

Inventory of historical contaminated sediment in Rhine Basin and its tributaries



(Foto: BfG)

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This report was written on behalf of the Port of Rotterdam

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Table of contents

Executive Summary (W. Salomons & S. Heise).....	I
Introduction (S. Heise & U. Förstner)	1
1. Characterization of Key Processes (U. Förstner)	5
1.1. Interaction of Key Processes in Fluvial Systems (U. Förstner)	6
1.2. Erosion and Transport: From Sediment to Suspended Matter	7
(B. Westrich)	
1.2.1. Beginning and Intensity of Erosion.....	7
1.2.2. Sediment Erosion Stability Tests.....	8
1.2.3. Sediment Depth Profiles.....	9
1.2.4. Transport of Resuspended Sediments.....	10
1.3. Mobilization of Sediment-Associated Contaminants (U. Förstner)	12
1.4. Availability of Contaminants from Sediment and Suspended Material to Organisms (S. Heise)	13
1.5. Processes Related to Remediation Measures on Contaminated Sediments (U. Förstner)	16
1.5.1. Risk Reduction by Ageing Processes.....	17
1.5.2. Enhanced In-Situ Stabilization based on Natural Processes.....	18
1.5.3. Processes Underlying Conventional Treatment Techniques.....	19
2. Requirement on Sediment Data Quality (U. Förstner)	27
2.1. Strategies for Water Quality Assessment: Particulate Matter	27
(U. Förstner & B. Westrich)	
2.1.1. Types of Assessment Programmes.....	27
2.1.2. Water Quality Assessment using Particulate Matter Data.....	27
2.1.3. Strategy of the Present Study.....	29
2.2. Quality Control of Field and Laboratory Chemical Data	31
(U. Förstner & B. Westrich)	
2.2.1. Quality Control and Quality Assurance in Water and Sediment Monitoring Data.....	31
2.2.2. Quality Control in the Analysis and Monitoring of WFD-Priority Substances.....	32
2.3. Quality Control of Chemical Sediment Analysis – Traceability Concept Extended to Secondary Sources	39
(U. Förstner)	
2.3.1. Surveillance Investigations.....	40
2.3.2. Monitoring.....	40
2.3.3. Resuspension – Secondary Source.....	41
2.3.4. Sampling and Filtration of Suspended Matter.....	43
2.4. Deriving Ecological Risk from Chemical Data (S. Heise)	44
2.5. Hydraulic Data Quality (B. Westrich)	47
2.5.1. Flood and Sediment Transport Parameters.....	47
2.5.2. Uncertainties and their Origin.....	49
3. Sediment Management at the Catchment Scale (U. Förstner)	61
3.1. Legal Aspects ¹	61
3.1.1. European Directives on Water, Soil and Waste (Landfills)	61
3.1.2. International Commission for the Protection of the Rhine (ICPR)	64

¹ compiled from Dutch-German Exchange on Dredged Material, Part I

3.1.3. National Legislation and Guidelines on Dredged Material.....	66
3.1.4. Dredged Material – Where Does Waste Term Apply and End?	68
3.1.5. Relocation of Dredged Material in German Inland Waterways.....	70
3.1.6. Subaquatic Disposal of Dredged Material.....	72
3.2. Management Practice in The Netherlands and Germany².....	73
3.2.1. Management Practice in The Netherlands.....	73
3.2.2. Management Practice in Germany.....	76
3.3. Biological Effects-based Sediment Quality in Ecological.....	77
Risk Assessment for Dutch and German Waters³.....	77
3.3.1. In situ Effect-Based Assessment.....	78
3.3.2. Ex situ Effect-Based Assessment.....	81
3.3.3. Outlook.....	82
3.4. Sediment Management Issues in the WFD-Strategies for Monitoring	
and Emission Controls of Priority Substances (U. Förstner)	83
3.4.1. Recommendations of the Expert Group on Analysis and	
Monitoring of Priority Substances (AMPS)	84
3.4.2. AMPS Drafting Group on Sediment Monitoring.....	85
3.4.3. Quality Standards for Sediments and Biota:Response of the	
Scientific Committee on Toxicity, Ecotoxicity and Environment.....	85
3.4.4. Priority Substances in Historical Contaminated Sediments.....	86
3.5. New Challenges for Catchment Scale Management.....	88
3.5.1. Risk Management at the Catchment Scale ¹ (S. Heise)	88
3.5.2. Sources and Measures at the Catchment Scale (U. Förstner)	91
3.5.3. Future Research on Soil-Sediment Contaminants	
at the Catchment Scale (W. Salomons)	94
4 Substances and Areas of concern.....	99
4.1 Introduction to the risk assessment approach	
for the Port of Rotterdam (S. Heise)	99
4.2.1 What substances are of concern for the Port of Rotterdam?	102
4.2.2. Assignment of hazard classes (HCC) to “substances of concern”	106
4.3 “Areas of concern” (S. Heise)	111
4.3.1 Methods to assign hazard indexes to areas of concern	
based on sediment data.....	111
4.3.2 Identified Areas of concern.....	114
4.4 Potential sources for contamination (S. Heise)	119
4.4.1 Industrial/diffuse sources in general.....	119
4.4.2 Historical sources for areas of concern.....	120
4.5 Special case area 1: Heavy metals in the Ruhr area (Th. Jancke)	134
4.6 Special case area 2: The Contamination of River Rhine	
with Hexachlorobenzene (H. Schönberger)	139
4.6.1 Introduction.....	139
4.6.2 Identification of the HCB source in the seventies –	
according to	140
4.6.3 Manufacture of chlorosilanes and the formation of HCB.....	141
4.6.4 Development of HCB emissions and of the immission situation.....	143
4.7 Ecotoxicological assessments along the River Rhine (S. Heise)	146
4.7 Summary (S. Heise)	149

² compiled from Dutch-German Exchange on Dredged Material, Part II

³ Compiled from den Besten et al. (2003)

5. Quantification of the Risk for the Port of Rotterdam.....	155
5.1 Introduction to the approach of risk quantification (S. Heise)	155
5.2 The hydrological regime, flood events, and sediment dynamics of the Rhine catchment area.....	159
(B. Westrich, T. Jancke, J. Karnahl & S. Heise)	
5.2.1 The hydrological regime and flood events.....	159
5.2.2 Sediment dynamics.....	163
5.3 Erosion thresholds in reservoirs of Rhine, Main and Neckar.....	168
(B. Westrich, T. Jancke & J. Karnahl)	
5.4 Estimated risk to the Port of Rotterdam due to substances of concern (S. Heise)	170
5.4.1 Introduction to the approach.....	170
5.4.2 Indication of risk by simulation of sediment transport from contaminated sites.....	177
5.5 Indications for resuspension and transport of contaminants in suspended matter – exemplarily described for Cadmium and HCB... ..	181
(B. Westrich, T. Jancke, J. Karnahl & S. Heise)	
5.5.1 Introduction.....	181
5.5.2 Evidence for Cd-resuspension.....	182
5.5.3 Evidence for HCB-resuspension.....	185
5.5.4 Other evidence for resuspension events.....	193
5.6 Summary – areas of risk for Rotterdam (S. Heise)	197
5.7 Sediment management at the areas of concern.....	200
(S. Heise)	
5.7.1 Institutional framework in water and sediment management.....	200
5.7.2 Planned and implemented measures for areas of concern.....	203
5.8 References Chapter 5.....	205
6 Summary and Conclusions (S. Heise)	207
6.1. Identification of areas risk in the Rhine catchment area and its tributaries for the Port of Rotterdam due to historic contamination.....	207
6.1.1 Identification and classification of substances of concern (chapter 4.2)	207
6.1.2 Identification and classification of Areas of Concern (chapter 4.3)	208
6.1.3 Identification and classification of Areas of Risk (chapter 5)	209
6.1.4 The processes.....	211
6.2. Knowledge Gaps and Uncertainties.....	212
6.3. Historical Contaminated Sediments under the WFD.....	212
6.4. Sustainable Sediment Management at the Catchment Level.....	213
 Abbreviations	 217
List of boxes	220
List of tables	221
List of figures	223

Acknowledgement

Annexe

Executive Summary

Sediments are an integral but ambiguous part of water systems. On the one hand they provide the substrate for organisms and through interaction with the overlying waters (e.g. nutrient cycling) play an essential role to the aquatic ecosystem. On the other hand, hazardous chemicals from various sources stick to the sediment, and even if water quality improves, sediment contamination will remain ("legacy of the past").

Today relatively uncontaminated sediment surface layers cover older contaminated sediments deposited in low flow area sites in the rivers, such as flood plains, river reservoirs, and groyne fields. Nevertheless, there is an increasing risk with increasing water discharge and frequency of flood events for the resuspension of old contaminated sediment layers and the transport of particle-bound contaminants downstream in the river system. Contaminated material can also be introduced to river systems from contaminated soil during surface run-off or erosion events. This report focuses on historic sediment contamination, terrestrial sites will only be dealt with to a minor extent.

In the scope of this project risks for the Port of Rotterdam were assessed arising from resuspension of historical sediment contamination upstream following natural events (e.g. floods) or anthropogenic activities (e.g. dredging activities).

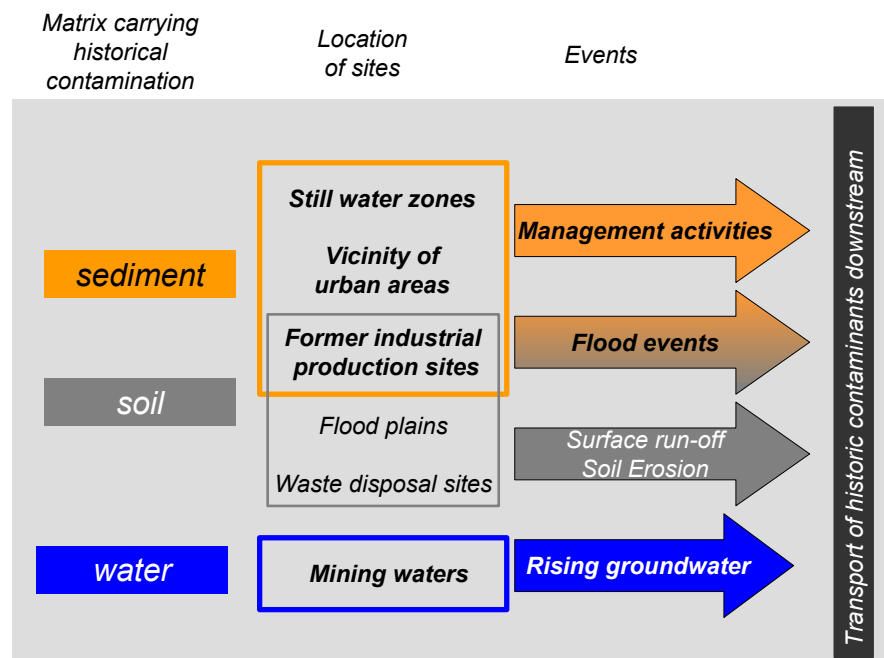


Figure ES.1 Pathways and processes for the transport of historic contamination downstream. Location of sites, that are of special importance in this report, are written in bold letters.

Until now, no comprehensive investigation on the current potentially buried sediment contamination in the river Rhine catchment had been performed nor has such a catchment wide assessment been carried out elsewhere. Hence a detailed review of relevant and scattered information was carried out as well as new conceptual approaches were developed.

Chapter 1 reviews the key processes controlling hydraulic and chemical mobilization as well as transfer of pollutants to organisms are described. Chapter 2 presents an overview on the requirements on sediment data quality, including strategies for water and sediment assessment as well as quality control of field and laboratory data. Quality requirements and uncertainties of hydraulic data, forming the key issue in the present study, are discussed. Chapter 3 summarizes recent developments in sediment management at the catchment scale. Information on chemical and biological sediment data from chapter 2 are discussed in relation to strategies for quality control in the analysis and monitoring of EU Water Framework Directive priority substances.

This extensive review shows gaps in knowledge on the potential impacts of high discharge on deposited sediments, making it necessary to develop a deductive approach. This approach comprises three steps (chapters 4 and 5).

Table ES.1 Substances of concern and their ranking

Substances of concern	Hazard class
Cadmium	2
Chromium	1
Copper	1
Mercury	2
Nickel	1
Lead	1
Zinc	1
DDT+DDD+DDE (SUM)	2
Dioxins and Furans	2
Hexachlorobenzene	2
Polycyclic aromatic hydrocarbons	2
Polychlorinated biphenyls	2
TBT	1
Aldrin (Dieldrin, Endrin)	1
γ -hexachlorocyclohexane	1
Nonyl-phenol compounds	1

Step 1. Selection of substances of concern.

Only those substances were chosen for further evaluation, that are of concern for the management of the Port of Rotterdam as they frequently exceed or reach the new Dutch "Chemistry –Toxicity Tests (CTT)-levels". These **substances of concern** were then assigned to different hazard classes according to a classification based on their behavior in the environment and the potential danger that they present for organisms.

Step 2. Selection of geographical areas of concern

In a second step, existing sediment analysis data from the last 10 years were used to identify those areas in the Rhine and its tributaries, which show increased concentrations of these substances of

concern above CTT level and therewith potentially provide a danger of increasing concentration levels

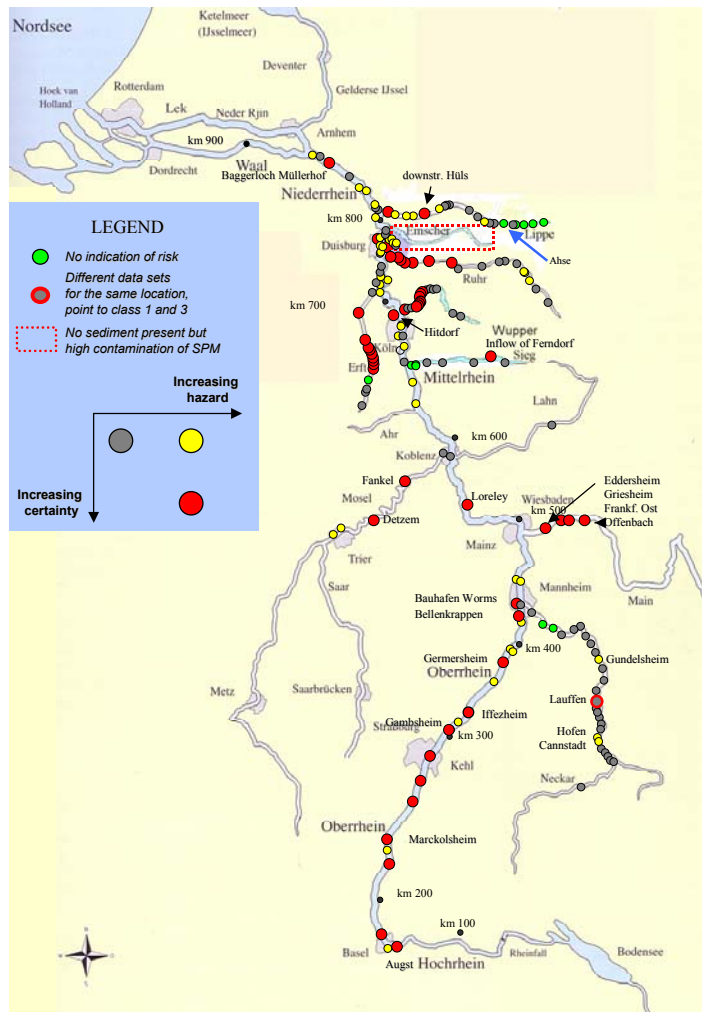


Figure ES.2 Areas of concern and their classification based on sediment contaminant concentrations

at the Port of Rotterdam. These **areas of concern** (figure ES.2) are classified with regard to the quantity of contamination and available data to give an overview over the distribution of persisting hazards in sediments along the river Rhine. A survey on information about historic emissions follows in order to a) clarify the sources of the sediment contamination; b) validate the possibility of persisting contamination at these sites; c) gather information on management options due to the potential persistence of sources and the distribution of contamination.

Step 3. Quantification of risk for the Port of Rotterdam

The risk assessment for the port sediments due to those “substances of concern” that could derive from the identified “areas of concern”

required estimating the extent of contamination, erosion and subsequent transport in the catchment. Due to lack of data on flood events, suspended contaminant load, and models to achieve a complete and comprehensive picture of areas of risk, an approach was used, in which results were based on different lines of evidence: In order to assess, whether the extent of contamination was high enough to exceed the CTT threshold in the Port of Rotterdam, a “worst case approach” was used taking into account normal water flow, and subsequently addressing “average high water” and “highest water discharge observed”. Furthermore it was assumed that suspended matter sediment concentrations are directly related to water flow resulting in concentrations of 20, 150 and 250 mg/l, that the whole sediment contamination at a specific site is transferred to the water phase, and that, sediment concentration equals the concentration of contaminants in the suspended material. In the port of Rotterdam no mixing with former deposited sediments was taken into account. Therewith CTT-values were directly compared with the calculated concentrations.

As a result of this final step, the number of “areas of concern” could be reduced from twelve to five:

1) The barrages in the Upper Rhine are the only ones, that may already present a risk during business as usual conditions (average water discharge, no management activities): Already at normal discharges, increased concentrations of hexachlorobenzene (HCB) have been measured in suspended matter at Iffezheim. With increasing discharges HCB (and possibly mercury) becomes resuspended and transported downstream. With the continuous inflow of contaminated sediments from the barrages further south, the existing sediment disposal sites reaching their upper limits, combined with still high HCB concentrations in the sediment and significant gaps in the understanding of its transport processes, this area becomes an important challenge for future sediment management.

2) The Ruhr currently represents a certain risk at increased water discharges. High concentrations of polycyclic aromatic hydrocarbons (PAHs) but also of the other substances that are of concern in that river, especially cadmium, are likely to be resuspended and transported downstream. It should be noted that there are a number of management projects initiated in the Ruhr, which may positively affect (decrease) the contaminant contribution of this river to the Rhine.

3) The Neckar may also represent a risk. A resuspension of cadmium in the barrage Lauffen has been predicted due to its low sediment stability, and increases in cadmium concentration in suspended matter at this site have been measured. However, whether this load arrives at the Rhine after passing 13 more barrages, is uncertain due to missing data during flood events from the measuring station Feudenheim near Mannheim, the last barrage before the Neckar reaches the Rhine. However, no cadmium source could be identified other than the Neckar that could account for the observed cadmium loads of more than 1000 mg/s at stations Koblenz (Rhine) and Bad Honnef.

4) Evidence of a risk from old contamination in the Wupper is derived from a comparison of contamination patterns of this tributary's sediments with those of the harbours in the Lower Rhine (downstream of the Wupper confluence) and here especially the monitoring station Hitdorf-Harbour. All show a similar contamination pattern, suggesting an influence of the Wupper's effluents on the Rhine sediments. However, available information is insufficient to determine whether this material is likely to be transported further downstream as the erosion thresholds of the sediments in these harbours are unknown.

5) There is some indication that the Lippe may contribute to the HCB load in the Rhine under high water situations. If the crest of the flood wave reaches the Rhine before the flood of the main river arrives, dilution of suspended matter from the Lippe may even be that low, that its contaminated suspended material could lead to an increase in the HCB concentration in the Port of Rotterdam. The latter case shows the complexity of making predictions in view of the inherent variability in discharge regimes in the Rhine catchment.

A review of the current regulations (chapter 3) showed that erosion of contaminated sediments and their potential impacts downstream and subsequently in deltaic and coastal regions is not covered by existing regulations. Existing regulations are focused on local impacts of the relocation of contaminated sediments and do not take the whole catchment into account. On the other hand, the Water Framework Directive, which focuses on the catchment scale, does not explicitly mention sediments nor sediment quality and quantity. However, the strategies against chemical pollution of surface

waters (WFD article 16), i.e. implementation of monitoring programs until 2006 and establishment of the program of measures until 2009, have to consider sediment quality at the catchment scale. With respect to the latter date, already the first step – screening of all generic sources that can result in releases of priority substances and priority hazardous substances – will include the specific source/-pathway “historical contamination from sediment”.

Introduction

The largest “sediment trap” and, therefore, potential concentration of contamination, can be found at the end of rivers, where an enormous amount of sediment is trapped yearly in estuaries and coastal zones, e.g. in ports and harbours. The already existing situation for these port areas to pay – in addition to the high capital costs for the maintenance of navigation channels – the expenses for the shortcomings in the emission control within their catchment areas can be aggravated further in an even less predictable manner (extreme flood events, climate change). In the scope of this project future risks for the Port of Rotterdam will be assessed that may arise from resuspension of historical sediment contamination upstream following natural events (e.g. floods) or anthropogenic activities (e.g. dredging activities).

Likely sites for the accumulation and potential exposure of contaminated sediments are:

- river reservoirs and barrages where sediment is accumulated and which can release the contaminants during floods events
- inland harbours with wide openings to the river Rhine
- dead arms which have been cut off due to straightening of the river during the 20th century, as they are potentially contaminated and exposed to high floods.
- tributaries and bypass channels which historically were industrially used but which have not been maintained by continuous dredging
- industrial areas which are located within the potentially flooded area and which contain waste deposits. The risk of these has been demonstrated during the Elbe flood in 2002, when flooding of the Bitterfeld area and the industrial site “Spolana” raised a lot of concern.
- the vicinity of larger cities (and emissions from municipal wastewater plants)

Contaminated material can also be introduced to river systems from contaminated soil during surface run-off or erosion events. As this report focuses on historic sediment contamination, terrestrial sites will only be dealt with to a minor extent.

To our knowledge there is no comparable approach to predict the effects of both extreme flood events and dredging activities on the transfer of historical contaminated sediment to a port area at the lower reaches of such a large catchment area. In fact, there are many uncertainties in this prognosis, arising from the complexity of influencing factors, but also from gaps in process knowledge and deficiencies at problem-specific databases:

- In Chapter 1 the **key processes** controlling hydraulic and chemical mobilization as well as transfer of contaminants to organisms are described. On the other side, there are stabilizing processes such as ageing, which can be used for developing cost-effective remediation techniques for in situ and dredged sediments.

- Chapter 2 presents an overview on the **requirements on sediment data quality**, including strategies for water and sediment assessment as well as quality control of field and laboratory data. In section 2.5 the quality requirements and uncertainties of hydraulic data, forming the key issue in the present study, are discussed.

The present project is an extension of the Rhine Research Project II (1999-2001) "Dredged Material in the Port of Rotterdam – Interface between Rhine Catchment Area and North Sea", which dealt with three major issues: (i) point and diffuse sources in the Rhine catchment and identification of their past, present and future inputs and how they determine sediment quality; (ii) the current and future policies and regulatory frameworks that are relevant for sediment/dredged material as well as their proposals for "new priority chemicals", and (iii) the issue of hazard assessment of contaminated sediments/dredged material through new methodologies and their relation to risk assessment at the disposal site. Since the publication of the report (February 2001) substantial progress has been made in the field of sustainable sediment management (SSM):

- Chapter 3 summarizes recent developments in **sediment management at the Rhine Catchment**. Legal aspects on a European and national level were covered in a review by the Dutch-German Exchange on Dredged Material program, Part 1 (DGE-1, 2003) and management practice, i.e. treatment and confined disposal, in both countries is reviewed by the same program, Part 2 (DGE-2, 2002). Another important new source of information is SedNet, a European sediment research network on environmentally and economically viable sediment management (EC FP5, contract No. EVKI-CT-2001-20002); a final version of the SedNet Strategy Paper has been published in June 2004 and in section 3.3 of the present study an overview is given on "biological effects-based sediment quality in ecological risk assessment for Dutch and German waters" summarizing the SedNet Working Group publication of Den Besten et al. (2003). In section 3.4 information on chemical and biological sediment data from chapter 2 is embedded in the forthcoming strategies for quality control in the analysis and monitoring of EU Water Framework Directive priority substances. Section 3.5 presents short articles on three themes closely related to the catchment scale sediment perspective: "Risk Management", "Sources and Measures", and "Future Research on Soil-Sediment Contaminants".

In the Rhine Research Project II report calculations were made of current emissions and immissions into the Rhine and its tributaries in order to analyze (or forecast) the quality of sediments and dredged material in the Port of Rotterdam. Emphasis lay on the development of acute diffuse and point sources over time. The report showed that total emissions of heavy metals, PCBs and PAHs had decreased since the beginning of the 80s with a strong decline of contribution by industrial emissions. In the present report, the scope of assessing the risk for the Port of Rotterdam is extended to sites and impact of historic contamination in sediments. "Historic" contamination with a potential to be re-introduced into the sediment-suspended matter cycle may gain in importance with further reduction of diffuse pollution. Due to the scarce and inhomogenous data base on "old" sediment contamination,

our conclusions on impact of historical contamination on the sediment in the Eastern part of the Port of Rotterdam had to be mainly deductive and comprised the following steps:

- Chapter 4 lists the substances that are of concern for this report and explains, why we focused on a limited amount of compounds: Only those substances are chosen for further evaluation, that are of concern for the management of the Port of Rotterdam as they frequently exceed or reach the new Dutch "Chemistry –Toxicity Tests (CTT)-levels" which decide about relocation at sea (clean sediment) and Slufter disposal facility (contaminated sediment). These **substances of concern** ("s.o.c.") are then assigned to different hazard classes (HC_c) due to their behaviour in the environment and the potential danger that they present for organisms (chapter 4.1.). In a second step, we used existing sediment analysis data from the last 10 years to identify those areas in the Rhine and its tributaries, which show increased concentrations of these substances of concern above CTT level and therewith potentially provide a danger of increasing concentration levels at the Port of Rotterdam. These **areas of concern** ("a.o.c.") are classified with regard to the quantity of contamination and available data to give an overview over the distribution of persisting hazards in sediments along the river Rhine. A survey on information about historic emissions follows in order to a) clarify the sources of the sediment contamination; b) validate the possibility of persisting contamination at these sites; c) gather information on management options due to the potential persistence of sources and the distribution of contamination.
- Chapter 5 is dedicated to the **quantification of risk for the Port of Rotterdam** through the contaminated sediments located in the respective areas of concern. Historic contamination can lead to a concentration gradient in a constrained area if it is continuously exposed like e.g. in mining areas or where waste disposal sites leak into groundwater or directly into rivers. More often, however, legacies of the past in rivers have been covered up by freshly deposited sediment and may be resuspended during flood events or in the process of management or construction activities. This chapter evaluates the possibility that these hazards lead to exposure of sediments downstream to elevated contaminant concentration levels. Information on the hydrodynamic in the Rhine, on erosion thresholds and events and their effect on contaminant transport, theoretical concentrations and calculated loads are discussed in order to conclude, which areas of concern may provide a risk under different discharge scenarios for the Port of Rotterdam. Where management options are planned or have already been implemented for these "areas of risk" these are described in 5.5.

The summary and conclusions (chapter 6) will focus on the results of this report, identifying those areas of concern, which are regarded as presenting a risk for the Port of Rotterdam with regard to potential exceedances of the CTT value(s).

The Rhine catchment area and its tributaries

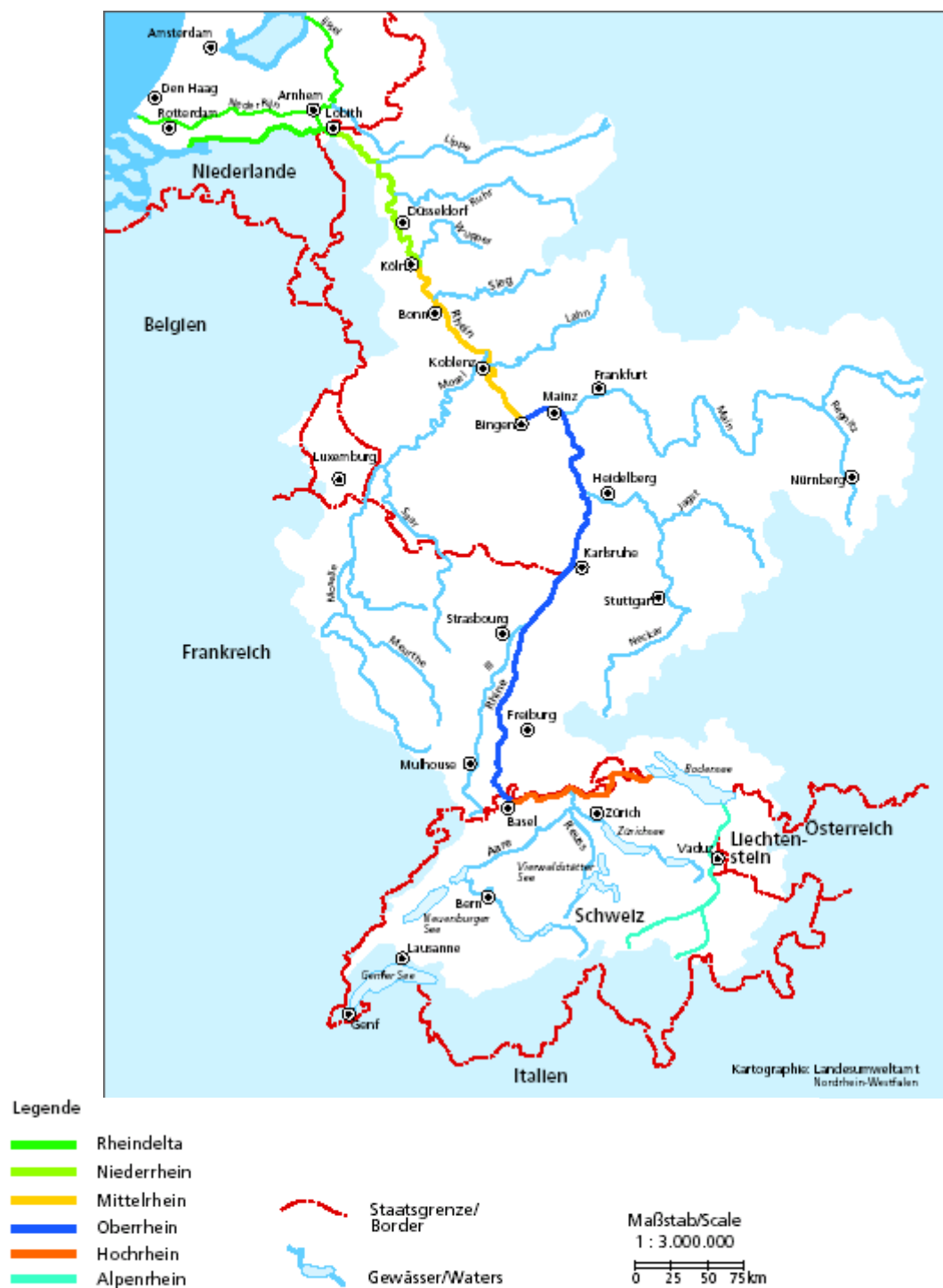


Figure I.1 Catchment area of the Rhine (indicating the area of the Delta Rhine ("Rheindelta"), the Lower Rhine ("Niederrhein"), the Middle Rhine ("Mittelrhein"), the Upper Rhine ("Oberrhein"), the High Rhine ("Hochrhein"), and the Alpine Rhine ("Alpenrhein").

1. Characterization of Key Processes

Both for establishing and interpreting sediment-related quality objectives and for developing and applying simulation techniques in different spatial and temporal scales a set of practical process knowledge is needed that uses specific information on interacting hydromechanical, biological and chemical processes.

In Table 1.1, the major processes influencing the cycling of contaminants in aquatic systems are arranged according to the primary research discipline involved, and phase (dissolved or particulate). There are characteristic interactions between chemistry and biology in the case of bioturbation of sediment deposits and between chemistry and photodegradation. Biological activity is involved in physical cycling of particulate matter both in the water column and at the sediment/water interface. Organic excretions may produce fecal pellets and may enhance aggregation and thus fasten settling of particles. There are well-documented effects of reworking and resuspension of sediments by benthic organisms such as tubifid worms, but also by amphipods, shrimps and clams. Bioturbation is a major post-sedimentation process, affecting the fate of particle-associated toxic metals and persistent organic chemicals, which are not primarily affected by volatilization, photolysis or bio- and photo-degradation (Allan 1986). In fluvial systems, cycling of pollutants is dominated by processes of resuspension, settling and burial of particulate matter.

Table 1.1 Processes Affecting the Cycling of Pollutants in Aquatic Systems

	Aqueous Species	Particulate Species
"Chemical"	Dissolution Desorption Complexation	Precipitation Adsorption Aggregation
	<i>Species Transformation</i>	
"Biological"	Decomposition Absorption, release Cell wall exchange	Food web transfer Filtering, digestion Pellet generation
	<i>Bioturbation</i>	
"Physical"	Advection Diffusion Photolysis	Resuspension Settling Burial

1.1. Interaction of Key Processes in Fluvial Systems

In the description of dynamic fluvial processes, three scientific disciplines are involved and three study objects can be distinguished (Fig. 1.1): Suspended matter, sediment and porewater or open water. In practice, emphasis has to be given to fine-grained sediments and suspended matter, since these materials exhibit large surface areas and high sorption capacities. Organic materials are highly reactive. Degradation of organic matter will induce depletion of oxygen and may enhance formation of flocs and biofilms. Study of variations of sediment and water chemistry should predominantly include changes of pH and redox conditions, competition of dissolved ions and processes such as complexation by organic substances. Major questions relate to the potential reduction of sorption sites on minerals and degradation of organic carrier materials. All these processes will influence solution/solid equilibrium conditions and have to be studied prior to modeling the overall effects on the water body and aquatic ecosystems.

Special study targets, as shown in Fig 1.1, are the formation of aggregates in turbulent water, flocs and biofilms from organic reactions, and formation of new surfaces for readsorption of dissolved pollutants. In the center of interactive processes is the degradation of organic matter, which affects both hydrodynamic processes – here erosion vs. sedimentation – and geochemical redox cycles. Here, the major question, after all possible interactions between both existing and newly formed solid and dissolved phases refers to the net release of dissolved organic carbon (DOC), nutrients and pollutants into the open water.

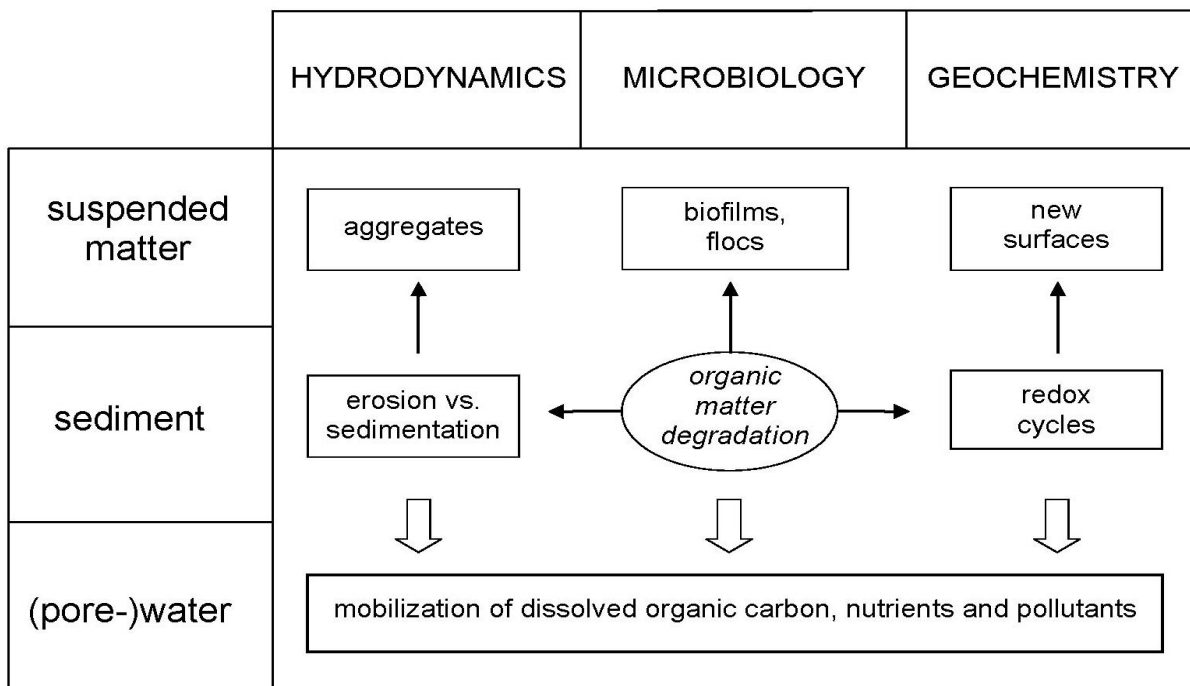


Figure 1.1 Scientific Disciplines and Study Objects in a Coordinated Research Programme of the German Federal Ministry of Education and Research, 2002-2006, on Fine Sediment Dynamics and Pollutant Mobility in Rivers (SEDYMO; Förstner 2001)

Due to their particular dynamics, two characteristic features of sedimentary and erosive processes in rivers should receive special attention: The dramatic effects of stormwater events on particle transport (section 1.2), and the rapid and far-reaching effects of chemical changes (section 1.3), both studied in the SEDYMO programme. Next to mobilization of contaminants, bioavailability and its changes over time and in dependency of the abiotic parameters determines the environmental impact (section 1.4). On the other hand, a common feature of sediments is their tendency to increase overall mechanical and chemical stability over time (section 1.5.1); the “intrinsic barrier concept” is probably one of the few realistic approaches to deal with contaminated soils and sediments in flood plain areas (section 1.5.2). In section 1.5.3 processes underlying conventional treatment techniques and those controlling the pollutants mobility in sub-aquatic depots of dredged material are presented.

1.2. Erosion and Transport: From Sediment to Suspended Matter

1.2.1. Beginning and Intensity of Erosion

In most cases contaminated sediments have a very small particle size of less than 20 micrometer, they exhibit cohesive properties and high sorption capacity reflected by the partitioning coefficient k_d . Those fine particles are characterized by high sediment specific interparticle bounding forces which are enhanced by natural consolidation and influenced by diagenetic processes, river water chemistry and sediment biology. Several historical sediment depositional areas in the river Rhine basin are known as highly contaminated and must be considered as a severe latent hazard for the river ecosystem because of their toxic potential (Witt et al. 2003). As for the contaminated sediment resuspension risk the sediment erosion stability is the key issue because of the triggering effect of hydrodynamic erosion which controls the contaminant mass flux and therefore, the initial concentration, the exposure conditions and the subsequent chemical and biological processes in the water body. Despite of several research activities on sediment stability we have only a weak understanding which physical, chemical and biological parameters are relevant and to what extent do they influence the sediment stability (Gerbersdorf et. al 2004; Haag and Westrich 2001). The evaluation and comparison of experimental data on cohesive sediment erosion show that there is no simple correlation between sediment properties and hydrodynamic shear force. Sediment samples from the river Neckar (Haag and Westrich 2001) show a reasonable correlation between sediment grain size smaller than 20 micrometer, water content and extracellular polymer substances (EPS). However, more intensive recent investigation on sediments from different sites, i.e. river Rhine, Neckar and Elbe, taken in different seasonal time and sediment depth revealed a very complex feature of sediment erosion stability. By applying a multivariate statistical analysis and, in particular the factor analysis major components influencing the sediment stability could be found such as chlorophyll content, EPS etc. (Gerbersdorf et. al 2004). By the correlation analysis some interaction of physical,

chemical and biological factors could be detected such as EPS with clay content but a conclusive generic description of cohesive sediment erosion processes is not yet possible because of the limited number of analyzed sediment types.

In addition, because of the large number of relevant sediment stability parameters which are expected to result in different river and site specific weighting factors, the experimental results cannot be directly transferred to another river basin or tributary. Although a lot of hydrological, morphological and sediment data of the river basin have been collected and analyzed by several authorities and institutes in the past there are still a lot of missing data required for erosion, transport and sedimentation description and modelling, respectively. Therefore, for all unexploited historical sites in the river Rhine basin sediment stability assessment must rely on engineering assumption and judging associated with uncertainties. Of course, there is always an option for sampling and testing sediments from unsampled sites to fill the data gap with actual data on sediment stability. To update the data base, specific and targeted field measurements and experiments by application of a new innovative techniques (Witt and Westrich 2003) can be performed focusing on sediment erosion threshold and erosion rates as well for different sediment layers as to enable to provide sediment depth profiles in terms of erosion and contaminant related parameters.

1.2.2. Sediment Erosion Stability Tests

The sediment stability testing facilities consist of a unique triple set developed by innovative experimental laboratory and field research. The instrumental facilities allow measuring not only the onset of erosion (critical bed shear stress) but also the erosion rate for different sediment layers. The mobile testing equipment facilitates to simulate local erosive events. The unique combination of laboratory and in situ experiments enables to upscale and transfer sediment erosion and sedimentation criteria to the nature, which is an essential prerequisite for numerical modelling of natural processes. In addition, it facilitates to collect freshly eroded particles on site for sedimentological (grain size etc.), geochemical and/or biological analysis.

As the river flow and transport conditions vary in space and time sediments must be sampled at selected sites with regard to the local flow pattern (groyne fields, harbours, headwaters) lateral mixing processes and contaminant point sources from municipal or industrial waste water plants (Ruhr etc.). Undisturbed sediment samples can be taken from contaminant sites, e.g. in near bank groyne fields, harbors, headwaters and reservoirs, in the river Rhine basin using appropriate and recently developed techniques: (1) core sampler (diameter 14 cm, length 150 cm) for sediment erodibility depth profiling, (2) box sampler (30x70 cm² top view area, 28 cm depth) for comparing and upscaling the results from (1). The objective is to analyze physical sediment properties such as grain size spectrum, water and gas content by a non intrusive high frequency capacity measurement method (Gerbersdorf et. al 2004) bulk density by γ -ray, to specify the depth profile of critical erosion shear stress as one key parameter which then, must be linked to the discharge which is hydrologically specified by its occurrence probability or statistical return period. In addition, the erosion rate as another key para-

meter can be quantified through laboratory experiments by applying the extended SETEG system called SEDCIA (Sediment Erosion Detection by Computer aided Image Analysis, Witt and Westrich 2003) and through the recently developed mobile in situ erosion stability testing facility EROMOB with a sediment surface area of $30 \times 70 \text{ cm}^2$ to be tested (Westrich and Schmid 2004).

For the sediments in the upper river Rhine reservoirs, especially in the Marckolsheim reservoir, a critical erosion shear stress between 2-8 Pa (N/m^2) and a erosion rate between 0,0001 and 0,011 ($\text{g/cm}^2 \text{ sec}$) could be found and finally used for numerical prediction of particulate mass of HCB eroded during the 1999 flood event as shown by Witt (2004).

With the sediment corer parallel samples can be taken for chemical and eventually biological sediment parameter profiling. As a more simple method a calibrated Cohesive Strength Meter can be applied and used for rough investigation and intercomparison (de Deckere et. al 2001). It also allows to correlate the sediment stability with the macrobenthos density.

1.2.3. Sediment Depth Profiles

Beside the physical sediment properties, the contamination level is subject to a great variability both in space and time which has to be taken into account when estimating and predicting the transport behavior and the environmental impact of particulate contaminants in the fluvial system. In most cases there is no information available about the depth profile of sediment contamination which in combination with the erosion parameter is an important parameter for any erosion induced contaminant mass flux calculation. To provide the input data for a 1-d (COSMOS, Westrich et. al 1999) or 2-d (TELEMAC -SUB 2, Jacoub 2004) numerical transport model, field and laboratory measurements must be conducted. As not enough data are available neither for a geostatistical evaluation nor an accurate extra- or interpolation the contaminated sediment bodies must be explored in three dimensions (surface and depth) to get a complete picture of the "areas of concern" which is necessary for modelling the total mass of contaminants resuspended by an erosive event.

