276	1.6	29	83	908
	Difference [%]	-45%	-30%	-20%	-30%	-29 %	-45%	-28%
New German States	1985 [mg/kgDM][3)]	16.9	467	301	-	128	262	2,565
	1995 [mg/kgDM][3)]	3.9	69	346	-	39	164	1,773
	Difference [%]	-77%	-85%	+14%	-30%	-70%	-37%	-31%

[1)] Average from 1982 (BMU, 1982) and 1986-1990 (BMU, 1992); [2)] BMU (1996); 4) Hornig/Lehmann (1994)

On the basis of the calculated heavy metal content in sewage sludge for 1985-1995 (see table 3-7), the PT specific 1995 influent loads from table 3-6 were converted into input values for 1985. This procedure is underlain by the assumption that a reduction of heavy metal in the sewage sludge reflects, being an integral measure, the changes of the municipal wastewater treatment plants' influent load. The emitted heavy metal loads may be calculated from the PT specific input values for 1985 and by means of the MONERIS wastewater treatment module.

Estimation of As input via municipal wastewater treatment plants

Effluent concentrations for As are merely available for 18 wastewater treatment plants in the Federal State of Schleswig-Holstein and originate from a special monitoring programme in 1995. An average concentration of 0,33 µg/l was calculated from the measured values. This concentration was applied to all river systems for 1995 and 2000 to generate a coarse estimate of the inputs via municipal wastewater treatment plants. For 1985, the As input was estimated according to the same method, as hardly any data was available for the content of As in sewage sludge and only one author described the separator rate for sewage purification. Firk (1986) took samples to determine As in the effluent of three North Rhine-Westphalian wastewater treatment plants in the mid-eighties. The concentrations fluctuated on average between 2-4 µg/l. The average effluent concentration was set to 3 µg/l. A differentiation in NFS and OFS was not possible.

3.1.2 Direct industrial discharges

In Germany every Federal State is in charge of the implementation and execution of water right regulations. The individual data on the approval and monitoring of both direct industrial and municipal discharges are usually available on the lower respectively medium administrative level. A co-ordinated summary revision of this data up to a federal level does, however, not exist so far. To respond to the required report commitments, the data was gathered and calculated case by case. Correspondingly, the data made available by the Federal States has also been used within the scope of this project. In addition to these, other data sources were used as well whenever it revealed to be necessary or meaningful. The following data sources were included in the surveys:

- data from the water resources respectively environmental protection authorities of the Federal States (in particular for 1995 and 2000)
- reports from river basin commissions (e.g. CIPR, ICPE) as well as international report commitments (e.g. data of the OFS for 1985),
- statements respectively reports on environmental protection published by companies (completing data respectively for comparison),
- further data sources such as e.g. results from research projects (in particular an inventory of sewage conditions in the former GDR), data of the Federal Statistical Office, publications of associations etc..

The quality of the available data was very uneven. It thus had to be thoroughly reviewed as for plausibility and compatibility. Usually, several iteration steps revealed to be necessary to clarify the differences between data from various sources. Formerly used emission figures had to be partly corrected. In some cases this led to deviations from previously published figures.

The basic figures for 1995 (period 1993-1997) originate from the report “Water Emission Inventory for the Federal Republic of Germany” (Böhm et al., 2000). In this case the most important change is the separation of the emissions originating from historic mining activities (chapter 3.1.3). In the former inventory they were counted among the direct industrial discharges. Moreover, even though to a small extent, the original data was completed and corrected.

For 2000 all Federal States were asked to provide the newest available data. Only for the Bavarian Danube no current data was made available.

For 1985, data regarding direct industrial discharges was available for the OFS. These data result from former inventories for the International Conference on the Protection of the North Sea. The data situation of the former GDR, however, is considerably less favourable as no data was available and had to be generated. The necessary calculations were based on the following reports:

- Brodtman/Karras (1991b) collected data on industrial point sources in the former GDR together with the responsible authorities. For most of the relevant industries they evaluated data on the quantity and quality of wastewater with a particular focus on heavy metals. The data generally dates from 1989 and 1990. It includes about 800 plants. The total number of industrial point sources was approximately 5000, but the 800 plants comprise the most important ones.

- The International Commission for the Protection of the Elbe carried out an inventory of inputs from point sources in the Elbe catchment area for the year 1989 (ICPE, 1992). Nearly 100 industrial point sources were listed in this inventory. As for the effluent loads, the focus was set on heavy metals.

On the basis of these data the input via direct industrial discharges was estimated for the GDR in 1985. It was assumed that the situation of these discharges barely changed in the GDR between 1985 and 1989/1990. Generally, the loads thus obtained for 1985 range close to a lower bound given the existing gaps and uncertainties during data collection. The actual input is supposed to be even higher.

3.1.3 Contaminated sites of historic mining activities

Mining activities always go along with considerable impacts on nature, both during the time of active mining but also for a very long time after the activities have come to an end. Surface waters may thus be considerably polluted by the runoff from inundated mines or seepage from waste dump sites. Heavy metal loads that, at least locally, have a considerable impact on the water quality, occur mainly on former ore production sites. However, the projects on input quantification in German water bodies realised so far could not consider this pathway in detail.

While the input from current mining activities is comprised in the data on direct industrial discharges, the input from contaminated sites that result from historic mining activities, however, could not be processed in a way to allow a qualitative comparison with the data from direct industrial discharges. This is mainly due to two reasons:

- In the concerned Federal States (Baden-Wuerttemberg, Bavaria, Hesse, Lower-Saxony, North Rhine-Westphalia, Rhineland-Palatinate, Saxony, Saxony-Anhalt and Thuringia) studies on heavy metal pollution have actually been realised, but usually only the pollutant concentrations in the soils have been considered (e.g.

problems with dump sites). Sediments (Wippermann, 2000; Steffen, 1993) or surface water concentrations were analysed (LfU, 1997; NLWK, 2000) and the and the problems related to historic mines were pointed out, but this information rarely resulted in estimations on inputs in surface waters (Christoffels et al., 1996).

- Whereas currently operating mines are subordinated to the mining authority, the surveillance passes over to environmental protection authorities (responsible for water and soil) when the mining activities end. As a result the responsibility is sometimes unclear. During the inquiry conducted in the Federal States, the mining authorities repeatedly referred to the water authorities which only in two cases disposed of data on emissions from historic mines.

An additional problem are the usually very low concentrations in the effluent from the mines, even though they cause considerable loads given their high water volume.

Potassium and coal mining are both of significant environmental relevance as they go along with water salinisation and ore separation, but they are no source for high priority heavy metals.

The best inventory on German historic mining activities is provided by an Austrian report drawn up on behalf of the authority for environmental protection of the regional government of the Federal State of Salzburg in 1994 (Spiekermann, 1994). The research of that time intended to describe the possible action to be taken for the areas in the Federal State of Salzburg. The survey represented in table 3-8 is based on this report even though it does not claim to be comprehensive.

It has to be considered that the mining areas partly extend over several square kilometres and that one may only speak of direct discharges into surface waters if, e.g., a mouth of an adit exists. Otherwise diffuse input has to be assumed. Some of these areas were even artificially extended, e.g. if excarvated material was used as a low-priced building material. A well-known example is the city of Bodenmais, where the town hall place is paved with excarvated material originating from silver mining. Today, disintegration releases heavy metals (Bergamt München, 2001).

A more recent, exploitable metal is, since the 1940ies, uranium, with considerable deposits in the Erzgebirge (‘ore mountains’). This region temporarily ranged among the most important uranium producers worldwide. Contaminated sites resulting from these activities may be found in the Federal States of Saxony, Thuringia and Saxony-Anhalt.

Table 3-8 Survey on historical mining sites in Germany.

Federal State	**Location (heavy metal)**	**Data available**
Baden-Wuerttemberg	Wiesloch (Pb/Zn)	Yes
	Südschwarzwald (Pb/Zn)	No
	Mittlerer Schwarzwald (Ag/Co)	No
Bavaria	Fränkische Alb (Fe)	No
	Oberpfalz (Fe. Ag)	No
Hesse	Westerwald (Cu. Pb. Zn)	No
	Taunus (Cu. Pb. Zn)	No
	Odenwald (Cu. Pb. Zn)	No
Lower Saxony	Harz (Cu. Ag. Pb)	No
North Rhine-Westphalia	Mechernich (Pb. Zn)	Yes
	Stolberg (Pb. Zn)	No
	Maulbach (Pb. Zn)	No
	Marsberg (Cu)	No
	Wintrop (Sb)	No
	Siegerland (Co. Ni)	No
	Müsen (Hg)	No
Rhineland-Palatinate	Nordpfälzer Bergland (Cu. Hg)	No
	Hunsrück (Cu. Hg)	No
Saxony	Ehrenfriedersdorf (Sn)	Yes
	Helmsdorf. Schlema. Pöhla (U)	Yes
Saxony-Anhalt	Mansfelder Land (Cu)	Yes
Thuringia	Ronneburg. Culmitzsch (U)	Yes

3.2 Heavy metal input via diffuse sources

3.2.1 Direct input on water surface areas via atmospheric deposition

The deposition data available for the calculation of direct atmospheric deposition on water surface areas (→ equation 2-3) were of extremely uneven quality. To obtain an optimum spatial resolution for every reference year and metal, various data sources were considered.

The deposition rates for 1985 were collected separately for the OFS (former FRG) and the former GDR, due to the varying conditions of atmospheric emissions. Table 3-9 shows the deposition rates of heavy metals collected from literature for the mid-eighties in the OFS. Average deposition rates were calculated on the basis of literature for 1985. As for Hg no data was available in literature, a Hg deposition rate was generated on the basis of model calculations for 1985 (TNO, 1991). This rate ranges from 0.6-1.8 g/(ha·a) for the Rhine catchment area.

Table 3-9 Atmospheric deposition rates for the OFS in 1985 in g/(ha·a).

Area	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
Mean (OFS) 1985	10.3	3.4	6.0	68	1.2[10)]	12.3	131	385
North Rhine-Westph. 1984-86[1)]	10.3	3.1	7.1			9.3	111	
Lower Saxony 1986[2)]		2.3		84			156	
Hesse 1984-86[3)]		4.6		75			181	443
Harz 1987-89[4)]	10.2	2.6	6.6	37		7.7	168	193
Black forest 1985[5)]		4.3		23			128	
Northern Germany 1983-85[6)]		2.0	3.2	24		7.1	115	199
Schleswig-Holstein 1986-87[7)]		2.1		62			47	335
Rhineland-Palatinate 1984-86[8)]		3.9		80			87	602
Various locations 1982-86[9)]		6.0	7.0	160		25.0	190	540

[1)] Schulte et al. (1996). Schulte/Gehrmann (1996); [2)] Dämmgen (1996); [3)] HLfU (1991); [4)] Siewers/Roostai (1990); [5)] Zöttl (1985); [6)] Schultz (1987); [7)] Peters (1990); [8)] Block (1989); [9)] Brechtel (1989); [10)] TNO (1991).

Data on atmospheric deposition in the former GDR was published for Cd, Cu, Pb and Zn between 1984 and 1989 by Moeller/Lux (1992) for seven sampling sites The two highly polluted sampling points Bitterfeld and Leipzig differed considerably from 5 less polluted rural points. Given the high dust deposition concentrations in

agglomerations, the deposition of atmospheric heavy metals was dry. However, the deposition concentrations decrease already at short distance from the emission centres and are comparable to the values found in rural areas (Moeller/Lux, 1992). To obtain a representative average value for the whole area of the former GDR, the sampling sites Bitterfeld and Leipzig were not considered. The average deposition rates are listed in table 3-10.

Table 3-10 Atmospheric deposition rates for the area of the NFS in 1985 in g/(ha·a).

Area	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
New Federal States 1985	32[2)]	41[1)]	7.9[3)]	131[1)]	2.2[2)]	41.5[3)]	153[1)]	730[1)]

[1)] Moeller/Lux (1992); [2)] Skoda/Santroch (1994) cited. in Vink et al. (1998); [3)] estimate of total deposition rates based on the reduction of atmospheric emissions 1985-1995 (UBA, 2000).

Moeller/Lux (1992) did not provide data from the former GDR for other metals. The deposition rate of As and Hg was completed on the basis of data obtained from the Czech Republic for the period 1988-1990 (Skoda/Santroch, 1994 cited in Vink et al., 1997). For Cr and Ni the deposition was estimated on the basis of the atmospheric emission reduction. For 1985-1995 the deposition is 69 % for Cr and 82 % for Ni in the NFS (UBA, 2000). The 1985 deposition was derived on the basis of the emission reduction of the known deposition for 1995 (see table 3-11). When using this procedure it has to be taken into account that the reduction of the atmospheric deposition is not only due to a reduction of atmospheric emissions, as heavy metals may partly originate from natural sources and as a transboundary transport of heavy metals occurs as well.

Atmospheric heavy metal pollution has considerably decreased in Europe over the last 15-20 years (Nordic Council of Ministers, 1987, 1994). Within the frame of the "Co-operative programme for monitoring and evaluation of the long range transmission of air pollutants in Europe (EMEP)" the Meteorological Synthesizing Centre East (MSC-East, Moscow) has been modelling the atmospheric deposition for Cd, Hg and Pb in a 50 x 50 km grid for Europe since 1996 (figure 3-3). From the data provided by MSC-East, grids were generated in Arc/Info and were subsequently overlaid and merged with the MONERIS river systems map. A spatially differentiated calculation of heavy metal inputs resulting from direct atmospheric deposition on the water surface area became thus possible for these metals for the years 1995 and 2000.

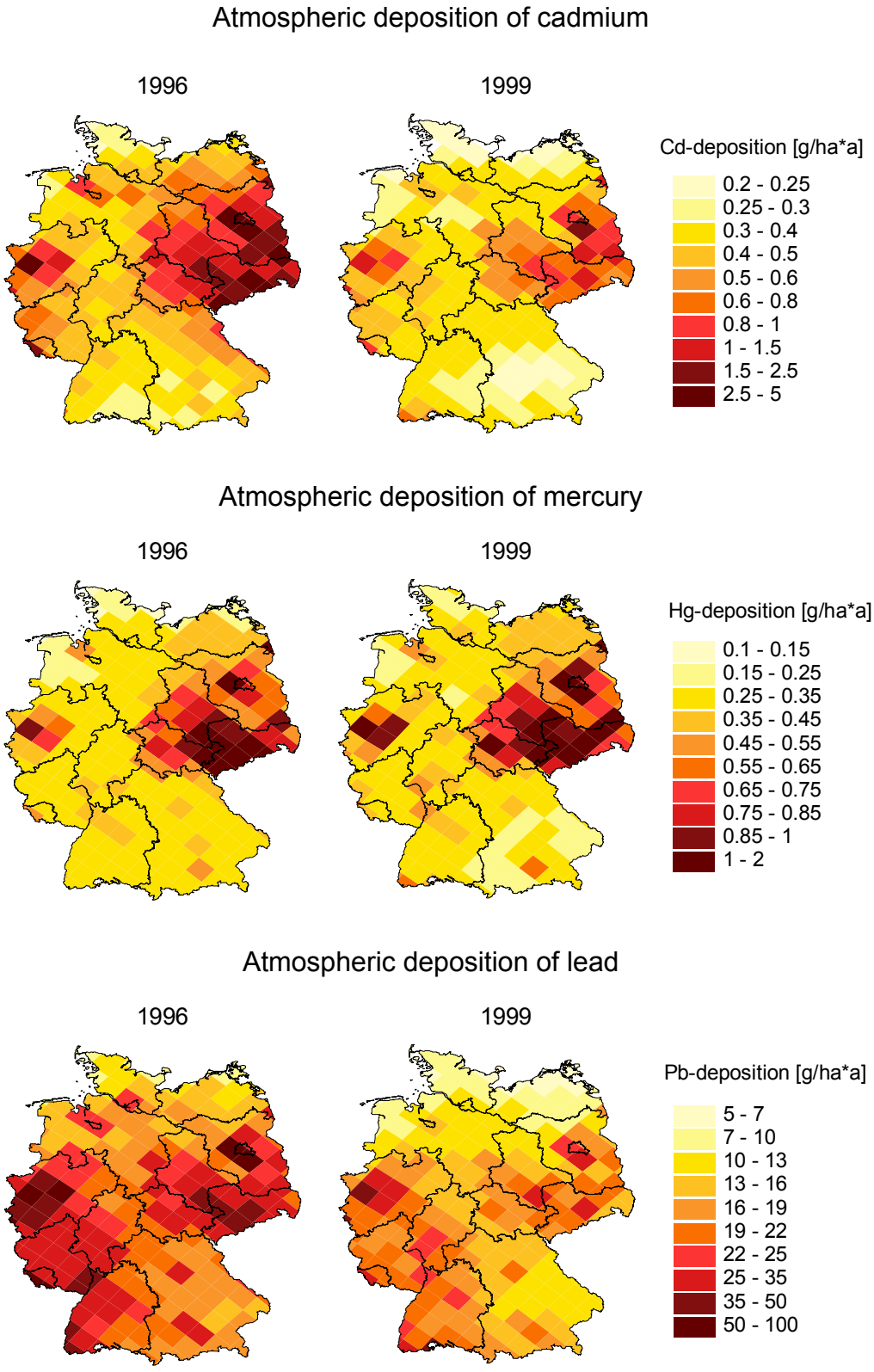

Figure 3-3 Deposition rates for the metals Cd, Hg and Pb for 1996 and 1999 in a 50x50 km grid (MSC-East, 2001).

The Federal Environment Agency (UBA, 2001) observes the bulk deposition of heavy metals on two stations in Germany (Waldhof, Lower Saxony and Deuselbach, Rhineland-Palatinate). For Cd, Cu and Pb data are available since 1989 and for the other metals since 1994/1995. From the annual deposition rates of the two stations a respective average value was generated for Germany. Subsequently, an average deposition rate was calculated for 1995 on the basis of the data obtained for 1994-1996. The deposition rates of the year 2000 are based on those of 1999. The average deposition rates are represented in table 3-11.

Table 3-11 Average heavy metal deposition rates for Germany calculated on the basis of the values of the Federal Environment Agency in g/(ha·a).

Year	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
1995	1.30	(1.25)[2)]	2.44	23.4	(0.1[1)])[2)]	7.5	(26.2)[2)]	253
2000	0.81	(0.83)[2)]	2.33	12.0	(0.08[1)])[2)]	10.4	(16.3)[2)]	230

[1)] Wet deposition only (UBA); [2)] values in brackets were not used as emission factors for the calculation (see figure 3-3)

3.2.2 Seepage on farmyards and spraydrift

The major source for heavy metal input from farms (→ equation 2-4) is the use of fertilisers. One distinguishes between organic manure and mineral fertilisers. The ICPR (1999) determines the percental share of fertiliser masses entering the waters via seepage on farmyards and spraydrift by 0.2 % for manure and by 0.01 % for mineral fertilisers.

The heavy metal concentrations in organic manure correspond to data provided by the Working Group of the Federal States on Soil Problems (Bannick et al., 2001) and Boysen (1992) (Table 3-12). Pig manures show especially high Cu and Zn contents given Cu and Zn enriched mineral feed (Boysen, 1992, Crößmann, 1999). A further source are galvanised stable facilities (Wilcke/Döhler, 1995).

The Federal Statistical Office (1986a, 1996a, 1999a) and the Statistical Yearbook (GDR, 1986) list the livestock populations (cattle, pigs, poultry) for the Federal States. The organic manure mass per cattle may be calculated from the total manure mass in Germany (Eurich-Menden, 1997). Annually, a cow produces 533 kgDM of liquid manure and 1028 kgDM of solid dung, for a pig it is 66 kgDM of liquid manure and 70 kgDM of solid dung and 6 kgDM are due to poultry.

Table 3-12 Heavy metal contents in organic manure in mg/kgDM (Bannick et al., 2001; Boysen, 1992).

Organic manure	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
Slurry, cattle	0.5[1)]	0.28	7.3	44.5	0.06	5.9	7.7	270
Solid dung, cattle	-	0.29	12.9	39.0	0.03	5.2	5.8	190
Slurry, pig	2.0[1)]	0.40	9.4	309.0	0.02	10.3	6.2	858
Solid dung, pig	-	0.33	10.3	450.0	0.04	9.5	5.1	1068
Slurry, poultry	-	0.25	4.4	52.6	0.02	8.1	7.2	336

[1)] Boysen (1992), converted into mg/kg dry mass (1992).

The heavy metal contents underlying the calculation of mineral fertiliser input are listed in table 3-13.

Table 3-13 Heavy metal contents in mineral fertilisers from literature data in mg/kgDM.

Mineral fertiliser	As[2)]	Cd	Cr	Cu	Hg	Ni	Pb	Zn
N-fertiliser mean	-	0.12	4.7	4.5	0.01	5.5	10.1	12.9
Calcium cyanamide fertiliser [1)]	-	0.25	8.7	4.0	0.02	3.8	21.4	38.3
Ammonium fertiliser (AHL)[1)]	-	0.03	1.3	6.3	-	0.3	0.2	2.3
Urea[1)]	-	0.13	0.5	0.5	<0.01[2)]	0.7	0.6	1.9
Other N-fertilisers[3)]	-	0.07	8.4	7.1	0.02[4)]	17.3	18.0	9.0
Super phosphate[1).5)]	3.7	18.80	201.0	22.3	0.04	32.6	15.3	362.5
Thomas meal[3)]	3.2	0.30	1743.0	39.0	0.03	31.0	8.8	73.3
Rock phosphate, various[1)]	3.6	7.80	168.0	15.6	0.07[2)]	15.6	1.3	199.0
K-fertiliser mean	-	0.07	6.5	3.0	0.01	3.7	1.2	7.6
Potassium salt[3)]	-	0.03	10.7	2.4	<0.01[2)]	5.4	0.6	1.6
Potassium chloride[1)]	-	0.08	3.5	2.9	0.02	1.5	0.5	3.7
Potassium sulfate[1)]	-	0.11	5.2	3.6	0.02[4)]	4.1	2.5	17.4
NP-fertiliser[1)]	3.1	9.15	91.4	21.5	0.02	18.0	5.5	151.0
PK- fertiliser [1)]	2.7	7.98	191.0	19.3	0.08	19.9	14.4	152.0
NKP- fertiliser [1)]	4.6	3.78	45.8	11.3	0.06	10.9	14.8	116.0
Ca-fertiliser mean	-	0.19	20.8	7.8	0.02	4.0	4.6	36.5
Carboniferous lime [1)]	-	0.30	7.5	8.2	0.04	6.1	5.9	41.2
Caustic lime[1)]	-	0.10	19.2	11.1	0.02[4)]	6.0	2.8	15.8
Slag lime[1)]	-	0.10	50.6	4.2	0.02[4)]	2.8	7.0	8.8
Other Ca-fetilizers[2)]	-	0.50	6.0	20.0	0.02[4)]	1.0	2.5	80.0

[1)] Bannick et al. (2001); [2)] Boysen (1992); [3)] Wilcke/Döhler (1995); [4)] Stotz/Knoche (1999b); [5)] inclusive triplesuperphosphate

P-fertilisers and phosphate containing compound fertilisers show especially relevant Cd-, Cr- and Zn contents. Thomas meal, which is generated during the processing of iron ore, contains the highest Cr concentrations (Boysen, 1992). The heavy metal contents in other P-fertilisers fluctuate depending on the origin of the used mineral phosphate, Cd and Zn contents usually being correlated (Boysen, 1992). Presently, only mineral phosphates are used for the production of P-fertilisers, their contents range considerably below 40 mg/kgDM. In the 1984 pledge of commitment of the German fertiliser industry, however, the thresholds were higher, i.e. 90 mg/kgDM (LABO, 2000; Müller, 1999). In the former GDR, P-fertilisers produced on the basis of the less polluted Kola apatite (1-2 mg Cd/kgDM) were used until 1989 (Podlesak et al., 1991). This is why diverging heavy metal contents in P-fertilisers, differentiated according to the OFS and NFS, were used for 1985 (Table 3-14).

Table 3-14 Heavy metal contents in mineral P-fertilisers from mineral phosphates of different origin in mg/kgDM for 1985, differentiated for OFS and NFS.

P-fertiliser 1985		**As**	**Cd**	**Cr**	**Cu**	**Ni**	**Pb**	**Zn**
OFS 1985	Superphsophate[1),2)]	1.4	20-38	215	20	33	2	470
	Rock phosphate[2)]	6	15	100	16	15	3	250
NFS 1985	Superphosphate		1.4[3)]					< 2[4)]
	Alkali phosphate		0.8[3)]					< 2[4)]
	Other P-fertilisers		0.2[3)]					< 2[4)]

[1)] Inclusive triplesuperphosphate; [2)] Boysen (1992); [3)] Podlesak et al. (1991); [4)] Wilcke/Döhler (1995)

The nutrient masses in mineral fertilisers were drawn from the data of the Federal Statistical Office (StaBu 1986b, 1998a, 2000) and the Statistical Yearbook of the GDR (1986). The Statistical Yearbook of the GDR (1986) merely contained the total nutrient masses for N-, P-, K- and lime fertilisers for the former districts. A differentiation in different fertiliser types was only possible for P-fertilisers on the basis of the data provided by Podlesak et al. (1991). For N-, K- and lime fertilisers an average heavy metal content was calculated respectively (Table 3-13).

The conversion of the nutrient mass to the total fertiliser mass occurred on the basis of the data obtained from LABO (2000) and Boysen (1992). Table 3-15 lists the masses resulting for mineral fertilisers. The relatively high N-, P-, and K-masses of the former GDR in 1985 also comprise compound fertilisers. A comparison of the total masses for Germany shows a distinct reduction of mineral fertiliser masses between 1985 and 1995 and for 2000 (see table 3-15).

Table 3-15 Relation of total fertiliser mass and nutrient content as well as mineral fertiliser masses.

	Fertiliser/ nutrient ratio	Fertiliser mass [t]			
		1985 OFS	1985 NFS	1995	2000
N-fertiliser total	(3.4)	3,536,716	2,715,300	5,319,723	6,231,332
Calcium cyanamide fertiliser	3.7	3,389,030	-	3,706,734	3,914,356
Ammonium fertiliser (AHL)	3.6	-	-	930,391	984,186
Urea	2.2	101,407	-	410,346	509,210
Other N-fertiliser	4.0	46,279	-	272,252	823,580
P-fertiliser total	-	674,701	1,080,139	164,079	195,547
Super phosphate	3.2	149,283[1)]	861,571[2),3)]	109,875[2)]	152,435[2)]
Thomas meal	6.7	373,163	89,345[3)]	14,284	0
Rock phosphate, various	3.7	152,255	129,223[3)]	39,938	43,112
K-fertiliser total	(3.1)	1,154,753	1,670,900	990,808	815,927
Potassium salt	8.3	344,732	-	188,144	112,971
Potassium chloride	2.5	746,235	-	730,833	623,928
Potassium sulfate	3.3	63,786	-	71,831	79,028
Compound fertiliser	-	3,514,329	-	2,126,547	1,681,492
NP-fertiliser	2.5	513,118	-	428,303	561,318
PK-fertiliser	2.9	931,924	-	566,828	536,660
NKP-fertiliser	2.2	2,069,287	-	1,131,416	1,120,174
Ca-fertiliser total	(2.0)	2,456,296	2,518,000	3,953,482	5,072,946
Carboniferous lime	2.1	1,160,159	-	2,773,592	3,907,880
Caustic lime	1.2	333,937	-	148,681	154,006
Slag lime	2.3	649,083	-	318,591	352,928
Other Ca-fertiliser	1.8	313,117	-	712,618	658,132
Total mineral fertiliser		19,344,181		12,416,320	13,043,347

[1)] Inclusive triplesuperphosphate; [2)] inclusive alkali phosphate; [3)] Podlesak et al. (1990)

All information was collected on the Federal State level. For the area of the former GDR in 1985, the former districts were combined to the present Federal States. The conversion of the respective Federal State data to the river basins occurred on the basis of the Federal State's relative areal share of the catchment areas.

3.2.3 Runoff from unpaved areas

When calculating the **dissolved** heavy metal input via surface runoff from unpaved areas (→ equation 2-6) the load from rainfall runoff and the load caused by fertiliser washoff were considered separately.

Heavy metal load in rainfall runoff

No literature values are available for dissolved heavy metals in the surface runoff of unpaved areas. Assuming an approximate sorption/desorption balance between topsoil and runoff, this balance may be described by means of adsorption isothermes. However, the required parameters have to be determined by laboratory tests and depend largely on the pH-value as well as on the respective soil and component characteristics (Scheffer/Schachtschabel, 1992). The laboratory characteristics could not be studied for all metals and soil types in Germany within the frame of this project. As a substitute, heavy metal concentrations in precipitation were thus taken as a basis. Considering that, due to the short time of contact during the runoff event, a total equilibrium may not be obtained – transport models such as e.g. GLEAMS recommend to use 50 % of the equilibrium concentration (Haider, 1996) – it may be assumed that this method approximately covers the actual concentrations. The average concentrations in rainfall used are shown in table 3-16.

Table 3-16 Heavy metal concentrations in rainfall in µg/l.

Reference	Year	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
Schultz, 1987	1985	3.09[1)]	0.25	0.40	2.70	0.064[2)]	0.86	13.0	26.0
UBA, 1994-96[1)]	1995	0.39	0.12	0.39	3.30	0.025	0.65	2.1	13.6
UBA, 1999[1)]	2000	0.12	0.06	0.14	2.75	0.013	0.85	1.2	13.5

[1)] UBA (2001); [2)] concentration back-calculated from the change in atmospheric deposition 1985/1995

Heavy metal input via fertiliser washoff

For agriculturally used areas, the heavy metal input via fertiliser washoff has to be calculated in addition to the input via surface runoff. For this purpose the amount of mineral fertilisers and organic manure as well as their heavy metal contents were taken over as derived in chapter 3.2.2. For this pathway, however, sewage sludge application has to be considered additionally.

Table 3-17 shows the heavy metal concentrations in agriculturally used sewage sludges as provided by the Federal Ministry for the Environment (BMU, 1992, 1997, 1999). No average data was available for the former GDR for 1985. A mean

value was thus generated from various data (see table 3-17). For As, no differentiation between NFS and OFS could be given and no temporal development of the concentrations could be specified either. As the Ordinance on Sewage Sludge (AbfKlärV, 1992) does not comprise any limiting values for As, barely any data are available.

Table 3-17 Heavy metal concentrations in agriculturally used sewage sludges from 1985 to 2000 in mg/kgDM.

Area	Year	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
OFS[1)]	1985	8.8[5)]	3.3	71.0	346	2.3	41	152	1263
NFS[2)]		8.8[5)]	6.4	185.0	186	3.6	57	134	1805
OFS[3)]	1995	8.8[5)]	1.8	49.7	276	1.6	29	83	908
NFS[3)]		8.8[5)]	1.8	64.7	192	1.9	31	82	1045
Germany[4)]	2000	8.8[5)]	1.4	46.0	274	1.0	23	63	809

[1)] Average from 1982 (BMU, 1982) and BMU (1990); [2)] average from data of the administrative region of Dresden 1987, Saxony-Anhalt 1985, Mecklenburg-Western Pomerania and Brandenburg 1991/92 (BMU, 1996); [3)] BMU (1996); [4)] BMU (1999); [5)] Koppe/Stozek (1999)

The agriculturally used sewage sludge masses were compiled for the different Federal States on the basis of data provided by the Federal Statistical Office (Stabu, 1983, 1987, 1998b, 2001a) and the Federal Ministry for the Environment (BMU, 2000). For the former GDR, no statistical data on sewage sludge yield and disposition was available for 1985. Brodtmann/Karras (1991a) collected data on the sewage sludge yield in the NFS for 1990. It may be assumed that these data approximately correspond to the 1985 sewage sludge yield. According to Brodtmann/Karras (1991a), sewage sludge was used on 65 % of agriculturally used land in the former GDR. The agriculturally used sewage sludge masses for the period 1985-2000 are listed in table 3-18.

The share of mineral fertilisers and organic manure entering the surface waters via washoff is 0.3 % according to ICPR data (1999). The same figure was assumed for sewage sludge as well.

Table 3-18 Sewage sludge yield and share of agricultural use from 1985-2000.

Area, year of elevation	Year	Sewage sludge yield [t DM/a]	Sewage sludge used in agriculture	
			[t DM/a]	[%]
OFS, 1983/87[1)]	1985	2,116,800	848,861	35 %
NFS, 1990[2)]		206,240	134,100	65 %
Total		2,323,040	982,961	42 %
OFS, 1995[3)]	1995	2,275,800	855,400	38 %
NFS, 1995[3)]		366,400	95,300	26 %
Total		2,642,200	950,700	36 %
Germany, 1997/98	2000	2,514,500[4)]	909,547[5)]	36 %

[1)] StaBu (1983,1987); [2)] Brodtmann/Karras (1991b); [3)] StaBu (1998b); [4)] StaBu (2001a); [5)] BMU (1999)

3.2.4 Erosion

Sediment input into surface waters represents a major parameter for the calculation of heavy metal input by erosion (→ equation 2-7). Within the scope of MONERIS, a model applicable on all German river basins was developed to calculate sediment input (Behrendt et al., 1999). The specific sediment loads obtained from MONERIS are shown in figure 3-4.

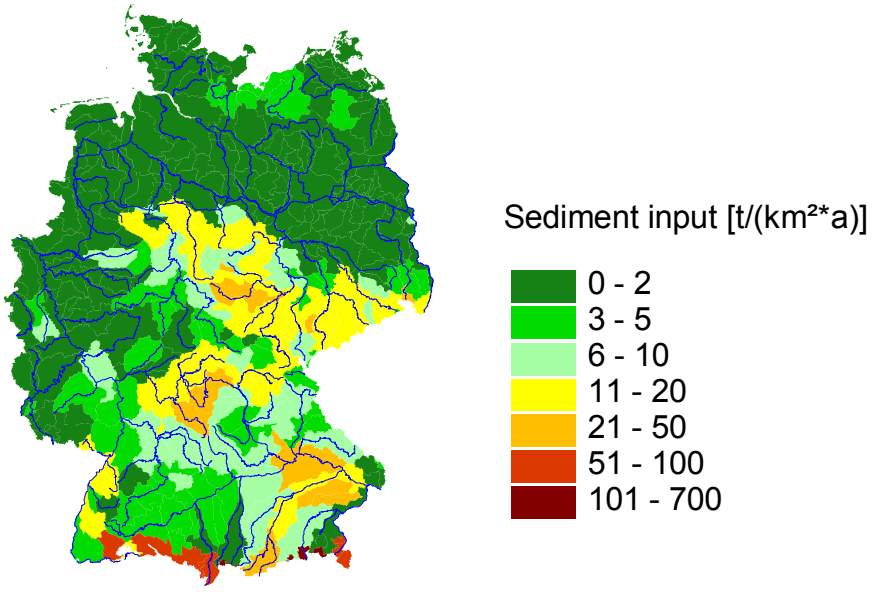

Figure 3-4 Specific sediment input in German river systems obtained from MONERIS for 1995.

Heavy metal contents in the topsoil

The Working Group of the Federal States on Soil Problems (LABO, 1998) compiled background values of heavy metal contents in topsoils of agricultural land on a Federal State level. They were taken as a basis for 1995.

The background value describes the concentration of a soil and is composed by the geogenous content and the ubiquitous substance distribution resulting from diffuse inputs into the soil. Given that the Working Group of Federal States on Soil Problems did not provide the heavy metal concentrations for Hg and As for all Federal States, the lacking data was complemented with values obtained for neighbouring states with comparable geological conditions. The solid rock regions of southern and central Germany exhibit particularly high heavy metal concentrations in the topsoil of agricultural land (table 3-19).

Table 3-19 Heavy metal concentrations in the topsoil of agricultural land of the Federal States in 1995 mg/kg (LABO, 1998).

Federal State	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
Baden-Wuerttemberg	12.0	0.20	36.0	19.0	0.10	27.0	27	60
Bavaria	11.0	0.23	49.0	17.0	0.08	26.0	35	73
Berlin	-	0.15	2.2	10.0	-	0.8	22	16
Brandenburg	4.0	0.10	4.0	4.5	<0.05	2.0	12	16
Bremen	2.9	0.10	13.0	8.0	0.05	3.0	50	31
Hamburg[1)]	-	0.12	12.0	8.2	0.04	8.9	14	34
Hesse	6.3	0.24	34.0	15.0	0.07	25.0	25	62
Meckl.-Western Pomerania	-	0.13	23.0	13.0	-	13.0	17	45
Lower Saxony	-	0.25	22.0	13.0	0.08	14.0	26	60
North Rhine-Westphalia	-	0.42	25.0	12.0	-	12.0	30	67
Rhineland-Palatinate	8.5	0.29	31.0	17.0	0.13	24.0	24	63
Saarland	-	0.29	26.0	14.0	0.06	21.0	29	77
Saxony	11.0	0.42	37.0	16.0	0.10	14.0	53	71
Saxony-Anhalt	-	0.15	22.0	13.0	0.09	17.0	27	57
Schleswig-Holstein	-	0.12	12.0	8.2	0.04	8.9	14	34
Thuringia	8.0	0.23	45.0	22.0	0.09	29.0	32	76

[1)] Equivalent to heavy metal content of Schleswig-Holstein

The result of agricultural management and atmospheric deposition is a heavy metal enrichment in the topsoil of agricultural land (Wilcke/Döhler, 1995; Crößmann, 1999; Müller, 1999; Bannick et al., 2001). To derive the heavy metal contents for 1985 and 2000, heavy metal balances were drawn for the periods 1985-1995 and 1995-2000.

For **inputs originating from agricultural production**, mineral fertilisers, manure and sewage sludge were considered. The fertiliser masses were taken from chapters 3.2.2 and 3.2.3 and were then converted to a specific input per hectare of crop land. While the total crop land was taken as a basis in the case of mineral fertilisers and manure, the specific loads for sewage sludge were exclusively limited to agriculturally used land after 1992, due to the fact that sewage sludge application on grassland was prohibited with the amendment of the Ordinance on Sewage Sludge (AbfKlärV, 1992). According to Wilcke/Döhler, the total crop land covers 16,950,100 ha, the share of arable land coming to 66 % (StaBu, 1997).

As for the evaluation of average **atmospheric depositions**, time series were generated on the basis of literature data and the values measured by the Federal Environment Agency (2001) (chapter 3.2.1) between 1985-1999. In a second step the mean deposition rate was calculated for 1985-1995 and 1995-2000.

The major **output pathways** for heavy metals from the soil are extraction caused by harvesting, wash-out with seepage water and wash-off via surface runoff. Heavy metal extractions resulting from crop harvesting were compiled by the Working Group of the Federal States on Soil Problems (Bannick et al., 2001). The seepage wash-out estimations were based on the heavy metal concentrations measured in seepage water by Bielert et al. (1999) (chapter 3.2.5), considering a mean annual net seepage volume of 200 l/m^2 (Bannick et al., 2001).

The heavy metal load caused by rainwater and fertiliser washoff has to be deduced, as these load shares do not contribute to a heavy metal enrichment in the topsoil. On the recommendation of the Working Group of the Federal States on Soil Problems (Bannick et al., 2001), output via erosion has not been considered. If less contaminated subsoil is intermixed through ploughing, this may lead to a reduction of the soil contents. The net output via erosion would then result from the difference between a possibly higher heavy metal content in the topsoil affected by erosion and the lower contents in the intermixed subsoil (Wilcke/Döhler, 1995). Given that the Working Group of the Federal States on Soil Problems (LABO, 1998) provided only data on heavy metal concentrations in the topsoil and no respective values below the plough horizon, this difference could not be estimated.

Table 3-20 Heavy metal balance for arable areas in Germany in g/(ha·a). Annual averages for the periods 1985-1995 and 1995-2000.

Heavy metal flow [g/(ha·a)]	**As**	**Cd**	**Cr**	**Cu**	**Hg**	**Ni**	**Pb**	**Zn**
Deposition 1985-1995[1)]	5.37	2.18	4.28	49.7	0.91	9.26	53.8	277
Deposition 1995-2000[1)]	0.94	1.19	2.23	20.0	0.48	8.97	18.1	226
Mineral fertiliser 1985-1995[2)]	1.02	1.51	71.1	9.08	0.03	8.52	10.1	48.3
Mineral fertiliser 1995-2000[2)]	0.54	1.14	21.1	6.56	0.02	5.28	8.72	42.2
Organic manure 1985-1995[2)]	1.34	0.58	21.2	166	0.08	12.0	12.6	621
Organic manure 1995-2000[2)]	1.11	0.49	17.6	137	0.06	9.98	10.5	516
Sewage sludge 1985-1995[3)]	0.48	0.19	4.75	20.4	0.14	2.49	8.01	77.8
Sewage sludge 1995-2000[3)]	0.58	0.13	3.99	22.5	0.10	2.12	5.90	70.8
Input total 1985-1995	**8.21**	**4.47**	**101**	**245**	**1.16**	**32.3**	**84.5**	**1023**
Input total 1995-2000	**3.17**	**2.95**	**44.9**	**186**	**0.67**	**26.4**	**43.2**	**855**
Loss by crop[4)]	-	0.67	5.27	33.9	-	10.3	5.92	173
Loss by seepage[5)]	1.44	0.28	9.20	8.00	0.14	17.8	0.56	38.0
Loss by surface runoff 1985-1995[6)]	0.58	0.07	0.43	1.68	0.01	0.34	2.59	9.13
Loss by surface runoff 1995-2000[6)]	0.14	0.05	0.29	1.82	0.01	0.31	0.91	7.37
Output total 1985-1995	**2.02**	**1.02**	**14.9**	**43.6**	**0.15**	**28.4**	**9.07**	**220**
Output total 1995-2000	**1.61**	**1.00**	**14.8**	**43.7**	**0.15**	**28.4**	**7.39**	**218**
Accumulation 1985-1995	**6.19**	**3.45**	**86.4**	**201**	**1.00**	**3.83**	**75.4**	**803**
Accumulation 1995-2000	**1.56**	**1.94**	**30.2**	**142**	**0.52**	**0**	**35.8**	**636**

[1)] See chapter 3.2.1; [2)] see Chapter 3.2.2; [3)] see chapter 3.2.3; [4)] Bannick et al. (2001); [5)] Bielert et al. (1999); Bannick et al. (2001); [6)] loss of heavy metals by surface runoff referring to agricultural area (see chapter 3.2.3)

The annual heavy metal accumulation for the periods 1985-1995 and 1995-2000 can be taken from table 3-20 and table 3-21. For the conversion in µg/kg the reference quantity consists in the upper 30 cm of the arable layer (generally corresponds to the Ap-horizon), the assumed soil density was of 1.3 g/cm^3 (Bannick et al., 2001).

Relative to the mean topsoil content of 1995 (mean value from table 3-19), the metals Cd (4.1 %), Cu (4.0 %), Zn (3.9 %) and Hg (3.8 %) show their highest accumulation for the period 1985-1995. For the other metals it was much lower and fluctuated between 0.06 and 0.9 %. During the period 1985-1995 the accumulation diminished for all metals due to smaller inputs via atmosphere and fertilisers (Table 3-21). For 1985 and 2000, the heavy metal contents in the topsoil were reduced respectively increased by the accumulation specified in table 3-21.

Table 3-21 Average annual heavy metal accumulation for arable soils in µg/kg and in % for the periods 1985-1995 and 1995-2000.

Accumulation of heavy metals		As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
1985-1995	[µg/(kg·a)]	1.59	0.88	22.20	51.60	0.26	0.98	19.30	206
	[%/a]	0.02	0.41	0.09	0.40	0.38	0.006	0.07	0.39
1995-2000	[µg/(kg·a)]	0.40	0.50	7.74	36.50	0.13	0	9.18	163
	[%/a]	0.01	0.23	0.03	0.28	0.20	0	0.03	0.31

Besides the erosion of arable areas, with 73 % being the major source for sediment input into surface waters, erosion also occurs on naturally open areas. To evaluate the heavy metal inputs originating from these areas, a mean geogenous heavy metal concentration was determined. The heavy metal concentrations contained in the most frequently occurring rock types in Germany were determined by Hindel/Fleige (1991). Based on a digital geological map (GK 1;000, BGR 2001) the shares of these rock formations were determined according to the data provided by Hindel/Fleige (1991) and a weighted mean value was calculated (Table 3-22). For the metals Cr and Ni it exceeds the mean content in arable soil. This is however plausible, given that agricultural management does not occur to the same extent in regions of different rock type. Especially in solid rock regions of higher situated low mountain range sites, which frequently show increased heavy metal contents, the soils are barely ever used for agricultural purposes.

Table 3-22 Geogenous heavy metal contents in the most frequently occurring rock types in Germany in mg/kg (Hindel/Fleige, 1991, GK 1000, BGR).

Rock type	Percentage	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
Sand and gravel	39.7 %	1.3	<0.3	1.5	1.5	0.005	5	10	11
Loam	10.5 %	3.4	<0.3	20	9	0.024	15	20	36
Clay	11.7 %	8.9	<0.3	103	22	0.044	60	39	98
Turf	3.9 %	6.0	0.4	-	10	0.056	12	17	29
Sandstone	8.8 %	4.7	<0.3	17	8	0.019	14	20	30
Limestone	10.8 %	3.6	<0.3	5	9	0.018	16	38	35
Shist	8.6 %	8.9	<0.3	65	28	0.015	39	35	124
Basalt	1.2 %	2.6	<0.3	317	50	0.027	207	31	103
Crystalline	4.6 %	1.8	<0.3	2	4	0.019	8	25	31
Weighted average	100 %	3.84	0.16	26.4	9.41	0.018	20.3	21.8	40.6

Enrichment ratio (ER)

The lower the soil erosion rate, the more selective will be the enrichment process due to transport processes (Auerswald, 1989). Behrendt et al. (1999) determined the enrichment ratio for phosphorus on the basis of suspended solids concentrations at high runoff rates in small catchments of the Danube River, as it may be assumed for these, that the share of autochtonous material and point sources is neglectable. The variation of the enrichment ratio may be described on the basis of the specific sediment input. The same procedure was chosen for heavy metals. However, the available data base is of considerably lower quality if compared to the nutrients, as for small river catchments no measured values are generally available for heavy metal contents in suspended solids. Moreover, the number of annual measurements is considerably lower. An evaluation of the data as a function of runoff conditions was thus not possible.

