Relative Significance of the Different Zinc Emissions for the Regional Zinc Concentrations in German Surface Waters

(FKZ 360 12 015)

A Survey within the Framework of the Risk Reduction Strategy for Zinc According to the Council Regulation No 793/93 on the Evaluation and Control of the Risks of Existing Substances and

the River Basin Management Plans According to the Water Framework Directive

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Abbreviations

a	share of fertilizer arriving directly in the surface water
A_{AL}	area of arable land
A_{DR}	drained area
A_{ROOF}	area of zinc covered roofs
A_{SW}	water surface area
A_{URBSS}	impervious urban area connected to separate sewer systems
C_{DR}	zinc concentration in drainage water
C_F	zinc concentration in fertilizer
C_{GW}	zinc concentration in groundwater
C_{MWWTP}	zinc concentration in the MWWTP effluent
C_{RO}	Zinc concentration in precipitation
CSO	combined sewer overflow
C_{TS}	zinc concentration in topsoil
D	area-specific deposition rate of zinc
E_D	zinc emission via atmospheric deposition
E_{DR}	zinc emission via tile drainage
E_{ERO}	zinc emission via erosion
E_F	load of zinc due to fertilizer wash off
E_{GW}	zinc emission via groundwater
E_{MWWTP}	zinc emission via municipal wastewater treatment plants
e_{MWWTP}	efficiency of wastewater treatment
ER	enrichment ratio
E_{RO}	zinc emission via surface runoff (from unpaved areas)
E_{ROOF}	zinc emission via wash off from roofs
E_{ship}	zinc emission via commercial shipping
E_{SP}	zinc emission via seepage and spraydrift
E_{SS}	emission via storm sewers
L_{ship}	zinc load emitted per ship
I_{MWWTP}	zinc input load of municipal wastewater treatment plants
LS_{URB}	zinc surface load from impervious urban areas
M_F	mass of fertilizer application
MWWTP	municipal wastewater treatment plant
n_{ship}	number of ships
PEC	predicted environmental concentration
PNEC	predicted no effect concentration
Q_{DR}	drainage flow
Q_{GW}	groundwater flow to surface water
Q_{MWWTP}	treated wastewater
Q_{RO}	surface runoff from unpaved areas
SED	sediment input into surface water
SS	storm sewers
wr_{Zink}	wash off rate for zinc

1 INTRODUCTION

Several studies that have focussed on zinc emissions into surface water and their impact on the environment come to different results regarding the amounts of zinc released into water bodies. Furthermore, the importance of emission sources is estimated differently.

The Federal Environment Agency of Germany commissioned the Institute for Water and River Basin Management (IWG) at the Universität Karlsruhe (TH) to examine the reason for the main differences in the results using three studies (Fuchs et al., 2002, Klasmeier et al., 2006 and the International Zinc Association IZA, 2006).

In the following the focus and aims of the three studies will be highlighted, the model approaches and the databases will be compared and the reasons for relevant deviations of the results will be illustrated. Finally the conclusions of the mentioned studies will be assessed.

2 FOCUSES AND AIMS OF THE STUDIES

The compared studies differ in their approach and the scale of the observed catchment (9,000 – 100,000 km²).

Fuchs et al. (2002) determined the overall load of heavy metals in surface water in Germany. The emitted loads from point and diffuse sources are quantified based on fifteen pathways (Figure 2). An adapted version of the model MONERIS[1] was used to calculate the emissions for about 300 river basins with an average catchment area of 1,000 km². There are several sources that serve as input data: databases from federal agencies, monitoring data of the counties, international reports, environmental reports of companies and industrial associations as well as comprehensive literature research on the zinc concentration in different runoff components.

The quality of the calculated loads is checked by the immission data of the available quality gauges. Therefore the substance-specific retention in each river had to be considered. The comparison between the calculated emissions reduced by retention and the loads in the rivers revealed an average deviation of 30% for zinc (Fuchs et al., 2002). The aim of the Fuchs et al. (2002) study was to estimate the average emission situation for all river basins in Germany.

For this survey the loads for the Ruhr basin were recalculated with the approach of Fuchs et al. (2002). To get a higher spatial resolution additional regional data was collected. Varying from Fuchs et al. (2002) the average catchment area is 100 km² (Figure 1).

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[1] Modelling Nutrient Emissions in River Systems (Behrendt et al., 1999)

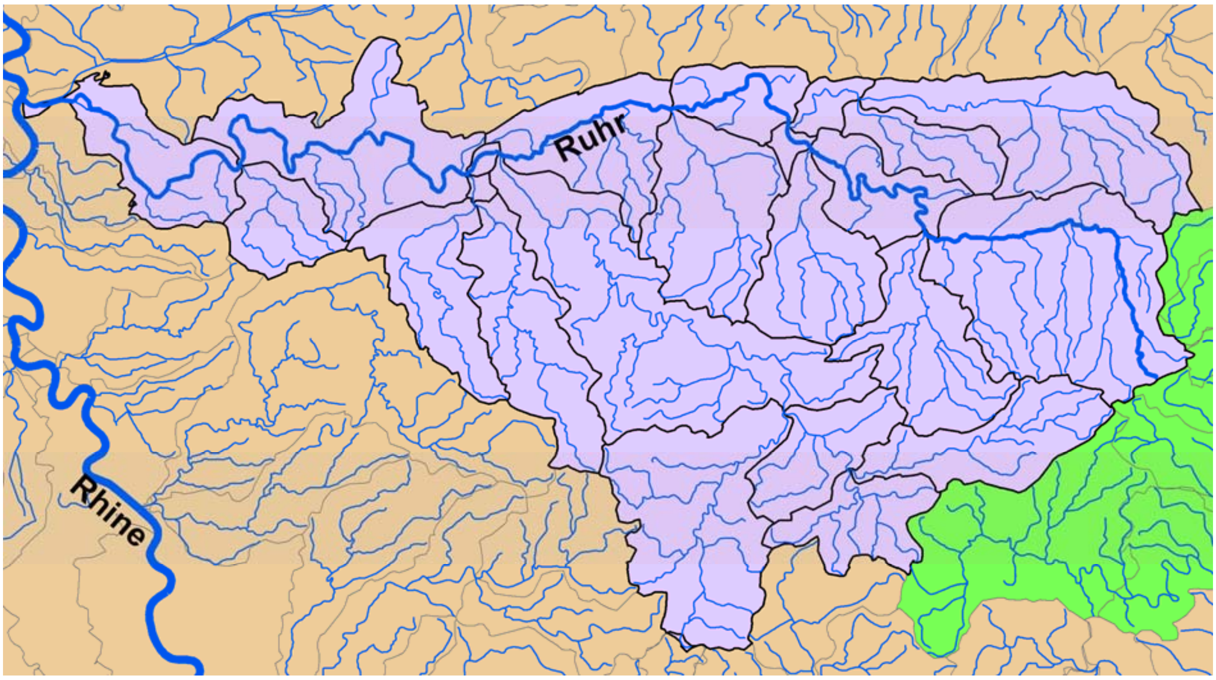

Figure 1: The basin of river Ruhr

The **Klasmeier et al. (2006)** study aims at mapping the zinc concentration gradients in rivers with the aid of the GREAT-ER model in the catchment area of the river. For this both a source-related analysis and quantification of zinc emissions are conducted. Considered point sources are industrial discharges, loads from mining activities as well as municipal wastewater treatment plants. Agriculture, geogenous loads and storm sewers are handled as diffuse sources. Like with Fuchs et al. (2002), retention is calculated for the rivers.

The IZA (2006) conducted a risk assessment of the bioavailable zinc concentrations in rivers for a so-called regional scenario on the basis of immission data. The authors did not calculate any loads in the rivers. In this study the regional concentrations were calculated using monitoring data. This is based on the data pool as given by the Dutch Organization for Applied Scientific Research TNO (2006). However, the data sets had been filtered intensely. After further processing, the 90 % percentile of the remaining data was used for the risk assessment.

The general descriptions of the different studies show that they aren’t easily comparable. Approaches based on emissions (Fuchs et al., 2002 und Klasmeier et al., 2006) cannot be set against a purely immission based approach with the aim of being a risk assessment (e.g. IZA, 2006). A direct comparison of the quantification approaches and input data as well as the achieved results can only be made between the studies by Fuchs et al. (2002) and Klasmeier et al. (2006) (chapters 3 and 4).

3 QUANTIFICATION APPROACHES FOR THE EMISSION ASSESSMENT BY FUCHS ET AL. (2002) AND KLASMEIER ET AL. (2006)

The current state of knowledge assumes that 15 pathways are relevant for the zinc emissions in surface water (Figure 2) which are elaborately described by Fuchs et al. (2002). This study will be taken as reference for this survey. The quantification approaches used here are to be compared to the emission assessment by Klasmeier et al. (2006) in the following.