The difficulties and uncertainties associated with the prediction of erosive mass flux of sediment bound contaminants released from historically contaminated sites has been investigated by Li (2004) based on data of the river Neckar. The results confirm the predominant influence of the shape of the hydrograph of a flood with given occurrence probability and the variance of the critical shear stress and the erosion rate as well. This can be illustrated by the attempt to quantify the concentration and total mass of particulate HCB released from the river Rhine reservoir Iffezheim during the flood event in May 1999. The existing data base of the post flood particulate contamination of the remaining reservoir sediments was quite poor. Therefore different assumptions on local bed shear stress and sediment contamination depth profile had to be made resulting in a great difference of the contaminant mass calculated by a 2- numerical flow model (Witt 2004).

1.2.4. Transport of Resuspended Sediments

The sediment erosion mass flux plays an important role because it controls the source strength of contaminants and therefore, determines the initial concentration field not only of the resuspended particulate contaminants but also of the dissolved components associated with the pore water. The erosion is followed up by the hydrodynamic transport potentially associated with desorption and remobilization of sediment bound contaminants and, finally results in sedimentation of remaining contaminated fractions downstream in headwaters and stagnant water bodies like groyne fields, inland harbors and flood plains.

The knowledge of the contaminated particle fraction and the interaction between the dissolved and particulate phase of micropollutants is necessary for determining the transport, fate, bioavailability and toxicity of such substances in river ecosystems. There is almost no information available on the suspended particle size distribution and the respective fall velocity spectrum, which is important for transport and sedimentation behavior.

The field-flow fractionation techniques provides a new possibility for the characterization and reproducible separation of colloidal solutions and particle suspensions (Giddings 1993; Beckett & Hart 1993). The technique which works with a cross flow of carrier liquid is one of the most powerful sub-techniques (Gimbert et. al. 2003). It is useful for separating particles of very different sizes (from about hundred microns to the submicron range).

Sedimentation rate measurements can be conducted by a new developed and calibrated sediment trap when deployed at representative sedimentation zones (e.g. groyne fields, flood plains) (Kozerski 2002).

After erosion, sedimentation of contaminated sediments is likely to occur in low flowing areas such as large reservoirs, flood plains, stagnant water bodies like inland harbors and groyne fields. Sedimentation of fine suspended material is primarily dominated by the bed shear stress, the flow velocity and flow depth, the fall velocity and concentration of the contaminated fraction and the microstructure of the river bed and the flood plains, respectively (Juraschek and Westrich, 1985). From the hydraulic point of view one can simply conclude that the flow velocity is the key parameter for sedimentation control. Up to now there is no quantitative description of fractional sedimentation possible under natural conditions encountering on flood plains where arable land, pasture land grass land , forest or other type of land are available. Large flood plain areas with vegetation show flow velocities lower than the critical velocity for the beginning of sedimentation (less than about 0,5 m/s) and hence, may be a temporary or final sink of the contaminants the strength of which is difficult to estimate. Measurements for the river Rhine flood plains by Müller and Yahya (1992) and data of the Elbe flood in 2002 clearly illustrate the sink effect of flooded areas. Sedimentation diminishes the remaining contaminant concentration and also load reaching the port of Rotterdam. For a rough conservative estimate such loss of contaminants is less than about 10 % of the total load.

Transport, mixing and sedimentation in the river system is a complex process varying both in space and time. If sedimentation in the main river, e.g. river Rhine itself or one of its tributaries, can be neglected the maximum concentration depending on the lateral and longitudinal dispersion due to mixing with low flowing or stagnant water bodies can be effected only. However, if the extension of the contaminated water body is about some kilometers caused by a several hours or even one day lasting erosive event the influence of the mixing process on the maximum concentration can be neglected provided there is no tributaries in between.

Tributaries always have an influence on the concentration and also on the total mass of contaminants if there is an additional input to the main river. As a first approach this effect can be described by applying the simple mixing equation in the following way

$$C_1 * Q_1 + C_{trib} * Q_{trib} = C_{mix} * (Q_1 + Q_{trib})$$

with $C_1 = C_{particulate} \text{ (mg/kg)} * C_{total \text{ suspended sediment (mg/l)}}$ and $Q \text{ (m}^3\text{/s)}$

This assumption can be applied only if the particulate contaminants are restricted to the grain size fraction smaller than 20 micrometer and the total suspended sediment grain size distribution of both the rivers, that is the tributary and the receiving river, is unchanged. Because of lack of data no evidence can be given that this assumptions is justified.

The mixing approach assumes a complete mixing of the contaminated fraction at the point of confluence in the main river and the joining tributary as well. In case of measurements taken in a contaminated plume with lateral concentration gradients the concentration profile must be known to allow the evaluation for the mass balance by integration of the product of local concentration and flow velocity. If the mixing approach is acceptable, it has to be applied at each point of confluence along the river Rhine until the last tributary. Knowing the residence time and specifying some reaction and degradation processes the final concentration at the destination, that is the port of Rotterdam, can be estimated. Only a few historical flood events have been recorded in detail and can provide a consistent data set which allows to trace the transport process over a long distance down to the Dutch-German border in terms of residence time, particulate contaminant concentration and pertinent contaminant mass. The data set of the flood event in February 1999 was almost complete as to facilitate a quantitative description of the relevant transport parameters. In lack of detailed data of contaminated transport processes in the tributaries the monthly averaged concentrations could not be assigned to flood events with a definite discharge. Prior to the historical flood events in 1999 some important tracer experiments have been performed after the chemical spill accident by Sandoz in 1986 in order to quantify the transport velocity and the longitudinal dispersion of dissolved substances in the river Rhine from the German-Swiss to the German-Dutch border (Steinebach and Hanisch 1991, DVWK-Arbeitskreis 1987). The evaluation of the tracer experiments provides reliable data on the residence time within different river portions and the longitudinal dispersion, which, however is only relevant for resuspension processes with short duration of approximately a few hours.

Opposite to contaminants which are released from industrial plants or municipal wastewater treatment plants or other drainage systems, historically deposited contaminants in river are likely to be resuspended by larger flood events with a duration of several hours or even days. The longitudinal profile of resuspended particulate contaminants depends on the spatial averaged erosion rate at the contaminated site as a function of the local bed shear stress and the erodibility of deposited sediment layers. If the local erosion rate averaged over the total contaminated side is approximately considered proportional to the second to third power of the discharge, the resulting concentration of resuspended particulate contaminants could be estimated. In addition to that, the assumption of the duration of the erosion process of several hours or even days leads to the conclusion that dispersion can be neglected. Consequently, the initial concentration at the contaminated side varies only due to the influence of tributaries, sedimentation processes on inundated areas or erosion in near bank groyne fields. The present data set, however does not allow the evaluation and interpretation of flood induced resuspension of historical contaminants in most of the river Rhine tributaries.

The driving force for erosion, transport and sedimentation is the discharge and hence, the risk for the port of Rotterdam must be related to the hydrological risk. This allows to investigate the impact of relevant discharge scenarios and to attribute a hydrological probability. In addition, the spatial variability and uncertainty of the sediment data must be taken into account, e.g. by applying the Monte Carlo method to come up with statistical model results, i.e. expected values and variance for the residual pollutant load and concentration at the port, the residence time and exposure duration etc. (Li, 2004) to be used for the final toxicological assessment in terms of CTT. Erosion and sedimentation, transport and mixing, residence time, sorption and 1-st order degradation can be approached by the basic model assumptions like COSMOS (Kern 1997). To account for specific river morphology a hierarchical model can be applied consisting of a 2-dimensional model with high spatial and temporal resolution (CTM-SUBIEFF-2D; Jacoub 2004), which can be coupled or nested, in a 1-dimensional model (COSMOS) which allows long term simulation for future exposure and environmental impact assessment very efficiently.

1.3. Mobilization of Sediment-Associated Contaminants

The concern associated with the chemicals sorbed to sediments is that many commercial species and food-chain organisms spend a major portion of their life-cycle living in or on aquatic sediments. This provides a pathway for these chemicals to be consumed by higher aquatic or terrestrial life and wildlife, as well as human. Direct transfer of chemicals from soils and sediments to organisms is now considered to be a major route of exposure for many species (Adams et al., 1992) (see section 1.4).

Due to the capacity of sediments to store and immobilize toxic chemicals in so-called "chemical sinks", direct effects of pollution may not be directly manifested. This positive function of sediments does not guarantee, however, that the chemicals are safely stored forever. Factors influencing the storage capacity of sediments or the bioavailability of the stored chemical can change and indirectly cause

sudden and often unexpected mobilization of chemicals in the environment (Stigliani 1988). Therefore, at first, it is imperative to know what sediment properties will control the toxicity levels of a chemical, and how sensitive the chemical toxicity is to changes in these properties; secondly, the relevance of a sediment property to significant release of sediment-associated pollutant depends on how this property is affected by long-term environmental changes, e.g., socioeconomic or climatic changes (Hesterberg et al., 1992).

Solubility, mobility, and bioavailability of sediment-bound metals can be increased by four major factors in terrestrial and aquatic environments (Förstner and Salomons 2004):

- lowering of pH, locally from mining effluents (Salomons and Förstner 1988), regionally from acid precipitation (examples from Rhine catchment area: Stigliani and Jaffe 1993; Stigliani et al. 1994, Stigliani 1995);
- increasing salt concentrations, by the effect of competition on sorption sites on solid surfaces and by the formation of soluble chloro-complexes with some trace metals (Salomons and Mook 1980);
- increasing occurrence of natural and synthetic complexing agents (DTPA, EDTA, NTA), which can form soluble metal complexes with trace metals that are otherwise adsorbed to solid matter (Salomons 1983); and
- changing redox conditions, e.g., after land deposition of contaminated anoxic dredged materials (Maass et al. 1985).

A typical combined effect of mechanical erosion and chemical changes – involving large scale mobilization of toxic metals – is the case of sulfide oxidation: Metal sulfides in sediment depots have an extremely low solubility and concentrations of metals in pore waters of sediments are generally low. However, an increase in the redox potential will cause metal sulfides to become unstable; this change is not gradual but rather sudden and an example of a non-linear response. This change occurs when contaminated anoxic sediments are resuspended by natural erosion processes or are dredged from ports and relocated either on land or in waterways (overview: Förstner 1995; experimental: Fengler et al. 1999).

1.4. Availability of Contaminants from Sediment and Suspended Material to Organisms

Bioavailability will be defined here as the extent to which a contaminant in a source is free for uptake (Newman and Jargoe, 1994). It is important in this context not only with regard to ecotoxicological test systems that are discussed as part of the sediment categorization in the Port of Rotterdam, but also with regard to persistence and ecological risk – both of which determine the importance that contaminant concentrations have for sediment managers now and with regard to future target levels.

Bioavailability – Limitations and Empirical Relationships (Dickson et al., 1994)

Since the form in which a compound or element occurs can effect the exposure, and thus toxicity, accurate estimates of the effects of toxicants and nutrients require a knowledge of both the short-term and long-term exposure, which is a function, in part, of bioavailability. However, speciation or bioavailability is seldom used in decision-making. There are several reasons for this, some of which can be addressed with additional information and understanding, while others cannot. The utility of bioavailability in decision-making is limited by the fact that there is little uniformity in the operational techniques used to measure bioavailability.

Environmental scientists have developed and used a number of empirical relationships to guide decision making regarding the fate and effects of organic and inorganic chemicals in the aquatic environment. These empirical relationships have been developed using scientific judgement and field and laboratory data. Examples of some of these relationships that have been used follow:

- The relationship between body residue, fat content, and the octanol:water partition coefficient,
- water hardness adjustments for metal toxicity, and
- pH effects on metal bioavailability.

Table 1.2 summarizes some of the more empirical relationships with their understanding of mechanisms, uses, problems or exceptions, and research needs.

Table 1.2 Examples for Empirical Relationships in Bioavailability (Dickson et al., 1994)

Empirical relationship	Understanding of mechanism	Use(s)	Problems or exceptions	Research needs
K_{oc} partitioning describes interactions with sediment and water	Good	Estimate exposure concentrations	All organic carbon not equal	Define sorption/desorption kinetics and add classes of compounds
Free metal ion controls bioavailability	Poor	Predictive	Ion pair small organic ligands	Activity should be used instead of concentration
Photochemical, redox, hydrolysis processes generally detoxify organic chemical	Limited	Regulation, EPA requires product studies across all species	Some	Compilation of compound that are photochemically active
Activities should be used instead of concentrations	Good	Used in research and modeling	Some	Availability of activity coefficients for organics
All metals cycle with Fe and Mn	Good	Prediction	Not always correct	Better empirical data needed
AVS control metal availability in sediments	Good	Prediction potential regulations	No evidence from intact sediments	Better empirical data needed

The bioavailability of inorganic contaminants in sediments and suspended matter is difficult to predict precisely. However, some general rules and processes do emerge from the literature with regard to the following processes: Uptake of contaminants, biotransformation, bioaccumulation and biomagnification.

The solid-phase concentrations influence bioavailability by dictating the concentrations in the interstitial waters surrounding the biota, by direct ingestion of solids by benthic species and by offering a reactive space for microbial enzymatic activity.

With regard to heavy metals, risks that are calculated on the basis of total heavy metal concentrations mostly overestimate the occurring effects because their bioavailability or toxicity is strongly correlated with the free-metal-concentration. And this is reduced by a number of adsorption processes under oxic and anoxic conditions in sediment: In oxic sediments, iron- and manganese oxides adsorb arsenic, cobalt, copper, lead and zinc. Organic compounds reduce the availability of Cu(II), Hg(II), Pb(II) and Zn(II) even further. The insoluble sulphide-complexes with heavy metals that are formed in anoxic sediments can diminish the toxicity of Cd(II) or Ni(II) if the sulphide concentration is sufficient. This is in accordance with the “free-ion activity model” (FIAM), which describes “the universal importance of free metal ion activities in determining the uptake, nutrition and toxicity of all cationic trace metals” (Campbell and Tessier, 1996). However, there are known exceptions to the FIAM or its derivative, the Biotic Ligand Model, such as passive diffusion of neutral lipophilic species (e.g. $\text{Hg}(\text{Cl})_2^0$) through membranes, accidental transport of metals as complexes with assimilable ligands and the formation of ternary complexes at the cell surface, which can alter the bioavailability significantly. Experiments have shown anomalously high metal toxicity in the presence of two common low molecular weight metabolites (citrate and alanine) or in the presence of an assimilable anion (thiosulphate) (Campbell, 2001).

So bioavailability of heavy metals remains to be difficult to assess on a routinely basis. Partial or sequential extractions, which are thought to grossly separate particular metal-binding fractions of the solid sediments, have shown promising results in their correspondence with ecotoxicological responses. An application for routine sediment testing however is not in sight. Additionally the normally continuous denaturing of the original matrix during sequential extraction is a significant drawback to its reduced transferability to *in situ* conditions. Development and establishment of heavy metal specific ecotoxicological test systems, e.g. using biosensors, and coupled with solid phase extraction could be a good step forward – however, despite EU networks like SENSPOL, there is no experience with long-term application so far.

Bioavailability of organic compounds has been described with *structure-activity relationships* (SAR) that use molecular qualities of the organic compound to predict reactivity, e.g. bioavailability. If expressed quantitatively, SAR becomes *quantitative structure-activity relationship* (QSAR). Molecular qualities include the degree of lipophilicity, steric conformation, molecular volume, reactivity, etc. Most commonly used are measures of lipophilicity such as K_{ow} (n-octanol – water-partition-coefficient) (Mackay, 1982), water solubility, and K_{TW} (triolein-water partition coefficient). Chiou used the K_{TW} in

order to better reflect partitioning between water and triglycerides in organisms (Chiou, 1985). In the simple K_{OW} approach, the organism is envisioned as a membrane-enveloped pool of emulsified lipids. Uptake and elimination are controlled by permeation of the membrane and/or permeation through aqueous phases with the predominant process being dictated by the qualities of the specific compound in question. While among $\log K_{OW}$ values of 3 to 6, uptake from the water phase increases linearly with K_{OW} - controlled by membrane permeation – bioavailability to benthic species usually decreases with increasing $\log K_{OW}$ as the non-polar organic compounds show enhanced partitioning to the solid phases, especially if these have an organic layer. Above a K_{OW} of 6, any uptake slows, as the large molecular size of the most-lipophilic compounds begins to impede diffusion in the aqueous phase of the organism (Connell and Hawker, 1988).

Other factors that influence toxicity of organic compounds are biodegradation processes and the pH-dependent transformation of ionisable contaminants. These become especially important during passage of intestinal tracts and in biofilms, where microorganisms control the pH of the environment.

Bioavailability for microbial degradation is determined by the rate of mass transfer to microbial cells relative to their catabolic activity. Bacteria have been shown to actively enhance bioavailability by:

- approaching the source of the compound, adhering to the surface and/or changing the hydrophobicity of the cell surface;
- changing their specific affinity to the compound (e.g. by switching the membrane-bound uptake systems);
- by producing detergents that increase solubility of the substance and allow a reduction of the distance to the organic compound (Wick et al., 2001).

1.5. Processes Related to Remediation Measures on Contaminated Sediments

As shown from the examples of large-mass wastes dredged material, mining residues and municipal solid waste, long-term immobilization of critical pollutants can be achieved by promoting less soluble chemical phases, i.e., by thermal and chemical treatment, or by providing respective environmental conditions. Selection of appropriate environmental conditions predominantly influence the geochemical gradients, whereas chemical additives are aimed to enhance capacity controlling properties in order to bind (or degrade!) micropollutants. In general, micro-scale methods, e.g., formation of mineral precipitates in the pore space of a sediment waste body, will be employed rather than using large-scale enclosure systems such as clay covers or wall constructions. A common feature of geochemically designed deposits, therefore, is their tendency to increase overall stability in time, due to the formation of more stable minerals and closure of pores, thereby reducing water permeation (Bambauer and Pöllmann 1998).

1.5.1. Risk Reduction by Ageing Processes

Initial findings from soil studies were that as the residence time of organic compounds such as phenanthrene in soil increases, they become increasingly unavailable to microorganisms and resistant to mild extraction (Hatzinger and Alexander 1995). Part of these effects may be related to specific geosorbents such as combustion residue particulate carbon (e.g., chars, soot, and ashes) that exhibit typical non-linear, hysteric sorption behaviour for organic and inorganic substances (Luthy et al. 1997). Preferential sorption of planar contaminants, such as chlorobenzenes and PAH on sootlike material has been found in sediments from Lake Ketelmeer, The Netherlands (Jonker and Smedes 2000). Investigations by Karapanagioti and Sabatini (2000) on organic matter from samples taken from different depths and locations in an alluvial aquifer demonstrated that opaque organic matter fractions dominate the sorption process and that quantifying this fraction alone can virtually predict the sample K_{OC} value.

For inorganic compounds, mainly heavy metals and arsenic, the effect of ageing mainly comprises enhanced retention via processes such as sorption, precipitation, co-precipitation, occlusion and incorporation in reservoir minerals (Salomons 1980, Förstner and Schoer 1984). In practice, non-destructive, "intrinsic" bonding mechanisms and their temporal development have so far found much less recognition compared to destructive processes such as biological degradation (Förstner and Gerth 2001). Nevertheless, these so-called "diagenetic" effects, which apart from chemical processes involve an enhanced mechanical consolidation of soil and sediment components by compaction, loss of water and mineral precipitations in the pore space, may induce a quite essential reduction of the reactivity of solid matrices (Table 1.3).

Table 1.3 Demobilization of Pollutants in Solid Matrices by Natural Factors (Förstner 2003)

Cause (Example)	Effect
Compaction	<i>Reduction of Matrix...</i>
Consolidation	Erodibility
Phytostabilization (Plant Roots)	Permeability
Penetration into Dead-End-Pores	Reactivity
Interlayer Collapse of Clay Minerals	<i>Reduced Pollutant...</i>
Co-precipitation (High-Energy-Sites)	Mobility
Occlusion and Over-coating	Availability
Absorption/Diffusion	Toxicity
"Diagenesis"	"Natural Attenuation"

Natural attenuation and ageing effects will characteristically influence the use of equilibrium partitioning models in developing sediment quality criteria (SQC) from final chronic value (FCV) water quality criteria. The example in Fig. 1.2 (Chen et al. 2000) indicates that the SQC of 1,4-dichloro-

benzene would be nearly 2 orders of magnitude less strict when the process of irreversible adsorption on the resistant fraction in sediment is taken into account.

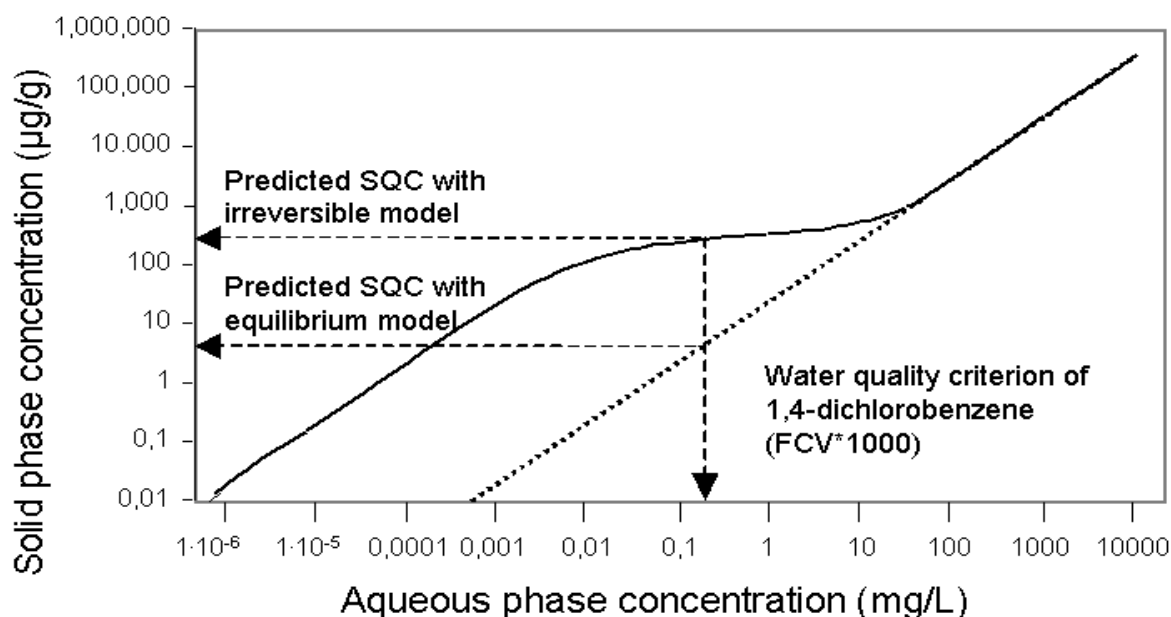


Figure 1.2 Implication of irreversible adsorption on sediment quality criteria (after Chen et al. 2000)

Geochemical influences on assimilation of sediment-bound metals have been evaluated by Griscom et al. (2000) in a series of experiments using suspension-feeding mussel *Mytilus edulis* and facultative deposit feeder *Macoma balthica*. Oxidized and reduced radiolabeled sediments were fed to the animals and the assimilation efficiencies (AEs) of ingested metals were determined. For oxic sediment, Cd and Co AEs in *M. edulis* decreased 3-4-fold with increased sediment exposure time to the metals with smaller but significant effect also noted for Zn and Se but not Ag. Sequential extractions of the oxidized sediments showed a transfer of metals into more resistant sediment components over time, but the rate did not correlate with a decrease in metal assimilation efficiencies. The results imply that metals associated with sulfides and anoxic sediments are bioavailable and that the bioavailability of metals from sediments decreases over exposure time.

1.5.2. Enhanced In-Situ Stabilization based on Natural Processes

Until now quantitative data of the effects of ageing and natural attenuation on sediment and pollutant stability are scarce and the conceptual basis of practical applications has still to be developed. However, it is quite obvious that any problem solution strategy in situations, where traditional remediation procedures become economically unacceptable, either due to the large volume of dredged material or because sediment-bound contaminants are dispersed in a hardly predictable manner, has to be based on natural processes, that simultaneously consider both the chemical demobilization and the reduction of mechanical erodibility.

In such cases the concept of “geochemical engineering” (Salomons and Förstner 1988) can provide both cost-effective and durable solutions. The latter are defined in terms of capacity controlling parameters, such as redox and pH buffers (Salomons 1995). Geochemical engineering applies geochemical principles such as stabilization, solidification, and other forms of long-term, self-containing barriers to determine the mobilization and biological availability of critical contaminants.

Recent developments in the Netherlands in “soft” (geochemical and biological) techniques on contaminated soils and sediments, both with respect to policy aspects as to technical developments have led to a stimulation of in-situ remediation options: (i) no longer remediation actions have to be executed within a very short period of time, (ii) the result is not necessarily a “multifunctional soil”, and (iii) advantage is taken of natural processes (the self-cleaning capacity of the soil). In Table 1.4 a number of potentially relevant options for metals are summarized: Phytoremediation, for instance degradation of contaminants near plant roots, may be beneficial in certain cases. As to the immobilization of contaminants by adsorption one can think of applying clay screens, or clay layers (with or without additives). The advective dispersion of contaminants toward ground water or surface water can be reduced by capping the contaminated sediment with a clay layer, with organic matter (humus) or other materials as possible additives.

Table 1.4 Selected options for in-situ sediment remediation (after Joziassse and Van der Gun 2000; the original version comprises more than 20 technological concepts)

Remediation type	Scope (type of contaminants)	Technological concept	Technological implementation
Fixation of contaminants (sorption/immobilisation)	Metals	Precipitation of metals as hydroxides or insoluble complexes	Precipitation or adsorption at plant roots (phytostabilisation)
Reduction of advective dispersion towards surface waters	All contaminants	Reduction of bank erosion/wash out	Introduction of plants
Reduction of dispersion towards ground water	All contaminants	Increased hydrological resistance	Application of a clay screen

It is stressed by Joziassse and Van der Gun (2000) that for every single case the effects of the actions (either dredging, or in-situ) on the aquatic ecosystem will have to be accounted for. In concrete cases, where a conventional approach encounters serious difficulties, an investigation dedicated to the prevailing conditions will have to give a judgement on the feasibility of an alternative approach.

1.5.3. Processes Underlying Conventional Treatment Techniques

Sediment remediation methods can be subdivided according to the mode of handling (e.g. in-place or excavation), or to the technologies used (containment or treatment). Important containment techniques include capping *in situ* and confined disposal. Biological processes may be applied with in-place-

treatment. Excavated sediments – apart from physical separation – can be treated to immobilize contaminants, mainly metals (Table 1.5).

Table 1.5 Technology types for sediment remediation (Anonymous 1994)

	In Place	Excavated
Containment	in situ-capping	confined aquatic disposal/capping
	contain/fill	land disposal
		beneficial use
Treatment	bioremediation	physical separation
	immobilization	chemical extraction
	chemical treatment	biological treatment
		immobilization
		thermal treatment

A general conceptual scheme related to excavated sediment material has first been proposed by TNO, the Netherlands scientific technological organization (Van Gemert et al. 1988). "A-" and "B-" techniques are distinguished: "A" is for large-scale concentration techniques like mechanical separation; these techniques are characterized by low costs per unit of residue, low sensitivity to variations, and they may be applied in mobile plants. "B"-techniques are decontamination procedures, which are especially designed for relatively small scale operations. They involve higher operating costs per unit of residue, are more complicated, need specific experience of the operators and are usually constructed as stationary plants. "B"-techniques include biological treatment, acid leaching, solvent extraction, and so on.

Classification of Dredged Material

As an example of "A"-techniques, the classification of harbour sediment from Hamburg is described (Detzner et al. 1993). In March of 1993, the first large-scale plant for treatment of sediments, known as METHA (mechanical separation of harbour sediments), commenced operation in the Port of Hamburg. This plant processes dredged material amounting to an annual quantity of approx. 2 million m³ for accommodation as filling material. The process for separation and dewatering of harbour sediments was systematically developed from initial laboratory tests followed by a pilote phase and then on an industrial scale. Contaminants such as heavy metals and organic contaminants contained in the sediments are separated as fine fractions and dewatered to such an extent that they can be stored on a sealed land disposal site.

The core of this technique is the combination of hydrocyclonage and elutriator as designed by Werther (1988). In the hydrocyclone the separation of the coarse fraction (relative clean sand) from the highly contaminated fine fraction is effected by the action of centrifugal forces. The coarse fraction leaves the cyclone in the underflow, while the fine fraction is contained in the overflow. The advantage of the hydrocyclone is its simplicity and its ability to handle large throughputs; a disadvantage is that the sharpness of the separation is fairly low. The elutriator, which follows in the classification scheme, effects a much better sharpness of separation.

Solidification/Stabilization

In general, solidification/stabilization technology is considered a last approach to the management of hazardous wastes. The aim of these techniques is a stronger fixation of contaminants to reduce the emission rate to the biosphere and to retard exchange processes. Most of the stabilization techniques aimed for the immobilization of metal-containing wastes are based on additions of cement, water glass (alkali silicate), coal fly ash, lime or gypsum (Goumans et al. 1991).

Laboratory studies on the evaluation and efficiency of stabilization processes on harbor sediments from Hamburg were performed by Calmano et al. (1986). Best results are attained with calcium carbonate, since the pH-conditions are not changed significantly upon addition of CaCO_3 . Generally, maintenance of a pH of neutrality or slightly beyond favors adsorption or precipitation of soluble metals (Gambrell et al., 1983). On the other hand it can be expected that both low and high pH-values will have unfavorable effects on the mobility of heavy metals.

Several factors negatively interfere with the objective to solidify or stabilize: Organic compounds, oil and grease, inorganic salts such as nitrates, sulfates and chlorides, small particles sizes, volatile organic compounds and low solids content.

Solvent Extraction

The primary application of solvent extraction is to remove organic contaminants such as halogenated compounds and petroleum hydrocarbons (Anonymous 1988). Extraction processes may also be used to extract metals, but these applications, which usually involve acid extraction, have not proven to be cost effective for contaminated sediments. Fine grained materials are more difficult to extract, and presence of detergents adversely impacts oil/water separation. The procedure is less effective for high molecular weight compounds and very hydrophobic substances. In any case, careful selection of reagents and laboratory testing is required.

Biodegradation and biore Restoration

Biological treatment has been used for decades to treat domestic and industrial wastewater, and in recent years has been demonstrated as a technology for destroying some organic compounds in contaminated soils. Bioremediation or biore Restoration may be applied in certain cases to organically contaminated sediments. However, since in large catchment areas contamination with only organic

compounds is rare, the expectations in this technique of remediation seem to be overestimated. Even in optimal cases, there are many limitations to biodegradation processes: Temperature, nutrients, oxygen, are the most important ones.

Bioremediation and other advanced techniques have been studied in the Dutch POSW Program, which is reviewed in more detail in the section 3.2.1.

Likelihood of Success, Costs

Remediation techniques on contaminated sediments are generally much more limited than for most other solid waste materials, except for mine wastes. The widely diverse contamination sources in larger catchment areas usually produce a mixture of contaminants, which is more difficult to treat than an industrial waste. For most sediments from maintenance dredging, there are more arguments in favor of "disposal" rather than "treatment". Mechanical separation of less strongly contaminated fractions, however, may be an useful step prior to final storage of the residues.

Similar to the experience in soil remediation, the initial hope that physical-chemical treatment would find a considerable market has not been realised for these materials. The only wide-spread application are the methods of separation according to grain size, but even with the positive effects of processing – less storage space needed, saving on the extraction of primary materials – the processing itself has negative side-effects (Rulkens 2001): The separation of sand is energy-consuming and requires water to dilute the input. The water is recycled during the process, but any surplus will have to be treated, either locally or in a purification plant elsewhere.

Cost estimations for decontamination techniques cover wide range for individual examples from the fields of bioremediation, chemical dechlorination, soil washing, solvent extraction, thermal desorption and vitrification (Anonymous 1994). These are mostly well-known examples from industrial waste technology. Typical cost factors for sediments include water quantity, moisture contents, physical and chemical characteristics (for example, grain size and organic material content).

In the centre of today's sediment management there is a science-based technology for the final storage of sediments – called 'sub-aquatic depot'. The EU Landfill Directive does not refer to waste disposal below the groundwater level, and here the two most promising conditions for a sediment depot can be found: (i) a permanent anoxic environment to guarantee extremely low solubility of metals, (ii) base layers of compacted fine-grained sediments which prevent the advective transport of contaminants to the groundwater (see Box on page 23). Together with advanced geochemical and transport modelling, such deposits offer the most cost-effective and sustainable problem solutions for dredged sediments. In the convoy of this technology – flagship is the Dutch 'Slufter' depot – innovative sediment-specific applications are developing, for example, techniques for active capping to safeguard both depot and in-situ contamination against pollutant release into the surface water.

In section 3.5.2. the contents of the DEPOTEC report on sub-aquatic depots in the Netherlands will be outlined.

Processes Controlling the Pollutants Mobility in Sub-Aquatic Depots of Dredged Material

Since the late 70s there is a controversy regarding the various containment strategies. Some experts have argued that upland containment (e.g., on heap-like deposits) could provide a more controlled management than, for example, containment in the marine environment; others have inferred, that contaminants released either gradually from an imperfect impermeable barrier (also to groundwater) or catastrophically from failure of the barrier could produce substantial damage.

In an early review of various marine relocation options, Kester et al. (1983) suggested that the best strategy for disposing off contaminated sediments is to isolate them in a permanently reducing environment. Disposal in capped mound deposits above the prevailing sea-floor, disposal in sub-aqueous depressions and capping deposits in depressions provide procedures for contaminated sediment (Bokuniewicz 1983). In some instances it may be worthwhile to excavate a depression for the disposal site of contaminated sediment which can be capped with clean sediment. This type of waste deposition under stable anoxic conditions, where large masses of contaminated materials are covered with inert sediment became known as "sub-aquatic deposit".

Under these conditions there is a particular low solubility of metal sulfides, compared to the respective carbonate, phosphate and oxide compounds. One major prerequisite is the microbial reduction of sulfate. Thus, this process is particularly important in the marine environment, whereas in anoxic freshwaters environment there is a tendency for enhancing metal mobility due to the formation of stable complexes with ligands from decomposing organic matter. Marine sulfidic conditions, in addition, seem to repress the formation of mono-methyl mercury, one of the most toxic substances in the aquatic environment, by a process of disproportionation into volatile dimethyl mercury and insoluble mercury sulfide (Craig and Moreton 1984). There are indications that degradation of highly toxic chlorinated hydrocarbons is enhanced in the sulfidic environment relative to oxic conditions (Kersten 1988).

Contaminants may propagate in two different modes: (1) by advective transport, e.g., dispersion of dissolved or particle-bound pollutants in the groundwater or surface water flow; (2) by diffuse transport, e.g., by transport of pollutants from a zone of high concentration into a zone of low concentration ("tea bag in warm water"). According to initial estimates on sediment depots like the Dutch Slufter the major transfer route of pollutants into the groundwater was expected from the squeezing out of porewater at the bottom of the depot during compaction and consolidation. However, measurements of water and soil tensions in the Slufter depot have shown that the permeability of the base layer of already consolidated dredged material is so small, that the compaction water cannot become squeezed out. In addition, the measurements at the Slufter depot indicate, that the hydraulic resistance of the whole depot 10 years after the start of filling has increased to 1.000.000 days. This means, that the potential porewater release and transfer into the groundwater as derived from model calculations has been overestimated (Anonymous 1998; Kamerling 1999; Anonymous 2002).

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2. Requirements on Sediment Data Quality

The present inventory of historical contaminated sediment in the Rhine basin and its tributaries uses a wide spectrum of already existing data of different origin and for different purposes. Such data represent a great source of potentially valuable information; however, the quality of data available can be quite variable. This chapter starts with an allocation of the present inventory within the different strategies for water quality assessment (2.1) and with an overview of quality control and quality assurance issues in water and sediment investigations (2.2); the subsequent sections 2.3, 2.4, and 2.5 deal with quality requirements in relation to chemical, biological and hydraulic sediment data, respectively, as used in the present study.

2.1. Strategies for Water Quality Assessment: Particulate Matter¹

The main reason for the assessment of the quality of the aquatic environment has been, traditionally, the need to verify whether the observed water quality is suitable for intended uses. The use of “monitoring” – in the wider sense – has also evolved to determine trends in the quality of the aquatic environment and how it is affected by the release of contaminants.

2.1.1. Types of Assessment Programmes

The implementation of the assessment programme objectives may focus on the spatial distribution of quality (great number of stations), on trends (high frequency of sampling) or on pollutants (in-depth inventories). Full coverage of all three requirements is virtually impossible, or very costly². Table 2.1 summarizes some common types of water quality assessments in relation to their main objectives.

In the past, many countries or water authorities have installed multi-purpose or multi-objective monitoring programmes without conducting the necessary preliminary surveys. Critical scrutiny of results after several years of operation has led to a second generation of programmes with more differentiated objectives such as impact assessment, trend analysis or operational management decisions.

2.1.2. Water Quality Assessment using Particulate Matter Data

Three principal media can be used for aquatic monitoring: water, particulate matter and living organisms. With respect to particulate matter, the preferred medium of the present study, characteristics have been noted such as: (1) good specificity to a given pollutant, (2) high sensitivity to low levels of

¹ Based on the UNESCO/WHO/UNEP Guidebook “Water Quality Assessment” edited by Deborah Chapman (1992), Chapter 2 on “Strategies for Water Quality Assessment” (Meybeck et al.) and Chapter 4 on “The Use of Particulate Material” (Thomas and Meybeck)

² Consequently preliminary surveys are used to determine the necessary focus of an operational programme

pollution, (3) medium to low sample contamination risk, (4) short (suspended matter) or long to very long (deposited sediment) time span, respectively of information obtained.

Table 2.1 Objectives and aims of water quality assessment operations (Meybeck et al. 1992)

Type of assessment		Major focus of water quality assessment
Common assessments		
1	Multipurpose monitoring	Space and time distribution of water quality in general
2	Trend monitoring	Long term evolution of pollution (concentrations and loads)
3	Basic survey	Identification and location of major survey problems and their spatial distribution
4	Operational surveillance	Water quality for specific uses and related water quality descriptors (variables)
Occasional assessments		
5	Background monitoring	Background levels for studying natural processes; used as reference point for pollution and impact assessments
6	Preliminary survey	Inventory of pollutants and their space and time variability prior to monitoring programme design
7	Emergency surveys	Rapid inventory and analysis of pollutants, rapid situation assessment following a catastrophic event
8	Impact surveys	Sampling limited in time and space, generally focusing on few variables, near pollution sources
9	Modelling surveys	Intensive water quality assessment limited in time and space and choice of variables, for example, eutrophication models or oxygen balance models
10	Early warning surveillance	At critical water use locations such as major drinking water intakes or fisheries; continuous and sensitive measurements

The objectives of an assessment programme for particulate matter quality can be (Thomas and Meybeck 1992):

- to assess the present concentrations of substances including pollutants found in the particulate matter and their variations in time and in space (*basic surveys*), particularly when pollution cannot be accurately and definitely shown from water analysis;
- to estimate past pollution levels and events (e.g., for the last 100 years) from the analysis of deposited sediments (*environmental archive*);
- to determine the direct or potential bioavailability of substances or pollutants during the transport of particulate matter through rivers and reservoirs (*bioavailability assessment*);
- to determine the fluxes of substances and pollutants to major water bodies (i.e., regional seas, oceans)(*flux monitoring*); and
- to establish the trends in concentrations and fluxes of substances and pollutants (*trend monitoring*).

Natural sediment formed during weathering processes may be modified quite markedly during transportation and deposition by chemicals of anthropogenic origin. Major point or diffuse sources of pollutants to sediments are summarized in Figure 2-1. Firstly, it must be noted that anthropogenic chemicals may be scavenged by fine sediment particles at any point from their origin to the final sink or their deposition. Secondly, to compute a geochemical mass balance for sediment-associated elements, it is imperative to derive, by measurement, a mass balance for the sediment in the system under evaluation (section 2.5).

To establish background levels of particulate matter composition, samples of bottom sediment should be taken in the upper reaches of the river basin. The effects of tributaries on the main river should be covered by sampling tributaries close to their junction with the main river. In practice different levels of monitoring sophistication can be distinguished (Table 2-2).

Table 2.2 Development of particulate matter quality assessment in rivers in relation to increasing levels of monitoring sophistication (after Thomas and Meybeck, 1992)

Monitoring level			
	A	B	C
Suspended matter (SPM)	Survey of SPM quantity throughout flood stage (mostly when rising)	Survey of SPM quality at high flow (filtration or concentration)	Full cover of SPM quality throughout flood stage
Deposited sediment	Grab sample at station (end of low flow period)	Longitudinal profiles of grab samples (end of low flow period)	Cores at selected sites where continuous sedimentation may have occurred

Level A: simple monitoring, no requirement for special field and laboratory equipment

Level B: more advanced monitoring requiring special equipment and more manpower

Level C: specialised monitoring which can only be undertaken by fully trained and equipped teams of personal

2.1.3. Strategy of the Present Study

In terms of the objectives and aims of water quality assessment operations (Table 2-1), the present study is (i) a basic survey, aiming to identify the spatial distribution of a number of point sources ("historical contaminated sediment") in the catchment area of the Rhine river, (ii) a [virtual] trend monitoring, performing a computational prognosis on the temporal changes of the contaminant input into the sediment of the port of Rotterdam, and (iii) an impact assessment in relation to the potential adverse effects on the target ecosystem, e.g. in the Port of Rotterdam and subsequent receiving systems for the Rotterdam water and particulate matter.

The use of particulate matter as an assessment medium has several advantages, at least compared to the water phase, mainly due to the high sensitivity to low levels of pollution and the medium to low sample contamination risk (section 2.1.2). However, considering the complex system of a large river basin and the novelty of the present approach, a closer look is necessary both with respect to state-of-the-art of quality control and quality assurance in these water quality assessment procedures

(section 2.2) and specifically to quality requirements in relation to chemical, biological and hydraulic sediment data (2.3-2.5).

