Emissions of heavy metals into river basins of Germany

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Abstract The input of seven heavy metals (Cd, Cr, Cu, Hg, Ni, Pb and Zn) into the large river basins of Germany via various point and diffuse pathways were estimated for the period of 1985 through 2000. To quantify the emissions via point sources a nationwide 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 functions given by Vink and Behrendt. 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 North Sea decreased for each metal during the period of 1985 to 2000. The reduction varies between 87% for Hg and 41% for Ni mainly caused by the decline 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 emission pathways are *"paved urban areas"* and *"erosion"*.

Keywords Diffuse source pollution; heavy metal emissions; river basin management

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Introduction

Several international agreements (International Conference on the Protection of the North Sea, Baltic Marine Environment Protection (HELCOM), International Commission for the Protection of the Rhine (ICPR) etc.) recommend diminishing the emission of priority pollutants into North and Baltic Sea significantly. The aim of this project was to quantify the emissions of seven heavy metals (Cd, Cr, Cu, Hg, Ni, Pb and Zn) into German river basins within the time period of 1985–2000.

The project was carried out in co-operation with the Fraunhofer Institute for Systems and Innovation Research (Karlsruhe, Germany) and the Institute of Freshwater Ecology and Inland Fisheries (Berlin, Germany). A detailed description of methods and results is published in Fuchs *et al.* (2002).

Materials and methods

The investigated river basins were those of the rivers Danube, Rhine, Meuse, Ems, Weser, Elbe, Odra and the coastal areas of North and Baltic Sea. A geographical overview of the large German river basins is shown in Figure 1. For each river basin the input of heavy metals via various point and non-point sources were calculated based on input data for the calculation periods of 1983–1987, 1993–1997 and 1999/2000.

The main sources and pathways taken into account to calculate the heavy metal input into the river systems and marine environments are shown in Figure 2.

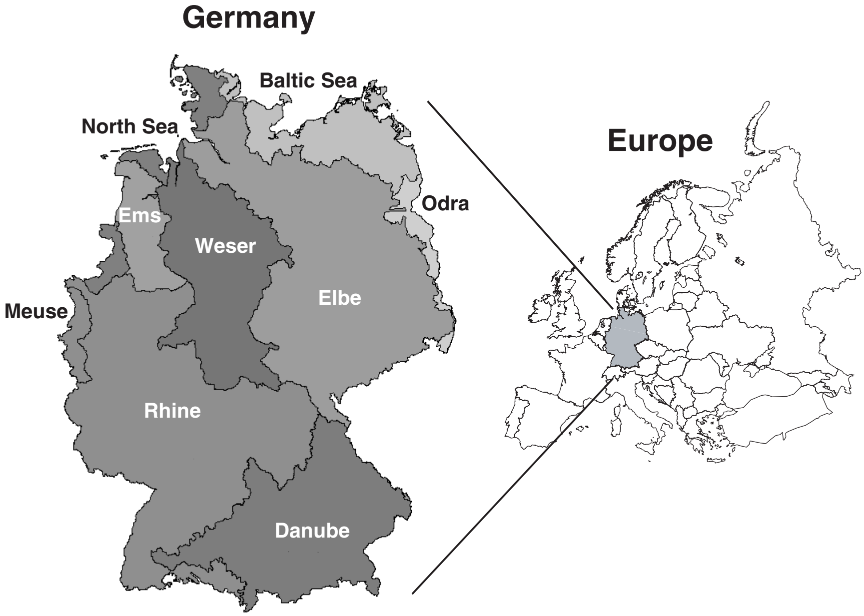

Figure 1 Geographical overview of the large German river basins

Heavy metal emissions via point sources

The emissions via point sources have been caused by *"municipal wastewater treatment plant effluents"* and *"direct industrial discharges"*.