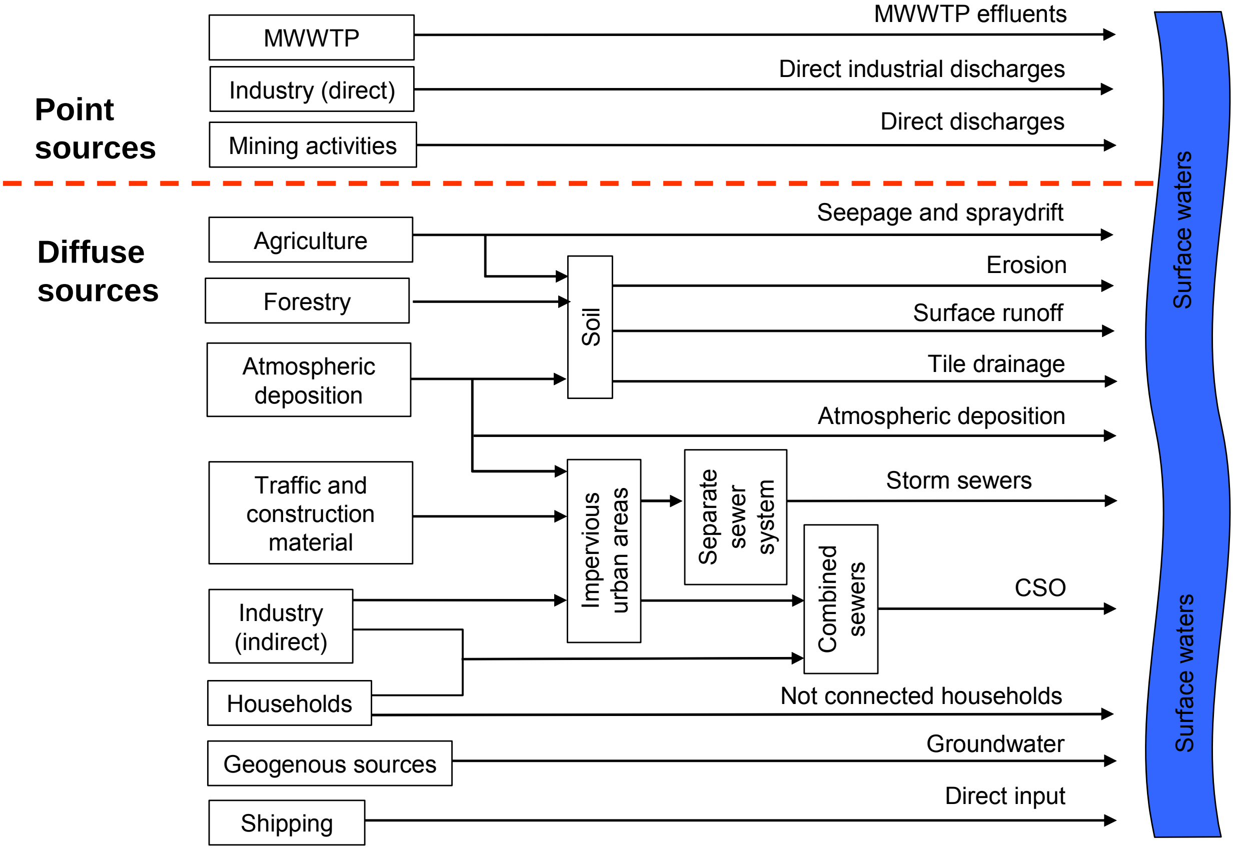

Figure 2: Sources and pathways of emissions into river basins

To keep track the fifteen pathways of this survey are classified into three blocks:

- Point-source pathways (chapter 3.1): effluents from municipal wastewater treatment plants, direct industrial discharges and mining activities,
- diffuse non-urban pathways (chapter 3.2.1): atmospheric deposition onto rivers, seepage and spraydrift, erosion, tile drainage, direct discharges from ships, runoff from unpaved areas, geogenous loads (groundwater),

- diffuse urban pathways (sewer systems, see chapter 3.2.2): storm sewers, combined sewer overflows (CSOs), households not connected to wastewater treatment plants[2] and not connected households[3].

3.1 Point-source pathways

Table 1 shows an overview of the quantification approaches of point-source pathways in both studies. To quantify the loads from **municipal wastewater treatment plants** Fuchs et al. (2002) use the effluent concentrations and the discharge of treated wastewater.

Klasmeier et al. (2006) detect the loads into the rivers from this pathway by taking the inhabitant-specific zinc loads, a specific pollutant load from surfaces (chapter 3.2.2) and zinc retention in wastewater treatment plants.

Table 1: Quantification approaches for point pathways

Pathway	Fuchs et al. (2002)	Klasmeier et al. (2006)
Municipal wastewater treatment plants	$E_{MWWTP} = C_{MWWTP} \cdot Q_{MWWTP}$	$E_{MWWTP} = I_{MWWTP} \cdot (1 - e_{MWWTP})$
Direct industrial discharges	Data from European Pollutant Emission Register	
Mining activities	Data from state environment agencies	

For the detection of **direct industrial discharges** Fuchs et al. (2002) as well as Klasmeier et al. (2006) rely on the discharge data from the emission registers (e.g. European Pollutant Emission Register EPER and the state environment agencies.).

Loads from **mining activities** are detected from data research (state environmental agencies) in both studies.

Due to estimations by Fuchs et al. (2002) the loads from mining activities are generally underestimated as there are only little data available in Germany. In a current project[4] attention is being drawn towards these sources.

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[2] households and areas that are connected to sewer systems but not to the MWWTP

[3] households and areas that are neither connected to a MWWTP nor to a sewer system

[4] Model-based Quantification and Internet-based Visualisation of Priority Emissions into River Basins in Germany. Project on the behalf of the German Federal Environmental Agency, FKZ 204 24 218, due to be finished by 12/2007. The currents status is available online at: http://www.umweltbundesamt.de/wasser/themen/stoffhousehold/Haushalt/schwermetalle-bergbau.htm

3.2 Diffuse pathways

3.2.1 Diffuse non-urban pathways

The quantification approaches for diffuse non-urban pathways are outlined in Table 2. Klasmeier et al. (2006) only considered the loads from runoff from unpaved areas and the groundwater.

Table 2: Quantification approaches for diffuse non-urban pathways

Pathway	Fuchs et al. (2002)	Klasmeier et al. (2006)
Atmospheric deposition	$E_D = A_{WS} \cdot D$	not considered
Seepage and spraydrift	$E_{SP} = M_F \cdot C_F \cdot a$	not considered
Erosion	$E_{ERO} = C_{TS} \cdot SED \cdot ER$	not considered
Tile drainage	$E_{DR} = Q_{DR} \cdot A_{DR} \cdot C_{DR}$	not considered
Shipping	$E_{ship} = n_{ship} \cdot L_{ship}$	not considered
Runoff from unpaved areas	$E_{RO} = Q_{RO} \cdot C_{RO} + E_F$	$E_{RO} = A_{AL} \cdot area\ spec. load$
Groundwater	$E_{GW} = Q_{GW} \cdot C_{GW}$	Concentration and discharge data on surface waters heavily polluted by geogenous sources

Fuchs et al. (2002) define the **atmospheric deposition,** which passes straight into the rivers, based on the measuring data of the German Federal Environment Agency.

The quantification of **seepage and spraydrift** is taken from the amount of fertiliser, the heavy metal content in the fertilisers as well as an estimated fraction which passes straight into surface water. In respect to zinc emissions into surface water this pathway is relatively meaningless in Germany and in the catchment area of the river Ruhr (Figure 4).

The **erosion** describes the particle-bound transport of pollutants into rivers. Loads from erosion are influenced by the amount of pollutant in the top soil, the sediment loads into the surface water and the accumulation factor (enrichment ratio).

Seepage water concentrations are used to quantify the loads via **tile drainage** into surface water.

Loads from **shipping** are calculated from the amount of traffic and an emission factor per ship. In respect to zinc emissions into surface water this pathway is meaningless in Germany and in the catchment area of the river Ruhr.

Fuchs et al. (2002) quantify the **surface runoff from unpaved areas** by the load in the rainwater runoff from all unpaved areas and completed by the heavy metal loads from the surface runoff of mineral fertilisers and manure from agriculturally used areas.

Klasmeier et al. (2006) only consider the surface runoff from agriculturally used areas. Otherwise used unpaved areas are not included in the calculation.

According to the approach by Fuchs et al. (2002) the loads from the **groundwater** are balanced by the zinc concentrations in sources of rivers and the base flow.

Klasmeier et al. (2006) estimate the emissions from the groundwater from the concentrations in highly geogenously loaded rivers and the discharge calculated with GREAT-ER.

3.2.2 Diffuse urban pathways (sewer systems)

For the emissions from urban areas the human influences are decisive. The emissions result mainly from traffic[5], corrosion of zinc-coated surfaces as well as atmospheric deposition on impervious urban areas. The discharge into the rivers takes the following pathways:

- storm sewers,
- combined sewer overflows (CSOs),
- sewerage systems that are not connected to the wastewater treatment plants, and
- households that are not connected (Figure 3 and Table 3).

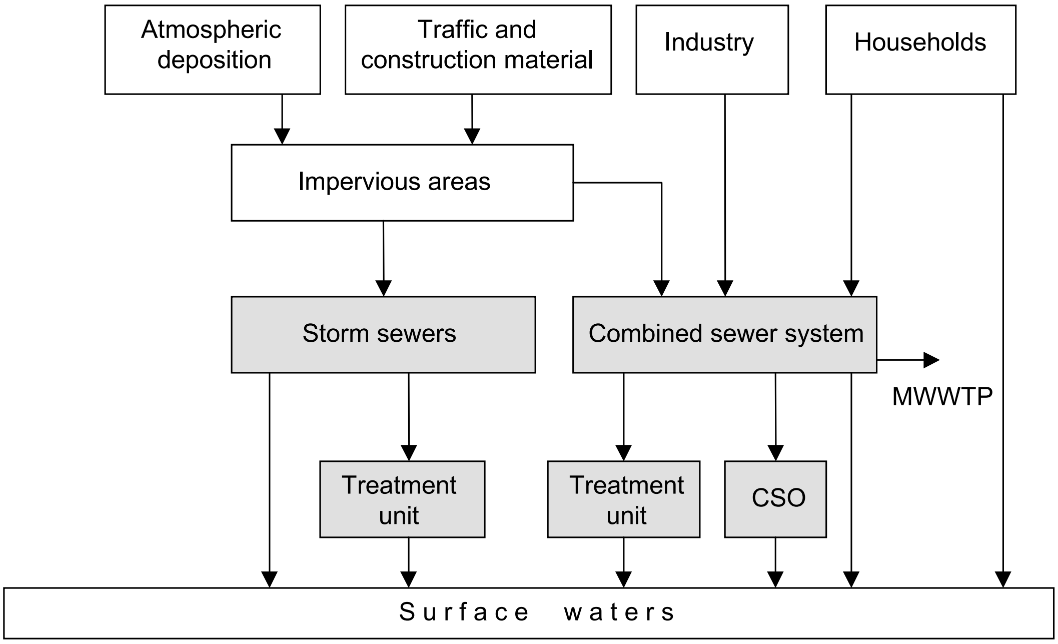

Figure 3: Sources and pathways of heavy metals from urban areas into surface waters (according to Stotz & Knoche, 1999 and Fuchs et al., 2002)

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[5] tyre, brake and road abrasions

To define the loads from **storm sewers** in separate sewer systems Fuchs et al. (2002) have calculated a specific surface load[6]. This emission load is at disposal for discharge on all impervious surfaces and completely mobilised over the years.