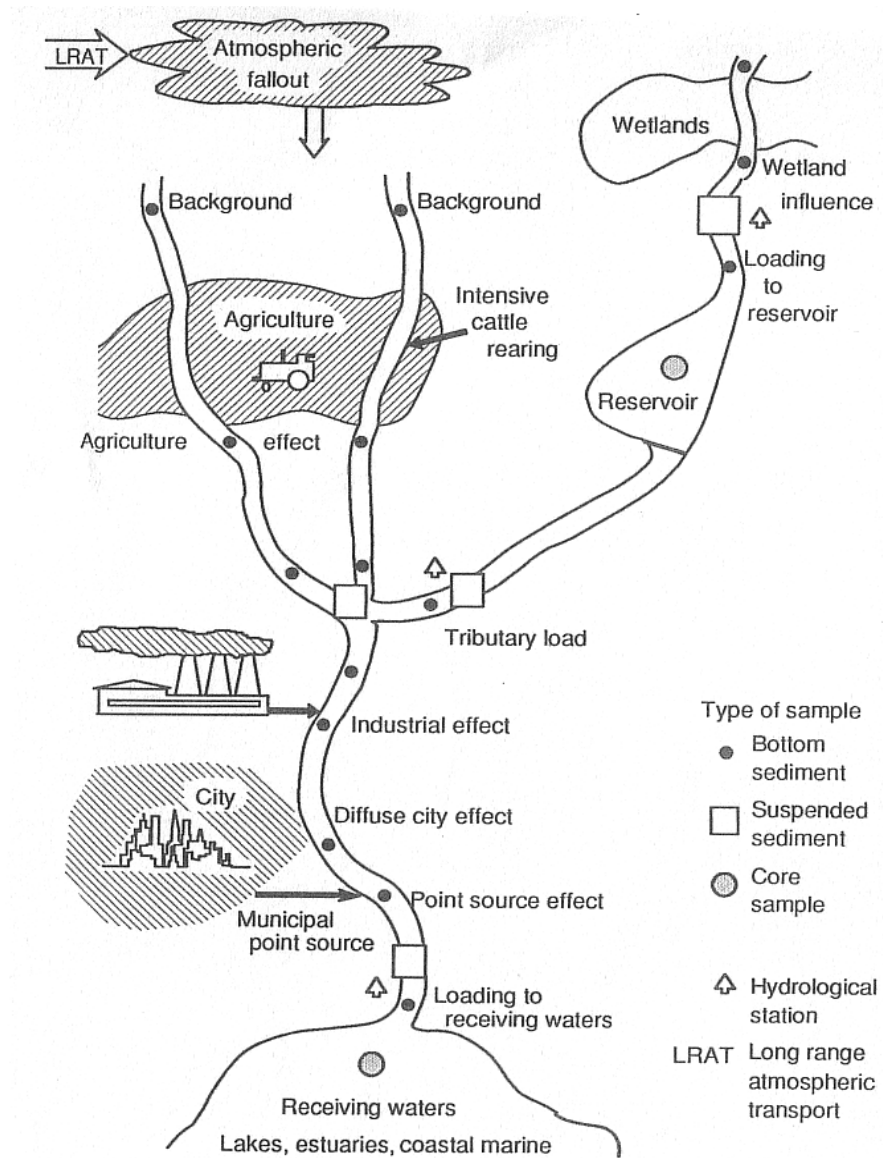


Figure 2.1 Sources of pollutants to sediments and the associated appropriate sampling operations for surveys of particulate pollutants (Thomas and Meybeck, 1992)

The present study is a typical example in the new way of thinking in terms of river basin scale, where sediment quantity can be critical in creating risk and determining management options. The flow of sediments, whether clean or contaminated, can impact the relative risk, quality or potential utility of downstream sites. The Conceptual Basin Model for such risk assessment, as presented by Apitz and White (2003), balances the mass flow of particles and contaminants, screening level assessment of sediment quality data, and base-scale objectives, e.g., for source control (local historical, remote historical, active point sources, quasi-diffuse sources, non-point sources). However, no indication has been given so far what type of data are needed and how to combine the various sets of quality and quantity data.

2.2. Quality Control of Field and Laboratory Chemical Data

2.2.1. Quality Control and Quality Assurance in Water and Sediment Monitoring Data

Data quality control is a complex and time-consuming activity which must be undertaken continuously to ensure meaningful water quality assessments. Errors can occur in many operations of the assessment process as indicated in Table 2-3.

Experts agree that 10 to 20 per cent of resources, including manpower, should be directed towards ensuring the quality of analytical determinations for common water quality variables (Anon. 1987). When trace pollutants (e.g., pesticides and trace elements) are measured, the resources required for quality control may reach 50 % (Meybeck et al. 1992). Regarding assessment strategies involving sampling and analysis of particulate matter, reference should be given to the quality-assurance project of the U.S. Geological Survey (Anonymous 1998).

In the framework of an integrated decision-making process, a systematic approach is needed starting with a critical examination to establish whether environmental measurements provide a suitable basis for monitoring and other assessment strategies. Major problem areas have been identified and discussed by the European thematic framework "Metropolis" (Metrology in Support of Precautionary Sciences and Sustainable Development Policies; Anon. 2004a):

- lack of harmonisation of the procedures applied by laboratories (starting with the sampling procedure, but also including the approach adopted for the calculation of the uncertainty); this lack of harmonisation makes the data obtained from different sources difficult to compare;
- lack of representativeness: data that do not reflect the reality that we want to represent are simply not fit for purpose;
- a too high level of uncertainty associated with the data collected makes the process of decision-making critical (on the other hand, in some cases the uncertainty is not expressed at all!);
- lack of metadata: information about the data (what, how and when measurements were made, who owns the data, etc.) and the way they are reported / used is an essential requirement to allow the use of the data for other purposes (e.g. compilation of databases);
- lack of traceability: The concept of traceability implies that measurement data are linked to stated references through an unbroken chain of comparison, all with stated uncertainties (Quevauviller 2004).

It is impossible to base decisions on data that are not sufficiently documented (not traceable to well established references and therefore not reliable). In section 3.3 the implications of the traceability concept for the quality control of chemical sediment analysis will be demonstrated with special reference to the objectives of the present study.

Table 2.3 Some possible sources of errors in the water quality assessment process with special reference to chemical methods (Meybeck et al. 1992)

Assessment step	Operation	Possible source of error	Appropriate actions
Monitoring design	Site selection	<ul style="list-style-type: none"> station not representative (e.g., poor mixing in rivers) 	Preliminary surveys
	Frequency determination	<ul style="list-style-type: none"> sample not representative (e.g., variations betw.samples) 	
Field operations	Sampling	<ul style="list-style-type: none"> sample contamination (micropollutant monitoring) 	Decontamination of sampling equipment, containers
	Filtration	<ul style="list-style-type: none"> contamination or loss 	Running field blanks
	Field measurement	<ul style="list-style-type: none"> uncalibrated operations (pH, conduct., temperature) inadequate understanding of hydrological regime 	Field calibrations Replicate sampling Hydrological survey
Sample shipments to Laboratory	Sample conservation and identification	<ul style="list-style-type: none"> error in chemical conservation 	Field spiking
		<ul style="list-style-type: none"> lack of cooling 	
		<ul style="list-style-type: none"> error in biological conservation 	Appropriate field
		<ul style="list-style-type: none"> error and loss of label 	Pre-treatment
Laboratory	Preconcentration	<ul style="list-style-type: none"> break of container 	Field operator training
		<ul style="list-style-type: none"> contamination or loss 	Decontamination of laboratory equipment and facilities
	Analysis	<ul style="list-style-type: none"> contamination 	Quality control of laboratory air, equipment and water
		<ul style="list-style-type: none"> lack of sensitivity 	Quality assurance tests
		<ul style="list-style-type: none"> lack of calibration 	(analysis of control sample or standards)
		<ul style="list-style-type: none"> error in data reports 	Check internal consistency of data (e.g., with adjacent sample, ionic balance etc.)

2.2.2. Quality Control in the Analysis and Monitoring of WFD-Priority Substances

Since the year 2000 any risk assessment in European waters will be made by the holistic river-basin approach of the Water Framework Directive (WFD) of the European Union (see overview in [Box](#) at page 33 after the concept paper on emission control of Expert Advisory Forum [EAF] from June 8, 2004). The chemical status of water bodies is to be assessed in terms of compliance with the Quality Standards (QSs) established in Annex IX, Article 16 of the Directive and under other relevant Community legislation setting Environmental Quality Standards (EQSs). WFD specifically requires (Article 8 and Annex V) that Quality Standards and related needs for analytical quality control (AQC) should be made according to a harmonised scheme for the analysis and monitoring of priority substances (AMPS).

Water Framework Directive (WFD) and Priority [Hazardous] Substances (PS/PHS)

Environmental objectives (WFD Article 4)

In relation to PS and PHS, the surface water section of **article 4(1)** WFD is most relevant:

- *"Member States shall implement the necessary measures ...with the aim of progressively reducing pollution from priority substances and ceasing or phasing out emissions, discharges and losses of priority hazardous substances".*

The combined approach of EQS and emission controls (WFD article 10)

The Water Framework Directive requires that a so called combined approach shall be applied to reach the environmental objectives. **Article 10(1)** requires that Member States

- *"ensure that all discharges [...] into surface waters are controlled according to the combined approach".*

The combined approach according to **articles 10(2) and 10(3)** means that Member States shall establish

- *"emission controls based on best available technique, relevant emission limit values or in the case of diffuse impacts the controls including, as appropriate, best environmental practice" and if quality objectives or quality standards "require stricter conditions than those which would result from paragraph 2, more stringent emission controls shall be set accordingly".*

Other requirements of the Water Framework Directive

Article 5 requires each Member State to undertake "a review of the impact of human activity on the status of surface waters". Annex II.1.4 specifies that this shall include an identification of pressures, that is *"the type and magnitude of the significant anthropogenic pressures"*. This shall include estimation and identification of "significant" point source and diffuse source pollution from *"urban, industrial, agricultural, and other installations and activities"*.

- In addition, **recital (43) of the WFD** requires to take account of *"all significant sources"*, when drawing up measures to be taken against pollution of water by substances considered for action as a priority. It is therefore important to carry out a sound and comprehensive source screening.

Strategies against pollution of water (WFD article 16)

Article 16 concerns strategies against chemical pollution of surface waters. **Article 16(1) and 16(6)** asks for specific measures against pollution of water to be adopted by the European Parliament and the Council upon the proposal of the Commission, of specific measures against pollution of water for:

- PS, aimed *"at the progressive reduction of discharges, emissions and losses"* and,
- PHS, aimed *"at the cessation or phasing-out of discharges, emissions and losses"*.

Progressive reduction of PS and cessation of PHS are not further qualified within the WFD. However, the progressive reduction should at least result in the achievement of good chemical status of surface waters.

Timetable of the WFD

- In **Article 16(6)** WFD it is specified that the timetable to achieve the objective for the cessation/-phase out of emissions, discharges and losses of **PHS** *"shall not exceed 20 years after the adoption of the proposals"* of the European Commission (on emission controls) by the European Parliament and the Council.

Initial steps for implementing measures under the WFD are:

- 2004 : first pressure and impact analysis (Article 5)
- 2006 : monitoring programmes to be operational (Article 8)
- 2009 : establishment of the programme of measures (Article 11)

Actually, the AMPS Expert Group under the Common Implementation Strategy (CIS) of the Water Framework Directive (Anonymous 2001, 2003) is preparing the WFD monitoring programme to be started in 2006. Water samples – which are proposed to form the centre of this monitoring programme – will be “whole water”, defined as “the water sample which is not subjected to phase separation, i.e. when solid matter and the liquid phase have not been separated”.

The WFD monitoring objectives require compliance checking with Environmental Quality Standards (EQS) but also the progressive reduction of pollution. The no-deterioration clause implies that trend studies should be foreseen for sediment and biota; this calls for further guidance under CIS, complementing the existing monitoring guidance. However, compliance monitoring for sediment is not yet appropriate because of lack of the definition of valid Environmental Quality Standards (EQSediment) in a European context, analytical limitations and anticipated costs involved to obtain full spatial coverage (see Box on next pages, AMPS 2004).

Sediment trend monitoring may be both spatial and temporal, and may be related to the chemical and ecological status of a water body. Sediment monitoring may also play a part in risk-assessment,

- in cases where the good-ecological-status/potential is not met or water quality is adversely affected by the bedded and/or resuspended sediment also in order to prioritise sites, where actions can take place and/or where monitoring should be intensified with respect to its effects along the river basin;
- to address the issue for sediments as potential carriers of long-lived bio-accumulative toxicants, bioavailability and combination toxicity;
- to assess the extent of organisms affected by sediments at less than “good ecological status” examined locations;
- to apply EDA (Effect Directed Analysis) to determine whether contaminants could be the causative factor and which these are..

It is still open to what level the various sediment monitoring approaches will become reality in the course of the WFD implementation process. A questionnaire on current practice in sediment monitoring circulated to EU Member States early 2004 revealed a wide range of different approaches; this may be because different programmes address different objectives but it mainly occurs in trend analysis – currently the primary objective of sediment monitoring – because the producers and users of data are reluctant to change the basic approach selected at the programme’s inception.

In principle, it has been recognized that harmonization of sediment monitoring is particularly relevant at a river basin level. Different objectives (trend monitoring, compliance monitoring, risk assessment and source control) will be involved and subsequently also different sampling strategies. However, technical issues such as sediment collection, sample treatment, sediment analysis and reporting results will have to follow a common level of quality requirements. An example is the application of the traceability concept (2.2.1) in chemical sediment analysis.

Spatial Monitoring

The present example of an “inventory of historical contaminated sediment in the Rhine basin and its tributaries” is a clear case requiring spatial monitoring. According to the drafting group of AMPS Expert Group spatial monitoring should provide an indication of the status of contamination over an area. Such monitoring is necessary to detect the horizontal spreading of a contaminant over a river basin, and possibly to locate its source. It will also provide basic information for appropriate sediment management. Historic contamination at hot spots is often reflected in the deeper sediment layers. Moreover, the spatial variation in sediment contamination is influenced by differences in sedimentation rate of newly formed particulate material as it influences the degree by which historic contamination is covered-up. Consequently, the choice of sediment sampling depth is therefore a critical issue in mapping the status of sediment quality. This type of sediment sampling and analysis can favourably be used in the determination of enrichment or concentration factors of typical environmental pollutants. The enrichment factor (EF) can be used to compare surface waters with different geochemical and deposition histories. It is a useful tool for geographical comparison between studies, since the ratio is insensitive to differences, e.g. in sediment focussing and sample digestion.

Metal Background Reference Concentrations (BRCs)

In the discussions on monitoring and implementation of measures for priority substances, an “added risk approach” has been proposed for metals, and a first step is the use of natural background concentrations. A respective AMPS working group has defined the background metal concentrations:

“The background concentrations of target metals (Pb, Cd, Ni, Hg) in the aquatic ecosystems of a river basin, river sub-basin or river basin management area is that concentration in the present or past corresponding to very low anthropogenic pressure.”

Various methodologies such as measurements of trace metals in pristine areas, groundwater, selection from long-term data sets applying appropriate statistical methodology, and long-term data sets and partitioning, are employed to provide estimates of the BC (AMPS draft final report, June 2004).

Study of Dated Sediment Cores

The study of dated sediment cores has proven particularly useful as it provides a historical record of the various influences on the aquatic system by indicating both the natural background levels and the man-induced accumulation of elements over an extended period of time. Marine and, in particular, lacustrine environments have the ideal conditions necessary for the incorporation and permanent fixing of metals and organic pollutants in sediments: reducing (anoxic) and non-turbulent environments, steady deposition, and the presence of suitable, fine-grained mineral particles for pollutant fixation. Various approaches to the dating of sedimentary profiles have been used but the isotopic techniques, using ^{210}Pb , ^{137}Cs and $^{239+240}\text{Pu}$, have produced the more unambiguous results and therefore have been the most successful (see review on “Historical Monitoring” by Alderton, 1985).

Analysis and Monitoring of Solid Matrices under the Water Framework Directive (Report of the Expert Group on Analysis and Monitoring of Priority Substances¹)

Sediment and biota

The aim of monitoring of sediment and biota is to assess compliance with the no deterioration objective of the Water Framework Directive and to assess the long-term impacts of anthropogenic activity. The monitoring of sediment and biota should take account of the aim of determining the extent and rate of change of levels of environmental contamination. Aspects of definitions of sediments and biota are dealt with in the reports produced by the corresponding expert drafting groups.

Relevant matrix

Article 16.7 of the WFD states that “the Commission shall submit proposals for quality standards applicable to the concentrations of the priority substances in surface waters, sediments or biota.” It has been noted that although Environmental Quality Standards (EQSs) are to be established for all substances in water, certain particularly hydrophobic substances may not be found in the liquid phase at significant concentrations. In such cases it may be more practical to address the question of EQS compliance via monitoring or assessment of SPM-bound concentration. Given this, the appropriateness of monitoring of a substance in different matrices, was discussed from the perspective of analysis and monitoring.

The AMPS Expert Group concluded that no specific requirements regarding which matrix (whole water, liquid or particulate phases) should be analysed could be made. This is because variations in individual circumstances, including the concentration and nature of SPM, preclude rigid categorisation. However, the Group did feel that it would be of value to provide guidance on the most relevant matrices for monitoring by giving an indication in which phase the chemical is most likely to be found.

Whole water, dissolved phase vs. suspended particulate matter (SPM)

Member States are primarily responsible for the provision of data to demonstrate compliance with EQS values. For organic compounds, this corresponds to data relating to whole water. For metals, the determinand of interest is dissolved metal and hence the requirement is to report metal concentrations in the dissolved phase.

A majority of AMPS expert group members agreed that whole water is the relevant matrix for compliance checking of the EQS derived for the priority substances other than metals. The approach recommended by the AMPS expert group is that the choice of how to generate the required data and the proof of its fitness for purpose should be the responsibility of Member States. Thus whole water data may be generated by analysis of the whole water sample, or by separate determinations on dissolved and solid phases.

¹ Expert Group on Analysis and Monitoring of Priority Substances: EAF PS

Analysis and Monitoring of Solid Matrices (continued)

Analytical perspective of compliance checking of SPM, sediment and biota EQS

Separate SPM QS (Quality Standards) have been proposed for certain substances as an alternative to whole water QS, if from an analytical perspective it is preferable (for cost reasons, characteristics of specific substances etc.) not to monitor the whole water.

The recommendation of the AMPS Expert Group is that, for the reasons stated below, it is not advisable to establish specific EQSs for SPM at this stage. It was noted the issue of monitoring compliance with any future quality standards will furthermore raise the questions of comparabilities of phase separation methodologies. The AMPS Group did furthermore not consider that, from a monitoring point of view, it would be technically feasible to propose EQSs in the near future for sediment and biota.

Waters with high SPM contents

The AMPS Group recommended that approaches to the assessment of EQS compliance in waters of high SPM should be examined further in technical guidance.

Design of monitoring programmes for sediments and biota

The purpose and nature of sediment and biota monitoring is different from water monitoring. Following the advice from the EAF PS, it is proposed not to establish quality standards for biota and sediment at this stage, but to designate monitoring requirements to assess the compliance with the no deterioration objective of the WFD and to assess long term impacts of anthropogenic pressures.

The AMPS expert group was asked to provide further insight and recommendations on the practices of sediment and biota sampling, for these purposes, but also to assess the practical aspects of checking compliance in these matrixes of specific EQS.

Separate requirements (for instance location and frequency of monitoring) on surveillance and subsequently operational monitoring of sediment and biota for the purpose of assessing long-term trends in impacts anthropogenic pressure and to ensure the no deterioration objective is reached may therefore be necessary, to ensure that comparable data can be collected.

The base line year for assessing long-term trends is 2004, in line with article 5 of the WFD. Specific requirements proposed as regards sediment and biota monitoring that may be introduced by any forthcoming legislative proposal, could then be taken into account in a confirmation or adjustment of the baseline data to be reported in the 2009 programme of measures.

The AMPS Expert Group convened two drafting groups to consider these issues. The groups assess current practices by means of questionnaires and then developed recommendations on the way forward. It emerged that the monitoring frequency varies widely and it was agreed that the appropriate frequency should be based on local circumstances.

Recommendations of the AMPS Drafting Group on Sediment Monitoring (06/2004)

A drafting group of the Expert Group on Analysis and Monitoring of Priority Substances (AMPS) including advisors from the European Research Network on Contaminated Sediments (SedNet) produced a 17 pages discussion document on sediment monitoring with the following recommendations:

- Initiate the development of a community-wide diagnostic guideline on the assessment of contaminated sediments in relation to the degradation of both ecological quality elements (benthic community, fish etc.) and water quality. Such a diagnostic guideline should be made available by 2006 in order to support Member States in their effort to implement the WFD are concerned;
- Initiate the development of a community-wide technical guidance on sediment sampling and handling, analytical techniques and normalization procedures. Such a technical guideline should be build on existing protocols/guidelines and be made available by 2006 in order to support Member States in their effort to implement the monitoring requirements of the WFD are concerned;
- Instruct Member States to apply sediment monitoring in selected waterbodies in order to determine the trends of those priority substances that are poorly soluble in water soluble (Table 2-4 is derived from these considerations);
- Stimulate the harmonization of sediment status & trend monitoring programmes of Member States at a river basin level.

Table 2.4 Priority substances of the Water Framework Directive list that are suggested for trend monitoring in sediment and or biota. P = preferred matrix over water phase, O= optional matrix

Priority Substance	Sediment	Biota
Anthracene	P	O
Brominated diphenyl ethers ^{a)}	P	P
C10-13-chloroalkanes	P	P
Fluoranthene	P	O
Hexachlorobenzene	P	P
Hexachlorocyclohexane ^{b)}	O	P
Pentachlorobenzene	P	O
Polycyclic Aromatic Hydrocarbons ^{c)}	P	O ^{d)}
Tributyltin compounds	P ^{e)}	P ^{e)}
DDT (including DDE, DDD)	P	P

^{a)} Including Bis(pentabromophenyl)ether, octabromo derivate and pentabromo derivate;

^{b)} gamma-HCH (Lindane);

^{c)} including Benzo(a)pyrene, Benzo(b)fluoranthene, Benzo(g,h,i)perylene, Benzo(k)fluoranthene, Indeno(1,2,3-cd)-pyrene;

^{d)} preferable in mussels;

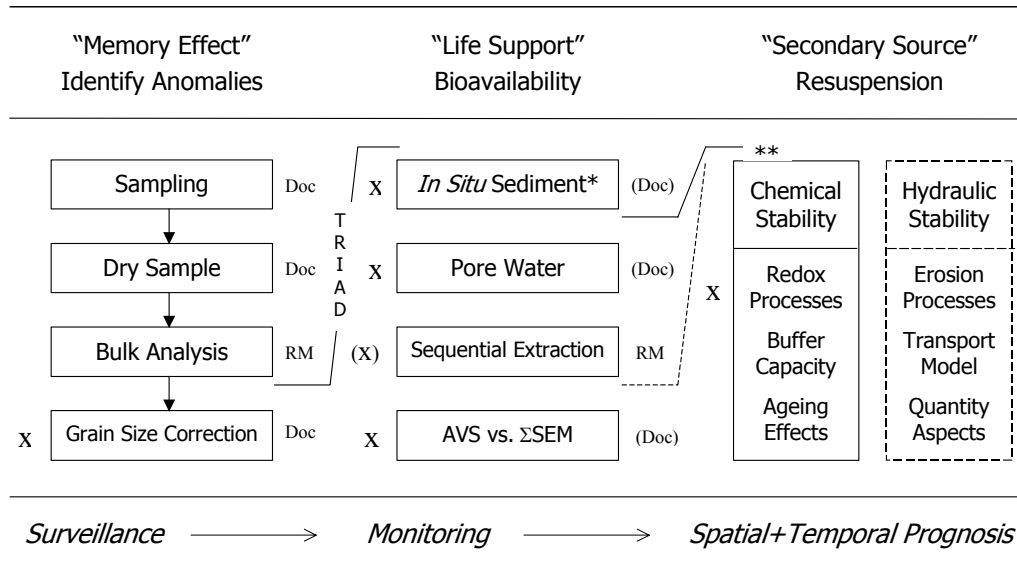
^{e)} marine environment

2.3. Quality Control of Chemical Sediment Analysis – Traceability Concept Extended to Secondary Sources

From a practical viewpoint, three functions of aquatic sediments can be distinguished (Table 2-5):

- Memory effect, mainly in dated sediment cores from lakes, reservoirs and marine basins, as historical records reflecting variations of pollution intensities in a catchment area.
- Life support, i.e., sediment as ecological, social and economic value, as an essential part of the aquatic ecosystem by forming a variety of habitats and environments (Anonymous 2003b). A system approach is needed comprising biotests and effect-integrating measurements due to the inefficiency of chemical analysis in the assessment of complex pollution.
- Secondary source, mobilisation of contaminated particles and release of contaminants after natural or artificial resuspension of sediments (Stigliani 1988).

Table 2.5 Overview on traceability aspects of chemical sediment analysis (Förstner 2004)
 X = Sediment-Specific Property; RM = Reference Material; Doc = Documented Procedure; TRIAD = Chemical Proportion of Triad Approach; AVS/ Σ SEM = Acid Volatile Sulfide/Sum Simultaneously Extractable Metals (DiToro et al. 1990); *Wet Sample (Mudroch & Bourbonniere 1994): Sub-sampling for tests under oxygen-free atmosphere (pore water, sequential extraction, etc.); **Depth Profile: Coupling of chemical/ecological risk data with critical shear stress (erosion probability) data



In the present context, memory effects will be used both from source material, e.g. historically contaminated sediment areas, and the target sediments from the port of Rotterdam, i.e. for the assessment of concentration trends for critical substances. Ecological effects (section 2.4) will be assessed or estimated from the target sediments. Resuspension effects (section 2.5) will be estimated from source materials and this information will form the input term for the transport calculations, which will eventually lead to a prognosis of both mass deposition rates and trends of contaminant concentration in the port of Rotterdam sediments.

2.3.1. Surveillance Investigations (1st Column in Table 2-5)

Surveillance is a “continuous specific observation and measurement relative to control and management” (Anonymous 1978a); the primary objective is to trace and observe sources and pathways of specified hazardous substances (Anonymous 1978b). If a simple aim of a study is to determine the presence or absence of a specific contaminant in bottom sediment at a given area, then the sediment can be sampled at one or a few sampling stations at fine-grained sediment deposition sites. However, after confirmation of the presence of the contaminant in the sediment, the study may be expanded to determine the extent of sediment contamination by the specific compound or element with the area, the contaminant’s sources, history of the loading of the contaminant, its transport, bioaccumulation, etc. (Mudroch and Azcue 1995).

In the view of the traceability concept, a basic sequence of measurements consists of three steps, which can be considered as an unbroken chain of comparisons:

- Sampling and sample preparation. Project planning, sampling stations, sampling devices, handling and storage, and quality control are not standardised, but well documented in all aspects (Mudroch and Azcue 1995).
- Analytical. Reference sediment materials are commercially available. While direct species analysis is still limited, standardised extraction schemes for metals and phosphorus in sediments as well as certified reference materials for comparisons were developed under the auspices of BCR/IRMM (Quevauviller 2002).
- Grain size as a characteristic sediment feature. Sampling on fine-grained sediment (Horowitz 1991) and grain size normalisation with “conservative elements” such as Cs, Sc, Li and Al (all reflecting clayey material content) is recommended as standard approach (Förstner 1989).

Uncertainties: Minor uncertainties, which will not affect the general applicability of the present approach, could arise from variations of typical matrix constituents and can be narrowed down by analysing parameters such as organic matter, carbonate and iron oxide contents.

2.3.2. Monitoring (2nd Column in Table 2-5)

Many national assessment schemes are based on a Triad approach, combining physical-chemical, biological and ecotoxicological assessment methodologies (section 3.3). The chemical parameters, that are included in the physical-chemical part of the Triad approach in many countries, are (example of Netherlands, Den Besten et al. 2003): mineral oil, chlorobenzenes, organochlorine pesticides, PCBs (standard group of 7 congeners), PAHs (16 of EPA) and the heavy metals Cadmium, Chromium, Copper, Nickel, Lead, Mercury, Zinc and Arsenic. The concentrations are normalized to values for sediment with a standard granular composition and organic carbon content; in the Netherlands “standard sediment” is defined as having a 25% particle fraction <2 µm and 10% organic matter on a dry weight basis.

Additional information, which can be used to bridge the gap between chemical analyses and biological effects (section 3.3) are:

Porewater. Tests on porewater (interstitial water) were considered suitable for several types of regulatory frameworks, but unsuitable for other, e.g., as stand-alone pass/fail methods or as a substitute for a solid phase test. Determination of chemical concentrations in pore waters is recommended, in addition to the regular contaminant measurements conducted in the whole sediment, as a means of providing information on routes and levels of exposure, and aiding in the interpretation of test results (Carr & Nipper 2001).

The leachable fraction does not necessarily correspond to the amount available to biota. Studies on the prediction of the trace metal levels in benthic organisms have shown, that the prognostic value of sequential extraction data is improved, when the trace metal concentrations are normalized with respect to the iron (hydrous oxide) and/or organic content of the sediments (Tessier and Campbell 1987).

It has been suggested that if the molar concentration of acid volatile sulfide (AVS) that is extracted from a sediment exceeds the molar sum of the simultaneously extracted metals (Σ SEM) that form more insoluble sulfides than iron sulfide – that is NiS, ZnS, CdS, PbS, and CuS, any one of which is denoted by MS – then those sediment metals should not be toxic to sediment dwelling organisms (DiToro et al. 1990).

Traceability/Uncertainties. Standing alone and for an individual sample, the physical-chemical proportion of the Triad does not seem to involve major practical problems. “Sampling”, “sample preparation” (using wet sediment) and “chemical analysis” (use of bulk or fractionated reference material; normalization to grain size and organic carbon) widely follows a standard sequence similar to the surveillance approach described in section 2.3.1. However, with a differentiated approach, e.g., when applying the BCR fractionation scheme (Quevauviller 2002), the question how to preserve the original physico-chemical forms of both matrices and critical contaminants becomes crucial. This question also relates to the way and extent, to which the findings within the chemical proportion can be compared with the results of the biological studies.

2.3.3. Resuspension – Secondary Source (3rd Column in Table 2-5)

Key processes in mechanical and chemical mobilization of sediments and their associated contaminants were described in Chapter 1. On a river-basin scale, i.e., when applied in a conceptual river basin model (CBM), chemical and ecological information need a strong basis of sediment quantity data. In a dynamic system, this assessment should include not just those materials that are currently sediments, but also materials such as soils, mine tailings, etc. that can reasonably be expected to become part of the sediment cycle during the lifetime of a management approach (Apitz & White 2003).

Sampling. For both erosion risk and chemical mobilization risk studies the chains of comparison are broken at early stages of sampling and sample preparation. Sampling of flood-plain soils and sedi-

ments is affected by strong granulometric and compositional heterogeneities arising from the wide spectrum of flow velocities at which the sediments were eroded, transported and deposited. These heterogeneities can be reduced by subsequent normalization procedures (section 2.3.1); however, the overall comparability of the samples will be significantly lower than in the applications described in sections 2.3.1 and 2.3.2 for surveillance and monitoring tasks, respectively. Sampling and sample preparation of *in situ* sediments primary has to avoid any modification of labile phases, in particular access of oxygen, which will inevitably change redox-sensitive minerals such as metal sulfides. For physical sediment property analysis, especially for erosion tests undisturbed samples should be taken to ensure *in situ* conditions in order to avoid disturbance of the sediment matrix and escape of gas.

All sediment tests and analysis should be performed for one sample. However, in most cases this is technically not possible. Hence, at least two sediment cores must be taken at the same sampling spot, one for the physical erosion test, the other for the chemical and biological tests. Since neighboring samples always show some different properties (known as the nugget effect in geostatistics) there will be no full correspondence of the physical and chemical/biological parameters for the same sediment depth, which implies a systematic uncertainty.

Reference materials. Sediment reference materials should be applied for erosion risk studies in a similar way as described in section 2.3.1 ("surveillance investigations"). Harmonized fractionation schemes and respective reference materials can be useful for studying ecotoxicological aspects, i.e., in the framework of comparative investigations of erosion stabilities and bioavailability of pollutants in sediment core samples. Regarding chemical mobilization studies, fractionated reference sediments, even if the chain of direct comparability has been broken, may offer some advantages in providing secondary information on the contents of calcium, iron and sulfur, from which the matrix parameters such as "acid producing potential" and "acid consuming capacity" can be calculated and predicted (Förstner 2002).

Uncertainties regarding the interpretation of findings both from erosion risk (I) and chemical mobilization studies (II) mainly arise from the fact, that the reliability of chemical analyses proper is masked by large variabilities of influencing factors such as: (I) granulometric and compositional heterogeneities as well as the fact that transfer of laboratory data into the field is still not at a routine level; (II) anoxic sediment/porewater extraction and preservation requires special experience; until now, lack of pore-water reference material is a significant deficiency with respect to chemical mobilization studies.

Outlook for secondary sources

In the process to develop measures against priority substances according to WFD Articles 11 and 16 a first step comprises the identification of all sources of "priority substances" (PS) and "priority hazardous substances" (PHS) to the environment – *source screening*. Historical contaminated sediments can be considered as possible secondary sources for releases of priority substances to the aquatic environment and the respective approach, including a first estimation on relevant substances, is presented in section 3.4.4.

2.3.4. Sampling and Filtration of Suspended Matter

In almost all cases of water quality studies, in which sediment sampling and subsequent chemical analysis can be included, either bed sediments or suspended matter could be used. However, given an option, bed sediments tend to be preferable to suspended sediments, mainly because of the simpler and easier collection of sufficient amounts of bed sediments and due to the much more marked spatial and temporal chemical and physical variability of suspended sediments (Horowitz 1991).

The two possible exceptions just refer to the present example: these are (1) studies designed to evaluate the transport (including the calculation of fluxes) and (2) short-term temporal variation of pollutants. Samples of suspended sediments, collected at selected sites (sampling stations; see Figure 2-1) in a river basin at short time intervals and related to water discharge, could provide valuable information on the specific inputs of pollutants from partial catchment areas. Typical influences from rocks, soils, waste materials, historical contaminations etc. can be indicated by characteristic mineral or element assemblages in the suspended solids, in particular when sample collection and data interpretation is performed in relation to typical meteorological and hydrological situation in the catchment area(s) (Baborowski et al. 2004).

Suspended-sediment sampler fall into three general categories (Anonymous 1982, Ongley and Blachford 1982, Horowitz 1991): (i) integrating samplers that accumulate a water-sediment mixture over time, (ii) instantaneous samplers that trap a volume of whole water by sealing the ends of a flow-through chamber, and (iii) pumping samplers that collect a whole-water sample by pump action. Integrating samplers usually are preferred because they appear to obtain the most representative fluvial cross-sectional samples. Cross-sectional spatial and temporal variations in suspended sediment and associated trace elements and their causes are discussed by Horowitz (1991).

Filtration may be carried out under positive pressure or vacuum; excessive pressure or vacuum should be avoided because this may cause rupture of algal cells and release of their intracellular contents into the filtered sample (Hunt and Wilson 1986). Filters having different structures, pore sizes, and composition are available (Brock 1983); the effective pore size of depth filters – having a complex system of channels – changes as the filter becomes more loaded with particles, whereas the effective pore size of screen filters is not affected by filter loading (Apte et al. 2002). Filtration and ultrafiltration can be used for size fractionation of aquatic particles, colloids, and macromolecules (Buffle et al. 1992).

Uncertainties: Handling of suspended sediments includes medium to high contamination risk, similar to the sampling and processing of water samples. Beside problems with filtration techniques (see above), it is important to minimize the time between sample collection and filtration because adsorption/desorption reactions involving particulates and bacterial activity can lead to changes in sample composition.

2.4. Deriving Ecological Risk from Chemical Data

Environmental managers often find themselves in the centre of different environmental, social and economical interests and expectations, which in current times of sustainability discussion and emission control are sought to be compatible with a reasonable amount of compromises on all sides. Environmental quality criteria fulfil hereby two tasks: They serve as a control mechanism to check the effectiveness of source control, and they are supposed to minimize the risk for the marine or estuarine environment as it has been claimed by the London Convention (1972).

The Dutch assessment framework UCT (uniform content test) for marine dredged material has been based on bulk sediment chemistry for a number of persistent compounds. No specific pathways were defined other than the input of these persistent compounds into the marine environment. The Chemistry-Toxicity Tests (CTT), that replaced the UCT in July 2004, differs in the following aspects:

- a number of 3 bioassays are included and will be tested for a period of 2 years with regard to their reproducibility and applicability in the decision making framework. They cannot overrule chemical quality criteria.
- TBT has been added because it is a chemical of concern.
- Sediment normalization procedures have been omitted, because they are not regarded as relevant for decisions on confined disposal of dredged material, and
- OCP²s have been omitted because their concentrations are low in nearly all cases.

The CTT values are used as pass/fail criteria regarding open water disposal. No exceedance of any CTT value (with the exception of bioassays) is permitted in material proposed for open ocean disposal. No attention is given to other compounds not represented on the CTT list, because the named ones are thought to be appropriate guides for other persistent contaminants. No exceedance of the CTT value is thought to guarantee a minimal ecological risk for the marine environment.

In this section, the uncertainty involved in deriving statements on ecological risk from chemical quality data will be discussed with respect to the compounds of concern that we will deal with in this project.

O'Connor and Paul (2000) critically evaluated sediment data with regard to their compliance with sediment quality guidelines and their ability to predict sediment toxicity as measured by the 10 days amphipod test³. Their conclusion was, that except in cases of extreme contamination, no chemical measurement reliably predicts sediment toxicity. They recommended that SQGs should not be used to attach biological meaning to chemical data.

This implies, that no chemical monitoring and decision-making procedures for dredged material could have any relevance with regard to the ecological risk when relocated at sea.

² OCP: DDT, Dieldrins, HCB, lindane

³ Sediment was considered to be toxic if there was less than 80% survival of amphipods during 10 days exposures to whole sediment

Opinion of the scientific committee on toxicity, ecotoxicity and the environment (CSTEE) on „The Setting of Environmental Quality Standards for the Priority Substances included in Annex X of Directive 2000/60/EC in Accordance with Article 16 thereof“, 28 May 2004

Question 3 – Quality standards for sediments and biota

At this stage, the Commission is not considering presenting specific Quality Standards for sediment and biota for three reasons:

- *data on toxic effects on benthic organisms and biota are of limited availability;*
- *difference in types of sediment are of varying importance at different locations;*
- *uncertainties regarding monitoring points, sampling and analytical methods, would make compliance checking in sediment and biota difficult for the purpose of implementation of Community legislation.*

Specific monitoring requirements for sediment and biota to ensure the environmental objective of “no deterioration” are however foreseen to be proposed. The Expert Group on Analysis and Monitoring is furthermore currently developing overview, assessment and guidance of practices required for this purpose.

CSTEE Response

We note that at this stage the Commission envisages presenting Quality Standards only for the water phase and that this would include reporting the concentration of a priority substance in the whole water; i.e. including the dissolved fraction and that bound to suspended organic matter. We believe that there are some difficulties with this being applied uncritically:

- To base protection on a water column standard ignores many of the biological complexities of exposure through absorption and ingestion by sediment organisms. Notwithstanding the view that “data on toxic effects on benthic organisms and biota are of limited availability,” the CSTEE believes, that information is now more available and should be taken into account whenever possible.
- The exposure of chemicals through the food chain is not only relevant for secondary poisoning in birds and mammals, but also for aquatic invertebrates and fish and the EQSs based on waterborne exposures are not protective in all cases. Monitoring programmes for lipophilic substances should be focussed on biota (and possibly sediment). As the number of chemicals selected as priority substances is very limited, the CSTEE strongly recommends producing the required ecotoxicological information for supporting sound QSs at least for these substances.
- Basing exposure concentrations on whole water may be very misleading with regard to bioavailability. For example the presence of algae and other organic matter in suspension may be important, particularly when there are blooms, and yet the bioavailability of substances in algal biomass is not straightforward. The concentrations of lipophilic substances will depend on the amount of suspended particulate matter (SPM) in the sample, which will depend on where, when and how the sample is taken.

As a general conclusion the CSTEE believes that specific quality standards can and should be developed for sediment and biota. This should be based on direct assessment and monitoring of sediments and biota directly.

The reasons for this misfit are manifold and many have been mentioned in this section already: Phases that strongly bind metals in oxic or anoxic sediments, unusual carbon types (soot, ash, black carbon) that do not behave according to equilibrium partitioning models, ageing processes. They all reduce bioavailability and are usually not incorporated into sediment quality guidelines.

Toxicity of sediment however strongly depends on the test system applied. In the extreme, the choice of a very sensitive test organism could render all measured sediments toxic although no impacts would be seen in the natural community. A battery of tests, which are carefully chosen in order to give complementary information, would increase the certainty of the ecotoxicological result (Ahlf et al. 2002). On the other side, toxicity can always be due to unmeasured chemicals in which case SQC would indicate no risk at all although the impact to the environment could be large. This could also occur due to interactions in mixtures of toxicants. In case that contaminants have similar modes of action like dioxins, dibenzofurans, and dioxin-like PCBs, their toxicity (or rather "toxic equivalences"⁴) can add up to a strong effect although single compounds are only present in low concentrations. Potentiation has been shown with sulfide and mineral oil in sediment (Tiemann and Ahlf, 2002), in which one chemical, not toxic itself at the exposure concentration or dose, enhances the toxicity of a second chemical in a mixture.

Because of the shortcomings of each assessment technique, the best choice to identify potential impacts towards the environment, would be an integrated approach as suggested by Chapman et al. (Chapman et al., 1997), in which the information from sediment chemistry, toxicity and resident community alterations are combined and collectively assessed with regard to the overall risk (sediment "Triad" approach, Figure 2.2). Grapentine et al. added a fourth line of evidence (LOE) to this: the bioaccumulation and biomagnification data (Grapentine et al., 2002). The different LOEs are supposed to end up in an overall weight of evidence (WOE) approach to assist in making a decision as to whether or not contaminated sediment has resulted in biological impairment (Wenning and Ingersoll, 2002).

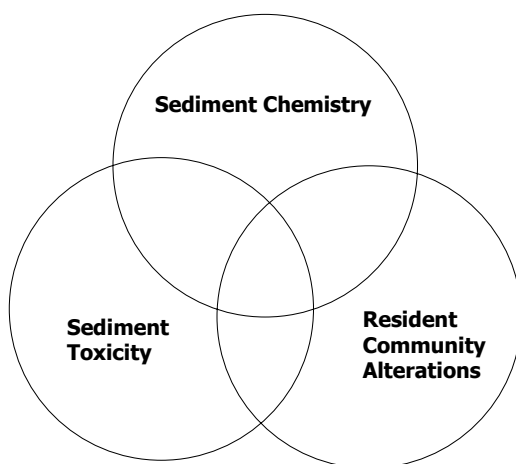


Fig. 2.2 Sediment „Triad“ approach

A method, which has been proposed to integrate environmental information from different systems, which each contain a certain amount of uncertainty, is fuzzy technology (Zadeh, 1965). This mathematical tool is capable to reflect natural variability, ambiguity and lack of quantitative data in environmental prediction (Silver, 1997) and has been applied to ecotoxicological sediment assess-

⁴ Toxic equivalence is calculated from the multiplication of the concentration of a dioxin or dioxin-like PCB and its "toxic equivalence factor", an empirical factor, which is scaled

ments (Heise et al., 2000; Ahlf et al., 2002; Hollert et al., 2002). The question, however, remains, how to value the outcome of such an extensive risk assessment with regard to the impact on the sediment community. The impact will have to be scaled according to the length, that an effect persists, and its severeness (in relation to the resilience⁵ of a community).

2.5. Hydraulic Data Quality

2.5.1. Flood and Sediment Transport Parameters

Hydrological and hydraulic data which are necessary for contaminated sediment risk assessment were collected from official reports issued by different authorities, institutes and agencies. All the data have been processed and aggregated as to present the results as daily, monthly or annually averaged values in terms of concentration and mass of contaminants. Most data are presented without specification of the sampling site, sampling method, uncertainty of the raw measuring data, data processing and data quality assessment. Little is known about the representativity of the measuring point for the whole flow cross section and only few information is given on the sampling frequency especially when single flood events are sampled. To answer these questions concerning the probability of resuspension of historical contaminated sediments and the risk for the port of Rotterdam more detailed data should be available as briefly described in the following.

Discharge gauging stations must provide calibrated discharge rating curves especially for the upper range of discharges with respective erosion potential. Although a spatial density of discharge gauging stations is sufficient, there might be some smaller tributaries without gauging stations and discharge data for flood events.

Aiming at the quantification of transport rates of contaminated fractional sediment, concentrations must be sampled in an appropriate cross section at different points in the vertical line a position of which has to be found as to cover the whole water depth at different discharges and to extrapolate on the full vertical concentration profile. The distribution of suspended material as well as the suspended sediment concentration for the different grain size sections should be available. Hence, the sediment fraction curves can be analyzed if necessary.