The enrichment ratio was determined for 16 middle-sized catchment areas in different regions of Germany (→ equation 2-8). To reduce the impact of peak values in suspended solids that may result from input via point sources, the median of heavy metal contents in suspended solids was used (UBA, 1999c). The mean heavy metal contents in the topsoil of the catchments were determined in consideration of the geological conditions (Digital Geological General Map of Germany, BGR, 2001 and Working Group of Federal States on Soil Problems, 1998).

The calculated enrichment ratios were then plotted against the specific sediment input of the water courses (from MONERIS) in log-log scale (figure 3-5). The respective shapes of the plotted curves are due to the different heavy metal contents in the different grain class fractions of the topsoil. The regression equation was determined for every metal and the enrichment ratio was calculated on this basis for the catchment areas. The resulting mean enrichment factors for Germany are listed in table 3-23.

Table 3-23 Mean enrichment ratios for heavy metals.

	As	**Cd**	**Cr**	**Cu**	**Hg**	**Ni**	**Pb**	**Zn**
Mean ER	1.6	3.0	1.6	3.0	3.9	1.7	1.5	3.3

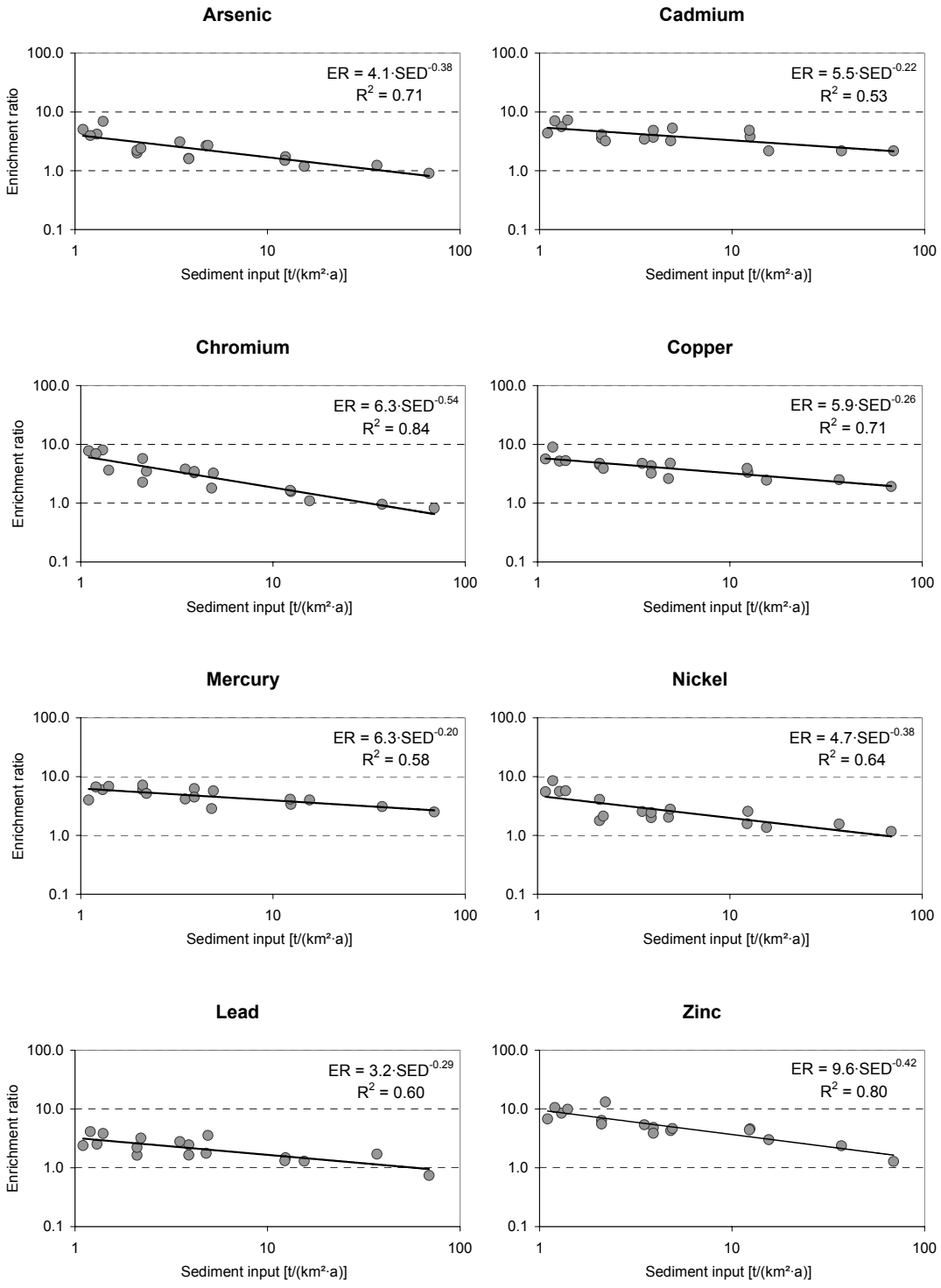

Figure 3-5 Correlation between enrichment ratio and the specific sediment input for 16 middle-sized German river catchments in log-log scale.

3.2.5 Drainages

The calculation of the input via drainages occurs according to equation 2-9. Figure 3-6 shows the specific drainage volume in mm (discharge from drainages relative to the respective catchment area). Especially the coastal areas and subcatchments of Ems and Elbe show high specific drain rates.

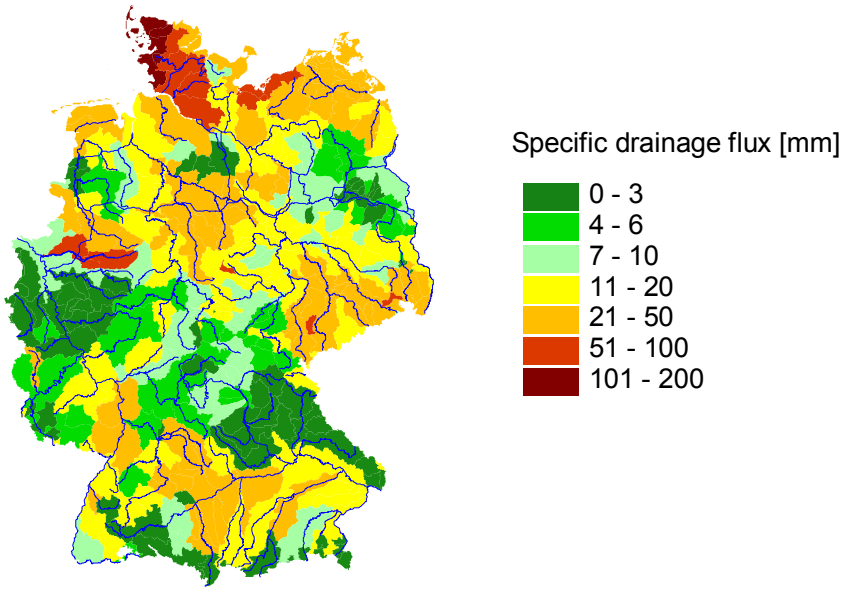

Figure 3-6 Specific drain rates for the German river basins from MONERIS (1995).

Literature barely provides any measured values on heavy metal concentrations in drainage water. Table 3-24 shows the results of two studies (Teichgräber, 1988, Hahn et al., 1992). Given that some metals were not considered and that the studies put a strong emphasise on specific aspects, the studies revealed to be inappropriate to estimate the heavy metal input via drainages.

Table 3-24 Measured heavy metal concentrations in the drainage water in µg/l drawn from literature.

Reference	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
Hahn et al. (1992)	-	<0.02	-	<3.0	-	-	<1.9	-
Teichgräber (1988)	-	0.5	13	2.0	n.d.	n.d.	4.0	200

n.d. = no data

The concentrations obtained in the seepage water of arable soils may be considered alternatively. Within the scope of a project on behalf of the Federal Environment Agency, lysimeter experiments were conducted with a total of 340 seepage water

samples from 16 arable soils of different sites in Germany (Bielert et al., 1999). The comparison of the median values of the different soils' seepage water concentrations did not show a unitary trend. Nor a classification according to the soil texture nor that according to the soil type showed a specific behaviour exceeding the natural fluctuation range (Bielert et al., 1999). A classification of seepage waters as a function of soil texture and soil type was thus not possible. The median values of all 340 seepage water samples were used to calculate the inputs via drainages (Table 3-25).

Table 3-25 Heavy metal concentrations measured in the seepage water (Bielert et al., 1999).

	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
Concentration [µg/l]	0.72	0.14	4.60	4.00	<0.14[1)]	8.90	0.28	19

[1)] Half the quantification limit was used as emission factor

For inputs from drainages during the period 1985-2000, only the changed drain rates were considered as a result of different rainfall conditions. The heavy metal concentrations were not varied, as it may be assumed that heavy metal load changes do not affect the seepage concentration below the root zone within the given time period .

3.2.6 Groundwater

This pathway allows to determine the heavy metal load which is transported with the base flow (→ equation 2-10). In a first step, it had to be verified whether the heavy metal concentrations measured in the groundwater were applicable. Heavy metal concentrations in the near-surface groundwater are substantially determined by the geology of the aquifer, water chemism (water hardness, pH-value, ionic strength) and oxygen content. Sand and gravel aquifers usually exhibit increased heavy metal concentrations as a result of the more intensive contact between water and aquifer material (NLfB, 2000). Attention has to be paid to the fact, that only oxic groundwaters reflect the water quality of the groundwaters streaming towards the surface waters, as chemical alterations occur during the natural discharge of anoxic groundwaters. This is particularly true for the north-eastern German lowland (Behrendt et al., 2000).

In the groundwater data base of the Federal Environment Agency, data from 786 German groundwater surveying spots is being administrated to be able to give evidence on mean groundwater conditions and possible long-term changes. However, at the time of data provision, no measured values on heavy metals were available for the Federal States of Bavaria and North Rhine-Westphalia and only a

few for Schleswig-Holstein. Moreover, the data are not characterised by a unitary measuring period and all heavy metals of the Ordinance on Drinking Water were not determined for all groundwater surveying spots. No data are available e.g. for Hg. Table 3-26 lists the number of measured values, the share of measured values exceeding the quantification limit and the median of the groundwater concentrations. For values remaining under the quantification limit, 50 % of the quantification limit were included in the median calculation. This, however, causes considerable uncertainties as for the quantification of the load, due to the fact that these quantification limits fluctuate within a broad range. The metals Cd, Cr and Pb show a particularly high number of values that remain under the quantification limit.

Table 3-26 Number of measured values, number of values exceeding the quantification limit and median of heavy metal concentrations in groundwaters (groundwater data base of the Federal Environment Agency).

	As	**Cd**	**Cr**	**Cu**	**Hg**	**Ni**	**Pb**	**Zn**
Number of data	1708	1620	1645	1633	-	1631	1619	1666
Percentage above DL[%]	41%	26%	25%	39%	-	43%	15%	48%
Median [µg/l]	1,0	0,15	1,0	2,5	-	2,5	1,5	15

Schleyer/Kerndorff (1992) studied the groundwater quality on the basis of 2,800 water samples of about 170 water suppliers in the OFS in 1989. For the metals Cd, Cr, Hg and Pb, the provided median values from individual samples correspond, however, to the mean quantification limit. For these metals only approximate evidence can thus be given on the mean concentration. Moreover, a differentiation according to groundwater storeys was not possible.

In the further course of the project, the use of groundwater concentrations was left out of consideration: besides the described uncertainties of the data, the principle question had to be posed on whether measurements in the groundwater are appropriate to estimate heavy metal loads in the base flow fraction of surface waters. The required measurements have to integrate both the specific geogenous conditions of the surface waters' subsoil catchments and the anthropogenic contaminations reaching the surface waters by groundwater passage (e.g. agriculture, mining, regional industrial emissions). However, groundwater catchments may considerably differ from surface water catchments. Moreover, only surface-near oxic groundwaters are suited for this purpose, as otherwise the precipitation of heavy metals has to be considered at the moment of the natural discharge of anoxic groundwater into surface waters. In addition to this, it may not be excluded that the material used for well constructions might influence the measured heavy metal values in the ground-

water. Especially the high Zn values measured in the groundwater (see table 3-26) might originate from zinciferous well materials.

This is why the measured values of the German Geochemical Atlas were used. They were mainly collected from brooks of 1st or 2nd order at low water levels (representative for the base flow) and thus describe the load actually entering the surface waters by groundwater flux. The Federal Institute for Geosciences and Natural Resources (BGR, Hannover) published the first Geochemical Atlas in 1985 (Fauth et al., 1985). A total of about 80,000 surveying spots in the rivers of the OFS were evaluated. The analysis was then effected by means of AAS (atomic absorption spectrometry), which is why the quantification limits for Cd and Pb were frequently too high in source water. As, Cr and Hg have not been evaluated (Table 3-26).

At present, the Federal Institute for Geosciences and Natural Resouces (branch office Berlin) is working on a New Geochemical Atlas for Germany for the period 1999/2000 (Birke et al., 2001). Even though the sampling site density is considerably lower featuring 954 surveying spots, the New Geochemical Atlas was favoured, as it considers the NFS and as measured values are available for all required metals. Moreover, the use of the ICP-MS method allowed a further reduction of the quantification limits for heavy metals, so that, except for Hg, no concentrations remaining under the quantification limit were measured. So far, the Federal Institute for Geosciences and Natural Resources provided the median of all measured values as well as the geochemical background (modal value of the distribution function of all measured values) (Table 3-27). To evaluate the heavy metal inputs via groundwater the median of all measured values was used. It may be assumed that the large river basins are sufficiently well represented by the median, as the sampling points are homogeneously distributed over Germany based on 350-400 km^2 units. The regionalisation of the data may only occur after the New Geochemical Atlas has been completed. It is however worth striving for a regionalisation in the future, as the regional geogenous heavy metal load may fluctuate dramatically, especially in smaller catchments.

The data of the New Geochemical Atlas were taken as a basis for all three calculation periods, due to the fact that the differences between Old and New Geochemical Atlas may not be attributed to the actual changes of water quality. A temporal change of heavy metal concentrations in the groundwater occurring over the studied period could possibly be attributed to acidification processes.

Table 3-27 Median of all samples of the Old Geochemical Atlas (OGA, Fauth et al., 1985) and median of all samples and geogenous background of the New Geochemical Atlas (NGA, Birke et al., 2001) in µg/l.

	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
OGA: median of concentration	-	0.3	-	1.5	-	2.0	1.0	9.0
NGA: median of concentration	0.76	0.02	0.26	1.03	<0.01[1)]	3.39	0.11	3.0
NGA: geogenous background	0.37	0.008	0.19	0.68	<0.005	2.13	<0.02	0.47

[1)] Half the quantification limit was used as emission factor for the calculation

3.2.7 Urban areas: Sewer systems and not connected inhabitants

The sources and pathways of heavy metals via diffuse sources in urban sewer systems are schematically represented in figure 3-7.

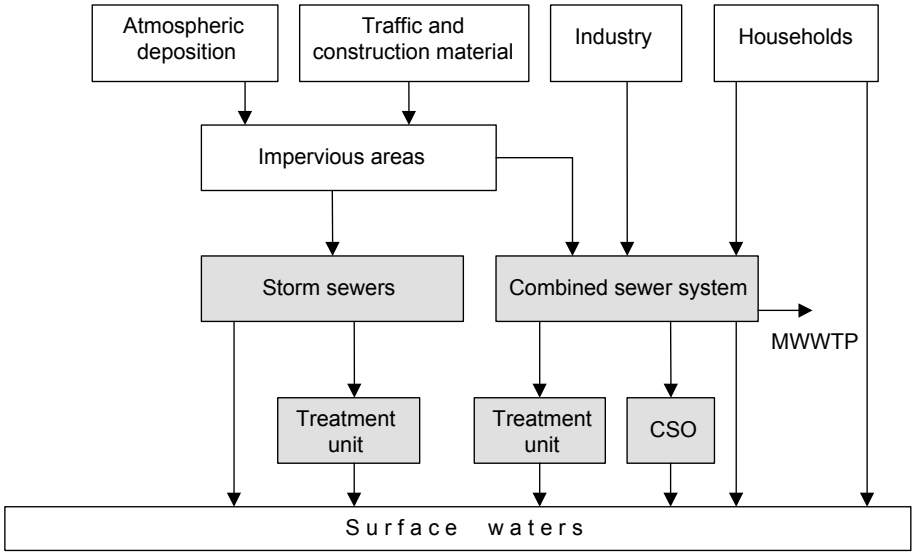

Figure 3-7 Sources and pathways of heavy metals from urban areas (changed according to Stotz/Knoche, 1999a).

The relative importance of the major pathways represented in figure 3-7 (combined/separate sewer systems, direct domestic discharge) may be derived from the distribution of the sewer systems and the share of households connected to sewers and wastewater treatment plants. For 1985 and 1995 this share may be drawn from

table 3-28. A mean value was generated for the OFS for 1985 on the basis of the 1983 and 1987 data (StaBu, 1983, 1987). No regional data was available in the Statistical Yearbook of the GDR (1986). Given that no topical statistical data was available for 2000 at the moment of the calculations, the 1995 data set was also taken as a basis for the year 2000.

Table 3-28 Share of households connected to sewer systems and wastewater treatment plants (Federal Statistical Office, 1983, 1987, 1998b, Statistical Yearbook of the GDR, 1986).

Federal State	**Population connected to sewer systems [%]**		**Population connected to MWWTPs [%]**		**Population connected neither to sewers nor MWWTPs [%]**	
	1985	**1995**	**1985**	**1995**	**1985**	**1995**
Baden-Wuerttemberg	97.6	98.2	95.3	97.6	2.4	1.8
Bavaria	86.6	92.2	82.6	90.5	13.4	7.8
Berlin	97.8	98.0	97.8	98.0	2.2	2.0
Brandenburg	-	61.9	-	61.1	-	38.1
Bremen	99.5	100	99.5	100	0.5	0.0
Hamburg	94.8	96.7	94.3	96.7	5.2	3.3
Hesse	98.2	99.3	89.2	97.2	1.8	0.7
Meckl.-Western Pomerania	-	75.3	-	70.7	-	24.7
Lower Saxony	84.4	90.5	83.2	90.3	15.6	9.5
North Rhine-Westphalia	91.8	95.5	91.0	95.3	8.2	4.5
Rhineland-Palatinate	93.3	97.5	83.0	94.1	6.7	2.5
Saarland	98.5	98.8	63.9	76.8	1.5	1.2
Saxony	-	78.8	-	64.2	-	21.2
Saxony-Anhalt	-	79.4	-	63.5	-	20.6
Schleswig-Holstein	83.7	90.5	82.1	89.9	16.3	9.5
Thuringia	-	89.4	-	53.6	-	10.6
Old Federal States	**91.6**	**95.2**	**87.8**	**94.0**	**8.4**	**4.8**
New Federal States	**70.8**	**77.3**	**55.3**	**62.5**	**29.2**	**22.7**
Germany	**-**	**90.2**	**-**	**85.7**	**-**	**9.8**

The percental share of separate and combined sewer systems for the Federal States is represented in figure 3-8.

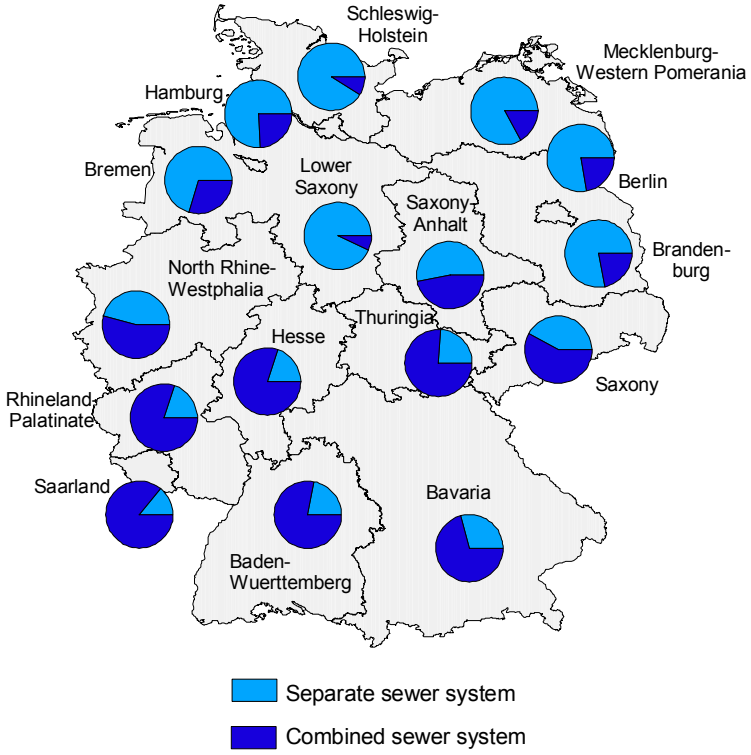

Figure 3-8 Share of separate and combined sewer systems for the Federal States (StaBu, 1998b).

Specific heavy metal input from impervious urban areas

The major sources for heavy metal pollution in runoff from urban areas are atmospheric deposition, road traffic (abrasion from tyres, brakes and asphalt, waste gases), contamination of paved areas as well as the corrosion of metallic surfaces. Experiences gathered in urban hydrology showed, that the annual pollutant loads washed-off from paved areas are mainly determined by the amount of pollutant deposition on the surface rather than by runoff concentrations during descrete storm events (Fuchs/Hahn, 1999). Literature, however, usually only specifies the pollutant concentrations measured in the runoff. Both the specific heavy metal input from impervious urban areas and its temporal development had thus to be derived from concentration data.

Within the frame of an ATV project (German Association for Water, Wastewater and Waste), heavy metal concentrations in stormwater runoff and combined sewer overflows were analysed among others (Brombach/Fuchs, 2002). From these data, measured values were extracted for “Central Europe” (Germany, Switzerland, France, the Benelux countries and Great Britain).

The heterogeneity of the sampling sites (storm sewers in residential areas, street runoff, runoff from metal roofs etc.) and the complexity of external factors such as e.g. the duration of precipitation respectively dry periods as well as the dynamic behaviour of pollutants in the wash-off process, lead to a broad range of concentrations during rainfall events (Boller, 1997). However, the data used should cover comparable ranges, as the fluctuations could otherwise overlay a possible temporal trend for the aforementioned reasons. To identify "outliers", a ranking was drawn up for all measured values of a metal. The values of the upper and lower end that could distinctly be identified as outliers, were eliminated. The result is illustrated in figure 3-9 for Cd.

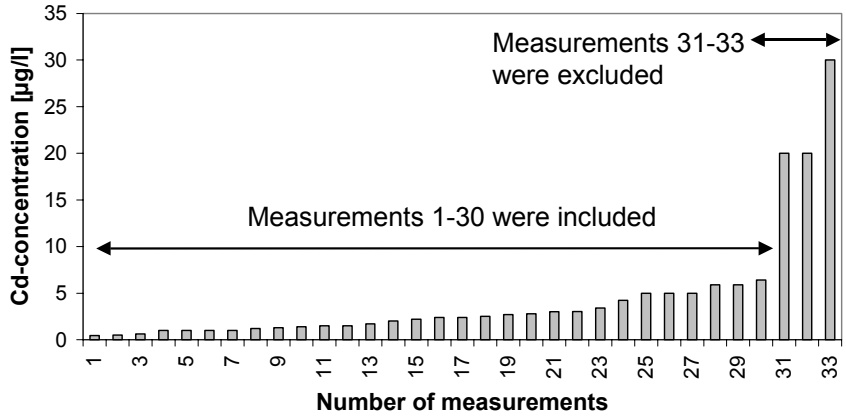

Figure 3-9 Ranking of Cd-concentrations in storm sewers.

The remaining data sets were used to calculate mean values for the measured years. Figure 3-10 shows the concentrations in the runoff for the period 1980-2000.

While the concentrations for Cd, Pb and Ni show a distinct downward trend, there is no clear tendency in the measured data over the studied period for Cr, Cu and Zn (figure 3-10). Both, the curve gradients and the results obtained on diffuse heavy metal inputs from urban areas are discussed in chapter 6.3.7.

The MONERIS model allows not only mere load calculations, but also an estimation of the runoff from storm sewers. Based on this model, specific heavy metal inputs from impervious urban areas were derived from the concentration. For this purpose, the prominent concentrations were determined from the regression lines for 1985, 1995 and 2000, see figure 3-10.

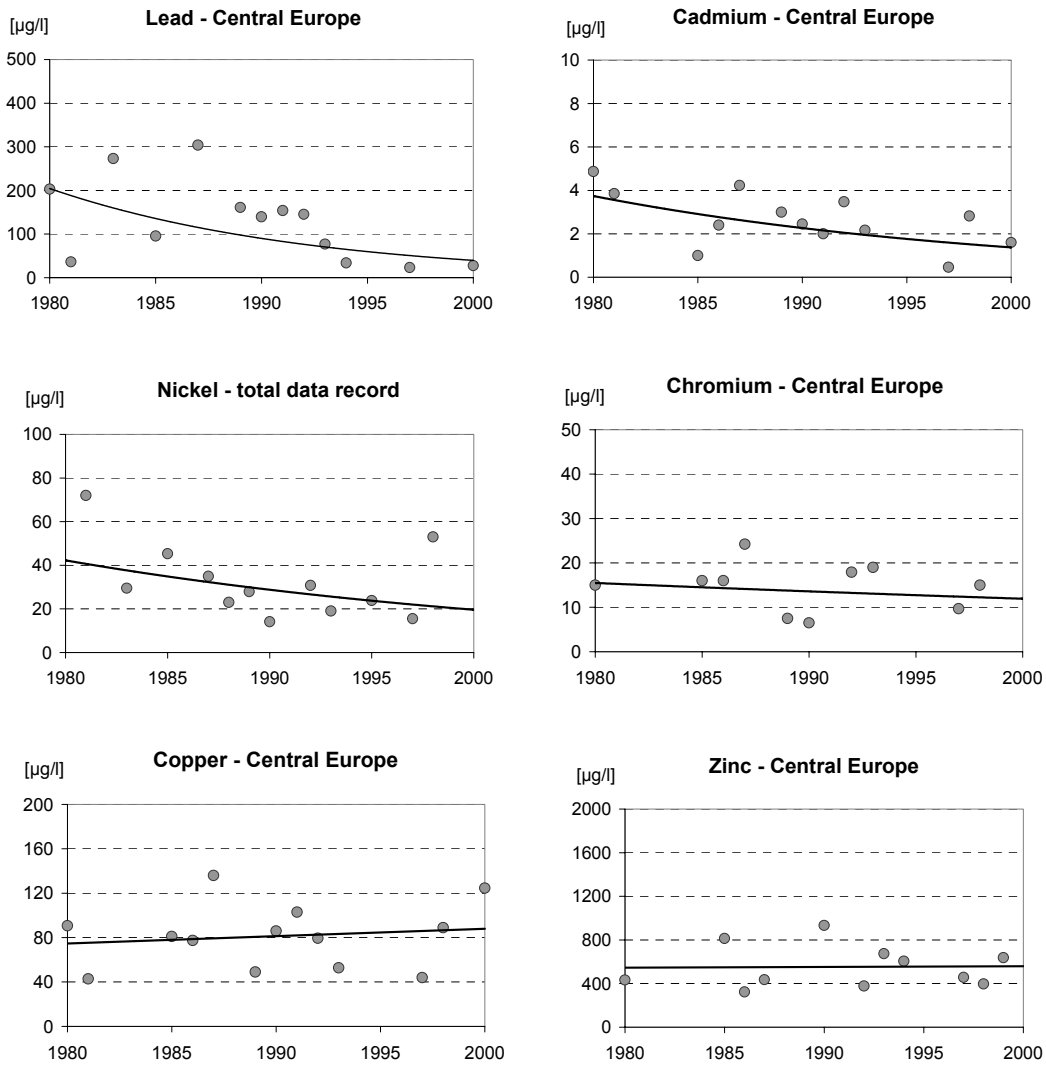

Figure 3-10 Concentrations in the runoff from paved areas for 1980-2000.

As for As and Hg the number of measured data did not allow to calculate the specific heavy metal input from impervious urban areas following the same procedure, they were directly derived from the data found in literature and from atmospheric deposition. Stotz/Knoche (1999a) specify a heavy metal input from impervious urban areas of 2 g/(ha·a) for Hg, which is taken as a basis for 1995. Buffleben et al. (2001) specify As-concentrations in the runoff of 1997/1998 corresponding to a heavy metal input from impervious urban areas of 9.4 g/(ha·a). Subsequently the values were extrapolated to the reference years, given the changes of the atmospheric deposition (→ chapter 3.2.1).

Due to the geographic situation of the sampling sites, the specific heavy metal inputs from impervious urban areas calculated for 1985 are only representative for the OFS. No data were available for the runoff from paved areas of the former GDR. Given the differing emission situations, the specific heavy metal input from

impervious urban areas of the former GDR was increased by the deposition difference between the OFS and the GDR in 1985 (chapter 3.2.1).

Moreover, it has to be considered for the former GDR that in 1985, both in the private sector and for newly constructed public buildings, no Cu was used as building material for roofs and gutters. This is why inputs via corrosion are only to be expected from Cu- roofs of historical buildings. For Cu the specific heavy metal input from impervious urban areas was thus reduced by the difference of inputs via corrosion in the OFS and the former GDR[2]. The resulting specific heavy metal inputs from impervious urban areas are listed in table 3-29.

Table 3-29 Specific heavy metal input from impervious urban areas for 1985, 1995 and 2000 in g/(ha·a).

	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
Old Federal States 1985	18.6	10.7	53	276	2.70	112	505	1950
New Federal States 1985	40.0	48.0	55	264	3.70	141	527	2295
Germany 1995	9.6	6.4	47	300	2.00	77	222	1972
Germany 2000	9.2	5.1	44	310	2.05	63	145	1985

3.2.7.1 Separate sewer systems

Altogether 46.5 % of the sewer pipes in Germany account for the separate sewer system, the northern Federal States being drained to about 80 % in mainly separate systems (figure 3-8). The pathways to be considered for the separate system are *storm sewer effluents* and *discharges from stormwater tanks* (figure 3-7). The storage volume of storm water tanks in separate sewer systems was 637,000 m^3 for 1987 in the OFS and 706,000 m^3 for 1995 for all of Germany. This corresponds to about 10 % of the total runoff entering the surface waters via storm sewers (StaBu, 1987, 1998b). Within the frame of a literature study, Stotz/Knoche (1999a) state that the published figures for the pathway *storm water tank* are not very telling and thus inappropriate for the calculation of loads, given that the studies concentrated on short periods and on a small data base. Moreover, it may be assumed that the

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2 For the Old Federal States the load share resulting from corrosion for 1985 corresponds to about 1/3 of the Cu-inputs via surface water sewers. This corresponds to a specific heavy metal input from impervious urban areas of about 100 g/(ha·a). About half of it originates from roof drainage (gutters), the other half from the roofs themselves (Wirtschaftsvereinigung Metalle, 2001 and chapter 6.3.7). The share of historical buildings within all buildings featuring Cu-roofs was estimated to about 50 % for the Old Federal States. Based on this information, the specific heavy metal input from impervious urban areas for Cu-roofs of the former GDR is 25 g/(ha·a).

retention efficiency of the tanks is very low for heavy metals. The impact of storm water treatment on heavy metal input has thus not been considered. The quantification of heavy metal inputs via storm sewers was effected according to equation 2-11 with the specific heavy metal input from impervious urban areas listed in table 3-29.

3.2.7.2 Combined sewer systems

The untreatable respectively unstorable water volumes of combined systems that contain both storm water runoff and sewage, are discharged into the receiving waters by means of *combined sewer overflows* or *stormwater tanks* (figure 3-7).

The surface specific portion of heavy metal inputs from impervious urban areas corresponds to the values determined for separate sewer systems (Table 3-29). To estimate the additional load from domestic and industrial-commercial sewage, data are required on inhabitant specific heavy metal emissions and the heavy metal concentrations in industrial-commercial sewage (→ equation 2-13).

Nolte (1986) estimated heavy metal loads in domestic sewage for all wastewater treatment plants in the Federal State of Hesse for 1985. Based on the number of Hessian inhabitants connected to wastewater treatment plants (StaBu, 1983, 1987), inhabitant specific loads were derived. The years 1995 and 2000 are mainly based on inhabitant specific loads determined by Zessner (1999) after literature studies.

For the former GDR it may be assumed, that in 1985 hardly any copper pipes were used for domestic water supply. The inhabitant specific Cu-input was thus reduced by the load originating from the corrosion of Cu-pipes[3].

Jenkins/Russel (1994) determine the inhabitant specific As-input with 0.16 g/(I·a), 73 % of which originate from detergents. This value is to be increased by the As-load of tap water. According to Schleyer/Kerndorff (1992), the median of As in Western German drinking water resources is of <0.5 µg/l. Assuming a water consumption of 130 l/(I·d) and 50 % of the quantification limit, an additional load of 0.012 g/(I·a) arises. The inhabitant specific heavy metal data used is listed in table 3-30.

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3 Zessner (1999) specifies the share of tap water Cu-load in domestic sewage with 19-58 % (average value: 38.5 %). The ATV (1984) specifies the Cu-load in tap water with 20 µg/l. The median of the Cu-concentrations in Western German drinking water resources is of 3.6 µg/l (Schleyer/Kerndorf, 1992). The 82 % of Cu contained in tap water do thus result from corrosion. On the basis of this information, the inhabitant specific Cu-discharge was reduced by 32 % for the area of the former GDR in 1985.

Table 3-30 Inhabitant specific heavy metal input in g/(I·a).

	Year	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
Total load[1)]	1985	0.17[6)]	0.08	1.5	4.2/2.5[5)]	0.06	1.4	2.3	27.6
Dissolved load[4)]		0.13[6)]	0.06	1.4	3.1/2.1[5)]	0.05	1.1	2.2	18.5
Total load[1)]	1995	0.17[6)]	0.05[2)]	1.5[1)]	4.0[2)]	0.018[3)]	1.4[1)]	1.6[2)]	23.0[2)]
Dissolved load[4)]	+2000	0.13[6)]	0.04	1.4	2.9	0.015	1.1	1.5	15.4

[1)] Nolte (1986); [2)] Zessner (1999); [3)] The Netherlands (2000); [4)] dissolved inhabitant specific load was calculated from total inhabitant specific load based on information given by Zessner (1999); [5)] inhabitant specific load of Cu for the former GDR in 1985; [6)] Jenkins/Russel (1994)

The evaluation of a mean heavy metal concentration in indirect discharges goes along with considerable uncertainties, given that industrial-commercial discharges depend to a very large extend on local conditions. Industrial-commercial sewage which is discharged into MWWTP has, according to the 1986 Water Resources Policy Act, to be pre-treated following the state of the art. For heavy metals the concentrations given in table 3-31 are to be reached according to guideline A 115 of the ATV (German Association for Water, Wastewater and Waste), (ATV-DVWK, 2000). The data represented corresponds to the state of 1994. The first draft of the working sheet dates from 1970, it was revised both in 1983 and 1994. The recommended monitoring values were constantly reduced respective to the technical development as for the pre-treatment of industrial sewage. It may thus be assumed that the heavy metal concentrations in industrial-commercial sewage have been drastically reduced since the mid-eighties until today.

The 1985 heavy metal concentrations in industrial-commercial sewage were derived on the basis of the heavy metal loads contained in the indirect discharges of all Hessian wastewater treatment plants (Nolte, 1986) and the treated commercial sewage volume in the Federal State of Hesse (StaBu, 1987). Ried (1990) gathered heavy metal concentrations in sewage for different branches. The fluctuation range may also be taken from table 3-31. All concentrations specified by Nolte (1986) are situated within the range determined by Ried (1990) and thus reveal to be plausible. Lacking data did not allow a differentiation between OFS and NFS. For 1995 and 2000 the concentrations specified by Schäfer (1999) were used. No data was available in literature for As.

Table 3-31 Heavy metal concentrations in industrial-commercial sewage in µg/l.

	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
1985	50[1)]	43	382	688	5.8	268	514	2,046
1995/2000	5.0[1)]	4.6	44	149	1.5	50	152	523
ATV A 115 (1994)	500	500	1,000	1,000	100	1,000	1,000	5,000
Nolte (1986)	-	43	382	688	5.8	268	514	2,046
Ried (1990)	-	3-134	60-20,140	37-7,040	3-134	40-740	-	280-3,890
Schäfer (1999)	-	4.6	44	149	1.5	50	152	523

[1)] Emission factors for As were estimated as percentage of the ATV critical values. It was assumed that the occurrence of As in commercial wastewater is corresponding to Cd.

3.2.7.3 Sewer systems not connected to wastewater treatment plants

If a sewer system is not connected to a wastewater treatment plant, the whole untreated sewage and storm water runoff is discharged into the receiving waters.

As regards the heavy metal input, urban areas are comparable to areas connected to storm sewers of the separate system (Table 3-29). Moreover, heavy metal inputs via domestic and industrial-commercial sewage also have to be considered (→ equation 3-14). For households it is assumed that the particle share of the heavy metal discharge is separated during primary sludge removal or in septic tanks and is transferred to the MWWTP. The whole dissolved share, however, is conducted into the sewer system and subsequently into surface waters. In the case of heavy metals, the major portion of the inhabitant specific heavy metal discharge exists in the dissolved phase and originates for its majority from detergents (Koppe/Stozek, 1999, Zessner, 1999). Zessner (1999) specifies the heavy metals originating from detergents and tap waters in domestic sewage with 71 % for Cd, 98.5 % for Cr, 73.5 % for Cu, 86 % for Hg, 80 % for Ni, 95.5 % for Pb and 67 % for Zn. The dissolved share of the inhabitant specific heavy metal discharge was calculated on the basis of this data (Table 3-30). The heavy metal concentrations in industrial-commercial sewage were taken over from table 3-31.

3.2.7.4 Not connected households

The emission factors used for the quantification of heavy metal loads originating from households that are not connected to a sewer system, are the specific heavy metal input from impervious urban areas from table 3-29 and the dissolved inhabi-

tant specific heavy metal discharge from table 3-30. For all heavy metals a soil retention of 95 % was assumed (→ equation 2-15).

3.2.8 Shipping

Heavy metal discharges into surface waters via direct uses for shipping are only significant for the metals Cu, Pb and Zn (→ equation 2-16).

The number of business ships is based on data provided by the Statistical Yearbook of Germany (1985, 1999b) and the Statistical Yearbook of the GDR (1986). The Statistical Yearbook of Germany collects the number of business ships by waterway regions. The classification of the ships occurs by their port of registration. Moreover, it is specified whether the ships dispose of a navigation licence for the Rhine River. Assuming that ships disposing of a licence for the Rhine do not exclusively navigate on this waterway, only half of the Rhine vessels were related to the Rhine catchment. The Statistical Yearbook of the GDR (1986) merely specified the total number of river vessels. The number of ships was thus proportionately allocated to the river basins, according to the share of the basins in the total area of the GDR.

Lead enters the surface waters via plombiferous propeller shaft grease, which is used for an estimated 80 % of business ships. The input per ship is of 1.5 kg/a. Zinc is emitted by electrodes used for corrosion protection purposes. According to information of the shipping industry (Dönneweg, 2000), zinc electrodes are only used on 5 % of the river vessels in brackish or sea water. Zn-inputs were thus merely considered for coastal areas. The lifetime of an electrode (100 kg) is of 2 years (Mohaupt et al., 1998).

The exact number of sporting boats is registered neither by the Federal Statistical Office nor by the navigation authorities. It was thus estimated following the ICPR relative to the total area of surface waters (58.8 ships/km^2) (Mohaupt et al., 1998). The changes in the number of sporting boats between 1985-2000 could not be determined either.

Cu-containing antifoulings are used on sporting boats to eliminate foulings on their submerged part. About 25 g Cu/a are emitted per boat (Mohaupt et al., 1998).

4 Lindane (γ-HCH)

Lindane is a universal pesticide used in Germany until the 1990ies. The persistence of lindane in the environment is of crucial importance. As it is only slowly degrading, it may be transported over long distances due to its long resident times within the various environmental compartments. This is why lindane has also been detected in regions that are very remote from the original sites of its application, e.g. the Arctic (AMAP, 2000).

Lindane enters the environment exclusively via anthropogenous activities. Knowing its major application fields and the quantities used are essential conditions for input quantifications. The first section of this chapter thus provides a survey on the required background information.

4.1 Characteristics and application of lindane

4.1.1 Behaviour of lindane in the environment

Lindane is synthesised from benzene and chlorine in the presence of ultra-violet light. The mixture thus generated comprises 8 to 9 streroisomere hexachlorcyclohexane (HDH)-compounds. Lindane (γ-HCH) is the only isomer presenting an insecticide effect and in technical mixtures ready for application lindane typically has a share of 15-20 % (Heinisch, 1992).

HCH-isomeres are distinguished by their physical-chemical characteristics and thus by their persistence, diffusion and biological and geological accumulation capacities. Lindane (γ-HCH) is extremely volatile and dominantly transported in the gas phase through the atmosphere (LfU, 1993). Given their low sorption coefficients, anorganic sediments merely dispose of a low sorption capacity for lindane. However, in organic matter it accumulates easily. It is thus strongly adsorbed in soils containing a large amount of organic matter, but its mobility increases in humus-poor, sandy soils (WHO, 1991). In surface waters, lindane is usually dissolved. In the Elbe river, a K_s-value (distribution coefficient between water and suspended matter phase) of 460 has been determined for lindane (Agency for the Environment Hamburg, 1991).

The half-lives of lindane given in literature fluctuate within a broad range. In soils, the half-life varies depending on soil type and climatic region and amounts to 40-70 days in Central Europe. (WHO, 1991). Bintein/Devillers (1996) report a half-life

in the air of about 2 years. Lindane is resistant against hydrolysis and stable to a high extent in pure water and at pH 7 to pH 3 and 25°C. In the water, the half-life may thus come to several months or years (Gunkel, 1994). The degradation products of lindane mainly consist in chlorinated benzenes and phenols. In soils and plants, further degradation products may occur due to microorganisms and UV-irradiation, including the generation of α- and β-HCH (Hoffmann et al., 1980).

Due to the fact that lindane is a broad-spectrum insecticide, it not only destroys specific damage causing insects but affects the whole biological environment. Given its lipophile characteristics, lindane is well resorbed in the adipose tissue and may thus be found in food items, especially in meat and milk products as well as in human milk. Lindane may also have a growth or function inhibiting effect on plants and microorganisms (Hoffmann et al., 1980).

4.1.2 Extent of use, production

The major fields of lindane application were the cultivation of maize and sugar beets as well as seed treatment. It was used furthermore in sylviculture, wood and timber protection as well as in pest control in general.

Lindane has been commercially used since 1949 (WHO, 1991). In the late 1980ies, production was brought down in the OFS (Detzel et al., 1998). In the former GDR lindane production had already been stopped in 1982 (Heinisch, 1992). The isomeres arising as by-products of lindane production were almost exclusively dumped on waste disposals, the sites of which cause considerable environmental problems today (Hoffmann et al., 1980; Heinisch, 1992; Davis, 1998).

Since the coming into force of the 1986 Pesticide Act, stipulating that the “use of chemical pesticides is to be limited to the necessary extent”, lindane has been increasingly replaced by new substances (Zschaler/Schmidt, 1999; Schmidt, 1999). Since 1992, the use of lindane has been prohibited for the storage of cereals and cereal products. However, the use of lindane-containing pesticides and wood preserving agents was still allowed (Kussatz et al., 1999).

Following a report of the Austrian Government, the European Committee on Plant Health voted for a prohibition of lindane in 2000 (Harvey, 2000). In Germany, lindane production was already stopped in 1999 (BBA, 2001). However, considering its worldwide production, the annual average for 1990-1995 was still of 3,222 t. In Western Europe alone, an annual average of about 2,055 t was produced (Detzel et al., 1998).

4.1.3 Applied masses

The Federal Biological Research Centre (branch office Kleinmachnow) provided data on lindane sales within the field of application of the Pesticide Act (corresponds to domestic sales) for the OFS for the period 1987-1990 and subsequently for the whole area of Germany (BBA, 2001). However, this data has not yet been published by the Federal Biological Research Centre and may thus merely be quoted qualitatively. The annual sales in the former GDR were published by Schmidt (1994).

Differentiated information on regional lindane masses as well as quantitative data on the major application sectors *agriculture, sylviculture* and *wood and timber protection* are only partly available and had thus frequently to be estimated. The extent of the use of lindane-containing hygiene products in households, camping sites and open-air swimming pools is unknown and the additional masses used in these sectors could thus not be considered.

Use of lindane in the Old Federal States before 1990

The domestic sales of lindane have only been collected since 1987 for the OFS in consequence of the Pesticide Act (BBA, 2001). This is why, for the period 1983-1987, precise mass data are only available for the last year. For 1981, the lindane mass used in the OFS is estimated to 250 t (Detzel et al., 1998), which is considerably higher than the figure known for 1987. It has thus been assumed that between 1983 and 1987 the mean lindane use was higher than in 1987.

TNO (1991) (Netherlands Organisation for Applied Scientific Research) recommends to estimate the total lindane mass for the early 1980ies on the basis of specific application masses of 2 kg lindane per km^2 of agricultural land and 0.2 g lindane per inhabitant. This provides for an annual total mass of 162 t for the OFS. Assuming that this figure is representative for the early 1980ies and for the mass sold in 1987, the average lindane mass used in 1983-1987 is of an estimated 150 t/a. This corresponds to a specific mass of 0.6 kg/km^2 relative to the surface of the OFS.

According to data of the WHO (1991), about 80 % of the total lindane volume produced is used in agriculture worldwide. In Germany, 70-80 % of the agriculturally used lindane was assigned to pesticide purposes, most of all in maize and sugar beet cultivation. 15-20 % were used for seed treatment (WHO, 1991). On the basis of this data and of the quantities assumed for the other major fields of application, the amount of lindane brought out in agriculture was estimated to 110 t/a. The share used in seed treatment was determined to 17.5 %.