The calculation of heavy metal emissions via *"municipal wastewater treatment plants (MWWTP)"* was based on a nationwide survey of MWWTP effluent concentrations. The quantity and quality of the data received from different authorities varied distinctly. Particularly the wide range of the notified quantification limits required a method to improve the data-basis. In a multistage checking process implausible data sets were removed (Böhm *et al.*, 2001). Using the remaining data (5,000–10,000 data for each metal) average effluent concentrations were calculated on the level of the 16 Federal states of Germany. Representative effluent concentrations for the river basins shown in Figure 1 were deduced subsequently taking into account the portion of population equivalents of each Federal state within a certain watershed. The heavy metal load via MWWTPs was calculated using the annual wastewater flow. Due to the lack of monitoring data, heavy metal emissions via MWWTPs for the period of 1983–1987 had to be generated using the average daily heavy metal load per treated population equivalent (heavy metal input) and the efficiency of wastewater treatment.

For the inventory of *"direct industrial discharges"*, different individual and aggregated data were used such as Federal state monitoring data, international reports, environmental reports of companies, reports from industrial associations and the results of various research projects. Whereas the emissions of working mines are included within the figures of *"industrial direct discharges"*, the input via discharges caused by *"historic mining activities"* are revealed separately (for details see Böhm *et al.*, 2001 and Fuchs *et al.*, 2002).

Heavy metal emissions via diffuse pathways

The diffuse emissions of heavy metals were calculated by using an adapted version of the model MONERIS (**MO**delling **N**utrient **E**missions in **RI**ver **S**ystems, Behrendt *et al.*, 2000, Behrendt *et al.*, 2002). The model is based on a Geographic Information System (GIS) which includes data on discharges via the various pathways as well as extensive

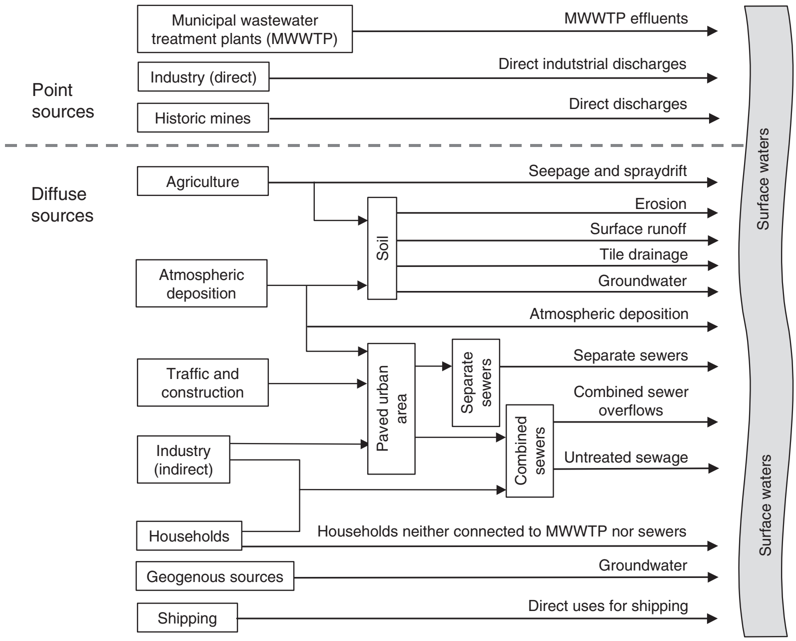

Figure 2 Sources and pathways of heavy metal input into river systems (Fuchs *et al*., 2002)

statistic information on each German catchment of a size between 500–1,000 km^2. The use of a GIS allowed estimating the regionalized heavy metal input into large river basins. Diffuse emissions of heavy metals into surface waters represent the sum of various pathways, which correspond to the different components of the runoff as shown in Figure 2.

A detailed description of the MONERIS approach is given by Behrendt *et al*. (2000). The input data used for the estimation of diffuse heavy metal emissions is described below. For the diffuse pathways that show a significant change over the investigated time period of 1985–2000, especially *"atmospheric deposition"* and diffuse input from *"urban areas"*, different input data according to each calculation period were used.