The sampling frequency must be adjusted to the discharge in order to provide an appropriate temporal resolution of the data and to account for the weight of the discharge as a key parameter for transport rate and mass balance. The evaluation of single flood events therefore requires a sampling frequency of the order of magnitude of 1 hour. The special density of sampling points depends on the local conditions with regard to the flow field and the contaminated sediment distribution. The situation in the headwater of the run-off power station Iffezheim can be presented as a typical example to illustrate how important it is to establish a clear measuring concept regarding the different flow field in front of the weirs and the turbines, the sedimentation pattern and the water depths. The total mass of

⁵ Resilience – the ability of a community to recover from a given stress

particulate HCB transported through the weir structure at Iffezheim was definitely underestimated since only one measuring point was selected in the low flowing zone of the headwater which was too far away to be representative for the whole flow cross section.

The weakest member in the information chain seems to be the sediment. There are only a few data available on the grain size distribution of deposited sediments, sediment bulk density and pore water content. No data are available on sediment erosion stability except for the upper river Rhine reservoirs where targeted sediment sampling and sediment erosion tests have been performed as to provide reliable field data for resuspension risk assessment in the upper river Rhine reservoirs as part of the ICPR (International Commission for the Protection of the Rhine) research contract.

Different experimental methods have been developed for cohesive sediment erosion tests, however, there is no intercomparison of the different methods available for quality assessment. Furthermore, it is still an open question how to upscale laboratory erosion tests, which where usually performed at low flow Reynolds numbers and boundary flow conditions which are different from the real river bed situation. The upscaling problem is currently pursuit at the University of Stuttgart by using a combined experimental setup, which allows comparing the results of the erosion tests with different size of sediment testing area exposed to the flow on one hand side and to compare laboratory tests with in-situ tests on the other hand side.

As for the sediment data no information is given on the vertical profiles of sediment properties and contaminant concentration except for the upper Rhine reservoirs, which where investigated within the framework of the ICPR research. To quantify the total mass flux of contaminated sediments including the pore water detailed knowledge about the vertical profile of the relevant physical sediment properties and the associated particulate contaminant concentration are essential and indispensable.

As for the data accuracy no figures are reported neither for the hydraulic parameters nor the sediment parameter. The key quantities, for instance the initial concentration of suspended particulate contaminants or the total mass of resuspended contaminants are a specific function of several independent variables such as the discharge, the actual bed shear stress versus the critical erosion shear stress, the erosion rate parameter, and the particulate contamination of the sediments which all have an uncertainty and, therefore all the uncertainties of the parameters have an impact on the uncertainty of the resulting objective quantity. Assuming statistical independence of the parameters the Gaussian law of error transmission can be applied for estimating the uncertainty of the resulting quantities at the port of Rotterdam. This holds not only for the hydraulic part of the process but also for the chemical and biological part, which increases the uncertainty of the assessment for the port of Rotterdam. It clearly shows that the uncertainty of the target quantity can be much larger than any of the input parameters.

2.5.2. Uncertainties and their Origin

Numerous models have been developed to describe the effect of flood events on river morphology and sediment transport, but most of them are deterministic and cannot account for the uncertainties involved in the input variables and model parameters. Computational results often show a wide spreading of the predicted quantities. Therefore, it is necessary to account for the uncertainties and to apply statistical methods to assess and improve the reliability of model results. In most stochastic approaches probabilistic distributions of the input variables and model parameters are used for uncertainty assessment. However, in most cases the data set is not sufficient to determine the probability distribution, or the data cannot be described by a distribution function. The integration of the stochastic concept into a deterministic model provides an useful alternative to cope with most important uncertainties.

For contaminated sediment resuspension risk assessment different sources of uncertainties must be considered. The most significant contribution to the uncertainty is due to discharge hydrology, which is known as the hydrological risk. Additional uncertainties originate from the imperfection of the model concept and, in particular from the erosion related sediment properties, which at least include the threshold of sediment erosion and the erosion rate as depending on different geochemical and biological factors. All of these quantities exhibit a specific measuring inaccuracy and show a high spatial variability in the nature. In case of environmental impact assessment the in-situ sediment contamination, sorption, transformation and degradation processes must be determined to quantify the final impact of the contaminants at their destination, i.e. the port of Rotterdam. The chemical and biological parameters usually show significant higher uncertainties than the physical parameters. Therefore, any quantity calculated at the far downstream end of the contaminant pathway, which is the port of Rotterdam is subject to all the uncertainties included and hence, exhibit the cumulative effect of uncertainties involved as shown in Figure 2.3. Because of the predominant influence of the hydrological risk the impact of the uncertainties of physical, geochemical and biological parameters on the results is directly linked to the hydrological discharge specified by its statistical return period.

Uncertainty assessment

To cope with the uncertainty of measurement based model parameters and the effect of the variability of hydrological input variables, the use of a stochastic concept for assessing the uncertainty and improving the reliability of the model results is advisable. Stochastic concepts can be applied and integrated into a deterministic hydrodynamic transport model. To reduce the uncertainty of the model output quantities such as eroded contaminated sediment mass, suspended particulate contaminant concentration, contaminated sediment redeposition and many other parameters, the uncertainties of the hydrological, hydraulic and sediment input data must be reduced, the capacity of the model itself and the validation of the model parameters must be enhanced (Fig. 2.4).

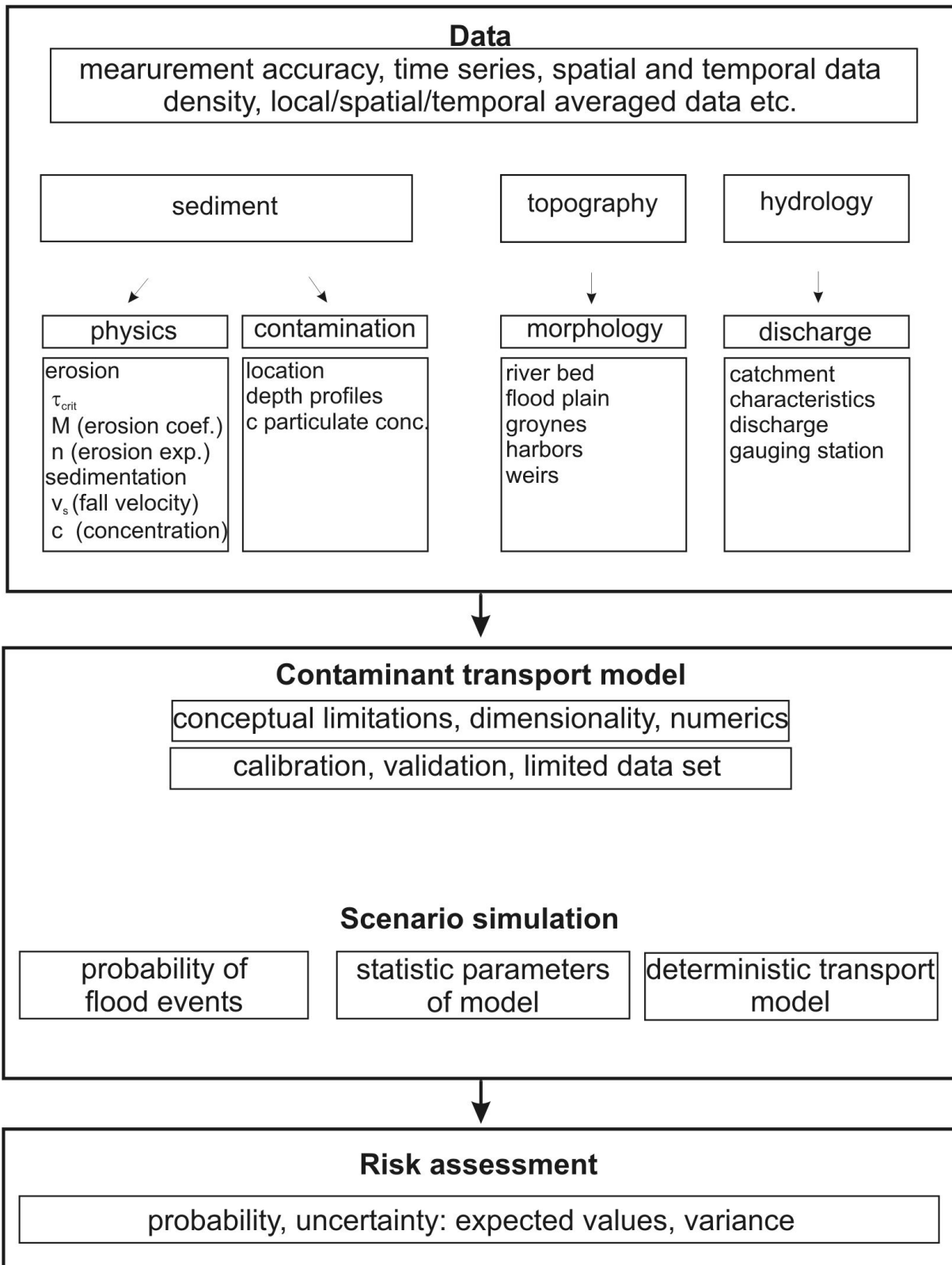


Figure 2.3 Origin and transmission of uncertainties

Reduction of uncertainties	data quality <ul style="list-style-type: none"> • higher accuracy • larger number of data • representativity
	model improvement <ul style="list-style-type: none"> • concept refinement • physical processes description
Quantification of the uncertainties	deterministic-stochastic model simulations
	statistical evaluation of results

Figure 2.4 Coping with uncertainties

The statistical components of the problem can be treated for instance by the Monte Carlo method which delivers the residual uncertainties in form of statistical parameters. The integration of deterministic and stochastic concept provides an approach to assess the influence of the variability of input variable or parameter. The bootstrap method is an effective method to evaluate the field data, especially when the number of available data is limited or there is no information about the uncertainties of the sediment data.

Since the hydrological component makes the dominant contribution to the sediment resuspension risk assessment the probability, i.e. the uncertainty with respect to time, of any model based quantity increases substantially with the complexity and size of the catchment area. As for the river Rhine there is a huge catchment consisting of different hydrological independent subcatchments like that of the river Neckar, Main or Mosel where contaminated sites are subject to potential resuspension by statistically almost independent regional or even local flood events. Therefore, one can hardly predict the impact of resuspended contaminants on the port of Rotterdam for floods with different return periods like 10-, 20 -.. - 100- years flood. This is just because of the large number of possible hydrological scenarios which for instance produce a 10-years discharge at Bimmen-Lobith. However, when focusing on the most important contaminated sites a qualitative risk assessment seems to be possible.

Case study Neckar

To demonstrate the influence of the sediment erosion parameters, i.e. critical erosion shear stress τ_{crit} , erosion coefficient M and erosion exponent n (see equation 1), numerical computations with a 1-dimensional transport model based on the Monte Carlo simulation method were made for the headwater of the river Neckar reservoir Lauffen focusing on floods with different discharge hydro-

graphs and spatial variability of the sediment erosion properties. Historical flood events were selected from the 50 –years data series to show the effect of the peak discharge and the flood volume, respectively on the erosion capacity of the flood and, in addition the resulting uncertainty of the eroded sediment mass caused by the statistical variation of the sediment erosion parameters.

Two field studies on sediment erosion were made in 1997 and 1998. All together 29 sediment cores were taken for experimental sediment erosion tests. In total, 460 data of the critical shear stress of sediment erosion are available.

Each value of the collected data is regarded statistically independent. The non-parametric bootstrapping method (Efron and Tibschirani, 1993) yields the mean of the data with unknown distribution or approximate the mean value of the variable on the base of the collected sample. Thus, a certain number bootstraps of the sample mean of the collected field data were produced. Each bootstrapped sample mean is assumed as mean critical erosion shear stress of the whole river reach, and was put into the function (equation 1) suggested by Kuijper et al. (1989) for calculating erosion rate (E),

$$E = M (1 - \tau_0 / \tau_{c,E})^n \quad (1)$$

where M erosion coefficient, τ_0 actual bed shear stress, $\tau_{c,E}$ critical erosion shear stress, n erosion exponent.

A data set of discharges covering almost 50 years from 1950 onwards was available for numerical simulations. The inflowing suspended sediment concentrations as a function of the discharge were calculated using an experimentally determined power law function (Kern, 1997). A field study of the flood event from 28th October 1998 to 4th November 1998 provided another data set of discharges and corresponding suspended sediment concentration (Haag et al., 2002).

A 1-dimensional flow and sediment transport model was applied to the lock-regulated river portion of the river Neckar upstream of the weir at Lauffen (Fig. 2.5) to study the effect of the variability of the hydrograph and the sediment erosion process.

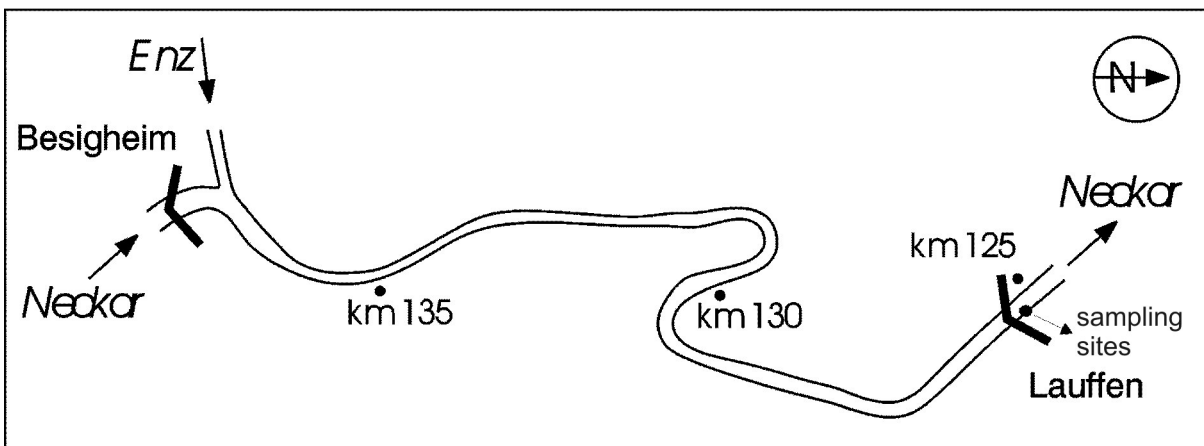


Figure 2.5 Sampling site at the River Neckar

In the study performed by Chen Chien Li (2004) the influence of all three sediment parameters according to the above shown basic equation and Figure 2.6, respectively were systematically investigated by a local sensitivity analysis. It turned out that each parameter has its specific impact on the erosion process which means that at least two parameters must be known which are the critical erosion shear stress and the erosion rate which itself is described by another two parameters, i.e. M (erosion coefficient) and n (erosion exponent).

In the following for simplicity two governing parameters are considered as stochastic. One is the hydrograph and the other is the critical shear stress of erosion ($\tau_{c,E}$). The influence of the two variables on the sediment erosion capacity of the flood is estimated by applying a one-dimensional flow and sediment transport model (Kern and Westrich, 1996) to the 11 km lock regulated river portion of the Neckar. The erosion parameters M and n were regarded as constant and set to be $7.5 \times 10^{-4} \text{ kg/m}^2\text{s}$ and 3.2, respectively.

➤ Data set

- 6 historical hydrographs and the associated SPM concentration
- erosion coefficient: $5,0 \times 10^{-5}$; $7,5 \times 10^{-5}$; $1,0 \times 10^{-4} \text{ kg/m}^2\text{s}$
- erosion exponent: 1,0 ; 1,5 ; 2,0 ; 3,0 ; 4,0
- critical erosion shear stress: 2 ; 4 ; 6 ; 8 ; 10 ; 15 ; 20 N/m^2

➤ Model

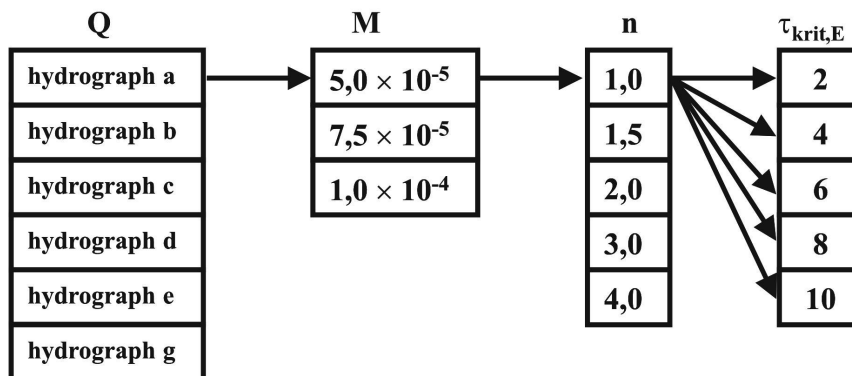


Figure 2.6 Sensitivity analysis (Li and Westrich 2004)

Four historical flood events with different peak discharge and duration in the period from 1950 to 1994 are chosen to demonstrate the effect of the shape of the hydrograph and the variability of the critical erosion shear stress on the sediment erosion potential of floods. The duration of each flood event is 10 days. 50 long term simulations were carried out for a period of 45 years using the measured discharges from 1950 to 1994. For each simulation following the Monte Carlo method the critical erosion shear stress was statistically determined and assumed to be constant in the entire river reach.

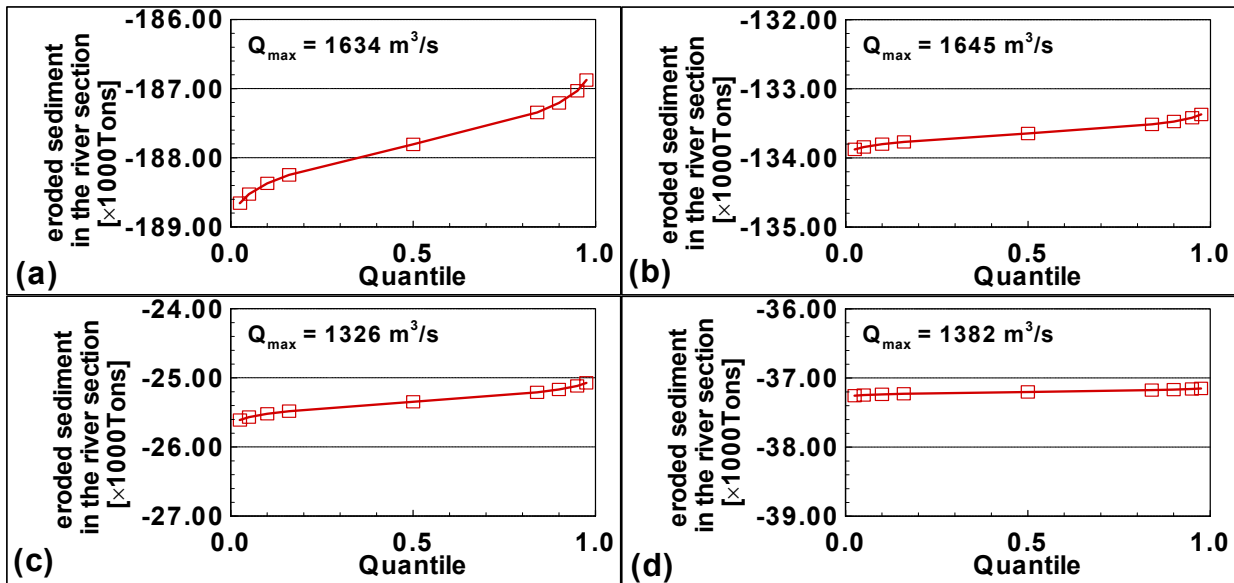


Figure 2.7 Calculated sediment mass eroded by historical flood events with variation of critical erosion shear stress from 2 to 10 N/m² (Li and Westrich 2004)

Figure 2.7 shows the calculated quantiles of eroded sediment for four representatively chosen flood events. The eroded sediment mass is the difference between the total amount of sediment in the river reach before and after the flood event. Q_{\max} stands for the flood peak discharge. Flood (a) differs from flood (b) by larger flood volume and longer erosion impact duration. Both floods (a) and (b) show higher peak flow rate compared to the floods (c) and (d) and hence, exhibit much higher eroded sediment mass. The gradient of the line indicates the effect of the variability of critical erosion shear stress. Among the four flood hydrographs in Figure 2.7 the flood (a) has the largest spreading of eroded sediment mass. A comparison between flood (a) and (b) shows that the bigger flood volume of the hydrograph (a) which is to be seen in Figure 2.8 results in a much larger erosion capacity compared to the flood hydrograph (b). The sediment mass eroded by the flood (a) is about 53.000 tons larger in comparison to flood (b). The calculated results in case (a) spread over 2.000 tons, i.e. ± 1.000 tons whereas, the spreading of the flood (c) is expectedly only about 1.000 tons, i.e. ± 500 tons maximum. It must be inferred from the numerical investigation that the peak flow rate as well as the duration of erosive flow velocities have a significant influence on the sediment erosion potential. This highlights the individual capacity and impact of a discharge hydrograph on sediment erosion.

Therefore, for instance when assessing the impact of a 100-years flood event on the resuspension of contaminated sediments a series of synthetic hydrographs with different peak discharge and duration must be investigated and analyzed to provide a probabilistic answer on how much sediment can be eroded by such an event. The joint effect of peak flow rate and the duration of the erosive flood discharge determines the concentration and load of resuspended sediments and, in conjunction with the contamination of the sediments it also controls the initial concentration of particulate contaminants and the event related total contaminant load.

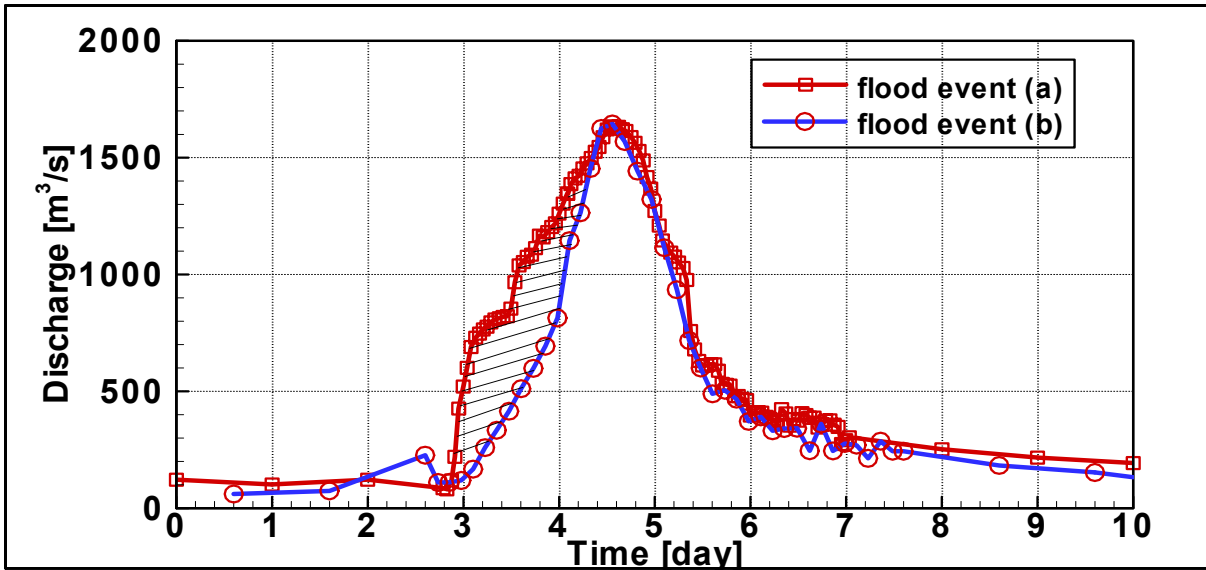


Figure 2.8 Hydrograph of two selected historical flood events with different flood volume (Li and Westrich 2004)

The impact of the spatial variability of critical shear stress on the erosion process can be demonstrated by the flood in 1998. In comparison to the flood events (c) and (d) in Figure 2.7 which have about the same peak discharge of 1634 and 1635 m^3/s , respectively more sediment is eroded by the flood in 1998 even though it had a lower peak discharge of 1055 m^3/s . The critical discharge of erosion in this river reservoir turned out to be some 600 m^3/s according to the investigation by Kern (1997).

Fifty simulations were carried out for the flood event from 28th Oct. 1998 to 4th Nov. 1998 using the measured discharge hydrograph with a peak flow rate of 1055 m^3/s . The value of the critical erosion shear stress was given by a random process for each simulation. The critical erosion shear stress was assumed to be constant both in space and time.

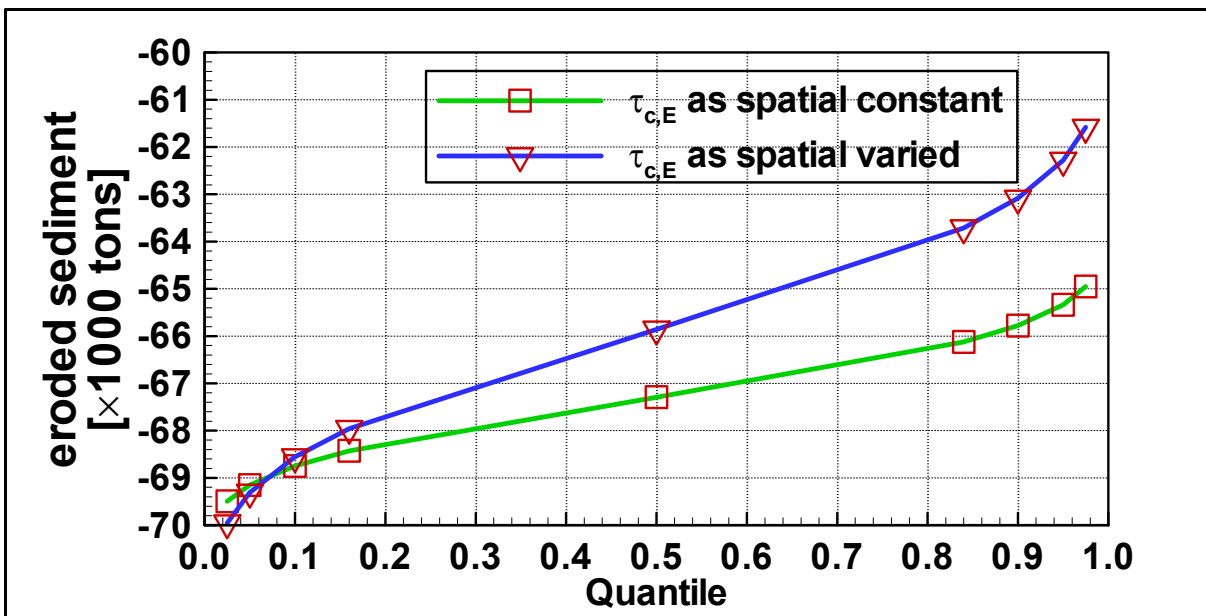


Figure 2.9 Quantile of calculated sediment mass eroded during flood event 1998 with a peak flow rate of 1055 m^3/s : (a) $\tau_{c,E}$ spatially constant and (b) $\tau_{c,E}$ spatially varied (Li and Westrich 2004)

Fifty bootstrap samples of critical erosion shear were generated using bootstrap sampling. Each bootstrap sample consisted of varied values drawn with replacement from the collected data. Each value is allocated to a river bed profile. 50 simulations were carried out for the flood event from 28th October 1998 to 4th November 1998 using the measured discharges of this period and 50 bootstrap samples of critical erosion shear stress.

Assuming the critical shear stress of erosion to vary along the river course which is usually the case in the field, the range of the statistical results is significantly increased and amounts up to 8.000 tons. The maximum deviation in the results could reach about ± 4000 tons which can be taken a maximum uncertainty of about $\pm 6\%$ related to the expected quantity of 65.000 tons. The graph of Figure 2.6 indicates that the statistical expected value of the eroded sediment mass is increased by about 1.500 tons due to the spatial variability of the critical erosion shear stress. Hence, the increase of the spatial variability of the sediment parameters has an impact not only on the variance but also on the expected mean value of the resulting quantity, i.e. the mass of eroded sediment.

The effect of the variability of the hydrograph that is the peak discharge and duration of erosive discharge is obvious. In addition, the eroded sediment mass is affected by the critical erosion shear stress, the erosion factor and erosion exponent which always vary in the field. When taking into account the variability of all sediment parameters, which are relevant for erosion, the variance of the resulting eroded sediment volume will definitely increase.

Parameter variability with sediment depth

Everywhere river bed sediments show large horizontal and even higher vertical inhomogeneity in terms of grain size, water content, bulk density and hence, the erosion behavior is expected to vary strongly from river to river and within confined sedimentation zones like reservoirs, harbors, groyne fields and other stagnant water bodies. Therefore, in addition to the horizontal variability of sediment parameters the variability in the vertical dimension has to be taken into account which definitely enlarges the variance of all the computational output such as initial concentration of resuspended contaminated sediments, sediment erosion depth, sediment erosion flux and eroded sediment mass as well resulting from the Monte Carlo simulation.

As for the resuspension of contaminated sediments the spatial variability of the concentration of contaminants associated with the sediments is important to know. Chemical analysis of sediment cores has shown a tremendous inhomogeneity of contaminant concentrations with sediment depth. Very high concentration gradients can be found within small sediment layer thickness as shown by the profile in Fig 2.10 for the HCB concentration of the sediments in the reservoir Marckolsheim (Witt, 2004). Only when assuming a constant concentration of contaminants in $\mu\text{g}/\text{kg}$ across the sediment layers the variance of the mass of resuspended contaminants would be the same as it is for the total eroded sediment mass.

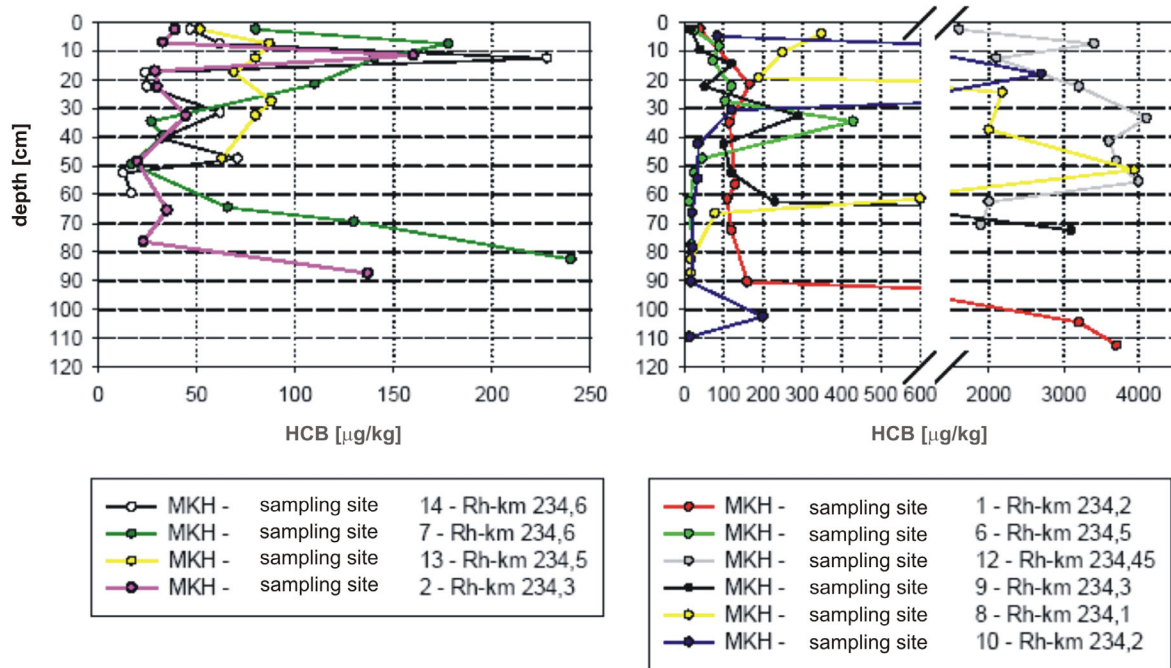


Figure 2.10 HCB content of sediment from different sampling sites in the upper river Rhine reservoir Marcholsheim (Witt 2004)

However, in the likely case of large vertical inhomogeneity of the contamination level this would cause a considerable increase of the variance of the released contaminant quantities. In this case the computation would be rather complicated because of the fact that the statistical sediment parameters, i.e. zero and higher cases of contaminant concentration will change with advancing erosion process and erosion depth, respectively. Therefore, it would be necessary to calculate those parameters for different time intervals during the erosion process.

Conclusion

The applied concept facilitates to quantify the uncertainty of the eroded sediment mass by statistical terms. When calculating the mass of contaminated sediments released by flood events the variability of the particulate concentration of sediments with depth, which has shown to be much larger than the horizontal variability must be taken into account. Consequently, the statistical range of results for the resuspended contaminants will be considerably higher. The more processes are involved on the pathway along the river course the higher the variance of the transport quantities involved and the larger the gap between the best and worst case assumption for the sediment management.

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3. Sediment Management at the Catchment Scale

Sediment quantity has been managed for centuries, mostly by dredging. This was, and still is, very much needed in order to keep waterways, that tend to silt up, open to the flow of water. This ensures a proper drainage capacity for precipitation and melting snow and ice, so it aids in flood prevention. However, the removal of sediments for the maintenance of waterways and water quality from locks, floodplains, harbours, navigation channels and river stretches is a high capital cost for responsible authorities and agencies.

Since the beginning of the industrial revolution, hazardous chemicals were emitted to our surface waters. Lots of these chemicals do not readily dissolve in water but rather stick to the sediment. Therefore, sediment quality rapidly deteriorated also because several chemicals do not readily break down in sediment. This introduced the need for a new type of management: sediment quality management (SedNet 2004).

This chapter deals with five aspects of sediment quality management: (1) Legislation on a European and national level, (2) management practice in The Netherlands and Germany, (3) biological effects-based sediment quality in ecological risk assessment for Dutch and German waters, (4) sediment management issues in the Water Framework Directive (WFD) for monitoring and emission controls of priority substances, and (5) future challenges on sediment management at the catchment scale.

3.1. Legal Aspects⁶

3.1.1. European Directives on Water, Soil and Waste (Landfills)

The *European Water Framework Directive (WFD)*, which came into force in 2000, will replace existing EC-directives for surface water and groundwater within the subsequent 7 years. Dredged materials (DM) and sediments are not mentioned explicitly in the WFD (Förstner 2002). Germany and The Netherlands expect that the WFD is likely to have implications on Dredged Material (DM) handling, since sediments have an influence on water quality. An increased monitoring requirement for selected substances (see priority list in Annex 10 of WFD) is expected (section 3.4). Furthermore, it is not clear yet whether and how the demands of the WFD about “heavily modified waters (e.g. waterways)” will affect the DM management.

A *European soil protection directive* does not exist, but the European Committee issued a communication paper as basis for discussion on the development of an *EU Soil Strategy*. The *European Construction Products Directive*, that aims to harmonise European legislation for the market of building materials in the EU, has relevance to this discussion. The Construction Products Directive regulates the re-use (beneficial use) of soils or soil material as building material and therefore could interfere with national soil policy (3.1.3).

Interactions of National and International Regulations (from: Rhine Research Project II Part D 2001)

Figure 3.1 indicates that the national, Dutch and German, European and international regulations concerning the immission and emission approach and dredged material management build a complex system of interactions. Both The Netherlands and Germany are contracting parties of the International Commission for the protection of the Rhine (ICPR, Rhine catchment area) and conventions as the Oslo and Paris (OSPARCON) concerning the receiving coastal environment (North Sea).

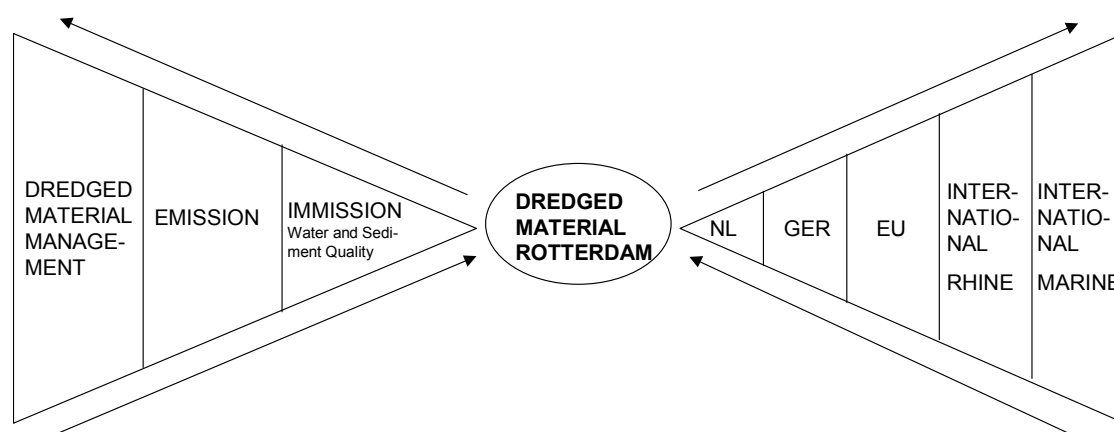


Figure 3.1 Overview over the interactions of national and international regulations

Differences between Dutch and German Regulations concerning Sediment Quality

Sediment Quality Targets (page 260)

The Netherlands have established two sets of sediment quality objectives for metals and organic substances, which are valid for both marine and freshwater sediments and which are based on ecotoxicological assessment and political decisions (environmental yield/costs ratio): the target level (long-term objective) and the limit level (short-term objective). In a long-term perspective a harmonisation of inland and marine quality targets is anticipated. The improvement of surface water quality aims as well at the unrestricted marine disposal of estuarine dredged material.

In Germany there are no marine sediment quality targets yet, but national freshwater sediment quality targets for seven metals currently do exist (German federal working group on quality targets, BLAK QZ). These sediment quality targets are based on ecotoxicological assessments. A comparison of the Dutch and German sediment quality targets for metals, lead, cadmium, chromium, copper, nickel, mercury and zinc shows, that in most cases the Dutch long-term sediment quality targets are more stringent than the German ones. On the other hand the Dutch short-term sediment targets are in most cases less stringent than the German quality targets.

⁶ selection from: Dutch-German Exchange on Dredged Material, Part 1 (DGE-1, 2003)

Feedback between dredged material quality and emission control (page 262)

The international conventions for the protection of the marine environment state in their dredged material management guidelines that high priority should be given to the identification of sources as well as the reduction and prevention of further contamination of sediments. Furthermore, both point and diffuse sources should be addressed adequately.

The Netherlands follow the principle that the quality of the dredged material to be disposed at sea should be improved by reducing inputs of contaminants in rivers and estuaries. These emission reductions should be achieved by the application of Best Available Techniques. The Dutch emission measures address both point and diffuse sources, with a current emphasis on the latter. Dredged material quality is not yet used in a feedback system to emission control, but it has been advised to implement such an effect-oriented emission approach. On the other hand, private initiatives to reduce emissions in the River Rhine by the Port of Rotterdam authorities have proven to be successful.

It is not obvious, whether Germany has a feedback system for dredged material quality to source control as required internationally. The environment objective of different German environmental laws include sediments as a compartment of nature. The emission principle (with its emission standards) is the main tool in German environmental law, e.g. for wastewater discharges to surface water the Best Available Technique is required to fulfil the environmental objectives. To assess whether the Best Available Technique is applied, a wastewater assessment is carried out by using bioassays. But at present the effects of effluents on organisms living in sediments (benthos) are not considered.

Dutch and German regulations for dredged material (page 263)

The Netherlands established five levels of sediment quality criteria, which are based on ecotoxicological assessment and political decisions. Coupled to these levels there is a sediment classification system on which the decision about the inland disposal option is based: the lowest 3 classes of sediment (below the testing value) can be disposed in surface water or on land, whereas the highest two classes should be treated or stored. In addition to this there are so-called Uniform Quality Criteria as (chemical) decision criteria for the marine disposal of estuarine dredged material. The use of bioassays in the assessment of estuarine dredged material quality is foreseen for 2002. (refer to current status)

In Germany two action levels are stated for dredged material management in Federal coastal waterways. They are derived from the prevailing contaminant concentrations measured in North Sea sediments from 1982 – 1992. Ecotoxicological and biochemical data support decision-making, but in general only one bioassay is used for that purpose. The action levels are not environmental quality targets or objectives, but guide values. The decision is generally guided by the values, but is made on a case-by-case basis. For Federal inland waterways the disposal decision is based on chemical and ecotoxicological criteria (applying a bioassay testset). The criterion for the disposal decision is that a deterioration of water and sediment quality at the disposal site is not allowed. The decision is, like for Federal coastal waterways made on a case-by-case basis.

The *European Landfill Directive (1999/31/EC)* regulates the landfilling of waste, including DM. If DM will be disposed of upland without any further use, it has to be decided which category of landfill has to be chosen. Technical demands for those landfill categories (disposal facilities) are defined in the European Landfill Directive. An important exemption for DM is made in article 3: “...*the deposit of non-hazardous dredging sludges alongside small waterways from where they have been dredged out and of non-hazardous sludges in surface water including the bed and its sub-soil*” is excluded from the scope of the European Landfill Directive. This exemption is implemented in the Dutch waste legislation (Environmental Act) for “slightly contaminated DM” as defined in the Dutch Soil Protection Act. The German Landfill Ordinance (DepV, 2002) does not explicitly highlight the exemption of the European Landfill Directive for aquatic disposal of DM.

3.1.2. International Commission for the Protection of the Rhine (ICPR)⁷

In 1950 the “International Commission of the Protection of the Rhine” (ICPR) was founded on the initiative of The Netherlands. The members are Switzerland, France, Luxembourg, Germany, The Netherlands and since 1976 the European Community. In 1963 the Commission’s contract was based on the Law of the Nations; the actual legal basis of the Commission’s work, the new Rhine Convention, was passed in 1999.

One of the objects of the ICPR is to achieve such a sediment quality of the River Rhine that all the dredged material can be relocated into the North Sea. But although the water quality of the River Rhine has improved significantly during the last 25 years – the actual concentrations of heavy metals in water (including suspended matter) are lower than the European Threshold for drinking water – the concentrations of heavy metals (except mercury) in the sediments of the upper Rhine are still frequently higher than the Dutch thresholds for relocation of DM into the North Sea. With regard to some PAHs and PCBs the Dutch contamination threshold was also exceeded.

The pollution reduction was quite successful and other topics such as flood protection or the ecological improvement of the river basins became more important. The ICPR elaborated a programme for the “Sustainable Development of the River Rhine” with the participation of NGOs and representatives from different industries. The ICPR is one of the important institutions to establish the river basin management plans required by the EU-WFD.

However, management of contaminated sediments remains a controversial issue. In 1995 the water quality working group analysed the national standards of the member states for the disposal of dredged material. The national regulations were embedded in other laws, as for example, for waste, waterways, environment or nature protection (see below). With regard to dredged material management, in 1997 the ICPR defined, among others, criteria for the relocation of dredged material in the River Rhine and its tributaries. The criteria are based on the “prevention of degradation principle” (see Box, selection and translation from the German version by U. Förstner).

ICPR - Recommendation to the Criteria for the Relocation of Dredged Material into the Rhine and its Tributaries (Document Ssed 06-04=No. 89=PLEN 40/97)

"An objective science-based assessment of the effects of contaminant contents during the relocation of dredged material at present is not possible. The second best assessment principle for dredged material is the "no deterioration requirement", which, however, only represents an interim solution. In the following, criteria are recommended, which refer to the actual quality of suspended particulate matter, and therefore imply a continuous improvement. Due to the very high anthropogenic inputs in former years contaminants have been enriched in the sediments and, with it, in the dredged material"

1. Purview of the recommendation – definitions and types of measures

Relocation in the sense of this recommendation is the relocation of dredged material (here aquatic sediments) within the aquatic system. In the regular case of relocation in the course of maintenance measure aquatic sediments are dredged and relocated at another site of the same aquatic system. Relocation is also performed under water, e.g., by means of a hydraulic dredge or jet stream.