To define the loads that reach the rivers via storm sewers Klasmeier et al. (2006) chose a source-specific approach. They balanced the loads from roofs- and street runoff. The approach is explained in Table 3 and chapter 4.2.2.2.

Klasmeier et al. (2006) neglect the seepage and atmospheric deposition on roofs as well as on impervious areas. Loads from the corrosion of zinc products[7] aren't quantified either.

Table 3: Quantification approaches for sewer systems (diffuse urban sources)

Pathway	Fuchs et al. (2002)	Klasmeier et al. (2006)
Storm sewers	$E_{SS} = LS_{URB} \cdot A_{URBSS}$	**Load from zinc covered roofs** $E_{ROOF} = A_{ROOF} \cdot wr_{zinc}$ **Load from street runoff** Assumptions: Surface load = 2,700 g Zn/(ha·a) Spraydrift = ⅓ Run off = $^2/_3$, diverted into infiltration, direct discharge and storm sewers (65 %) Efficiency of storm water treatment 80 %
Combined sewer overflows (CSO)	**Surface load**: overflow rate according to Meißner (1991) and specific surface load plus **Wastewater load** discharged during overflow events according to Brombach & Wöhrle (1997)	not considered

If the capacity of a wastewater treatment plant is exhausted during a rainfall event then the combined sewer system discharges the untreatable storm sewage via CSOs straight into the rivers. CSO discharges consist of wastewater and the surface load (Table 3).

Klasmeier et al. (2006) do not balance the loads from CSOs.

Fuchs et al. (2002) consider the loads from sewer systems that are not connected to wastewater treatment plants and from households that are not connected to the sewer system. In North Rhine-Westphalia 97% of all households are connected to wastewater treatment plants (Federal Statistical Office / Statistisches Bundesamt, 2007). Locally, both pathways could be

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[6] an area-specific yearly pollutant load

[7] e. g. street furniture, scaffolding, rails

of importance but due to the high amount of connected households they are an exception. They are hardly relevant for North Rhine-Westphalia.

3.3 Summary of the differences in the quantification approaches

As shown in chapter 3.1 and 3.2, there are noticeable differences in the quantification approaches between Fuchs et al. (2002) and Klasmeier et al. (2006). In sum the following can be said for the pathways:

- **Municipal wastewater treatment plants**: Fuchs et al. (2002) calculate the loads based on the total treated sewage and effluent concentrations, whereas Klasmeier et al. (2006) first calculated the inflow load for each source and detected the released loads by using the purification efficiency of the wastewater treatment plants.
- **Diffuse non-urban pathways** such as erosion, tile drainage and atmospheric deposition are not considered in the Klasmeier et al. (2006) study.
- **Diffuse urban pathways:**
    - To calculate the loads from storm sewers Fuchs et al. (2002) assume a specific surface load, Klasmeier et al. (2006) balance the pollutant load of roofs and streets[8].
    - Klasmeier et al. (2006) do not balance loads from CSOs.

A comparison of the calculated loads into the river Ruhr and the importance of the different pathways will follow in chapter 4.

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[8] Neither the atmospheric deposition on non-zinced roofs nor the loads from zinced products other than roofs are included in the calculations.

4 COMPARISON OF THE INPUT DATA AND RESULTS OF FUCHS ET AL. (2002) AND KLASMEIER ET AL. (2006)

On the scale of large river basins in Germany Fuchs et al. (2002) calculated zinc emissions into surface water for the year 2000 to be almost 3,200 t.

The most important pathways seen from a federal point of view are the emissions from sewer systems with about 40% (Figure 4). Further important pathways are the loads from erosion (16 %) as well as municipal wastewater treatment plants (14 %). 8 % of the zinc emissions reach the rivers via the groundwater.

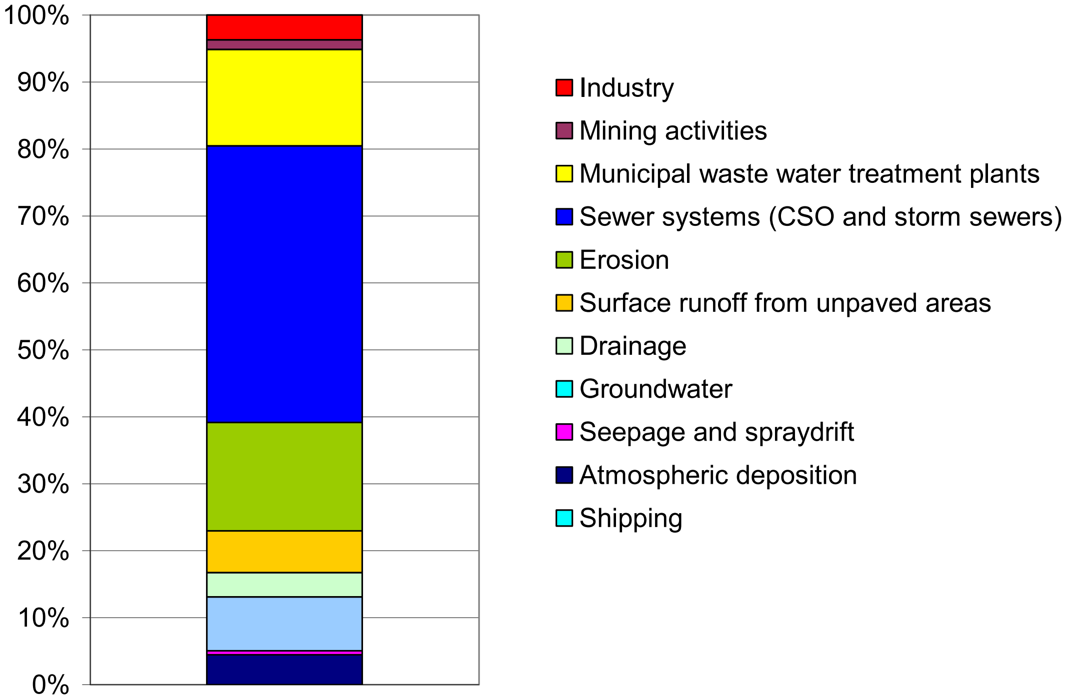


Figure 4: Portion of different pathways on total zinc emissions into river basins of Germany (Fuchs et al., 2002)

Due to regional conditions these numbers can vary. Especially in areas with high geogenous charges high zinc emissions can reach the surface water via the groundwater. This situation is amplified by mining activities. As an example for an area with typical mining activities and therefore with high geogenous background loads the Ruhr catchment area was explored.

As already mentioned in chapter 2, the surveyors recalculated the emissions into the Ruhr with taking the local conditions into consideration.

Apart from the two studies that will be compared the surveyors have included a further study which they see as relevant, namely the inventory report for the Water Framework Directive for the catchment area of the Ruhr (Raschke & Menzel, 2004).

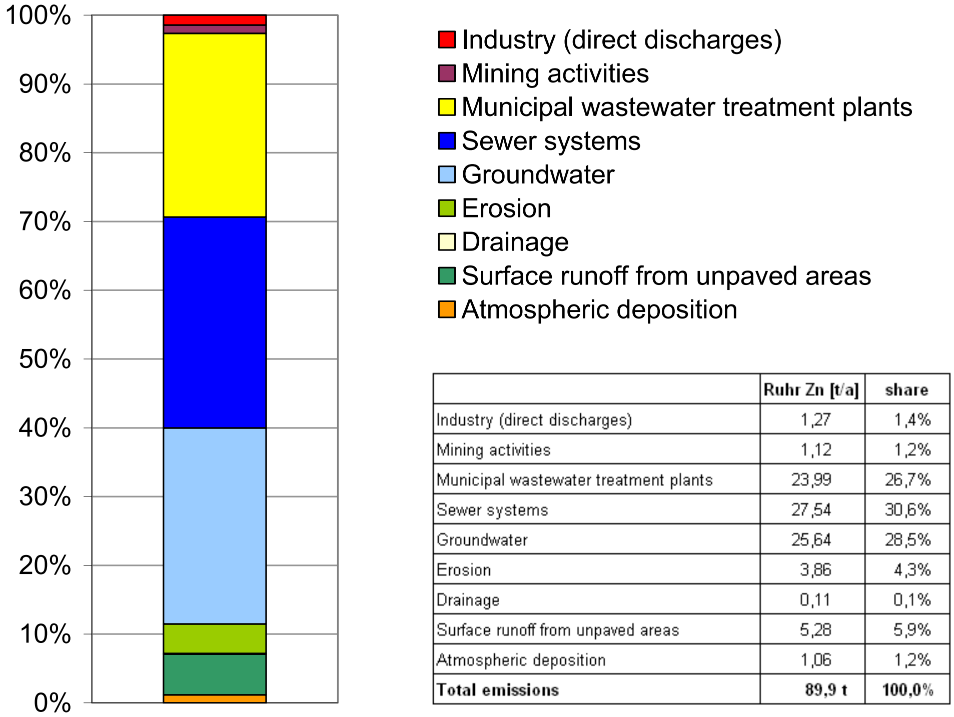
A comparative illustration of the loads from the research by the surveyors, Klasmeier et al. (2006) as well as Raschke & Menzel (2004) can be found in Table 4. This shows that the absolute loads in the individual studies vary a great deal as well as the relative meaning of the different pathways. The reasons for these large deviations will be explained in chapter 4.2.