The direct input of heavy metals on the water surface area by *"atmospheric deposition"* for the metals Pb, Cd and Hg was estimated by using data on the basis of a 50×50 km grid provided by EMEP/MSC-East. For the other metals, average deposition rates measured by the Federal Environmental Agency of Germany as well as data from literature were used.

Within the pathway *"seepage and spraydrift"* emissions of heavy metals to surface waters due to the use of organic manure and mineral fertilizer on farmyards are summarized. The calculation was carried out by determining the masses of mineral fertilizer, organic manure used and their mean metal content. It is assumed that a certain share of these masses is entering surface waters (ICPR, 1999).

Emissions of heavy metals via *"erosion"* were determined using the sediment input into surface waters, the concentration of heavy metals in topsoil and an enrichment factor of metals in eroded sediments. Heavy metal concentrations in the topsoil of agricultural land were provided for each Federal state of Germany by the LABO (Federal state working group on soil quality, 1998). According to the method suggested by Behrendt *et al*. (2000) enrichment ratios were calculated based on metal contents in suspended solids within the rivers (at high flow conditions) and the upper soil of arable land.

The dissolved share of heavy metals within *"surface runoff"* from unpaved areas caused by high rainfall events was calculated based on heavy metal concentrations in the rainwater. In the case of agricultural land, the resulting load was supplemented by the runoff of fertilizer, manure and sewage sludge.

The input via *"tile drainage"* was calculated as the product of the drained area, drainage water volume and average heavy metal concentrations within drainage water. Mean heavy metal concentrations within drainage water were assumed to correspond with concentrations within seepage water given by Bielert *et al.* (1999).

Heavy metal input through *"groundwater"* was calculated from the product of groundwater outflow and heavy metal concentrations in springs of small streams given by the geochemical survey of German surface waters (Birke *et al.*, 2001). The heavy metal load discharged into river systems via groundwater flux is predominantly caused by geogenous sources.

The main pathways of non-point heavy metal emissions from paved urban areas are *"separate sewer systems"* and *"combined sewer overflows"*. For calculating the heavy metal input discharged from the paved urban area during rainfall events, specific heavy metal loads from paved urban areas were derived from concentrations within separate sewers given by the literature. Combined sewer systems collect the input from households, indirect industrial input and rainwater runoff from paved urban areas. During stormwater events, the quantity of water that exceeds the realized storage volume is discharged to surface water. Inhabitant specific metal loads and metal concentrations in industrial-commercial wastewater were used to estimate the additional heavy metal load of households and industrial indirect discharges.

Heavy metal loads in rivers and heavy metal retention

Data on heavy metal concentrations and discharge from several monitoring stations of the large river basins and their tributaries (> 1,000 km^2) were used to calculate the transported heavy metal loads for the period of 1993–1997. The average five-year heavy metal transport was calculated according to OSPAR (1996). The application of this method strongly depends on the quality of the data set used. When measurements were below the quantification limit, the concentration was considered to be half the quantification limit concentration. Heavy metal loads of the rivers Rhine and Elbe were completed using data published by Vink and Behrendt (2002).

According to the retention of heavy metals – mainly by sedimentation along floodplains – a discrepancy exists between the sum of heavy metal emissions and measured heavy metal loads at monitoring stations. Behrendt and Opitz (1999) found that the loss of nutrients in a river system is related to the specific runoff of a catchment as given in the equation below. Low specific runoff causes higher losses due to increased retention processes.

$$\frac{L}{E} = \frac{1}{1 + a \cdot q^b}$$

L = total transported heavy metal load at the monitoring station [$kg \cdot a^{-1}$], E = total estimated heavy metal emission at the monitoring station [$kg \cdot a^{-1}$], q = specific runoff of the catchment [$l \cdot km^{-2} \cdot s^{-1}$], a,b = constants [–].

For the dependency on specific runoff Behrendt and Opitz (1999) determined the parameters a and b on the basis of 89 European river basins. Vink and Behrendt (2002) adapted a and b for the retention of each of five heavy metals using data of the river basins Rhine and Elbe. For this study the parameters a and b were chosen according to Vink and Behrendt (2002).