For sylviculture, the applied annual pesticide mass was limited to an estimated 1.5 % of the areas covered by forests in the mid-eighties (Wulf, 1986), yet, wood

engraver beetles were controlled by means of lindane-containing products up to the mid-eighties (Wulf, 1985, Wulf et al., 1993). Data on specific application quantities are not available. In the former GDR about 0.5 kg/ha lindane were used to control heavy nun-moth infestations (Heinisch, 1992). Taking this figure as a basis, a total of 56 t results for 1.5 % of the forest surface of the OFS. This result certainly has to be considered as the upper limit. The lindane masses used in sylviculture were thus estimated to 20 t/a.

In 1994, an estimated 30 t of lindane were contained in wood preservatives in Germany (Detzel et al., 1998). Literature does not specify to what extent the lindane quantity contained in wood protection agents has changed since 1985. Given that no legal limitations were issued for a use in this field, one may proceed from the fact that the quantities applied in 1985 were comparable to those applied in 1994. This quantity was assumed to be of 20 t/a for the OFS.

Use of lindane in the former GDR before 1990

In the former GDR lindane was very important as active substance in numerous pesticides in agriculture and sylviculture, horticulture, veterinary and stable hygiene as well as in some fields of material protection and was frequently applied in combination with DDT. After DDT had been gradually replaced by other pesticides in almost every application field since 1971, the importance of lindane grew thereafter. However, in the course of the 1980ies, it became subject to a downward trend (Heinisch, 1992). The lindane quantities used in the GDR are shown in figure 4-1. Altogether, the lindane consumption was reduced from 200 t in 1980 to 76 t in 1989 (Schmidt, 1993). For the period 1983-1987, the total lindane quantity was calculated with 110 t/a. Relative to the area of the former GDR this corresponds to a specific mass of 1 kg/km^2.

In the mid-eighties, an extremely high nun-moth occurrence in the forests led to a special authorisation to apply DDT-containing products (see figure 4-1). Combination products of lindane and DDT were applied via plane on about 60,000 ha in 1983 and on 250,000 ha in 1984 (Schmidt, 1993, press office „der Wald“, 1993). The sales volume of the two major DDT/lindane products “Aerosuper” and “Spritzaktiv” allowed an evaluation of the lindane volume used in sylviculture. It was of 28 t in 1983 and 116 t in 1984. For the period 1983-1987 an annual average of 30 t/a was applied (Heinisch, 1992).

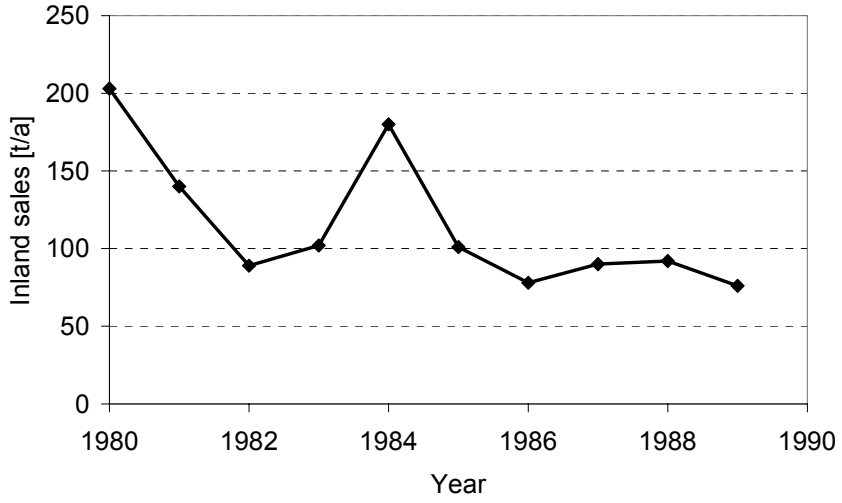


Figure 4-1 Lindane sales volume in the former GDR between 1980-1989 (Schmidt, 1993).

Lindane-containing agents for the protection of materials represent a quantitative uncertainty factor. Until 1988, wood preservatives such as “Hylotox” contained an estimated annual 7.5 t of lindane (Heinisch, 1992). The total volume of lindane used in material preservation was estimated to about 10 t for 1985.

For 1985, no precise data is available on lindane masses used in agricultural plant protection. The pesticide register of the former GDR specifies for 1989, that 25 t of lindane were supplied for agricultural purposes (Heinisch, 1992). For 1985, however, this figure appeared too low. The lindane volume supplied to agriculture was thus estimated as the difference between the total amount (110 t) and the quantities used in sylviculture (30 t) and material preservation (10 t), e.g. 70 t/a.

Use of lindane in Germany after 1990

The development of German inland sales between 1990 and 2000 is shown in figure 4-2, based on the data provided by the Federal Biological Research Centre for Agriculture and Forestry (2001, unpublished).

For the mid-nineties, only lindane emissions from wood preservatives are available. The masses may be derived from German wood preservative consumption data and from its average lindane content. With an average lindane content of 0.15 % for solvent- containing wood preservatives and a sales volume of 200,000 t/a, the total volume amounts to 30 t/a. In early 1997, lindane was to be replaced by another active substance (Detzel et al., 1998).

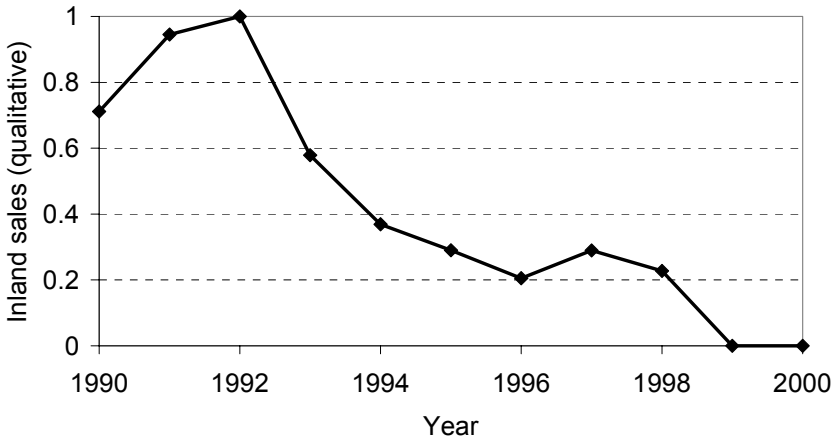


Figure 4-2 Development of German lindane inland sales (standardised) from 1990-2000 (according to BBA information, 2001, unpublished).

Following a bill passed by the German Bundestag in 1993, the NFS were entitled to use up, until late 1994, the remaining stocks of pesticides that were in part no longer authorised. For lindane-containing products the bill provided a sales prohibition. However, the products could be used up without restriction outside the spa and water protection zones (Ökologische Briefe, 1993).

In the field of sylvicultural plant protection, the last lindane-containing product against wood breeding insects was used in the OFS until late 1993 and in the NFS until 1994. In agriculture a lindane-containing product was still authorised until late 1997, no data are however available on precise masses (Detzel et al., 1998). The quantities applied in agriculture and sylviculture in 1995 were thus evaluated as the difference between the mean lindane mass for 1993-1997 (figure 4-2) and the known lindane content in wood protection agents. The resulting difference was apportioned as follows: for sylviculture it was assumed, that lindane-containing products were used only up to 1993 in the OFS and up to 1994 in the NFS. Its application in agriculture was assumed until 1997. Compared to the lindane contents in wood preservatives, its application in agriculture is only of little importance in the mid-nineties.

4.2 Lindane input into surface waters

The following sections describe the emission factors for the evaluation of lindane input via point and diffuse sources into surface waters. The considered relations existing between sources and pathways are shown in figure 4-3.

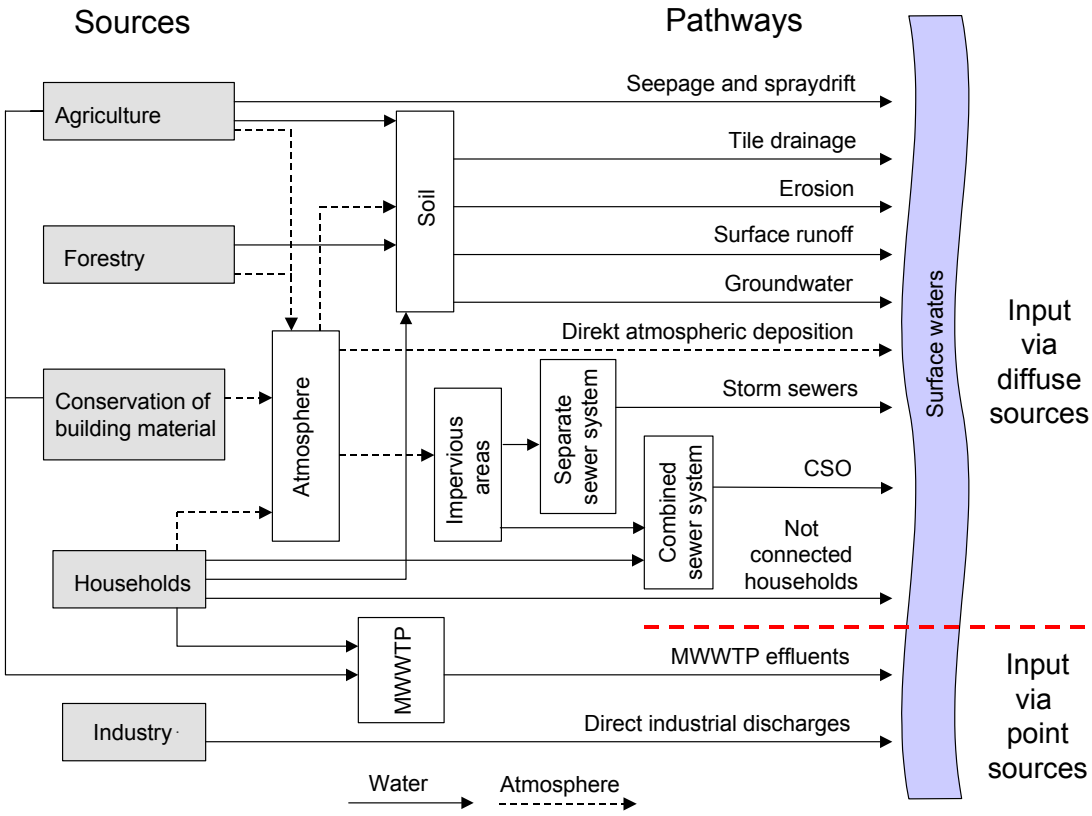


Figure 4-3 Sources and pathways for lindane.

4.2.1 Lindane input via point sources

4.2.1.1 Municipal wastewater treatment plants

Seel et al. (1994) and Fischer (1996) emphasised the significance of effluents from municipal wastewater treatment plants for pesticide input into surface waters. The substances enter the wastewater treatment plants by spray gun cleaning, disposal of pesticide remainders, trickling losses and storm water runoff (Seel et al., 1994). Moreover, domestic lindane inputs should also be considered due to the use of lindane for hygiene purposes and its presence in human excrements.

The evaluation of lindane input via municipal wastewater treatment plants for the periods 1993-1997 and 1999/2000 was conducted following equation 2-1. Lindane concentrations in the effluent of wastewater treatment plants range between 19-28 µg/l according to Hansen/Dizer (1998). Additionally, the measured values of two wastewater treatment plants in Schleswig-Holstein were available (Fischer, 2001).

The mean concentrations were calculated with < 10 and 29.2 µg/l for these plants and are thus comparable to those of Hansen/Dizer (1998). For both years the mean value of 23.5 µg/l from the data by Hansen/Dizer was taken as a basis.

No effluent concentrations were available for the period 1983-1987, the lindane input into surface waters was thus calculated following equation 2-2 by means of the MONERIS model. The domestic lindane input was determined on the basis of the number of connected inhabitants and a specific lindane discharge of 12 mg/(I·a) (The Netherlands, 2000). An additional input caused by runoff components was considered by multiplication of the treated runoff portion and an average lindane concentration of 24 µg/l (chapter 4.2.2.3). Based on sewage sludge concentrations, the eliminated fraction in wastewater treatment plants was assumed with 10 % for mechanical respectively 50 % for biological processes.

4.2.1.2 Direct industrial discharges

The data on lindane as well as the heavy metal inputs via direct industrial discharges were gathered from the respective authorities for the years 1995 and 2000 within the frame of a nation-wide study (see chapter 3.1.2). It has to be considered, however, that the quantities of lindane which are still emitted via direct industrial discharges are very low and that the concentrations generally remain under the quantification limit. The evaluation of lindane emissions for 1985 in the former GDR revealed particularly complicated. At that time, lindane was no longer produced in the GDR, some lindane-containing end products were, however, still composed. Data on lindane pollution in sewage water is available for a total of four plants. Together with additional data on sewage volumes it contributes to the evaluation of the 1985 lindane loads (Heinisch, 1992; ICPR, 1992).

4.2.2 Lindane emissions via diffuse sources

4.2.2.1 Atmospheric deposition on the water surface

Model results of the Meteorological Synthesizing Centre (MSC-East, Moscow) were available for the calculation of inputs via atmospheric deposition on the water surface (→ equation 2-3). The data was provided in a 150 x 150 km grid for 1985 and 1995. At the moment of the conclusion of the project, the calculations for 1999 and 2000 were not yet finished (MSC-East, personal information), no data was thus available for 2000. Figure 4-4 shows the atmospheric deposition for 1985, 1990 and 1995. Deposition visibly decreased between 1985 and 1990. Despite of reduced

lindane emissions in Germany since 1990 (chapter 4.1.3), the deposition rate increased again between 1990 and 1995 in Southern and Central Germany, in the West it even reached values exceeding those of 1985. The lindane emissions underlying the MSC-East model calculations are based on expert estimations (MSC-East, 2001). For France the emissions into the atmosphere doubled between 1990 and 1996. A transboundary atmospheric transport may thus be assumed to have caused the load increase in Germany.

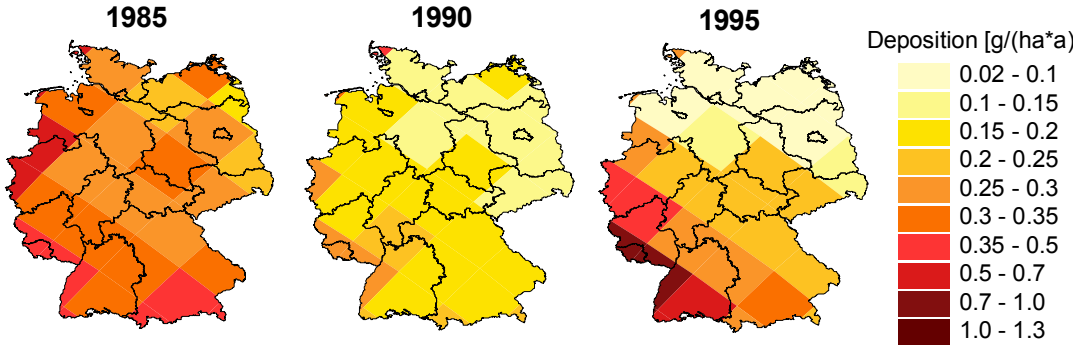


Figure 4-4 Lindane deposition rates for 1985, 1990, 1995 (MSC-East, 2001).

To estimate the atmospheric deposition for 2000, measured values of the Federal Environment Agency were additionally evaluated (UBA, 2000, 2001). Since 1994 the wet-only deposition has been collected at the surveying station Zingst (figure 4-5). As can be seen in figure 4-5, the measured values of the observed period show a high fluctuation rate and do not suggest any trend. This may be caused by fluctuating annual precipitation depths (UBA, 2000). Given that no temporal variations may be derived from the measured data, the same atmospheric deposition was supposed for both 1995 and 2000 (figure 4-4). The actual development of lindane deposition in Germany from 1995-2000 may finally only be estimated when the MSC-East simulation results are available for 1999/2000.

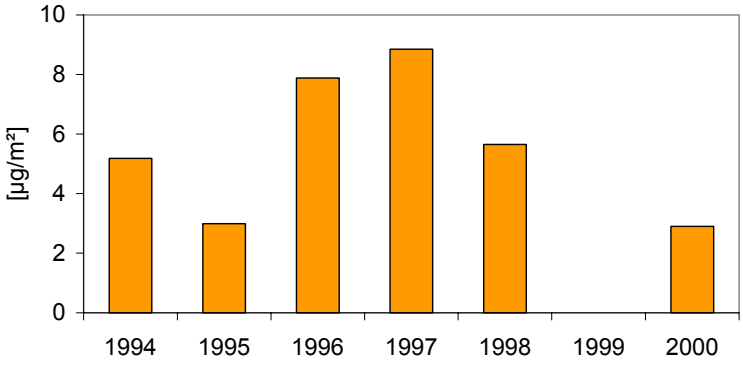


Figure 4-5 Lindane deposition at the surveying spot Zingst (wet-only) (UBA, 2000, 2001).

4.2.2.2 Seepage on farmyards and spraydrift

The input via seepage on farmyards and spraydrift (→ equation 2-5) was calculated on the basis of the total lindane quantity used in agriculture. This quantity was determined in chapter 4.1.3 for the OFS and NFS. No data is available on the regional distribution of the masses. The lindane quantities were thus distributed separately to the river basins of the OFS and NFS in relation to their agricultural areas. No emissions were calculated for the year 2000 (see chapter 4.1.3). The share of lindane entering the surface waters via seepage on farmyards and spraydrift was assumed of 0.1 % (ICPR, 1999).

4.2.2.3 Runoff from unpaved areas

The lindane load washed off into surface waters as a consequence of lindane application on agricultural areas and forests was quantified on the basis of the lindane quantities used in plant protection, i. e. the quantities applied in sylviculture and agricultural plant protection were used (chapter 4.1.3). The calculation was performed according to the method described in chapter 4.2.2.2. Following the method used in agriculture, the lindane masses applied in sylviculture were distributed separately to the river basins of the OFS and NFS, in relation to their forested areas. The ICPR (1999) specifies the share of lindane input discharged into surface waters by runoff from unpaved areas with 0.1 %.

Moreover, the lindane load resulting from rain water concentrations has to be considered (→ equation 2-6). Due to its seasonal application, concentrations in the

precipitation exhibit pronounced variations over the year (Dubus et al., 2000). This is why only annual averages are to be used. For 1995 and 2000, measured values of the surveying station Zingst were available (UBA, 2000, 2001). For 1985 the mean rain water concentration was calculated from the data provided by MSC-East on wet-only deposition (MSC-East, 2001). Mean lindane concentrations in rainfall may be drawn from table 4-1.

Table 4-1 Lindane concentrations in rain water in µg/l.

	Year	**Lindane [ng/l]**
Average from wet deposition (MSC-East)	1985	24
Station Zingst, wet-only (UBA)	1995	5.0
Station Zingst, wet-only (UBA)	2000	4.2

4.2.2.4 Erosion

The calculations on input via erosion (→ equation 2-7) are based on data regarding the lindane content in the topsoil, provided by MSC-East in a 150 x 150 km grid for the period 1985-1998 (figure 4-6). Due to the fact that the lindane content in the soil changes slower as compared to the atmospheric deposition, the 1998 topsoil contents were taken as a basis for the year 2000. The high values in Saxony-Anhalt (figure 4-6) result from lindane production near Bitterfeld-Wolfen until 1982. The Federal Environment Agency also reports on high HCH-concentrations in the soils of this region for the 1990ies (UBA, 1999b).

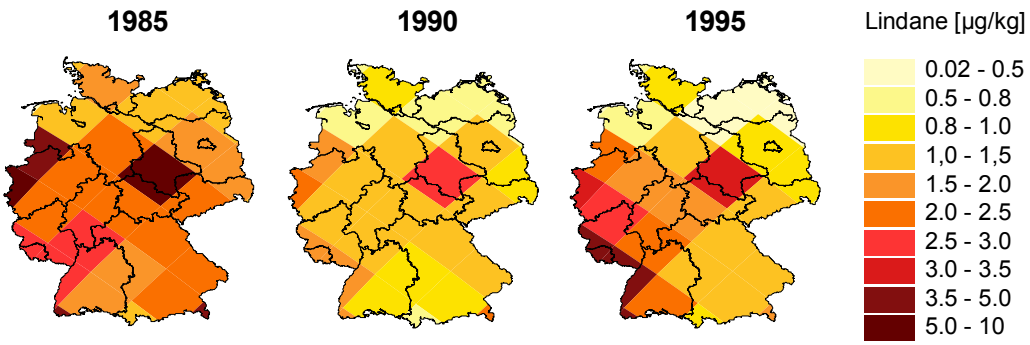


Figure 4-6 Lindane contents in the topsoil for 1985, 1990 and 1995 (MSC-East, 2001).

The enrichment ratio (ER) resulting from transport was determined on the basis of lindane contents in suspended solids of rivers (UBA, 1999c; HLUG, 2001) and in the topsoil (→ equation 2-8). Lindane is rarely determined in the suspended solids of rivers, as its major part is dissolved (see chapter 4.1.1). Moreover, numerous values remain under the quantification limit. Table 4-2 lists the enrichment ratios for eight medium-sized to large river basins. Given the small amount of data, the enrichment factors were summarised to a mean value of 2. This mean value was applied to all river basins.

Table 4-2 Lindane contents in suspended solids of rivers and in the topsoil, calculated enrichment ratios (ER).

Monitoring station	**Suspended solids (median) [µg/kg]**	**Top soil (median) [µg/kg]**	**ER [-]**
Elbe/Schnakenburg	2.6	0.68	3.8
Elbe/Magdeburg	3	2.29	1.3
Saale/Groß-Rosenburg	2.5	2.29	1.1
Schwarze Elster	4.3	2.29	1.9
Mulde/Dessau	12.6	2.29	5.5
Nidda/Frankfurt-Nied	<2.5	1.89	<1.3
Fulda/Wahnhausen	<1.2	1.89	<0.6
Rhine/Koblenz	1.1	3.03	0.33

4.2.2.5 Drainages

Literature does not provide any measured values on lindane concentrations in drainage water. The input quantifications were thus determined on the basis of the lindane masses applied in agriculture, according to the procedure described in chapter 4.2.2.2 and to the seepage water concentration.

According to the ICPR (1999), 1.1 % of the applied lindane (chapter 4.1.3) enter the surface waters via drainages. This value widely differs from other literature data. Huber (1998) calculated e.g. that only 0.005 % of the total pesticide mass applied in Germany enters the surface waters via drainages. Lindane was not considered in this study (see chapter 1). It may be assumed, however, given the high persistence rate of lindane, that a higher percentage is emitted via drainages as compared to newer substances. This is why the lindane share was evaluated on the basis of the simulation results obtained by Bintein/Devillers (1996). The authors specify that 0.35 % of the applied lindane reaches the subsoil via seepage. The portion of drained agricultural land was determined with 11.6 % by Behrendt et al. (1999).

From these data it can be concluded that 0.04 % of the applied lindane enters the surface waters via drainages.

Given its high persistence, lindane can still be found in the seepage water of agriculturally used soils to which lindane was applied in earlier years. The estimation of this load share was done by means of the MONERIS model (→ equation 2-9). For the period 1983-1987 a seepage water concentration of 4.55 µg/l was assumed according to Schleyer/Hammer (1992). Given the highly reduced masses applied in 1993-1997 and 1999/2000, a lower value of 2 µg/l (Walther, 1999) was used for these periods.

4.2.2.6 Groundwater

Literature reports on numerous lindane findings in groundwater (e. g. Hurle et al., 1987; Simmleit, 1988; Nordmeyer/Pestemer, 1989; Skark/Zullei-Seibert, 1996; DVWK, 1998). Once HCH-isomeres reach the groundwater, their degradation appears very uncertain. The aquifers are frequently poor in organic matter, allowing thus the HCH-isomeres to be transported over long distances without any remarkable concentration loss (LfU, 1993).

The input via base flow (→ equation 2-10) was calculated on the basis of measured values provided by the groundwater data base of the Federal Environment Agency. The data base disposed of 511 measured values for 1991-1999, 11.5 % of which remained under the quantification limit. The fluctuation range of the specified quantification limits was 1-100 µg/l. Given that values remaining under the quantification limit are considered with a concentration of 50 % of the quantification limit in the calculations, all QL exceeding 5 µg/l were eliminated, as they are not analytically justified. The median of the remaining 264 values (22.34 % exceeding the quantification limit) was 1 µg/l. This concentration was used for all 3 periods, as it may be assumed that lindane concentrations in the groundwater are only subject to slow changes.

4.2.2.7 Urban areas: Sewer systems and not connected inhabitants

The procedure as for the calculation of lindane inputs from *storm water sewers, combined sewer overflows, sewer systems that are not connected to a wastewater treatment plant* and *inhabitants not connected to a sewer system* is described in chapter 2.2.7.

Atmospheric deposition is the major source for pollution of impervious urban areas by lindane. The specific heavy metal input from impervious urban areas was thus chosen relative to the mean atmospheric deposition (see chapter 4.2.2.1).

Inhabitant specific lindane loads were collected for a literature study realised on behalf of The Netherlands within the scope of the report commitment for the North Sea Conference (The Netherlands, 2000). Lindane pollution of industrial-commercial sewage was excluded, as production and formulation did not occur in small commercial plants. The input data for the calculation of diffuse lindane input from urban areas are listed in table 4-3. The share of lindane reaching surface waters via households that are not connected to a sewer system, was estimated to 20 %.

Table 4-3 Emission factors for the quantification of diffuse lindane inputs from urban areas.

	Reference	**1985**	**1995**	**2000**
Specific lindane input [g/(ha·a)]	MSC-East, 2001	0.33	0.19	0.19
Inhabitant specific load [mg/(I·a)]	The Netherlands, 2000	12	1.5	1.5

5 Immission and retention

The calculation of the river loads serves the verification of the results obtained from emission estimations. The following chapter describes the methodology and data base for the calculation of immission and retention of substances in river systems. The relations are schematically shown in figure 5-1.

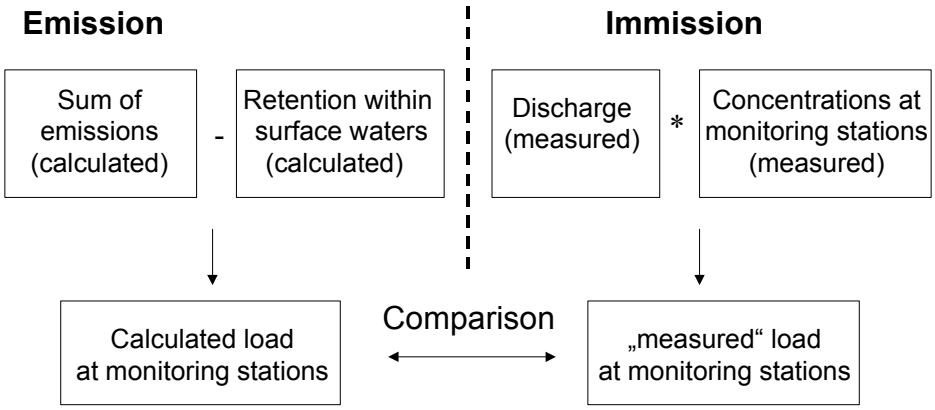


Figure 5-1 Relation between emission and immission.

Due to the fact that the loads of rivers featuring transboundary catchments (Rhine, Elbe, Odra) also comprise emissions from abroad, they had to be considered all the same. The MONERIS model could be applied to determine diffuse input, as it also disposes of the basis data of the neighbouring countries. For this purpose, the German emission factors were applied to Switzerland, France, the Czech Republic and Poland. Within the scope of this project, no research on specific emission factors of the foreign parts of the catchments could be done. The inputs via French and Swiss point sources were collected by the ICPR (1999) for the Rhine catchment. For the Elbe they were gathered by Vink (2002). No data on point source inputs are available for the Odra in Poland.

5.1 Calculation of the loads of rivers

The procedure for the quantification of heavy metal and lindane loads occurred following the same methodology as for nutrients (Behrendt et al., 1999). When calculating the loads of rivers, one has to distinguish the concentrations obtained

from individual or mixed samples. The load calculations from individual samples occurred according to the method favoured by OSPAR (1996) with equation 5-1:

$$L_J = \frac{Q_d}{Q_{mess}} \cdot \left(\frac{1}{n} \cdot \sum_{i=1}^{n} C_t \cdot Q_t \cdot U_f \right) \qquad \textbf{Equation 5-1}$$

L_J = annual load [kg/a]
Q_d = mean annual runoff of daily flow measurements [m³/s]
Q_{mess} = mean annual runoff for the days of quality monitoring [m³/s]
n = number of annual measured values
C_t = measured concentrations at time t [µg/l]
Q_t = mean discharge at time t [m³/s]
U_f = conversion factor (flow gauge to quality gauge)

If measured values of weekly or two-weekly mixed samples were available, the annual load was calculated on the basis of the following equation:

$$L_J = \left(\frac{1}{n} \cdot \sum_{i=1}^{n} C_{misch} \cdot Q_{misch} \cdot U_f \right) \qquad \textbf{Equation 5-2}$$

C_{misch} = concentration of the mixed sample[µg/l]
Q_{misch} = runoff during the measuring period[m³/s]

To calculate the surface water loads of the periods 1983-1987 and 1993-2000, the respective federal authorities were inquired about the measured values on water quality by the Institute of Freshwater Ecology and Inland Fisheries (IGB, Berlin). For measured values not exceeding the quantification limit, the value used for the calculation was set to 50 % of the quantification limit. A mean value was then generated for the periods 1983-1987, 1993-1997 and 1998-2000 from the calculated annual loads, given that the loads in the river are subject to heavy fluctuations depending on runoff conditions and that emission estimations are based on average conditions of a 5-year-period. Barely any data were made available by the authorities of the Federal States for the mid-eighties and the year 2000, a comparison of calculated inputs and loads revealed thus only meaningful for the mid-nineties.

5.2 Retention within the river system

When comparing the calculated emissions and the loads obtained at the quality monitoring stations, considerable differences arise which are not solely due to methodological errors such as an underestimation of the emissions or an overestimation of the river loads (Behrendt/Opitz, 1999).

Behrendt/Opitz (1999) analyzed the relation between total emissions and measured loads in a river basin for nutrients. The model is based on the mass balance in a river basin over a period of several years. It arises from the balance of total emissions from point and diffuse sources and the total sum of all retention and loss processes occurring in the river:

$$L = E - R = \sum EP + \sum ED - \sum R \qquad \textbf{Equation 5-3}$$

L = river load [kg/a]
E = total emissions [kg/a]
EP = total sum of all point source emissions [kg/a]
ED = total sum of all diffuse source emissions [kg/a]
R = retention [kg/a]

Considering the load weighted retention the following relation is given:

$$L = \frac{1}{1 + R_L} \cdot E \qquad \textbf{Equation 5-4}$$

R_L= retention factor [-]

To describe the relation between retention and possible controlling parameters, Behrendt/Opitz analysed the nutrient data of 89 European river basins. For nutrients it became apparent that relations exist as well between retention and specific runoff and the hydraulic load in the river basins. The retention of heavy metals mainly results from sedimentation processes, i. e. it depends on the specific runoff rate. Behrendt/Opitz (1999) chose a power function to describe this dependence:

$$R_L = a \cdot q^b \qquad \textbf{Equation 5-5}$$

q = specific runoff rate [l/(km^2·s)]
a,b = empirical factors

If the retention amount of a substance is known, the loads transported in the river may be calculated from the emissions by means of equation 5-4. These loads may then be compared to the loads obtained at the quality monitoring stations (see figure 5-1).

As for the dependence on the specific runoff, the *a* and *b* factors determined by Behrendt et al. (1999) were adapted for phosphorus with $a = 26.6$ and $b = -1.71$, based on the data obtained from 89 European river basins. Vink/Behrendt (2002) determined *a* and *b* for the metals Cd, Cu, Hg, Pb and Zn following the proceeding used for nutrients on the basis of the data available for Rhine and Elbe. These factors have also been used for the aforementioned metals. For Cr and Ni the factors had to be derived from our own data. Factor *b* was assumed to be constant and set to the value of phosphorus. Table 5-1 lists the factors *a* and *b* that were used to calculate the retention.

Table 5-1 Factors *a* and *b* used for the heavy metals retention model.

Factor	P	Cd[1)]	Cr[2)]	Cu[1)]	Hg[1)]	Ni[2)]	Pb[1)]	Zn[1)]
a	26.60	31.53	93.49	16.91	0.90	9.19	7.32	12.31
b	-1.71	-2.19	-1.71	-1.72	-0.12	-1.71	-0.83	-1.81

[1)] *a* and *b* according to Vink/Behrendt (2001); [2)] *a* and *b* according to data of this study

5.3 Immission analysis for the estimation of load shares from point and diffuse sources

Given that for lindane the data basis is less reliable than for heavy metals, additional studies were conducted to find out whether the estimated load shares emitted by point and diffuse sources may be verified by an analysis of the relations existing between measured lindane concentrations in the water and runoff conditions. For this purpose, the method developed for nutrients by Behrendt et al. (1999) was used to separate load shares from point and diffuse sources in the surface water.

The basis for the separation is the definition of point and diffuse sources for input of substances established by Novotny/Olem (1994) and Novotny (1988), summarised by Behrendt et al. (1999) as follows:

- *"The input via point sources is almost constant as for its volume and consistence. The input volume depends little or not on meteorological factors. Generally, the point of input may be distinctly identified."*

- *„The input via diffuse sources usually exhibits a very high variability. The resulting variability of the substance load may easily cover several orders of magnitude. The input volume is strongly related to meteorological factors such as precipitation. The point of input may not be distinctly identified."*

Based on the consideration of anthropogenic and natural runoff components, a separation of load shares from point and diffuse sources in the water body is thus possible. To apply this method it is necessary to dispose of the highest possible number of measured values obtained over several years in order to collect as many typical hydrological set-ups as possible. Moreover, the emission situation should not be subject to dramatic changes within the considered period.

The objective of the immission method is to determine a value for the load share from point sources, using the observed total load at a measuring spot and the respective measured flows covering the various hydrological set-ups. To do so, the water volume discharged by the point sources must be known for the considered measuring spot. The diffuse load share then arises from the difference between the total load and the input via point sources.

The following equation is to be used for the most simple case, i. e. the dilution of a constant load (point source):

$$L_P = L_0 + C_D \cdot Q_P \qquad \textbf{Equation 5-6}$$

L_P = load from point sources [kg/a]
L_0 = hypothetical load for a runoff of 0 [kg/a]
C_D = mean concentration of diffuse inputs [µg/l]
Q_P = runoff from point sources [m³/s]

The parameters L_0 and C_D are determined by the linear regression between concentration (respectively load in g/s) and flow (see figure 5-1).

If the concentration is not diluted by an increased runoff, equation 5-6 cannot be applied in a meaningful way, due to the fact that the regression between concentration respectively load and flow shows a steeper ascending gradient and thus results in negative values for parameter L_0. Hence it follows that the regression relation in its linear form cannot be applied up to zero within the studied flow range. Given the small water volume input from the point sources, their substance inputs are that much diluted, that they no longer significantly contribute to the concentration and substance load of the flow. However, for $L_0 < 0$, the flow for which the input merely originates from point sources may be derived. Whereas in the case of $L_0 > 0$, the load from point sources corresponds to the intersection point of the regression lines at Q_P (see figure 5-2), the intersection point is $Q_P + Q_{min}$ for $L_0 < 0$. Q_{min} corresponds to a flow with zero load and is determined by the intersection point of the regression lines with the x-axis.

$$L_P = L_0 + C_D \cdot (Q_P + Q_{\min}) \qquad \textbf{Equation 5-7}$$

Q_{min} = *minimum flow [m³/s]*

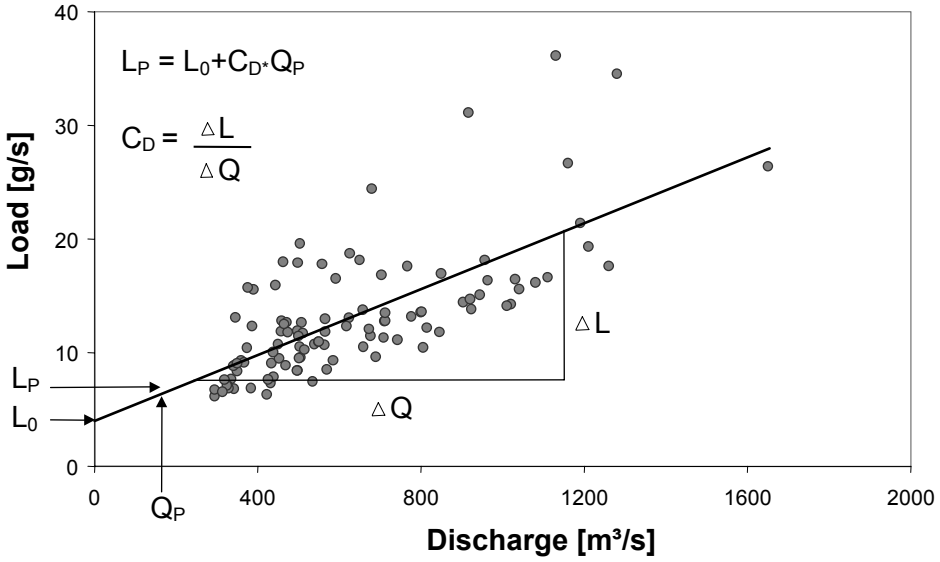


Figure 5-2 Graphical representation of the procedure for the estimation of L_0 and C_D on the example of lindane near Schnackenburg for 1996/1997 (representation according to Behrendt et al., 1999).

PART III RESULTS

6 Emissions of heavy metals into German river basins

6.1 Overview of the emissions

Figures 6-1 to –8 provide an overview on heavy metal emissions in the large German river basins and on their changes since the mid-eighties. Apart from the area-specific total inputs, they describe the significance of the pathways and provide a tabular survey of point, diffuse and total emissions. Individual results may be drawn from appendix 2a to h for all river basins and pathways.

For 1985, data on *direct industrial discharges* were not available for all river basins. It thus revealed necessary to sensibly complement the lacking emission values in the graphical representation of the results. This was the case for Danube, Odra, the coastal area of the Baltic Sea and, for As, also for Rhine and Ems. For the Danube river basin, the industrial emissions of the year 1985 were estimated on the basis of both the 1995 loads and the mean reduction of industrial discharges in the OFS between 1985 and 1995. Correspondingly, the reduction in the Elbe catchment area was taken as a reference for the Odra and the coastal areas of the Baltic Sea. For Hg the direct industrial discharges into the Elbe represent 95 % of the total input, due to a limited number of individual industrial sites (chlor-alkali electrolysis). This situation could thus not easily be transferred to the Odra catchment area. The reduced industrial Zn emissions in the Elbe catchment area may not be applied to the Odra either and would lead to unrealistic results, given that the major share of Zn emissions into the Odra is emitted by one big discharger (steel industry Eisenhüttenstadt). For Hg and Zn, the reduction rate of the OFS was thus taken as a basis for the NFS. This method could not be applied to As, due to the fact that barely any data on industrial discharges were available for this metal for 1985. For the graphical representation it was assumed in this case, that in 1985 the volume of industrial emissions was comparable to the emissions originating from municipal wastewater treatment plants. It has to be considered, however, that the emission estimations for wastewater treatment plants are fairly unreliable for As (see chapter 3.1.1). The question marks (“?”) used in the graphical presentations indicate complemented load shares from industry. Given the high unreliability of the estimated load shares they were not complemented in the tables. The emissions respectively the emission reductions obtained between 1985 and 2000 have thus to be considered as the lower limit and are provided with a “greater then”-sign (">").

The emission reductions actually reached since the mid-eighties and up to the year 2000 may only be calculated for the total catchment area of the North Sea (Rhine, Ems, Weser, Elbe and North Sea coast). However, given that the subsumed sub-catchments make up 76 % of the total area of Germany, the results may actually be representative. It has to be stated, however, that the quantitative statements summarised in the following are always related to the catchment area of the North Sea.

In 1985 the major part of the inputs was caused by point sources. For Cd, Cr, Cu, Hg and Zn the shares originating from point sources fluctuated between 56 % (Cd) and 86 % (Hg). Merely for the metals As, Pb and Ni more than half of the input results from diffuse sources already in 1985. The main pathways for Pb are *sewer systems and not connected inhabitants.* For As and Ni, the most significant share originates from *groundwater inflow*. In 1985, high surface specific loads were determined for the highly industrialised catchments of Rhine, Elbe and Odra. The highest specific Hg-loads occur for example in the Elbe river and are due to direct industrial discharges originating from the former GDR. Compared to the Rhine catchment, the total load in the Elbe catchment is 240 Hg/km², i. e. 8 times higher. For Cd, the area specific loads in the Eastern river basins of Elbe and Odra exceed those of the Rhine by factor 3. However, in addition to point source inputs, diffuse sources such as *sewer systems* and *atmospheric deposition* also contribute significantly to the Cd-load in these river basins. Rhine, Elbe and Odra exhibit a comparably high specific total load for Cr, the major part originating from direct industrial discharges. For Cu and Zn the loads are comparable. For the Rhine, however, the major share of Cu and Zn consists of point source emissions from municipal wastewater treatment plants.

Between 1985 and 2000 the inputs from point sources were considerably reduced. Reduction rates of 74 % for Ni up to 95 % for Hg are mainly due to the reduction of direct industrial discharges (see chapter 6.2). The dramatic changes as for point sources reduce the total pollution load and, at the same time, emphasise the importance of diffuse pathways. The pollution load of the year 2000 is dominated by diffuse inputs. Their shares range from 70 % (Hg) to 93 % (As). *Sewer systems and not connected inhabitants, erosion* and *groundwater inflow* were identified as the most prominent pathways.

The calculated reduction of diffuse emissions since the mid-eighties fluctuates between 5 % for Cu and 72 % for Cd. It may generally be stated that the reduction of diffuse inputs is mainly due to changed atmospheric emissions. Besides the reduction of direct inputs on the water surface, representing a small share in the total load, atmospheric deposition also has a direct impact on inputs via *surface runoff*, particularly from *impervious urban areas.* No distinct changes of the basic data determining the input into surface waters were identified respectively assumed for other significant diffuse sources such as *erosion* and *groundwater* since the mid-eighties.

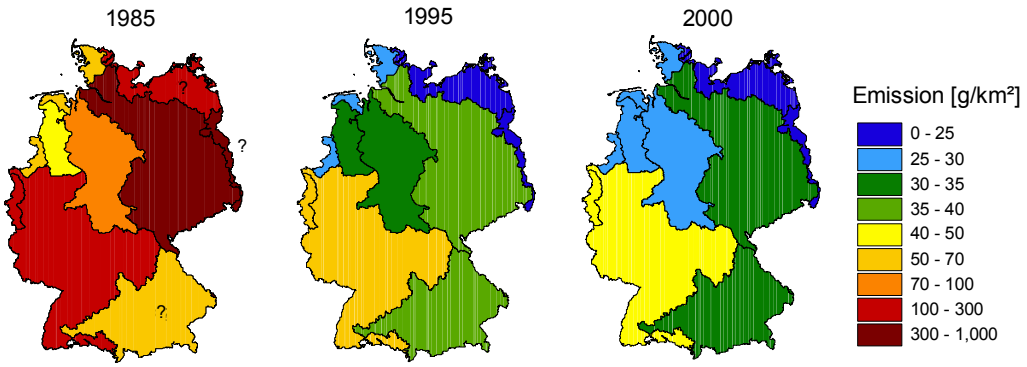
For 1995 and 2000, the highest surface specific loads in Germany were established for the Rhine catchment. This is due to a high population density and a respective high urbanisation and industrialisation degree (about half of Germany's population is living in the Rhine basin which, however, merely comprises 30 % of the surface). This is why the major share of the emitted Cd, Cu, Hg, Pb and Zn load originates from urban sources such as *municipal wastewater treatment plants, sewer systems* and *industry*. Since the reunification in 1990 and due to decreased industrial activities in the NFS, no increased loads have been calculated for the Eastern German river basins of Elbe and Odra.

As for the decrease of the total input into the North Sea, a reduction target of 70 % was determined for the metals Cd, Hg and Pb within the framework of the 3th International Conference on the Protection of the North Sea (The Hague Declaration, 1990). For As, Cr, Cu, Ni and Zn a load reduction of about 50 % was agreed. These reduction targets referred to the time period between 1985 and 1995. Since these reduction targets were only partly fulfilled by 1995, the 4th International Conference on the Protection of the North Sea (Esbjerg, 1995) agreed to fulfil these goals by the year 2000.

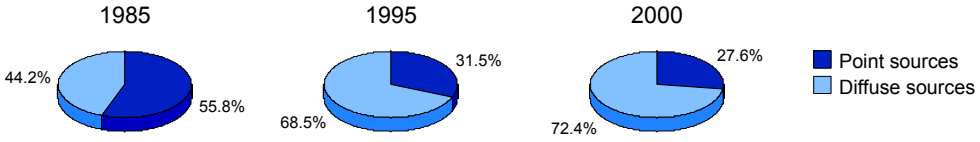
The most important reduction of emissions into surface waters was identified for Hg with 87 % and mainly results from decreased industrial activities in the Elbe catchment. An 83 % reduction of the total emissions was calculated for Cd. It is mainly due to smaller *direct industrial discharges* and to reduced diffuse emissions from *sewer systems* and *atmospheric deposition*, most of all in the NFS. Since 1986, the substitution of Pb as additive in fuels implied a reduction by 63 % of the emissions from diffuse sources into the North Sea. Relative to the total Pb-emissions, the 70 % reduction goal has, however, with 68 %, been missed by a low margin. The values for Cr (75 %), Cu (51 %) and Zn (60 %) were mainly obtained by the reduction of emissions from point sources. For Ni and As the major share of the emissions originates from diffuse sources. Even though the reduction of point source emissions amounts to 74 % for Ni, the total inputs into the North Sea were merely lowered by 41 % due to a high diffuse load. The actual emission reduction for As may not be specified as barely any data are available on direct industrial discharges for 1985. The total emissions from diffuse sources and municipal wastewater treatment plants were reduced by 39 %.