Table 4: Pathway specific emissions into the river Ruhr according to different studies

	Own quantifications		**Klasmeier et al. (2006)**		**Raschke & Menzel (2004)**	
Pathways	**Zn [t/a]**	**Share of total load [%]**	**Zn [t/a]**	**Share of total load [%]**	**Zn [t/a]**	**Share of total load [%]**
Point sources						
MWWTP	24.0	26.7	6.2	16.1	>13.8	12.3
Industry (direct discharges)	1.3 1)	1.4	0.8	2.1	1.3	1.1
Mining activities	1.1 1)	1.2	2.8	7.3	1.1	1.0
Diffuse sources 2)						
Atmospheric deposition	1.1	1.2	n.c.	n.c.	n.c.	n.c.
Erosion	3.9	4.3	n.c.	n.c.	n.c.	n.c.
Tile drainage	0.1	0.1	n.c.	n.c.	n.c.	n.c.
Runoff	5.3	5.9	0.9	2.3	n.c.	n.c.
Groundwater	25.6	28.5	23.6	61.5	n.c.	n.c.
Sewer systems	27.5	30.6	4.1 3)	10.7 3)	96.5	85.6
Total emissions [t]	**89.9**	**100.0**	**38.5**	**100.0**	**> 112.6**	**100.0**

1) Taken from Raschke & Menzel (2004)
2) Emissions from seepage, spraydrift and shipping are insignificant and therefore not included.
3) Only emissions from storm sewers

Figure 5 shows the relative proportions of the pathways according to the recalculations for this survey and the absolute numbers of the loads by the calculations of the surveyors for the Ruhr.



	Ruhr Zn [t/a]	share
Industry (direct discharges)	1,27	1,4%
Mining activities	1,12	1,2%
Municipal wastewater treatment plants	23,99	26,7%
Sewer systems	27,54	30,6%
Groundwater	25,64	28,5%
Erosion	3,86	4,3%
Drainage	0,11	0,1%
Surface runoff from unpaved areas	5,28	5,9%
Atmospheric deposition	1,06	1,2%
Total emissions	**89,9 t**	**100,0%**

Figure 5: Zinc emissions into the Ruhr river basin and portion of different pathways (according to recent calculations based on Fuchs et al., 2002)

The surveyors calculate a load of 90 t of zinc per year into the Ruhr when using the Fuchs et al. (2002) method. The sewer systems (30.6 %) and the wastewater treatment plants (26.7 %) together form the main part. Furthermore, loads via the groundwater are identified as relevant (28.5 %). This distribution differs from the average situation in Germany, therefore reflecting the specific characteristics of the Ruhr catchment area. Statistics help to clarify the interrelations: the average population density in Germany can be safely set at 230 inhabitants per km², in the catchment area of the Ruhr however amounts to 512 inhabitants per km². This implies that the amount of MWWTP effluent and with that the relative importance of wastewater treatment plants must be higher. By contrast the retention volume in combined sewer system (28 m³/ha) is higher than the federal average (20.3 m³/ha), which leads to a relative reduction of loads from CSOs. But the conclusion from the federal point of view that urban areas contribute a large amount of the total load does not change, even if the specifics for the Ruhr catchment area are considered.

The sum of the emissions from the Ruhr according to Klasmeier et al. (2006) should be about 40 t/a, whereas geogenous loads from the groundwater have the largest share with approximately 62 %. Also emissions from wastewater treatment plants (16 %) and sewer systems (11 %) are of importance.

Raschke & Menzel (2004) estimated the municipal wastewater treatment plants and sewer systems to be responsible for a total load into the Ruhr of >113 t/a. By their estimations the sewer systems alone stand for 97 t/a of zinc emitted into the Ruhr. This yearly load seems to be exorbitantly high and not plausible. In comparison to the calculations of the surveyors, the overflow and discharge rate are set very high as well as the zinc concentrations in combined and storm sewers. A rough calculation shows the amount discharged from combined and separate sewers into the Ruhr to be about 241 Mio m³/a according to Raschke & Menzel (2004).

But if the yearly rainfall amount (1,100 mm) and an effective urban runoff area in the Ruhr catchment area of 238 km² is applied then this leads to a total rainfall runoff of only 183.5 million m³/a. With 70 % drained by combined sewer systems and an overflow rate of 40 %, it would mean that in sum (combined and separate sewer system) only 106.4 million m³ are discharged into the Ruhr. Even if this calculation is only a first-cut estimation and even if it wasn't possible to understand all of Raschke & Menzel's (2004) assumptions, it does show how high the amount of water was scheduled to be.

Raschke & Menzel (2004) assume that the concentrations concerning combined and storm sewer to be 387 or 430 µg/L resp. Own analyses of more recent measurements lead to concentrations of 218 µg/L in combined sewer systems and 294 µg/L in separate sewer systems.

4.1 Comparison of the calculated overall emissions with loads from immission measurements in the Ruhr

The loads emitted into rivers are not completely found in the liquid phase. In rivers the sediment acts as heavy metal sink. After deducting the retention in the individual rivers from the calculated emissions it should theoretically leave us with measured loads from the quality and discharge measurements.

The long-time discharge average at Duisburg[9] is set at 76.8 m³/s (Ruhrverband, 2004). The median of the zinc concentration for the years 2000 to 2004 according to the LAWA (2006) at the same measurement point shows 31 µg/L. Shortly before it flows into the Rhine there's a calculated yearly load of 75.1 t of zinc (Figure 6). As there are no continuous measurements for zinc, the load for the rivers from immission measurements is generally underestimated. In a flood event higher zinc loads are brought into the rivers and are mobilised from the sediments. Quality measurements are rare during these times. The yearly load should thereby be noted as ≥ 75 t.

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[9] Ruhr-kilometre 5.4

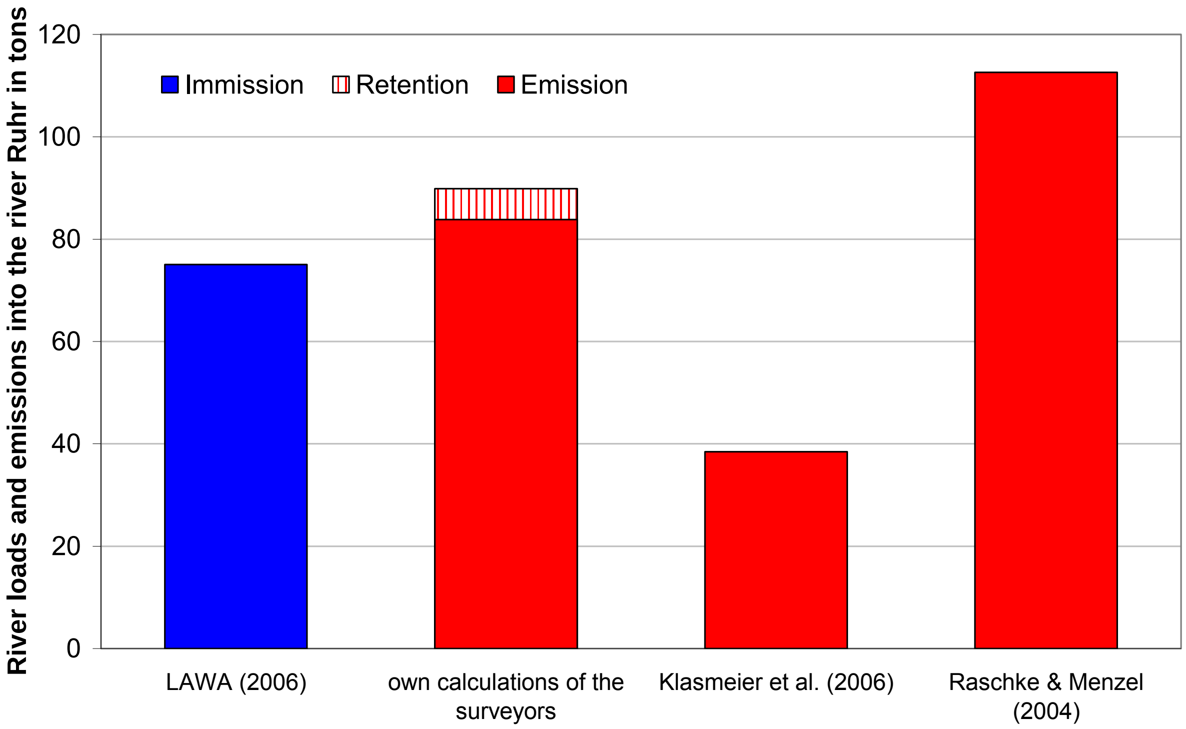

Figure 6: Comparison of river loads to emissions resulting from different quantification approaches

If the total emissions from Table 4 are compared to the immission loads into the Ruhr (Figure 4) then there are considerable differences between the different studies. Own load calculations should be reduced by the individual river retention before comparing emissions and immissions. Klasmeier et al. (2006) have already done this for the emission calculation. Raschke & Menzel (2004) do not calculate any retention as the authors only display a part of the loads. The emissions-immissions comparison shows the following deviations: the recalculation using the Fuchs et al. (2002) methods leads to an overestimation of 8.7 t/a or 12 %. The load assessment of Klasmeier et al. (2006) underestimates the river loads by 36.6 t/a or 49 %. Raschke & Menzel (2004) considerably overestimate the river's load by > 37.5 t/a or 50 %. But it must be said that the latter did not consider several pathways.

The above mentioned numbers show that the recalculation of the emissions according to Fuchs et al. (2002) describes the real zinc loads into the Ruhr relatively close to the actual river loads.

4.2 Comparison of the input data and the results

The following chapters 4.2.1 and 4.2.2 compare the pathway-specific input data and results of the own calculations with the approaches by Fuchs et al. (2002) and by Klasmeier et al. (2006) for the catchment area of the Ruhr.

For this comparison it must be pointed out that the study made by Klasmeier et al. (2006) is based on a source-specific analysis of the emission situation, whereas Fuchs et al. (2002)

combine the loads from different sources to pathways and balance them. Due to these different approaches some sources and pathways could overlap. Despite overlapping the loads can clearly be allocated to appropriate pathways. For a better idea of the connection between sources and pathways Figure 2 is helpful.