Results and conclusions

The portion of each pathway of total heavy metal emission into the North Sea (sum of the emissions into the river basins of Rhine, Ems, Weser, Elbe, Meuse and North Sea Coast) and its change since the mid-eighties are shown in Figure 3.

For the period of 1983–1987 the heavy metal input is mainly caused by *"direct industrial discharges"*. Except for the metals Ni (main input via *"groundwater"*) and Pb (main input via *"paved urban areas"*) diffuse emissions are more important than emissions via point sources. Due to policies that led to the reduction of emissions via *"industrial direct discharges"* and *"MWWTPs"* today's emissions of heavy metals into river basins of Germany are dominated by the input via diffuse pathways. The most important diffuse emission pathways are *"paved urban areas"* and *"erosion"*.

The target for the emission reduction of the metals Cd, Hg and Pb for the North Sea in the period of 1985–2000 was 70% while a 50% reduction was envisioned for Cr, Cu, Ni and Zn.

A reduction of 83% was achieved for Cd, mainly caused by reductions via point sources. In the East German states, a significant decrease occurred for the input via *"paved urban areas"* resulting from the decline of atmospheric Cd emissions. For Hg a reduction of 87% was reached, mainly caused by the reduction of Hg input via *"industrial direct discharges"* into the river Elbe. Following the substitution of Pb as gasoline additive and the decrease of industrial emissions to the atmosphere, a reduction of 63% for the input of Pb via diffuse pathways can be seen. Taking into account the remaining pathways, the annual Pb load entering the North Sea was reduced by 68%. As input via *"groundwater"* is the main source

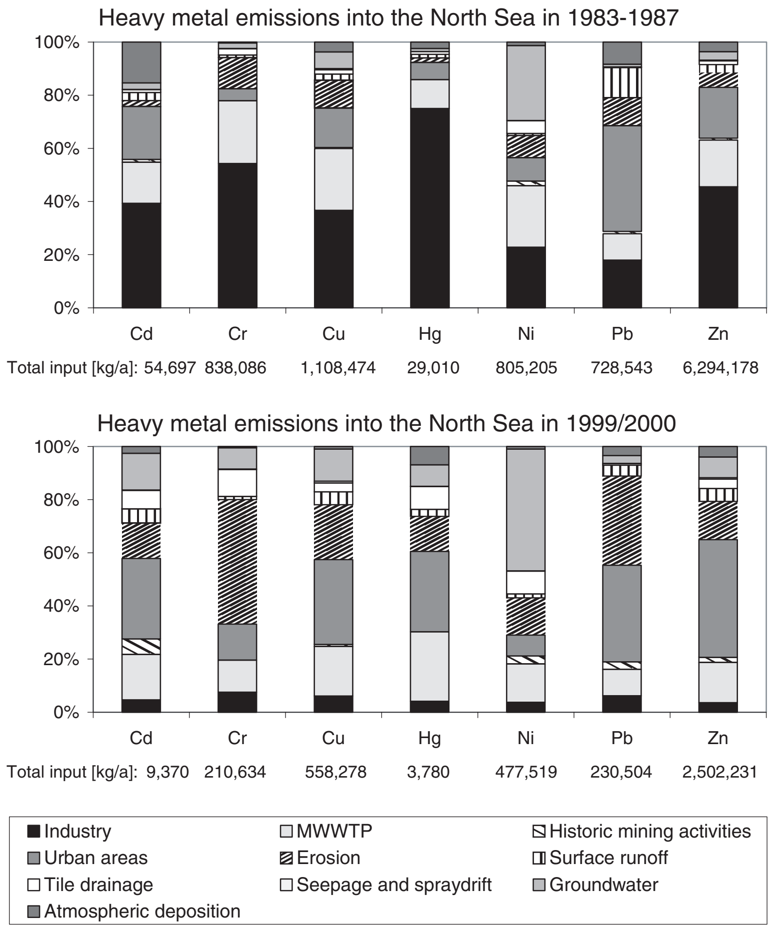

Figure 3 Heavy metal emissions into the North Sea [kg/a]

for Nickel emissions into surface waters the decrease of total Nickel input is only 41%. For the metals Cr, Cu, and Zn a reduction of 75%, 50% and 60%, respectively, was achieved mainly through decreasing the input via point sources.