Cadmium

Total area specific emissions



Mean percentage of point and diffuse sources



Cadmium emissions [kg/a] and change for the period 1985 to 2000

River basin	Point sources			Diffuse sources			Total emissions		
	1985*	2000	Change*	1985	2000	Change	1985*	2000	Change*
Danube	>476	148	>-69%	3,007	1,588	-47%	>3,483	1,735	>-50%
Rhine	5,963	1,449	-76%	6,054	2,980	-51%	12,017	4,429	-63%
Ems	160	73	-54%	459	281	-39%	619	354	-43%
Weser	1,666	220	-87%	2,270	1,099	-52%	3,936	1,319	-67%
Elbe	22,647	819	-96%	14,915	2,160	-86%	37,562	2,979	-92%
Odra	>222	30	>-86%	792	73	-91%	>1,014	104	>-90%
North Sea Coast	105	26	-76%	458	264	-42%	563	289	-49%
Baltic Sea Coast	>302	10	>-97%	3,832	402	-89%	>4,134	412	>-90%
Black Sea total	>476	148	>-69%	3,007	1,588	-47%	>3,483	1,735	>-50%
North Sea total	30,541	2,587	-92%	24,156	6,784	-72%	54,697	9,370	-83%
Baltic Sea total	>524	40	>-92%	4,623	476	-90%	>5,147	516	>-90%
Germany total	>31,541	2,774	>-91%	31,786	8,847	-72%	>63,327	11,622	>-82%

*Values marked by ">"-character do not include direct industrial discharges of 1985.

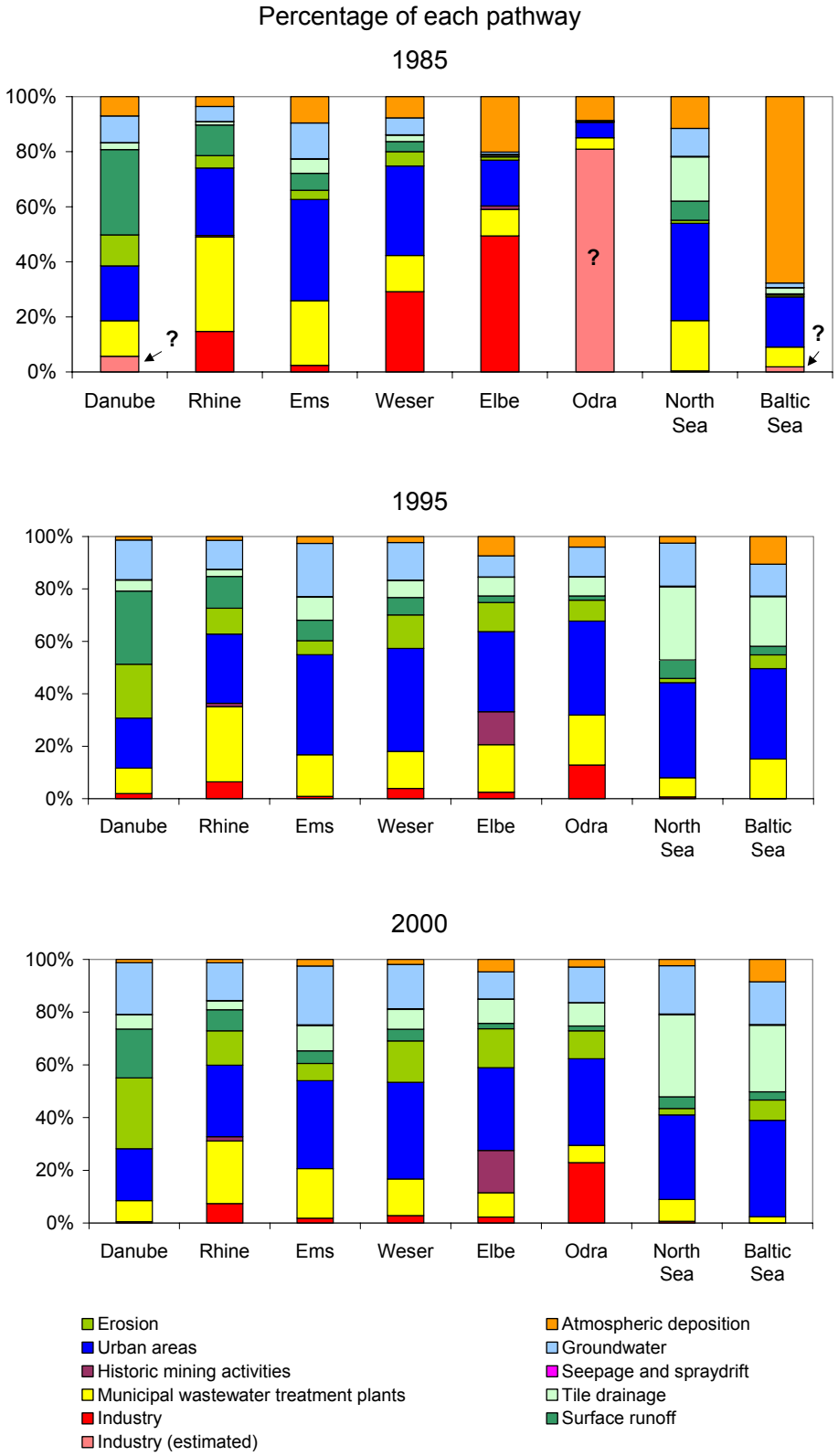
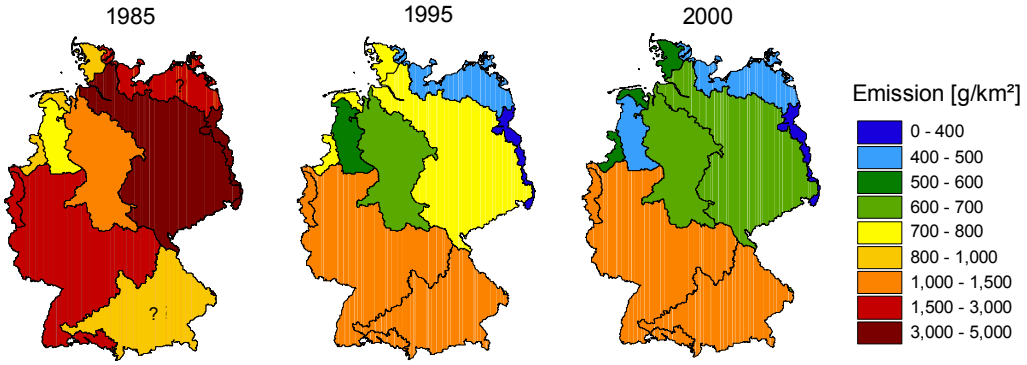


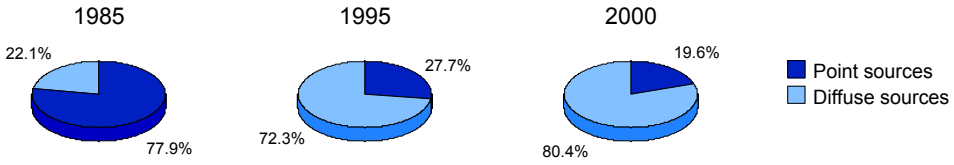
Figure 6-1 Cadmium emissions into German river basins.

Chromium

Total area specific emissions



Mean percentage of point and diffuse sources



Chromium emissions [kg/a] and change for the period 1985 to 2000

River basin	Point sources			Diffuse sources			Total emissions		
	1985*	2000	Change*	1985	2000	Change	1985*	2000	Change*
Danube	>13,004	4,789	>-63%	56,611	55,793	-1%	>69,615	60,581	>-13%
Rhine	296,881	30,720	-90%	85,082	77,725	-9%	381,963	108,446	-72%
Ems	3,606	1,186	-67%	5,269	4,946	-6%	8,875	6,132	-31%
Weser	29,914	3,435	-89%	28,206	25,781	-9%	58,120	29,216	-50%
Elbe	321,195	5,138	-98%	60,655	55,736	-8%	381,850	60,874	-84%
Odra	21,191	201	-99%	1,948	1,754	-10%	23,139	1,955	-92%
North Sea Coast	1,657	901	-46%	5,622	5,065	-10%	7,279	5,967	-18%
Baltic Sea Coast	>5,698	126	>-98%	10,744	10,193	-5%	>16,442	10,319	>-37%
Black Sea total	>13,004	4,789	>-63%	56,611	55,793	-1%	>69,615	60,581	>-13%
North Sea total	653,253	41,381	-94%	184,833	169,253	-8%	838,086	210,634	-75%
Baltic Sea total	>26,889	327	>-99%	12,691	11,947	-6%	>39,580	12,275	>-69%
Germany total	>693,146	46,497	>-93%	254,136	236,993	-7%	>947,282	283,490	>-70%

*Values marked by ">"-character do not include direct industrial discharges of 1985.

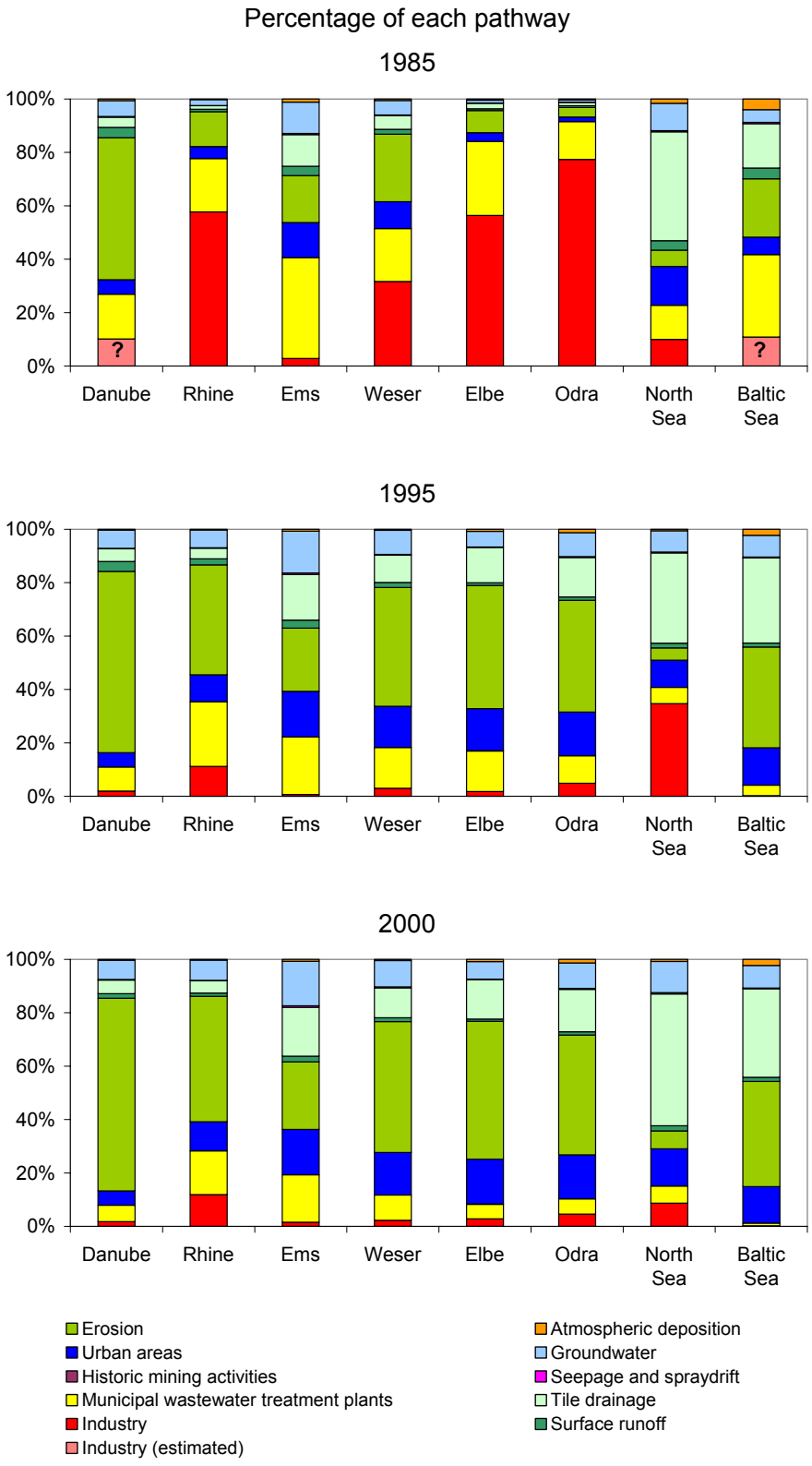
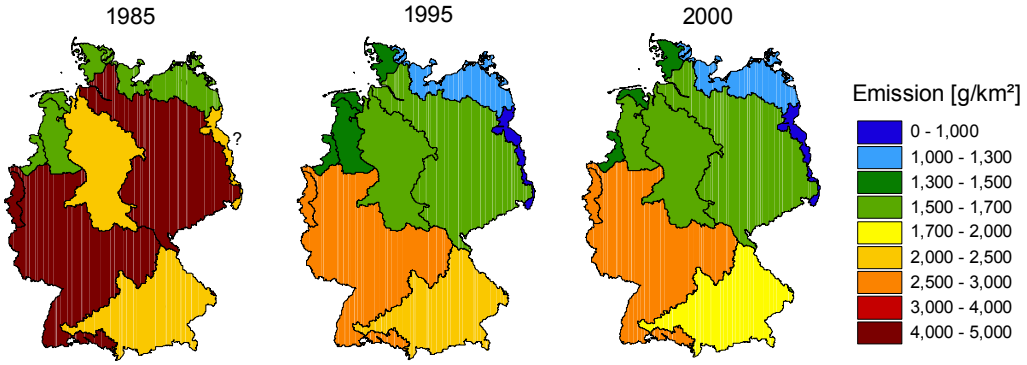


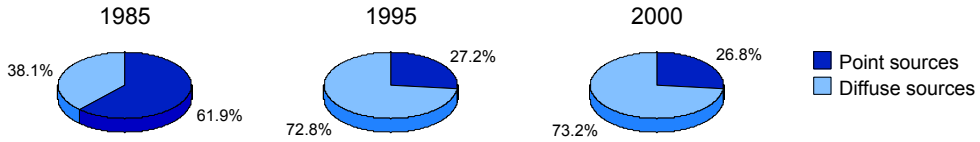
Figure 6-2 Chromium emissions into German river basins.

Copper

Total area specific emissions



Mean percentage of point and diffuse sources



Copper emissions [kg/a] and change for the period 1985 to 2000

River basin	Point sources			Diffuse sources			Total emissions		
	1985*	2000	Change*	1985	2000	Change	1985*	2000	Change*
Danube	>35,298	15,429	>-56%	89,753	90,866	1%	>125,051	106,295	>-15%
Rhine	275,375	96,660	-65%	183,036	173,212	-5%	458,411	269,872	-41%
Ems	6,399	5,337	-17%	14,629	15,229	4%	21,028	20,566	-2%
Weser	33,022	10,701	-68%	62,750	62,484	0%	95,772	73,185	-24%
Elbe	344,135	25,543	-93%	134,369	120,298	-10%	478,504	145,842	-70%
Odra	>942	603	>-36%	5,332	4,388	-18%	>6,274	4,991	>-20%
North Sea Coast	4,674	2,181	-53%	13,773	13,037	-5%	18,447	15,218	-18%
Baltic Sea Coast	>6,276	2,040	>-67%	28,536	22,291	-22%	>34,812	24,331	>-30%
Black Sea total	>35,298	15,429	>-56%	89,753	90,866	1%	>125,051	106,295	>-15%
North Sea total	663,605	140,421	-79%	408,558	384,262	-6%	1,072,163	524,683	-51%
Baltic Sea total	>7,218	2,643	>-63%	33,868	26,679	-21%	>41,086	29,322	>-29%
Germany total	>706,121	158,494	>-78%	532,179	501,806	-6%	>1,238,300	660,300	>-47%

*Values marked by ">"-character do not include direct industrial discharges of 1985.

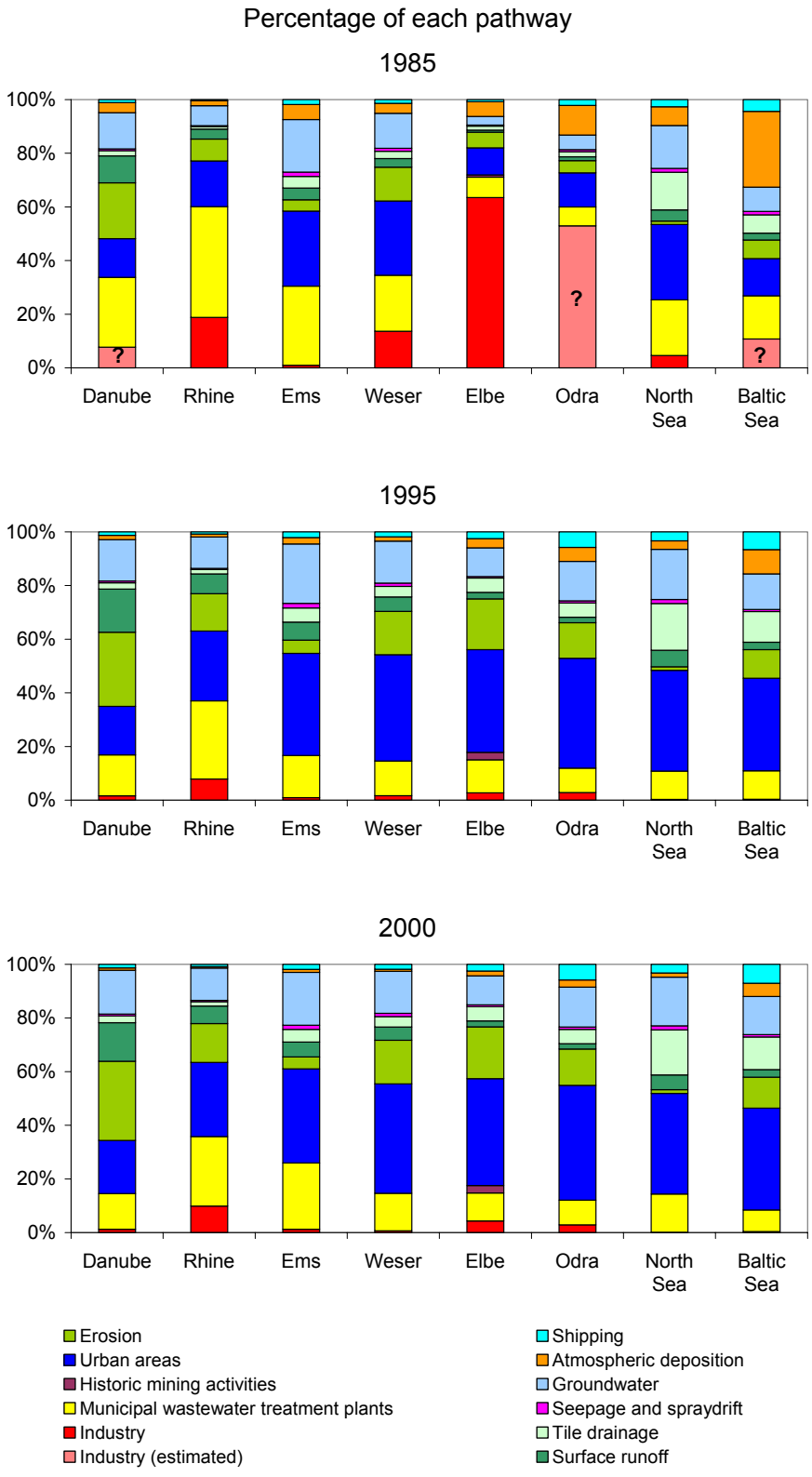
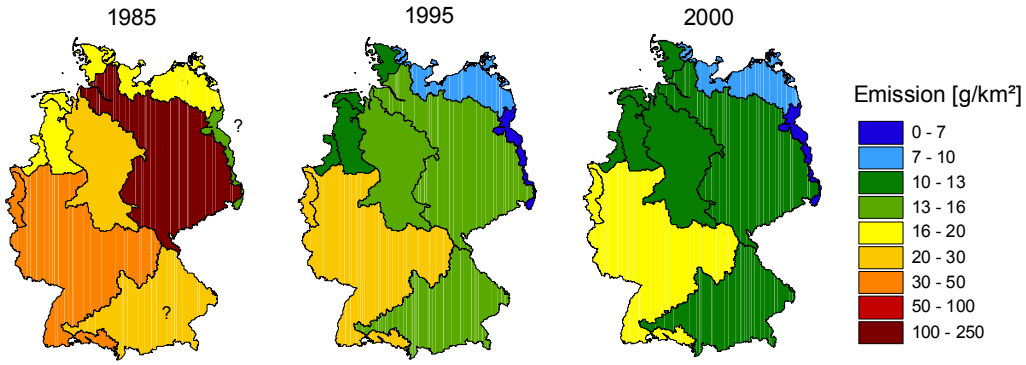


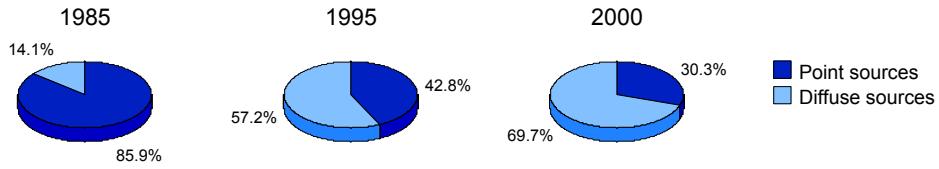
Figure 6-3 Copper emissions into German river basins.

Mercury

Total area specific emissions



Mean percentage of point and diffuse sources



Mercury emissions [kg/a] and change for the period 1985 to 2000

River basin	Point sources			Diffuse sources			Total emissions		
	1985*	2000	Change*	1985	2000	Change	1985*	2000	Change*
Danube	>314	125	>-60%	855	526	-39%	>1,169	650	>-44%
Rhine	2,695	762	-72%	1,743	1,068	-39%	4,438	1,830	-59%
Ems	80	47	-41%	129	102	-21%	209	149	-29%
Weser	505	134	-73%	562	413	-27%	1,067	547	-49%
Elbe	21,605	185	-99%	1,510	946	-37%	23,115	1,132	-95%
Odra	>16	6	>-64%	62	29	-53%	>78	35	>-55%
North Sea Coast	37	17	-55%	144	106	-26%	181	123	-32%
Baltic Sea Coast	51	5	-89%	336	184	-45%	387	190	-51%
Black Sea total	>314	125	>-60%	855	526	-39%	>1,169	650	>-44%
North Sea total	24,922	1,145	-95%	4,088	2,636	-36%	29,010	3,780	-87%
Baltic Sea total	>67	11	>-83%	398	213	-46%	>465	225	>-52%
Germany total	>25,303	1,281	>-95%	5,342	3,375	-37%	>30,645	4,656	>-85%

*Values marked by ">"-character do not include direct industrial discharges of 1985.

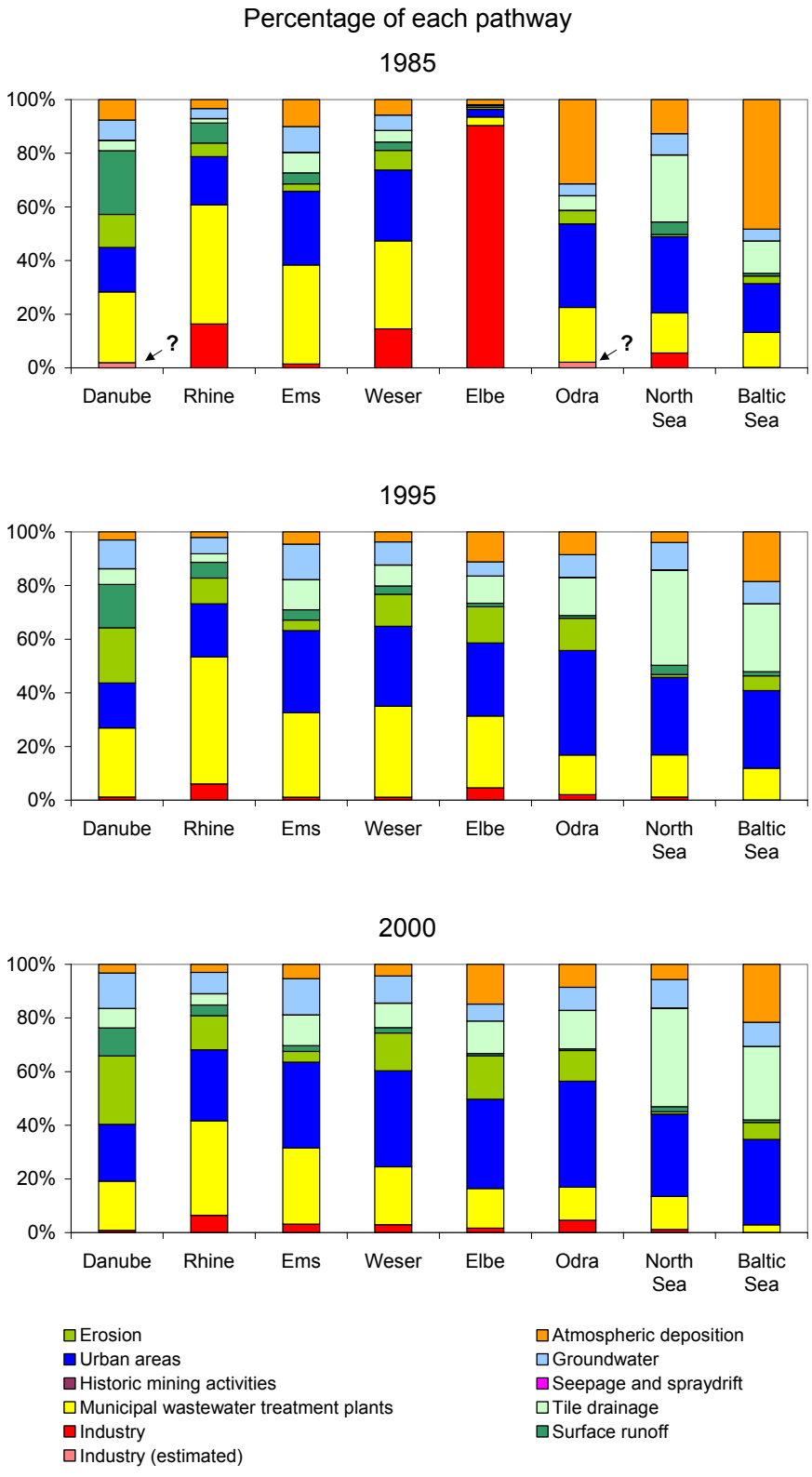
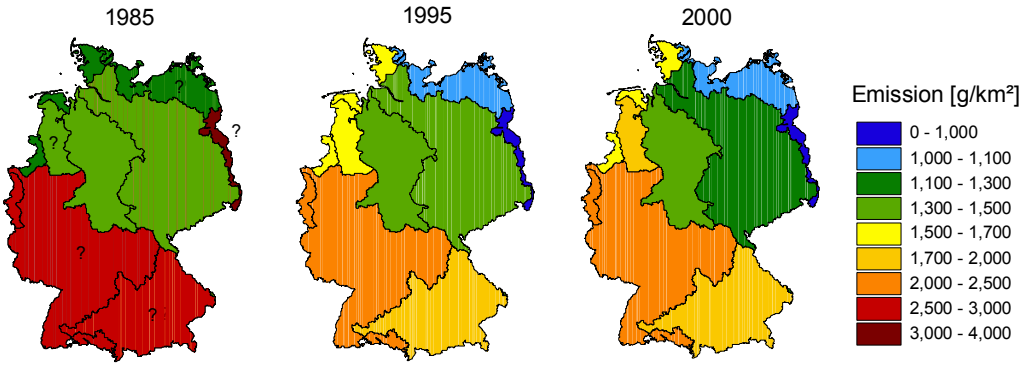


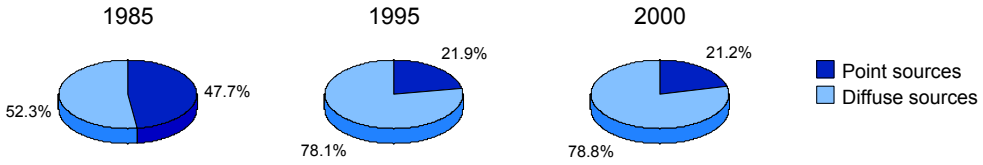
Figure 6-4 Mercury emissions into German river basins.

Nickel

Total area specific emissions



Mean percentage of point and diffuse sources



Nickel emissions [kg/a] and change for the period 1985 to 2000

River basin	Point sources			Diffuse sources			Total emissions		
	1985*	2000	Change*	1985	2000	Change	1985*	2000	Change*
Danube	>14,534	5,938	>-59%	105,943	101,606	-4%	>120,477	107,544	>-11%
Rhine	182,110	73,689	-60%	194,199	174,707	-10%	376,309	248,396	-34%
Ems	4,025	3,952	-2%	19,108	18,177	-5%	23,133	22,129	-4%
Weser	35,829	7,822	-78%	69,496	61,190	-12%	105,325	69,012	-34%
Elbe	159,963	14,282	-91%	120,301	105,745	-12%	280,264	120,027	-57%
Odra	>2,659	582	>-78%	4,845	4,165	-14%	>7,504	4,746	>-37%
North Sea Coast	2,043	1,454	-29%	18,131	16,501	-9%	20,174	17,955	-11%
Baltic Sea Coast	>4,903	813	>-83%	25,800	23,248	-10%	>30,703	24,061	>-22%
Black Sea total	>14,534	5,938	>-59%	105,943	101,606	-4%	>120,477	107,544	>-11%
North Sea total	383,970	101,199	-74%	421,235	376,320	-11%	805,205	477,519	-41%
Baltic Sea total	>7,562	1,395	>-82%	30,645	27,412	-11%	>38,207	28,807	>-25%
Germany total	>406,066	108,532	>-73%	557,822	505,339	-9%	>963,888	613,871	>-36%

*Values marked by ">"-character do not include direct industrial discharges of 1985.

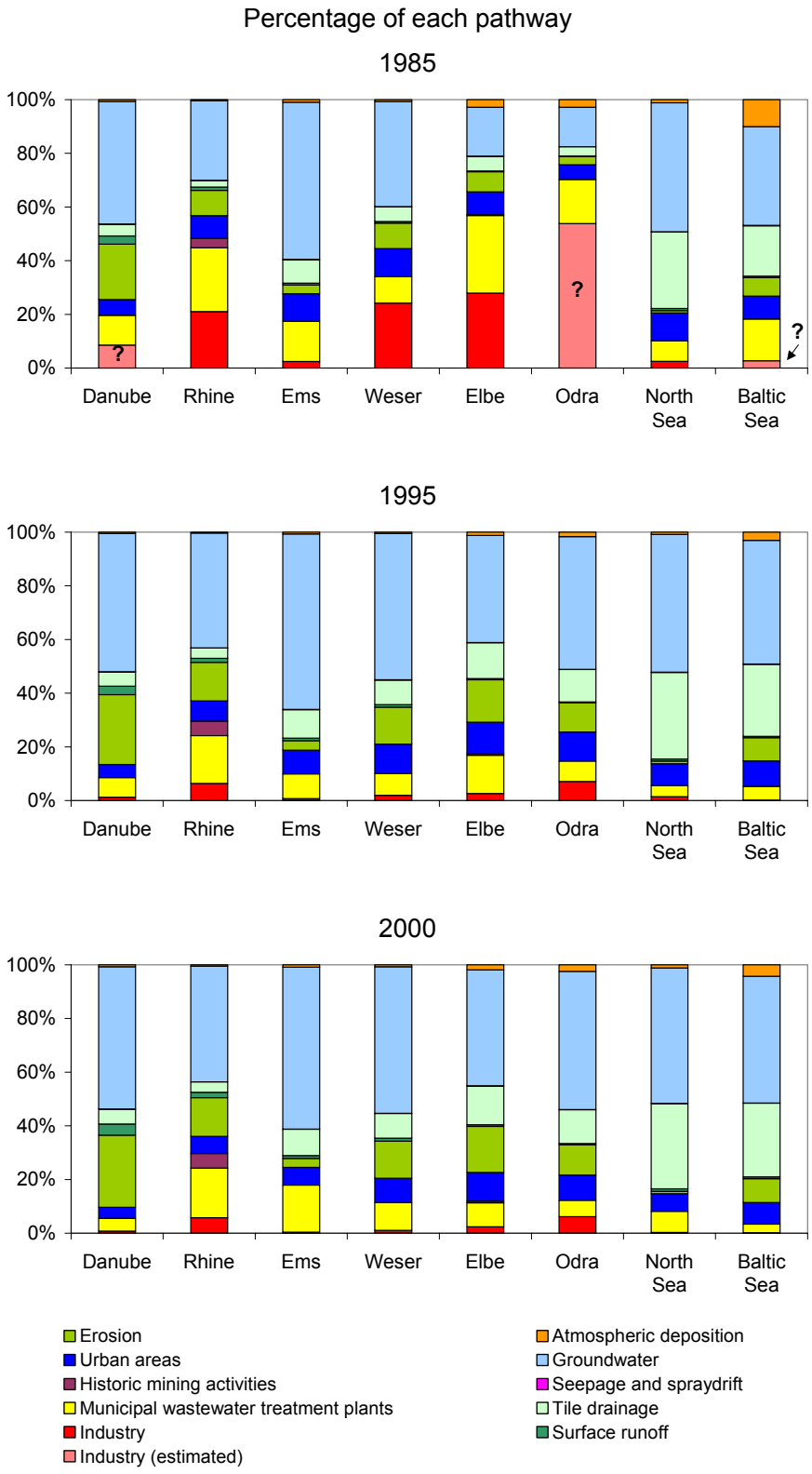
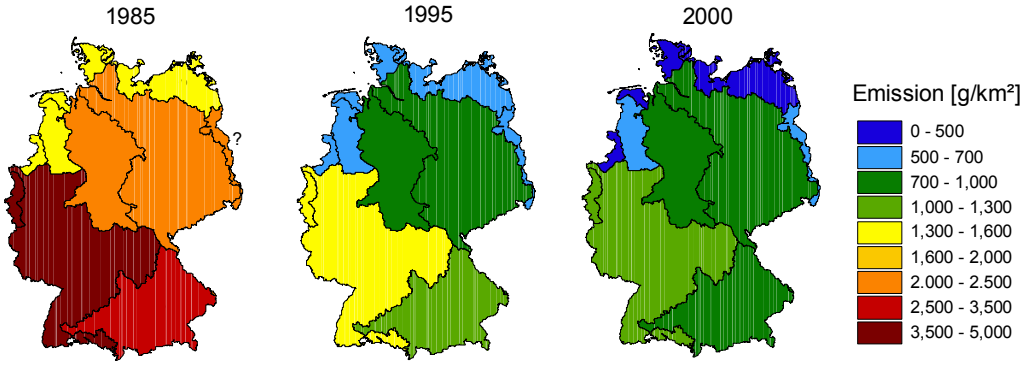


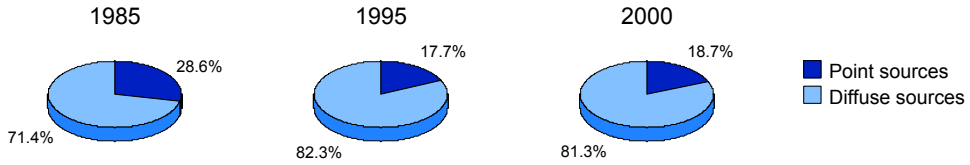
Figure 6-5 Nickel emissions into German river basins.

Lead

Total area specific emissions



Mean percentage of point and diffuse sources



Lead emissions [kg/a] and change for the period 1985 to 2000

River basin	Point sources			Diffuse sources			Total emissions		
	1985*	2000	Change*	1985	2000	Change	1985*	2000	Change*
Danube	>13,038	3,332	>-74%	133,796	51,202	-62%	>146,834	54,534	>-63%
Rhine	126,970	26,693	-79%	258,367	85,311	-67%	385,337	112,004	-71%
Ems	2,049	1,181	-42%	16,409	5,703	-65%	18,458	6,884	-63%
Weser	28,956	4,323	-85%	73,144	28,519	-61%	102,100	32,842	-68%
Elbe	48,993	10,504	-79%	158,132	63,937	-60%	207,125	74,441	-64%
Odra	>649	1,087	>67%	5,885	1,917	-67%	>6,534	3,004	>-54%
North Sea Coast	1,280	452	-65%	14,242	3,882	-73%	15,522	4,334	-72%
Baltic Sea Coast	>2,391	136	>-94%	28,472	8,153	-71%	>30,863	8,288	>-73%
Black Sea total	>13,038	3,332	>-74%	133,796	51,202	-62%	>146,834	54,534	>-63%
North Sea total	208,248	43,153	-79%	520,295	187,351	-64%	728,543	230,504	-68%
Baltic Sea total	>3,040	1,223	>-60%	34,357	10,069	-71%	>37,397	11,292	>-70%
Germany total	>224,326	47,708	>-79%	688,448	248,622	-64%	>912,774	296,330	>-68%

*Values marked by ">"-character do not include direct industrial discharges of 1985.

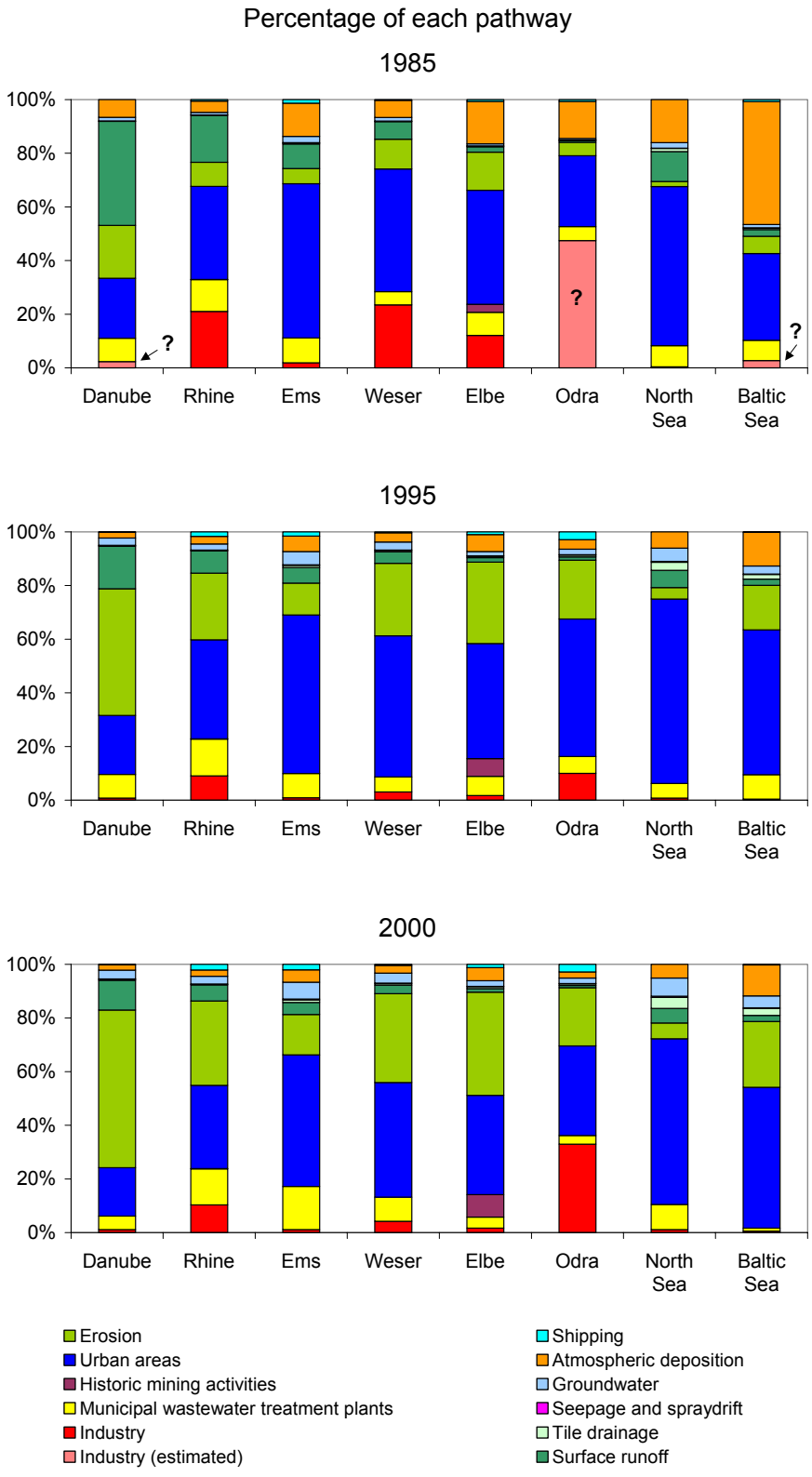
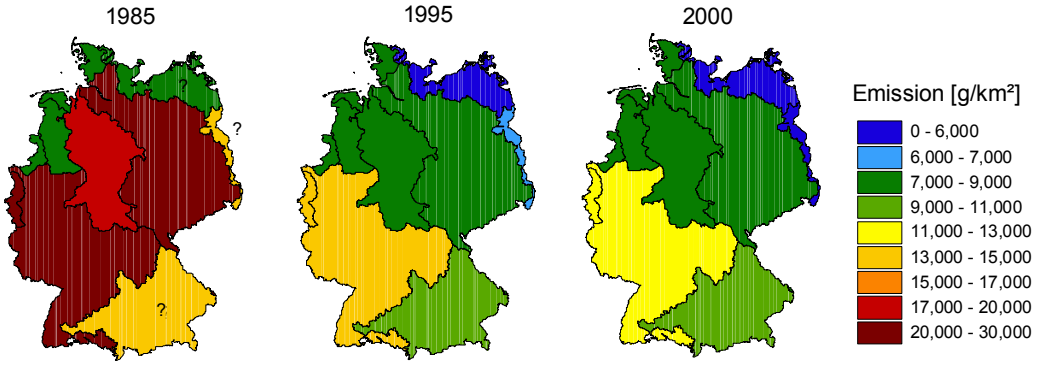


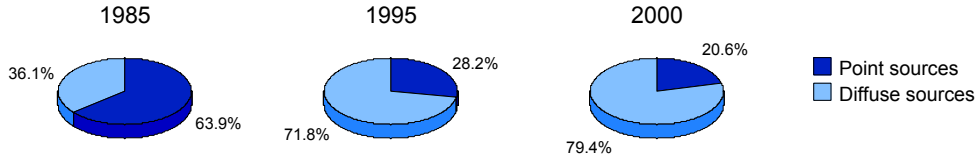
Figure 6-6 Lead emissions into German river basins.

Zinc

Total area specific emissions



Mean percentage of point and diffuse sources



Zinc emissions [kg/a] and change for the period 1985 to 2000

River basin	Point sources			Diffuse sources			Total emissions		
	1985*	2000	Change*	1985	2000	Change	1985*	2000	Change*
Danube	>193,541	91,437	>-53%	482,260	430,817	-11%	>675,801	522,254	>-23%
Rhine	1,293,939	375,561	-71%	1,024,033	878,058	-14%	2,317,972	1,253,619	-46%
Ems	31,088	16,296	-48%	77,115	79,273	3%	108,203	95,569	-12%
Weser	572,413	40,744	-93%	338,780	325,182	-4%	911,193	365,926	-60%
Elbe	2,113,312	69,300	-97%	761,963	636,413	-16%	2,875,275	705,713	-75%
Odra	>7,219	10,889	>51%	29,845	23,221	-22%	>37,064	34,109	>-8%
North Sea Coast	9,413	14,034	49%	72,121	67,370	-7%	81,534	81,404	0%
Baltic Sea Coast	>16,124	4,397	>-73%	148,712	124,039	-17%	>164,836	128,436	>-22%
Black Sea total	>193,541	91,437	>-53%	482,260	430,817	-11%	>675,801	522,254	>-23%
North Sea total	4,020,165	515,935	-87%	2,274,013	1,986,296	-13%	6,294,178	2,502,231	-60%
Baltic Sea total	>23,343	15,286	>-35%	178,556	147,260	-18%	>201,899	162,546	>-19%
Germany total	>4,237,049	622,658	>-85%	2,934,829	2,564,373	-13%	>7,171,878	3,187,031	>-56%

*Values marked by ">"-character do not include direct industrial discharges of 1985.