Dredged material from maintenance measures mostly consists of aquatic sediments of varying grain size composition, depending from the availability and respective flow conditions. There is a characteristic high proportion of fine grain sizes in zones of low water velocity; this fine-grained material (silt, clay) is oftenly contaminated.

2. Obligation of investigations for dredging plans

Prior to each relocation measure investigation of the dredging site, the dredged material and the depositional area have to be made. Morphological and biological criteria must be respected and, if needed, respective investigations have to be performed. Laying down the extent of investigations of chemical-physical parameters is made on the basis of available measuring data (not older than 5 years) and the local peculiarities (discharges, harbours). Accordingly the extent can be reduced or enlarged. Samples must be representative for the dredging site and must allow statistical evaluation.

3. Obligation to discard

If dredged material cannot be relocated, e.g., because of the criteria indicated below, it has to be discarded according to national criteria.

4. Qualitative criteria for the relocation of dredged material

The qualitative criteria must not be attained by mixing less and strongly contaminated dredged material..

Chemical-physical criteria: Dredged material is allowed to be relocated only when the mean concentration of every pollutant is less than three times (nationally partly stricter criteria are valid, see Table 3.1) the mean concentration in suspended matter of three years before dredging occurred.

Ecotoxicological criteria: In principle, for the assessment of dredged materials ecotoxicological criteria should be applied with priority. However, at present this cannot be achieved at an international level due to the lack of an uniform assessment procedure.

The concentration of oxygen in the water must be higher than 4 mg/l.

5. Quantitative limitations of the contaminant

Relocations of dredged material are permitted only when the actual river flow is significantly above the mean longstanding minimum flow. General care should be taken that the contaminant load of the dredged material has only minor effects on the annual contaminant load in the aquatic system.

⁷ after Hagner and Peters in Rhine Research Project II report (2001)

3.1.3. National Legislation and Guidelines on Dredged Material

Water Regulations

In The Netherlands there is a national policy document on water-management in use (NW4) for the period 1998-2006. It gives an overall strategy for water-management in The Netherlands including specific quality criteria (target and/or risk levels) for surface water, and sediments (DM). The policy document also contains specific criteria for aquatic relocation of DM in sea-water. In general, quality criteria for DM, and surface water (freshwater) have a regulatory link to the Soil Protection Act (WBB) and the Pollution of Surface Waters Act (for seawater WVZ, and freshwater WVO) too. In addition to the policy document on water-management, there is a governmental policy document on the removal of DM (BVB, 1994), which describes the policy on DM management in The Netherlands. A national directive for large (aquatic) disposal sites is part of the governmental policy document on the removal of DM. Very important are the criteria for the protection of groundwater quality. Recently, also a master plan for the removal of DM was presented in The Netherlands (*Tienjarens scenario*). The master plan made clear that in recent years the amount of DM did not equalise the sedimentation-rate. Consequently the total amount of sediments that have to be removed from Dutch waterways has increased. In order to make up these arrears in dredging, large efforts have to be made in the near future.

In Germany, comparable policy documents for DM do not exist. National water quality criteria for inland waters (freshwater) were developed by the LAWA (Länder Expert Group on Water). This classification includes quality criteria for suspended matter but not for DM. The system is going to be revised and is foreseen for implementation as part of the EC-Water Framework Directive. For DM in the coastal region there is a political mandate between the federal government and the regional (Länder) governments at the coast to work out a national recommendation for the handling of DM in coastal waters (North Sea and Baltic Sea). A recommendation for the handling of TBT-contaminated DM in coastal waters was introduced in November 2001 (BLABAK TBT-Concept).

Soil Protection

The *Dutch Soil Protection Act* includes aquatic soils (sediments/DM) and gives quality criteria for soils, aquatic soils and groundwater. The Soil Protection Act is divided into a soil protection section and a soil remediation section. Both sections deal with aquatic and terrestrial soils and groundwater. The protection section prevents soil degradation and addresses all kinds of soil quality threatening activities. The soil remediation section regulates whether or not action should be taken on contaminated soils and what kind of action that should be. Quality standards for soil and groundwater are included. An ordinance to the prevention section of this act (but also to the Pollution of Surface Waters Act) is the *Building Material Decree*, which makes a difference between 3 categories of building materials. The difference is based upon the leaching of the building material. The Dutch Building Material Decree has been notified to conform to the *European Construction Products Directive*.

In Germany the *Federal Soil Protection and Contaminated Site Act* has in general the same goals as the Dutch Soil Protection Act. The rules for practice were set into force by the *Federal Soil Protection and Contaminated Site Ordinance*. The main difference between the Dutch and the German Soil legislation regarding DM is that the aquatic soils (bottom sediments) are not in the scope of the German Soil legislation (BBodSchG). The German soil regulations (act and ordinance) relate to upland disposal (re-use/beneficial use) of DM. There is a close connection to waste legislation with regard to restoration of contaminated sites. Permits are needed if DM shall be placed on soils for further (e.g. agricultural) use. These permits have to include an expertise about the soil planned to be covered by DM and the DM itself with regard to possible deterioration of soil and groundwater quality or other subjects of protection connected with soil. In consequence of the introduction of the Federal Soil Protection Act and Ordinance (BBodSchV) the soil standards in different environmental regulations are going to be harmonised with regard to groundwater protection.

Waste Regulations

National waste regulations in both Germany and The Netherlands are strongly influenced by the European waste policy. Main goals of the European waste policy are the avoidance of waste, the stimulation of re-use or beneficial use of waste, and to ensure that the handling of waste is safe. Waste which cannot be used environmentally sound has to be treated and/or to be disposed of in waste facilities (landfill). The superior definition of waste is given by the *European Framework Directive on Waste* and is implemented as such in the national waste regulations of The Netherlands and Germany. Because of this superior definition of waste all DM that has to be discarded without any further use is waste irrespective of its contamination.

In The Netherlands there is a national ministerial decision under the Environmental Management Act for the disposal of non-hazardous DM in landfills. By means of this ministerial decision the European Landfill Directive was implemented in Dutch legislation. The ministerial decision can be regarded as the Dutch directive for upland (*above groundwater*) confined disposal facilities (CDFs) for DM. It defines the “maximum” impact on groundwater that is regarded as tolerable. This Directive is similar to the Dutch directive for large-scale (aquatic) disposal sites for DM that is part of the policy document (BVB) on the removal of DM, and has to be applied on CDFs within groundwater. Both directives do not prescribe specific isolative means, but define the maximum tolerable effects on groundwater quality. The maximum tolerable effects are in line with the goals of the Dutch soil protection policy. Possibly in the near future both Dutch directives for confined disposal facilities for DM will be combined.

Germany does not have comparable national DM guidelines for the disposal alongside small waterways and for confined disposal facilities. The term “small waterway” is not defined in any German law or standard. Within the new German Landfill Ordinance the special characteristics were considered with some compromises, which allow waste authorities to permit upland DM disposal sites in an adequate way. The German DM directives HABAK (coast) and HABAB (inland, see 3.1.4) apply to all German federal waterways (7700 km), which do not include waterways/ports/reservoirs/rivers/lakes under the competence of the 16 Länder. HABAK and HABAB do not regulate the disposal of DM along-

side small waterways (exemption in the European Landfill Directive) or in a confined disposal facility in a special way. Despite the complex situation, there are presently no political activities in Germany to create a harmonised national guideline that regulates all aspects of DM handling.

3.1.4. Dredged Material – Where Does Waste Term Apply and End?

Dutch considerations

In the Dutch situation all dredged material is regarded as waste if there is a need for disposal. Based upon the quality, the dredged material is divided into classes. Class 0 is clean material (target-values are not exceeded). Class 1 and 2 are regarded as lightly contaminated and classes 3 and 4 are heavily contaminated. In general the Dutch Environmental Management Act forbids the disposal of waste outside a facility (WM art. 10.2). All waste should be disposed of in specific facilities like prescribed in the decision on facilities and permits (WM, Inrichtingen en vergunningen-besluit, Ivb). Facilities for the disposal of soils are mentioned in category 11 of the IVb, but since contaminated DM is regarded as industrial waste (bedrijfsafvalstof) facilities for contaminated dredged material are belonging to category 28 of appendix 1 of the IVb (facilities for the disposal of waste).

In the Environmental Management Act (WM) an exception on article 10.2 of the WM is made for DM of classes 0,1 and 2 (besluit vrijstelling stortverbod buiten inrichting, 1993 (1) Stb 616, revised 28-07-2000, staatsblad 2000, 352). Clean material (class 0) can be relocated in surface-waters without restrictions from an environmental point of view. DM of Classes 1 and 2, originating from maintenance dredging, can be relocated in - or alongside waterways within certain conditions.

Permits based upon the Pollution of Surface Waters Act are needed for relocation in waterways. For the excavation of contaminated DM a permit based upon the Soil Protection Act is needed also. In order to obtain both permits the sediment (soil) quality has to be known. In this way before the dredging operation takes place the quality of the DM is known. This is necessary because the sediment quality determines indirectly if waste regulations or water or soil regulations apply to the dredging project. Transport of contaminated DM needs a permit based upon the provincial environmental ordinances. The Dutch Building Materials Decree allows re-use DM of class 1, 2 or 3 as a secondary building material. Waste regulations allow this if the DM quality complies with the demands of the Building Materials Decree. During the use of DM as a building material the waste regulations are no longer relevant.

German considerations

The issue of whether dredged material should be classified as waste and when the term should apply is based on the definition of waste in the Closed Substance Cycle and Waste Management Act (*Kreislaufwirtschafts- und Abfallgesetz* - KrW-/AbfG). Under Article 3 para. 1 of this Act, which corresponds with Article 1 a of the EC Framework Directive on Waste (Council Directive 75/442/EEC), waste is defined as "all movable property in the categories set out in Annex I which the holder discards, or intends or is required to discard". In order for the term waste to apply to dredged material, the individual fea-

tures of the definition must be met. Ultimately, the deciding factor is whether one of the statements with regard to discarding can be applied. The "desire to discard", which must always be checked if movable property occurs unintentionally due to certain processing or treatment activities, is particularly significant. Pursuant to Article 3 para. 3 no. 1 of the KrW-/AbfG, "desire to discard" must be assumed in the case of property occurring in connection with certain treatment measures or services, when such occurrence is not the purpose of the action. Under Article 3, par. 3 no. 2, the desire to discard must also be assumed for such movable property whose original purpose no longer exists, or is given up, without being directly replaced by a new purpose.

Since the extraction of dredged material is not the primary purpose of dredging in waterways, it could be assumed that there is a desire to discard in the sense of Article 3 par. 3 No. 1 of the KrW-/AbfG, when dredged material is relocated. It should be noted, however, that a particular measure can also have secondary objectives. Under the European Court of Justice (ECJ) ruling of 18 April 2002 (case C-9/00), the term waste and in particular the feature of discarding must be given a wide interpretation, and therefore stringent requirements have to be met in order for sediment to qualify as a by-product. Under this decision, the sediment could only be classed as a by-product if its environmentally sound re-use without prior processing and following directly on from the extraction process is certain. Uncertain, potential re-uses, or those only possible in the long-term, are not sufficient. Before dredging begins, therefore, and taking ecological aspects into account, it must be clear what role the relocated sediments will play in navigational safety, hydrology, morphology or water management.

Where sediments must be defined as waste they are subject to the waste regime of the KrW-/AbfG. Under the obligations and requirements of this Act, priority must be given to the environmentally sound recovery of dredged material (cf Articles 5 ff KrW-/AbfG) or "if recovery is not technically possible or economically reasonable (cf Article 5 par. 4 KrW-/AbfG)" dredged material must be disposed of in a manner compatible with public interest (cf Articles 10 ff KrW-/AbfG). The waste producer also has the option of recovery in water rather than recovery on land. The decisive factor is whether the material resources are used, or, as formulated in the ECJ decision of 27 February 2002 (case C-6/00), whether the dredged material can fulfill a useful task in the proposed recovery, which entails substituting the materials which must otherwise be used for this purpose and thus enabling conservation of natural resources. Here too, hydrological, morphological, water management and navigational safety aspects all play an important role in the technical assessment. Whether or not discarding dredged material classified as waste in water bodies can be seen as recovery must be decided on a case-by-case basis by the competent authorities on site.

As soon as wastes are discharged or dumped into water bodies, however, they are no longer subject to the provisions of the KrW-/AbfG (cf Article 2 par. 2, no. 6). However, all material and formal requirements of waste law apply without restriction until the moment the wastes are introduced into the water body. The principle of waste avoidance has priority over waste management obligations (cf Article 4 par. 1). Before beginning the measure, therefore, a study must be undertaken to determine whether and to what extent it is possible to avoid or reduce wastes as defined under waste law. The

waste characteristic ends when a material obtained from dredged material is actually used in an environmentally sound way, or if a secondary raw material is produced of such a quality as would appear to ensure its environmentally sound use (e.g. pre-treated and purified sand as building material).

3.1.5. Relocation of Dredged Material in German Inland Waterways

The general approach to dredging and relocation (aquatic disposal) of DM is in principle the same in Germany and The Netherlands, including permissions and standards. DM can be relocated in surface waters (freshwater and saltwater) under specific conditions, which guarantee no harm to the environment or on the banks alongside small regional waterways (freshwater), instead of disposal in specific landfills/facilities. Quality criteria are used both in Germany and The Netherlands to decide if relocation in water/waterways is possible environmentally sound. However, contents and levels of standards are different, and in addition standards for sediments are more detailed in The Netherlands.

Similar to the international guidelines on dredged material management the tiered procedure according to Directive for the Handling of Dredged Material on Federal Inland Waterways (HABAB-WSV, BfG 1997, 2000) includes: planning of the project, avoidance of dredged material; physical, chemical and if necessary ecotoxicological and ecological characterisation; relocation or direct beneficial use; pre-treatment and recovery on land or aquatic disposal besides the Federal waterways; and as the last option, disposal on land; examination of the disposal site and selection of the suitable option. Here, some aspects of the chemical and biological characterisation, and the criteria for the different management options will be highlighted (Peters & Hagner 2001):

- 1) The physical characterisation of the dredged material is compatible with international guidelines. The chemical parameters include As, Cd, Cr, Cu, Pb, Hg, Ni, Zn, and Fe (metals) and organic contaminants such as PCBs (7 congeners), α -HCH, γ -HCH, HCB, Pentachlorobenzene, p,p'-DDT, p,p'-DDE, p,p'-DDD, total of six PAHs, Σ HC, DBT, mineral oil. However, the programme can be adjusted to regional and local special conditions.
- 2) Ecotoxicological studies have to be conducted, if chemical analysis and biological structure analysis indicate that ecotoxicological effects might be possible and the option of relocation is not excluded because of the chemical analysis. According to the HABAB-WSV, the bioassays, which have to be applied in such cases, are in general porewater tests with bacteria (bioluminescence inhibition of *Vibrio fischeri*), algae (freshwater algae growth inhibition test) and crustacea (Daphnia toxicity test). In addition other tests are conducted in special cases.

Criteria for relocation of dredged material in the Federal waterways are summarized in Table 3.1.

In cases of relocation of dredged material in Federal waterways, the Federal Waterway Act (*Bundeswasserstraßengesetz* – WaStrG) has to be considered. For maintenance dredging no permission is necessary (§ 7 III WaStrG), but in case that interests of the *Länder* are affected, they have to give their consent to such actions (Einvernehmen)(§ 4 WaStrG).

Table 3.1 Criteria for the decision of relocation according to HABAB-WSV (Federal Inland Waterways)

Chemical criteria and decision		
Case	Criteria	Decision
Case 1	The median concentration of each single contaminant in the dredged material does not exceed the 1.5 times value of the median concentration of contaminants of the suspended matter (3-annual-median) at the relocation site.	The dredged material can be relocated.
Case 2	The median concentration of at least one contaminant in the dredged material exceeds the 1.5 times value but none exceeds the 3 times value of the median concentration of contaminants of the suspended matter (3-annual-median) at the relocation site.	The decision about relocation has to be proven in every single case. Inputs of pollution into the water body have to be considered. In addition the ecotoxicological assessment of the dredged material can be considered.
Case 3	The median concentration of at least one contaminant in the dredged material exceeds the 3 times value of the median concentration of contaminants of the suspended matter (3-annual-median) at the relocation site.	It is not allowed to relocate the dredged material in principle.
Biochemical Criteria		
The relocation must not cause an oxygen consumption in the water body below 4 mg/l		
Ecotoxicological Criteria		
Case 1	Porewater of the dredged material in a dilution of 1:4 does not cause toxicological effects.	The dredged material can be relocated.
Case 2	Porewater of the dredged material in a dilution of 1:4 causes toxicological effects.	A case-by-case decision will be made, further ecotoxicological studies might be necessary.
Ecological Criteria		
Negative effects on the benthos have to be avoided. The extent of acceptable effects has to be decided on a case-by-case basis		

In addition, the Federal Nature Conservation Act (*Bundesnaturschutzgesetz* - BNatSchG) has to be considered. Pursuant to § 3 III 2 BNatSchG the other authorities shall inform and consult the authorities in charge of conservation of nature and of landscapes as early as in the preparatory stages of any public plan or measures which may affect the interests of nature and landscape conservation. If the dredging operation causes encroachments on nature and landscapes, as defined in the BNatSchG, compensation or substitution measures have to be carried out (§ 8 I, II, VI and IX BNatSchG). In parallel to the relocation option it should be proven, whether the dredged material might be directly used (without technical treatment). If the dredged material cannot be relocated or directly used, then in general also one of the three alternatives of disposal is fulfilled.

If the dredged material is waste in the sense of KrW-/AbfG (see 3.1.4), the basic principles of the KrW-/AbfG must be applied: avoidance, recovery and disposal (§ 4 KrW-/AbfG). For recovery of dredged material, a treatment step is necessary. There are in general different treatment techniques possible (see HABAB-WSV). Several regulations regarding recovery exist, which have to be considered depending on the purpose, e.g. for agriculture and forestry use the technical guidelines of the *Länder* Working Group Soil (LABO) and the Ordinance on Sewage Sludge (*Klärschlammverordnung* - AbfKlärV). For land disposal of dredged material, several regulations, e.g. the Technical Directive on Waste Disposal (*TA-Abfall*) have to be applied (HABAB-WSV, Bertsch & Köthe, 1996 & 1999).

Aquatic disposal is part of the Water Management Act (*Wasserhaushaltsgesetz* - WHG) and its implementation by the *Länder*. For any aquatic disposals a permit or concession is necessary (§ 2II Nr.6 WHG). Generally, solid matter shall not be introduced into waters for the purpose of disposal. However, sludge and dredged material shall not be deemed to be solid matter. Substances may only be stored or deposited near waters if no pollution of the water or any other detrimental change in the properties of the water or in water flow is caused (§ 26 I, II WHG). To summarise, the German dredged material management consists of a complex system of regulations. The Federal approach, stated by the HABAK-WSV and HABAB-WSV is not based on environmental quality objectives but on prevailing contaminant concentration and therefore a prohibition of deterioration is stated. The Federal and *Länder* regulations differ in their evaluation of contamination of dredged material that results in different disposal strategies. There is a strong need for a harmonised, nation-wide regulation (Netzband 1997; Köthe et al. 1998). The German Association for Water Pollution Control (ATV) has compiled a Memo M 362 Recommendation for the Handling of Dredged Material (1997) for German inland waters. However, this association did not have a political mandate for co-ordination between the *Länder*. Such a mandate was given by the Conference of *Länder* Ministers for the Environment to the *ad-hoc* Working Group on Dredged Material of the Working Group of the Elbe (*Arbeitsgemeinschaft Elbe* - ARGE Elbe).

3.1.6. Subaquatic Disposal of Dredged Material

Dutch considerations

The EC Landfill Directive (1999/31/ES) (see 3.1.1) is relevant to disposal sites for DM on land only. In the Dutch point of view this does not mean that subaquatic disposal is prohibited. A confirmation to this point of view can be found more or less in Art. 3 of the EC Landfill Directive. Article 3 states that the relocation of non-hazardous dredging sludges alongside waterways or in surface waters is excluded from the scope of the Directive. Also the Dutch definition of surface water is relevant to this question (Annex I). For example the CDF "Ijsseloog" is situated in the lake Ketelmeer. However the water inside the facility (pit) is not surface water according to the Pollution of Surface Waters Act. The water in the pit is part of the facility because of the surrounding dike (protection of the surface water).

In The Netherlands a way was found to deal with this issue. The EU Landfill Directive was implemented in 2001 by means of the Ministerial Decision under the Environmental Management Act, for dispo-

sal facilities for non-hazardous DM on land (above groundwater). A directive for Subaquatic disposal of DM is part of the policy document on the removal of DM (1993). In the Dutch point of view DM is a very specific kind of waste. Because of the specific properties (low permeability, low leaching under anaerobic conditions) of the DM, subaquatic disposal is possible without severe effects on the environment, including groundwater-quality. The Ministerial Decision on upland disposal and the Dutch directive for subaquatic disposal take the specific properties of the waste category DM into account. Specific isolative measures are not prescribed for disposal facilities for DM, but both documents define the maximum tolerable effects on the environment and especially on groundwater quality. Those definitions are in line with the Dutch Soil Protection Policy. The isolative measures that will be taken to ensure the protection of the environment can therefore be site-specific and differ between facilities. In this way the regulations do not exclude the use of innovative isolative techniques. In general isolative measures must be taken to reduce emission of pollutants *As Far As Reasonably Achievable* (ALARA). However subaquatic disposal sites are only allowed if (amongst others) permits are issued based on the Environmental Management Act and the Pollution of Surface Waters Act (for the discharge of waste-water originating from the disposal facility on the surrounding surface water). Studies carried out in The Netherlands have even pointed out that, under certain conditions, disposal of contaminated DM directly in pits in surface waters is possible without intolerable effects on water quality.

German considerations

In subaquatic (stationary) disposal, DM is placed below the water surface in such a way that no hazard to the environment occurs. The regulations of the commercial and industrial waste management act (*Kreislaufwirtschafts- und Abfallgesetz (KrW-/AbfG vom 27. September 1992)* are pursuant to §2, Section 6 not applicable to substances if these are introduced or discharged into water bodies or wastewater facilities. Neither does the landfill ordinance (*DepV*) regulate subaquatic disposal. Article 3 (2) of the European Landfill Directive expressly excludes subaquatic disposal of non-hazardous sludges. Consequently, subaquatic, stationary disposal of DM is not governed by waste legislation, but by water and waterway legislation. Many internationally available experiences, partly documented in PIANC reports show that - due to the specific properties of aquatic sediments - this special form of disposal at suitable sites is both economically and environmentally acceptable and is regulated outside waste legislation. It would be desirable to establish this disposal practice legally at the European level.

3.2. Management Practice in The Netherlands and Germany⁸

3.2.1. Management Practice in The Netherlands

In The Netherlands each year 25-30 million m³ partly contaminated dredged material has to be removed. More than half of this amount comes from maintenance dredging for the main port Rotterdam,

⁸ selection from: Dutch-German Exchange on Dredged Material, Part 2 (DGE-2, 2002)

which has a leading position in the world. Dredging is mainly done by Rijkswaterstaat (Ministry of Transport, Public Works and Watermanagement), waterboards and municipal authorities.

About $\frac{3}{4}$ of the dredged material is marine sediment, transported inland by sea currents. The major part (90 %) of these marine sediments is clean or hardly contaminated and can be relocated in the sea. Only 30 % of the dredged material from fresh waters can be relocated because of higher contamination levels. Another reason that hampers relocation on the banks of waterways is lack of space. Source control is a prerequisite for a sustainable strategy on the management of dredged material. The target for the Dutch policy is that within 25 years the sediment quality will have improved to the level that the dredged material can be completely relocated or beneficially used. For the dredged material that is too much contaminated for relocation there are two options: treatment for beneficial use and disposal. The major part (approximately 90%) of this contaminated dredged material (CDM) is disposed (3-5 million m³/year). Disposal is mainly subaquatic in confined disposal sites (CDFs), but on a small scale also dewatered DM is stored in upland disposal sites. The largest CDF is the Slufter with a design capacity of 95 million m³ mainly meant for the contaminated dredged materials near Rotterdam. Recently a CDF was constructed in the Ketelmeer (IJsselmeer) with a capacity of 23 million m³. New CDFs in combination with treatment facilities are in preparation e.g. in the southwestern part (Koegorspolder) and downstream of the Meuse (Hollandsch Diep). For these CDFs an open and careful communication process was carried out to gain public support.

The Dutch Development Program for Treatment Processes for Contaminated Sediments (POSW), starting in 1989 and running until 1996, was aimed at the development of ecologically sound dredging and processing techniques to be used in the remediation and reuse of polluted sediments (Anonymous 1997; Rulkens 2001). Typical research issues of the POSW Stage II (1990-1996) program were:

- Separation of DM into subflows (hydrocyclone separation, upstream separation, settling, flotation, dewatering of fine fractions, practical experience in pilot remediation),
- Thermal and chemical treatment methods (thermal desorption, incineration, solvent extraction),
- Biological treatment (land farming, greenhouse farming, slurry treatment in bioreactors),
- Immobilization of pollutants in products (melting, sintering, experience in pilot remediation),
- Assessment of the environmental effects of processing chains (based on life cycle analysis, LCA),
- Scenarios for large-scale processing, varying from natural processes in treatment plants (e.g.: sedimentation, dewatering, landfarming, ripening) to maximum deployment of classifying and polishing methods.

Until now treatment of CDM is very limited (0.5 million m³/year) and has been done on a small scale only, because of the higher costs of treatment compared with disposal, no guaranteed supply of dredged material for treatment and the lack of a market for the products of treatment. Ripening is commonly applied in the rural areas on a small scale mainly for clean or lightly contaminated dredged material from regional waterways. The dewatered dredged material (clay) is locally used to raise the

land. A pilot project to use the clay from dredged material for road construction is in preparation. Landfarming and phytoremediation is restricted to small scale pilot projects. Next to ripening, the separation of sand from dredged material is the most frequently applied treatment technique. This is mainly done in sedimentation basins near the large CDFs Slufter and IJsseloog. Separation of sand by hydrocyclones is practised on a smaller scale. Stabilization of dredged material has been applied in small pilot projects only. Thermal immobilization is not (yet) operational.

Dutch policy on treatment and disposal

The Dutch government has approved the Master plan in April 2002 (Tienjarens scenario), what has resulted in the release of an extra budget of € 150 Million to tackle the dredging arrears. This budget is only the first step and will be invested mainly in maintenance of waterways in urban area and the remediation of contaminated sites in the next 4 years. A decision on a structural increase of budgets, which is needed to solve the problem in the future, will be taken by the next government.

In order to find more destinations for dredged material, the Dutch policy is aiming at enlarging the share of treatment of CDM into building materials. First, a national inventory and assessment of the possibilities of large-scale treatment has been set up (project Impulse B2). Second, several measures have been taken to stimulate the treatment of CDM. The inventory of treatment has led to the conclusion that in general treatment is still more expensive than large-scale disposal for most of the dredged materials. Furthermore, treatment should not be done at the expense of dredging, which means that more budgets are needed.

Based on this inventory, the Dutch government has set aside a budget of more than € 70 million for treatment of CDM during a test period of four years. This budget is meant for two purposes: a large-scale pilot project and a subsidy for treatment of contaminated sediments. The objective of the pilot project is treatment of at least 50% of the supply of dredged material, which has to be reused as construction material. A tender for this pilot project resulting in a private-public partnership is expected for the second half of 2004. The subsidy for treatment is meant to bridge the financial gap between disposal and treatment in order to stimulate treatment. Another financial instrument, meant to stimulate treatment and reduce disposal, is the Minimal Treatment Standard, which at the 1st of January 2005 will replace tax on the disposal of CDM that can easily be treated. For the time being, the criterion for treatability is 60% or more sand in the DM. The aim for the subsidy is to encourage new technologies not yet commonly applied in practice on a large scale. Legislative obstacles to the re-use of products will be removed by adaptation of the Dutch Building Materials Act on the parameters sulphate, mineral oil and fluoride. Furthermore, measures will be taken to promote markets for products from treatment. The policy of the Dutch government is aiming at a step-by-step conversion to increased treatment by an integral approach of measures. The effectiveness and effects on dredging activities will be closely monitored and evaluated to ensure that the objectives of treatment are met and that treatment will not frustrate the dredging activities.

3.2.2. Management Practice in Germany

In Germany about 40 to 50 million m³ of sediments have to be dredged annually for maintenance of ports and waterways, mainly in the coastal areas of the North Sea. Maintenance of the waterways is done by the Federal Waterways Administration; maintenance of the ports is done by the federal states or the cities. The same applies to capital dredging. Rehabilitation works are of minor importance in the coastal area. Most of the above mentioned material stems from the sea and is more or less uncontaminated and can therefore be relocated. Due to exceeding given standards some of the material especially in ports cannot be relocated. In the North Sea area contaminants like heavy metals, organic contaminants or TBT are of main concern. In the Baltic Sea often the nutrient load does not allow relocation into the sea. Generally, source control is necessary to solve the problem of contaminated sediments not only to the environment, but also for those responsible for maintenance of ports and waterways. For example the International Commission for the Protection of the River Elbe foresees that the sediments shall be clean by the year 2010 in a way that they can be used, for example, for agricultural purposes.

German policy on treatment and disposal

There is no common, coherent German policy on dredged material. However, the deputies of the state ministries for environment have set up some guidelines (LAGA, 1997) and requirements for the treatment and beneficial use of mineral waste based on classification of contaminated sediments and target values. The guidelines have to be applied for maintenance or other sediment related activities in inland rivers, harbours, lakes, flood retention and drinking water reservoirs. In practice however, the states have their own policy, which often deviates from these guidelines for several reasons. By the end of 2003 the German Organisation for Water Resources Management, Waste Water and Solid Waste (ATV- DVWK) has produced a draft report on "Treatment of dredged material, Part II, case studies" which presents quite a large spectrum of how different practical problems with contaminated sediment have been solved throughout Germany in the past in compliance with the existing guidelines. The draft is still under revision but it can be expected that it will be finished in 2004. Treatment and disposal are especially known from the Ports of Hamburg, Bremen, and Rostock. Besides that, flushing fields etc. are in operation on a smaller scale.

Hamburg. Dredged material is treated in Hamburg in the large-scale METHA-plant. Its main task is to separate sand and fine sand from silt and to dewater the (contaminated) silt for further beneficial use and / or disposal. The throughput capacity is roughly 1 Mio. m³ sediment *in situ* per year corresponding to more than 500.000 tons dry matter. Total investment cost was € 70 Mio. (in the year of construction 1993). Including capital costs and expenditure for operation, maintenance and personnel, the calculatory specific costs average to 15-20 €/m³ sediment in-situ. The same task as in the METHA can be accomplished by flushing fields (for classification) and dewatering fields. Advantage are lower operating costs, disadvantages are large areas needed and dependence on

climate. The pre-treated silt is mainly disposed in two specially constructed silt mounds which fulfil German criteria for landfills. Each has a capacity for ca. 20 Mio. m³ untreated sediment and will reach a final height of 38 m above the ground. In these mounds, the separated sand is beneficially used as drainage material. The mineral seals are made by selected, pre-treated silt.

Bremen. In the Port of Bremen, about 300.000 m³ of sediments (mainly silt) have to be dredged annually. The contamination is predominantly caused by heavy metals (cadmium, zinc, lead) coming from sources upstream and organic substances like TBT. The dredged sediments are dewatered and stabilised in dewatering fields within 1 year. After the dewatering process, the material is deposited in a landfill / silt mound with an upper and a lower seal system. The mineral bottomsealing system was constructed by using specially selected silt. The dewatered silt has a permeability coefficient less than $1 \cdot 10^{-9}$ m/s and meets other soil mechanic parameters for liners as well. Excess water is collected via drainage layers and diverted to a treatment plant. Treatment and silt mound cover 127 ha in total, additional 124 ha are for compensation. The mound capacity comprises 4 Mio m³. The planned filling time is 20 years. In parallel, Bremen has examined possibilities to integrate various sediment treatment techniques into the existing management concept. The costs for dredging and disposal of the material range between € 10 - 13 Million per year.

Rostock. In the Port of Rostock at the Baltic coast, dredged sediments cannot be relocated into the sea due to nutrient contents, contaminants are of minor importance. The dredged material is dewatered in ripening fields. Then it is used as earthworks material or for agricultural purposes.

3.3. Biological Effects-based Sediment Quality in Ecological Risk Assessment for Dutch and German Waters⁹

Historically, sediment quality has been assessed by making comparisons between concentrations of contaminants with (numeric) sediment quality guidelines (SQGs). Based on such a comparison, the potential risks, or hazard of (groups of) sediment-bound contaminants can be estimated. A recent overview of the use of SQGs in Europe has been given by Babut et al. (2002). An important aspect in the risks caused by sediment-bound chemicals is the degree of exposure encountered by sediment-dwelling organisms. It is well documented that only part of the contaminants are biologically available, because desorption can be thus slow, that the actual exposure level is less than what would be expected on the basis of the total concentrations of the compounds in the sediment (Hamelink et al. 1994; Kraaij 2001). However, it is also known that mixtures of contaminants can have synergistic effects, which may not be well addressed by single SQGs (Hermens et al. 1984; De March 1987; Von Danwitz 1992). For these reasons, and because of the large number of unknown contaminants as explained above, ecological risk assessment of sediment quality has received much attention in the past decades. The advantages of biological endpoints, such as effect bioassays, over chemical quality

⁹ selected from Den Besten et al. (2003)

assessment are that biological testing integrates the effects of all contaminants present at their actual bioavailability (and detect possible synergistic effects).

Most so-called ecological risk assessment (ERA) frameworks deploy biological effect-based sediment quality assessments (BEBA). The basic principle of most of ERA is the use of multiple lines of evidence (Burton et al., 2002). Important lines of evidence are: 1) Assessment of the condition of the benthic macroinvertebrate community; 2) Assessment of sediment toxicity using bioassays (BEBA); and 3) Assessment of the potential effect occurring through food chain poisoning. The present chapter (extracted from Den Besten et al. 2003) gives an overview of ecological risk assessment frameworks that are used in The Netherlands and Germany. Two main goals for sediment quality assessment in these countries are distinguished:

- Biological Effects-Based Assessment of *in situ* risks (in situ BEBA) at sites where sediment remediation is to be considered;
- Biological effects-based assessment of the *ex situ* quality of dredged sediments (ex situ BEBA) in order to select sediment management options (e.g., confined disposal or treatment options).

Comparing in situ and ex situ BEBA, it is likely that the assessments lie at very different levels in a decision making process. In situ BEBA is a front-end investigation necessary to evaluate whether sediments create a risk, before any decision if some action would be needed. Ex situ BEBA is something that is carried out after it has already been decided to dredge (e.g. dredging for nautical reasons), but when disposal options have to be considered. Apart from the ERA approaches explained above, there may be different concepts using risk information for other questions, such as prioritizing.

3.3.1. In situ Effect-Based Assessment

The biological effects-based assessment of the *in situ* risks in sediment (in situ BEBA) focusses on location-specific conditions with respect to the bioavailability of contaminants and the assessment of damage to the ecosystem. Assessment of damage to the ecosystem can be both prognostic and retrospective. *In situ* BEBA can be considered as one of the lines of evidence in ERA (Burton et al., 2002). ERA can be combined with studies focusing on risks related to transportation of contaminants back to the surface water, or to deeper sediment layers, and subsequently to the ground water.

With the growing concern for the potential problems caused by sediment contaminations, ecological risk hazard assessment approaches have been proposed as decision support tools or instruments for prioritization. These approaches generally rely upon a tiered process, in order to allocate properly limited technical and financial resources.

In general, three main purposes can be identified for which in situ BEBA frameworks have been developed (Ingersoll et al. 1997):

- Integration of information from large numbers of parameters that use different lines of evidence (e.g., sediment chemical concentrations, sediment toxicity, benthic community diversity, tissue concentrations, etc.);
- Proof of causality between environmental effects and sediment contamination;
- Tiered approach for increasing confidence in a cost-effective manner.

The Netherlands

Assessments of *in situ* sediment quality in the Netherlands follow a tiered approach. The *in situ* BEBA is part of a broader evaluation of risks caused by sediment contamination:

- 1) 1st tier assessment: comparison of levels of priority pollutants with national standards/guidelines. Contaminant levels are normalised according to the approach described by CUWVO (1990), in order to compensate for differences in sorption characteristics between sediments¹⁰. Normalised contaminant levels are then compared with the Dutch sediment quality criteria (developed for 1st tier assessment of risks for human health and ecosystems). According to the resulting classification, most contaminated sediments (class 4 on a 0 to 4 scale) require a risk assessment (2nd tier).
- 2) 2nd tier assessment: The primary statement for this second line assessment is as follows: if a priority contaminant exceeds the intervention value, the site needs to be remediated urgently, unless it is shown that there are actually no high risks at that particular site. (so, there is an assumption of risk, until it is disproven). When the data from the 2nd tier show no high risk at a site where a priority contaminant exceeds the intervention value, the need for remediation is not considered as urgent anymore. Conversely, if actual high risks were confirmed, the next step would review different remedial options, that are to be compared for the expected risk reduction. Three main pathways are seen for a complete risk assessment, the third being an *in situ* BEBA approach:
 - Human exposure: model calculations are carried out in order to quantify the extent to which humans (adults/children) can be exposed to contaminants via food consumption or via recreation activities in water. When the exposure exceeds maximum permissible risk criteria, actual risk is concluded. The model is based on general assumptions with regard to behavior and diet of human populations.
 - Investigation of the risk for transport of contaminants from the sediment to groundwater, or to surface water. Model calculations are carried out in order to quantify the extent to which these processes occur. When contaminant fluxes (preferably calculated from field data) exceed high risk criteria, actual risk is concluded.
 - *In situ* BEBA. The evaluation of risks for the ecosystem is done using the TRIAD assessment. In the Dutch version of the TRIAD (integrating chemical measurements, biological investigations and ecotoxicological measurements; section 2.4) bioaccumulation measurements are also consi-

¹⁰ standard sediment is defined as having a 25% particle fraction < 2 µm and 10% organic matter on a dry weight basis

dered, using the results of laboratory tests, or preferably by measurements in indigenous organisms (Den Besten et al., 1995). Based on the *most sensitive* parameter, sediments are classified for the categories "field observations" and "bioassays" as either "-" (no effect/risk), "±" (moderate effect/risk) or "+" (strong effect/high risk). The goal is to elucidate the relationship between effects on macrozoobenthos and responses of bioassays, which, in turn, can be related to levels of chemical contamination. For that purpose, chemical concentrations are converted into "toxic units" (TU): These are the ratio between the chemical's normalized concentration and the lowest no-effect-concentration (NOEC) reported in the literature, among the bioassays included in the battery (Den Besten 1995). High risk is inferred when strong effects are observed in field surveys and/or bioassays that can be related to chemicals present in the sediment.

Table 3.2 NL-classification of effects in bioassays in the Triad approach^{*})

Daphnia	parameters (equal, take most sensitive)			
	NOEC-mortality (in % dilution of pore-water)	Mortality in undiluted pore water	NOEC-reproduction	Inhibition of reproduction in undiluted pore water
Criterion 1	NOEC < 100% NOEC > 10%	-----	NOEC < 100% NOEC > 10%	Inhibition >10% Inhibition <50%
Criterion 2	NOEC ≤ 10%	mortality ≥ 50% within 48h	NOEC ≤ 10%	Inhibition ≥50%
Chironomus	Parameters (equal, take most sensitive)			
	Mortality of eggs, prior to start sediment bioassay (incubation in elutriate)	Mortality larvae	Inhibition of development	Effect on weight (negative effects are scored only)
Criterion 1	mortality > 25%	mortality > 10% mortality < 50%	inhibition > 10% inhibition < 50%	effect > 10% effect < 25%
Criterion 2	mortality ≥ 50%	mortality ≥ 50%	inhibition ≥ 50%	effect ≥ 25%
Microtox	parameter: 1/EC20 (5, 15, 30 min: equal, take most sensitive)			
Criterion 1	1/EC20 > 2			
Criterion 2	1/EC20 ≥ 10			

^{*} Exceedance of criterion 1 results in class 2 toxicity (moderate effects); exceedance of criterion 2 results class 3 toxicity (strong effects); otherwise, class 1 (no toxicity).

Classification of sediment can be done on each of the bioassays independently (i.e., most sensitive bioassay determines the toxicity score).

Effects on which score depends should be significant at $p < 0.05$

- 3) Prioritization. When the supplied data from the second tier show that there are actually no high risks at a site where a priority contaminant exceeds the intervention value, the need for remediation is not urgent anymore. In case actual high risks were confirmed, a next step is possible in which different remedial options are considered for the risk reduction that can be achieved. The information from the sediment quality assessment can be used again in setting priorities within the group of locations that need to be remediated urgently. In the Netherlands some experience exists with the use of multi criteria analysis (MCA; also called Analytic Hierarchy Process (AHP);

Saaty 1980) for this purpose. MCA enables a ranking of sites based on risks for the ecosystem. This method (described by Den Besten et al., 1995) is based on the same classification of results as described above. For each criterion (= parameter), standard numerical values (scores) were assigned to the effect/risk classes, from the value 1 for the class representing the strongest effect or highest risk, to for example 0.5 and 0.25 for the classes representing moderate risk and no risk, respectively. Then the criteria are given a specific place and weight in a hierarchy. The scores are multiplied by the weight of the corresponding criterion and subsequently totalized bottom-up using a computer program, resulting in a final score between 0 and 1. The difference between the final score and the theoretical score 1 (the score for a site with strong effects / high risk for all parameters) gives an indication of the risks for ecosystem health at each of the sites. For this method all available information from the field surveys can be used, including site-specific information from bioaccumulation studies. At a higher level of hierarchy, information from human risk studies, ecological risk assessment, and estimates of contaminant mobility (transport) can be integrated. In the MCA, specific weights can be attributed to the different criteria (=parameters) and higher in the hierarchy, at branch points. This makes the method useful for decision makers, who have to deal with all these aspects at the same time and therefore need integrated information. In the near future, estimates of the expected beneficial effects of remedial action will also be integrated in the step of prioritization of dredging locations.

Germany

Several research groups have recommended application of a Triad approach, (Neumann-Hensel et al. 2000; Ahlf and Förstner 2001; Ahlf et al. 2002, Hollert et al. 2002). Based on an inventory of bioassays and biological classification methods to establish ecological quality criteria (Ahlf & Gratzner, 1999), a classification scheme for screening of ecotoxicological sediment quality was developed, that integrates results of 5 biotests including whole sediment toxicity tests (Heise et al. 2000).

Recently, recommendations were made for the use of an integrated stepwise approach combining toxicological, chemical and ecological information to assess and evaluate the quality of sediments (Neumann-Hensel et al., 2002). A difference with the approaches followed in most other countries is that bioassays are used as a trigger for further research steps, instead of chemical data that is more commonly used. In Henschel et al. (2002) a stepwise approach is described for an integrated assessment of ecosystem health effects and the consequences of sediment contamination for human health.