A comparison of transported heavy metal loads for several monitoring stations of river basins of a size between 1000 and 50,000 km^2 and simulated loads (estimated heavy metal emission minus losses within the river system according to the retention functions given by Vink and Behrendt, 2002) is depicted in Figure 4.

The total variance of measured and estimated transported loads is lowest for Zn and Cu with 23.6 and 25.2% respectively. The metals Cd and Pb show a higher total variance of 40.6 and 42.6% respectively. The higher variance is correlated with increased uncertainties of heavy metal concentration measurements at the monitoring stations since many measurements of these heavy metals are below the quantification limit.

In general the variance from the 1:1 line increases with decreasing catchment size, because the specific conditions within small catchments could not be described exactly. Another reason for the inconstancies shown in Figure 4 are strong declines of heavy metal loads after the passage of reservoirs and lakes which are not included within the used retention model.

With regard to the large river basins the estimated transported heavy metal loads correspond well with the measured heavy metal loads.

The results shown allow the following conclusions.

- The MONERIS approach is an appropriate tool for estimating heavy metal emissions into river systems.
- The most important pathways of water pollution could be identified with an adequate precision for the large watersheds.
- Because of the limited availability of reasonable input data for both the emission and immission side it is currently not possible to reach a spatial resolution comparable to the nutrient analysis.

In order to improve the estimation of heavy metal emissions into river basins, further research should focus on the following:

- Better spatial regionalization especially of areas which show significant geogenous heavy metal contents as well as for urban areas.

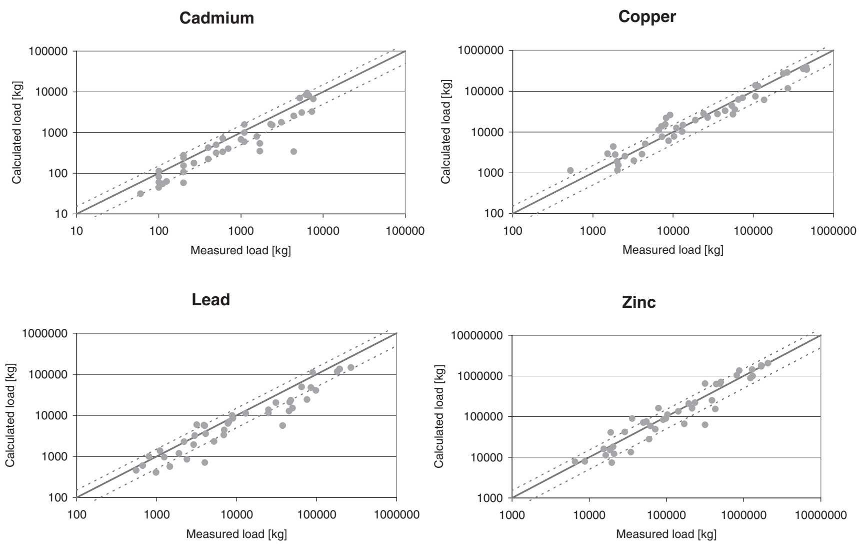

Figure 4 Relationship between measured and simulated heavy metal loads (estimated heavy metal emission minus losses according to retention processes) for several monitoring stations of German river basins

- The MONERIS approach of individual pathways being of importance to heavy metal emissions should be adapted to heavy metal specific transport processes.
- Methods of chemical heavy metal analyses should be improved especially for the metals Cd, Hg and Pb, to minimize the uncertainties in both measured loads at the monitoring stations and estimated heavy metal emissions.

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