4.2.1 Pathways of point sources

4.2.1.1 Municipal wastewater treatment plants

The surveyors used the effluent concentrations and the yearly amount of treated wastewater to quantify the loads from municipal wastewater treatment plants. With an average effluent amount of 443 m³ in the catchment area of the Ruhr (Raschke & Menzel, 2004) with an average concentration of 54.16 µg/L for North Rhine-Westphalia (Fuchs et al., 2002) the calculated zinc emissions come up to 24 t/a.

In their approach Klasmeier et al. (2006) quantify the inflow loads to the wastewater treatment plants. The loads from households (in the combined and separate sewer system) are detected based on a load per inhabitant[10] and the population number[11]. The roof surfaces which are drained in the combined sewer system are considered via the corrosion of zinc surfaces and the loads from traffic via an area-specific pollutant load. The basic database is according to the specifications in chapter 4.2.2.2. Loads from indirect dischargers are not balanced.

Klasmeier et al. (2006) assume that the purification rate of wastewater treatment plants in terms of zinc is 84 %. They refer to the results of Hamel (2001). According to this the loads from wastewater treatment plants into surface water amount to 6.2 t/a (Table 4).

4.2.1.2 Direct industrial discharges

To list the balances of direct dischargers in the catchment area of the Ruhr the surveyors took the data of Raschke & Menzel (2004). This delivers an annual load of 1.3 t of zinc into the rivers.

Klasmeier et al. (2006) consider one discharger according to the European Pollutant Emission Register EPER and forty emitters according to the State Environment Agency of North Rhine-Westphalia (2004). This sums up to a yearly amount of 0.8 t zinc (Table 4).

4.2.1.3 Mining activities

The surveyors resort to the data on mining activities by Raschke & Menzel (2004). According to these the emissions from the coal-mine in Meggen are 1.1 t zinc for the year 2002.

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[10] 15.4 ± 2.2 g/(inh·a)

[11] According to Klasmeier et al. (2006) 2.3 million people live in the Ruhr area. Following Hüffmeyer (2007) the balances were made on the data of the State Environment Agency of North Rhine-Westphalia. Hence only 1.9 million people live in that area.

Klasmeier et al. (2006) consider two locations[12], whereas the authors estimate that the loads represent a minimum level. They specify an amount of 2.8 t zinc per year.

4.2.2 Diffuse pathways

4.2.2.1 Diffuse non-urban pathways

Although the Ruhr area is well industrialised the loads from atmospheric depositions to the rivers due to the relatively small river surfaces are negligible. Due to the low sediment discharge in the catchment area of the Ruhr the erosion does not play a large role either. Furthermore, the loads from tile drainage are negligible. Less than 10% of the loads in the catchment area of the Ruhr come from the above mentioned diffuse non-urban pathways (Table 4).

Klasmeier et al. (2006) do not balance the mentioned diffuse non-urban pathways.

Two non-urban diffuse pathways are left and of relevance for the zinc emissions into the Ruhr: surface runoff from unpaved areas and groundwater. To define the **surface runoff from unpaved areas** the surveyors have calculated the loads from the runoff[13] from all unpaved areas. For the agriculturally used areas the amount of washed-out mineral fertilisers and manure must be considered additionally. Surface runoff strongly depends on the regional conditions. For the Ruhr area yearly loads of 5.3 t zinc are calculated.

Klasmeier et al. (2006) only calculate the surface runoff of agriculturally used areas based on an average specific load of 7.32 g/(ha·a) according to Fuchs et al. (2002). The load from this pathway comes to 0.9 t zinc.

As can be taken from Table 4 the load via the groundwater represents a considerable pathway. According to statistics of the Ruhrverband (Ruhrverband, 2007) high concentrations have been measured in the upper reaches of the Ruhr (Neger, Elpe, Valme and Nierbach) as well as in several tributaries of the river Lenne (Hundem, Olpe and Silberbach). Klasmeier et al. (2006) act on the assumption that these rivers have no relevant anthropogenic effect and that the observed concentrations are solely based on geogenous sources. From the concentrations in these rivers and the corresponding discharge they calculate the geogenous load into the Ruhr to be 24 t/a zinc.

The surveyors use the method by Fuchs et al. (2002) based on zinc concentrations in spring water (Ruhrverband 2005) and the base flow to quantify the groundwater loads. The Ruhrverband also supplied spring concentrations for very small catchment areas which were not considered due to the chosen area classification (in average 100 km², see Figure 1). Area-weighted average concentrations were calculated for the 100 km² sized basins enabling

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[12] The coal mines ‚Friedlicher Nachbar' and ‚Meggen'

[13] The rainfall with a average concentration of 13.5 µg/L (UBA, 2001) was considered according to Fuchs et al. (2002).

the concentrations of the smaller areas to be incorporated into the calculations (see Annex 4). The above mentioned heavily geogenously loaded tributaries of the river Ruhr (Neger, Elpe, Valme, Palme and Nierbach) have yet proved to have no high geogenous charge at their source (Ruhrverband, 2005). These only occur shortly before they join the Ruhr. Concentrations of up to 720 µg/l (Valme) were registered (Ruhrverband, 2007). To be able to consider these loads as well, the Klasmeier et al. (2006) procedure is followed: For these heavily geogenously polluted rivers a load is estimated from the concentration and discharge in those rivers. The surveyors calculate a zinc emission of approximately 26 t/a from geogenous sources.

4.2.2.2 Diffuse urban pathways (sewer systems)

Fuchs et al. (2002) used a specific surface load for the pathway **storm sewers**. This was found from average concentrations and estimated runoffs into storm sewers in a widely applied study (Brombach & Fuchs, 2002) and is 1,985 g/(ha·a) for zinc. The different loads from impervious surfaces are not considered any closer and enter the calculation as a sum. Fuchs et al. (2002) further assume that due to the fine particulate character of the pollutant load from urban areas there will be no significant retention by sedimentation in storm water treatment.

Klasmeier et al. (2006) calculate the loads from impervious areas specifically for each source separately. In doing so the atmospheric deposition on non-zinced roofs as on other impervious areas is ignored.

According to the specifications of Klasmeier et al. (2006) 30 % of the surfaces in the catchment area of the Ruhr are drained by the separate sewer system. Their loads from roofs consider the corrosion of zinc-covered roofs as a specific load of 3 g/(m²·a) according to Hillenbrand et al. (2005). As the zinc from corroded roofs mainly exists as solute it is expected that there is no retention in the storm water treatment.

When acquiring the loads of streets the authors revert to a specific load of 2,700 g Zn/(ha·a) from Stotz & Knoche (1999). It is assumed that one third of this contaminant load is blown away and two thirds are collected in the street runoff. The street runoff can thereafter either seep away[14] or can be discharged into the surface water or into the sewer system[15]. (Table 3). According to Klasmeier (2007) 80 % of the zinc used in tyres and brakes exists permanently as particles and therefore do not solubilise. This is why Klasmeier et al. (2006) assume that the particulate portion of the contaminant load of streets is retained anywhere in the sewer system.

The average annual overflow duration of combined sewer systems is 230 h/a according to Brombach & Wöhrle (1997). Thereby about 3 % of the household and commercial wastewa-

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[14] on roads outside of inhabited areas up to 80%

[15] 65% of the runoff from roads in inhabited areas is discharged into the sewer system.

ter is lead into the surface water without being treated. The loads from stormwater discharge are added, too. The calculated overflow rate of the the combined sewer system in North Rhine-Westphalia is 40 % according to Meißner (1991).

The surveyors calculated the zinc loads from diffuse urban pathways to be 27.5 t. For diffuse urban pathways Klasmeier et al. (2006) only consider loads from storm sewers and defined the emissions as being 4.1 t of zinc (Table 4).

An assessment of the quantification approaches and results from Klasmeier et al. (2006) will be given in chapter 6.1.

5 PRESENTATION OF THE IZA METHOD (2006)

In this study regional concentrations are calculated based on monitoring data in rivers to assess the risk of bioavailable zinc fractions.

For this the same data pool is used as the Netherlands Organisation for Applied Scientific Research TNO (2006). The approach to determine the regional concentrations contains the following steps:

1. The original TNO-data is heavily filtered:
   - **a.** Only data from 1995 onwards is used.
   - **b.** If the value is noted as „below detection limit“ then they are only considered if the detection limit is smaller than the concentration that has no effect on the environment (PNEC[16]). Data noted as below detection limit is accepted as half of the detection limit for the calculations.
   - **c.** If there are values on the concentration of dissolved zinc then these are favoured.[17]
2. Elimination of data that
   - **a.** does not reflect the current emissions (e.g. measuring points in areas with historic mining),
   - **b.** is influenced by point sources of industrial discharges,
   - **c.** is from areas with naturally high background concentrations.
3. Eliminating the data according to the above criteria leaves a smaller amount of data left[18]. From these the 90 % percentile is calculated. This concentration is called „predicted environmental concentration“ (PEC [19]). It was found that the remaining concentrations for some of the river basins were 1.7 times lower after eliminating the historically influenced measurement points as those from the original risk assessment data pool of the TNO (IZA 2006).
4. The remaining data is yet again reduced by the natural background concentration (3 – 12 µg/L).
5. To calculate the dissolved zinc the remaining concentration is reduced by the factor 2.7 if there’s only a value given for the total zinc concentration.

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[16] Predicted No Effect Concentration PNEC (for the total amount of zinc: 25 µg/L)

[17] Otherwise the total zinc concentration would be converted with a fixed value for the ratio of dissolved to particulate zinc to calculate the dissolved zinc concentrations. (no. 5)

[18] About one quarter of the approx. 120 measurement points was filtered out of the original database.

[19] Predicted Environmental Concentration PEC

6. In addition the bioavailable concentration is corrected according to the approach of the TNO (2006). This reduces the concentration further (by about the factor 1.25 to 2.5).
7. Finally, the ratio between the bioavailable concentration and the concentration that has no predicted effect on the environment (PNEC) is calculated[20]. If the ratio is smaller than one then the IZA (2006) assumes that the use of products containing zinc and the resulting diffuse emission pose no risk to the environment.