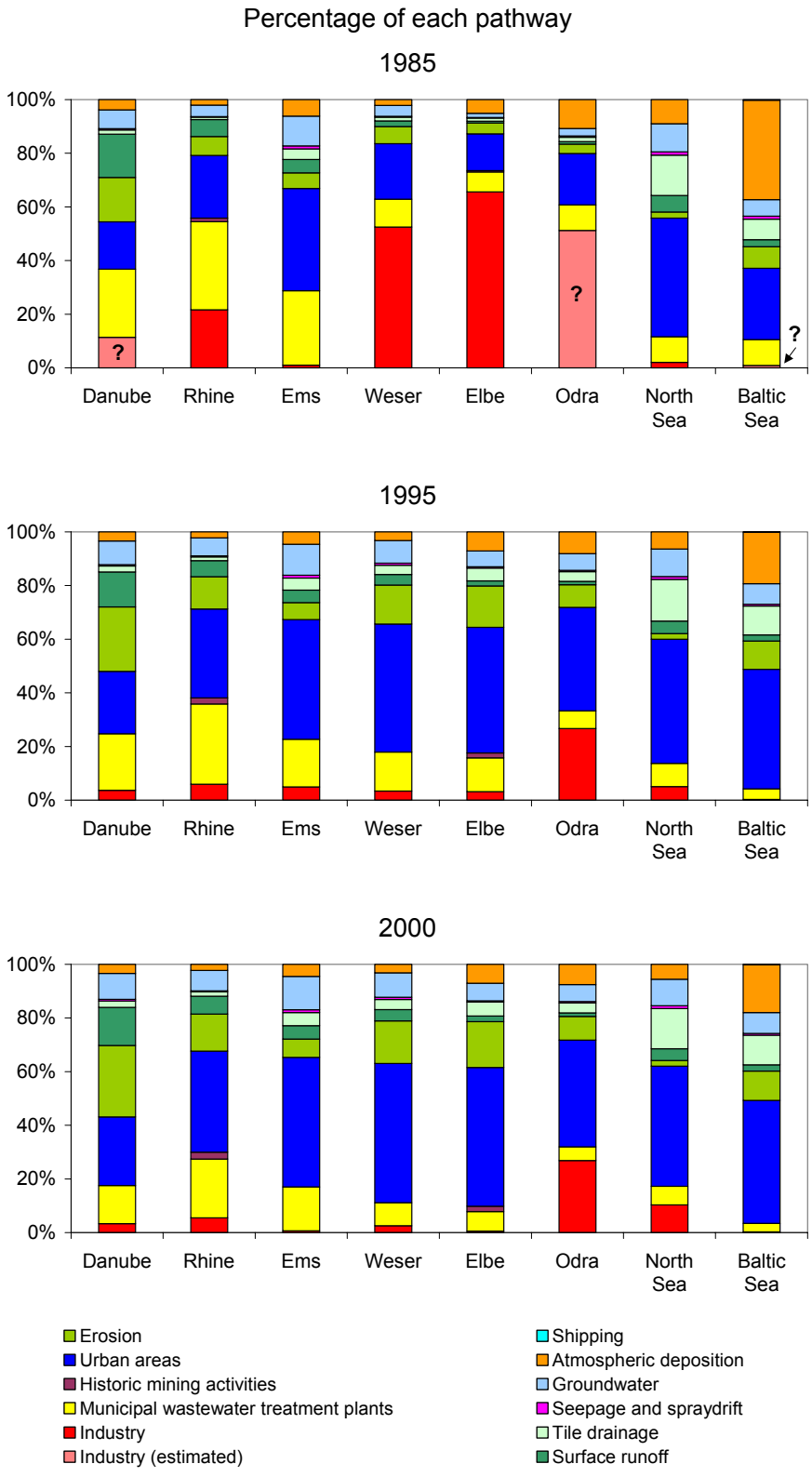
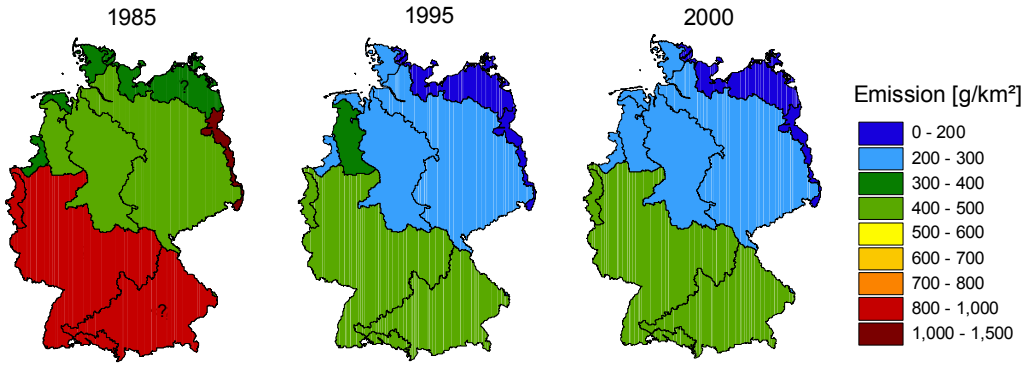


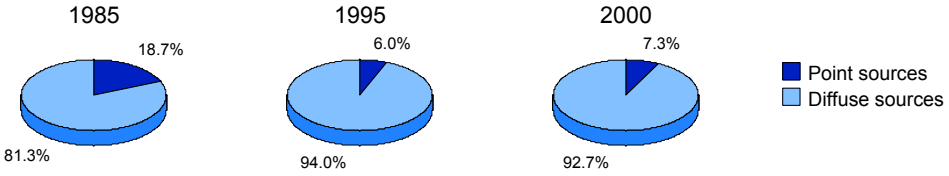
Figure 6-7 Zinc emissions into German river basins.

Arsenic

Total area specific emissions



Mean percentage of point and diffuse sources



Arsenic emissions [kg/a] and change for the period 1985 to 2000

River basin	Point sources			Diffuse sources			Total emissions		
	1985*	2000	Change*	1985	2000	Change	1985*	2000	Change*
Danube	>3,560	413	>-88%	38,666	23,951	-38%	>42,226	24,364	>-42%
Rhine	>17,549	4,606	>-74%	59,986	39,681	-34%	>77,534	44,287	>-43%
Ems	>720	119	>-83%	4,398	3,650	-17%	>5,117	3,769	>-26%
Weser	2,734	309	-89%	16,542	12,618	-24%	19,276	12,927	-33%
Elbe	5,757	1,378	-76%	33,795	23,076	-32%	39,552	24,454	-38%
Odra	7,060	23	-100%	1,457	936	-36%	8,517	959	-89%
North Sea Coast	424	61	-86%	3,647	2,753	-25%	4,071	2,813	-31%
Baltic Sea Coast	>590	56	>-91%	7,112	4,129	-42%	>7,702	4,185	>-46%
Black Sea total	>3,560	413	>-88%	38,666	23,951	-38%	>42,226	24,364	>-42%
North Sea total	>27,184	6,472	>-76%	118,367	81,778	-31%	>145,551	88,250	>-39%
Baltic Sea total	>7,650	79	>-99%	8,569	5,065	-41%	>16,219	5,144	>-68%
Germany total	>38,394	6,964	>-82%	165,602	110,793	-33%	>203,996	117,758	>-42%

*Values marked by ">"-character do not include direct industrial discharges of 1985.

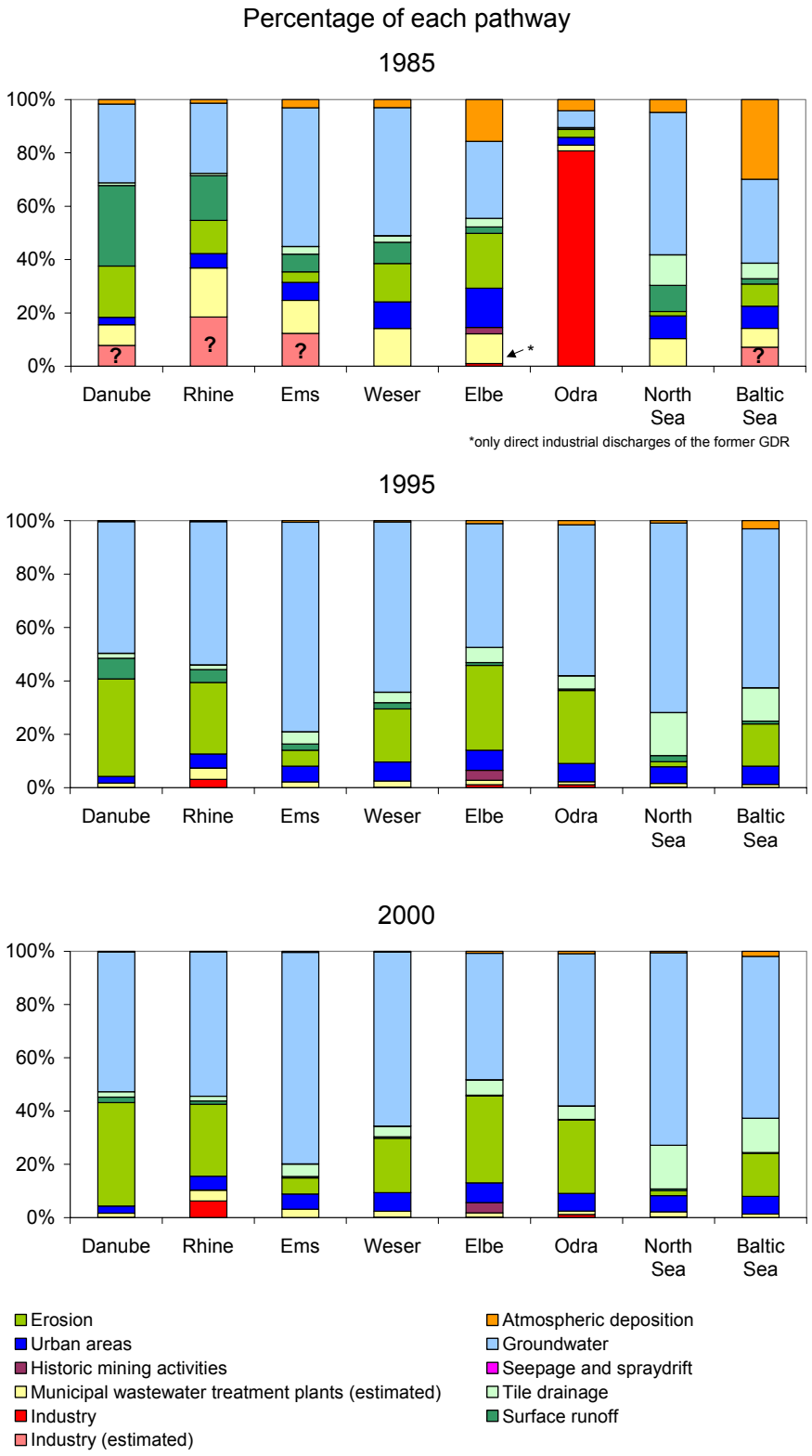


Figure 6-8 Arsenic emissions into German river basins.

6.2 Heavy metal emissions from point sources

6.2.1 Heavy metal emissions from municipal wastewater treatment plants

Emissions from municipal wastewater treatment plants contribute with between 10 % (Pb) and 24 % (Cr) for 1985 respectively between 10 % (Pb) and 26 % (Hg) for 2000 to the total water pollution load. Considering the contribution of municipal wastewater treatment plants to the sum of all point source inputs, it becomes clear that they do not represent the decisive pathway for 1985, with 13 % (Hg) to 48 % (Ni). In the following years this is no longer true. As a result of the very successful efforts made by industry to reduce direct inputs, the importance of emissions originating from municipal wastewater treatment plants already grew considerably in the 1990ies. In 2000, the largest share of the heavy metal load entering the waters via point sources (52 % (Pb) to 86 % (Hg)) originates from the effluents of municipal wastewater treatment plants.

Figure 6-9a to g represents the inhabitant specific heavy metal emissions of municipal wastewater treatment plants for the years 1985, 1995 and 2000. The percentages complemented in the diagrams show the emission reduction achieved between 1985 and 2000. All heavy metals show a distinct emission reduction of between 60 % (Cu) and 87 % (Cr). This reduction was mainly reached within the period 1985-1995. The reasons for this reduction are: measures taken with regard to indirect discharges following the 1986 Water Resources Policy Act, reduction of heavy metal concentrations in domestic sewage, strongly decreasing atmospheric deposition and modernisation of municipal wastewater treatment plants. Due to an ongoing nutrient elimination in municipal wastewater treatment plants, the average efficiency to eliminate heavy metals has been improved. Biological processes and phosphorus precipitation in particular led to increased heavy metal separation rates (see table 3-5 in chapter 3.1.1). The average efficiencies obtained in Germany are listed in table 6-1. A comparison of these mean values with the efficiencies of various sewage treatment processes shows, that in the mid-nineties the purification level corresponded to that of biological plants in all Germany.

Table 6-1 Comparison of mean efficiencies for heavy metals in sewage treatment between 1985 and 1995.

Year	Cd	Cr	Cu	Hg	Ni	Pb	Zn
1985	0.59	0.60	0.63	0.70	0.36	0.78	0.65
1995	0.62	0.67	0.71	0.73	0.44	0.81	0.70

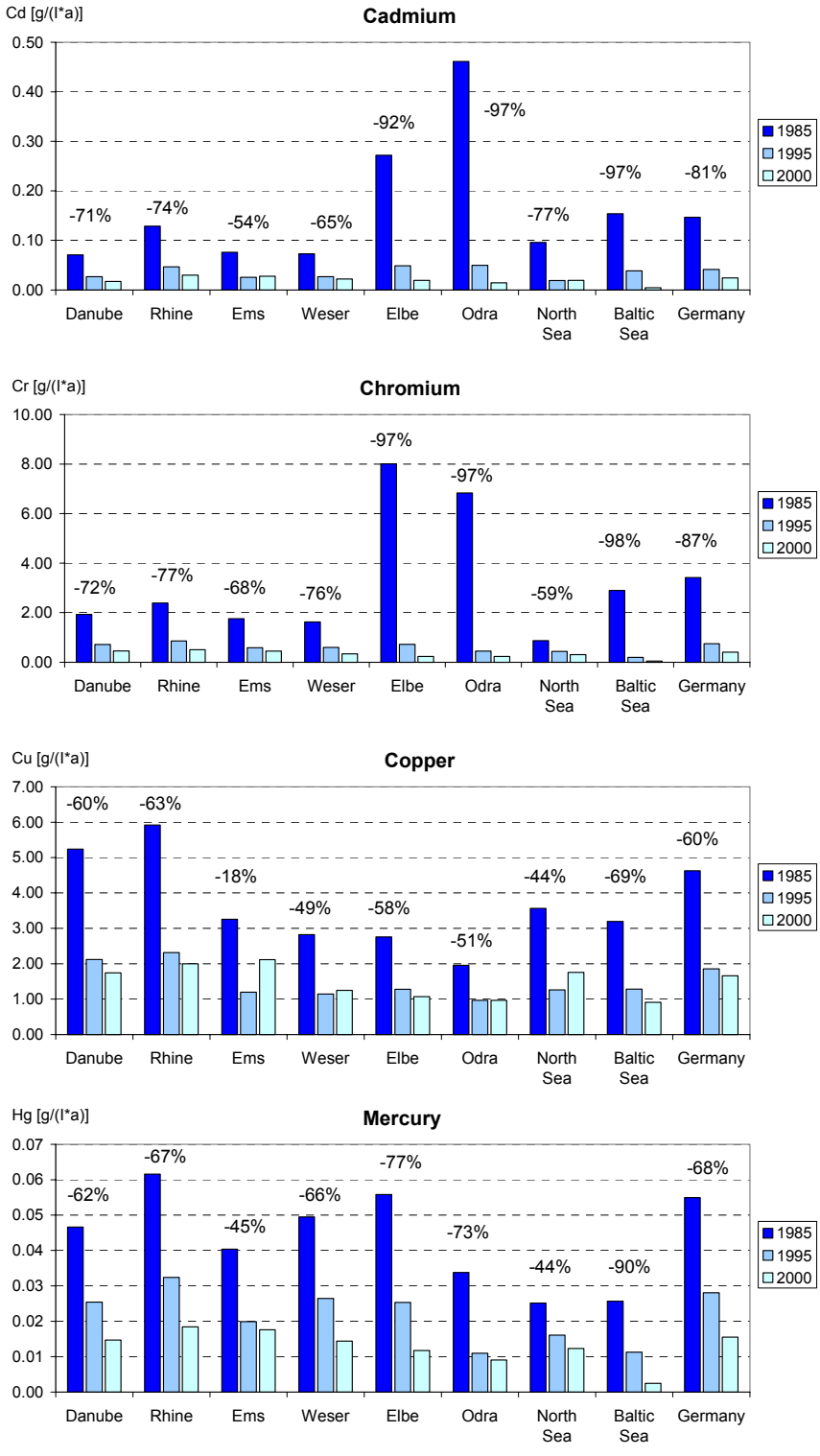


Figure 6-9a-d Specific heavy metal input per connected inhabitant via municipal wastewater treatment plants in g/(I·a).

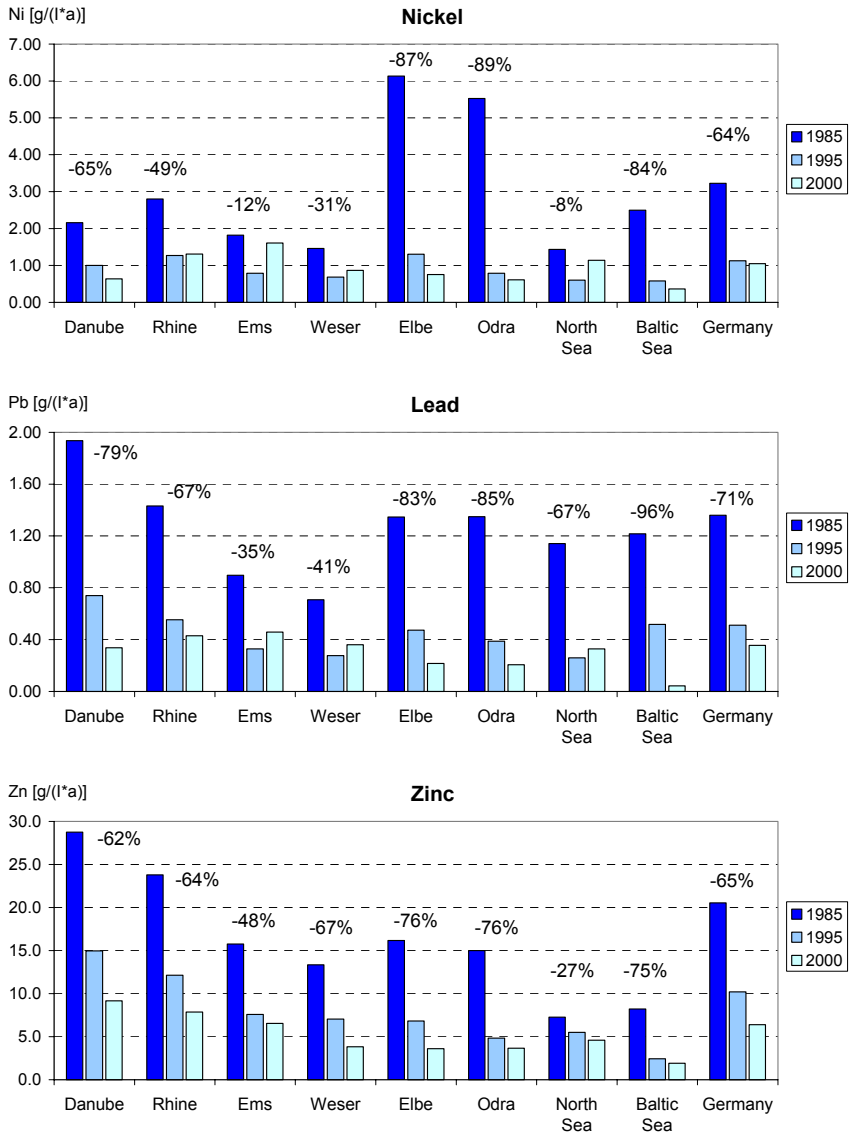


Figure 6-9e-g Specific heavy metal emissions per connected inhabitant via municipal wastewater treatment plant in g/(I·a).

The highest load reductions were obtained for Cd, Cr and Ni in the river basins of Elbe and Odra as well as in the coastal area of the Baltic Sea. However, these successes are not to be attributed to the implementation of the aforementioned measures regarding water resources management or the improvement of environmental conditions, but are rather due to the collapse of industrial production after the German reunification in 1990. The main source for heavy metals in municipal sewage are indirect industrial discharges (Zessner, 1999, Hornig/Lehmann, 1994). In the NFS, the breakdown of numerous industrial and commercial works caused a considerable reduction of the load originating from indirect industrial discharges

which has to be treated in municipal wastewater treatment plants. The Odra is a perfect example to illustrate this phenomenon. In 1995, merely 29 % of the 1985 indirect dischargers were connected to MWWTP in the Odra catchment (see table 3-4 in chapter 3.1.1). The Ems catchment shows the opposite effect: compared to other river basins, the Ems is characterised by a very low percental reduction of inputs from MWWTP plants. This results from an outstanding increase by 26 % of inhabitants connected to MWWTP between 1985 and 1995. The average increase in Germany was only 11.5 % over the same period.

In 1995 and 2000, the Rhine catchment supplied more than half of the loads emitted from MWWTP in Germany. This is due to various reasons: About half of the German population is living in the Rhine catchment area. Moreover, compared to German average values, the highest sewage volumes per inhabitant were measured in this area, with about 450 l/(I·d) (StaBu, 1998b) due to a predominance of combined sewer systems. Only the Danube catchment area exhibits a comparably high inhabitant specific water volume with 430 l/(I·d). For all other river catchments the sewage volume is only around 300 l/(I·d). The combined sewer system also entails that Cu, Pb and Zn, which have their main sources in the surface runoff of urban areas (Zessner, 1999; Gutekunst, 1988), are increasingly discharged into wastewater treatment plants. In separate sewage systems, the loads resulting from surface runoff are immediately discharged into the water bodies. In Germany, the distribution of combined and separate systems is thus reflected among others by the inhabitant specific Cu and Zn loads. This observation cannot be made for Pb, given that numerous measured values in the effluent of MWWTP plants remain below the quantification limit. Especially for the year 2000, some Federal State data sets could not be used to quantify the effluent load, as the number of measured values situated beyond the quantification limit revealed to be too small.

As for the accuracy of the quantified loads from MWWTP it has to be stated that the quantification was much more reliable for 1995 and 2000 than for 1985. This is due to the fact that in the first case measuring data on effluent concentrations were available and that for 1985 several assumptions had to be made.

However, the quality of the effluent concentrations specified for 1995 and 2000 differed a lot for the various metals and Federal States (see chapter 3.1.1). The load calculations for Cu and Zn are thus extremely reliable, given that all data of the Federal States could be used for the quantification of the loads. On the other hand, in the case of the remaining heavy metals and especially for the year 2000, many data sets had to be excluded from quantification as the laboratory methods used were not sufficiently sensitive and as implausible quantification limits were specified. This might be due to the fact that in many cases only the compliance with the threshold values of the Wastewater Levy Act (appendix 1 of § 3 AbwAG) was controlled and recorded. These values, however, usually exceed by far the actual concentrations in the effluent of the wastewater treatment plant.

6.2.2 Heavy metal emissions from direct industrial discharges

The methodological proceeding as for data acquisition requires plausibility and compatibility controls of the various data sources. As a result, data regarding the emissions from direct industrial discharges are of comparatively good quality, especially for 1995 and 2000. However, the data available for 1985 is much less reliable, as for the area of the former GDR the only data that could be used dates from 1989/1990. The examination of the data occurs by comparison with the data collected by the river basin authorities in the Rhine and Elbe river catchments.

Comparison with the ICPR inventory

For the year 2000, the ICPR also prepared an inventory of the heavy metal inputs in the Rhine catchment area (ICPR, 2001). The comparison of both surveys (see table 6-2) shows a very good correspondence for all parameters. The arising differences, even though minor, are due to the fact, that small differences exist in the delineation of the Rhine catchment area (consideration of the Maas and Ijssel areas). Moreover, in our own data acquisition attention was put on a most exhaustive collection of direct discharge sources, even of the small ones.

Table 6-2 Comparison of the results obtained for the Rhine catchment area in the year 2000 with the ICPR inventory 2000 in kg/a.

	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
This study	2,752	325	12,906	26,648	118	14,318	11,489	68,726
ICPR	2,742	307	12,831	27,205	112	14,410	11,408	67,645

Comparison with the ICPE inventory

The ICPE also elaborated an inventory of direct industrial discharges for the Elbe basin for the year 2000 (ICPE, 2001). It does, however, comprise the inputs via historic mining activities, which in the present calculations were reported separately. For the comparison the ICPE inventory was reduced by this share. The ICPE did not consider discharges with sewage concentrations remaining under certain quantification limits (for Hg, Cd: 10 kg/a; for Cr, Ni: 50 kg/a; for Cu, As, Pb: 100 kg/a; for Zn: 250 kg/a). In comparison with the present data collection, this inventory is thus less complete. Table 6-3 compares the results of the data collections. For some parameters the data show a good correspondance. For Zn, Pb, As and Cr the ICPE inventory showed considerably lower sewage loads.

On the whole, the results obtained for direct industrial discharges show a strong reduction of sewage loads in the observed period 1985-2000. The reduction amounted between 88 % for Pb and 99 % for Hg. Figure 6-10 shows that the reduction in the NFS (96 % for Zn to 99.9 % for Hg) was even stronger as compared to the OFS (79 % for Zn to 94 % for Cr).

Table 6-3 Comparison of the results for the Elbe catchment area in the year 2000 with the ICPE inventory 2000 (without mining) in kg/a.

	As	**Cd**	**Cr**	**Cu**	**Hg**	**Ni**	**Pb**	**Zn**
This study	33	68	1,735	6,291	18	2,825	1,205	3,823
ICPE	23	62	1,240	6,060	15	2,410	860	2,312

The reduction of emissions from direct industrial discharges was considerably higher than for the other pathways (municipal wastewater treatment plants, diffuse inputs). Correspondingly, in the total inputs the share of inputs arriving along this pathway decreased heavily. Figure 6-11 shows the changes of this share during the period 1985-2000: while in 1985 this pathway was the most important for Hg, Cr and Zn, it remains below 10 % for all metals by now.

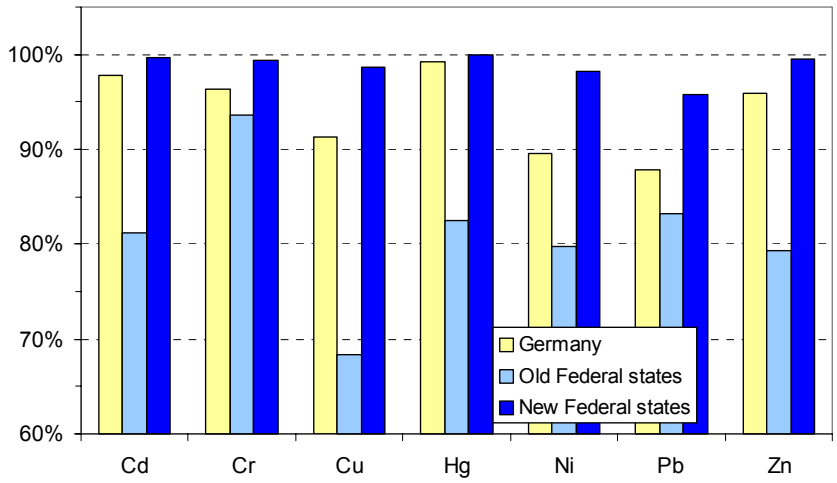


Figure 6-10 Reduction of sewage load inputs via direct industrial discharges for the period 1985-2000 for all of Germany and separately for the OFS and NFS.

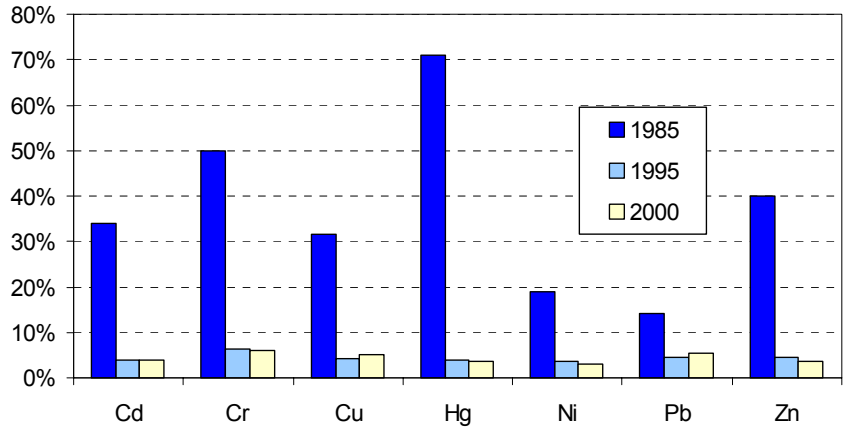


Figure 6-11 Changes of the share of direct industrial discharges in the total emissions of the years 1985-2000.

Fig 6-12 shows how much the reduction of the industrial sewage content affected the total reduction rate in the NFS. The reduction rate obtained for the total emissions in the period 1985-2000 is contrasted with the reduction rate that would result if emissions via direct industrial discharges in the NFS had not been considered. The results show that the impact is especially obvious for Hg, Cu, Zn and Cd.

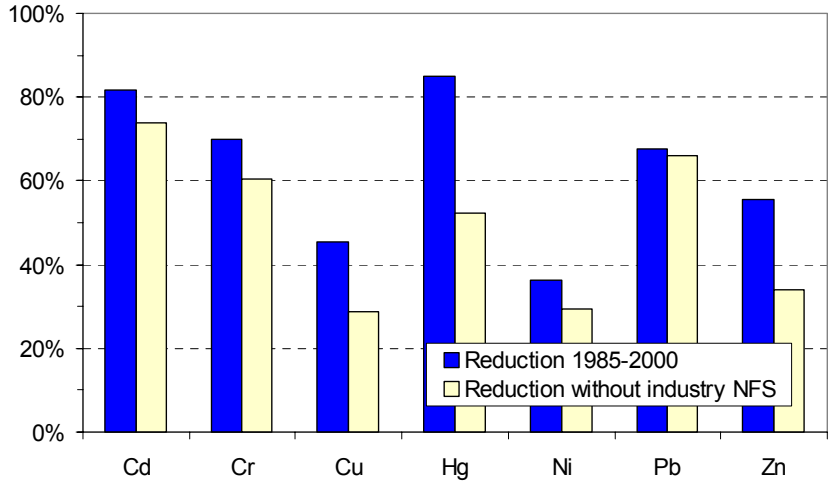


Figure 6-12 Comparison of emission reduction rates in Germany for the period 1985-2000, with and without consideration of direct industrial discharges in the NFS.

The main reasons for the dramatic reduction of discharged sewage loads via direct industrial discharges are:

- improved wastewater treatment in industrial works (implementation and further development of the requirements of § 7a WHG (Water Resources Policy Act) respectively stimulus function of the wastewater levy according to the Wastewater Levy Act);
- major economical changes in the NFS after the reunification which led, among others, to the closure of numerous environmentally harmful plants;
- connection of direct discharge sources to the public sewer system. Their sewage loads are now subject to an additional wastewater treatment in MWWTP and are no longer counted among the direct discharges;
- an altogether considerable structural change towards less sewage intensive industries and
- the reduction of water consumption for industrial purposes (sewage poor/free manufacturing procedures, water recirculation systems) allowing a more efficient wastewater treatment.

To illustrate the impact of the last three points in particular, figure 6-13 represents an evaluation of data from the Federal Statistical Office on the situation of industrial sewage (StaBu, 2001b). It shows a decrease of the treated sewage volume which amounted to over 40 % in the period 1991-1998 (the untreated sewage volume, usually cooling water, may be neglected here). This decrease is mainly due to a reduction by 64 % of the directly discharged sewage volume. The indirect sewage discharges changed considerably less (reduction by 17 %), which is caused, among others, by a displacement from direct to indirect discharges[4].

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4 According to official statistics, a differentiation between treated and untreated sewage water is not possible for directly discharged sewage. This is why in this case, the entire untreated respectively unused and derived (sewage) water volume was deducted, given that it is usually discharged directly.

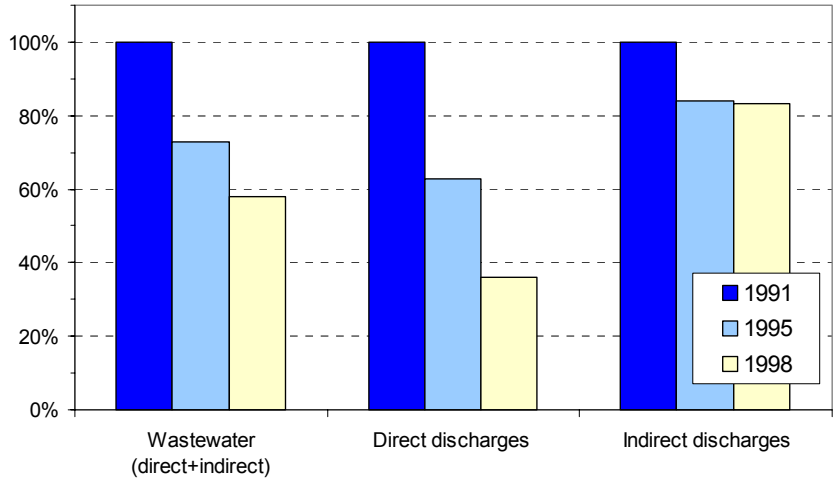

Figure 6-13 Development of industrial sewage water volumes for 1991-1998 (Evaluation of the statistics of the Federal Statistical Office) (1991 = 100 %).

6.2.3 Heavy metal emissions from historic mining activities

For the reasons described in chapter 3.1.3, the emissions determined by historic mining activities merely cover a small share of potential emission sources. A more accurate differentiation for every reference year is not possible. However, given that emissions from mines that had been shut down a longer time ago remain constant over a long period, the topical values may also be used for the former years. A research project is planned to bundle the existing data of the various Federal State authorities and, as far as possible, to quantify the input masses.

However, the comparison with the inputs via direct industrial discharges (table 6-4) shows that the loads determined for As, Cd, Ni, Pb and Zn range in comparable orders of magnitude.

Table 6-4 Heavy metal inputs originating from the registered historic mining activities and direct industrial discharges in 2000 in kg/a.

	As	**Cd**	**Cr**	**Cu**	**Hg**	**Ni**	**Pb**	**Zn**
Emissions via historic mining	973	549	107	4,027	-	14,272	6,371	45,891
Direct industrial discharges	2,851	469	17,128	35,200	165	19,092	15,822	117,542

6.3 Heavy metal emissions from diffuse sources

6.3.1 Heavy metal emissions by atmospheric deposition on the water surface

Direct atmospheric deposition contributes with between 0.4 % (Cr) and 15 % (Cd) in 1985 respectively between 0.5 % (Cr) and 6.9 % (Hg) in 2000 to the heavy metal pollution of surface waters (see figure 6-1 to -8). Figures 6-14a-h represent the surface specific heavy metal emission via atmospheric deposition on the water surface as well as its decrease between 1985 and 2000. The reference area for the calculation of the specific input was taken to be the respective total surface area of the catchments under consideration. Given that the coastal areas of the Baltic Sea comprise a large share of surface waters, they feature the highest specific inputs as compared to other river basins (figures 6-14a-h). The decrease of direct atmospheric deposition was calculated for Germany and for the period 1985-2000 with 56 % (Zn) to 97 % (Cd). The highest reduction for all metals was obtained in Eastern Germany. After the German reunification in 1990 numerous outdated furnaces and industrial plants were shut down respectively rapidly adapted to the state of the art.

Besides anthropogenic emissions, natural sources do also contribute to the heavy metal content in the atmosphere. Complex transport processes and meteorological factors determine the deposition rate in Germany which is not only ascribable to national emissions into the atmosphere. All changes of the atmospheric deposition (increases and decreases) as well as the reduction observed between 1985 and 2000 do thus not only result from reduced German emissions into the atmosphere. Nevertheless, the changes that occurred over the last years in the field of production and consumption contributed to a considerable extent to an improvement of environmental conditions.

Cd-emissions result, for instance, from the production of nonferrous heavy metals, the combustion of fossil fuels and waste as well as iron and steel production (Siewers/Herpin, 1998). In the 1980ies, a twelve-fold atmospheric deposition was measured in the former GDR as compared to the OFS (Möller/Lux, 1992). In 1995 and 2000, only the Ruhr basin, Berlin and the NFS with the exception of Mecklenburg-Western Pomerania exhibit increased Cd deposition rates (see figure 3-3 in chapter 3.2.1). According to Ilyin et al. (2001), the contribution of internal emissions into the atmosphere in the German Cd deposition rate is one third for 1999.

In the 1980ies the major share of Pb emissions (about 90 %) resulted from the use of leaded fuel. Further sources are the iron and steel industries as well as the combustion of highly sulphurous coal (Siewers/Herpin, 1998). Compared to the OFS, slightly increased deposition rates were measured for Pb in the former GDR in 1985 (see chapter 3.2.1). Despite of a lower traffic volume as compared to the OFS,

the emissions from traffic were higher and result from a higher Pb content in the fuel used in the former GDR (Siewers/Herpin, 1998). The introduction of unleaded fuels since 1985 led to an 89 % reduction of direct atmospheric inputs into surface waters between 1985-2000. In 1995, increased Pb deposition rates were still measured in urban-industrial conglomerates of Baden-Wuerttemberg, in the Ruhr basin and in Saxony (see figure 3-3 in chapter 3.2.1). The share of German emissions into the atmosphere in the deposition rate is 41 % for 1999. Another 18 % originate from France, Italy and Belgium (Ilyin et al., 2001).

Given that only few data on atmospheric deposition were available for 1985, the calculated 67 % reduction of direct inputs into surface waters is merely approximate. In 1995 and 2000, the Ruhr basin, Berlin, Saxony-Anhalt and Thuringia exhibit increased Hg deposition rates (see figure 3-3 in chapter 3.2.1). The share of German emission sources in the Hg deposition amounts to 50 % (Ilyin et al., 2001).

No deposition data allowing a differentiated observation on a river basin level for the 1990ies was available for As, Cr, Cu, Ni and Zn. This is why merely a spatial differentiation between OFS and NFS could be conducted for 1985 (see chapter 3.2.1). The introduction of more efficient dust filters in coal power plants contributed substantially in the 96 % reduction of As inputs (Jockel, 1993). The main emission source for Cr into the atmosphere is the iron and steel industry. Cu and Zn are emitted during the production and processing of Cu and Zn products, in the nonferrous heavy metal industry and in coal combustion (Siewers/Herpin, 1998). The highest reduction has been determined for these metals in Eastern Germany as a result of the decrease of industrial activities since 1990.

In the OFS the atmospheric deposition of nickel merely exhibits a slight reduction for the period 1985-2000, despite of a decrease of Ni-emissions into the atmosphere by 52 % between 1985 and 1995 (UBA, 2000) (see figure 6-14f). This was proven in North Rhine-Westphalia by time series measured by Schulte/Gehrmann (1996) for the period 1984-1993 and the time series of UBA for 1994-1999 (UBA, 2001). According to Schulte/Gehrmann (1996), the relatively small decrease of the atmospheric deposition is due to a Ni-consumption increased by 18 % (Metallstatistik, 1995, 2000) which could overlay the measures taken to reduce air pollution that were started in the 1980ies. The main anthropogenic sources are metal smelting and the combustion of fossil fuels (especially diesel and fuel-oil-mixtures). The heavy reduction of Ni inputs observed in the Eastern river basins is partially due to the substitution of the two-cycle engines commonly used in the former GDR (UBA, 2000).

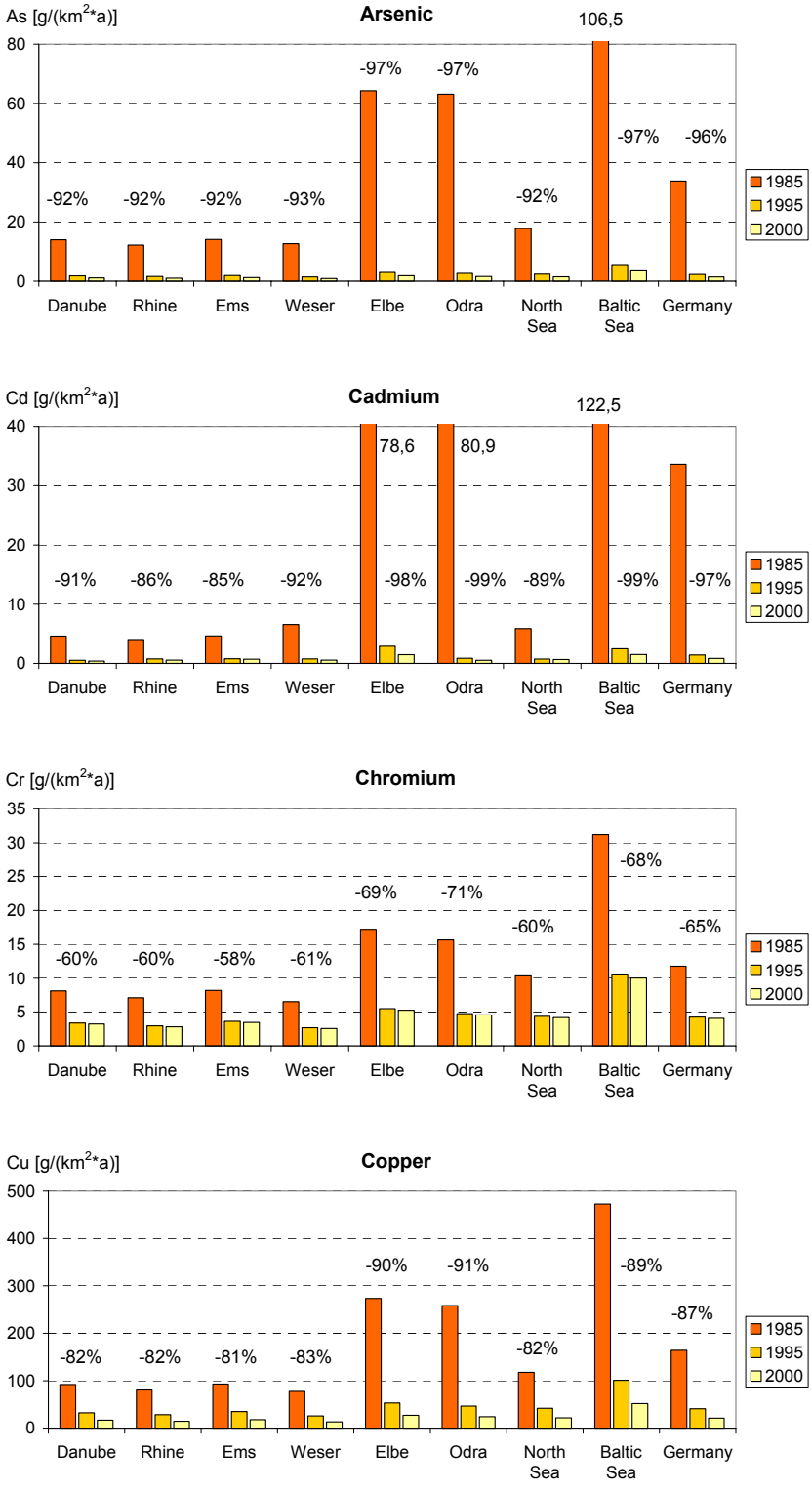

Figure 6-14a-d Surface specific heavy metal emissions from direct atmospheric deposition on the water surface in g/(km^2 catchment area·a).

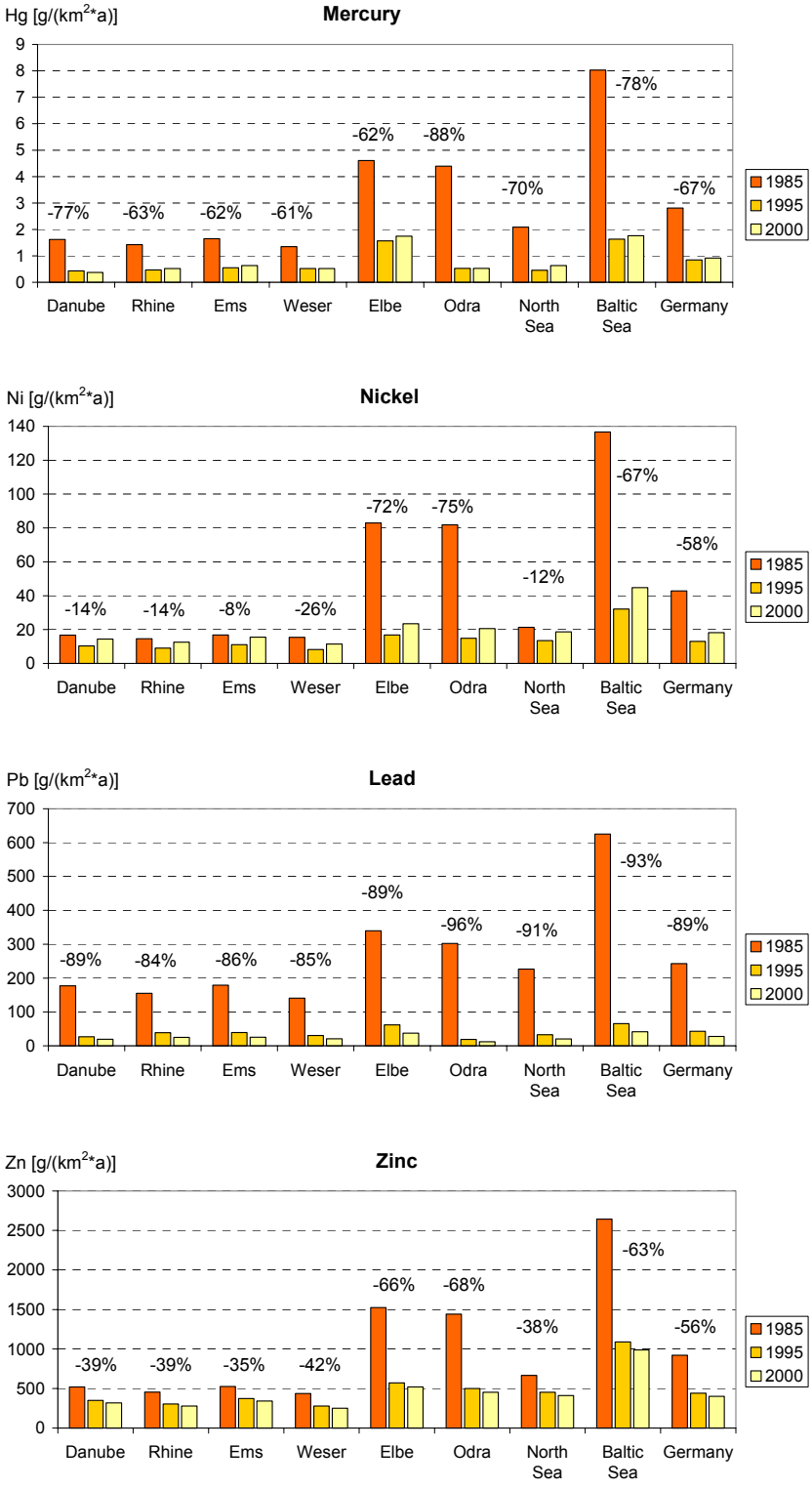

Figure 6-14e-h Surface specific heavy metal emissions from direct atmospheric deposition on the water surface in g/(km^2 catchment area·a).