3.3.2. Ex situ Effect-Based Assessment

Ex situ BEBA is a *hazard assessment*, in which biological/toxicological endpoints are used as predictors of possible effects that may occur when the sediment is disposed of in the environment. In this BEBA, often bioassays are included in the sediment quality assessment or added as a second Tier. The approach is more prognostic, i.e. based on the outcome of the assessment, predictions are made of the consequences of free disposal of dredged sediments in the environment. In that respect this

approach, using sediment toxicity assessment bears resemblance with total effluent risk assessments (see e.g. Grothe et al. 1996; Tonkes et al. 1999).

The Netherlands

For the assessment of the possibilities of disposal of marine dredged material in the coastal waters of The Netherlands, recently a new sediment quality approach was developed, the chemistry toxicity test (CTT; Stronkhorst et al. 2001). Three bioassays have been selected for routine application in the CTT approach (Table 3.3), viz a mud shrimp toxicity test, a bacterial test (Microtox solid phase) and the DR-Calux assay, which reacts specifically to dioxin-type compounds. In the CTT approach, in order to allow free marine disposal of sediments, sediment quality guidelines need to be met both for the concentrations of a list of chemicals (see par. 4.2.1). The degree of effect observed in the bioassays are not yet implemented as quality criteria for marine disposal.

Table 3.3 Ecotoxicological criteria for the CTT test for evaluation of dredged marine sediment

Test/compound	Group	Units	Criterion ¹
Amphipod <i>C. volutator</i>	combination toxicity	Mortality (%)	50
Microtox SP, bacteria <i>V. fischeri</i>	combination toxicity	Decrease bioluminescence (1/EC _{50,corr}) ²	100
DR-CALUX, cell-line	dioxine-type	ng TEQ/kg dw	50

¹ concentrations without standard correction, ² EC₅₀ corrected for fraction of fine silt

Germany

For an ex situ BEBA type of application, Krebs (1988) proposed an ecotoxicological sediment quality assessment that is based on the number of dilutions steps, that are necessary to decrease inhibition in elutriates or pore water below 20 %. This is expressed as pT-value and part of the HABAB regulation (see Table 3.1: a dilution of 1:4 corresponds to a pT-value of 2).

3.3.3. Outlook

The application of bioassays provide ERA approaches with more information about the exposure of organisms in contaminated sediment. At the same time, this step forward also creates concern with regard to quality assurance of the techniques. Several issues are of great importance when using bioassays for the evaluation of sediment quality. Firstly, bioassays are subject to a number of confounding factors that may have nothing to do with contaminant load (such as grain size, ammonia, and countless other issues). Secondly, it is very important to define references and controls that are meaningful for the site under consideration. A third point of concern is the question whether all relevant modes of action can be covered by a set of bioassays. For instance, if only bioassays are used

that measure acute toxicity, sublethal modes of toxicity (effects on fecundity, growth, immuno-competence etc.) could be overlooked with important consequences for ecosystem health.

In order to be able to harmonize *in situ* and *ex situ* BEBA approaches between countries, it is necessary to discuss the goals for sediment management. From the perspective of the EU Water Framework Directive (EU WFD), it seems logical to harmonize the approaches on a river basin level. Because the EU WFD focuses primarily on water quality, it can be expected that *in situ* BEBA approaches will be used mostly as a diagnostic tool, i.e. to determine whether a poor ecological status of waters is caused by sediment contamination. These approaches may already be part of regulations, or will be. Therefore, harmonization will be difficult, or take a long time, and probably dependent on a top-down approach (European directive). But for *in situ* sediment quality assessment this may not be necessary, except for the fact that clearly a need is felt to intensify the exchange of information on the criteria used to infer effects and to classify sediment quality. The situation might be different for *ex situ* BEBA approaches. When the relocation of dredged material in surface water is concerned, harmonizing the sediment quality assessment in river basins is needed. The *ex situ* BEBA can help to more effectively prioritize dredged sediment with high ecological risks, that should be transported to confined disposal sites. Such prioritization can better be made based on effect observations than on chemical measurements, because biological responses integrate the effects of all biologically available contaminants.

3.4. Sediment Management Issues in the WFD-Strategies for Monitoring and Emission Controls of Priority Substances

A main objective of the WFD is to achieve good ecological or good ecological potential and chemical status for each water body. Therefore a singly source/pathway or when considered collectively with other sources/pathways may have a potential to result in the failure of the objective if it contributes to a concentration in excess of the Environmental Quality Standards (EQS) set in the aquatic environment for a specific priority substance (chemical status) and/or if it contributes to the failure of meeting the ecological status. It is also important to note under Article 16 of the WFD there is a requirement to achieve the progressive reduction of discharges, emissions and losses of priority substances and cessation or phasing out of emissions, discharges and losses of priority hazardous substances. A further objective of the WFD is the “no deterioration” requirement. These objectives need to be taken into account when assessing the different sources/pathways.

It is interesting to see that while sediments and dredged materials are not explicitly mentioned in the Water Framework Directive they will play an important role in the forthcoming steps for the implementation of measures against pollution from priority [hazardous] substances (PS/PHS) under WFD Article 16 – monitoring programmes to be operational (Article 8, 2006) and establishment of the programme of measures (Article 11, 2009). In the previous sections of chapters 2 and 3 of the present study, the discussion process among the relevant expert groups has been described:

3.4.1. Recommendations of the Expert Group on Analysis and Monitoring of Priority Substances (AMPS)

In the draft final report from 10 June 2004 the Expert Group on Analysis and Monitoring of Priority Substances (AMPS), based on discussions during their meetings in Brussels (22-23 January 2004) and in Ispra (31 March to 1 April 2004) provided recommendations to sediment-related issues (see Box on pages 36 and 37):

- A majority of AMPS expert group members agreed that whole water is the relevant matrix for compliance checking of the EQS derived for the priority substances other than metals. The approach recommended by the AMPS expert group is that the choice of how to generate the required data and the proof of its fitness for purpose should be the responsibility of Member States. Thus whole water data may be generated by analysis of the whole water sample, or by separate determinations on dissolved and solid phases.
- The recommendation of the AMPS Expert Group is that, it is not advisable to establish specific EQSs for suspended particulate matter (SPM) at this stage. It was noted that the issue of monitoring compliance with any future quality standards will furthermore raise the questions of comparabilities of phase separation methodologies. The AMPS Group did furthermore not consider that, from a monitoring point of view, it would be technically feasible to propose EQSs in the near future for sediment and biota.

The AMPS expert group was asked to provide further insight and recommendations on the practices of sediment and biota sampling, for these purposes, but also to assess the practical aspects of checking compliance in these matrixes of specific EQS.

Separate requirements (for instance location and frequency of monitoring) on surveillance and subsequently operational monitoring of sediment and biota for the purpose of assessing long-term trends in impacts anthropogenic pressure and to ensure the no deterioration objective is reached may therefore be necessary, to ensure that comparable data can be collected.

- The AMPS Expert Group convened two drafting groups to consider these issues. The groups assessed current practices by means of questionnaires and then developed recommendations on the way forward. It emerged that the monitoring frequency varies widely and it was agreed that the appropriate frequency should be based on local circumstances.

Metal Background Reference Concentrations (BRCs)

In the discussions on monitoring and implementation of measures for priority substances an “added risk approach” has been proposed for metals, and a first step is the use of natural background concentrations. A respective AMPS working group has defined the background metal concentrations as follows:

"The background concentrations of target metals (Pb, Cd, Ni, Hg) in the aquatic ecosystems of a river basin, river sub-basin or river basin management area is that concentration in the present or past corresponding to very low anthropogenic pressure."

Various methodologies such as measurements of trace metals in pristine areas, groundwater, selection from long-term data sets applying appropriate statistical methodology, and long-term data sets and partitioning, are employed to provide estimates of the BRC (AMPS draft final report, June 2004).

3.4.2. AMPS Drafting Group on Sediment Monitoring

Recommendations of a drafting group on Sediment Monitoring of the Expert Group on Analysis and Monitoring of Priority Substances (AMPS) were, among others (see Box on page 38):

- Initiate the development of a community-wide diagnostic guideline on the assessment of contaminated sediments in relation to the degradation of both ecological quality elements (benthic community, fish etc.) and water quality. Such a diagnostic guideline should be made available by 2006 in order to support Member States in their effort to implement the WFD;
- Initiate the development of a community-wide technical guidance on sediment sampling and handling, analytical techniques and normalization procedures. Such a technical guideline should be build on existing protocols/guidelines and be made available by 2006 in order to support Member States in their effort to implement the monitoring requirements of the WFD.

The drafting group outlined a list of priority substances of the Water Framework Directive that are suggested for trend monitoring in sediment and or biota (Box on page 38).

3.4.3. Quality Standards for Sediments and Biota: Response of the Scientific Committee on Toxicity, Ecotoxicity and Environment

The opinion of the scientific committee on toxicity, ecotoxicity and the environment (CSTEE) on „The Setting of Environmental Quality Standards for the Priority Substances included in Annex X of Directive 2000/60/EC in Accordance with Article 16 thereof" was adopted by the CSTEE 43rd plenary meeting of 28 May 2004 (see Box 46):

"We note that at this stage the Commission envisages presenting Quality Standards only for the water phase and that this would include reporting the concentration of a priority substance in the whole water; i.e. including the dissolved fraction and that (fraction) bound to suspended organic matter. We believe that there are some difficulties with this being applied uncritically:

- To base protection on a water column standard ignores many of the biological complexities of exposure through absorption and ingestion by sediment organisms

- The exposure of chemicals through the food chain is not only relevant for secondary poisoning in birds and mammals, but also for aquatic invertebrates and fish and the EQSs based on waterborne exposures are not protective in all cases
- Basing exposure concentrations on whole water may be very misleading with regard to bioavailability... The concentrations of lipophilic substances will depend on the amount of suspended particulate matter (SPM) in the sample, which will depend on where, when and how the sample is taken

As a conclusion the CSTEE believes that specific quality standards can and should be developed for sediment and biota, and should be based on direct assessment and monitoring.

3.4.4. Priority Substances in Historical Contaminated Sediments¹¹

In order to record the different steps undertaken to identify the measures under Article 16 of the Water Framework Directive, the Expert Advisory Forum (EAF) on Priority Substances and Pollution Control formulated a concept paper on the control of emissions, discharges and losses of priority substances and priority hazardous substances. The process proposed to develop the appropriate mix of emission controls until the year 2009 has the following steps.

1. Inventory of all generic sources that result in releases and their pathways – source screening
2. Identify existing control measures at EU level
3. Identify appropriate sources where measures could be taken under the WFD and possibly other EU legislation (taking into account the effect of the present measures and changes in releases that will take place irrespective of existing and new reduction measures)
4. Set priorities
5. Develop the measure

Under step (1) "source screening" the following systematic presentation of pathways and underlying sources was proposed: (A) Losses to surface water by diffuse sources (S1: Atmospheric deposition on the water surface; S2: drainage and deep ground water; S3: agricultural activities; S4: transport and infrastructure without connection to canalisation/sewers; S5: accidental spills; S6: release from materials and constructions in non urban area); (B) Discharges to surface waters by point sources (S7: discharges in sewage effluents or storm water; S8: discharges in sewage effluents or storm water as a result of household, consumer use; S9: industrial activities; S10: solid waste management; S11: historical pollution: **S11.1 historical pollution from sediments**; S11.2 historical pollution from contaminated land; S12: natural sources).

To effectively identify key sources and pathways a stepwise approach for source screening has been developed. The first step is the identification of potential sources and the second step assesses whether the source/pathway can contribute to a failure of the objectives of the WFD. The final steps 3 and 4 of the methodology deal with the development of measures. The key outcome of the process is to identify Category 1 sources, which may potentially require additional measures for their control.

Priority Substances in Historical Contaminated Sediments as Possible Secondary Sources for Releases to the Aquatic Environment – WFD Article 16 “Measures”

(from: Concept Paper on Emission Controls to the Seventh Meeting of the Expert Advisory Forum on Priority Substances and Pollution Control, Brussels 14-15 June 2004)

Systematic presentation of sources and pathways. Discharges to surface waters by point sources include: discharges in sewage effluents or storm water due to run off in paved urban areas (S 7), as a result of household consumer use (S 8), due to industrial activities (S 9), via solid waste management (S 10), and due to historical pollution from sediments (S 11.1) and contaminated land (S 11.1).

Categorisation of importance of sources and pathways. *Category 1:* The available information indicates that the source/pathway contributes to the concentration of the substance in the aquatic environment, which may lead to a risk of failing to meet the objectives of WFD (Chapter 3.1.1). *Category 2:* All other sources and pathways that have not been identified as category 1 or 3, in particular those where insufficient information is available. *Category 3:* The available information shows that the source/pathway does not have a potential for the release of the substance directly or indirectly to the aquatic environment.

Categories for source/pathway S 11.1 “historical pollution from sediments”. S 11.1 will be a *category 1* source if monitoring data show that this pathway results in increased concentrations in the aquatic environment; S 11.1 is *category 3* if it is not present in sediment or if it is not released in detectable concentrations to the aquatic environment or if it is biodegraded in sediment (e.g., half life less than 180 days).

Identification of possible control measures for sources/pathways S 11 according to WFD 16(6). Explore the possibilities for establishing a strategy at EU level on contaminated sediments and links with the Thematic Strategy on Soil Protection (mainly for S 11.2).

Table 3.4 gives examples of priority substances (PS) and priority hazardous substances (PHS) as defined in article 2 (30) of the WFD. There is some indication that historic contaminated sediments might serve as a source for releases into the aquatic environment. Underlying data in most cases are still very insufficient and will have to be completed by further assessments.

Table 3.4 Examples of Substances for further Assessment on Historically Contaminated Sediments (numbers in brackets refer to the WFD list of priority substances)

Anthracene (2): category 1*	Cadmium (6): category 2 ⁺	Lead (20): category 2
Fluoranthene (15): category 1*	Hexachlorobenzene (16): category 2 ⁺	Mercury (21): category 2
Naphthalene (22): category 1*	Hexachlorobutadiene (17): category 2	Nickel (23): category 2
PAHs (28) category: 1*	Hexachlorocyclohexane (18): category 2	TBT (30): category 2 ⁺

*contaminated sediment as one possible source of various PAHs that may all contribute at the end to a failure of WFD objectives. ⁺ Additional indications for classification in category 1 given in data sheets

¹¹ from the “Concept Paper on Emission Control from 8 June 2004” of the Expert Advisory Forum (EAF) on Priority Substances and Pollution Control (7th EAF-Meeting at Brussels, 14-15 June 2004)

The process of source screening using different categories of importance of sources and pathways is demonstrated for historical contaminated sediments in the Box on page 87. Table 3.4 lists several examples; for some of them there are already additional data, indicating a possible change from category 2 to category 1, e.g., for cadmium, hexachlorobenzene, and tributyltin. In most cases, however, information is still insufficient and further efforts are needed in particular for sources such as historical contaminated sediments.

3.5. New Challenges for Catchment Scale Management

The Rhine Research Project II study "Dredged Material in the Port of Rotterdam – Interface between Rhine Catchment Area and North Sea" (Salomons & Gandrass, 2001) has described the changes at the catchment level as a major challenge to river basin managers and to the coastal zone managers who are 'at the receiving end' of the catchment. In the comprehensive EU-funded project "European Catchments: catchment changes and their impact on the coast (EuroCat) the scientific coordinator stressed the fact, that the main issue for this interface ("first order coastal zone", Meybeck et al. 2004a) is the *"achievement of 'hydro solidarity' within the basin, i.e. a full upstream/downstream integration of monitoring, stakeholder consultation, models and expert systems that can link basin pressures to transfers, across various administrative and/or political boundaries, and between the various land users, water users and other stakeholders"* (Salomons, 2004).

In the following short overviews are given on three themes closely related to the catchment scale perspective: "Risk Management" (section 3.5.1), "Sources and Measures" (section 3.5.2), and "Future Research Soil-Sediment Contaminants" (section 3.5.3)

3.5.1. Risk Management at the Catchment Scale¹²

The sediment risk management objective, as defined by SedNet Working Group 5, is *"to reduce risk posed by contaminated sediments to humans and ecological receptors to a level deemed tolerable by society and to control and monitor sediment quality and ensure public communication with the final aim of complying with the EU WFD and Habitats Directive."*

The objectives that drive sediment management activities are generally combinations of the following needs: a) to meet regulatory criteria, b) to maintain economic viability, c) to ensure environmental quality and nature development and d) to secure the quality of human life. Although often interrelated, these distinctions help to make the decision making processes transparent, informing the public of the overall aims, and helping managers to structure the decision process. To this end, measurable risk indicators defined for each objective (such as "decrease of fish yields" for "maintaining economic viability") will help simplify complex information, trigger management activities and support decision and communication processes.

Recommendations of SedNet WG 5 “Risk Management and Communication”

Development of a basin-scale decision framework

- Effective and sustainable management strategies must focus on the entire sediment cycle
- A basin scale framework should be comprised of two principal levels of decision-making: the first for basin-scale evaluation (site prioritisation) and the second for site-specific risk assessment (risk ranking).
- A basin-scale assessment should involve the balancing of a Conceptual Basin Model, which considers the mass flow of particles and contaminants, and the basin-scale objectives (BOs) to generate a Basin Use Plan. This Basin Use Plan should define the goals for both the river basin and specific parcels of sediment.
- In those cases in which sediment management decisions begin at the site-specific level, it is essential that the impacts of these actions upon adjacent sites, and basin-scale quality and objectives are considered.

Risk assessment, site-prioritisation and risk ranking

A prerequisite for sediment management on river basin scale is the harmonisation of site prioritisation and site-specific assessment/risk ranking schemes. This comprises

a) for prioritisation at the basin scale

- Development of (an) appropriate indicator(s) for sediment mobility at catchment scale
- Determination of the sediment dynamics and budget in a river
- Development of databases for implementing, testing (and improving) prioritisation methods
- Development/improvement of models that address the basin scale risk implications of site-specific conditions and actions

b) for risk assessment / risk ranking at the local scale

- Development of explicit measures of exposure, related to ecological processes which must be selected based upon site-specific conditions and management options (or scenarios)
- Collection and gathering of data from (local) risk assessment studies (establishment of data bases)
- Harmonisation of risk assessment/ranking approaches
- Establishment of obligatory monitoring after sediment management (collate data, use them for “validating” effect or exposure assumptions (class boundaries etc))
- Establishment of a tiered approach for risk assessment for remediation purposes, in which the first tier comprises of “easy to use” bio-tests and chemical analyses for risk assessment.

Diversity of sediment regulations and monitoring

- Assessment of sediment quality and risks: For a basin-scale/site specific sediment quality assessments and subsequent management decisions, harmonised sediment quality criteria and assessment procedures should be developed.
- Regulatory situation: From the scientific-hydrological point of view, dredged material is comprised of natural sediment (sometimes contaminated by external sources) while from the political / legal point of view, it is considered a waste. A new definition and new views of the role of sediments and dredged material within river basins should be developed in support of sustainable basin-wide sediment management strategies.

Management objectives and risk indicators

- There is the need for the development of a modified DPSIR approach¹³ for the respective river basins, in which the requirements and interactions between social and societal forces, the objectives of risk management and potential management options are explicitly addressed.

¹² Synthesis paper of SedNet Working Group 5 “Risk Management and Communication” (S. Heise, 30.06.2004)

¹³ DPSIR: “Driver-Pressure-State-Impact-Response-Analysis

Because of the dynamic, complex and interconnected nature of sediments, from sources and rivers to estuaries and the sea, effective and sustainable management strategies must focus on the entire sediment cycle, rather than on one unit of sediment at a time. Such an approach will help focus limited resources to maximise the achievement of management objectives, including basin-scale risk reduction. A basin-scale risk management framework should be comprised of two principal levels of decision making; the first being a basin-scale evaluation (prioritisation of sites for further evaluation and/or management) and the second being an assessment of specific sites for risks and management options (site-specific risk ranking). Sites should be prioritised at the basin scale according to a number of criteria, preferably quantifiable at a screening level, including: the location along the up- and downstream gradient (e.g., how are downstream sites affected by contaminated sediment sources upstream?), quantity of sediment (e.g., is the volume large enough to present a risk?), evaluation of sediment quality (e.g., how contaminated is the sediment?), sediment dynamics (e.g., is (contaminated) sediment transported downstream?) and the potential expected benefit of proposed management actions at a given site and for the river basin.

Sediment risk assessment (or risk ranking) generally falls into two categories, based upon different management objectives, and thus requiring different assessment procedures: a) Assessment of the in situ risks caused by contaminated sediments in place, and b) Assessment of risks of contaminants in sediments during and after dredging (ex situ). There is a need for harmonisation of risk ranking approaches; a tiered approach for in situ risk assessment has been proposed by the working group.

In summary, a comprehensive Basin Scale/Site specific risk management approach is suggested that includes the following steps: 1) The communication between managers and the public, throughout the decision process, 2) The identification of management objectives, 3) The determination of appropriate risk indicators, 4) The usage of risk indicators to prioritise sites on a river basin scale and to rank risks on site-specific scale, 5) The decision making process in which potential effects on the river basin and on the site-specific scale are weighed against each other, taking into account the economic, societal and environmental risk, and finally 6) The selection, implementation and monitoring of the final management option(s).

In this report, some of the steps in the site prioritization process of risk management have been taken: The identification of areas of concern in combination with evaluation of resuspension, transport phenomena and the distance of the sites from the Port of Rotterdam results in a site prioritization, that indicates what areas of concern need to be addressed in the first place and where management options should be favoured. A risk assessment at the prioritized site could make use again of the hazard classes of compounds, integrating them into the risk ranking which eventually should be undertaken on the basis of chemical, ecotoxicological and ecological aspects in order to identify the minimally impacting (?), maximally efficient management option, which would – in our case – refer to the level of contamination in the Port of Rotterdam.

3.5.2. Sources and Measures at the Catchment Scale

In the process of implementing emission control of priority substances, some key terms are defined in article 2 WFD. For example, the “emission limit values” for substances shall normally apply at the point where the emissions leave the installation, dilution being disregarded when determining them. With regard to indirect releases into water, the effect of a wastewater treatment plant may be taken into account when determining the emission limit values of the installations involved (article 2(40) WFD). The term “sources” is not defined in article 2 of the WFD, and definitions have been given by the Expert Advisory Forum on Priority Substances and Pollution Control Implementation of Article 16 of Directive 2000/60/EC (WFD) in their Concept Paper on Emission Control from 8 June 2004):

- **“Discharges”**: *“shall mean the release of priority substances from individual or diffuse sources in the installation through effluent directly or indirectly into surface waters as defined under Article 2(1) of Directive 2000/60/EC”*
- **“Emissions”**: *“shall mean the direct or indirect release of priority substances from individual or diffuse sources in the installation into air, water or land including ‘discharges’ as defined above”*
- **“Installation”** : *“shall mean a stationary technical unit where one or more industrial activities are carried out, and any other directly associated activities which have a technical connection with the activities carried out on that site and which could have an effect on emissions and pollution” (Based on Integrated Pollution Prevention Control [IPPC] Directive 96/61/EC definition)*
- **“Losses”** : *“shall mean any intentional or unintentional release or transfer of priority substances, other than discharges, emissions or the result of accidents, directly or indirectly into surface waters as defined under Article 2(1) of Directive 2000/60/EC”*

The latter source type is probably closest to the case of historical contaminated sediments. Apart from the definition, however, the spatial situation of a source is of prime importance. There are a number of types of sediment and contamination sources in a dynamic system (Apitz and White, 2003):

- Active point sources – in general these are being controlled by legislation. However, catastrophic failures and isolated spillages may still occur.
- Quasi-diffuse sources – these, rather than being specific point sources, can be residues of controlled point sources (as above) or diffuse (but not entirely ubiquitous) sources from the basin. These can be sources of contaminants such as pesticides, veterinary pharmaceuticals, nutrients, inputs from atmospheric deposition ect.; to control such risk requires basin-wide changes in agricultural and industrial practices. Such contamination is not manageable until sources are controlled.
- Non-point sources. If contaminants in sediments result from ubiquitous background levels, either from natural or anthropogenic sources, there is little that can be done about risks as a result of such inputs, so even if present, risk is not manageable in an active way.

- Local historical – in this case, the source of contaminant or sediment is from nearby, has been controlled, and the major concerns are to prevent spreading and to control risk in place. These risks, in general, are controllable at the site (dependent upon site-specific conditions).
- Remote historical, point source – in this case, contamination or sediment came from upstream, but the source has been controlled. Concerns include residual diffuse input (e.g. metals in river bank and flood protection banks).

One of the goals of sediment parcel prioritisation in basins is to assure that such potential risk sources are managed, if possible, before downstream parcels (barring cases in which very high site-specific risk moves a parcel up in priority, in which case the upstream input is not the primary risk driver).

An increasingly important challenge in river basin management is to develop strategies and solutions for the legacy of the past, based on a multidisciplinary, co-ordinated and harmonized approach (Brils, 2002). As outlined in section 1.5.2., the selection of remedial measures should primarily be based on the concept of “geochemical engineering”, applying principles such as stabilization, solidification, and other forms of long-term, self-containing barriers to determine the mobilization and biological availability of critical pollutants. A combination of various existing or planned techniques, examples mainly from the Elbe catchment areas, has been proposed by Förstner (2003):

- Predominantly in the upper and middle course of river systems, sediments are affected by contamination sources like wastewater, mine water from flooded mines and atmospheric deposition. Measures at the source are particularly important and may include improvement of traditional wastewater purification, but also more approaches for in-situ treatment of highly contaminated effluents such as introducing active barriers (fly ash, red mud, tree bark, etc.) into ore mines to prevent heavy metal dispersion during flooding (Zoumis et al. 2000).
- During floods, sediment bound pollutants can undergo a large-scale dispersion of contaminants in flood-plains, dike foreshores and polder areas. The complex mixtures of toxic compounds and the dimension of pollution often preclude technical measures like chemical extraction or solidification of contaminated soil material. Instead, alternative measures have to be taken considering the different local factors such as soil, sediment and water quality, flow velocity, and the dynamic of the water-level. From an initial example of the Spittelwasser case comparison (Anonymous 2000) in a 60 km² flood plain of the upper Elbe River it has been shown that problem solutions for such areas deserve thorough consideration of legal and socio-economic aspects. The measures implemented should be flexible and easy to adjust to changing conditions; they have to be planned comprehensively and need controlling for extended periods of time.

Sub-aquatic depots are an emerging science-based technology for the final storage of sediments. The EU Landfill Directive does not refer to waste disposal below the groundwater level, and just there the two most promising prerequisites for a sediment depot can be found (Box on page 25): (i) permanent anoxic conditions to guarantee extremely low solubility of heavy metals, (ii) base layers of compacted fine-grained sediments, which avoid advective transport of contaminants to the groundwater.

Die subaquatische Unterbringung von Baggergut in den Niederlanden DEPOTEC Amersfoort/NL by order of Freie und Hansestadt Hamburg (2002)

1. Einführung und Überblick über den Bericht

2. Politik

3. Umweltauswirkungen subaquatischer Depots

4. Technik der subaquatischen Depots

- 4.1 Merkmale des Depots
- 4.2 Der Weg zu einem Depotentwurf
- 4.3 Rahmenbedingungen bestimmen die Eingliederung eines Depots
- 4.4 Entwurfaspekte des Baggergutdepots
- 4.5 Ausführungstechnische Aspekte
- 4.6 Der Betrieb eines Depots
- 4.7 Verwaltung und Monitoring eines Depots
- 4.8 Ausgleichs- und Ersatzmaßnahmen
- 4.9 Arbeiten und Verfahren in der Nachsorgephase
- 4.10 Nebenfunktionen
- 4.11 Kostenschätzung für subaquatische Ablagerungen

ANLAGEN

- Anlage 1 Niederländische Normen für die Qualitätsbeurteilung des Oberflächenwassers, Schwebstoffen, Sedimenten und Grundwasser
- Anlage 2 Niederländische Vorschriften für subaquatische Ablagerungen von Baggergut
- Anlage 3 Der Niederländische Baustoffbeschluss
- Anlage 4 Ablagerungen von Baggergut in Grubendepots
- Anlage 5 Verwertung von Baggergut in den Niederlanden (Impuls B2)
- Anlage 6 Berechnung und Überprüfung der Verteilung von Schadstoffen aus Baggergutdepots an Land
- Anlage 7 Die Wirksamkeit von Isolationsmaßnahmen für Baggergutdepots
- Anlage 8 Diffusion von Schadstoffen
- Anlage 9 Numerische Modelle
- Anlage 10 Übersicht zusätzlicher Reinigungstechniken für Rückwasser
- Anlage 11 Methodik der Bewertung und des Vergleichs der Depotvarianten im Umweltverträglichkeitsbericht (UVB)
- Anlage 12 Subaquatische Depots in der Praxis

Together with advanced geochemical and transport modelling such deposits offer the most cost-effective and durable problem solutions for dredged sediments.

Actually there are 16 sites of sub-aquatic depots for harbor sediment in The Netherlands (Depotec 2002), most of them at near coast sites. World-wide known is the “Slufter” peninsula disposal facility in the mouth of Rhine and Meuse, the largest example to contain more than 95 Mio m³. Much experience has been gained during the last 20 years with the planning, operating and supervising this site. The preparation work before construction took between 4 and 7 years. Filling for the smaller depots will take place within 5 years, for the larger ones within 20 year. Cost estimations for construction, operation and aftercare are between 5 and 10 Euro per m³, much less than the costs for conventional separation, drying and land deposition of dredged material.

This cost-efficiency together with the operational safety of sub-aquatic depots should be a convincing argument for the application of these containment technologies at upstream sites as well. Here, some additional precautionary measures should be considered, e.g. an armoring layer which provides erosion protection of the depot. Implementation of sediment capping is a typical example for collaborative projects involving strategic research, applied research and development, and technology sharing projects (Azcue et al., 1998). Major steps are (1) characterization of sediment materials (reactivity, mobility of pollutants), (2) suitability of capping techniques (currents, steep gradients, groundwater seepage), (3) provision of capping material (sand, granular materials, geotextile, additives; logistics; soft sediment/coarse, dense cover; impermeable materials, water flow); (4) thickness of capping material, (5) reactive additives; (6) monitoring of the sediment/cap system, early warning systems.

Application of a combined sub-aquatic depot and active capping technology can be considered for small yachting harbors. For the Hitzacker/Elbe harbour site, a draft approval has been made which involves the excavation of approx. 10.000 m³ fine grained, polluted sediments from the harbour area and their sub-aquatic deposition close to the site, in a communication channel between the Elbe River and the harbour. Active capping of the sediment depot will include natural zeolite additives and monitoring of the site will be performed using dialysis sampler and diffusional gradient technique (DGT) probes (Jacobs 2003).

Examples from sediment depots in gravel pits, separated river branches and harbour basins in Germany, where similar geochemical conditions can be expected as in the specially designed sub-aquatic depots, are described in a recent compilation of case studies by ATV-DVWK (2004).

3.5.3. Future Research on Soil-Sediment Contaminants at the Catchment Scale

Many and various sources contribute to the contaminant concentrations in fluvial sediments. The more important pathways are depicted in figure 3.2.

The Rhine Research Project II study showed the increasing importance of diffuse sources compared to point sources for sediment contamination. Historical analysis as well as future scenarios shows this trend.

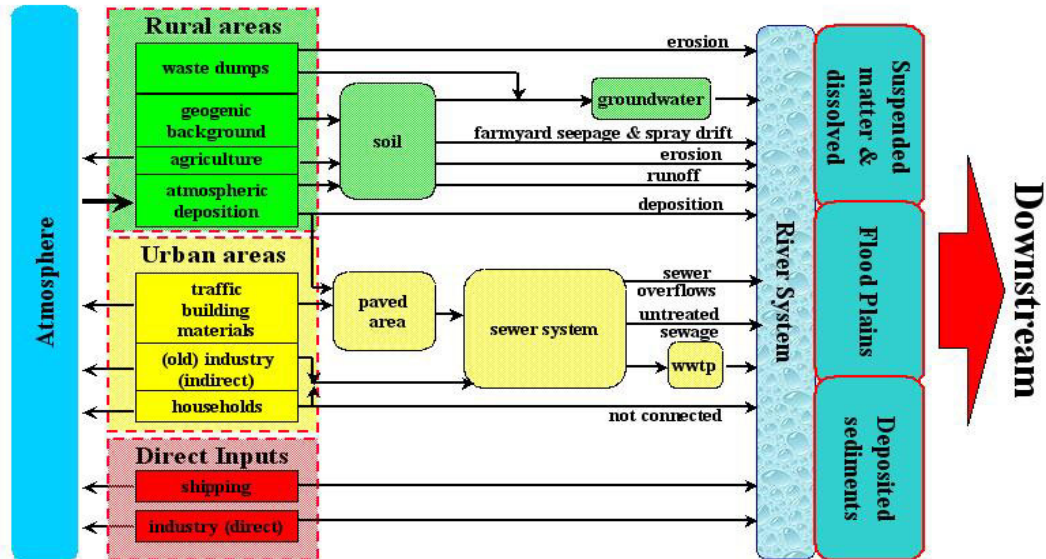


Figure 3.2 Sources and Pathways of Contaminants in River Basins

Not considered in the Rhine Research Project II analysis were possible contributions of the “legacy” of past industrialisation in the Rhine catchment, which are the subject of the current study.

On land these are waste deposits and contaminated industrial and mining areas. In the river system contaminated sediments in harbours and upstream of barrages and dams as well as river flood plains have to be considered.

The Rhine Research Project II focused on averages, often over years, to identify and predict future behaviour of pathways. In contrast, the present study tackles the issue of isolated events of high discharge and its effects on sediment transport and the potential for erosion of historic contaminated sediments. In addition, as a prerequisite, a survey of potential sites of erosion of contaminated deposits in the catchment was carried out.

Hence the following three issues have to be solved (in theory) for a quantitative prediction of the Rhine catchment “legacy” on dredged material quality in the port of Rotterdam.

- Identification of the contaminated sites
- Application of an erosion model to each identified site
- Application of a sediment transport model for the isolated events at the site of erosion (sub-catchment) and subsequently for the whole catchment

On the basis of available data, numerous potential areas/sites of concern could be identified (Fig. 4.2). For some areas, only few or no data were available (no circles). To fill this gap relatively simple, basic investigations like additional monitoring data and sediment survey will be required.

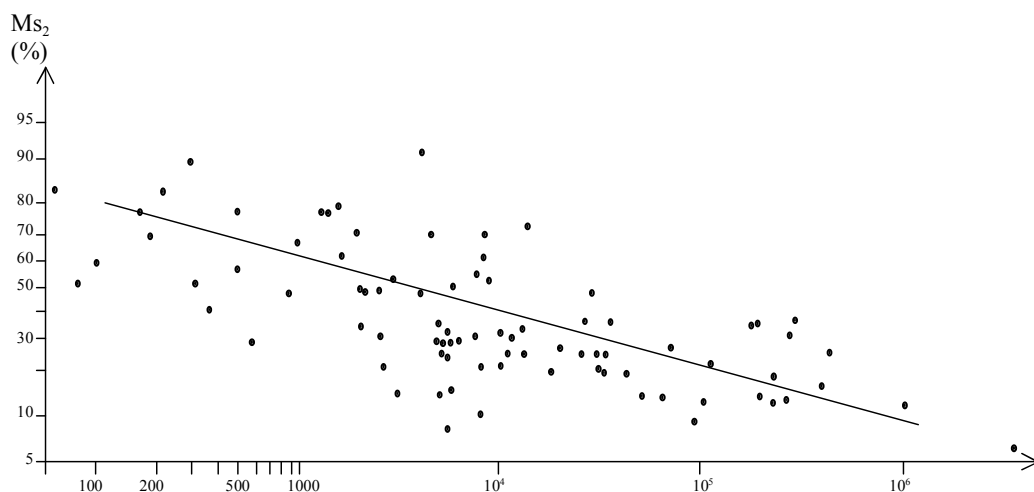


Figure 3.3 Percentage of suspended solids flux discharged in 2% of time (Ms_2) vs log of basin area (km^2). Meybeck et al. 2004b

The review part on erosion gave detailed description on the intricacies of erosion modelling, the sediment properties required and the laboratory sediment testing procedures. In principle these data have to be measured for each identified site to arrive at quantitative erosion potential for a modelling effort.

Anyhow, the analysis of available data on contaminant load and discharge showed that under average conditions, the contaminants do not show up. Only during periods of high discharge, high loads for some specific contaminants become apparent: a positive proof for the contribution of erodable formerly contaminated deposits.

The next issue is the sediment transport during events of high discharge. There is a significant relationship between sediment flux discharged and the basin size. In particular in small sub-basins but also in larger basins most of the sediment transport takes place during relatively short time periods. Figure 3.3 shows the relationship between basin size and the sediment transport that occurs in 2 % of the time. These high transport event periods are relevant for the impact from contaminated sites on downstream dredged material quality.

Many studies have dealt with these isolated events on sediment transport and it is well described in the literature. However, validated models for the Rhine catchment seem to be lacking let alone an application of these models to isolated contaminated areas in the Rhine catchment. To fill in this gap will require massive efforts, in particular with regard to obtaining field data and monitoring data sufficient for validating this kind of model. In this respect European research is needed, in particular since the phenomenon of the legacy of past pollution in sediments and waste dumps is not restricted to the Rhine catchments but occurs in other European regions as well.

As such the “worst case approach” taken in this study appears currently to be the Best Available Technique for a first order risk assessment of contaminated sites in river catchments.

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4 Substances and Areas of concern

4.1 Introduction to the risk assessment approach for the Port of Rotterdam

The intention of this report is to analyse and conclude, what kind of risk derives from historical contaminated sites in the Rhine catchment area and its tributaries for the Port of Rotterdam. Risk in this respect refers to the requirement that the Port of Rotterdam have to costly dispose dredged material to a disposal site (de Slufter) rather than being allowed to relocate it into the marine environment. Decisions on management options for the 15-20 Mio m³ that are annually dredged in Rotterdam, are based on the "Chemistry Toxicity Tests" (CTT), giving the chemical concentration thresholds in sediments, above which relocation of dredged material is forbidden (see Annex 1).

With the Action Program "Rhine" in 1987 of the International Commission for the Protection of the Rhine (ICPR), extensive improvements of the water quality of the Rhine have been achieved by reduction of industrial and municipal point sources. In future, diffuse pollution and possibly pollution through secondary sources such as historic contaminated sites will gain in importance. Both will be more difficult to reduce than point sources – either because they are by definition "highly dynamic spreaded pollution sources" (definition of diffuse sources, (Vink & Behrendt, 2001)) because their location and resuspension risk is not known as is often the case with historic contaminated sediments. They may presently be hidden by freshly deposited clean material, and only become resuspended if the current velocity increases the shear stress on the bottom, e.g. during flood events, or they may be consolidated to such an extent, that no resuspension occurs any more.

In this report, an inventory of historical contaminated sites along the Rhine and its tributaries was undertaken and those sites are identified that represent a risk for the Port of Rotterdam with respect to a possible exceedance of the CTT thresholds.

Hereby a three-step approach was followed:

- Identification of **substances of concern (s.o.c.)** and their classification into "**hazard classes of compounds**" (HC_c)
- Identification of **areas of concern (a.o.c.)** and their classification into "**hazard classes of sites**" (HC_s)
- Identification of **areas of risk (a.o.r.)** and their assessment relative to each other with regard to the probability of contaminating the sediments within the Port of Rotterdam.

Conclusions regarding "hazards" and "risks" were differentiated. A **hazard** describes the potential danger of a substance or a specific site without referring to exposure occurring in reality. The **risk** is the magnitude of hazard multiplied by the probability of exposure.

Hazards, which are in this report the hazards of “substances of concern” and of “areas of concern”, can be determined with higher certainty than the risks, as they lack the additional exposure assessment, comprising resuspension and transport phenomena, that are part of the later risk assessment.

The steps in detail were the following:

1st step: “substances of concern” (s.o.c.) (Chapter 4.2)

This chapter describes the characterization and identification of substances that are of concern for the Port of Rotterdam with regard to current regulatory threshold levels and future developments. This comprises compounds, which sometimes exceed regulation values and those that might become of increasing importance under the aspects of implementation of bioassays and the long-term shift in the contamination pattern.

According to chemical characteristics like persistence, sediment-water partitioning, and their (bio)accumulative potential, s.o.c. are assigned to 2 classes of increasing hazard ($HC_C^{13}1 < HC_C2$), which refer to the magnitude of potential impact they could cause in the Port. At this stage, no risk assessment is carried out, because no transport and therewith no exposure and final concentration in the Port of Rotterdam is taken into account.

2nd step: “Areas of concern” (a.o.c.) (Chapter 4.3)

“Areas of concern” comprise those locations that show an exceedance of CTT thresholds in sediments. As this again – at this point – does not refer to any resuspension or transport mechanism, a hazard has to be dealt with (as opposed to “risk”) and accordingly the a.o.c. needs to be classified into different hazard classes.

The CTT threshold values are used as a yardstick, because a concentration below that management level will not be of direct concern for the port, even if that material would be resuspended and transported downstream without dilution.

Assessments of areas of concern and the hazard classification are based on analytical data on surface sediments from publications and databases from federal environmental agencies.

As has been described extensively in Chapter 2, available data on suspended matter and sediment data are subject to some degree of uncertainty. To conclude hazard classes for areas of concern, the quantity of contamination (from available sediment surveys), the quality of contamination (of which hazard classes (HC_C) are the substances that exceed the CTT-thresholds) and the likelihood, that the assumption, that a hazard exists, is true, have to be taken into account.

¹³ HC_C Hazard Class Compounds

Four hazard classes for sites (HC_s) have been determined:

- (0) There is no indication for a hazard
- (1) A potential hazard is present, meaning that there is a possibility that these sediments, if transferred directly to the Port of Rotterdam lead to an exceedance of the local CTT-values
- (2) A potentially high hazard, meaning that there is a possibility that these sediments, if directly transferred to the Port of Rotterdam would lead to a significant exceedance of the local CTT-values
- (3) High hazard with high certainty, meaning that there is a high certainty that these sediments, if directly transferred to the Port of Rotterdam lead to a significant exceedance of the local CTT-values

In order to integrate the different properties, a fuzzy logic based classification scheme is used, which takes into account gradual differences in the concentrations of s.o.c. and the uncertainties involved, and which is able to deal with linguistic descriptions of classes (e.g. potentially high).

Information on historical contamination has been gathered in order to identify the sources and to estimate, how long ago the contaminants have been discharged.

3rd step: Risk Quantification for the Port of Rotterdam (Chapter 5)

In order to quantify transport of contaminated material, information has to be provided about its resuspension and transfer into the suspended matter fraction, its transport as suspended matter and its deposition, and about the total load that is transported. The available data base however, is limited. Only comparatively few data exist on critical erosion thresholds of sediments (Universität Stuttgart). Contaminant concentration in suspended matter and depth-dependent concentration in sediment are only available for a limited number of monitoring stations and a selected number of rivers, respectively. A risk assessment can therefore only be a rough estimation, based on assumptions that have to be made, and needs to address a worst case scenario to be on the safe side when drawing conclusions.

At first, information of erosion thresholds in the catchment area have been gathered. Therewith, the likelihood of sediment resuspension depending on the discharge could be estimated.

Secondly, a calculation was done to assess the minimal concentration, that sediment would need to have before it could potentially raise the concentrations in the Port of Rotterdam above CTT-level upon resuspension. This was done by taking into account dilution effects in the Rhine river due to the confluence of its tributaries, using generalized hydrological schemes for different discharge scenarios.

Thirdly, concentrations of s.o.c. in suspended matter and its loads at different flow regimes were examined for evidence of resuspension events. Special emphasis was put upon Cadmium and HCB as model compounds with different historic sources and distribution within the Rhine basin.