All that is left after these steps is the amount of dissolved zinc concentrations in rivers which is generated by loads from urban areas, agriculture and direct atmospheric deposition on river surfaces. These are mainly discharges from municipal wastewater treatment plants and diffuse urban pathways (sewer systems) as the emission calculations for Germany show (Figure 4).

An estimation of the load for the Rhine can be taken to find out how far the filtering of databases leads to different conclusions than from the immission situation and emissions quantification by Fuchs et al. (2002). To be able to compare this estimation with the own load calculations and the loads observed by the LAWA resp., the load is not calculated by the 90% percentile but by the 50% percentile. Based on the original data (www.umweltbundesamt.de/hid/index.htm) the 50% percentile was looked up and verified for the outlet gauge (Kleve-Bimmen).

If filtering criteria 1 and 2 are considered the arithmetic average of the median concentration for the total amount of zinc is 14.72 µg/L. With an average discharge of 2,923 m³/s for the year 2001 (Deutsche Kommission zur Reinhaltung des Rheins, 2007) this results in a yearly load of almost 1,400 t for the gauge at Kleve-Bimmen. This calculated load which results from urban areas and agriculture according to the filtering criteria of the IZA (2006) would have to be compared to the calculated load[21] of about 1,890 t at the gauge at Kleve-Bimmen. This comparison shows that the urban areas and the agricultural use of the catchment areas would cause over 70% of the load into the Rhine in a regional scenario proceeded like the IZA.

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[20] According to the TNO (2006) the following point is critical: A PNEC value of 7.8 µg/L is used for low as well as for relatively high natural background concentrations. If e.g. low background concentrations are doubled by the additional concentrations then the impact is different from when the same additional concentration is added to high background concentrations (which is now relatively less significant). This seems to be a conceptual uncertainness of this approach but „it is very hard to make any comments on the dimension of the uncertainness.“ (TNO, 2006).

[21] Measured average zinc concentration at the Kleve-Bimmen gauge = 20.5 µg/l, measured average drainage for the year 2001 = 2,923 m^3/s

6 ASSESSMENT OF THE RESULTS BY KLASMEIER ET AL. (2006) AND THE IZA (2006)

In the following the results by Klasmeier et al. (2006) and the IZA (2006) will be assessed.

6.1 Klasmeier et al. (2006)

In the Klasmeier et al. (2006) study the loads into the rivers are balanced specifically for each source. In the point of view of the surveyors the following points lead to the deviations as mentioned in 4:

1. **Municipal wastewater treatment plants**
   - **a.** Efficiency: enquiries of the surveyors say Hamel (2001) states the average efficiency to be 63 % with a maximum of 84 %. Why the maximum efficiency is included in the balancing could not be clarified in a discussion with the authors Klasmeier and Hüffmeyer. Fuchs et al. (2002) have stated an efficiency of 73% for wastewater treatment plants with a mechanical and activated sludge treatment. In the Ruhr water quality report 2003 (Ruhrverband, 2003) retention rates of 64 and 72 % resp. are mentioned.
   - **b.** It can generally be said that the approach to balance the emissions from wastewater treatment plants via input loads and a purification rate of the effluent (as e.g. used by Klasmeier et al., 2006) shows a large amount of uncertainties regarding the input data. Especially the loads from indirect dischargers cannot be estimated correctly as the metal loads strongly depend on the local situation and these data are usually not available. Therefore, Klasmeier et al. (2006) cannot consider this load source.

     Fuchs et al. (2002) quantify the discharge loads of wastewater treatment plants based on monitoring data (effluent volume and concentration). This approach reduces the number of assumptions noticeably and the overall emissions of wastewater treatment plants are included.
2. **Sewer systems**
   - **a.** Klasmeier et al. (2006) do not consider any loads from deposition on non-zinced roofs an other impervious areas. From the point of view of the surveyors this parameter could provide a substantial load in the industrialised Ruhr area. The deposition rates for zinc in the urban areas in some parts of North Rhine-Westphalia were above an average of 4.000 g/(ha·a) in 2005 (LANUV, 2007). Due to calculations by Hillenbrand et al. (2005) the emissions from the corroded zinc-plated products represent about one fifth of the overflow load. These, too, are not considered by Klasmeier et al. (2006).
   - **b.** When balancing the emissions from sewer systems into rivers, Klasmeier et al. (2006) do not consider the loads of CSOs. They justify this by saying that the impact on the

concentrations in rivers is only temporary. This is no doubt true but the CSOs significantly contribute to the overall load in rivers and can therefore not be left out in the opinion of the surveyors.

3. **Diffuse non-urban pathways**

   a. Klasmeier et al. (2006) only consider agriculturally used areas for surface runoff and therefore only calculate a load proportion of 2.3 %. But when balancing the surface runoff all unpaved areas have to be considered.

   b. Further non-urban diffuse pathways are not taken into consideration by Klasmeier et al. (2006). But according to the estimations on a national scale they cause about 25 % of the total load (Figure 7). Even if they are negligible in the Ruhr area (see 4.2.2.1), this cannot be extended to other catchment areas.

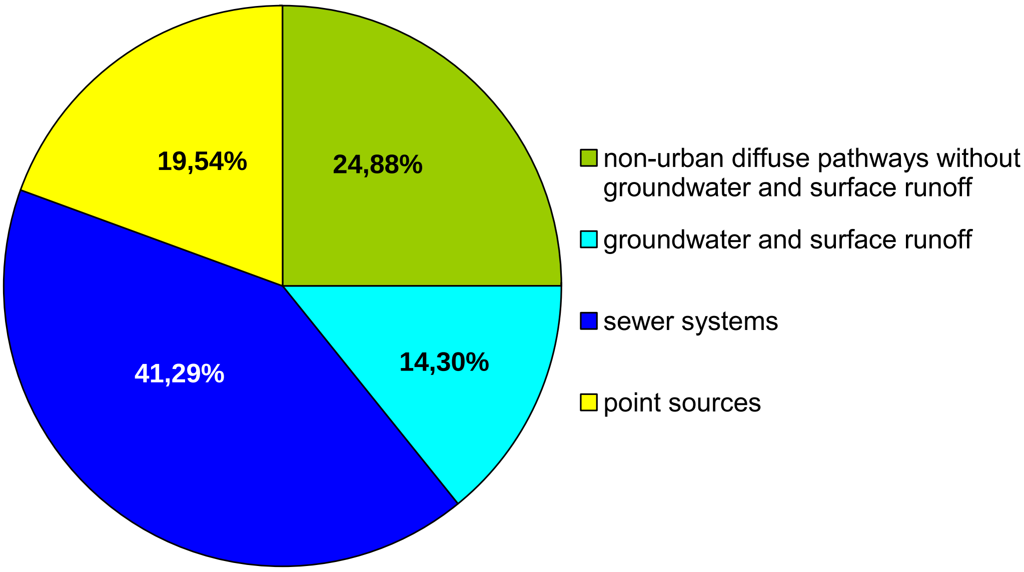

Figure 7: Importance of aggregated emissions for German water bodies

(according to Fuchs et al., 2002)

In sum it can be noted that a main conclusion of the Klasmeier et al. (2006) study that the zinc load in the Ruhr is largely based on geogenous sources, cannot be retraced. Without a doubt the geogenously caused loads play an important role in this area. But when all pathways are completely exposed it shows that despite of the special conditions in the Ruhr area the discharge via municipal wastewater treatment plants and the sewers systems respectively have the same importance as the discharge from the groundwater.

From the point of view of the surveyors the results from the Ruhr are not allowed to be generalised. A quantification of the emission load for the catchment area of the Neckar which was done using the same approach and regional input data back this conclusion (Figure 8).

The Neckar catchment area shows comparable usage but generally different geogenous boundary conditions (no extensive orebodies, no mentionable mining activities). The main pressures here, like the national average, are a result of urban areas and the connected activities (traffic, production, consumption).

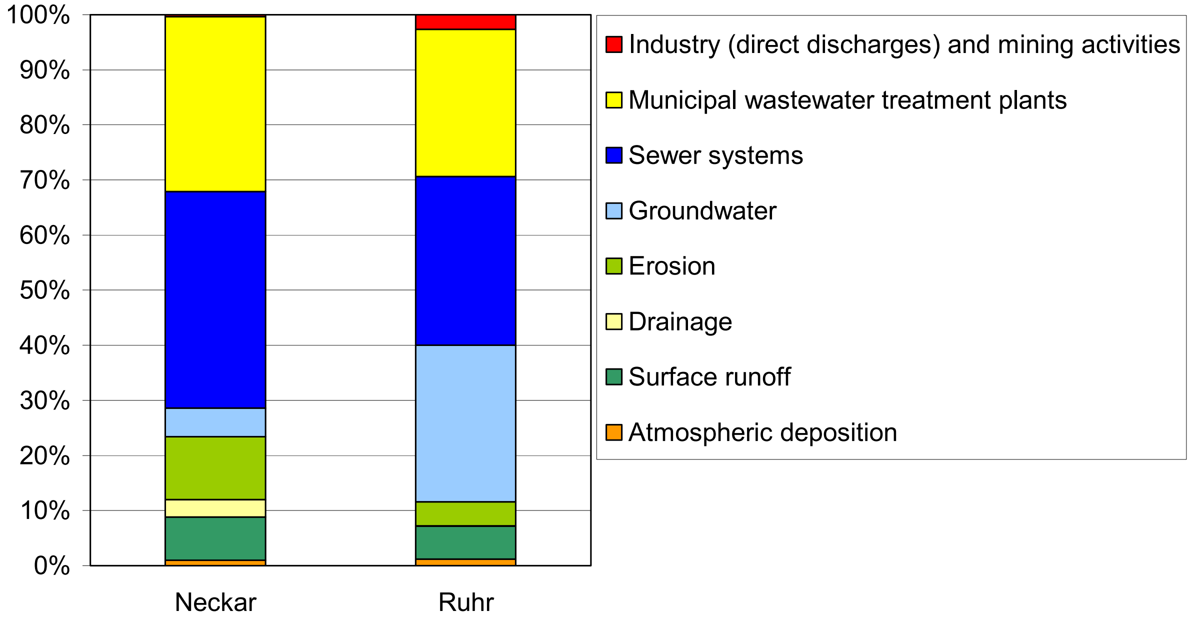

Figure 8: Significance of zinc emissions within the catchment of Neckar and Ruhr

It finally needs to be said that when approached in a professional way the question, whether a single pathway dominates the overall load or not, is directly and exclusively connected to the scale of analysis (local or regional).