6.3.2 Heavy metal emissions via seepage on farmyards and spraydrift

Heavy metal emissions via seepage on farmyards and spraydrift decreased by between 28 % (Pb) and 40 % (Cr) during the period 1985-2000. In the case of mineral fertilisers, especially the application of P- (and K) fertilisers was halved. The heavy reduction of Cr inputs is due to the diminishing importance of Thomas meal. Whereas in 1985 the share of Thomas meal in the total P-fertiliser volume still amounted to about 50 % in the OFS, it is no longer applied today (see table 3-15 in chapter 3.2.2). P-fertilisers from natural phosphate deposits may be heavily polluted with Cd and Zn, depending on the source of the rock phosphates. The preferred use of cadmium-poor rock phosphates led to a reduction of the Cd input in the OFS (LABO, 2000). In the former GDR, Kola apatite containing very low Cd and Zn concentrations was used before 1990. However, since the 1990ies, the Cd contents have been comparable to the P-fertilisers produced in the OFS (Podlesak et al., 1991). The inputs from organic manure decreased correspondingly to the reduction of the animal stock of pigs and cattle by about 30 % between 1985 and 2000.

The river basin of the Ems and the coastal area of the North Sea exhibit the highest surface specific inputs due to the high number of farms (agricultural crop land 80 % respectively 77 %). Relative to the total heavy metal emissions, input via seepage on farmyards may almost be neglected. The share of Cu and Zn inputs originating mainly from organic manure merely amounts to about 1 % of the total emission. For the other metals, this share remains below 0.2 %.

6.3.3 Heavy metal emissions via runoff from unpaved areas

Heavy metal emissions via runoff from unpaved areas such as arable land and grassland as well as from mountain areas and areas with natural vegetation, are relevant most of all in the river basins of Danube and Rhine (figure 6-1 to –8). This results from the high specific surface runoff in the foothills of the Alps and the higher annual precipitation in the upper Rhine basin.

The major portion of the load originates for most of the metals with at least 90 % from rainfall runoff. Only in the case of Cr, 49 % of the load resulting from surface runoff originate from fertiliser washoff. This is not only due to very high Cr contents in P-fertilisers (Thomas meal), but also results from the neglectable importance of atmospheric deposition for Cr compared to the inputs via other sources (see figure 6-1). Washoff also contributes a significant share of Cu and Zn mainly originating from organic manure. Their emission share via surface runoff amounts to 20 respectively 15 %.

As a result of meteorological conditions, the surface runoff was by 16 % higher in the mid-nineties as compared to the mid-eighties. The Cu and Ni concentration in rainfall barely changed between 1985 and 2000. For these metals the load increase was thus calculated with 5 respectively 7 % (see table 3-16 in chapter 3.2.3). For the other metals this reduction amounts to between 38 % (Zn) and 89 % (Pb), due to extremely lower concentrations in rainfall (see chapter 6.3.1) and decreased fertiliser applications (see chapter 6.3.2).

6.3.4 Heavy metal emissions via erosion

The contribution of erosion in the total heavy metal emission fluctuates between 2 % (Cd, Hg) and 12 % (Cr) in 1985 and between 13 % (Cd, Hg) and 47 % (Cr) in 2000. As can be taken from figure 6-2, erosion is the major pathway for Cr in most of the river basins in the 1990ies. For Pb, As and Cu as well, considerable emissions enter the surface waters via erosion. The regional distribution of heavy metal inputs via erosion may be taken from the maps in figure 6-15 for 1995.

Due to high sediment inputs and heavy metal contents in the topsoil, the focal points of emissions via erosion are situated on the lower Danube (Inn, Isar, Vils), the Upper Rhine, the Main (upper Main, Tauber, the Franconian Saale), the upper part of the Elbe (Mulde, Saale, Unstrut) and the middle part of the Weser. The foothills of the Alps, the eastern Danube, the Main and the Unstrut exhibit especially high surface specific sediment inputs. As they are situated in medium altitudes and due to the high percentage of arable land, these areas are particularly threatened by erosion. Low specific sediment inputs are quantified for the river basins of the lower Ems and Weser, the coastal region of the North Sea, the central north-eastern lowlands (Black Elster, Spree, Havel) and the Lower Rhine (see figure 3-4 in chapter 3.2.4).

High natural (i.e. geogenous) heavy metal contents in the soil are mainly found in the hardrock areas of Baden-Wuerttemberg, Bavaria, Saxony and Thuringia. Acid eruptive stones and metamorphites as well as argillaceous slate series of the Erzgebirge (‘ore mountains’) exhibit the highest As, Cd and Pb contents. High Cr, Cu and Ni contents may be observed in shelly limestone, keuper marl and argillaceous slate series in Thuringia. Moreover, the tertiary basalts of Hesse represent a major source for Cr and Ni. However, the tertiary and quaternary, mainly sandy sediments of Northern Germany exhibit relatively low heavy metal contents.

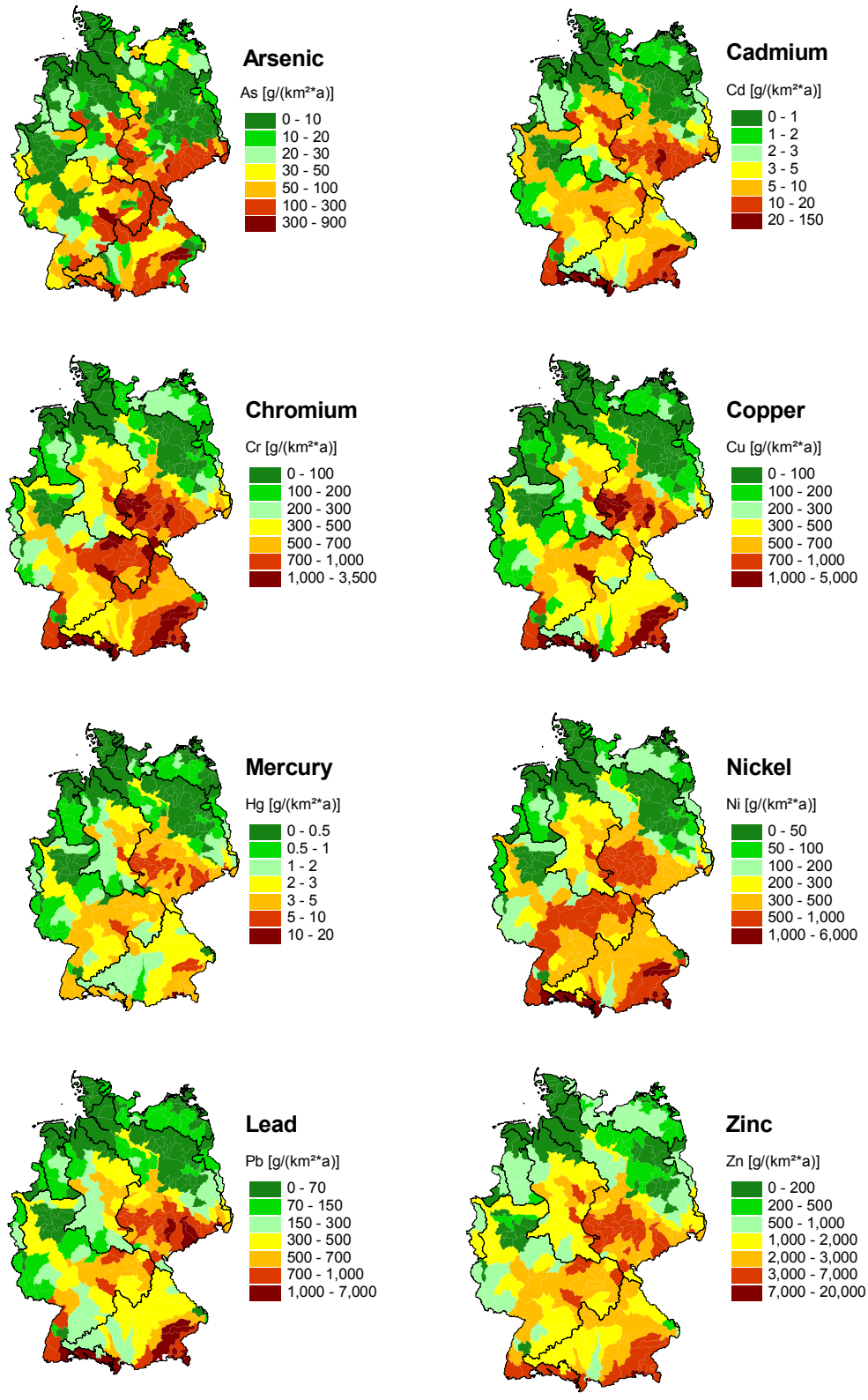

Figure 6-15 Distribution of heavy metal emissions by erosion.

For all heavy metals, an input increase caused by erosion was calculated for the period 1985-2000. Within the studied period, a significant input increase was found for Cd with 6 %, Cu and Zn with 5 % and Hg with 4 %. An increase by 2 % was observed for As, Cr and Pb. The reason for this is the accumulation of heavy metals in the topsoil as a result of atmospheric deposition and the application of mineral fertilisers, organic manure and sewage sludge. While the enrichment of Cd in the topsoil is mainly due to atmospheric deposition and the application of mineral fertilisers, Cu and Zn mainly originate from organic manure. The major sources for Hg are atmospheric deposition and agricultural sewage sludge use. Ni exhibits the lowest enrichment rates in the topsoil over the period under consideration, with a mere 1 %.

With the coming into force of the Federal Soil Protection Act (BBodSchV), a settled balance for heavy metal inputs and emissions in agricultural soils should be the goal (Bannick et al., 2001). The balances established within the frame of this project showed that the annual accumulation in the topsoil was reduced for all metals between 1985 and 2000. A settled balance could however only be established for Ni between 1995 and 2000.

6.3.5 Heavy metal emissions via drainages

Heavy metal emissions via drainages were quantified on the basis of mean seepage water concentrations that were unitary for all river basins (chapter 3.2.5). Different surface specific loads do thus exclusively result from the various drain rates corresponding to figure 3-6 (chapter 3.2.5). The coastal area of the North Sea exhibits the highest specific heavy metal inputs via drainages.

Relative to the total heavy metal emissions, the share originating from drainages was of between 0.2 % (Pb) and 5 % (Ni) in 1985 respectively between 0.6 % (Pb) and 10 % (Cr) in 2000.

In principle, if the same amounts of heavy metals are adsorbed, their solubility usually decreases in the following sequence (Scheffer/Schachtschabel, 1992):

$$Cd \geq Zn \geq Ni > Cu > Cr = As \geq Pb \geq Hg$$

The low Pb loads from drainages are thus to be attributed to the low solubility of Pb in the soil. Compared to this, the Hg loads appear relatively high. They might have been overestimated, as all measured values of Hg in seepage water remained under the quantification limit (Bielert et al., 1999) and thus 50 % of the quantification limit was used in the balance.

For all reference periods, the same drainage area size (Behrendt et al., 1999) and metal concentrations in the drainage effluent were taken as a basis. The changes in

emissions from drainages during the period 1985-2000 are thus merely due to differences in the amount of the drain rate. On a German average it was by 7 % higher in the 1990ies than in the 1980ies.

6.3.6 Heavy metal emissions via groundwater inflow

The major source for Ni and As emissions into surface waters is the groundwater inflow. In 2000, its share in the total input is 46 % Ni and 56 % for As. For the other metals between 3 % (Pb) and 14 % (Cd) of the inputs enter the surface waters via the groundwater.

The heavy metal input via groundwater inflow was quantified on the basis of median values taken from the New Geochemical Atlas of Germany (Birke et al., 2001). One fraction of the heavy metal load in the groundwater originates from geogenous sources. The geogenous share may be quantified on the basis of mean geochemical background values that were also determined within the scope of the New Geochemical Atlas of Germany. For Germany, the geogenous share amounts on average between 15 % for Zn and 73 % for Cr.

No regionalisation of heavy metal concentrations in the groundwater inflow could be established within the frame of this research project, given that the New Geochemical Atlas will only be completed in 2003. Spatially differentiated data will only be available at that time.

6.3.7 Diffuse heavy metal emissions from urban areas

Heavy metal inputs from *sewer systems and not connected inhabitants* supply a considerable share of the total Cd, Cu, Hg, Pb and Zn loads discharged into the river basins. Already in 1985, diffuse emissions from urban areas represented the most important pathway for Pb with 40 %. In 1995 the share in the total emission was between 24 % (Hg) and 42 % (Pb) respectively, in 2000, between 30 % (Hg, Cd) and 44 % (Zn). Diffuse inputs from urban areas are of little importance for As, Cr and Ni (see figures 6-1 to –8).

Figures 6-16a-h represent the specific inputs via urban areas relative to the catchment surface of the river systems. A differentiation was made between the inputs from *storm water sewers, combined sewer overflows, sewer systems that are not connected to wastewater treatment plants* and *households that are not connected to sewer systems*. The surface specific loads are represented for the years 1985, 1995 and 2000 respectively.

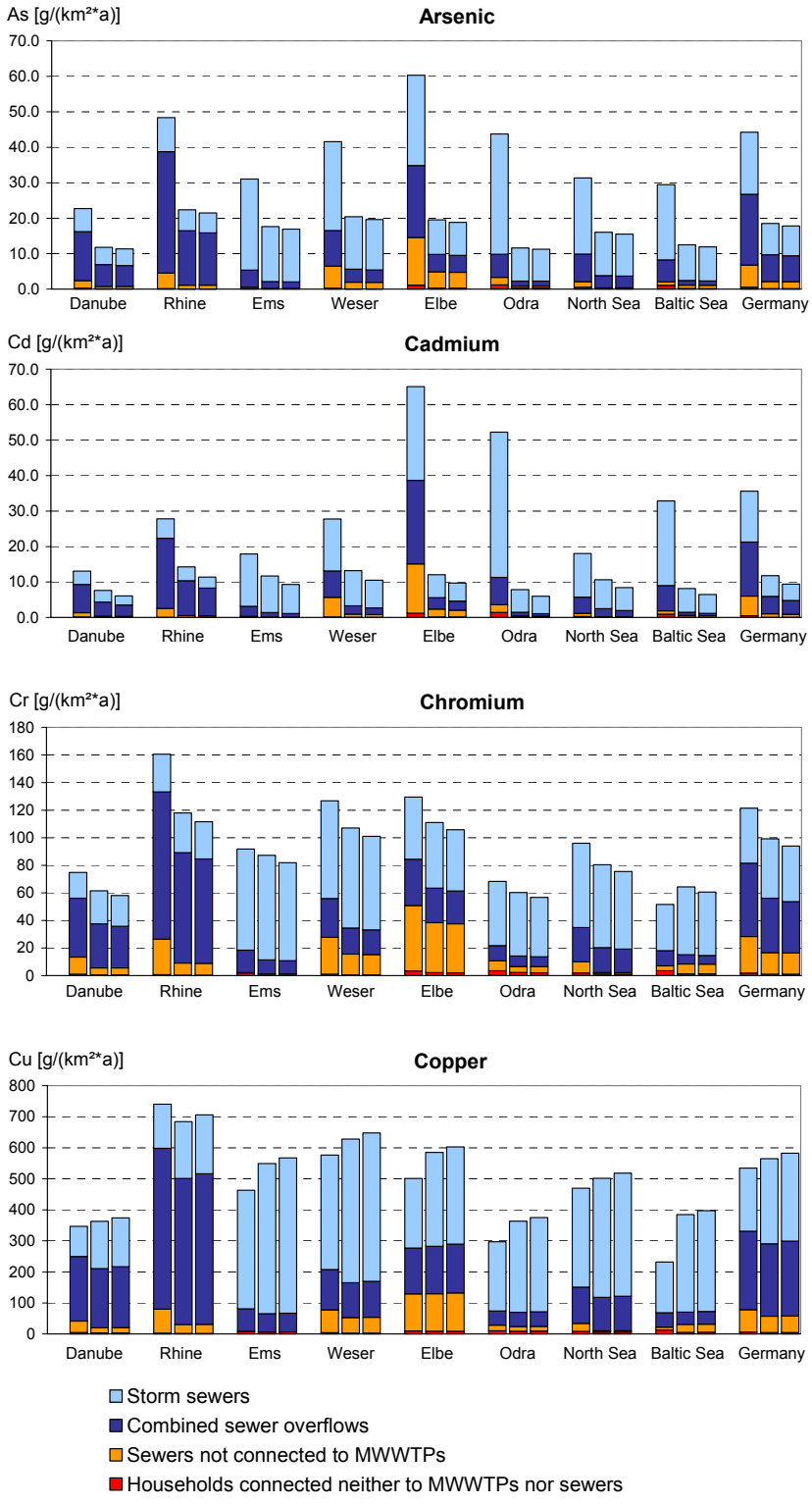

Figure 6-16a-d Specific emissions from urban areas in g/(km2 catchment area ·a).

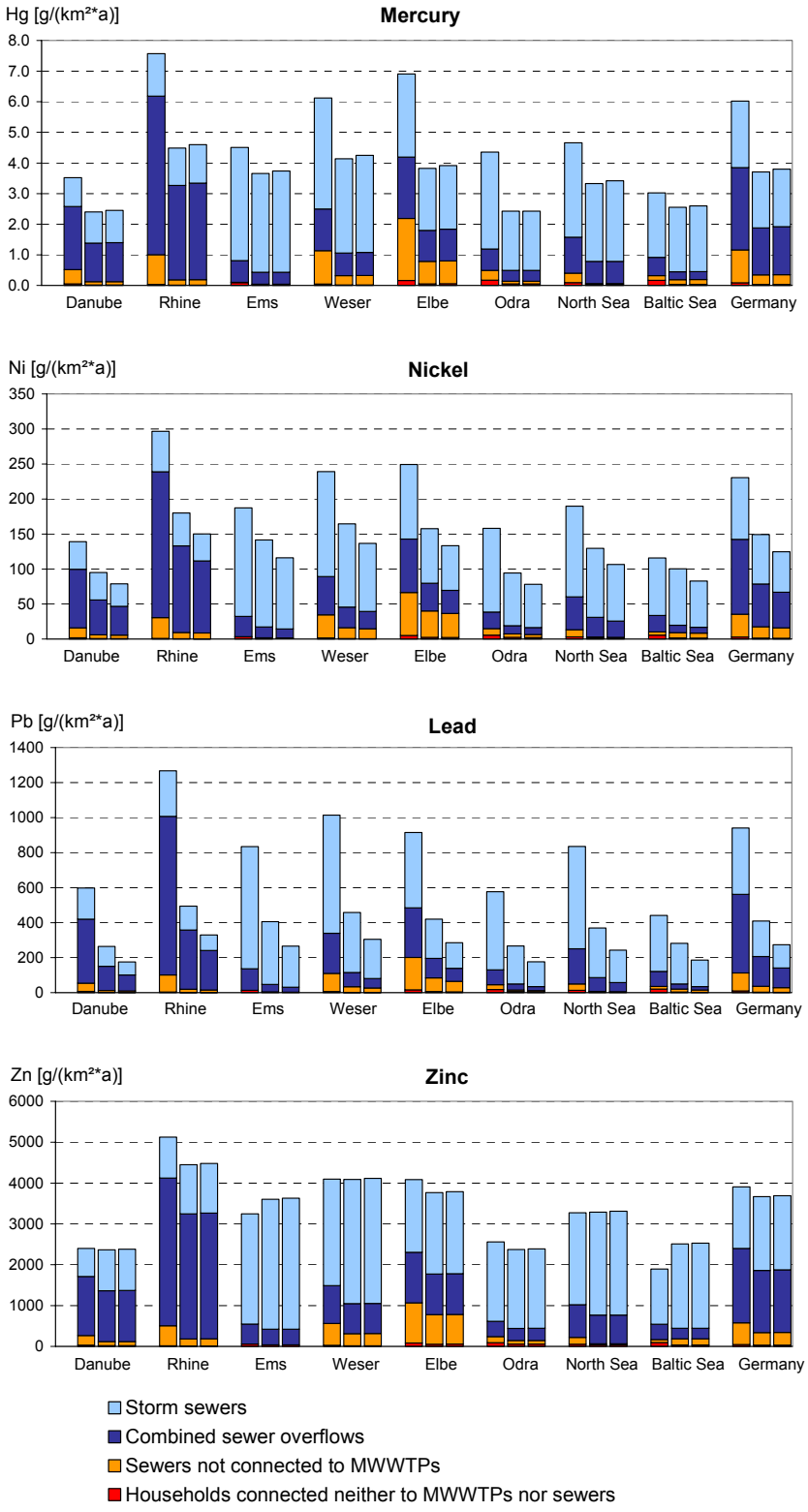

Figure 6-16e-h Specific emissions from urban areas in g/(km2 catchment area ·a).

The major share of the inputs originates from storm sewers and combined sewer overflows. According to their area of application, in Southern Germany the largest load share originates from combined sewer overflows, in the North it originates from separate sewer systems (see figure 3-8 in chapter 3.2.7).

In 1985, inputs via *sewer systems that are not connected to a wastewater treatment plant* are still of importance for Danube, Rhine, Weser, Elbe, Odra and the coastal area of the Baltic Sea. Whereas in 1985, in the OFS only 3.8 % of the population was connected to a sewer system but not to a wastewater treatment plant, in 1995 this share merely amounted to 1.2 %. In 1995, still 14.8. % of the population were only connected to a sewer system in the NFS. This is why this pathway was still of importance for Elbe and Odra in the mid-nineties (table 3-28 in chapter 3.2.7).

Even though in 1995 the share of inhabitants not connected to a sewer system was 4.8 % in the Old respectively 22.7 % in the New Federal States, heavy metal emissions originating from this pathway are of subordinate importance, assuming that a major part of the heavy metals is retained during their passage through the soil.

The amount of surface specific inputs from urban areas is substantially determined by the percentage of paved area in the river basins. The highest specific emissions from urban areas were calculated for the Rhine, Ems, Weser and Elbe rivers, given the high percentage of paved surfaces of between 3 % (Weser) and 5 % (Rhine).

The changes as for the diffuse inputs via urban areas is of between –74 % (Cd) and +9 % (Cu) for the observation period 1985-2000 for Germany.

For Cd, the most important pollution sources are combustion processes, industrial emissions and traffic (abrasion from tyres and brakes) (Duncan, 1999). Given the dramatic reduction of atmospheric deposition, the highest reduction of diffuse inputs from urban areas was observed for the eastern river basins, between 80 % (coastal area of the Baltic Sea) and 89 % (Odra). For the other river basins, the reduction is 53 % (North Sea) to 62 % (Weser). The major reason for a reduction by 71 % of Pb concentrations in storm water runoff is the use of unleaded fuels since 1986. Diffuse As, Cr, Hg and Ni emissions via urban areas decreased by between 23 % (Cr) and 60 % (As) from 1985 to 2000. For these metals the reduction of the concentrations mainly results from the reduction of the atmospheric deposition already described in chapter 6.3.1.

For Cu and Zn no reduction of the concentrations in the discharged runoff was established in chapter 3.2.7. The reasons herefore may be found in the sources these two metals originate from in urban areas. Given that Cu and Zn are used as building material for roofs and gutters, corrosion is a major pollution source. The Wirtschaftsvereinigung Metalle (2001) (trade association) specifies the total load washed off by corrosion in 2000 with 90 t for Cu and 780 t for Zn. With a separate

sewer system share of 46.5 % (StaBu, 1998b), about 42 t Cu and 363 t Zn of this load directly enters the surface waters via storm sewer outlets. Relative to the total load from storm water sewers of 101 t Cu and 647 t Zn, the share originating from surface corrosion amounts to 41 % for Cu and 56 % for Zn in the year 2000.

The copper surface in the entire building inventory exposed to the weather was specified by the Wirtschaftvereinigung Metalle (2001) with 23.8 Mio m^2 for the OFS in 1985 and with 64.1 Mio m^2 for all of the FRG in 2000. For 1985, a higher corrosion rate as compared to the year 2000[5] had to be assumed, given the higher atmospheric SO_2- and NO_X-concentrations of the time (Landner/Lindström, 1999). However, due to a simultaneous 2.7-fold increase of the exposed Cu surfaces, a reduction of inputs via corrosion is not to be supposed for the period 1985-2000. No data are available on the increase of the exposed areas for the period 1985-2000. The Wirtschaftsvereinigung Metalle (2001) specifies the average market size for zinc used for building construction purposes in the last 30 years with 69,000 t/a. A considerable increase of surfaces will thus also occur for Zn.

A further important source for Cu and Zn in storm water runoff is traffic, i.e. the release of brake abrasion and abrasion from tyres. Since asbestos containing brake linings have been substituted in the early 1980ies, they now consist of brass (70 % Cu, 30 % Zn) for 25-50 % of their weight. For a supposed durability of the linings of 40,000 km, about 1-2 mg Cu are released per driven km (Landner/Lindeström, 1999). Given an increasing traffic volume in Germany (1990-1999 by 12 %, UBA, 2000), the source “traffic” has to be quantified with constantly growing Cu and Zn loads discharged into the sewer systems.

For the reasons described, the diffuse Cu input from urban areas increased by an average of 9 % in Germany for 1985-2000. A particularly high increase is identifiable in the NFS, caused by a growing use of Cu for water supply installations and roofing (see figure 6-16d).

For Zn the emission from urban areas decreased by altogether 6 %, even though an increase of the specific heavy metal input from impervious urban areas was observed. This is mainly to be attributed to the decrease of *sewer systems that are not connected to a wastewater treatment plant* as well as to a reduced domestic and industrial-commercial sewage load.

In Germany, the share of the domestic and commercial sewage load in the total load of combined sewer overflows amounts to between 2.4 % (Pb) and 14 % (Cr) for 1985 and between 4.9 % (Zn) and 13 % (Cr) for 2000. The comparison with the minimum mixing ratio of 1:7 between wastewater and surface runoff that had to be

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5 The Wirtschaftsvereinigung Metalle (2001) specifies the corrosion rate for Cu in 2000 with 1.3 g/(m^2Pa). The exact corrosion rate for 1985 is not known.

guaranteed before the CSO start to work (ATV-DVWK, 2000, A 128) shows, that the calculated sewage share is of a plausible order. The share of heavy metals in the total discharged sewer load originating from commercial activity (households and industry) still lies between 19 % (Zn) and 64 % (Cd) in 1985. In the year 2000, however, merely between 6.2 % (Zn) and 22 % (Cd, Pb) of the inputs originate from industrial-commercial sewage.

Over the last years a trend towards separate systems could be observed. Whereas in Germany the channel length merely increased by 13 % between 1991 and 1998, the channel length of the separate system increased by altogether 39 %. Considering anthropogenic pollutants, this does not necessarily go along with an improvement of water quality. In the combined system, one fraction of the pollution load originating from paved surfaces is discharged into the wastewater treatment plant where it is efficiently retained. However, in the separate system this pollution load is usually discharged into the surface waters without any adequate treatment. A further expansion of separate systems devoid of an adequate storm water treatment goes thus along with additional pollution loads for the surface waters.

6.3.8 Heavy metal emissions originating from shipping activity

Heavy metal inputs originating from shipping activity only had to be considered for Cu, Pb and Zn. Cu is emitted by sporting boats. Given that no exact figures are available on the number of sporting boats existing in the river catchments, no changes as for the emission situation of Cu could be calculated. Pb and Zn inputs into the rivers are mainly due to enter business ships. For 2000, a lower number of business ships was recorded by the Federal Statistical Office, especially for the NFS. Since 1985, a reduction amounting to 17 % for Pb and to 91 % for Zn could thus be calculated. The dramatic reduction of Zn inputs is to be attributed to the assumption that Zn electrodes used for corrosion protection purposes are exclusively used in brackish inland waters, i.e. only in the coastal area of the Baltic Sea (see chapter 3.2.8). This is why in the shipping sector of the NFS the decreased number of business ships is especially apparent in the coastal area of the Baltic Sea.

6.4 Comparison of the calculated heavy metal emissions with the loads measured at the quality monitoring stations

In consideration of the retention capacity of a river it is possible to compare the calculated emissions with the river loads obtained from the measured quality and discharge values (chapter 5.2). Despite of measurement and calculation mistakes occurring both for emission and immission, this comparison may allow to detect significant deviations and the result of the emission calculation may be checked as for its plausibility.

Figures 6-17a-f represent the relation between calculated load (emission – retention) and measured load (established from monitoring data). Besides our own evaluations, the loads calculated for Cd, Cu, Pb and Zn by Vink/Behrendt (2002) on the basis of the same method could also be used. In the diagrams, the 50 % deviation from the 1:1 line is indicated by a pointed line. Barely any river load data are available for Hg and As.

The mean total deviation is 38.7 % for Cd, 42.1 % for Cr and 41 % for Pb. The concentrations of these metals in the rivers frequently remain under the quantification limit, which leads to considerable uncertainties. On the other hand, a comparably small deviation was determined for Cu with 19.7 %, Ni with 17.4 % and Zn with 28.2 %, as for these metals the quantification limits measured rarely remained under the quantification limit. An inaccurate evaluation of the river loads may however also be attributed to the discharges taken into account. The catchment areas of the gauging stations for water quality respectively discharge differ considerably in some parts.

In general it may be stated that the deviations between calculated and ‘measured’ load increase considerably for smaller catchments. Given the available data basis and the scale level of the large German river basins to be considered, heavy metal emissions had, in part, to be quantified on the basis of mean emission factors. By doing so, the peculiarities of smaller river basin units as e.g. an increased geogenous load or major regional and local loads resulting from industrial or agricultural uses, may not be considered. Meteorological as well as geographical or landuse-dependent characteristics cannot be adequately collected by means of the available respectively applied data basis and methodology. Especially in the areas of former ore mines it was not possible to quantify all loads resulting from historic mining activities (see chapter 3.1.3 and 6.2.3).

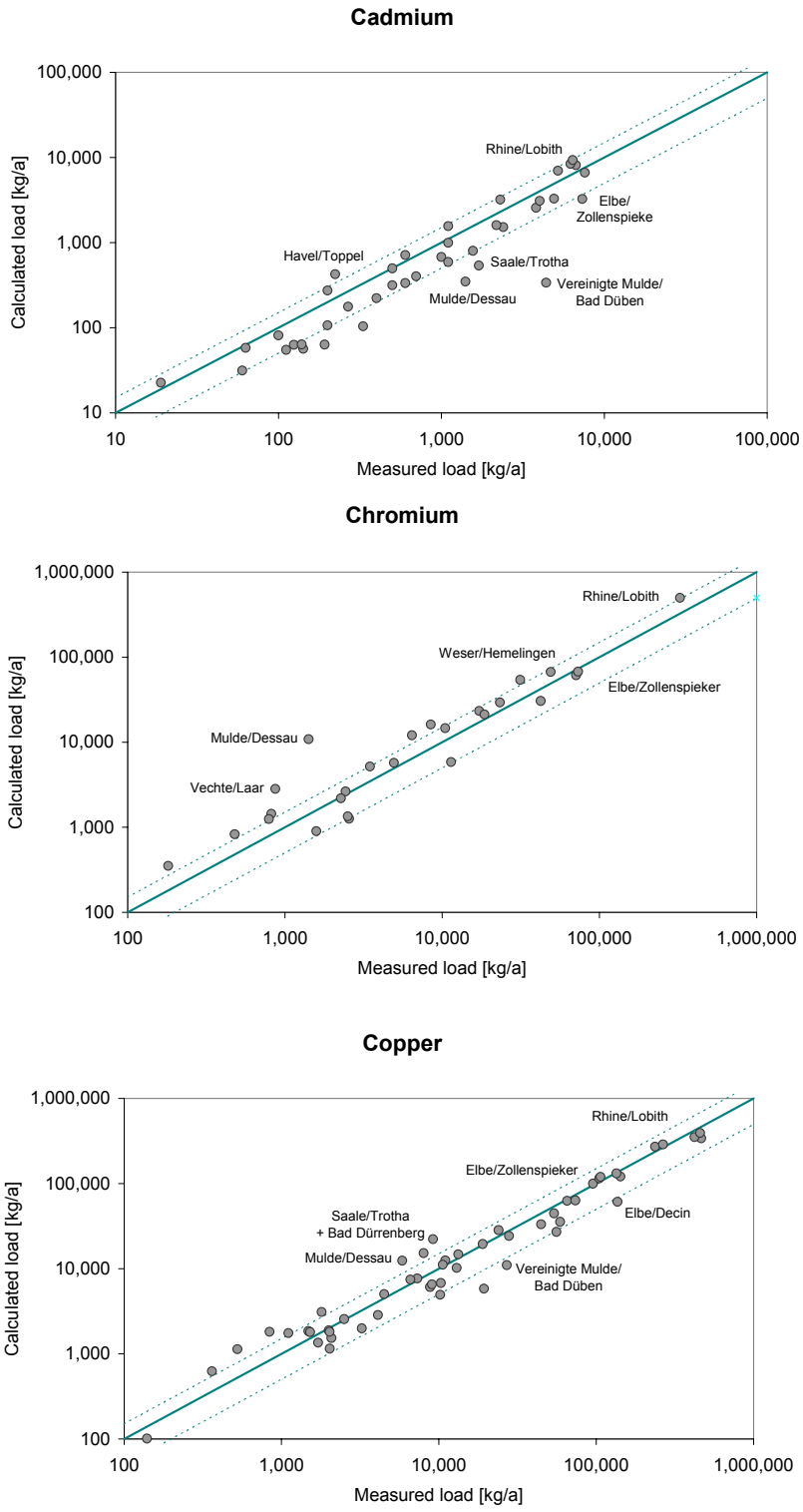


Figure 6-17a-c Comparison between calculated loads with loads measured at monitoring stations.

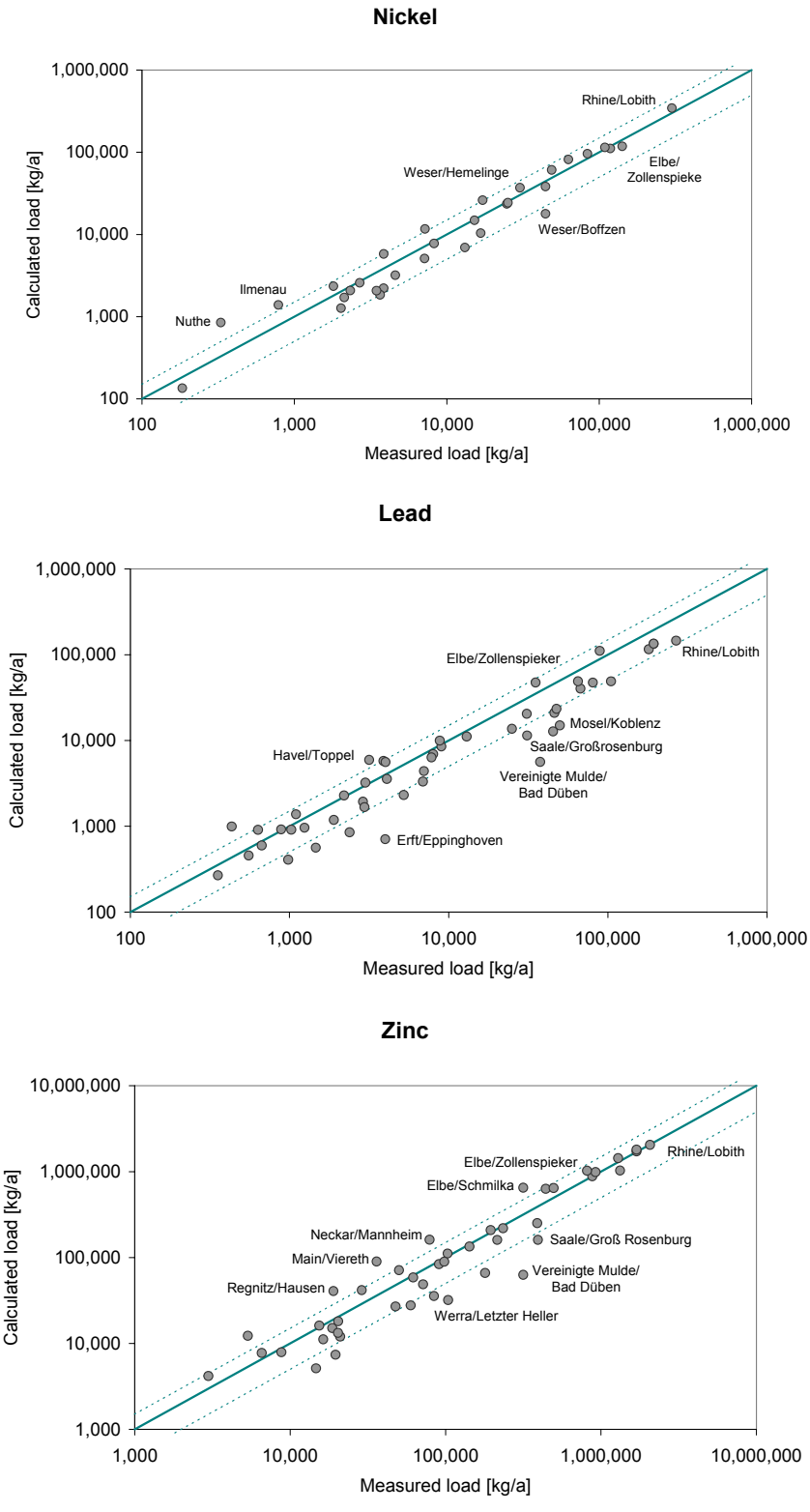


Figure 6-17d-f Comparison between calculated loads with loads measured at monitoring stations.

More significant differences have been identified e.g. for the Elbe river basin and the catchments of the Mulde and Saale, which exhibit high geogenous heavy metal concentrations originating from the Erzgebirge (‘ore mountains’) and the Thuringian Slate Mountains. In the Rhine river basin, the Pb inputs from the Erft have been largely underestimated. Tunnel waters of a former lead mine (Burgfeyer tunnel) are discharged into the Erft, leading to a considerable sediment pollution (Christoffels, 1989).

The relation between catchment size and percental deviation is represented for Cu in figure 6-18. For large river basins, a good correspondence could usually be obtained between calculated loads and loads measured at monitoring stations. Only for the Elbe, a higher deviation of beyond 50 % was identified on the German/Czech border near Decin. For Cu, Vink/Behrendt (2002) derived a load of 137 t near Decin. However, at the monitoring station Schmilka situated downstream, the Cu load amounted to a mere 65 t, which corresponded well to the calculated loads. Vink/Behrendt (2002) attribute this difference to the fact that the two sampling sites are situated on different banks of the Elbe river. Behrendt et al. (1999) observed a comparable phenomenon for nutrients.

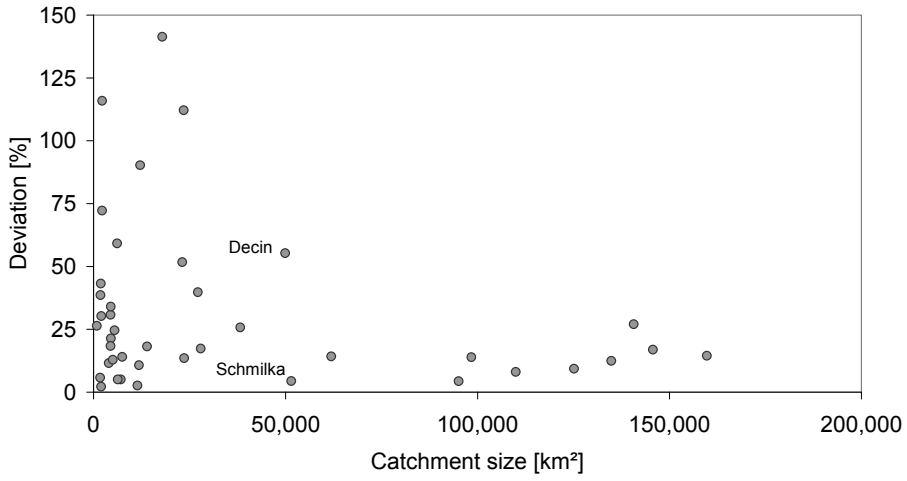


Figure 6-18 Deviation of calculated loads and loads measured monitoring stations versus catchment size on the example of Cu.

For some river basins it became apparent that the inputs are considerably higher than the river loads. An analysis revealed that for most of these rivers the monitoring stations were situated directly downstream a lake or a dam. It has to be supposed that the retention factor for these rivers is underestimated by the retention approach derived for free-flowing surface waters. In the case of the Bitterfeld dam

for example, 80-90 % of the suspended solid load (Müller et al., 1995, cited in Vink/Behrendt, 2002) is retained. This is why near Dessau the heavy metal load carried by the Mulde is low. The overestimation of the inputs into the Mulde shows best for Cr, as for this metal erosion is the essential pathway.

Despite of the characteristics that had to be considered for nearly every river basin and the available, sometimes unsatisfactory data basis used to quantify the emissions and river loads, the emission/immission comparison led to a pleasing result. The loads evaluated for the large river basins of Germany showed a deviation of below 50 % for the metals Cd, Cr, Hg and Pb. For Cu, Ni and Zn, the error is of even less than 30 %.

A further improvement of this result may only be achieved if, both on the emission and on the surface water side, reliable measurements with a higher spatial resolution are conducted for all metals. Within the frame of this project for instance, only loads of Cu, Zn and Ni could be quantified reliably at the monitoring stations.

7 Lindane emissions in the river basins of Germany

7.1 Overview of lindane emissions

Figure 7-1 provides a survey on lindane emissions in the river basins and on their changes between 1985 and 2000. The specific total emissions are related to the catchment area, the share of point and diffuse sources as well as the importance of the studied pathways. A detailed listing of the emissions may be found in appendix 2i.

Between 1985 and 2000 a mean lindane emission reduction by 76 % was calculated for Germany. This is closely related to the fact that the application of lindane has first been largely limited since the mid-eighties and then prohibited in Germany since 1999. Nevertheless, given the persistence of lindane, it may still be found in the atmosphere, in the soil and in the water and is thus still discharged into surface waters in 2000.

As it is highly volatile and persistent, its distribution via the atmosphere is of great importance. The lindane contained in the atmosphere enters the rivers via *direct atmospheric deposition on the water surface, runoff from unpaved areas* as well as through *sewer systems* and *effluents of municipal wastewater treatment plants.*

Wastewater treatment plants were identified as the most important pathway. The share in the total load for Germany is of an average 25 % for 1985 and 36 % in 2000. Since 1985, a decrease of inputs by 52 % via MWWTP has been found as a result of heavily reduced lindane applications and lower concentrations in the surface runoff from urban areas. Significant industrial inputs were still found for the Elbe until 1994, due to the lindane formulation in Bitterfeld-Wolfen. The share of point sources amounts to about one third of the total emissions.

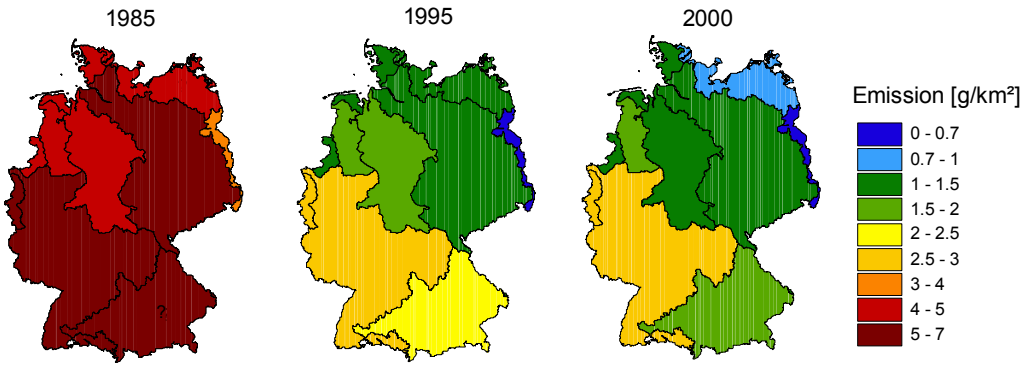
In 1985, the major diffuse pathway with a share of 24 % in the total emission is *runoff from unpaved areas*. In the OFS about half of the emissions originate from rainfall, the other half results from washoff of applied lindane. For the catchments of Danube and Rhine the load share from rainfall dominates due to a higher specific runoff described in chapter 6.3.4. However, given higher application masses in the former GDR (see chapter 4.1.3), the major load share in the eastern German river basins of Elbe, Odra and Baltic Sea coast results from lindane washoff. Further important diffuse pathways in 1985 are *sewer systems and not connected inhabitants* with a share of 15 %, *atmospheric deposition* with 11 % and *seepage on farmyards and spraydrift* with 10 % of the total emissions.

Even though in 1985 Eastern Germany was supposed to have higher specific lindane applications as compared to the OFS, lindane emissions into surface waters were not higher. It is true that the specific lindane inputs via *seepage on farmyards and spraydrift, runoff* and *drainages* are higher compared to the other river basins, however, relative to the total emission, they merely amount to an average 25 %.

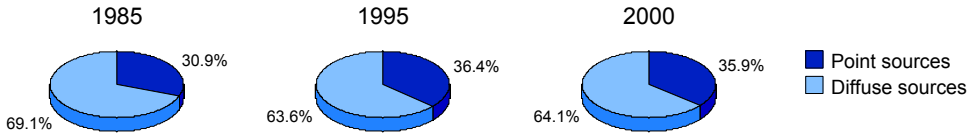
In 1995 and 2000, the major diffuse pathways were *diffuse emissions from urban areas* with 18 % respectively 20 % and *direct atmospheric deposition on the water surface* with 17 % respectively 19 %. No changed emission factors were assumed for input via *groundwater* between 1985 and 2000 (see chapter 4.2.2.6). Due to decreased total emissions, the input share originating from the *groundwater pathway* increased and amounts to 13.5 % in 2000. *Erosion* causes only about 1 % of the total lindane emission in Germany, given the low sorption capacity of lindane (see chapter 4.1.1).