The information from these three approaches were treated as three lines of evidence to finally conclude which areas represent a risk for the Port of Rotterdam.

4.2 “Substances of concern”

4.2.1 What substances are of concern for the Port of Rotterdam?

The sediment transport from the River Rhine is significant in the respect that even though about half of it is directly transported through the port to the North Sea, the amount that settles increases the contamination level especially in the Eastern part of the port.

Sediments that do not meet CTT thresholds values are not allowed to be relocated in the North Sea but have to be disposed of in a confined site, e.g. in the Slufter (see Chapter 3). According to the former UCT (Uniform Contest Test) that was valid until the end of year 2002 for Rotterdam, copper, zinc, mercury, cadmium, lead, PAH and PCB often exceeded the sea/Slufter thresholds as was shown in sediment samples from Brienenoord between 2000 and 2002 (Gerard van den Berg, KIWA, pers. communication¹⁴). In the CTT¹⁵ (Chemistry Toxicity Tests) changes were not or only slightly (PCB, PAHs) done with regard to the actual limit values, but the calculation of contaminant levels was modified with substantial consequences:

- 1) No normalisation of contaminant values to the content of organic material and clay takes place any more with the consequence that now the nominal concentrations of heavy metals, that have to be compared to the limit values, are often higher than before (if clay content exceeds 25%) and the organic contaminants show lower concentrations at organic matter content below 10 %.
- 2) No individual concentrations of PAHs and PCBs but the sum value is considered in CTT meaning that a moderate excess of one component can be made even by lower concentrations of the other substances.
- 3) Bioassay tests may be included in two years. Therewith synergistic effects of contaminants or even the possibility of potentiation has to be considered (see section 2.4 and 3.3.2)
- 4) No limit values for γ -HCH, Aldrine, Dieldrine, and Endrine are set in the CTT because these proved to be present in only low concentrations in the DM.
- 5) Tributyltin (TBT) is newly added to the list of contaminants because it is a chemical of concern.

¹⁴ see also DONAR database, http://www.donarweb.nl/pub/geinteresseerde/geint_links/index.html

¹⁵ Annex 1

Considering the implication of the new CTT, the list of substances that are of concern for the sediment management in Rotterdam because they may all pose a risk in future, and which will specifically be dealt with during this project, is extended to the following list:

Cadmium, Chromium, Copper, Mercury, Lead, Nickel, Zinc, PCBs and PAHs (although to a smaller extent), **and HCB**. Arsenic will not be included in this report, as it has not been shown to be present in any significant amount in the sediments in the Port of Rotterdam (Gerard van der Berg, pers. communication).

However, also substances that may not frequently exceed the CTT-values may still become a problem in future and should also be mentioned in this report, such as

TBT: No surpassing of limit values due to historic sources outside of the port is expected from mineral oil and TBT, as their concentration will originate to the most extent from the port itself. Nevertheless, external sources for TBT compounds will be looked for as these compounds show a long half-life in sediments and may still present a problem long after production and emissions have ceased. A strong increase of copper in the sediment can be expected in future because of the shift in antifoulings from TBT to copper-based paints – but this, again, will mostly derive from ships in the port and not from historic contamination in the Rhine.

Insecticides like γ -HCH, Aldrine, Dieldrine, and Endrine may pose a problem in port sediments as even though they may be present in only low concentration and were therewith skipped from the CTT-list, they may interfere with the activity of one of the biotests, the amphipod *Corophium volutator*, because crustacea are often sensitive to insecticides as they are relatively closely related to insects – on evolutionary terms.

HCH: Estimation of the persistence of HCH in the environment without microbial degradation varies from half-lives of months to years up to environmental stability (Callahan *et al.*, 1979; Mabey *et al.*, 1982). Microtox bacteria (one of the biotests) and algae (*Scenedesmus subspicatus*) react to HCH-concentrations of more than 1 mg/L (Calleja *et al.*, 1994) (Stephan *et al.*, 1986) and therewith will probably not be affected by the environmental concentrations that persist in the Rhine. But it has been shown that crustaceans like *Crangon septemspinosa* and *Pagurus longicarpus* show EC₅₀-values of 5 μ g/L. Similar sensitivity has been reported for Aldrin (*Crangon septemspinosa*: EC₅₀: 8 μ g/L; (WHO, 1989)) and Dieldrin (Adema & Vink, 1981). No data on the sensitivity of *Corophium volutator* to sediment-bound γ -HCH has been available, but it cannot be ruled out, that this amphipod shows a similar sensitivity and will be affected by a mixture of insecticides. In order to assess the future risk to the port of Rotterdam on the basis of the new CTT regulation, these substances should be included in our survey.

Dioxins: Toxicity of PCDD and PCDF vary greatly with target organism, raising some controversy about their significance as environmental contaminant. The 2,3,7,8,-tetrachlorinated congeners are the most toxic form and are often the compounds that are considered when the more general terms "dioxin" and "dibenzofuran" are used. The sensitivity to 2,3,7,8,-tetrachlordibenzo-p-dioxin can be as

low as 1.7 ng/L (EC₅₀ of Fathead Minnow, *Pimephales promelas*, 24 hour test (Cooper, 1989)) but toxicity data are scarce. Because of very similar modes of action, dioxins, dibenzofurans, and dioxin-like polychlorinated biphenyls (PCB), ecotoxicological effects will be additive and related to the sum of individual concentrations. Therefore also information on dioxins will be included where available, as the DR-Calux assay, which is specifically sensitive to dioxins, is suggested for introduction into the CTT in two years.

Nonylphenols should be addressed where possible, as these are considered as priority substances in the Water Framework Directive (WFD). It can therewith be expected that they may become part of sediment quality criteria as well. However, nonylphenols have not been included in the list of Rhine-relevant substances ("Koordinierungskomitee Rhein", 2003), and data on chemical analysis of sediments are scarce.

EDTA: It has been shown, that complex-building compounds like NTA and EDTA remobilize heavy metals, especially Zn, from aerobic sediments, whereby no or only minor remobilization occurs with anaerobic material (Lorenz, 1997). Compared with the concentrations that were used in experiments (0,5 mg/L Na₂H₂-EDTA*2H₂O, 2 mg/L Na₂H-NTA), the concentrations in the Rhine are low with 14,7 µg/L for EDTA and 3.2 µg/L for NTA at Kleve-Bimmen (BMU) shifting towards NTA as this increasingly replaces EDTA. Additionally, complex-building compounds in the natural environment will have bound heavy metals before they reach the sediment. It is therefore concluded, that EDTA or NTA will not have an important effect on the resolubilization of heavy metals from sediments.

Priority substances: In the scope of implementation of the WFD, the EC assigned several substances and substance classes to a list of "priority substances", partly identified as "dangerous priority substances" (Decision Nr. 2455/2001/EC of the European Parliament and its Commission from November 20th 2001). Although these currently refer to the water column only, those compounds, which adsorb to sediment, can be expected to become part of the national sediment regulations in near future. With regard to historically contaminated sites, especially those compounds that are currently not produced any more and are only applied to a small extent, are of interest, because increases in concentrations originate from historic accumulation (or diffuse emissions). Cadmium, Mercury, PAHs, HCB, Nonylphenol compounds, TBT and the pesticides Atrazin and Simazin belong to these substances. The EC has not yet decided whether the pesticides will be considered as "dangerous priority substances".

Table 4.1 depicts the substances of concern in this project, the limit values according to the CTT and the target values of the ICPR. The ICPR-values are mostly based on suspended matter or water concentrations and are shown here because some reference will be given in this report to publications that refer to quality assessments in the terms of the ICPR.

While in some cases, ICPR target values and CTT threshold values are in the same order of magnitude, they differ largely with regard to PCBs, PAHs, DDT, HCB, HCH, the Drins, and TBT. This is due to different objectives of the regulations. The ICPR target values are set for Rhine water quality and also take the function of drinking water into account. CTT threshold values on the other side are

determined as protection levels towards the (marine) aquatic community. Substances with known human health risk and bioaccumulative potential have therefore been assigned much lower values in the ICPR regulation. This has to be kept in mind when comparing exceedance of criteria.

Table 4.1 “substances of concern” with limit values according to CTT, and target values according to ICPR determined in solid phases (DW: dry weight) or per volume water (L: liter).

SUBSTANCES OF CONCERN	LIMIT VALUES acc. to CTT	TARGET VALUES acc. to ICPR
Cadmium	4 mg/kg DW	1 mg/kg
Chromium	120 mg/kg DW	100 mg/kg
Copper	60 mg/kg DW	50 mg/kg
Mercury	1,2 mg/kg DW	0,5 mg/kg
Lead	110 mg/kg DW	100 mg/kg
Nickel	45 mg/kg DW	50 mg/kg
Zinc	365 mg/kg DW	200 mg/kg
PCB	0,1 mg/kg DW sum PCBs ¹⁶	0,0001 µg/L ¹⁷ each substance
Sum PAHs	8 mg/kg DW ¹⁸	0,1 µg/L ^{17, 19}
SUM DDT+DDD+DDE	0,02 mg/kg DW	0,001 µg/L ¹⁷ each substance
HCB	0,02 mg/kg DW	0,001 µg/L ¹⁷
γ-HCH	-	0,002 µg/L
Aldrin, Dieldrin, and Endrin	-	0,001 µg/L ¹⁷ each substance
Dioxins	-	-
TBT	100 – 250 µg Sn/kg DW	0,001 µg/L ^{17,20}

¹⁶ Sum of 7 PCB: PCB-28, PCB-52, PCB-101, PCB-118, PCB-138, PCB-153, PCB-180

¹⁷ checked for compliance from measurements in suspended matter

¹⁸ sum of 10 PAHs: Naphthalene, Phenanthrene, Anthracene, Fluoranthene, Chrysene, Benzo(a)anthracene, Benzo(a)pyrene, Benzo(k)fluoranthene, Indeno(123-cd)pyrene, Benzo(ghi)perylene,



¹⁹ sum of 5 PAH: Benzo(b)fluoranthene, Benzo(k)fluoranthene, Benzo(ghi)perylene, Indeno(1,2,3-cd)pyrene. Benzo(a)pyrene: 0,01 µg/L

²⁰ with regard to the organotin-cation

4.2.2. Assignment of hazard classes (HC_C) to “substances of concern”

In various regulations, substances are assigned to specific classes of danger or “priority” usually with respect to a specific objective, e.g. to protect a marine aquatic community or aim at drinking water quality. Often their resistance to photolytic, biological and chemical degradation, their semi-volatility as an indicator of their long-range transport (Ritter *et al.*, 1995, ???) (persistent organic pollutants, POPs, Stockholm Convention), and sometimes their toxicity and bioaccumulative potential (“priority hazardous substances”, Water Framework Directive; §7.6 of the OSPAR 2002 Summary Record) are taken into account when adjusting the threshold values. In the Rhine Research Project II-Report, it has been shown, that only 9 substances were shared by three lists on a) EU-WFD priority chemicals, b) the ICPR Rhine relevant substances, and c) the OSPAR priority chemicals (Gandrass & Eberhardt, 2001). From the EU list for priority hazardous substances, which comprises 11 out of the 32 as priority substances declared chemicals (Decision No 2455/2001/EC of the European parliament and of the Council, Nov. 20, 2001) only 7 are shared with the OSPAR list (Table 4.2).

Different criteria for classification of chemicals lead to different selections as substances of concern. Also the relevance of chemicals for certain environments can be different, so it is not surprising, that the lists with priority substances only overlap to some extent. HCB for example is not a compound that is usually expected in marine waters, whereby industrial emissions made it a problem in some rivers. Sediments that accumulate in the large ports are contaminated by rivers, but are often relocated in coastal waters. Therewith two environments have to be addressed and there is substantial overlap with both the OSPAR and the priority hazardous substances of the WFD, which addresses primarily the water phase.

Table 4.2 Persistent organic pollutants (POPs), priority hazardous substances (WFD), priority substances (OSPAR) are depicted by grey cells. Substances of concern in this report are shown, assigned to different risk classes: 2() and 1()

Substances	POP (UNEP)	EU: priority hazardous substances	OSPAR ²¹	subst. of concern, this report
Cd				2
Cr				1
Cu				1
Hg			+ Hg-organic comp.	2
Ni				1
Pb			+ Pb-organic comp.	1
Zn				1
Aldrine (Dieldrine, Endrine)				1
Brominated Diphenylether / Flame Retardants				
Chloralkanes				
Chlordane				
DDT+DDD+DDE (SUM)				2
Dioxins and Furans				2
HCB				2
γ-HCH				1
Heptachlor				
Hexachlorobutadien				
Mirex				
Nonyl-phenol compounds				
PAH (z.B. Benzo(a)pyrene)				2
PCB				2
Pentachlorobenzene				
TBT			Organotin-comp.s	1
Toxaphene				
4-tert- Butyltoluene				
Neodecanoic Acid, Ethenyl Ester				
Tetrabromobisphenol A				
Hexachlorocyclopentadiene				
Trichlorobenzenes				
4-(Dimethylbutylamino)diphenylamine (GPPD)				
Triphenyl Phosphine				
Hexamethyldisiloxane (HMDS)				
Dicofol				
Endosulphan				
Methoxychlor				
PCP (Pentachlorophenol)				
Trifluralin				
Clotrimazole				
2,4,6-tri-tert-Butylphenol				
Octylphenol				
certain Phthalates				
musk xylene				
short chained chlorinated paraffins				

²¹ OSPAR List of Chemicals for Priority Action, category A-chemicals (up-date 2002), ref. nr. 2002-18; OSPAR 02/21/I-E, Annex 5

Focussing on the risk that contaminants in sediments and suspended matter may bring about for the Port of Rotterdam, the previously identified substances of concern were scrutinized with respect to:

- **Persistence of the compounds in sediments.** Hereby, information on the half-life of a compound is used as an indicator. Different from the POP-classification of UNEP, within the group of persistent chemicals, a further differentiation of persistent substances is made into 3 categories according to the respective time scale of their half-lives. Differences in terms of years may well have influences on management decisions. Therefore the following categories were chosen:

Category 1: Half-life < one year

Category 2: Half-life 1 – 10 years

Category 3: Half-life > 10 years

- **Sediment-water partitioning.** Partitioning of non-polar organic chemicals between water and particulate matter in aquatic systems is general well correlated with their partitioning to octanol (Larson *et al.*, 2000) and can thus be described by the octanol-water partitioning coefficient. With regard to the risk for the port due to contaminated sediment, the potential hazard increases with the binding tendency to solids and the resulting accumulation of compounds in sediments. The importance to widen the approach to multimedia partitioning is demonstrated in fig. 4.1. Henry's law constant "H" is an indicator of the air-water partition, " H / K_{ow} " an indicator of the partitioning of a substance between air and octanol. Partitioning processes strongly depend on the water temperature. HCB tends to partition towards air and cold solids, but is little soluble in water. Due to these properties, it is widely distributed around the earth and seen as capable of being transported over a long-range. Dioxins (PCDDs) and DDTs partition towards solids and towards cold water accounts for their higher water-solubility. Similarly, HCH is fairly water-soluble, and has a higher tendency to cold solids. So although HCH is considered a persistent compound, its persistence in the sediment fraction is limited.
- **(Bio)accumulative potential.** Bioaccumulative compounds will probably be included into future sediment monitoring programmes, following the Water Framework Directive (WFD).

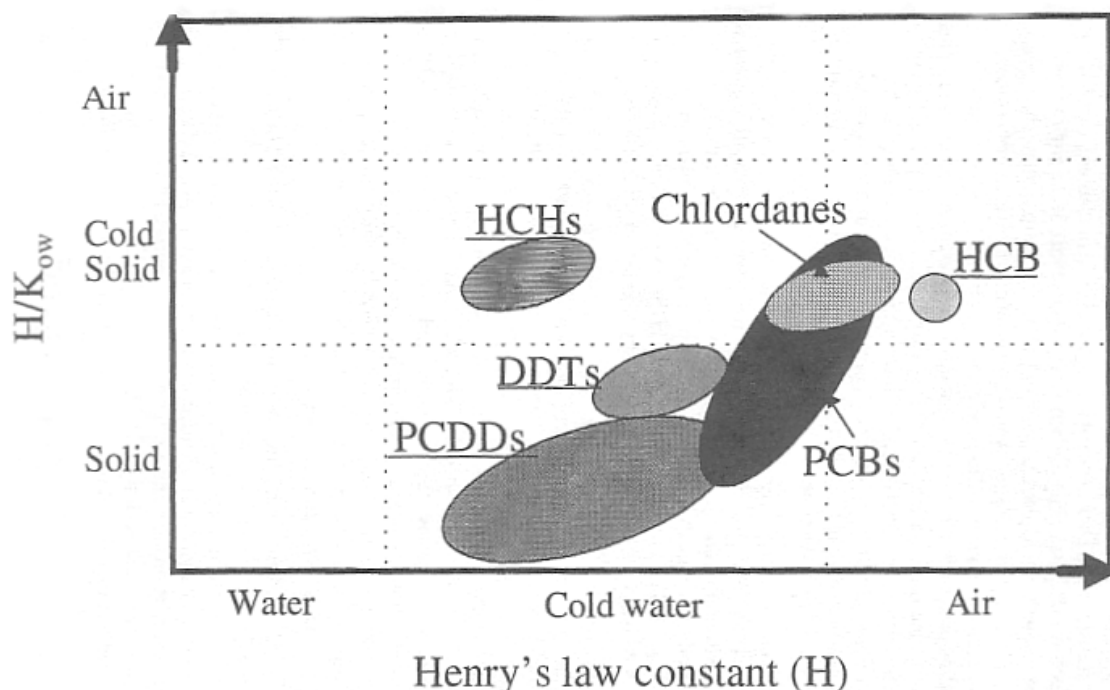


Figure 4.1. Schematic illustration of redistribution of certain organochlorine compounds based on their partitioning coefficients among air, water, and solids and the influence of temperature (Iwata, 1994)

The following compounds have been assigned to the higher hazard class 2:

Heavy metals: Cadmium and mercury, here following the guideline of the Water Framework Direction. This is done for two reasons:

- It is very likely that the WFD list of priority hazardous substances of the WFD will be transferred to sediments in future (Kott, Umweltbehörde Hamburg, personal communication). In order to be proactive in this study, this development will be taken into account.
- Cadmium and mercury are known to be highly toxic and bioaccumulative.
- Mercury is particularly dangerous in sediments, as it can be microbiologically transformed to methyl-mercury, which has a much more toxic due to its better lipid-solubility.
- Cadmium has been shown to be highly toxic to amphipods like *Corophium*, and its toxicity is even enhanced in the presence of nickel (Paquin *et al.*, 2003) (Bat *et al.*, 1998), so that this heavy metal requires special attention with regard to the bioassays that are part of the CTT.

As heavy metals are not degradable and one of the biotests that has been suggested for the inclusion in the CTT regulation (amphipod test with *Corophium volutator*) has been shown to react to relatively low concentrations of 2 mg/L of Arsenic, Zinc, Nickel, Chromium (Bryant *et al.*, 1984; Bryant *et al.*, 1985), all heavy metals are classified at least into risk group 1.

With regard to organic compounds, PCB, DDT, HCB, dieldrin and dioxins are assigned to hazard class 2, because they all show a high persistence (and have been classified as "persistent organic

pollutants” by the UNEP) and a strong partition to sediments. HCH, TBT and nonylphenol are less persistent (table 4.2) and have lower K_{ow} -values. They are classified as “1” (Table 4.2). In the case of HCH this may be very conservative, as it has been shown to degrade within days in a water-sediment environment (Callahan *et al.*, 1979). There is, however, a strong influence of the ambient temperature, prolonging the half-life to more than 100 years in cold ocean waters (Ngabe *et al.*, 1993).

PAHs are difficult to assign to one class only, as the half-lives vary depending on the specific polycyclic aromatic hydrocarbon. PAHs are considered as priority hazardous substance in the WFD but not as POP by the UNEP. Estimations of the half-lives of PAHs range from 5 to 10 years (Rippen, 2003). As, however, some of them can even show dioxin-similar effects, they will be classified in HC_C:2 (Table 4.3).

Table 4.3 Organic substances of concern with the assigned hazard classes (Hazard Class Compound HC_C) due to their chemical properties:

Substance of concern	<p>persistence</p> <p>1 : half life < 1 yr</p> <p>2: half life > 1 yr</p> <p>3: half life > 10 yrs</p>	log K_{ow}	Remarks	<p>Hazard Class (Comp.)</p> <p>HC_C</p>
PCB	3 ²²	8,2 ²³	POP synthetic compounds, not readily metabolized or degraded	2
PAH (z.B. Benzo(a)pyrene)	2 ²⁴	6,13	some PAHs (e.g. Benz(a)pyrene show dioxin-similar effects	2
Sum DDT+DDD+DDE	3 ²⁵	6,19	POP, synergistic effects: elevation of toxicity by lindane	2
HCB	3 ²⁶	5,91	POP	2
γ-HCH	1 ²⁷	3,66	Creation of (toxic) metabolites during degradation	1
Aldrine (Dieldrine, Endrine)	3	5,59	POP	2
Dioxins	3	6,78	POP	2
TBT	2 ²⁸	3,59		1
Nonyl-phenol compounds	2 ²⁹	3,28		1

²² Higher chlorinated PCBs (>5 chlorine atoms) are resistant to biodegradation under natural conditions (Rippen, 2003)

²³ K_{ow} for PCBs vary between <5 and 11, depending on their degree of chlorination. 8.2 is an average K_{ow} that is mostly used (Rippen, 2003)

²⁴ half life 5 to 10 years (Rippen, 2003)

²⁵ in soil and sediment: 0-20% transformation after 3 years (Rippen, 2003)

²⁶ Chemical Fact sheet: CAS 118741

²⁷ Transformation in Water /Sediment: 90% in 87 days (anaerobic) (Rippen, 2003)

²⁸ Half life in sediment: 22 months (Rippen, 2003)

²⁹ Degradation of 80% within 70 days (Rippen, 2003)

4.3 “Areas of concern”

An area of concern, a.o.c., in this report is defined as a hazardous site. Ranking of a hazardous site is done with regard to the CTT regulation. Using CTT threshold values as the yardstick makes it possible to compare the sediments at their present location with the effect they would have if they were transferred to the Port of Rotterdam.

4.3.1 Methods to assign hazard indexes to areas of concern based on sediment data

No risk is addressed at this stage. Hence, information on erosion and transport will not be considered in this chapter. The data base for the determination of hazard indexes for areas of concern contains sediment data, that were gained from reports of the environmental offices of the different Federal States, (Baden-Württemberg, Hessen, Rheinland-Pfalz, Nordrhein-Westfalen), reports of the Erft- and Emscher-Verband, reports from the ICPR, data that have been made available by various institutions (BfG, ICPR, LUA, LfU, RIZA, UBA etc), personal communication with people in charge of sediment and suspended matter monitoring, and publications.

Monitoring programs of suspended matter and – where it is done at all – of sediments – are carried out in Germany by the different Federal States. Sampling data and monitoring periods are often not consistent which hampers the analysis and conclusions for effects along the river basin. Hence, higher degrees of uncertainty have to be accepted. Choosing a fuzzy logic tool facilitates consideration of these uncertainties when calculating the hazard index of areas of concern, of transport loads and effects for the Port of Rotterdam. The fuzzy set theory (Zadeh, 1965) has been commonly recommended for the assessment of ecological data, as it makes it easy to integrate information from different fields (Ahlf *et al.*, 2002; Heise *et al.*, 2000). It can reflect natural variability, ambiguity and lack of quantitative data in environmental prediction (Silvert, 1997). It presents an interesting alternative to stochastic analysis since fuzzy logic models reflect very well how humans think and take decisions (Mohamed & Côté, 1999). The big difference to stochastic models is that it is easy to include uncertainties in the data and that the whole information of a data set is sustained throughout the calculation, as no early decisions need to be made e.g. into black or white, but “shades of grey” can be worked with.

The calculation of contamination indexes for areas in Nordrhein Westfalen are based on chemical data of surface sediments that were taken by the LUA along the Rhine, generally in sedimentation areas like small harbours, and along the tributaries Sieg, Wupper, Erft, Ruhr and Lippe between 1993 and 2003. Data from 1997 till 2002 that were gathered by the „Waterways and Shipping Administration“ (WSA) and are collected by the Federal Institute of Hydrology, hold information on sediment that was sampled during dredging activities mainly in small harbours. Heavy metal concentration is measured in

Nordrhein Westfalen in the <40 µm fraction. Data on grain size distribution are not available for every sediment sample. Median values of the percentage of the <40 µm fraction have been used for the tributaries as these do not change to a large extent, in order to compare the contaminant concentration with those levels that are given in the CTT regulation. The grain size distribution for the Rhine stations differ to a larger extent. Here different values were determined for the various Rhine locations.

Concentrations in surface sediments between 1999 and 2001 along the High and Upper Rhine were received from the LfU Baden-Württemberg (*Landesanstalt für Umweltschutz*, Institute for environmental protection of the Federal State Baden-Württemberg). For every sediment sample, the grain size distribution has been provided and the calculation for concentration in the whole sediment sample has been done on the basis of the <20 µm fraction, in which heavy metals are analysed in Baden-Württemberg. The same has been done for the data from the „Waterways and Shipping Administration“.

Only few sediment data were available for the Main and Mosel, as only a few sediment analyses have been carried out in Rheinland-Pfalz and Hessen. Data that were provided for these rivers have been taken from the report on ecotoxicological sediment mapping in the large German rivers (Duft *et al.*, 2002) by the German Environment Agency. No grain size distribution is available for those sediments.

In the calculations, the amount to which a compound exceeds the CTT threshold, the hazard rank of this compound, and the uncertainty of the data are used to categorize the hazard index of an area of concern. The number of compounds, exceeding the CTT thresholds, only influences the outcome in the respect that the certainty of a conclusion, that a specific site is hazardous, increases with the number of contaminating compounds.

In detail, the following assumptions are made for the calculations:

In most cases, the sedimentation patterns in a harbour or tributary are not known. Therewith no statement can be made about the analysed sediment's age and whether old or only "new" sediment has been measured. Therefore, relying on the provided data on sediment surface contamination, those sediments, which show contamination above the CTT-levels in subsequent years are regarded as potentially dangerous, and the concentration of contaminants is averaged over the sampling years, if no trend towards decreasing contamination was obvious. Such a trend is obvious with TBT concentrations in all measured sediments and with PCB-concentrations in the Lippe and Wupper. In those cases, no averaging is done and only the most recent data on concentrations are used.

When single measurements exceeded the CTT values and these extremes were before 1999, they are also not taken into account.

In general, only few significant improvements in sediment quality over time could be identified on the basis of the available data. Often recent sediment samples show high concentrations. Although sampling surveys did not specifically target floodings, these may well have effected the sediment data by exposing deeper and more contaminated sediments. This, however, does not corrupt the

estimation procedure: If the sediment is exposed, it may also become transported towards the port. This topic of resuspension and transport will be dealt with in the next chapter.

Data are not available for every location from all years and all compounds, e.g. there are only data from 1994 and 1997 for the River Ruhr, whereby some locations at the Lippe have been sampled in 4 to 5 different years. In the Rhine harbours, up to 10 measurements from different years are available.

The uncertainty of drawing conclusions on a limited number of data points is integrated in the calculations:

- n = 1; uncertainty is high
- n = 2; uncertainty is medium
- n ≥ 3; uncertainty is low

With the number of compounds that exceed the CTT thresholds, the probability of a hazard increases which is taken into account.

On the basis of the available data and applying the assumptions above, the sediments were assigned to 4 hazard classes:

- 0 – low or no hazard
- 1 – potential hazard
- 2 – potentially high hazard
- 3 – high hazard with high certainty.

Class 1, a potential hazard, is the second lowest category, indicating that there are some concentrations above CTT thresholds but that these exceed those values only to a small extent (up to 1.5 times with substances of hazard rank 2; up to 2 with substances of hazard rank 1).

Class 2, a potentially high hazard is assigned, when the concentrations are higher than class 1 (more than 1.5 times with substances of hazard rank 2; more than 2 times with substances of hazard rank 1) and there is some uncertainty involved.

Class 3, a “high hazard with high certainty” comprises those areas with the same concentration levels as in class 2, but where the amount of available data and / or the number of compounds exceeding the CTT make a hazard highly probable.

4.3.2 Identified Areas of concern

Figure 4.2 gives an overview of the hazard classes in the sediments in the River Rhine. The table with the assigned hazard classes is provided in the annex 2.

High and Upper Rhine up to Iffezheim.

Most sediment samples in the high and upper Rhine down to the weir of Iffezheim are assigned to hazard class 3 indicating a “high hazard with high certainty” due to exceptionally high HCB concentrations and some elevated amounts, in particular of PCB, lead, DDT. HCB in these sediments is a consequence of emissions from a former chlorosilane production site in Rheinfelden. It is still retained in high amounts in sediments of the upper and high Rhine – especially in the weirs with decreasing concentrations downstream. Extreme values are 2500 µg/kg in surface sediments in Augst (Zipperle & Deventer, 2003), and 3000 µg/kg in Marckolsheim (Witt *et al.*, 2003). In all 15 locations that were sampled between Augst and Iffezheim, the CTT values were exceeded 4 to 23 fold. An exception here is Kehl. These sediments are regarded as hazardous because of PCB concentrations of 341 µg/kg.

Downstream of the last barrage Iffezheim, sediment samples were assigned to class 2 and 3. Both classes indicate a high hazard, differentiating between results of different certainties, in this case because the concentrations of HCB at the class 2 areas are significantly lower (between 53 and 90 µg/kg) than those of class 3 (180 up to 900 µg/kg in Gernersheim).

Small harbours in the High and Middle Rhine

Further downstream sediment data are mainly available for small river harbours which usually serve as sedimentation areas and are therewith analysed in order to keep track of downstream transported material and accumulating suspended material. Under certain conditions of high water flow and harbour construction works, these sinks can serve as contamination sources and are therewith classified here as well. Data are available for the 3 harbours Worms-Bauhafen (km 443), Loreley (km 555) and Ehrenbreitstein (km 591) near Koblenz for which data have been provided by the Federal Institute of Hydrology. Between Koblenz and Duisburg, the environment agency of the Federal State Nordrhein-Westfalen (*Landesumweltamt Nordrhein-Westfalen*, LUA) sampled 17 small harbours.

The class 3 classification of Bauhafen near Worms, “high hazard with high certainty”, is due to HCB concentrations of 460 µg/kg, in addition to slightly elevated levels of Cu and Hg. The Loreley harbour, 100 km further downstream, shows high amounts of zinc, cadmium, copper, mercury, lead, PCB, PAH, sum DDT+DDD+DDE, and HCB-concentrations of 106 µg/kg.

There is none of the especially hazardous chemicals present in the Ehrenbreitstein-Hafen: no PCB, no cadmium, no HCB. Most other heavy metals show only low concentrations.

All harbours between Koblenz and Duisburg are assigned to hazard classes 1 or 2 with one exception: Hitdorf-harbour. Apart from increased values for most heavy metals, including mercury, copper, chromium and lead, PCB concentrations of 228 µg/kg were measured in this class 3-area. HCB content in the sediment was higher than 40 µg/kg.

All other harbours up to Duisburg show (slightly) elevated concentrations of heavy metals (no cadmium, no mercury). Those that are classified as class 2 have increased HCB concentrations between 34 (km 639,1, Hafen Oberwinter) and 75 µg/kg (Sporthafen Golzheim; km 747).

Duisburg / The Ruhr-area and harbours downstream

Five out of seven sampling areas in the vicinity of Duisburg are categorized as class 3. The kind and distribution of contaminating compounds vary: Whereas in Duisburg-Hüttenheim (km 770,3), concentrations of Zn (563 mg/kg) and Pb (135 mg/kg) are elevated, Duisburg-Wanheimerort (km 774,2) shows peaks in copper (125 mg/kg) and PAHs (108 mg/kg). In sediment from Duisburg-Aussenhafen (km 776,6) cadmium is enriched (4,4 mg/kg), zinc reaches values of 484 mg/kg, chromium accumulates to 147 mg/kg, and PCB is slightly increased with 126 µg/kg. Diergard-harbour is exceptional in its contamination with dioxins: concentrations of 470 with peaks of more than 2900 International Toxicity Equivalents (TEQ) were determined.

In the Ruhrort Becken and the Duisburg-Eisenbahnhof, a categorization of class 2 is determined by increased PAH levels between 17 and 26 mg/kg.

Most other harbours in the Lower Rhine do not show any significant peaks with the exception of the Baggerloch Müllerhof, in which heavy metal concentrations are increased, PCBs levels are 332,5 µg/kg and HCB reaches 96 µg/kg.

HCB concentrations in Duisburg and the Lower Rhine harbours are frequently elevated, though remaining in the range of 20 to 55 µg/kg.

Tributaries

Few data are available for Mosel and Main, as the respective environment agencies of the Federal States ("Landesämter") do not carry out sediment monitoring.

Sufficient data are available for Neckar, Sieg, Erft, Wupper, Ruhr, and Lippe.

Along the NECKAR, on 30 locations surface sediment was sampled between 1999 and 2001 (Zipperle & Deventer, 2003). To most of the stations, class 1 can be assigned, indicating a (low) potential hazard. Exceptions are class 2 station Gundelsheim (increased cadmium concentrations of 36 mg/kg), Hofen (class 2: PCB: 209 µg/kg) and Cannstadt (class 2: mercury: 2,7 mg/kg). The barrage Lauffen was also classified as class 1 on the basis of data from Zipperle and Deventer (2003), but classified as

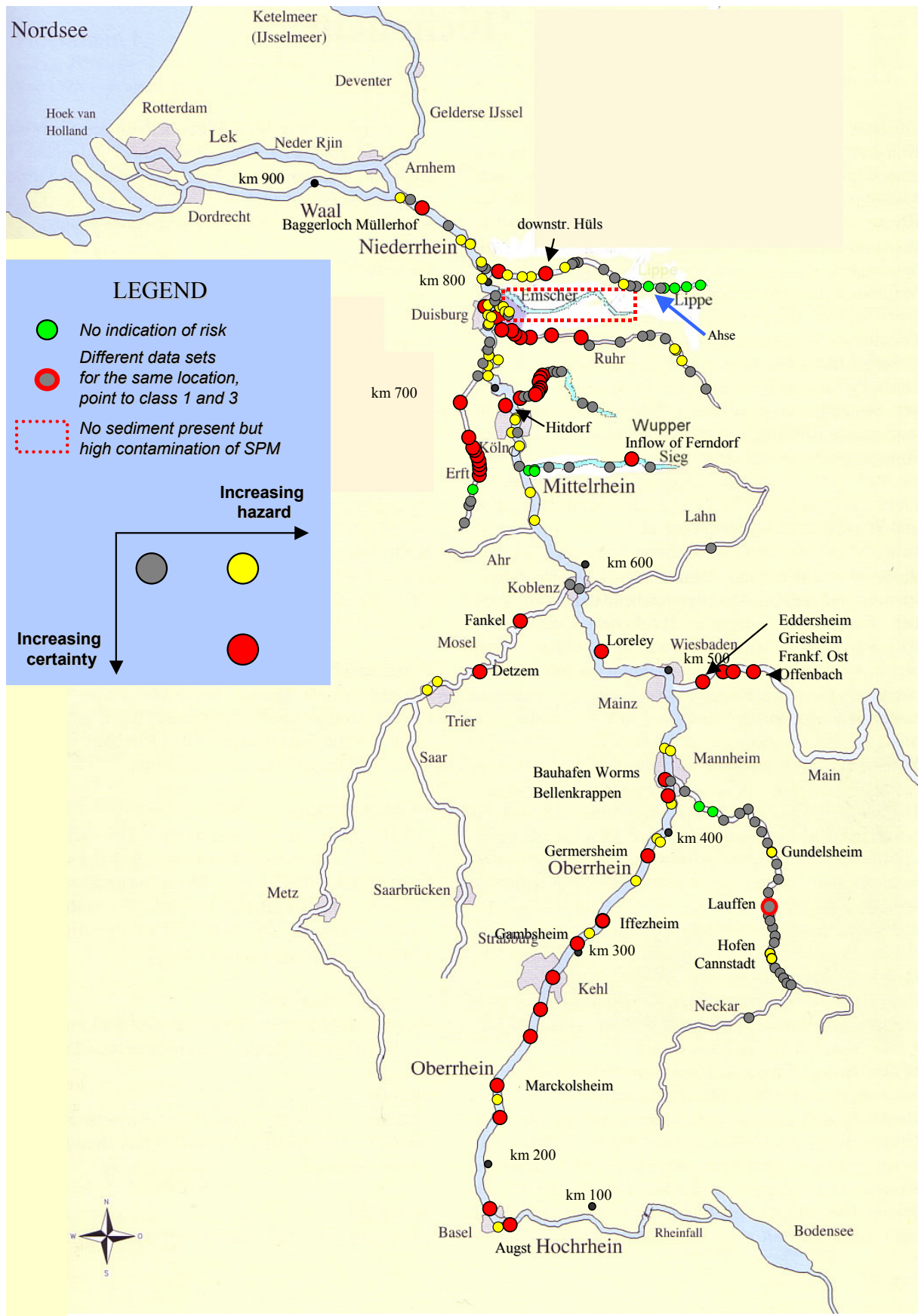


Figure 4.2 Hazard classes for the areas of concern along the River. All data except Mosel and Main data are corrected for the contaminant concentration in the whole sediment sample (background map taken from (Fenzl, 2003) with kind permission of the publishing house "Edition Maritime GmbH")

3 due to data from the „Waterways and Shipping Administration“ in which cadmium concentrations up to 18.4 mg/kg were recorded.

The SIEG showed a low potential hazard near its mouth (class 1). From River km 24 upstream, concentrations increase in zinc (up to 811 mg/kg at Eiserfeld), copper (up to 78 mg/kg), chromium (up to 194 mg/kg), lead (up to 161 mg/kg), and nickel (67 mg/kg). At the inflow of the Ferndorf, sediments are assigned to class 3. No organic contamination except a slight increase in PAH (8 mg/kg) has been recorded.

WUPPER: The Wupper is mostly categorized as class 3: Apart from cadmium (which was often below a detection limit of 5 mg/kg; LUA) all heavy metals show strongly increased concentrations with peaks in zinc (780 mg/kg), copper (244 mg/kg), chromium (176 mg/kg), mercury (5,2 mg/kg), lead (374 mg/kg), and nickel (94 mg/kg). Also PAH are increased in some locations up to 36.2 mg/kg.

RUHR: The Ruhr sediment is classified completely as highly hazardous with high certainty (class 3). It contains high peak levels of zinc (1596 mg/kg), cadmium (up to 11 mg/kg), copper (300 mg/kg), chromium (230mg/kg), lead (282 mg/kg), and nickel (104 mg/kg) up to river km 136. In addition it is enriched with high levels of PCBs (up to 462.8 µg/kg) and PAHs (up to 1277 mg/kg).

ERFT: The Erft shows low concentrations near the mouth (mainly class 1), but again high heavy metal concentrations of zinc (up to 5203 mg/kg), copper (98 mg/kg), lead (641 mg/kg), and nickel (1678 mg/kg), which all exceed the highest values that have been measured in the Wupper and in the Ruhr with the exception of copper. Accordingly these sediments are assigned to class 3.

Only little information is available on the MAIN and the MOSEL. For the barrage Eddersheim at the Main, high concentrations of mercury and cadmium of up to 60 mg/kg were found. According to data released by the Environment Agency, the locations Offenbach, Frankfurt Osthafen and Griesheim at the Main are extremely high contaminated with PAHs (class 3), the stations Fankel and Detzem at the Mosel with heavy metals (class 3) (Duft *et al.*, 2002).

LIPPE: The Lippe shows few class 3 sediments compared to the other rivers. Zinc (up to 603 mg/kg) and copper (up to 137 mg/kg) concentrations are elevated. PCB levels are increased (up to 222 µg/kg) and also PAH values (up to 15 mg/kg). Very high HCB concentrations are found near the mouth of the river (436 µg/kg) and downstream of Hüls (140 µg/kg). Increased levels are found up to river km 46.

4.4 Potential sources for contamination

4.4.1 Industrial/diffuse sources in general

In the tables 4.4. and 4.5 general information about potential and diffuse sources of heavy metals and organic contaminants are gathered in order to compare what is known about former locations of industries with the areas that have been identified as being of concern in chapter 4.3.

Most production sites for heavy metals and organic s.o.c. are located in Germany, and here mainly in the Ruhr area, which had the highest density of industries in Europe in the 70s. Use and production of most of the organic s.o.c. (table 4.5) is restricted today with the exception of PAHs and HCB. PAHs and dioxins are produced through incomplete combustion of fossil fuels. Their input into the environment can therefore not be prevented completely. Emission of HCB as a by product of various processes has been reduced to a large extent. Any significant concentrations of the organic s.o.c. can therewith be regarded as stemming from a historic source or from accidental release.

Table 4.4. Potential industrial sources of heavy metals of concern in the Rhine catchment from 1985 to 1996 (main source: ICPR Rhein Bestandsaufnahme der Emissionen prioritärer Stoffe 2000, Mai 2003, modified)

Source industry	Zn ³⁰	Cu	Hg	Cd	Ni	Cr	Pb
/	Pigment production Zinc plate production Petrochemical plants Chlor-alkali-production Fertilizer Production Steal -Industry	Galvanic processes Paper industry Fertilizer production Steal-industry	Chlor-alkali production Pesticide production Paper industry Fertilizer production Steal-industry	Pigment production Zn-production Petrochemical plants Chlor-alkali-production Fertilizer production steal-industry	Paper industry Fertilizer production Steal-industry	Paper industry Petrochemical plants Chlor-alkali-production Fertilizer production steal-industry leather produc. industry	Chlor-alkali- production Pesticide production Paper industry Fertilizer production Steal-industry
Diffuse source	Surface run-off	Antifouling paint ³¹ , surface run-off	surface run off	Agricul. battery			
Location of production	Krefeld Duisburg Kaysersberg (Elsass) Düsseldorff		Rheinberg Uerdingen Dormagen Leverkusen Hürth Weseling Ludwigshafen Frankfurt Marl (Lippe)	Ludwigshafen Leverkusen Krefeld Duisburg Düsseldorff			

³⁰ Until 1995 untreated waste water release from paper industry in Kaysersberg

³¹ Will increase in the future due to replacing TBT containing paints

Table 4.5 Potential industrial sources of organic substances of concern in the Rhine area

	PAH	PCB	HCB ³²	TBT (and other organotin-comp)	DDT+DDD+DDE	Dioxins	Chlororganics esp. γ-HCH
Source industry	/ coking plant Aluminium-industry ³³	PCB production ³⁴ Use in transformers use in condensators as hydraulic oil in plastics	Production of: - Pentachlorothiophenol - Tetrachlorethylen - Trichlorethylen - Tetrachlorkohlenstoff - PCNB ³⁵ Electrode, PVC- prod.	Antifouling Fungicides (stabilisators for PVC)	Industrial emissions Insecticides	Production of chlorophenol Steel, iron and metal working industries	Pesticide PVC-produc. paper
Diffuse source	incineration	Building-material Wood-protection Disposal sites	Tyres Seed protection Agriculture Wood protection			Incineration Combustion	Disposal sites
Location of production	Duisburg-Hochfeld Linz	Leverkusen (?) Ludwigshafen	Leverkusen Rheinfelden Arnheim (NL) Rheinberg Uerdingen Dormagen Hürth Weseling Ludwigshafen Frankfurt Marl (Lippe) Mannheim	Seseke (Lippe)			Köln Mohnheim Mannheim currently only one production site in Europe (located in Eastern Europe)
production restricted ?		selling and use prohibited since 1989 (Germany) restricted in marketing and use by Council Directive 76/769/EEC		Application of TBT- containing Antifouling paints for ships <25 m 10.12.89	In most countries application is forbidden. Insecticides widely restricted under Council Directives 76/769/EEC and 79/117/EEC or not used in Member States	no intentional production	Marketing and use prohibited under Council Directive 79/117/EEC,

³² Technical grade contains dioxins

³³ due to Graphit electrodes

³⁴ until 1982, since 1989 use is restricted in Germany and since 1991 in Europe

³⁵ Pentachloronitrobenzol

4.4.2 Historical sources for areas of concern

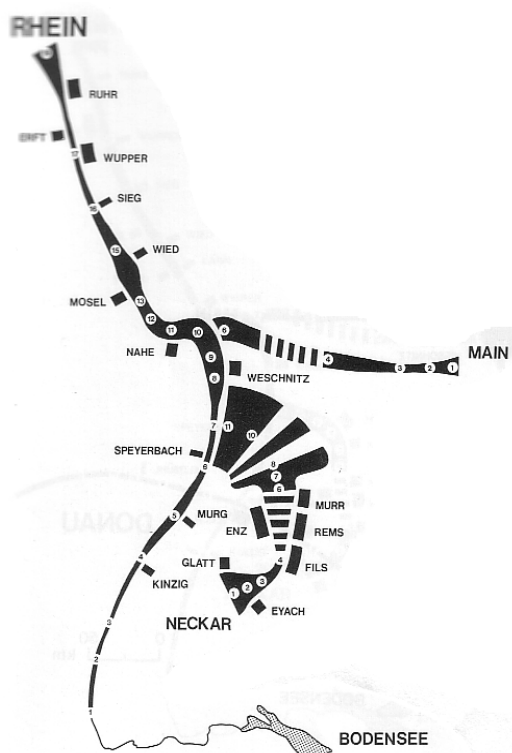
A comparison of identified areas of concern (depicted below in grey boxes) with knowledge about historical sources is carried out for two reasons:

- In order to identify the original source of the contamination that is still measurable today in surface sediment. Any measures for reduction of the risk that spreads from these sediments have to take into account the original source – its location and whether it still continuous to emit contaminants.
- In order to make sure, that no sites have been overlooked (e.g. if no sediment data were available for a river) although their historical contamination may be well known.