6.2 IZA (2006)

According to the TNO (2006) the latest technical guidelines for risk assessment by the EU commission (EC, 2003) do not include any detailed information on how to handle essential elements which are usually found in a natural environment. This is why the IZA (2006) adopts the „Added Risk Approach“of the TNO (2006). For the risk assessment this only uses the concentration which is found in waterbodies in addition to the natural concentration. This concentration is called “added concentration”. This way only anthropogenic emissions are taken into account for the risk assessment. A possible toxic effect due to the natural background concentrations is ignored (TNO, 2006).

In general this approach can be followed. But it must be questioned whether the method is reasonable, especially for persistent emissions which don’t reach dangerous levels at the discharge point when emitted nowadays but will accumulate in a long-term perspective and further away from the discharge point.

Connected to this the following approaches to the work should be questioned:

1. The share of higher natural background concentrations is excluded even though they no doubt contribute to a regional risk.

2. Point sources don’t have any influence on regional scenarios – even if they contribute a regional risk considering the above mentioned environmental relevance of heavy metals.
3. The risk assessment only refers to the bioavailable dissolved form of the appropriate pollutant. It is correct that primarily the bioavailable dissolved form would have serious consequences. But from the point of view of the surveyors is not clear, especially for zinc, when and for how long zinc rests in a particulate phase. Changing redox conditions in the sedimentation zones of the rivers can bring along massive resolution. Furthermore, flood events go along with a massive sediment erosion and consequently a resuspension of the accumulated sediments.

From the point of view of the surveyors it is not clear which advantage can be taken out of the definition of regional scenarios if the above boundary conditions apply.

A decisive part of the work of the IZA (2006) is dedicated to making sure the input data is of a good quality. Apart from the exclusion of gauges influenced by geogenous and point sources there are more conventions to be considered:

1. The detection limit should be halved for further calculations if certain limits should not be exceeded, here being 0.025 mg/L (PNEC). This approach seems to be appropriate and is used in similar cases of balancing.
2. Use of the 90 % percentile (90P) for risk assessment. This regulation is appropriate and connected to a confident valuation, too.
3. Averaging the 90P values along a river or for a river basin respectively as input value for further calculations on risk assessment. Two problems emerge from this approach:
    a. The surveyors were not able to comprehend the way the averages were calculated, even though the original data was given. This approach was barely transparent.
    b. It must be asked whether the arithmetic mean of all leftover concentrations can express the exposure of a region / a river. A calculation for the Rhine basin could clarify this:

       At the quality gauge in Kleve-Bimmen (last gauge on the German side) an average river concentration of 20.5 µg/L as median is calculated for 2001. According to the surveyors this concentration at the outlet of the area represents all input, transport and retention processes in the river system.

       The IZA (2006) approach reveals two different concentration values: the averaging of all medians of Rhine gauges would lead to a concentration of 7.94 µg/L. In contrast, the average of all medians from quality gauges in the Rhine catchment is 12.7 µg/L. An analogue effect occurs for the 90P values and from the point of view of the surveyors leads to a blatant misinterpretation. Calculating an arithmetic mean of all quality data is therefore not seen as appropriate by the surveyors. However, if this approach is chosen it would be essential to assess the individual concentrations by the discharge at the gauges. Currently, the zinc concentration of the river Rotach at the gauge at Friedrichshafen (catchment area: 130 km²) is included in the calculation of the mean with the same importance as the mean concentration of the Rhine (e.g. last monitoring gauge) with a considerably larger catchment area (190,000 km²).

As a basis for the definition of regions that are based on the regional scenarios the IZA (2006) is geared to the river basin areas of the Water Framework Directive. The approach chosen by the IZA (2006) leads to relatively small river basin areas such as the river basin districts Maas (on the German side: 4,000 km²) or Ems (on the German side: 14,000 km²) representing a region as well as the river basin districts Rhine or Elbe. The consideration of all filtering criteria for a regional scenario within a large river basin leads to the fact that relatively large area units (e.g. the Ruhr with 4,500 km² or the Mulde with 7,400 km²) are not taken into consideration. To be able to compare particular river basins it could be thought of defining a minimum and maximum size of areas which are taken into account for the assessment of risks to the environment.

Finally, it is noted that according to the surveyors the IZA (2006) study does not lead to an improvement of the risk assessment for zinc emissions. Regardless of this study it seems doubtful whether a general risk assessment like the one presented is of any help or even possible when based on such data and findings.

7 SUMMARY AND CONCLUSIONS

In this survey three studies were examined that deal with zinc pollution into surface waters or their impact on waterbodies.

The differences in the quantification methods and input data obviously deliver different results. These three studies can't easily be compared. The survey by Fuchs et al. (2002) is purely based on the emissions with the aim to estimate the total amount of pollutant discharge into river systems.

In contrast Klasmeier et al. (2006) focuses on the spatially mapping of waterbody concentrations. In addition the authors estimate the emissions into the waterbodies.

The risk assessment presented by the IZA (2006) is exclusively based on the analysis and assessment of bioavailable zinc concentrations in rivers and does not include any estimations on emissions.

Apart from the aims the compared studies also differ in the size of the research area: Klasmeier et al. (2006) analysed the connections between the concentration of waterbodies and the emissions for the catchment area of the river Ruhr. Fuchs et al. (2002) reported on the zinc emissions for the large river basins in Germany. The estimations of the IZA (2006) are based on the concentrations of zinc in watercourses for some European states.

Due to the above mentioned reasons it was only possible to compare the approaches of Fuchs et al. (2002) and Klasmeier et al. (2006). For the direct comparison the emissions for the rivers Ruhr and Neckar are recalculated with the method of Fuchs et al. (2002) considering the local circumstances. Before this, a meeting was held with the authors of the Klasmeier et al. (2006) study in January 2007 to clarify questions.

Klasmeier et al. (2006) come to the conclusion that the geogenic emissions into the river Ruhr contribute 62 % of the 40 t/a overall emissions and with that represent the most significant source. They quantified the load at 24 t/a zinc from this source. With regard to geogenic emissions the surveyors come to a similar result of 26 t/a zinc for the river Ruhr (see Table 4). However, the surveyors determined an overall emission of 90 t/a which lies in the dimension of the load transported in the river Ruhr (Figure 6) thus making the geogenic emissions only 29 % of the overall discharge. According to the calculations of the surveyors the anthropogenic emissions of the urban areas (point sources and sewer systems) were identified as main contributors with a share of 59 % (Figure 5). The comparison of pathways with those of the Klasmeier et al. (2006) study has shown that Klasmeier et al. (2006) did not consider important sources like combined sewer overflows, indirect discharges of industry and atmospheric deposition on impervious surfaces. Furthermore they assume very high grades of zinc elimination in municipal wastewater treatment plants and urban runoff treatment facilities. Due to the "underestimation" of these sources the relative meaning of the geogenic emissions rises considerably in the Klasmeier et al. (2006) study.

A direct comparison of Fuchs et al. (2002) and IZA (2006) is not possible as the latter is a purely immission-based work. Nevertheless, the river loads at the water gauge Kleve-Bimmen were able to be compared based on the medians of the observed concentration, considering all filter criteria for determining a regional scenario according to the IZA (2006) and the average annual discharge measured at Kleve-Bimmen. This calculation shows that the river load after filtering the data makes up about 70 % of the medium overall load at the water gauge Kleve-Bimmen. Following the approach of the IZA this would be almost exclusively the contributions from urban areas and agriculturally used areas.

It should be pointed out that for the risk assessment for the 'regional scenario' the IZA (2006) approach excludes what they call local and geogenic loads such as direct industrial discharges, high geogenic background levels or abandoned mines. It's especially in the case of zinc that the surveyors think that risk assessment as well as appropriate mitigation measures should always be made with the consideration of overall loads and overall concentrations respectively. Determining 'regions' with a risk assessment based on the arithmetic mean of the 90P-values also does not seem to yield suitable results. The extreme differences in the size of the individual regions as well as the calculation of the mean do seem critical.

In conclusion, a critical look at the studies as well as the own calculations show that the main statement made towards the meaning of urban sources for zinc emissions generally does not have to be changed. Even in the Ruhr area where the catchment is partly characterized by high geogenic background concentrations and mining activities the urban areas still have a share of 57 % of the total emissions.

The catchment area of the river Neckar, an area without high geogenic charge but intensive land use, has its share of 71 % from urban sources and according to the IZA (2006) approach the Rhine catchment area would have a load share of approx. 45 %[22] resulting from urban sources.

The main causes for other estimations and conclusions are that:

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[22] Emissions from agriculturally used areas are alleged to be responsible for 25 %. According Fuchs et al. (2002) the urban areas account for 58 % of emissions into the river Rhine.

- Klasmeier et al. (2006) did not consider important emission sources (combined sewer overflows, indirect discharges of industry, atmospheric deposition on urban areas as well as corrosion of diverse zinc coated products). This alone justifies the high share of groundwater emissions into the river systems (Table 4).
- The use of filtering criteria of the IZA considerably reduces the database of the original data pool of the TNO (2006). As a consequence of this some regions within large river basins are not considered for regional scenarios.
- The calculation of mean values using all data within a river basin compared to the outlet gauge of the main watercourse systematically leads towards lower water body concentrations. Especially if values below detection limit are included. From the point of view of the surveyors the concentration at the outlet gauge of a region reflects all upstream emission and retention processes.
- The risk assessment is only made by analysing the dissolved / bioavailable form of zinc. But environmental problems with heavy metals arise rather from the accumulation in different environmental compartments than from acute toxicity.