Lindane

Total area specific emissions



Mean percentage of point and diffuse sources



Lindane emissions [kg/a] and change for the period 1985 to 2000

River basin	Point sources			Diffuse sources			Total emissions		
	1985	2000	Change	1985	2000	Change	1985	2000	Change
Danube	51	28	-46%	243	81	-66%	294	109	-63%
Rhine	227	132	-42%	416	146	-65%	643	277	-57%
Ems	14	9	-39%	42	15	-65%	56	23	-59%
Weser	60	21	-65%	140	45	-68%	200	66	-67%
Elbe	208	30	-86%	336	88	-74%	544	118	-78%
Odra	4	1	-78%	15	3	-83%	19	3	-82%
North Sea Coast	8	4	-53%	37	12	-69%	45	15	-66%
Baltic Sea Coast	16	4	-75%	84	18	-78%	100	22	-78%
Black Sea total	51	28	-46%	243	81	-66%	294	109	-63%
North Sea total	517	195	-62%	972	305	-69%	1,489	500	-66%
Baltic Sea total	20	5	-76%	99	21	-79%	119	26	-78%
Germany total	588	228	-61%	1,313	407	-69%	1,901	634	-67%

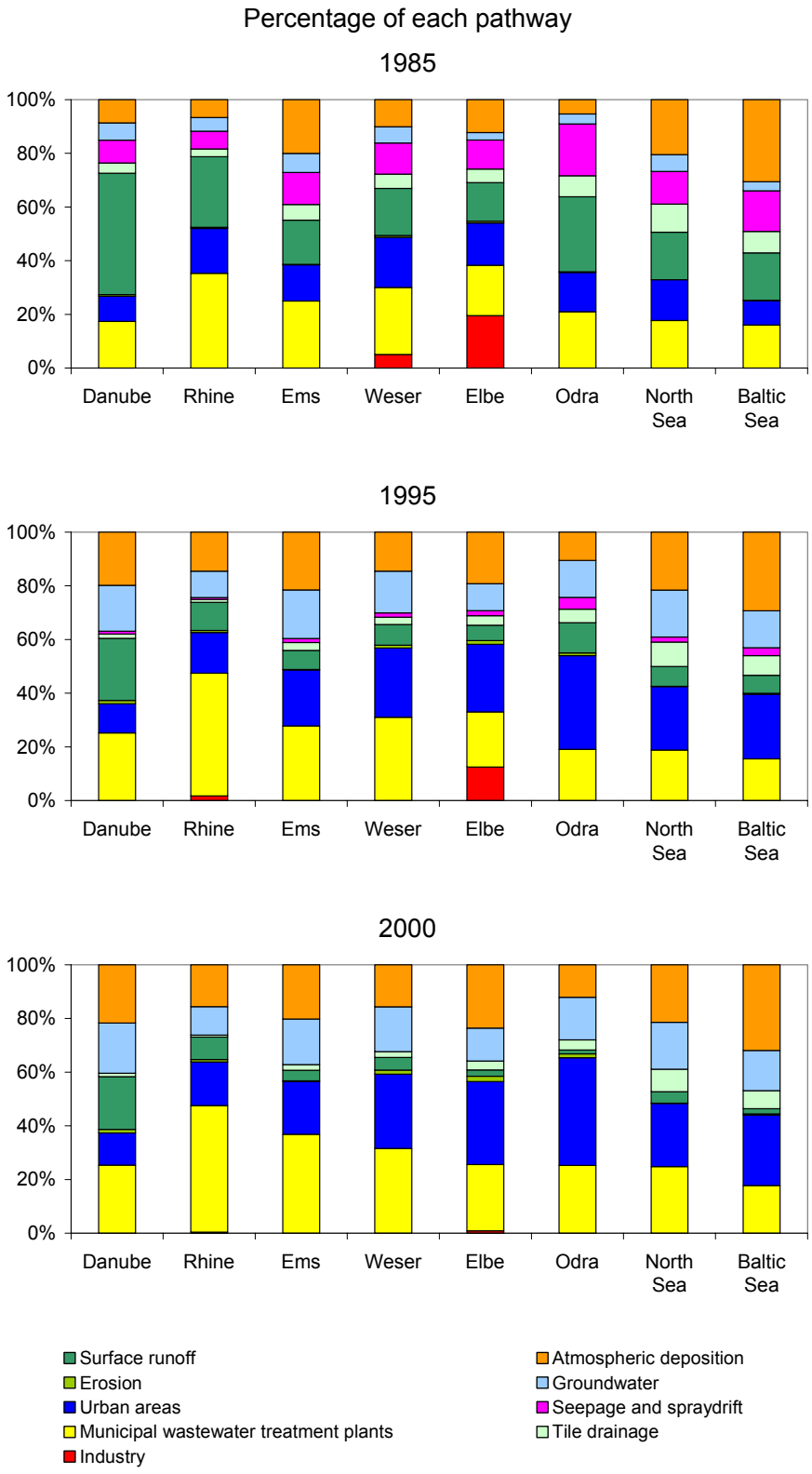


Figure 7-1 Lindane emissions into German river basins.

7.2 Comparison of calculated lindane emissions with loads measured at quality monitoring stations

Only very few data on concentrations in rivers are available for lindane. Data have only been collected for the Elbe since 1996 at various gauges. For the Rhine, only the data published by ICPR, i. e. a load of 250 kg lindane near Bimmen/Lobith in 1995, could be cited by way of comparison (ICPR, 1997). Figure 7-2 represents the relation between the calculated lindane emissions and the river loads. The deviations may be due to both emission and immission, as has already been described for heavy metals in chapter 6.4. For lindane as well, many concentrations measured at the monitoring stations remained below the quantification limit. Moreover, retention was not considered. It was assumed to be very low in the river system, given that lindane is decomposed very slowly and that it is mainly transported in the dissolved phase. The reasons for a faulty emission estimation are mainly due to the fact that for lindane, even more than for heavy metals, a number of assumptions had to be made, as the data on application masses and their spatial distribution were lacking. As for heavy metals it holds true for lindane as well that the deviation of the calculated emissions and the loads measured at the monitoring stations increases in smaller catchments. The examples by Vechte and Neisse shown in figure 7-2 illustrate this relation. However, it may be stated for the large river basins that lindane emissions could be established with a deviation of less than 50 %.

Figure 7-2 Comparison between calculated lindane emissions and loads measured at monitoring stations (1995 and 2000).

The ICPE (2000) provided data on the transported lindane load and the discharge of the Elbe river for the monitoring station Schnackenburg between 1985 and 1999 (figure 7-3). The lindane load largely depends on the discharge and thus exhibits a

high fluctuation range. Considering the linear trend lines for both gradients, the lindane load distinctly shows a downward trend. The emission reductions calculated since 1985 may thus be considered to be plausible.

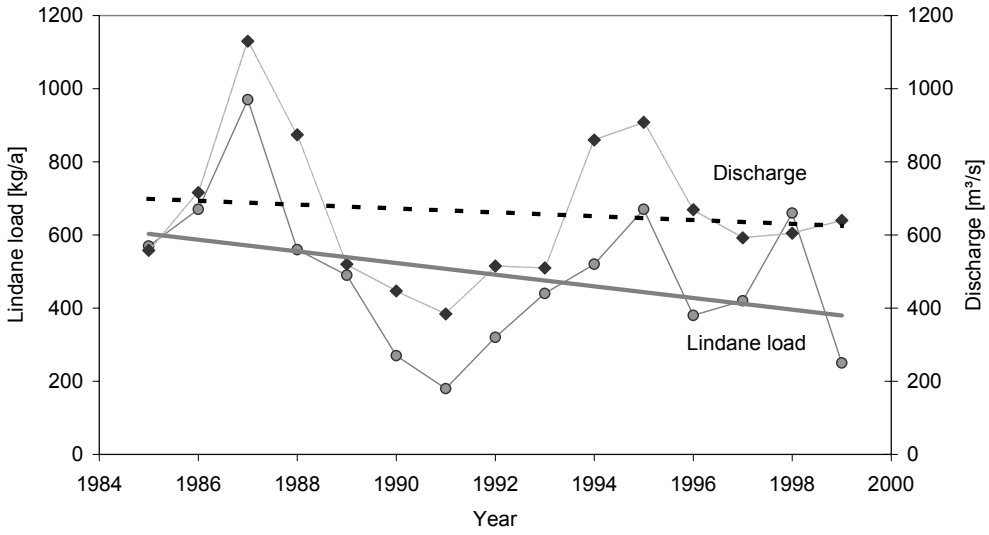


Figure 7-3 Relation between discharge and lindane load in the Elbe river (Schnackenburg) between 1985 and 1999 (ICPE, 2000).

The fact that the load strongly depends on the discharge leads to the assumption that the major share of the lindane inputs originates from diffuse sources. The evaluation of point and diffuse load shares was additionally verified by the "immission method" (chapter 5.3). The method could, however, only be applied to the monitoring stations of Schnackenburg (1983-1987 and 1996-2000) and Magdeburg (1996-1998), given that only for these stations a sufficient number of measured values was available of the required quality and over several years (i.e. as many measured values exceeding the quantification limit as possible). Data on direct industrial discharges from Bitterfeld-Wolfen were only available until 1994. Figure 7-4 shows the comparison between the immission and emission method for Schnackenburg and Magdeburg.

For 1985, the point and diffuse source load shares evaluated following the two methods corresponded very well for Schnackenburg. For the mid-nineties however, the immission method identified a higher share for point sources. The low coefficient of determination (R^2) of 0.38 indicates, however, that the used data exhibits a high dispersion. The same is true for the relation between discharge and lindane load near Schnackenburg represented in figure 7-5. The emission estimation of the monitoring station Magdeburg corresponded very well to the immission estimation for the period 1996-1998. Figure 7-5 also shows a distinct increase in load along with an increasing discharge. It may thus be assumed that the point and diffuse

source load shares were altogether satisfactorily quantified by means of the emission method.

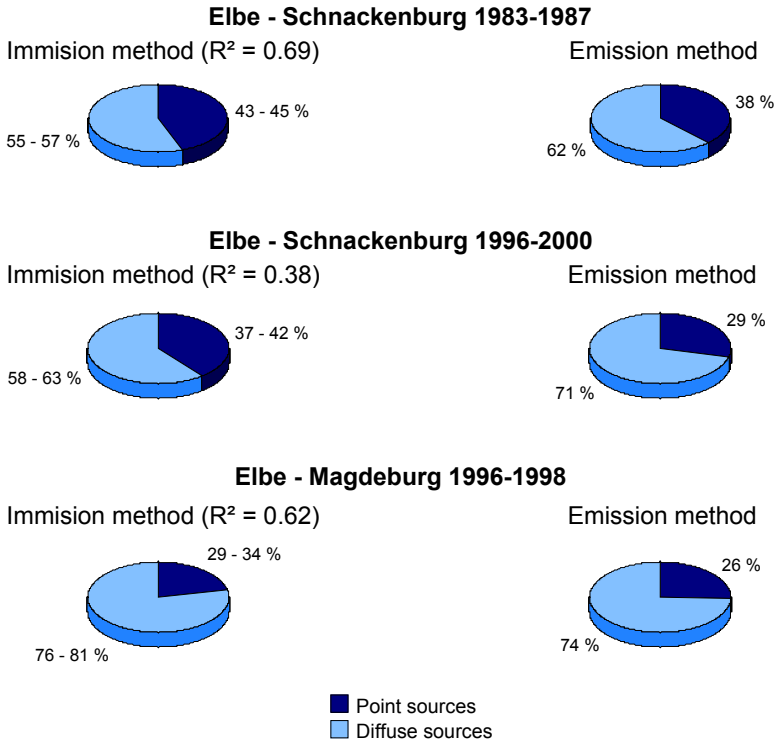


Figure 7-4 Comparison of the load shares from point and diffuse sources established following the immission and emission methods for the Elbe near Schnackenburg and Magdeburg.

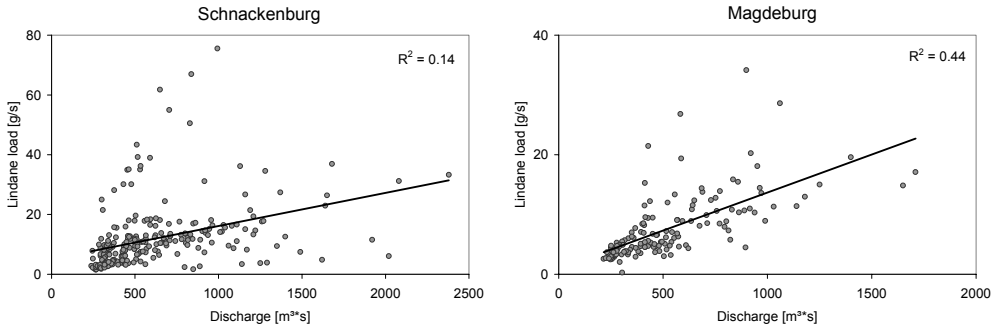


Figure 7-5 Relation between lindane load and discharge for Schnackenburg (1996-2000) and Magdeburg (1996-1998).

PART IV REFERENCES AND APPENDIX

8 References

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9 Appendix

Appendix 1

Appendix 1 supplies a survey on the data provided by the Federal States on heavy metal emissions via municipal wastewater treatment plants for the years 1993-1997 and 1999/2000. The number of measured values, the percental fraction exceeding the quantification limit and the mean calculated heavy metal concentration are specified for each Federal State. The values in brackets were not used for the quantification of heavy metal inputs via municipal wastewater treatment plants (see chapter 3.1.1).

No data were provided by Brandenburg and Saxony for the year 2000.

Annotations:

[1)] the former mean value for 1995 (Böhm et al., 2001) was corrected

[2)] Mean values calculated from several individual values were used for 'number of values'.

[3)] The specified quantification limit is not analytically justified. The data set was thus not used for balancing purposes.

Federal State	Year		Cd	Cr	Cu	Hg	Ni	Pb	Zn
Baden-Wuerttemberg	**1993-1997**	Number	1404	1369	1395	1298	1403	1315	45
		Percentage > DL	23%	39%	75%	19%	53%	33%	91%
		Mean conc. [µg/l]	**0.39**	**4.27**	**12.3**	**0.17**	**6.48**	**3.04**	**73.0**
	1999/2000	Number	383	393	415	381	412	369	9
		Percentage > DL	17%	28%	74%	20%	48%	30%	89%
		Mean conc. [µg/l]	**0.18**	**2.38**	**10.64**	**0.11**	**5.13**	**2.47**	**49.44**
Bavaria	**1993-1996**	Number	1563	1813	1851	1358	1826	1762	514
		Percentage > DL	64%	85%	99%	61%	94%	83%	99%
		Mean conc. [µg/l]	**0.14**	**4.57**	**13.59**	**0.16**	**6.34**	**4.93**	**98.01**
	1997	Number	373	409	413	346	408	395	98
		Percentage > DL	60%	91%	99%	45%	93%	71%	100%
		Mean conc. [µg/l]	**0.11**	**3.25**	**12.18**	**0.1**	**4.27**	**2.29**	**64.96**
Berlin	**1993-1997**	Number	364	938	948	771	929	947	951
		Percentage > DL	28%	14%	68%	1.6%	77%	4%	41%
		Mean conc. [µg/l]	**0.25**	**2.58**	**9.66**	(0.11)	**10.21**	(2.87)	**31.58**
	1999/2000	Number	12[2)]	12[2)]	12[2)]	12[2)]	12[2)]	12[2)]	12[2)]
		Percentage > DL	0%	8%	92%	0%	67%	0%	0%
		Mean conc. [µg/l]	(<0.5)	(2.4)	**9.85**	(<0.2)	**7.0**	(<5)	(<50)
Brandenburg	**1993-1997**	Number	151	161	171	95	171	172	172
		Percentage > DL	60%	55%	74%	85%	83%	65%	79%
		Mean conc. [µg/l]	**0.78**	**6.66**	**14.2**	**0.10**	**12.4**	**4.44**	**63.3**
Bremen	**1993-1997**	Number	47	47	47	47	47	47	47
		Percentage > DL	30%	85%	100%	2.1%	98%	45%	98%
		Mean conc. [µg/l]	**0.21**	**3.69**	**15.26**	(0.11)	**9.99**	**1.06**	**37.4**
	1999/2000	Number	11	11	11	3	11	11	8
		Percentage > DL	0%	0%	82%	0%	100%	0%	75%
		Mean conc. [µg/l]	(<0.2)	(<2)	**2.94**	(<0.2)	**5.87**	(<2)	**32.13**
Hamburg	**1995**	Number	22	13	19	16	19	14	24
		Percentage > DL	96%	87%	90%	89%	100%	88%	100%
		Mean conc. [µg/l]	**0.61**	**16.19**	**14.35**	**0.13**	**54.04**	**2.53**	**39.33**
	1999/2000	Number	5	2	8	10	13	8	17
		Percentage > DL	45%	100%	47%	63%	76%	50%	100%
		Mean conc. [µg/l]	**0.64**	(11.9)	**9.92**	**0.07**	**16.49**	**1.46**	**34.69**
Hesse	**1995**	Number	8[2)]	8[2)]	27[2)]	15[2)]	4[2)]	21[2)]	62
		Percentage > DL	-	-	-	-	-	-	100%
		Mean conc. [µg/l]	**0.24[1)]**	**6.33[1)]**	**13.02[1)]**	**0.33[1)]**	**5.29[1)]**	**1.94[1)]**	**44.65**
	1999/2000	Number	6[2)]	55[2)]	134[2)]	4[2)]	84[2)]	60[2)]	31[2)]
		Percentage > DL	67%	-	-	50%	-	-	-
		Mean conc. [µg/l]	**0.32**	**4.37**	**10.22**	**0.14**	**5.36**	**3.97**	**40.1**
Mecklenburg-Western Pomerania	**1993-1997**	Number	436	447	447	363	447	443	359
		Percentage > DL	76%	79%	94%	58%	90%	91%	97%
		Mean conc. [µg/l]	**1.15**	**4.05**	**12.4**	**0.23**	**11.5**	**14.5**	**52.0**
	1999/2000	Number	186		186	186	186	186	186
		Percentage > DL	19%	82%	100%	18%	99%	66%	100%
		Mean conc. [µg/l]	**0.06**	**0.58**	**9.81**	**0.03**	**3.54**	**0.3**	**26.31**

Federal State	Year		Cd	Cr	Cu	Hg	Ni	Pb	Zn
Lower Saxony	**1993-1997**	Number	139	140	133	37	154	138	119
		Percentage > DL	27%	4%	94%	89%	55%	49%	78%
		Mean conc. [µg/l]	**0.22**	(2.56)	**6.52**	**0.57**	**3.61**	**2.37**	**64.2**
	1999/2000	Number	65	92	76	65	76	63	18
		Percentage > DL	6%	5%	11%	1.5%	8%	95%	88%
		Mean conc. [µg/l]	(<0.5)	(<30)	(<30)	(<0.5)	(<40)	**3.54**	**28.89**
North Rhine-Westphalia	**1995**	Number	2295	2068	2037	2265	2394	421	497
		Percentage > DL	2.4%	20.7%	51%	0.5%	30%	26%	62%
		Mean conc. [µg/l]	(0.24)[1)]	**5.76[1)]**	**14.72[1)]**	(0.15)[1)]	**10.2[1)]**	**3.59**	**80[1)]**
	1999/2000	Number	4223	4280	4265	4134	4290	4201	884
		Percentage > DL	3.3%	0.7%	14.5%	0.3%	13.4%	7.4%	68.1%
		Mean conc. [µg/l]	(0.22)	(11.81)	**15.2**	(0.14)	**12.79**	(2.68)	**54.16**
Rhineland-Palatinate	**1993-1997**	Number	284	776	904	160	771	927	1
		Percentage > DL	3.2%	77%	83%	3.1%	83%	64%	100%
		Mean conc. [µg/l]	(0.3)	**3.73**	**18.5**	(0.1)	**4.75**	**2.80**	(50.00)
	1999/2000	Number	28	19	28	14	16	28	5
		Percentage > DL	0%	26%	11%	7%	31%	4%	40%
		Mean conc. [µg/l]	(<0.5)	**4.92**	**11.32**	(0.12)	**6.21**	(2.16)	**21.0**
Saarland	**1993-1997**	Number	1266	447	350	343	2247	350	2255
		Percentage > DL	16%	82%	11%	7%	36%	10%	100%
		Mean conc. [µg/l]	**0.76**	**8.93**	**6.79[1)]**	**-**	**7.31**	**3.16[1)]**	**54.4**
	1999/2000	Number	42	427	424	429	427	42	425
		Percentage > DL	0%	2%	44%	0.8%	14%	2%	99%
		Mean conc. [µg/l]	(<0.5)	(<3/<5)	**5.29**	(<0.2)	**5.1**	(<5)	**48.6**
Saxony	**1993-1997**	Number	46	40	38	14	36	46	2
		Percentage > DL	33%	65%	63%	43%	47%	63%	100%
		Mean conc. [µg/l]	**0.61**	**6.67**	**14.4**	**0.34**	**9.2**	**9.40**	(93.5)
Saxony-Anhalt	**1993-1997**	Number	394	314	831	328	314	398	105
		Percentage > DL	23%	68%	69%	20%	55%	61%	98%
		Mean conc. [µg/l]	**0.97**	**20.0**	**20.1**	**0.44**	**19.5**	**8.25**	**164.5**
	1999	Number	(16)[3)]	(19)[3)]	33	18	11	(19)	8
		Percentage > DL	(19%)	(0%)	52%	0%	36%	(0%)	100%
		Mean conc. [µg/l]	(2.0)[3)]	(<20)	**14.6**	(<0.2)	**12.8**	(<10)[3)]	**41.5**
Schleswig-Holstein	**1993-1997**	Number	576	582	599	574	576	581	151
		Percentage > DL	50%	67%	99%	50%	91%	55%	100%
		Mean conc. [µg/l]	**0.08[1)]**	**1.6[1)]**	**20.6[1)]**	**0.1[1)]**	**5.2[1)]**	**1.9[1)]**	**18.4[1)]**
	1999/2000	Number	245	269	269	268	269	269	180
		Percentage > DL	20%	42%	100%	64%	87%	23%	100%
		Mean conc. [µg/l]	**0.05**	**0.6**	**12.9**	**0.03**	**5.3**	**0.66**	**22.2**
Thuringia	**1995**	Number	172	165	218	65	220	217	-
		Percentage > DL	10%	55%	67%	98%	62%	38%	-
		Mean conc. [µg/l]	**0.4**	**5.98**	**16.9**	**0.98**	**14.34**	**3.7**	**-**
	1999/2000	Number	328	275	446	105	461	282	-
		Percentage > DL	11%	44%	69%	46%	56%	55%	
		Mean conc. [µg/l]	**0.34**	**1.69**	**13.96**	**0.52**	**5.69**	**3.47**	

Appendix 2a Cadmium emissions into river basins of Germany.

River basin	Year	Industry [kg/a]	MWWTPs [kg/a]	Historic mining activities [kg/a]	Atmospheric deposition [kg/a]	Seepage and spraydrift [kg/a]	Surface runoff [kg/a]	Erosion [kg/a]	Tile drainage [kg/a]	Separate sewers [kg/a]	Combined sewer overflows [kg/a]	Sewers without MWWTP [kg/a]	Households without connection [kg/a]	Ground-water [kg/a]	**Point sources total [kg/a]**	**Nonpoint sources total [kg/a]**	**Total [kg/a]**
	1985		476		258.7	4.6	1143	418	90	211	450	66	9	356	476	3007	3483
Danube	1995	44.2	218		30.0	3.6	627	461	94	183	225	17	4	340	262	1984	2247
	2000	7.8	140		22.0	3.5	321	467	94	144	179	15	3	340	148	1588	1735
Difference	**1985-2000**		**-71%**		**-91%**	**-25%**	**-72%**	**12%**	**4%**	**-32%**	**-60%**	**-78%**	**-68%**	**-5%**	**-69%**	**-47%**	**-50%**
	1985	1775.0	4117	71	423.6	6.7	1335	547	148	582	2086	258	10	658	5963	6054	12017
Rhine	1995	365.0	1635	71	80.0	5.3	687	567	151	413	1033	55	4	632	2071	3627	5698
	2000	324.5	1053	71	59.0	5.1	354	577	151	326	825	47	3	632	1449	2980	4429
Difference	**1985-2000**	**-82%**	**-74%**	**0%**	**-86%**	**-25%**	**-73%**	**5%**	**2%**	**-44%**	**-60%**	**-82%**	**-66%**	**-4%**	**-76%**	**-51%**	**-63%**
	1985	15.0	145		59.1	1.2	38	21	32	188	36	0	4	80	160	459	619
Ems	1995	3.5	61		10.0	1.0	30	21	34	131	16	0	2	79	65	324	389
	2000	6.4	67		9.0	1.0	17	23	34	104	13	0	1	79	73	281	354
Difference	**1985-2000**	**-57%**	**-54%**		**-85%**	**-18%**	**-55%**	**12%**	**7%**	**-45%**	**-64%**	**0%**	**-64%**	**-1%**	**-54%**	**-39%**	**-43%**
	1985	1150.0	516		302.8	3.7	145	203	91	677	343	253	8	244	1666	2270	3936
Weser	1995	60.2	219		35.0	3.0	103	198	100	455	109	42	3	222	279	1269	1548
	2000	36.8	183		25.0	2.9	58	207	100	359	87	36	2	222	220	1099	1319
Difference	**1985-2000**	**-97%**	**-65%**		**-92%**	**-20%**	**-60%**	**2%**	**10%**	**-47%**	**-75%**	**-86%**	**-74%**	**-9%**	**-87%**	**-52%**	**-67%**
	1985	18577.7	3591	478	7567.1	6.6	100	426	245	2547	2267	1339	117	301	22647	14915	37562
Elbe	1995	91.2	692	478	279.0	3.7	95	423	273	623	310	212	17	306	1261	2541	3802
	2000	68.1	273	478	142.0	3.7	59	440	273	492	247	183	14	306	819	2160	2979
Difference	**1985-2000**	**-100%**	**-92%**	**0%**	**-98%**	**-43%**	**-40%**	**3%**	**12%**	**-81%**	**-89%**	**-86%**	**-88%**	**2%**	**-96%**	**-86%**	**-92%**
	1985		222		460.5	0.4	2.3	9	9	233	44	12	8	14	222	792	1014
Odra	1995	15.9	24		5.0	0.2	1.9	10	9	36	6	2	1	14	40	85	124
	2000	23.7	7		3.0	0.2	1.9	11	9	28	4	1	1	14	30	73	104
Difference	**1985-2000**		**-97%**		**-99%**	**-47%**	**-15%**	**26%**	**3%**	**-88%**	**-91%**	**-89%**	**-90%**	**-1%**	**-86%**	**-91%**	**-90%**
North Sea	1985	2.0	103		64.8	1.1	39	6	90	136	50	10	3	57	105	458	563
Coast	1995	2.1	24		8.0	0.9	23	5	90	90	25	1	1	53	26	297	323
	2000	1.8	24		7.0	0.9	13	7	90	71	20	1	1	53	26	264	289
Difference	**1985-2000**	**-10%**	**-77%**		**-89%**	**-21%**	**-67%**	**9%**	**0%**	**-48%**	**-60%**	**-92%**	**-65%**	**-7%**	**-76%**	**-42%**	**-49%**
Baltic Sea	1985		302		2853.3	1.9	21	28	93	555	166	22	22	69	302	3832	4134
Coast	1995	0.3	83		58.0	1.1	18	29	104	156	20	11	3	67	83	466	550
	2000	0.3	9		35.0	1.1	13	32	104	123	16	9	2	67	10	402	412
Difference	**1985-2000**		**-97%**		**-99%**	**-42%**	**-39%**	**14%**	**11%**	**-78%**	**-90%**	**-58%**	**-90%**	**-2%**	**-97%**	**-89%**	**-90%**
Black	1985		476		258.7	4.6	1143	418	90	211	450	66	9	356	476	3007	3483
Sea	1995	44	218		30.0	3.6	627	461	94	183	225	17	4	340	262	1984	2247
total	2000	8	140		22.0	3.5	321	467	94	144	179	15	3	340	148	1588	1735
Difference	**1985-2000**		**-71%**		**-91%**	**-25%**	**-72%**	**12%**	**4%**	**-32%**	**-60%**	**-78%**	**-68%**	**-5%**	**-69%**	**-47%**	**-50%**
North Sea	1985	21520	8472	549	8417.4	19.2	1657	1203	607	4130	4782	1860	141	1339	30541	24156	54697
total	1995	522	2631	549	412.0	13.9	937	1214	648	1712	1493	309	26	1292	3702	8057	11760
	2000	438	1600	549	242.0	13.5	502	1254	648	1352	1192	267	22	1292	2587	6784	9370
Difference	**1985-2000**	**-98%**	**-81%**	**0%**	**-97%**	**-30%**	**-70%**	**4%**	**7%**	**-67%**	**-75%**	**-86%**	**-85%**	**-4%**	**-92%**	**-72%**	**-83%**
Baltic Sea	1985		524		3313.8	2.2	23	37	102	788	210	35	30	83	524	4623	5147
total	1995	16	107		63.0	1.3	20	39	113	192	26	13	4	81	123	551	674
	2000	24	16		38.0	1.3	15	43	113	151	20	11	3	81	40	476	516
Difference	**1985-2000**		**-97%**		**-99%**	**-43%**	**-37%**	**17%**	**11%**	**-81%**	**-90%**	**-69%**	**-90%**	**-2%**	**-92%**	**-90%**	**-90%**
Germany	1985	21520	9472	549	11989.9	26.1	2824	1657	799	5129	5442	1961	180	1778	31541	31786	63327
total	1995	582	2956	549	505.0	18.7	1584	1714	855	2087	1744	339	33	1713	4088	10593	14680
	2000	469	1756	549	302.0	18.3	837	1764	855	1647	1391	293	27	1713	2774	8847	11622
Difference	**1985-2000**	**-98%**	**-81%**	**0%**	**-97%**	**-30%**	**-70%**	**6%**	**7%**	**-68%**	**-74%**	**-85%**	**-85%**	**-4%**	**-91%**	**-72%**	**-82%**

Appendix 2b Chromium emissions into river basins of Germany.

River basin	Year	Industry [kg/a]	MWWTPs [kg/a]	Historic mining activities [kg/a]	Atmospheric deposition [kg/a]	Seepage and spraydrift [kg/a]	Surface runoff [kg/a]	Erosion [kg/a]	Tile drainage [kg/a]	Separate sewers [kg/a]	Combined sewer overflows [kg/a]	Sewers without MWWTP [kg/a]	Households without connection [kg/a]	Ground-water [kg/a]	**Point sources total [kg/a]**	**Nonpoint sources total [kg/a]**	**Total [kg/a]**
	1985		13004		457	179	3013	41174	2962	1046	2406	691	64	4619	13004	56611	69615
Danube	1995	1252	5782		189	127	2378	43665	3071	1343	1798	284	36	4376	7034	57267	64301
	2000	1090	3699		181	122	1078	43697	3071	1258	1697	279	34	4376	4789	55793	60581
Difference	**1985-2000**		**-72%**		**-60%**	**-32%**	**-64%**	**6%**	**4%**	**20%**	**-29%**	**-60%**	**-47%**	**-5%**	**-63%**	**-1%**	**-13%**
	1985	220400	76481		748	251	3761	49960	4872	2880	11266	2720	70	8554	296881	85082	381963
Rhine	1995	13794	29998		311	184	2803	50906	4970	3033	8445	922	42	8211	43792	79827	123619
	2000	12907	17813		297	173	1355	50954	4970	2839	7981	905	40	8211	30720	77725	108446
Difference	**1985-2000**	**-94%**	**-77%**		**-60%**	**-31%**	**-64%**	**2%**	**2%**	**-1%**	**-29%**	**-67%**	**-43%**	**-4%**	**-90%**	**-9%**	**-72%**
	1985	253	3353		104	42	314	1557	1046	932	207	2	26	1039	3606	5269	8875
Ems	1995	44	1410		46	33	192	1550	1120	964	129	0	16	1024	1454	5075	6528
	2000	98	1088		44	32	132	1553	1120	903	122	0	16	1024	1186	4946	6132
Difference	**1985-2000**	**-61%**	**-68%**		**-58%**	**-23%**	**-58%**	**0%**	**7%**	**-3%**	**-41%**	**0%**	**-38%**	**-1%**	**-67%**	**-6%**	**-31%**
	1985	18400	11514		301	132	1052	14712	2999	3264	1295	1238	47	3166	29914	28206	58120
Weser	1995	962	4916		123	101	615	14288	3287	3341	874	690	27	2889	5878	26235	32113
	2000	668	2767		118	98	423	14309	3287	3128	825	678	26	2889	3435	25781	29216
Difference	**1985-2000**	**-96%**	**-76%**		**-61%**	**-26%**	**-60%**	**-3%**	**10%**	**-4%**	**-36%**	**-45%**	**-45%**	**-9%**	**-89%**	**-9%**	**-50%**
	1985	215401	105687	107	1658	289	2637	31657	8043	4330	3238	4569	328	3906	321195	60655	381850
Elbe	1995	1225	10287	107	529	128	665	31372	8983	4575	2423	3478	215	3978	11619	56347	67966
	2000	1735	3296	107	506	125	540	31416	8983	4283	2282	3413	209	3978	5138	55736	60874
Difference	**1985-2000**	**-99%**	**-97%**	**0%**	**-69%**	**-57%**	**-80%**	**-1%**	**12%**	**-1%**	**-30%**	**-25%**	**-36%**	**2%**	**-98%**	**-8%**	**-84%**
	1985	17901	3290		89	17	161.9	824	284	265	63	41	20	183	21191	1948	23139
Odra	1995	103	215		27	7	26.4	876	310	262	43	25	13	187	318	1776	2094
	2000	90	111		26	7	24.0	878	310	245	41	25	12	187	201	1754	1955
Difference	**1985-2000**	**-100%**	**-97%**		**-71%**	**-61%**	**-85%**	**7%**	**9%**	**-8%**	**-35%**	**-39%**	**-40%**	**2%**	**-99%**	**-10%**	**-92%**
North Sea	1985	724	933		114	38	258	439	2969	676	274	89	21	744	1657	5622	7279
Coast	1995	3027	533		48	31	156	397	2947	663	198	13	13	695	3560	5161	8721
	2000	520	381		46	30	117	397	2947	621	187	13	12	695	901	5065	5967
Difference	**1985-2000**	**-28%**	**-59%**		**-60%**	**-21%**	**-54%**	**-10%**	**-1%**	**-8%**	**-32%**	**-85%**	**-43%**	**-7%**	**-46%**	**-10%**	**-18%**
Baltic Sea	1985		5698		727	82	746	4029	3067	779	257	83	83	891	5698	10744	16442
Coast	1995	20	426		244	37	169	4054	3421	1146	154	168	31	870	446	10293	10740
	2000	20	106		233	36	159	4062	3421	1073	145	164	30	870	126	10193	10319
Difference	**1985-2000**		**-98%**		**-68%**	**-56%**	**-79%**	**1%**	**12%**	**38%**	**-44%**	**98%**	**-64%**	**-2%**	**-98%**	**-5%**	**-37%**
Black	1985		13004		457	179	3013	41174	2962	1046	2406	691	64	4619	13004	56611	69615
Sea	1995	1252	5782		189	127	2378	43665	3071	1343	1798	284	36	4376	7034	57267	64301
total	2000	1090	3699		181	122	1078	43697	3071	1258	1697	279	34	4376	4789	55793	60581
Difference	**1985-2000**		**-72%**		**-60%**	**-32%**	**-64%**	**6%**	**4%**	**20%**	**-29%**	**-60%**	**-47%**	**-5%**	**-63%**	**-1%**	**-13%**
North Sea	1985	455178	197968	107	2925	753	8021	98325	19929	12082	16280	8618	492	17409	653253	184833	838086
total	1995	19052	47144	107	1057	477	4432	98513	21307	12576	12069	5103	313	16797	66303	172644	238946
	2000	15928	25346	107	1011	458	2568	98629	21307	11774	11397	5009	303	16797	41381	169253	210634
Difference	**1985-2000**	**-97%**	**-87%**	**0%**	**-65%**	**-39%**	**-68%**	**0%**	**7%**	**-3%**	**-30%**	**-42%**	**-38%**	**-4%**	**-94%**	**-8%**	**-75%**
Baltic Sea	1985	17901	8988		816	99	908	4853	3351	1044	320	124	103	1074	26889	12691	39580
total	1995	123	642		271	44	195	4930	3731	1408	197	193	44	1057	765	12070	12834
	2000	110	217		259	43	183	4940	3731	1318	186	189	42	1057	327	11947	12275
Difference	**1985-2000**	**-99%**	**-98%**		**-68%**	**-57%**	**-80%**	**2%**	**11%**	**26%**	**-42%**	**52%**	**-59%**	**-2%**	**-99%**	**-6%**	**-69%**
Germany	1985	473079	219960	107	4198	1030	11942	144352	26242	14172	19006	9433	659	23102	693146	254136	947282
total	1995	20427	53567	107	1517	647	7005	147108	28109	15327	14064	5580	393	22230	74101	241980	316082
	2000	17128	29262	107	1451	623	3828	147266	28109	14350	13280	5477	379	22230	46497	236993	283490
Difference	**1985-2000**	**-96%**	**-87%**	**0%**	**-65%**	**-40%**	**-68%**	**2%**	**7%**	**1%**	**-30%**	**-42%**	**-42%**	**-4%**	**-93%**	**-7%**	**-70%**

Appendix 2c Copper emissions into river basins of Germany.

River basin	Year	Industry [kg/a]	MWWTPs [kg/a]	Historic mining activities [kg/a]	Atmospheric deposition [kg/a]	Seepage and spraydrift [kg/a]	Surface runoff [kg/a]	Erosion [kg/a]	Tile drainage [kg/a]	Separate sewers [kg/a]	Combined sewer overflows [kg/a]	Sewers without MWWTP [kg/a]	Households without connection [kg/a]	Ground-water [kg/a]	Shipping	**Point sources total [kg/a]**	**Nonpoint sources total [kg/a]**	**Total [kg/a]**
	1985		35298		5174	880	13638	28221	2576	5446	11706	2087	255	18293	1477	35298	89753	125051
Danube	1995	1772	17135		1815	732	18104	31096	2671	8574	10720	936	174	17322	1477	18907	93621	112528
	2000	1314	14115		931	738	15316	31360	2671	8860	11058	953	179	17322	1477	15429	90866	106295
Difference	**1985-2000**		**-60%**		**-82%**	**-16%**	**12%**	**11%**	**4%**	**63%**	**-6%**	**-54%**	**-30%**	**-5%**	**0%**	**-56%**	**1%**	**-15%**
	1985	86000	189375		8473	1627	16941	37491	4236	15000	54672	8182	279	33886	2250	275375	183036	458411
Rhine	1995	21859	81014		2982	1366	20572	38837	4321	19357	49620	3024	203	32528	2250	102873	175060	277933
	2000	26649	70011		1529	1376	17552	39201	4321	20002	51167	3078	209	32528	2250	96660	173212	269872
Difference	**1985-2000**	**-69%**	**-63%**		**-82%**	**-15%**	**4%**	**5%**	**2%**	**33%**	**-6%**	**-62%**	**-25%**	**-4%**	**0%**	**-65%**	**-5%**	**-41%**
	1985	190	6209		1181	344	917	886	910	4854	920	5	105	4118	389	6399	14629	21028
Ems	1995	166	2876		440	308	1237	902	974	6155	748	0	80	4058	389	3042	15291	18333
	2000	249	5088		226	320	1133	915	974	6360	771	0	83	4058	389	5337	15229	20566
Difference	**1985-2000**	**31%**	**-18%**		**-81%**	**-7%**	**23%**	**3%**	**7%**	**31%**	**-16%**	**0%**	**-21%**	**-1%**	**0%**	**-17%**	**4%**	**-2%**
	1985	13050	19972		3557	1023	3087	12039	2608	16985	6009	3380	184	12540	1338	33022	62750	95772
Weser	1995	1190	9411		1183	867	3948	11762	2858	21326	5200	2292	126	11443	1338	10601	62342	72943
	2000	454	10247		607	895	3576	11904	2858	22037	5363	2334	129	11443	1338	10701	62484	73185
Difference	**1985-2000**	**-97%**	**-49%**		**-83%**	**-12%**	**16%**	**-1%**	**10%**	**30%**	**-11%**	**-31%**	**-30%**	**-9%**	**0%**	**-68%**	**0%**	**-24%**
	1985	303742	36366	4027	26320	1899	3943	27768	6994	21542	14291	11457	960	15473	3722	344135	134369	478504
Elbe	1995	3928	18225	4027	5077	859	3576	27861	7811	29204	14693	11636	862	15759	3722	26180	121060	147239
	2000	6291	15225	4027	2604	878	3280	28168	7811	30178	15163	11852	883	15759	3722	25543	120298	145842
Difference	**1985-2000**	**-98%**	**-58%**	**0%**	**-90%**	**-54%**	**-17%**	**1%**	**12%**	**40%**	**6%**	**3%**	**-8%**	**2%**	**0%**	**-93%**	**-10%**	**-70%**
	1985		942		1471	108	191.1	606	247	1274	257	103	59	724	292	942	5332	6274
Odra	1995	141	460		263	40	103.2	667	269	1671	262	83	52	742	292	601	4444	5045
	2000	143	460		135	40	99.0	676	269	1727	270	85	53	742	292	603	4388	4991
Difference	**1985-2000**		**-51%**		**-91%**	**-63%**	**-48%**	**12%**	**9%**	**36%**	**5%**	**-17%**	**-10%**	**2%**	**0%**	**-36%**	**-18%**	**-20%**
North Sea	1985	844	3830		1296	263	782	229	2582	3518	1283	290	88	2946	497	4674	13773	18447
Coast	1995	35	1555		463	228	908	205	2563	4232	1184	49	67	2754	497	1590	13151	14740
	2000	17	2164		237	233	830	209	2563	4373	1222	50	69	2754	497	2181	13037	15218
Difference	**1985-2000**	**-98%**	**-44%**		**-82%**	**-11%**	**6%**	**-9%**	**-1%**	**24%**	**-5%**	**-83%**	**-22%**	**-7%**	**0%**	**-53%**	**-5%**	**-18%**
Baltic Sea	1985		6276		11007	512	982	2713	2667	3815	1072	225	293	3528	1722	6276	28536	34812
Coast	1995	84	2758		2344	212	708	2772	2975	7317	923	590	129	3448	1722	2842	23140	25982
	2000	84	1956		1202	215	669	2813	2975	7561	952	602	132	3448	1722	2040	22291	24331
Difference	**1985-2000**		**-69%**		**-89%**	**-58%**	**-32%**	**4%**	**12%**	**98%**	**-11%**	**168%**	**-55%**	**-2%**	**0%**	**-67%**	**-22%**	**-30%**
Black	1985		35298		5174	880	13638	28221	2576	5446	11706	2087	255	18293	1477	35298	89753	125051
Sea	1995	1772	17135		1815	732	18104	31096	2671	8574	10720	936	174	17322	1477	18907	93621	112528
total	2000	1314	14115		931	738	15316	31360	2671	8860	11058	953	179	17322	1477	15429	90866	106295
Difference	**1985-2000**		**-60%**		**-82%**	**-16%**	**12%**	**11%**	**4%**	**63%**	**-6%**	**-54%**	**-30%**	**-5%**	**0%**	**-56%**	**1%**	**-15%**
North Sea	1985	403826	255752	4027	40827	5155	25670	78413	17330	61899	77175	23314	1616	68963	8196	663605	408558	1072163
total	1995	27178	113080	4027	10145	3628	30240	79567	18527	80274	71445	17001	1338	66542	8196	144285	386903	531188
	2000	33660	102734	4027	5203	3702	26371	80397	18527	82950	73686	17314	1373	66542	8196	140421	384262	524683
Difference	**1985-2000**	**-92%**	**-60%**	**0%**	**-87%**	**-28%**	**3%**	**3%**	**7%**	**34%**	**-5%**	**-26%**	**-15%**	**-4%**	**0%**	**-79%**	**-6%**	**-51%**
Baltic Sea	1985		7218		12478	620	1173	3319	2914	5089	1329	328	352	4252	2014	7218	33868	41086
total	1995	225	3217		2607	252	811	3439	3244	8988	1185	673	181	4190	2014	3442	27584	31027
	2000	227	2416		1337	255	768	3489	3244	9288	1222	687	185	4190	2014	2643	26679	29322
Difference	**1985-2000**		**-67%**		**-89%**	**-59%**	**-35%**	**5%**	**11%**	**83%**	**-8%**	**109%**	**-47%**	**-1%**	**0%**	**-63%**	**-21%**	**-29%**
Germany	1985	403826	298268	4027	58479	6655	40481	109953	22820	72434	90210	25729	2223	91508	11687	706121	532179	1238300
total	1995	29175	133433	4027	14567	4612	49155	114102	24442	97836	83350	18610	1693	88054	11687	166635	508108	674744
	2000	35201	119266	4027	7471	4696	42455	115246	24442	101098	85966	18954	1737	88054	11687	158494	501806	660300
Difference	**1985-2000**	**-91%**	**-60%**	**0%**	**-87%**	**-29%**	**5%**	**5%**	**7%**	**40%**	**-5%**	**-26%**	**-22%**	**-4%**	**0%**	**-78%**	**-6%**	**-47%**

Appendix 2d Mercury emissions into river basins of Germany.

River basin	Year	Industry [kg/a]	MWWTPs [kg/a]	Historic mining activities [kg/a]	Atmospheric deposition [kg/a]	Seepage and spraydrift [kg/a]	Surface runoff [kg/a]	Erosion [kg/a]	Tile drainage [kg/a]	Separate sewers [kg/a]	Combined sewer overflows [kg/a]	Sewers without MWWTP [kg/a]	Households without connection [kg/a]	Ground-water [kg/a]	**Point sources total [kg/a]**	**Nonpoint sources total [kg/a]**	**Total [kg/a]**
	1985		314		91	0.5	283.3	147	45	53	116	26.1	2.9	90	314	855	1169
Danube	1995	9.5	206		24	0.4	129.1	165	47	57	71	5.7	1.1	86	215	586	802
	2000	5.3	119		21	0.4	67.6	166	47	59	72	5.7	1.1	86	125	526	650
Difference	**1985-2000**		**-62%**		**-77%**	**-21%**	**-76%**	**13%**	**4%**	**11%**	**-38%**	**-78%**	**-62%**	**-4%**	**-60%**	**-39%**	**-44%**
	1985	725.0	1970		150	0.8	330.4	224	74	147	546	102.8	3.1	165	2695	1743	4438
Rhine	1995	143.6	1134		49	0.6	140.5	231	76	129	325	18.3	1.3	146	1277	1116	2394
	2000	117.5	645		55	0.6	73.7	232	76	132	333	18.5	1.3	146	762	1068	1830
Difference	**1985-2000**	**-84%**	**-67%**		**-63%**	**-22%**	**-78%**	**3%**	**3%**	**-10%**	**-39%**	**-82%**	**-58%**	**-11%**	**-72%**	**-39%**	**-59%**
	1985	3.0	77		21	0.1	8.6	6	16	47	9	0.1	1.2	20	80	129	209
Ems	1995	1.7	48		7	0.1	5.9	6	17	41	5	0.0	0.5	20	50	102	152
	2000	4.6	42		8	0.1	3.2	6	17	42	5	0.0	0.5	20	47	102	149
Difference	**1985-2000**	**53%**	**-45%**		**-62%**	**-14%**	**-63%**	**3%**	**7%**	**-11%**	**-44%**	**0%**	**-58%**	**0%**	**-41%**	**-21%**	**-29%**
	1985	155.0	350		62	0.4	32.9	78	46	167	63	50.1	2.1	61	505	562	1067
Weser	1995	7.1	217		24	0.3	20.1	76	50	142	34	13.9	0.8	55	224	416	641
	2000	15.8	118		24	0.3	10.9	77	50	146	35	14.1	0.8	55	134	413	547
Difference	**1985-2000**	**-90%**	**-66%**		**-61%**	**-17%**	**-67%**	**-2%**	**10%**	**-13%**	**-44%**	**-72%**	**-62%**	**-10%**	**-73%**	**-27%**	**-49%**
	1985	20867.6	737		444	0.8	21.1	182	122	261	193	195.1	15.8	75	21605	1510	23115
Elbe	1995	62.2	361		151	0.4	17.7	182	137	195	97	70.6	5.4	71	423	927	1350
	2000	18.3	167		168	0.4	9.7	183	137	200	100	71.7	5.5	71	185	946	1132
Difference	**1985-2000**	**-100%**	**-77%**		**-62%**	**-46%**	**-54%**	**1%**	**12%**	**-23%**	**-48%**	**-63%**	**-65%**	**-6%**	**-99%**	**-37%**	**-95%**
	1985		16		25	0.0	0.1	4	4	18	4	1.8	1.0	4	16	62	78
Odra	1995	0.7	5		3	0.0	0.4	4	5	11	2	0.5	0.3	3	6	29	35
	2000	1.6	4		3	0.0	0.2	4	5	11	2	0.5	0.3	3	6	29	35
Difference	**1985-2000**		**-73%**		**-88%**	**-49%**	**46%**	**3%**	**16%**	**-39%**	**-50%**	**-72%**	**-70%**	**-14%**	**-64%**	**-53%**	**-55%**
North Sea	1985	10.0	27		23	0.1	8.4	2	45	34	13	3.4	1.0	14	37	144	181
Coast	1995	1.5	20		5	0.1	4.3	1	45	28	8	0.3	0.4	13	21	105	127
	2000	1.4	15		7	0.1	2.4	1	45	29	8	0.3	0.4	13	17	106	123
Difference	**1985-2000**	**-86%**	**-44%**		**-70%**	**-14%**	**-72%**	**-33%**	**0%**	**-15%**	**-38%**	**-91%**	**-60%**	**-9%**	**-55%**	**-26%**	**-32%**
Baltic Sea	1985	0.7	50		187	0.2	3.8	11	47	49	14	3.5	3.9	17	51	336	387
Coast	1995	0.1	24		38	0.1	3.1	11	52	49	6	3.6	0.8	17	24	181	205
	2000	0.1	5		41	0.1	1.8	12	52	50	6	3.7	0.8	17	5	184	190
Difference	**1985-2000**	**-86%**	**-90%**		**-78%**	**-44%**	**-53%**	**8%**	**11%**	**2%**	**-57%**	**6%**	**-79%**	**-1%**	**-89%**	**-45%**	**-51%**
Black	1985		314		91	0.5	283.3	147	45	53	116	26.1	2.9	90	314	855	1169
Sea	1995	10	206		24	0.4	129.1	165	47	57	71	5.7	1.1	86	215	586	802
total	2000	5	119		21	0.4	67.6	166	47	59	72	5.7	1.1	86	125	526	650
Difference	**1985-2000**		**-62%**		**-77%**	**-21%**	**-76%**	**13%**	**4%**	**11%**	**-38%**	**-78%**	**-62%**	**-4%**	**-60%**	**-39%**	**-44%**
North Sea	1985	21761	3161		700	2.2	401.4	492	303	656	824	351.5	23.2	335	24922	4088	29010
total	1995	216	1779		236	1.6	188.5	496	325	535	469	103.1	8.4	305	1995	2668	4663
	2000	158	987		262	1.6	99.8	499	325	549	481	104.6	8.5	305	1145	2636	3780
Difference	**1985-2000**	**-99%**	**-69%**		**-63%**	**-29%**	**-75%**	**1%**	**7%**	**-16%**	**-42%**	**-70%**	**-63%**	**-9%**	**-95%**	**-36%**	**-87%**
Baltic Sea	1985	1	67		212	0.3	3.9	15	51	67	18	5.3	4.9	21	67	398	465
total	1995	1	29		41	0.2	3.4	16	57	60	8	4.1	1.1	20	30	210	241
	2000	2	10		44	0.1	2.0	16	57	61	8	4.2	1.1	20	11	213	225
Difference	**1985-2000**	**143%**	**-86%**		**-79%**	**-45%**	**-50%**	**7%**	**12%**	**-9%**	**-56%**	**-21%**	**-78%**	**-3%**	**-83%**	**-46%**	**-52%**
Germany	1985	21761	3542		1003	3.0	688.6	654	399	776	958	382.9	31.0	446	25303	5342	30645
total	1995	226	2015		301	2.2	321.0	677	429	652	548	112.9	10.6	411	2241	3465	5706
	2000	165	1116		327	2.2	169.4	681	429	669	561	114.5	10.7	411	1281	3375	4656
Difference	**1985-2000**	**-99%**	**-68%**		**-67%**	**-29%**	**-75%**	**4%**	**7%**	**-14%**	**-41%**	**-70%**	**-65%**	**-8%**	**-95%**	**-37%**	**-85%**

Appendix 2e Nickel emissions into river basins of Germany.

River basin	Year	Industry [kg/a]	MWWTPs [kg/a]	Historic mining activities [kg/a]	Atmospheric deposition [kg/a]	Seepage and spraydrift [kg/a]	Surface runoff [kg/a]	Erosion [kg/a]	Tile drainage [kg/a]	Separate sewers [kg/a]	Combined sewer overflows [kg/a]	Sewers without MWWTP [kg/a]	Households without connection [kg/a]	Ground-water [kg/a]	**Point sources total [kg/a]**	**Nonpoint sources total [kg/a]**	**Total [kg/a]**
	1985		14534		936	81	4052	27117	5731	2210	4713	797	101	60205	14534	105943	120477
Danube	1995	1353	8110		579	65	3460	28868	5942	2201	2803	292	48	57003	9463	101261	110725
	2000	783	5155		807	64	4483	28868	5942	1801	2330	268	41	57003	5938	101606	107544
Difference	**1985-2000**		**-65%**		**-14%**	**-21%**	**11%**	**6%**	**4%**	**-19%**	**-51%**	**-66%**	**-59%**	**-5%**	**-59%**	**-4%**	**-11%**
	1985	79000	89610	13500	1533	121	4790	35509	9425	6087	21972	3123	110	111529	182110	194199	376309
Rhine	1995	15928	44564	13500	952	99	3819	35856	9615	4968	13027	945	56	107059	73992	176396	250388
	2000	14318	45871	13500	1325	96	4914	35856	9615	4065	10861	869	48	107059	73689	174707	248396
Difference	**1985-2000**	**-82%**	**-49%**	**0%**	**-14%**	**-21%**	**3%**	**1%**	**2%**	**-33%**	**-51%**	**-72%**	**-56%**	**-4%**	**-60%**	**-10%**	**-34%**
	1985	556	3469		214	22	165	748	2024	1970	369	2	41	13553	4025	19108	23133
Ems	1995	135	1891		141	19	186	735	2166	1580	197	0	22	13355	2026	18401	20427
	2000	83	3869		196	19	229	735	2166	1293	165	0	19	13355	3952	18177	22129
Difference	**1985-2000**	**-85%**	**12%**		**-8%**	**-12%**	**39%**	**-2%**	**7%**	**-34%**	**-55%**	**0%**	**-54%**	**-1%**	**-2%**	**-5%**	**-4%**
	1985	25500	10329		708	68	612	10007	5802	6909	2517	1524	75	41274	35829	69496	105325
Weser	1995	1302	5624		378	58	619	9520	6359	5474	1361	713	35	37663	6926	62179	69105
	2000	712	7110		526	57	769	9520	6359	4479	1132	654	30	37663	7822	61190	69012
Difference	**1985-2000**	**-97%**	**-31%**		**-26%**	**-15%**	**26%**	**-5%**	**10%**	**-35%**	**-55%**	**-57%**	**-60%**	**-9%**	**-78%**	**-12%**	**-34%**
	1985	78213	80978	772	7991	134	705	20962	15561	10265	7341	5922	494	50926	159963	120301	280264
Elbe	1995	3343	18569	772	1621	70	588	20608	17380	7496	3825	3609	251	51867	22684	107315	129999
	2000	2824	10686	772	2257	69	734	20608	17380	6133	3168	3307	222	51867	14282	105745	120027
Difference	**1985-2000**	**-96%**	**-87%**	**0%**	**-72%**	**-49%**	**4%**	**-2%**	**12%**	**-40%**	**-57%**	**-44%**	**-55%**	**2%**	**-91%**	**-12%**	**-57%**
	1985		2659		466	8	31.3	508	550	680	134	54	31	2383	2659	4845	7504
Odra	1995	350	374		84	4	16.4	537	599	429	68	26	15	2444	724	4222	4946
	2000	291	291		117	4	19.4	537	599	351	57	24	13	2444	582	4165	4746
Difference	**1985-2000**		**-89%**		**-75%**	**-54%**	**-38%**	**6%**	**9%**	**-48%**	**-57%**	**-56%**	**-58%**	**3%**	**-78%**	**-14%**	**-37%**
North Sea	1985	505	1538		235	19	158	187	5745	1428	517	112	35	9695	2043	18131	20174
Coast	1995	248	741		148	17	141	165	5702	1086	310	15	18	9064	989	16666	17655
	2000	46	1408		206	17	174	165	5702	889	257	13	15	9064	1454	16501	17955
Difference	**1985-2000**	**-91%**	**-8%**		**-12%**	**-13%**	**10%**	**-12%**	**-1%**	**-38%**	**-50%**	**-88%**	**-57%**	**-7%**	**-29%**	**-9%**	**-11%**
Baltic Sea	1985		4903		3181	37	171	2170	5933	1910	545	108	131	11613	4903	25800	30703
Coast	1995	34	1254		748	19	117	2142	6619	1878	241	180	37	11348	1288	23329	24618
	2000	34	779		1042	19	145	2142	6619	1537	200	163	32	11348	813	23248	24061
Difference	**1985-2000**		**-84%**		**-67%**	**-49%**	**-15%**	**-1%**	**12%**	**-20%**	**-63%**	**51%**	**-76%**	**-2%**	**-83%**	**-10%**	**-22%**
Black	1985		14534		936	81	4052	27117	5731	2210	4713	797	101	60205	14534	105943	120477
Sea	1995	1353	8110		579	65	3460	28868	5942	2201	2803	292	48	57003	9463	101261	110725
total	2000	783	5155		807	64	4483	28868	5942	1801	2330	268	41	57003	5938	101606	107544
Difference	**1985-2000**		**-65%**		**-14%**	**-21%**	**11%**	**6%**	**4%**	**-19%**	**-51%**	**-66%**	**-59%**	**-5%**	**-59%**	**-4%**	**-11%**
North Sea	1985	183774	185924	14272	10681	364	6430	67413	38557	26659	32716	10683	755	226977	383970	421235	805205
total	1995	20956	71388	14272	3240	263	5352	66884	41222	20604	18720	5282	382	219008	106616	380958	487574
	2000	17983	68944	14272	4510	258	6820	66884	41222	16859	15583	4843	334	219008	101199	376320	477519
Difference	**1985-2000**	**-90%**	**-63%**	**0%**	**-58%**	**-29%**	**6%**	**-1%**	**7%**	**-37%**	**-52%**	**-55%**	**-56%**	**-4%**	**-74%**	**-11%**	**-41%**
Baltic Sea	1985		7562		3647	45	203	2678	6483	2590	679	162	162	13996	7562	30645	38207
total	1995	384	1628		832	23	134	2679	7218	2307	309	206	52	13792	2012	27551	29564
	2000	325	1070		1159	23	165	2679	7218	1888	257	187	45	13792	1395	27412	28807
Difference	**1985-2000**		**-86%**		**-68%**	**-50%**	**-19%**	**0%**	**11%**	**-27%**	**-62%**	**15%**	**-72%**	**-1%**	**-82%**	**-11%**	**-25%**
Germany	1985	183774	208020	14272	15264	489	10685	97208	50771	31459	38108	11642	1018	301178	406066	557822	963888
total	1995	22693	81127	14272	4651	352	8946	98431	54382	25112	21832	5780	482	289803	118092	509770	627862
	2000	19091	75169	14272	6476	344	11467	98431	54382	20548	18170	5298	420	289803	108532	505339	613871
Difference	**1985-2000**	**-90%**	**-64%**	**0%**	**-58%**	**-30%**	**7%**	**1%**	**7%**	**-35%**	**-52%**	**-54%**	**-59%**	**-4%**	**-73%**	**-9%**	**-36%**

Appendix 2f Lead emissions into river basins of Germany.

River basin	Year	Industry [kg/a]	MWWTPs [kg/a]	Historic mining activities [kg/a]	Atmospheric deposition [kg/a]	Seepage and spraydrift [kg/a]	Surface runoff [kg/a]	Erosion [kg/a]	Tile drainage [kg/a]	Separate sewers [kg/a]	Combined sewer overflows [kg/a]	Sewers without MWWTP [kg/a]	Households without connection [kg/a]	Ground-water [kg/a]	Shipping	**Point sources total [kg/a]**	**Nonpoint sources total [kg/a]**	**Total [kg/a]**
	1985		13038		9968	90	58348	29661	180	9964	20574	2633	404	1955	19	13038	133796	146834
Danube	1995	504	5987		1499	73	10715	31961	187	6345	7765	604	123	1817	78	6491	61168	67659
	2000	609	2723		1096	71	6074	32015	187	4144	5161	474	85	1817	78	3332	51202	54534
Difference	**1985-2000**		**-79%**		**-89%**	**-21%**	**-90%**	**8%**	**4%**	**-58%**	**-75%**	**-82%**	**-79%**	**-7%**	**311%**	**-74%**	**-62%**	**-63%**
	1985	81000	45824	146	16323	128	67712	34446	297	27445	95530	10278	440	3619	2149	126970	258367	385337
Rhine	1995	12724	19363	146	4063	106	11689	35168	302	14324	35722	1948	143	3222	2355	32233	109042	141275
	2000	11489	15058	146	2648	101	6660	35225	302	9356	23813	1530	99	3222	2355	26693	85311	112004
Difference	**1985-2000**	**-86%**	**-67%**	**0%**	**-84%**	**-21%**	**-90%**	**2%**	**2%**	**-66%**	**-75%**	**-85%**	**-78%**	**-11%**	**10%**	**-79%**	**-67%**	**-71%**
	1985	340	1709		2276	22	1686	1049	64	8882	1560	7	167	440	256	2049	16409	18458
Ems	1995	73	789		498	20	508	1033	68	4555	543	0	57	433	140	862	7855	8717
	2000	78	1103		321	19	308	1034	68	2975	366	0	39	433	140	1181	5703	6884
Difference	**1985-2000**	**-77%**	**-35%**		**-86%**	**-13%**	**-82%**	**-1%**	**6%**	**-67%**	**-77%**	**0%**	**-77%**	**-2%**	**-45%**	**-42%**	**-65%**	**-63%**
	1985	23950	5006		6491	69	6641	11351	183	31098	10573	4771	296	1339	332	28956	73144	102100
Weser	1995	1202	2266		1383	60	1724	10850	200	15782	3780	1483	88	1216	141	3468	36707	40175
	2000	1361	2962		951	58	1038	10866	200	10308	2521	1159	61	1216	141	4323	28519	32842
Difference	**1985-2000**	**-94%**	**-41%**		**-85%**	**-16%**	**-84%**	**-4%**	**9%**	**-67%**	**-76%**	**-76%**	**-79%**	**-9%**	**-58%**	**-85%**	**-61%**	**-68%**
	1985	24989	17779	6225	32674	135	4231	29408	490	41392	27249	17820	1617	1653	1463	48993	158132	207125
Elbe	1995	1612	6741	6225	5972	76	1564	28633	547	21611	10735	7544	583	1566	938	14578	79769	94348
	2000	1205	3074	6225	3607	74	989	28674	547	14115	7119	5883	425	1566	938	10504	63937	74441
Difference	**1985-2000**	**-95%**	**-83%**	**0%**	**-89%**	**-45%**	**-77%**	**-2%**	**12%**	**-66%**	**-74%**	**-67%**	**-74%**	**-5%**	**-36%**	**-79%**	**-60%**	**-64%**
	1985		649		1718	8	85.1	613	17	2542	480	161	101	77	83	649	5885	6534
Odra	1995	295	185		107	4	35.4	649	19	1237	192	54	35	61	85	480	2478	2958
	2000	989	98		69	4	25.0	651	19	808	128	42	25	61	85	1087	1917	3004
Difference	**1985-2000**		**-85%**		**-96%**	**-49%**	**-71%**	**6%**	**12%**	**-68%**	**-73%**	**-74%**	**-75%**	**-21%**	**2%**	**67%**	**-67%**	**-54%**
North Sea	1985	54	1226		2498	20	1720	297	181	6437	2231	398	145	315		1280	14242	15522
Coast	1995	44	320		359	18	379	255	179	3132	862	33	48	294		364	5559	5923
	2000	48	404		222	17	235	255	179	2046	575	25	33	294		452	3882	4334
Difference	**1985-2000**	**-11%**	**-67%**		**-91%**	**-14%**	**-86%**	**-14%**	**-1%**	**-68%**	**-74%**	**-94%**	**-77%**	**-7%**		**-65%**	**-73%**	**-72%**
Baltic Sea	1985		2391		14562	38	772	2043	187	7450	1995	338	483	377	227	2391	28472	30863
Coast	1995	43	1113		1528	22	282	2022	208	5415	677	389	88	367	20	1156	11017	12173
	2000	43	93		960	21	195	2030	208	3537	453	298	63	367	20	136	8153	8288
Difference	**1985-2000**		**-96%**		**-93%**	**-44%**	**-75%**	**-1%**	**11%**	**-53%**	**-77%**	**-12%**	**-87%**	**-3%**	**-91%**	**-94%**	**-71%**	**-73%**
Black	1985		13038		9968	90	58348	29661	180	9964	20574	2633	404	1955	19	13038	133796	146834
Sea	1995	504	5987		1499	73	10715	31961	187	6345	7765	604	123	1817	78	6491	61168	67659
total	2000	609	2723		1096	71	6074	32015	187	4144	5161	474	85	1817	78	3332	51202	54534
Difference	**1985-2000**		**-79%**		**-89%**	**-21%**	**-90%**	**8%**	**4%**	**-58%**	**-75%**	**-82%**	**-79%**	**-7%**	**311%**	**-74%**	**-62%**	**-63%**
North Sea	1985	130333	71544	6371	60262	375	81990	76551	1215	115254	137143	33274	2665	7366	4200	208248	520295	728543
total	1995	15655	29479	6371	12275	279	15865	75939	1296	59404	51642	11008	919	6731	3574	51505	238932	290437
	2000	14181	22601	6371	7749	270	9229	76054	1296	38800	34394	8597	657	6731	3574	43153	187351	230504
Difference	**1985-2000**	**-89%**	**-68%**	**0%**	**-87%**	**-28%**	**-89%**	**-1%**	**7%**	**-66%**	**-75%**	**-74%**	**-75%**	**-9%**	**-15%**	**-79%**	**-64%**	**-68%**
Baltic Sea	1985		3040		16280	46	857	2656	204	9992	2475	499	584	454	310	3040	34357	37397
total	1995	338	1297		1635	26	317	2671	227	6652	869	443	123	428	105	1635	13495	15131
	2000	1032	191		1029	25	220	2681	227	4345	581	340	88	428	105	1223	10069	11292
Difference	**1985-2000**		**-94%**		**-94%**	**-45%**	**-74%**	**1%**	**11%**	**-57%**	**-77%**	**-32%**	**-85%**	**-6%**	**-66%**	**-60%**	**-71%**	**-70%**
Germany	1985	130333	87622	6371	86510	510	141196	108868	1599	135210	160192	36406	3653	9775	4529	224326	688448	912774
total	1995	16497	36764	6371	15409	378	26897	110571	1710	72401	60276	12055	1165	8976	3757	59632	313595	373226
	2000	15822	25515	6371	9874	366	15523	110750	1710	47289	40136	9411	830	8976	3757	47708	248622	296330
Difference	**1985-2000**	**-88%**	**-71%**	**0%**	**-89%**	**-28%**	**-89%**	**2%**	**7%**	**-65%**	**-75%**	**-74%**	**-77%**	**-8%**	**-17%**	**-79%**	**-64%**	**-68%**

Appendix 2g Zinc emissions into river basins of Germany.

River basin	Year	Industry [kg/a]	MWWTPs [kg/a]	Historic mining activities [kg/a]	Atmospheric deposition [kg/a]	Seepage and spraydrift [kg/a]	Surface runoff [kg/a]	Erosion [kg/a]	Tile drainage [kg/a]	Separate sewers [kg/a]	Combined sewer overflows [kg/a]	Sewers without MWWTP [kg/a]	Households without connection [kg/a]	Ground-water [kg/a]	Shipping	**Point sources total [kg/a]**	**Nonpoint sources total [kg/a]**	**Total [kg/a]**
	1985		193541		29294	3684	122821	126014	12234	38477	81540	13177	1740	53279		193541	482260	675801
Danube	1995	20717	121036		19622	3043	74671	137662	12685	56360	69861	5586	1110	50446		141753	431046	572799
	2000	17235	74202		17838	3007	74092	138993	12685	56731	70300	5608	1117	50446		91437	430817	522254
Difference	**1985-2000**		**-62%**		**-39%**	**-18%**	**-40%**	**10%**	**4%**	**47%**	**-14%**	**-57%**	**-36%**	**-5%**		**-53%**	**-11%**	**-23%**
	1985	501000	761330	31609	47972	6088	145884	164488	20121	105975	381268	51638	1901	98698		1293939	1024033	2317972
Rhine	1995	83263	424674	31609	32240	5079	83944	170929	20526	127241	322972	18034	1295	94742		539546	877002	1416548
	2000	68727	275225	31609	29309	4998	83155	172859	20526	128080	324983	18104	1302	94742		375561	878058	1253619
Difference	**1985-2000**	**-86%**	**-64%**	**0%**	**-39%**	**-18%**	**-43%**	**5%**	**2%**	**21%**	**-15%**	**-65%**	**-32%**	**-4%**		**-71%**	**-14%**	**-46%**
	1985	1036	30052		6689	1195	5318	6336	4322	34297	6214	34	715	11994		31088	77115	108203
Ems	1995	5041	18215		4762	1075	4799	6436	4624	40458	4835	0	514	11819		23256	79322	102578
	2000	585	15711		4329	1092	4783	6520	4624	40724	4865	0	517	11819		16296	79273	95569
Difference	**1985-2000**	**-44%**	**-48%**		**-35%**	**-9%**	**-10%**	**3%**	**7%**	**19%**	**-22%**	**-100%**	**-28%**	**-1%**		**-48%**	**3%**	**-12%**
	1985	478000	94413		20094	3613	19209	58155	12386	120206	42592	24716	1284	36525		572413	338780	911193
Weser	1995	13248	57712		12788	3101	15545	57608	13575	140186	33802	13702	799	33330		70960	324436	395396
	2000	9320	31424		11626	3136	15467	58365	13575	141110	34014	13756	803	33330		40744	325182	365926
Difference	**1985-2000**	**-98%**	**-67%**		**-42%**	**-13%**	**-19%**	**0%**	**10%**	**17%**	**-20%**	**-44%**	**-37%**	**-9%**		**-93%**	**-4%**	**-60%**
	1985	1885524	213506	14282	146896	6834	19074	117510	33219	171529	118994	94670	8170	45067		2113312	761963	2875275
Elbe	1995	24325	96970	14282	54895	3386	14657	119022	37103	191968	95806	69641	5358	45900		135577	637736	773314
	2000	3822	51196	14282	49905	3382	14621	120544	37103	193234	96417	69922	5385	45900		69300	636413	705713
Difference	**1985-2000**	**-100%**	**-76%**	**0%**	**-66%**	**-51%**	**-23%**	**3%**	**12%**	**13%**	**-19%**	**-26%**	**-34%**	**2%**		**-97%**	**-16%**	**-75%**
	1985		7219		8199	389	754.0	2661	1175	11071	2118	856	513	2109		7219	29845	37064
Odra	1995	9333	2296		2842	167	440.9	2945	1279	10987	1697	497	322	2163		11629	23340	34968
	2000	9153	1736		2583	164	437.5	3003	1279	11060	1708	499	324	2163		10889	23221	34109
Difference	**1985-2000**		**-76%**		**-68%**	**-58%**	**-42%**	**13%**	**9%**	**0%**	**-19%**	**-42%**	**-37%**	**3%**		**51%**	**-22%**	**-8%**
North Sea	1985	1622	7791		7340	974	5007	1839	12265	24856	8802	1850	609	8580		9413	72121	81534
Coast	1995	3917	6781		5006	856	3616	1664	12173	27820	7702	299	434	8022		10698	67592	78290
	2000	8373	5661		4551	857	3591	1686	12173	28003	7750	300	437	8022		14034	67370	81404
Difference	**1985-2000**	**416%**	**-27%**		**-38%**	**-12%**	**-28%**	**-8%**	**-1%**	**13%**	**-12%**	**-84%**	**-28%**	**-7%**		**49%**	**-7%**	**0%**
Baltic Sea	1985		16124		61539	1862	4415	13298	12666	31545	8679	1740	2217	10277	473	16124	148712	164836
Coast	1995	326	5208		25342	884	2981	13833	14130	48098	5982	3565	807	10042	43	5534	125707	131242
	2000	326	4071		23038	879	2989	14092	14130	48415	6020	3580	811	10042	43	4397	124039	128436
Difference	**1985-2000**		**-75%**		**-63%**	**-53%**	**-32%**	**6%**	**12%**	**53%**	**-31%**	**106%**	**-63%**	**-2%**	**-91%**	**-73%**	**-17%**	**-22%**
Black	1985		193541		29294	3684	122821	126014	12234	38477	81540	13177	1740	53279		193541	482260	675801
Sea	1995	20717	121036		19622	3043	74671	137662	12685	56360	69861	5586	1110	50446		141753	431046	572799
total	2000	17235	74202		17838	3007	74092	138993	12685	56731	70300	5608	1117	50446		91437	430817	522254
Difference	**1985-2000**		**-62%**		**-39%**	**-18%**	**-40%**	**10%**	**4%**	**47%**	**-14%**	**-57%**	**-36%**	**-5%**		**-53%**	**-11%**	**-23%**
North Sea	1985	2867182	1107092	45891	228991	18704	194492	348328	82313	456863	557870	172908	12679	200864		4020165	2274013	6294178
total	1995	129794	604352	45891	109691	13497	122562	355659	88001	527673	465117	101676	8400	193813		780037	1986088	2766126
	2000	90827	379217	45891	99720	13465	121617	359974	88001	531151	468029	102082	8444	193813		515935	1986296	2502231
Difference	**1985-2000**	**-97%**	**-66%**	**0%**	**-56%**	**-28%**	**-37%**	**3%**	**7%**	**16%**	**-16%**	**-41%**	**-33%**	**-4%**		**-87%**	**-13%**	**-60%**
Baltic Sea	1985		23343		69738	2251	5169	15959	13841	42616	10797	2596	2730	12386	473	23343	178556	201899
total	1995	9659	7504		28184	1051	3422	16778	15409	59085	7679	4062	1129	12205	43	17163	149047	166210
	2000	9479	5807		25621	1043	3427	17095	15409	59475	7728	4079	1135	12205	43	15286	147260	162546
Difference	**1985-2000**		**-75%**		**-63%**	**-54%**	**-34%**	**7%**	**11%**	**40%**	**-28%**	**57%**	**-58%**	**-1%**	**-91%**	**-35%**	**-18%**	**-19%**
Germany	1985	2867182	1323976	45891	328023	24639	322483	490301	108388	537956	650207	188681	17149	266529	473	4237049	2934829	7171878
total	1995	160170	732893	45891	157497	17591	200654	510099	116095	643118	542657	111324	10639	256464	43	938954	2566181	3505135
	2000	117541	459226	45891	143179	17515	199136	516062	116095	647357	546057	111769	10696	256464	43	622658	2564373	3187031
Difference	**1985-2000**	**-96%**	**-65%**	**0%**	**-56%**	**-29%**	**-38%**	**5%**	**7%**	**20%**	**-16%**	**-41%**	**-38%**	**-4%**	**-91%**	**-85%**	**-13%**	**-56%**

Appendix 2h Arsenic emissions into river basins of Germany.

River basin	Year	Industry [kg/a]	MWWTPs [kg/a]	Historic mining activities [kg/a]	Atmospheric deposition [kg/a]	Seepage and spraydrift [kg/a]	Surface runoff [kg/a]	Erosion [kg/a]	Tile drainage [kg/a]	Separate sewers [kg/a]	Combined sewer overflows [kg/a]	Sewers without MWWTP [kg/a]	Households without connection [kg/a]	Ground-water [kg/a]	**Point sources total [kg/a]**	**Nonpoint sources total [kg/a]**	**Total [kg/a]**
	1985		3560		784.0	8.6	13826	8807	464	367	777	118	16	13498	3560	38666	42226
Danube	1995	28.3	417		101.0	6.9	2009	9457	481	274	348	36	6	12783	445	25502	25947
	2000	28.3	385		63.0	6.8	521	9458	481	263	334	35	6	12783	413	23951	24364
Difference	**1985-2000**		**-89%**		**-92%**	**-21%**	**-96%**	**7%**	**4%**	**-28%**	**-57%**	**-70%**	**-63%**	**-5%**	**-88%**	**-38%**	**-42%**
	1985		17516	33	1283.0	13.8	16018	11802	762	1011	3613	462	17	25004	17549	59986	77534
Rhine	1995	1385.4	1896	33	166.0	11.3	2180	11966	778	619	1616	115	7	24001	3315	41459	44774
	2000	2751.5	1821	33	103.0	11.1	551	11969	778	594	1554	113	7	24001	4606	39681	44287
Difference	**1985-2000**		**-90%**	**0%**	**-92%**	**-20%**	**-97%**	**1%**	**2%**	**-41%**	**-57%**	**-76%**	**-59%**	**-4%**	**-74%**	**-34%**	**-43%**
	1985		720		179.0	2.6	388	231	164	327	61	0	7	3038	720	4398	5117
Ems	1995	0.0	84		24.0	2.3	90	227	175	197	24	0	3	2994	84	3737	3821
	2000	0.0	119		15.0	2.3	21	227	175	189	23	0	3	2994	119	3650	3769
Difference	**1985-2000**		**-83%**		**-92%**	**-11%**	**-94%**	**-2%**	**7%**	**-42%**	**-62%**	**0%**	**-57%**	**-1%**	**-83%**	**-17%**	**-26%**
	1985		2734		583.0	7.9	1540	2772	469	1155	463	287	12	9253	2734	16542	19276
Weser	1995	26.0	306		66.0	6.6	307	2636	514	682	169	87	4	8444	332	12916	13248
	2000	19.1	290		41.0	6.6	70	2637	514	654	162	85	4	8444	309	12618	12927
Difference	**1985-2000**		**-89%**		**-93%**	**-16%**	**-95%**	**-5%**	**10%**	**-43%**	**-65%**	**-70%**	**-67%**	**-9%**	**-89%**	**-24%**	**-33%**
	1985	387.2	4430	940	6193.0	15.3	955	8146	1259	2451	1958	1290	111	11417	5757	33795	39552
Elbe	1995	289.6	414	940	282.0	7.4	269	7979	1406	935	475	439	31	11628	1643	23451	25094
	2000	32.7	405	940	176.0	7.3	66	7981	1406	896	456	430	30	11628	1378	23076	24454
Difference	**1985-2000**	**-92%**	**-91%**	**0%**	**-97%**	**-52%**	**-93%**	**-2%**	**12%**	**-63%**	**-77%**	**-67%**	**-73%**	**2%**	**-76%**	**-32%**	**-38%**
	1985	6879.3	181		359.0	0.9	17.8	251	45	193	37	12	7	534	7060	1457	8517
Odra	1995	11.5	11		15.0	0.4	5.8	265	48	53	8	3	2	548	22	948	970
	2000	10.9	12		9.0	0.4	1.8	265	48	51	8	3	2	548	23	936	959
Difference	**1985-2000**	**-100%**	**-93%**		**-97%**	**-59%**	**-90%**	**6%**	**7%**	**-74%**	**-78%**	**-75%**	**-71%**	**3%**	**-100%**	**-36%**	**-89%**
North Sea	1985		424		196.0	2.2	399	65	465	237	86	17	6	2174	424	3647	4071
Coast	1995	7.8	40		26.0	1.9	66	55	461	135	38	2	2	2032	48	2819	2866
	2000	7.8	53		16.0	1.9	16	55	461	130	37	2	2	2032	61	2753	2813
Difference	**1985-2000**		**-88%**		**-92%**	**-14%**	**-96%**	**-15%**	**-1%**	**-45%**	**-57%**	**-88%**	**-67%**	**-7%**	**-86%**	**-25%**	**-31%**
Baltic Sea	1985		590		2480.0	4.2	170	689	480	494	144	23	25	2603	590	7112	7702
Coast	1995	1.2	52		130.0	2.0	46	675	535	234	30	22	5	2544	54	4223	4276
	2000	1.1	55		81.0	2.0	13	676	535	224	29	21	4	2544	56	4129	4185
Difference	**1985-2000**		**-91%**		**-97%**	**-54%**	**-92%**	**-2%**	**11%**	**-55%**	**-80%**	**-9%**	**-84%**	**-2%**	**-91%**	**-42%**	**-46%**
Black	1985	0.0	3560		784.0	8.6	13826	8807	464	367	777	118	16	13498	3560	38666	42226
Sea	1995	28.3	417		101.0	6.9	2009	9457	481	274	348	36	6	12783	445	25502	25947
total	2000	28.3	385		63.0	6.8	521	9458	481	263	334	35	6	12783	413	23951	24364
Difference	**1985-2000**		**-89%**		**-92%**	**-21%**	**-96%**	**7%**	**4%**	**-28%**	**-57%**	**-70%**	**-63%**	**-5%**	**-88%**	**-38%**	**-42%**
North Sea	1985	387	25823	973	8434.0	41.9	19300	23016	3119	5181	6181	2056	153	50886	27184	118367	145551
total	1995	1709	2740	973	564.0	29.5	2913	22863	3334	2568	2322	643	47	49099	5422	84382	89804
	2000	2811	2688	973	351.0	29.2	724	22869	3334	2463	2232	630	46	49099	6472	81778	88250
Difference	**1985-2000**	**626%**	**-90%**	**0%**	**-96%**	**-30%**	**-96%**	**-1%**	**7%**	**-52%**	**-64%**	**-69%**	**-70%**	**-4%**	**-76%**	**-31%**	**-39%**
Baltic Sea	1985	6879	771		2839.0	5.1	188	940	525	687	181	35	32	3137	7650	8569	16219
total	1995	13	63		145.0	2.3	52	940	583	287	38	25	7	3092	76	5171	5247
	2000	12	67		90.0	2.3	15	941	583	275	37	24	6	3092	79	5065	5144
Difference	**1985-2000**		**-91%**		**-97%**	**-55%**	**-92%**	**0%**	**11%**	**-60%**	**-80%**	**-31%**	**-81%**	**-1%**	**-99%**	**-41%**	**-68%**
Germany	1985	7267	30155	973	12057.0	55.6	33313	32763	4108	6235	7139	2209	201	67521	38394	165602	203996
total	1995	1750	3220	973	810.0	38.7	4973	33260	4398	3129	2708	704	60	64974	5943	115055	120997
	2000	2851	3140	973	504.0	38.4	1260	33268	4398	3001	2603	689	58	64974	6964	110793	117758
Difference	**1985-2000**	**-61%**	**-90%**	**0%**	**-96%**	**-31%**	**-96%**	**2%**	**7%**	**-52%**	**-64%**	**-69%**	**-71%**	**-4%**	**-82%**	**-33%**	**-42%**

Appendix 2i Lindane emissions into river basins of Germany.

River basin	Year	Industry [kg/a]	MWWTPs [kg/a]	Atmospheric deposition [kg/a]	Seepage and spraydrift [kg/a]	Surface runoff [kg/a]	Erosion [kg/a]	Tile drainage [kg/a]	Separate sewers [kg/a]	Combined sewer overflows [kg/a]	Sewers without MWWTP [kg/a]	Households without connection [kg/a]	Ground-water [kg/a]	**Point sources total [kg/a]**	**Nonpoint sources total [kg/a]**	**Total [kg/a]**
	1985		51.0	25.5	24.8	133.0	1.8	11.2	6.5	14.4	4.8	1.8	19.0	51.0	242.8	293.8
Danube	1995	0	30.0	23.7	1.3	27.6	1.4	1.9	5.4	6.6	0.5	0.4	20.4	30.0	89.3	119.2
	2000	0	27.7	23.7	0.0	21.4	1.5	1.4	5.4	6.6	0.5	0.4	20.4	27.7	81.4	109.1
Difference	**1985-2000**	**0%**	**-46%**	**-7%**	**-100%**	**-84%**	**-17%**	**-87%**	**-16%**	**-54%**	**-89%**	**-76%**	**8%**	**-46%**	**-66%**	**-63%**
	1985	0	227.0	43.2	42.3	169.0	2.7	18.8	17.9	68.5	19.1	2.0	32.9	227.0	416.3	643.3
Rhine	1995	5	136.3	43.3	2.1	31.2	2.4	3.0	12.3	30.5	1.7	0.5	29.3	141.3	156.4	297.7
	2000	1	130.9	43.3	0.0	23.1	2.6	2.2	12.3	30.5	1.7	0.5	29.3	131.9	145.5	277.4
Difference	**1985-2000**	**100%**	**-42%**	**0%**	**-100%**	**-86%**	**-3%**	**-88%**	**-32%**	**-55%**	**-91%**	**-75%**	**-11%**	**-42%**	**-65%**	**-57%**
	1985	0	14.0	11.2	6.7	9.3	0.1	3.3	5.8	1.1	0.0	0.7	4.0	14.0	42.2	56.2
Ems	1995	0	6.1	4.7	0.3	1.5	0.0	0.6	3.9	0.5	0.0	0.2	3.9	6.1	15.7	21.8
	2000	0	8.6	4.7	0.0	0.9	0.1	0.5	3.9	0.5	0.0	0.2	3.9	8.6	14.7	23.2
Difference	**1985-2000**	**0%**	**-39%**	**-58%**	**-100%**	**-90%**	**-14%**	**-85%**	**-33%**	**-59%**	**0%**	**-71%**	**-2%**	**-39%**	**-65%**	**-59%**
	1985	10	50.0	20.2	23.2	35.1	1.2	10.6	20.3	7.3	8.6	1.3	12.2	60.0	140.1	200.1
Weser	1995	0	22.0	10.3	1.2	5.5	0.8	1.9	13.5	3.2	1.3	0.3	11.1	22.0	49.0	71.0
	2000	0	20.8	10.3	0.0	3.1	1.0	1.4	13.5	3.2	1.3	0.3	11.1	20.8	45.2	66.1
Difference	**1985-2000**	**-100%**	**-58%**	**-49%**	**-100%**	**-91%**	**-21%**	**-87%**	**-33%**	**-56%**	**-85%**	**-76%**	**-9%**	**-65%**	**-68%**	**-67%**
	1985	106	102.0	66.8	58.7	78.4	3.2	27.4	26.4	18.0	31.6	9.9	15.3	208.0	335.7	543.7
Elbe	1995	18	29.7	27.8	2.8	8.3	2.0	5.1	18.5	9.1	6.7	2.1	14.5	47.7	96.8	144.5
	2000	1	29.1	27.8	0.0	2.7	2.3	3.9	18.5	9.1	6.7	2.1	14.5	30.1	87.6	117.7
Difference	**1985-2000**	**-99%**	**-71%**	**-58%**	**-100%**	**-97%**	**-26%**	**-86%**	**-30%**	**-49%**	**-79%**	**-79%**	**-5%**	**-86%**	**-74%**	**-78%**
	1985		4.0	1.0	3.7	5.3	0.1	1.5	1.6	0.3	0.3	0.6	0.7	4.0	15.1	19.1
Odra	1995	0	0.8	0.4	0.2	0.4	0.0	0.2	1.1	0.2	0.1	0.1	0.6	0.8	3.2	4.0
	2000	0	0.9	0.4	0.0	0.1	0.1	0.1	1.1	0.2	0.1	0.1	0.6	0.9	2.6	3.5
Difference	**1985-2000**		**-78%**	**-59%**	**-100%**	**-99%**	**0%**	**-91%**	**-34%**	**-47%**	**-83%**	**-80%**	**-21%**	**-78%**	**-83%**	**-82%**
North Sea	1985	0	8.0	9.3	5.5	8.0	0.0	4.8	4.2	1.5	0.6	0.6	2.9	8.0	37.3	45.3
Coast	1995	0	2.9	3.3	0.3	1.1	0.0	1.4	2.7	0.7	0.0	0.2	2.7	2.9	12.4	15.2
	2000	0	3.8	3.3	0.0	0.7	0.0	1.3	2.7	0.7	0.0	0.2	2.7	3.8	11.5	15.3
Difference	**1985-2000**	**0%**	**-53%**	**-65%**	**-100%**	**-92%**	**-30%**	**-73%**	**-36%**	**-51%**	**-95%**	**-72%**	**-7%**	**-53%**	**-69%**	**-66%**
Baltic Sea	1985		16.0	30.5	15.1	17.6	0.1	8.0	4.7	1.3	0.6	2.4	3.4	16.0	83.7	99.7
Coast	1995	0	3.8	7.1	0.7	1.6	0.1	1.8	4.6	0.6	0.3	0.3	3.3	3.8	20.5	24.2
	2000	0	3.9	7.1	0.0	0.4	0.1	1.5	4.6	0.6	0.3	0.3	3.3	3.9	18.3	22.3
Difference	**1985-2000**		**-75%**	**-77%**	**-100%**	**-98%**	**-21%**	**-81%**	**-1%**	**-57%**	**-43%**	**-87%**	**-3%**	**-75%**	**-78%**	**-78%**
Black	1985	0	51.0	25.5	24.8	133.0	1.8	11.2	6.5	14.4	4.8	1.8	19.0	51.0	242.8	293.8
Sea	1995	0	30.0	23.7	1.3	27.6	1.4	1.9	5.4	6.6	0.5	0.4	20.4	30.0	89.3	119.2
total	2000	0	27.7	23.7	0.0	21.4	1.5	1.4	5.4	6.6	0.5	0.4	20.4	27.7	81.4	109.1
Difference	**1985-2000**	**0%**	**-46%**	**-7%**	**-100%**	**-84%**	**-17%**	**-87%**	**-16%**	**-54%**	**-89%**	**-76%**	**8%**	**-46%**	**-66%**	**-63%**
North Sea	1985	116	401.0	150.7	136.4	299.9	7.2	64.8	74.6	96.4	59.9	14.5	67.2	517.0	971.6	1488.6
total	1995	23	196.9	89.5	6.7	47.7	5.2	12.0	50.9	44.0	9.8	3.3	61.4	219.9	330.3	550.2
	2000	2	193.2	89.5	0.0	30.5	6.0	9.3	50.9	44.0	9.8	3.3	61.4	195.2	304.5	499.7
Difference	**1985-2000**	**-98%**	**-52%**	**-41%**	**-100%**	**-90%**	**-16%**	**-86%**	**-32%**	**-54%**	**-84%**	**-78%**	**-9%**	**-62%**	**-69%**	**-66%**
Baltic Sea	1985	0.0	20.0	31.5	18.8	23.0	0.2	9.5	6.3	1.6	0.9	3.0	4.1	20.0	98.8	118.8
total	1995	0.0	4.5	7.5	0.9	2.1	0.1	2.0	5.7	0.7	0.4	0.4	3.9	4.5	23.7	28.2
	2000	0.0	4.8	7.5	0.0	0.5	0.2	1.6	5.7	0.7	0.4	0.4	3.9	4.8	20.9	25.7
Difference	**1985-2000**	**0%**	**-76%**	**-76%**	**-100%**	**-98%**	**-16%**	**-83%**	**-10%**	**-55%**	**-57%**	**-86%**	**-6%**	**-76%**	**-79%**	**-78%**
Germany	1985	116	472.0	207.8	180.0	455.9	9.2	85.5	87.4	112.4	65.6	19.3	90.3	588.0	1313.2	1901.2
total	1995	23	231.4	120.7	8.8	77.3	6.8	15.9	62.0	51.3	10.7	4.1	85.7	254.4	443.2	697.6
	2000	2	225.7	120.7	0.0	52.4	7.6	12.3	62.0	51.3	10.7	4.1	85.7	227.7	406.8	634.5
Difference	**1985-2000**	**-98%**	**-52%**	**-42%**	**-100%**	**-88%**	**-17%**	**-86%**	**-29%**	**-54%**	**-84%**	**-79%**	**-5%**	**-61%**	**-69%**	**-67%**

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