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9 ANNEX

Annex 1: Parameters used for the emission calculation in the basin of Ruhr and Neckar

Input data	Ruhr	Neckar
Atmospheric deposition on water surface		
Specific zinc deposition in g/(ha·a)	230	230
Area of water surface in km²	46	20
Municipal wastewater treatment plants		
Treated wastewater in million m³/a	443	836
Effluent zinc concentration in µg/L	54.16	52.08
Erosion		
Sediment input into surface waters in t/a	9,652	56,075
Zinc concentration in topsoil in mg/kg	67.8	60
Runoff from unpaved areas		
Zinc concentration in precipitation in µg/L	13.5	13.5
Surface runoff in m³/a	12.4	25.1
Diffuse emissions from urban areas		
Inhabitant related zinc emissions in g/(cap·a)	21.9	21.9
Population connected to sewer and MWWTP in %	97	99
Portion of combined sewer systems in %	66	84
Portion of separate sewer systems in %	34	16
Specific storage volume in the combined sewer systems in m³/ha	28	28.3
Specific surface load of in g/(ha·a)	1,985	1,985
Overflow rate in combined sewer systems in %	41	40

Annex 2: Land use and population in the catchment area of Ruhr and Neckar

Parameter	Ruhr		Neckar	
	absolute	relative	absolute	relative
Total catchment area in km^2	4,489.87		13,925.93	
Urban area	595,67	13.27%	1,419.67	10.19%
Agricultural used area	1,714.99	38.20%	7,325.66	52.60%
Arable land	1,205.01	26.84%	6,169.27	44.30%
Pasture land	509.98	11.36%	1,156.39	8.30%
Forestry	2,107.54	46.94%	4,979.92	35.76%
Area of water surface	46.05	1.03%	19.96	0.14%
Population	2,302,855		5,336,248	

Annex 3: Distribution of land use within the Ruhr basin

Name of sub basin	**Urban in km²**	**Agriculture in km²**	**Arable land in km²**	**Pasture land in km²**	**Forestry in km²**	**Water surface in km²**
DENW_Ruhr von Quelle bis oh Wenne	22.4	177.1	120.8	56.3	288.1	3.3
DENW_Wenne von Quelle bis Mdg	6.1	121.2	85.7	35.5	90.9	0.6
DENW_Ruhr von uh Wenne bis oh Röhr	15.2	22.5	16.9	5.6	89.7	0.3
DENW_Rühr von Quelle bis Mdg	14.5	64.2	35.8	28.4	120.1	3.9
DENW_Ruhr von uh Röhr bis oh Möhne	6.4	2.9	1.2	1.6	6.6	0.0
DENW_Mühne von Quelle bis oh Heve	22.5	150.9	112.5	38.4	148.0	7.3
DENW_Heve von Quelle bis Mdg	0.5	8.4	6.5	1.9	89.8	2.9
DENW_Möhne von uh Heve bis Mdg	4.5	13.6	12.8	0.8	17.2	0.9
DENW_Ruhr von uh Mühne bis oh Hönne	11.7	63.6	52.6	11.1	24.2	0.2
DENW_Hönne von Quelle bis Mdg	35.9	97.7	68.9	28.8	122.3	0.7
DENW_Ruhr von uh Hönne bis oh Lenne	38.1	117.0	84.2	32.8	42.6	0.5
DENW_Lenne von Quelle bis oh Hundem	8.4	45.4	17.5	27.9	136.1	0.5
DENW_Hundem von Quelle bis Mdg	7.0	29.7	15.0	14.7	92.6	0.3
DENW_Lenne von uh Hundem bis oh Bigge	10.3	50.8	45.9	5.0	74.5	0.3
DERP_Bigge von Quelle bis Mdg	0.0	0.5	0.0	0.5	1.4	0.0
DENW_Bigge von Quelle bis Mdg	28.5	151.0	93.5	57.5	177.2	9.9
DENW_Lenne von uh Bigge bis Mdg	66.8	137.6	92.5	45.1	314.9	3.5
DENW_Ruhr von uh Lenne bis oh Volme	3.6	2.2	2.0	0.2	2.3	1.3
DENW_Volme von Quelle bis oh Ennepe	33.6	81.3	42.6	38.7	116.6	0.6
DENW_Ennepe von Quelle bis Mdg	34.3	88.8	69.5	19.3	63.3	1.2
DENW_Volme von uh Ennepe bis Mdg	6.6	0.7	0.7	0.0	0.7	0.1
DENW_Ruhr von uh Volme bis oh Deilbach	122.1	143.8	118.3	25.5	45.0	3.6
DENW_Deilbach von Quelle bis Mdg	14.7	72.7	46.8	25.8	23.2	0.3
DENW_Ruhr von uh Deilbach bis Mdg	82.2	71.6	62.8	8.8	20.6	3.7
Total	**595.7**	**1,715.0**	**1,205.0**	**510.0**	**2,107.5**	**46.1**

Annex 4: Zinc concentrations in the base flow of different tributaries of the Ruhr

Name of sub basin	Average concentration in µg/L	Base flow in m³/s
DENW_Ruhr von Quelle bis oh Wenne		6.34
DENW_Wenne von Quelle bis Mdg	0.50	2.83
DENW_Ruhr von uh Wenne bis oh Röhr	2.00	1.68
DENW_Rühr von Quelle bis Mdg	2.80	2.68
DENW_Ruhr von uh Röhr bis oh Möhne	2.00	0.21
DENW_Mühne von Quelle bis oh Heve	0.50	4.13
DENW_Heve von Quelle bis Mdg	62.00	1.30
DENW_Möhne von uh Heve bis Mdg	0.50	0.47
DENW_Ruhr von uh Mühne bis oh Hönne	2.00	1.35
DENW_Hönne von Quelle bis Mdg	11.00	3.58
DENW_Ruhr von uh Hönne bis oh Lenne	2.37	2.84
DENW_Lenne von Quelle bis oh Hundem	1.10	2.45
DENW_Hundem von Quelle bis Mdg	26.99	1.68
DENW_Lenne von uh Hundem bis oh Bigge	1.10	1.78
DERP_Bigge von Quelle bis Mdg	8.90	0.02
DENW_Bigge von Quelle bis Mdg	21.42	4.72
DENW_Lenne von uh Bigge bis Mdg	17.91	7.16
DENW_Ruhr von uh Lenne bis oh Volme	2.00	0.12
DENW_Volme von Quelle bis oh Ennepe	0.50	3.22
DENW_Ennepe von Quelle bis Mdg	2.30	2.60
DENW_Volme von uh Ennepe bis Mdg	0.50	0.11
DENW_Ruhr von uh Volme bis oh Deilbach	2.00	4.44
DENW_Deilbach von Quelle bis Mdg	5.22	0.40
DENW_Ruhr von uh Deilbach bis Mdg	2.00	0.45

Annex 5: Parameter used for the quantification of emissions from sewer systems within the Ruhr basin

Name of sub basin	Population	Area connected to separate sewer system in km²	Area connected to combined sewer system in km^2	Area not connected to sewers in km^2	Volume of combined sewer overflow in m³/a
DENW_Ruhr von Quelle bis oh Wenne	64,359	2.62	5.10	0.19	843.03
DENW_Wenne von Quelle bis Mdg	21,340	0.79	1.53	0.06	267.53
DENW_Ruhr von uh Wenne bis oh Röhr	39,576	1.69	3.29	0.12	524.78
DENW_Rühr von Quelle bis Mdg	36,033	1.58	3.08	0.12	483.28
DENW_Ruhr von uh Röhr bis oh Möhne	6,320	0.43	0.85	0.03	101.10
DENW_Mühne von Quelle bis oh Heve	41,790	2.08	4.05	0.27	610.31
DENW_Heve von Quelle bis Mdg	19,846	0.13	0.26	0.02	82.12
DENW_Möhne von uh Heve bis Mdg	8,619	0.42	0.82	0.05	118.74
DENW_Ruhr von uh Mühne bis oh Hönne	42,751	1.52	2.96	0.17	529.43
DENW_Hönne von Quelle bis Mdg	105,383	4.19	8.16	0.47	1,365.53
DENW_Ruhr von uh Hönne bis oh Lenne	174,257	5.55	10.82	0.48	2,180.42
DENW_Lenne von Quelle bis oh Hundem	20,912	0.91	1.78	0.07	276.76
DENW_Hundem von Quelle bis Mdg	12,489	0.64	1.25	0.07	174.35
DENW_Lenne von uh Hundem bis oh Bigge	29,994	1.20	2.34	0.13	384.35
DERP_Bigge von Quelle bis Mdg	65	0.00	0.00	0.00	0.19
DENW_Bigge von Quelle bis Mdg	87,423	3.39	6.61	0.38	1,099.43
DENW_Lenne von uh Bigge bis Mdg	262,796	8.99	17.51	0.98	3,236.64
DENW_Ruhr von uh Lenne bis oh Volme	13,005	0.47	0.91	0.04	173.11
DENW_Volme von Quelle bis oh Ennepe	133,359	4.53	8.83	0.52	1,634.80
DENW_Ennepe von Quelle bis Mdg	118,781	4.21	8.20	0.85	1,465.58
DENW_Volme von uh Ennepe bis Mdg	10,081	0.57	1.10	0.03	157.88
DENW_Ruhr von uh Volme bis oh Deilbach	538,186	17.20	33.53	2.33	6,510.84
DENW_Deilbach von Quelle bis Mdg	139,645	2.96	5.78	0.37	1,424.49
DENW_Ruhr von uh Deilbach bis Mdg	375,847	12.22	23.82	0.32	4,423.72
Total	**2,302,855**	**78.3**	**152.6**	**8.1**	**28,068**