Heavy metals

Most information on historical sources that are used here, derive from one of the first comprehensive studies on metals in rivers and lakes in 1972. Contaminant levels are presented in the graphs, shown here, in such a way, that the thickness of the black river outline corresponds to the concentration level (e.g. in Figure 4.3). Broken lines indicate that no data were available on these areas.

CADMIUM:



Cadmium has been identified in Chapter 4.3 as dominant contaminant in the following areas of concern:

- Duisburg, Ruhr area
- small harbours of the Lower Rhine
- Neckar
- Main
- Ruhr
- Erft

In 1972, high cadmium concentrations could be found in the Neckar, the Main, partly the Wupper and the Ruhr, and the Ruhrarea downstream of the Lippe-inflow (upper end of the graph). With exception of the Wupper, which today showed only insignificant cadmium-concentrations in the upper sediment, all other sources are still contaminated with cadmium today.

Figure 4.3 Cd in the clay fraction of sediments in the Rhine and its main tributaries in Germany (from (Förstner & Müller, 1974))

In the **Neckar**, sediment contamination was most severe upstream of the weir Lauffen where extreme cadmium concentrations up to 300 mg/kg were measured in 1975 (Stiefel, 1975) and where also today high cadmium levels can be found (Chapter 4.3). Metal working industry along the Enz was probably responsible for the cadmium emissions in the Neckar. Also a plant in Besigheim (Neckar) seemed to be responsible for a large part of the pollution, as it decreased significantly with the start-up of an industrial treatment plant 1973 (Förstner & Müller, 1974).

Cadmium-levels up to 22.3 mg/kg have been recorded for the **Erft** in 1986 (Christoffels, 1989) that originated from an industrial plant that was situated at Iversheim near Bad Münstereifel where zinc-leach was processed for production of metallic soap. As zinc co-occurs with cadmium in the natural environment due to high similarity of both metals, cadmium is often a by-product when zinc is processed. Modifications in the production of zinc leach led to a decrease in cadmium emissions in the following years. In addition to industrial emissions, the Erft is highly influenced by the effects of lead and zinc exploitation which has been going on in that area for 2000 years. Although exploitation of the ore deposit stopped in 1957, weathering of the highly damaged ground still caused high heavy metal concentrations in the mine water, which flowed into the Erft via the Veybach in 1987 (Christoffels, 1989). The emissions from the Erft into the Rhine may be the reason for the high cadmium concentration of more than 8 mg/kg in the **Neuss-Hafenbecken**, which is just 5 km downstream of the Erft-inflow into the Rhine.

While recent data only showed insignificant cadmium concentrations in the Wupper, considerable concentrations of cadmium, chromium, copper, mercury, nickel, lead, zinc, and arsenic were measured in 1995. Heavily contaminated sediments were found downstream of the cities Wuppertal, Remscheid and Solingen, due to the location of industrial heavy metal sources there (Schenk, 1995). Cadmium concentrations in Hitdorf (706,9 km, right side), however, do not show the increased levels, that would have been expected if this harbour, which is influenced by the Wupper, would have contained high contaminant loads (LUA, 1997).

In 1992, 40% of the overall cadmium load in the Rhine was estimated to derive from Cologne and the **Duisburg-area** (LWA, 1993), due to its high density of various industrial production sites and its high population density. Anderberg and Stigliani (Anderberg & Stigliani, 1994) made a mass balance for two zinc smelters before 1980 in Duisburg which had no economic interest in refining cadmium, but rather treated it as an unwanted waste product. Anderberg & Stigliani detected that the companies must have discharged what would normally have been considered as solid wastes directly to the river. This strategy only changed in the 1980s when the wastes were recycled in a nearby zinc/cadmium refinery. This assumption is supported by measurements shown in Figure 4.4 depicting cadmium concentrations of more than 50 mg/kg in sediments (<40 µm fraction) in this area at the Duisburger Aussenhafen (776,6 km, right) in 1980. Also today, cadmium concentrations in the Duisburger Aussenhafen are elevated with 8.2 mg Cd/kg (<40 µm fraction) (LUA data base).

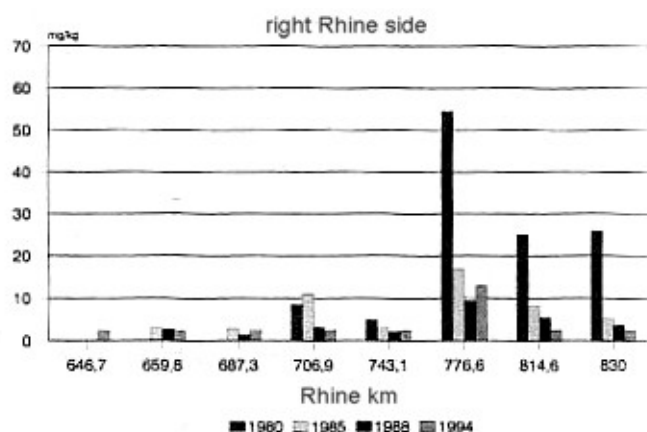


Figure 4.4 Cadmium concentrations along the right Rhine side in the years 1980, 1985, 1988 and 1994 (<40 µm fraction) (LUA, 1997)

The River **Ruhr** is the main source of drinking water in the Ruhr area. Nevertheless it has been polluted with heavy metals by industry and communal wastewater. Four impounding lakes were constructed to increase self-purification of the river. It has been estimated in 1980, that about 40% of the total heavy metal load of the River was deposited in the sediments of these lakes along the middle and the lower Ruhr (Imhoff *et al.*, 1980). The tributaries River Ennepe and River Volme and their catchment area were regarded as the potential main source for the input of contaminated sediment into the river Ruhr due to anthropogenic contamination through foundries, battery factories, wastewater treatment plants and steel works upstream (see chapter 4.5).

Compared to the Ruhr, the pollution of the **Emscher** was more severe. The 3 rivers Ruhr, Emscher and Lippe are in close proximity to each other. Their environmental fate was determined about a hundred years ago, when Lippe and Emscher were “sacrificed” for the sake of the Ruhr which was supposed to provide drinking water. The Emscher is still considered to be one of the highest contaminated rivers in the Federal Republic with regard to its concentration of contaminants and nutrients. Known historic sources of contamination, which continue to pollute the river are in the region of an old fertilizer plant and a former coking plant that emitted PAHs, heavy metals, cyanide and coking plant typical organic compounds into the water (LWA, 1993). The Emscher can theoretically be responsible for the difference between chemical concentrations measured at the monitoring station Bimmen on the left side of the Rhine and Lobith on the right side. Lobith is still within the trail of the Emscher discharge and the difference in the cadmium concentration between the 2 stations in 2000 (Bimmen: 0.83 mg/kg; Lobith 4.85 mg/kg) could be an indicator for the effect of the Emscher discharge. Nowadays, however, the whole river water is treated (see Chapter 5.7.2) and effects of this kind are unlikely to occur.

CHROMIUM

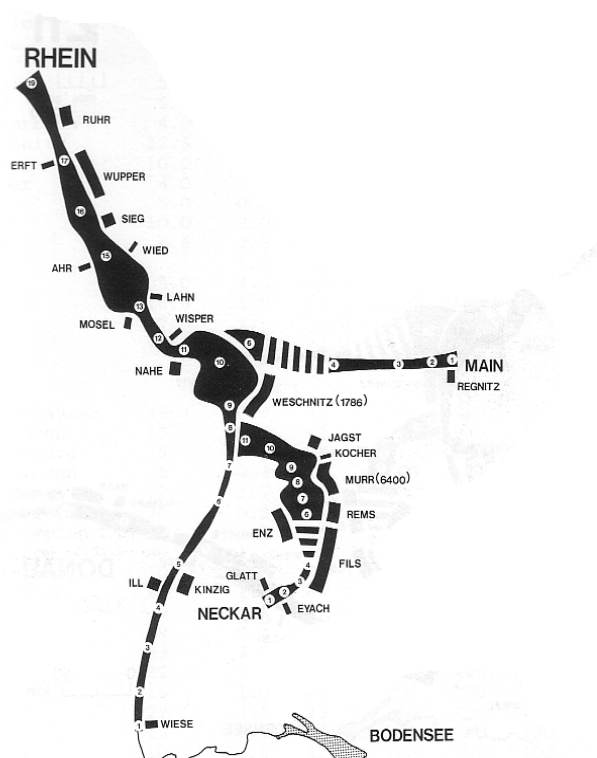


Fig. 4.5 Cr in the clay fraction of sediments in the Rhine and its main tributaries in Germany (from (Förstner & Müller, 1974))

Chromium has been identified in Chapter 4.3. as dominant contaminant in the following areas of concern:

- Duisburg, Ruhr area
- small harbours and flooded quarries of the Lower Rhine
- Wupper

Figure 4.5 shows the sediment contamination for chromium in 1972 in the Rhine and its tributaries where concentrations were especially high in the **Neckar, the Main, the Weschnitz**, and the **Wupper**. The Wupper is still classified as an area of concern with respect to chromium in this report.

The only recently high chromium concentrations that are recorded for the Neckar were observed in dredged material from Lauffen and Feudenheim at the

confluence (Data from the Waterways and Shipping Administration/BfG). Only few recent sediment data are available for the Main, which do not allow an assessment on chromium concentration.

The Weschnitz, which combines with the Rhine downstream of Mannheim, was carrying large amounts of chromium in 1972. The peak was near Weinheim at a large leather processing industry.

No recent sediment data are available for the Weschnitz but its discharge is too low and the distance to Rotterdam too long, to represent a potential risk.

Extremely high concentrations of more than 800 mg/kg were measured in Hitdorf in 1985. This has been explained by the environment agency of the Federal State Nordrhein-Westfalen as being due to sampling at high water level and therewith of older sediments (Nordrhein-Westfalen, 1997). The small and open harbour Hitdorf contains contaminated material which can relatively easily be exposed.

High values until 1994 were measured in the **Duisburger Aussenhafen** (776,6 km, right side) (Nordrhein-Westfalen, 1997) and elevated chromium levels are also presently recorded in various harbour basins in Duisburg and in the flooded quarry "Müllerhof".

COPPER

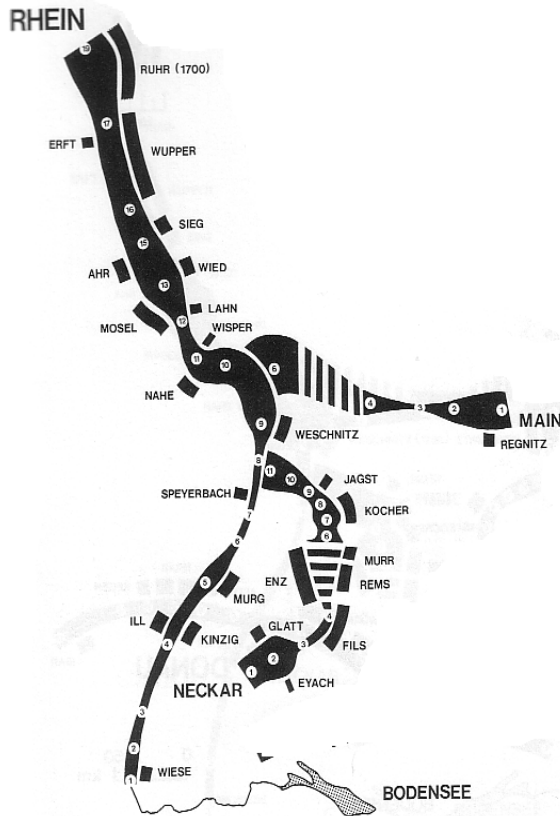


Fig. 4.6 Cu in the clay fraction of sediments in the Rhine and its main tributaries in Germany (Förstner and Müller, 1974)

Copper has been identified in Chapter 4.3 as dominant contaminant in the following areas of concern:

- small harbours and flooded quarries of the Lower Rhine
- Neckar
- Mosel
- Wupper
- Ruhr

In contrast to the other heavy metals cadmium, chromium, lead, mercury, nickel, and zinc, which originate to a large extent from the area between Cologne and Bimmen (e.g. Duisburg), copper is emitted extensively from sources upstream of Cologne.

As sediments in the reservoir Iffezheim have been described to carry a contamination with copper (they reach twice the ICPR target values) with almost no vertical trend, it can be assumed that the copper concentrations originate from

eroded upstream reservoir material from Lauterbourg. However, due to the importance of diffuse sources for copper and here especially precipitation dependent processes like run-off from houses and vineyards, where copper-based compounds are applied as anti-foulings or pesticides, it will be difficult to differentiate between resuspension of historic contaminated sites and increased emission of diffuse sources. However, the recent data show no increased copper levels in High, Upper and Middle Rhine barrages.

In the catchment area of the **Neckar**, mechanical engineering industry, electronic industry, and motor industry prevailed already in the 80ies and were certainly partially responsible for elevated copper contamination of the river sediments. The tributary Enz was especially contaminated with copper in 1972 (Fig. 4.6), but sources of copper contamination in sediments could also be attributed to the upstream section of the Neckar below Schwenningen (Müller *et al.*, 1993). In the 70ies, galvanic industries that settled along the Elsenz, a tributary that conflues with the Rhine in its downstream section (about 20 km upstream from Heidelberg), added to historic copper contamination (Müller & Nagel, 1980). Nowadays, contamination of suspended matter in the Neckar is most distinct below the large metropolitan areas Stuttgart and Heilbronn (LfU, 2001).

High concentrations in the **Mosel** probably also derive from surface run-off off vineyards and houses.

The elevated concentration in **Wupper and Ruhr** have also been reported in 1972 (Fig. 4.6).

The **Emscher** has been highly contaminated with heavy metals. Five wastewater treatment plants reduce the heavy metal load in the small river but till the year 2000 were not able to increase the quality of the river water to more than class III-IV (on a scale from I: *very good* to IV: *very bad*). Partly high values in Maassluis may be an indication of the expected future trend of increasing copper concentrations due to the replacement of TBT as antifouling paint on ships by copper.

MERCURY:

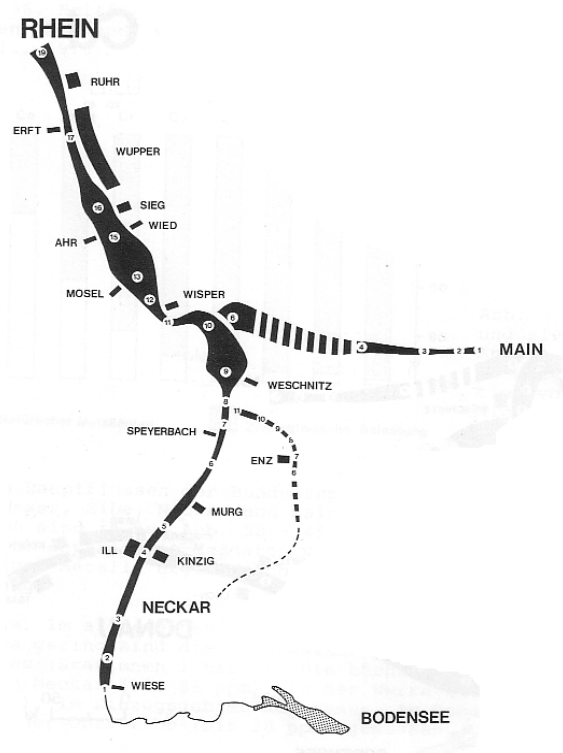


Fig. 4.7 Hg in the clay fraction of sediments in the Rhine and its tributaries in Germany (Förstner and Müller, 1974)

Mercury has been identified in Chapter 4.3 as dominant contaminant in the following areas of concern:

- The reservoirs of the High and Upper Rhine
- Harbours in the Upper and Middle Rhine
- small harbours and flooded quarries of the Lower Rhine
- Main
- Wupper

The chart of historic contamination of sediments with mercury (Figure 4.7) shows only few areas of heavy concentrations in 1972: In the **Main River** and in the **Wupper**. Still in 1995, the Wupper was considered to be heavily contaminated with heavy metals. The concentration of 40 mg Hg/kg in 1985 and of 13 mg Hg/kg in 1992 in **Hitdorf-Leverkusen** at the Rhine emphasizes the effect that the Wupper

efflux has on this site and the persistence of historic contaminated sites in this area can be suspected.

Recent data verify this assumption, as the same areas – Main, Wupper, and small harbours in the Lower Rhine like Hitdorf, have been identified as areas of concern with mercury as one dominant contaminant. The increased levels of mercury in the sediment of the **barrages in the High and Upper Rhine** and in **the harbours in the Middle Rhine** (e.g. Loreley), however, are not reflected in the former data shown in Figure 4.7. In a study that was carried out by Förstner and Müller only a

short time afterwards, sediments from around the city Basel were examined for mercury because a high contamination of fish downstream had become obvious. A significant increase in mercury concentration towards Basel was reported und assigned to emissions by large chemical industries around that city. The slow transport of this contamination and distribution downstream may be the reason for the elevated mercury levels in Iffezheim.

LEAD and ZINC

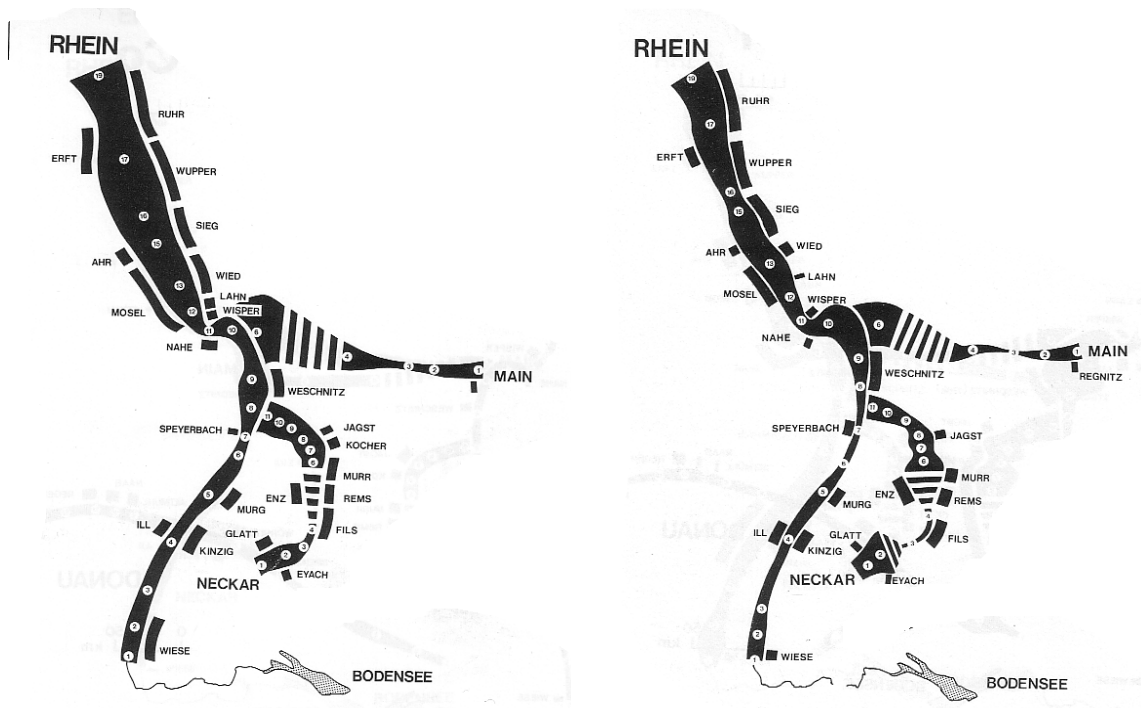


Figure 4.8 Pb (left) and Zn (right) in the Clay fraction of sediments in the Rhine and its main tributaries in Germany (Förstner and Müller, 1974)

Lead and zinc have been identified in Chapter 4.3 as dominant contaminant in the following areas of concern:

- Duisburg, Ruhr area
- small harbours and flooded quarries of the Lower Rhine
- Mosel
- Wupper
- Ruhr
- Erft

Lead as well as zinc showed increasing concentrations in 1972 in the **Neckar**, **Main**, the **Mosel** and downstream. Lead as well as Zinc are extensively emitted through diffuse sources near cities and communal point sources: High zinc emissions derive to a large extent from corrosion of pipes, lead from traffic. Accordingly, sediment concentrations of zinc and lead in the Wupper increased strongly at the city of Wuppertal. In 1995, 500 to 1000 mg/kg sediment were measured for Zn, 600 to 1383 mg/kg for lead (Schenk, 1995).

The transport from the **Wupper** into the Rhine is indicated again at the Hitdorf-Leverkusen station at 706.9 km (right side). However, concentrations of both heavy metals are even higher at Duisburg-Aussenhafen, another area of concern for these compounds.

Along the **Erft**, lead and zinc were exploited extensively for 2000 years, resulting in highly damaged ground. Accordingly, high concentrations of these heavy metals were carried with mine waters in the Rhine even after the end of mining activities in 1957. Additionally, a zinc-leach was processed for production of metallic soap in the Erft catchment.

Also the **Ruhr** catchment is characterized by former extensive exploitation of lead and zinc. The deposit *Ramsbeck*, exploited until 1974, was one of the largest zinc and lead ore deposits (Ruhrverband, 1998) The Ruhr and several of its tributaries (Neger, Elpe, Valme, Nierbach) that flow through this region are certainly contaminated by heavy metal laden mine waters.

NICKEL

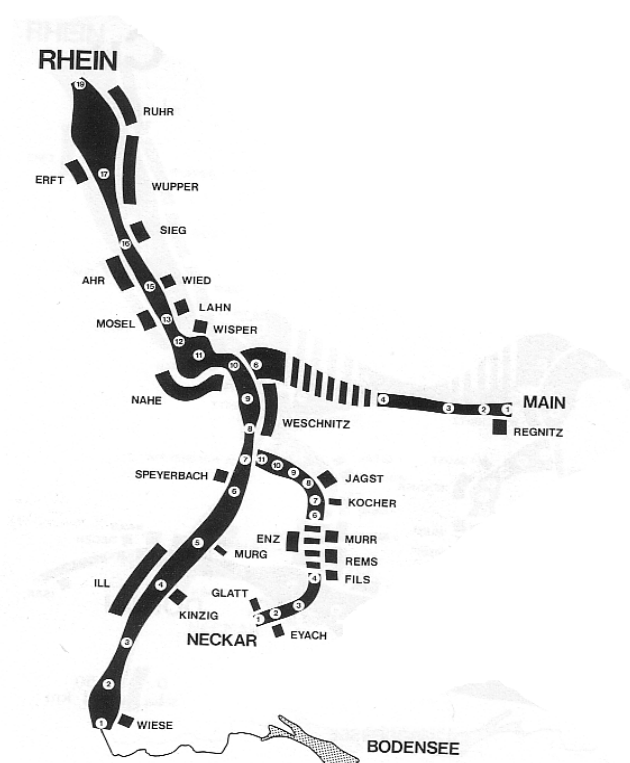


Figure 4.9 Nickel in the clay fraction of sediments in the Rhine and its main tributaries in Germany (Förstner and Müller, 1974)

Nickel has been identified in Chapter 4.3. as dominant contaminant in the following areas of concern:

- small harbours and flooded quarries of the Lower Rhine
- Mosel
- Wupper
- Erft

Ni As nickel emissions derive to a large extent from steel, galvanic and petrochemical industry, high concentrations were found in the **Ruhr-area** in 1972 (Figure 4.9). High concentrations were also found along the Ill tributary.

Also the **Mosel** was identified as area of concern with regard to nickel. Few sediment measurements are available and none were available for this report from former times. Settlement of steel industry, however, is mainly connected with the Saar area (a tributary of the Mosel). In opposite to the Mosel, a variety of industries settled

in the **Wupper** catchment (Schenk, 1995) of which probably former galvanic, chemical and metal processing industries were the most likely source for elevated nickel concentration in historic sediments. Increased concentrations in the **Erft** are caused again by drainage of former mines, as nickel is an abundant metal in the ores (Christoffels, 1992).

Organic substances

As can be seen in table 4.5, production and most extensive use of the organic s.o.c. is connected to coal mining and chemical industry. Accordingly, most extensive, historically contaminated sites will be found in the "Ruhrarea" (Chapter 4.5), near Leverkusen and in the Saar-Mosel area. An exception here is the HCB-emission which was caused by an industry near Rheinfelden, in the Upper Rhine.

In contrary to the paragraph on heavy metals, relating recently measured concentrations of organic substances of concern to former immission data is only possible to some extent, as determination of environmental concentrations of organics has not been done routinely until 20 years ago and is often limited even today due to economical constraints. This chapter will therewith focus on available information about the location of potential sources and from there conclude on the pathways that may have led to the recently measured contaminant concentration in surface sediments.

Polycyclic Aromatic Hydrocarbons (PAH)

PAHs have been identified in Chapter 4.3 as dominant contaminant in the following areas of concern:

- Emscher
- Ruhr

PAHs are produced through incomplete combustion of fossil fuels in coking plants, power plants, and in automobiles (Table 4.5). Their emission into the water and hence the sediment occurs diffusively. As PAHs strongly adsorb to sediments, the areas around former coking plants are potential legacies of the past.

The highest number of coking plants in Germany was located in the Federal State of Nordrhein-Westfalen. Of these, 454 out of 1313 plants that existed in Germany in the 70ies were positioned in this area due to the high population density, the large number of industries and the vicinity of mining areas: These concentrated around the cities of Dortmund, Bochum and Essen, all of them being located between the rivers **Ruhr** and **Emscher** (Annex Ruhrgebiet).

Polychlorinated Biphenyls (PCB)

PCBs have been identified in Chapter 4.3 as dominant contaminant in the following areas of concern:

- Higher and Upper Rhine
- Harbours and flooded quarries in the Lower Rhine
- Neckar
- Mosel
- Emscher
- Ruhr

Until their ban in 1989, PCBs were extensively used as condensator liquid in transformers and as hydraulic oils in hard coal mining. Environmental contamination was mainly due to leakages of the hydraulic systems that caused the oil to mix with mine waters, which then flowed into nearby rivers. These leakages were not minor: the institute of Nordrhein-Westfalen for water and waste (*Landesamt für Wasser und Abfall Nordrhein-Westfalen*) (LWA, 1988) calculated the volume of annual loss of the later PCB-substitute, Tetrachlorbenzyltoluol ("Ugilec 141") to 700 to 1000 tons between 1985 and 1987, indicating the dimension of PCB emission from mining sites before.

Extensive mining areas in the Rhine catchment are the **Ruhr area** and the Saarland at the German-French border. Elevated PCB concentrations can accordingly be found at sites, where mine waters flowed into the rivers and the areas downstream: The rivers **Lippe**, **Emscher**, **Ruhr** and Rheinberger Altrhein are still strongly contaminated with PCBs (Figure 4.10). Also the Saar, a **Mosel-tributary**, shows PCB contamination, which probably gets transported to and through the main river.

As also the **Erft** is highly influenced by mining activities, this should also be expected to be an area of concern for PCBs. However, no analytical data on organics from Erft sediments were available!

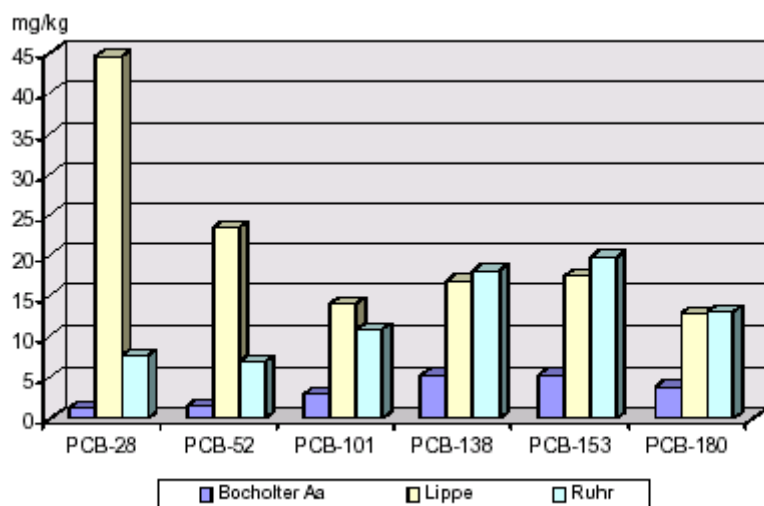


Figure 4.10 Average PCB concentration in suspended matter. Measurements at monitoring stations 1997-1999. Lippe (n=9, Ruhr (n=6), Bocholter Aa (n=2). modified from (Busch & Büther, 2000).

Interestingly, the PCB pattern differs between Lippe, where low chlorinated congeners dominate, and the Ruhr where the PCBs 138, 153 and 180 are found in higher concentrations (Figure 4.10). As the lower chlorinated congeners are easier degraded, the contamination in the Lippe seems to be younger and perhaps even persisting, but no polluter has been identified so far (Busch & Büther, 2000).

PCB concentrations at Duisburger Aussenhafen reached with 360 µg/kg in 1995 the highest PCB concentration along the Rhine from Königswinter to Rotterdam that had been measured in an ICPR survey (ICPR, 1999) (Figure 4.11). Therewith that Duisburger harbour basin contained almost twice the concentration of Hitdorf, that was also considered as polluted with PCB due to emissions from a former industrial plant, which ended their PCB-production in 1983.

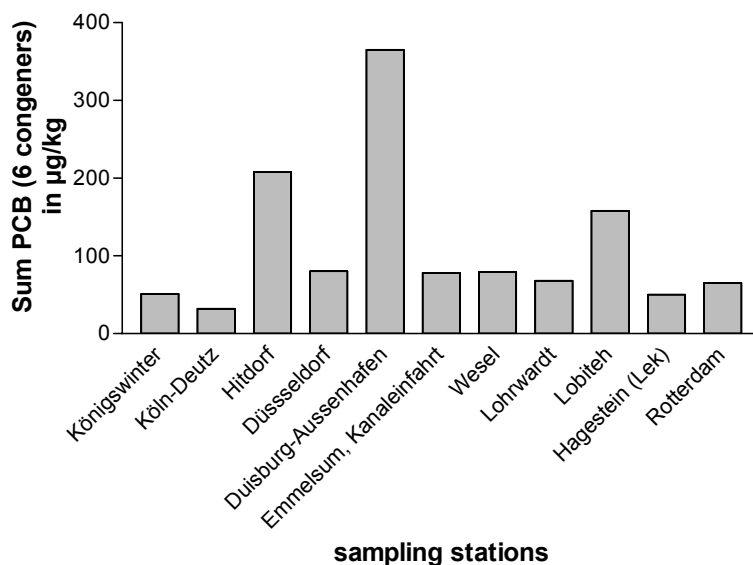


Figure 4.11 sum PCB (PCB 28, PCB 52, PCB 101, PCB 118, PCB 138, PCB 153) in the Rhine between Königswinter and Rotterdam in 1995 (modified from ICPR, 1995)

Concentrations in sediments that have been accumulated in reservoirs also show increased PCB levels in both Neckar and Main barrages. In sediments from Lauffen (Neckar) concentrations varied between 0.5 and 281 µg/kg.

No historic point sources were identified for the **High and Upper Rhine** and the **Neckar. Harbours and flooded quarries in the lower Rhine** are influenced by the PCB contamination, which transported into the Rhine by its tributaries.

Hexachlorobenzene (HCB) (see case study chapter 4.6)

HCB has been identified in Chapter 4.3 as dominant contaminant in the following areas of concern:

- Higher and Upper Rhine
- Upper and Middle Rhine
- Harbours and flooded quarries in the Lower Rhine

The most important compound of the chlorinated benzenes for the Rhine is hexachlorobenzene, as it provides the main environmental issue in the **High and the Southern part of the Upper Rhine**. Large HCB amounts were discharged from a former production site for pentachlorophenol (PCP) near Rheinfelden. During this industrial process and the consequent chlorsilane-production, HCB was produced and released into the Rhine between 1960 and 1985 until the production site was closed.

Apart from the site in Rheinfelden, a company in Marl in the **Middle Rhine** emitted HCB as a byproduct during chlorosilane production, although generally in much smaller amounts than in Rheinfelden. But in 1994, increased amounts of HCB were released to the Marl during cleaning procedures. This emission that flowed into the Rhine via Marl and Lippe was probably causing the high concentration of HCB that was measured in Bimmen in 1994.

Other important chlorobenzenes are di- and trichlorobenzene, which are important by-products in paint, rubber, pesticide, and textile industry. At the monitoring station **Hitdorf harbour**, increased concentrations of more than 270 µg/kg were measured in the sediment, which is assumed to derive partly from old industrial legacies that slowly emit through the groundwater.

Tributyltin (TBT)

TBT has been identified in Chapter 4.3 as dominant contaminant in the following area of concern:

- Lippe

Tributyltin is a general-purpose biocide that has been used as a fungicide and as an additive to antifoulant paints to prevent the growth of barnacles and other fouling organisms. Highest TBT-concentrations in the Rhine basin

area were found in the **Lippe**. Figure 4.12 shows values up to 600 µg/kg in sediments in 1994, and still almost 400 µg/kg in sediment in 1998 downstream of the confluence of the river Seseke at Lippe stream kilometer 95.08.

The emission stems from the only German (and world's largest) producer of TBT. In 1996, they covered 99% of the European TBT-demand. Origin of the high concentrations in 2000 was an insufficient elimination process of organotin compounds in the wastewater: The industrial effluents were collected and canalized to the wastewater treatment plant of another industrial company, where they underwent biological treatment. Afterwards the wastewaters were released into the Seseke, where they had to pass the river water treatment plant before entering the Lippe. As these treatments were not specifically adapted to remove or destroy the organotin compounds, elimination did not occur to a sufficient extent. After an investigation into this issue, the responsible environmental ministry in Nordrhein-Westfalen demanded that a specifically TBT-adapted waste water cleaning step

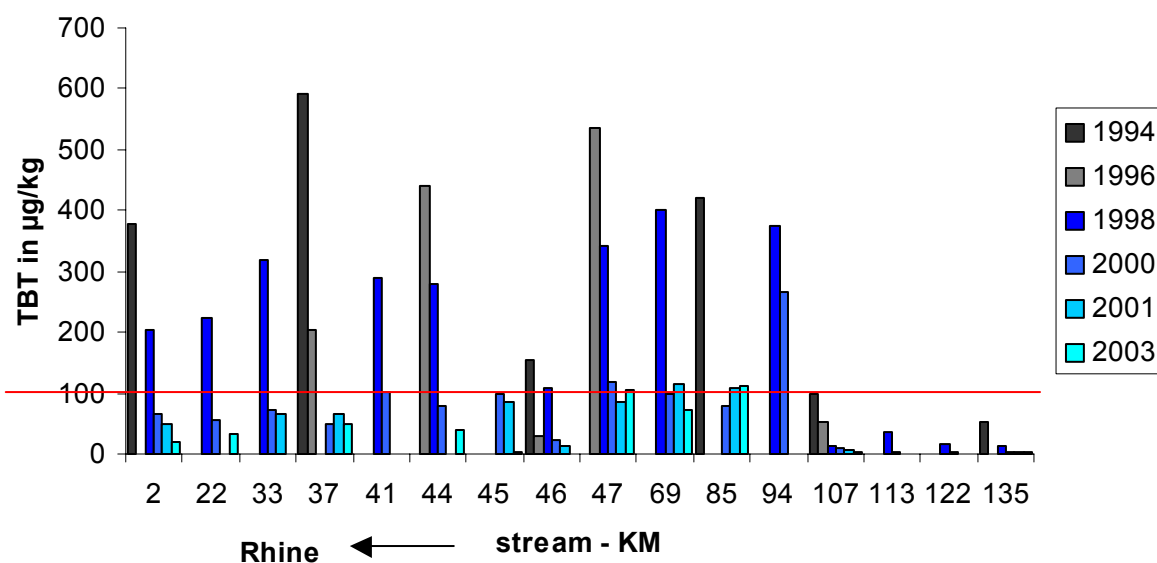


Figure 4.12 TBT concentrations in Lippe sediments between 1994 and 2003 in µg/kg. The red line indicates the lower range of the Dutch CTT level for TBT

had to be integrated into the production process and sludge from the Seseke treatment plant had to be incinerated which had previously been used for agricultural purposes.

Figure 4.12 shows that TBT concentrations in sediments were very high downstream the inflow of the Seseke at km 107. An efficient reduction occurred not before 2000. Currently, TBT reaches everywhere along the Lippe values in the range of the lower CTT-threshold.

Apart from Seseke and Lippe, various yacht harbours (Neuss-Gnadenthal, Oberwinter, Hitdorf, Industriehafen Düsseldorf, Krefeld, Duisburger Aussenhafen and Wesel) show elevated TBT concentrations up to concentration of 60 µg/kg TBT due to its use as an antifouling substance.

Dioxins and Furans

Dioxins and Furans have been identified in Chapter 4.3 as dominant contaminant in the following area of concern:

- Duisburg, Ruhr area

Polychlorinated dibenzodioxins (PCDD) and dibenzofurans (PCDF) are compounds that differ from the others of this list as they are not intentionally manufactured and have no commercial value. Like PCBs they are a group of related compounds with varying degrees of contamination. They

are formed as by-products during the production of chlorophenols and the herbicide 2,4,5-T., as combustion products and during the bleaching process at kraft pulp mills (Table 4.6).

On the basis of relatively few analytical data, as the measurements are expensive, one area of concern with regard to dioxins could be identified: The **Diergardt harbour at Duisburg** with up to 2900 ng/kg TEQ¹.

There is a particular lack of information on releases to water (Quass *et al.*, 2000) and no specific information on the source of dioxins in the Diergardt harbour basin has been found, other than the statement of the general impact of iron, metal, and steel producing plants, which potentially emit dioxins – depending on the filter system for the off-gas (Staatliches Umweltamt Duisburg, 2003). In the European Dioxin Inventory, a number of sources for release of dioxins and furans to water and their likelihood has been published (Table 4.6). They state the high probability of input through chemical and pesticide production (Quass *et al.*, 2000), which is concentrated in the Duisburg area.

The harbors in Duisburg are likely to be the only heavily dioxin-contaminated sites as the ICPR reported relatively low dioxin concentrations of 25ng/kg TEQ, increasing on the right Rhine side until Lobith to 73 ng/kg, never exceeding the protection value for children's playgrounds of 100 ng/kg (ICPR, 1999).

¹ TEQ: Toxic equivalent factors: Dioxins are often present in mixtures and in order to assess their "net"-effect, TEQ are calculated for each compound by multiplication of its concentration with an empirically determined "toxic equivalency factor" (TEF). One of the most toxic dioxins, the TCDD is given a TEF of 1, and the other dioxins, furans and some similarly acting PCBs are scaled accordingly. The sum of all single toxic equivalent factors is chosen as concentration value for the sediment.

Table 4.6 Estimation of likelihood of dioxin and furan releases to water from certain sources from (Quass *et al.*, 2000)

Source	Potential release to land (min. – max.) g I-TEQ (1994)	Likely trends in release from 1994	Additional notes
Pesticide Production	High (no data)	↓	
Chemical Production	High (no data)	↓	Estimated release from PVC processes in Germany 0,15-51 g I-TEQ
Accidental Fires	High (no data)	?	
Disposal of MSW to Landfill	High (no data)	?	
Pesticide Use	High (no data)	↓	
Paper & Pulp Production	Medium (8 – 27)	↓	
Incineration	Medium (0,3 – 16)	↓	Estimated release for industrial waste incineration only
Waste oil disposal	Medium (1,8 – 7,9)	?	
Textile treatment	Medium (no data)	?	
Non-ferrous metal production	Medium (no data)	?	
Iron & steel industry	Medium (no data)	?	
Sinter plant	Medium (no data)	?	
Waste water treatment	Low (no data)	↓	

DDT+DDD+DDE

DDT (dichloro-diphenyl-trichloroethane) was one of the first widely used organochlorine pesticides and was praised for its toxicity to a wide range of insects, its low mammalian toxicity and its persistence in the environment.

DDT+DDD+DDE have been identified in Chapter 4.3 as dominant contaminant in the following areas of concern:

- High and Upper Rhine – Reservoirs
- Upper and Middle Rhine - Harbours

In most countries, use and production was banned in the seventies. DDT undergoes degradation in the environment to DDD and DDE with a half-life in the order of years. Therefore environmental samples usually contain

predominantly DDD and DDE. Elevated concentrations (sum DDT+DDD+DDE) that are only found in the High and Upper Rhine point to a former industrial source in the **High Rhine**. There is no reason why diffuse emission by surface run-off should be higher in the High Rhine than at areas, where DDT application may have been much more extensive, e.g. in the agricultural areas in the **Middle Rhine**.

Sum γ -HCH and Drines (Aldrine, Dieldrine, Endrine)

No increased concentrations for γ -HCH and the Drines (Aldrine, Dieldrine, Endrine), which are no longer parameters in the CTT any more, have been reported and, hence, no areas of concern were identified.

4.5 Special case area 1: Heavy metals in the Ruhr area

In the 60ies and 70ies the Ruhr was loaded with a great variety of contaminants. For the year 1980 a heavy metal load of 283 tons was transported into the River Rhine (Imhoff et. al 1980). In the year 1996 the input had decreased to 132 tons per year (Figure 4.13)

In 16 years, between 1980 and 1996, industrial discharges vanished as one of the former contaminating sources. The relative percentage of diffuse sources and those from geochemical origin increased from 45% in 1980 to 69% in 1996.

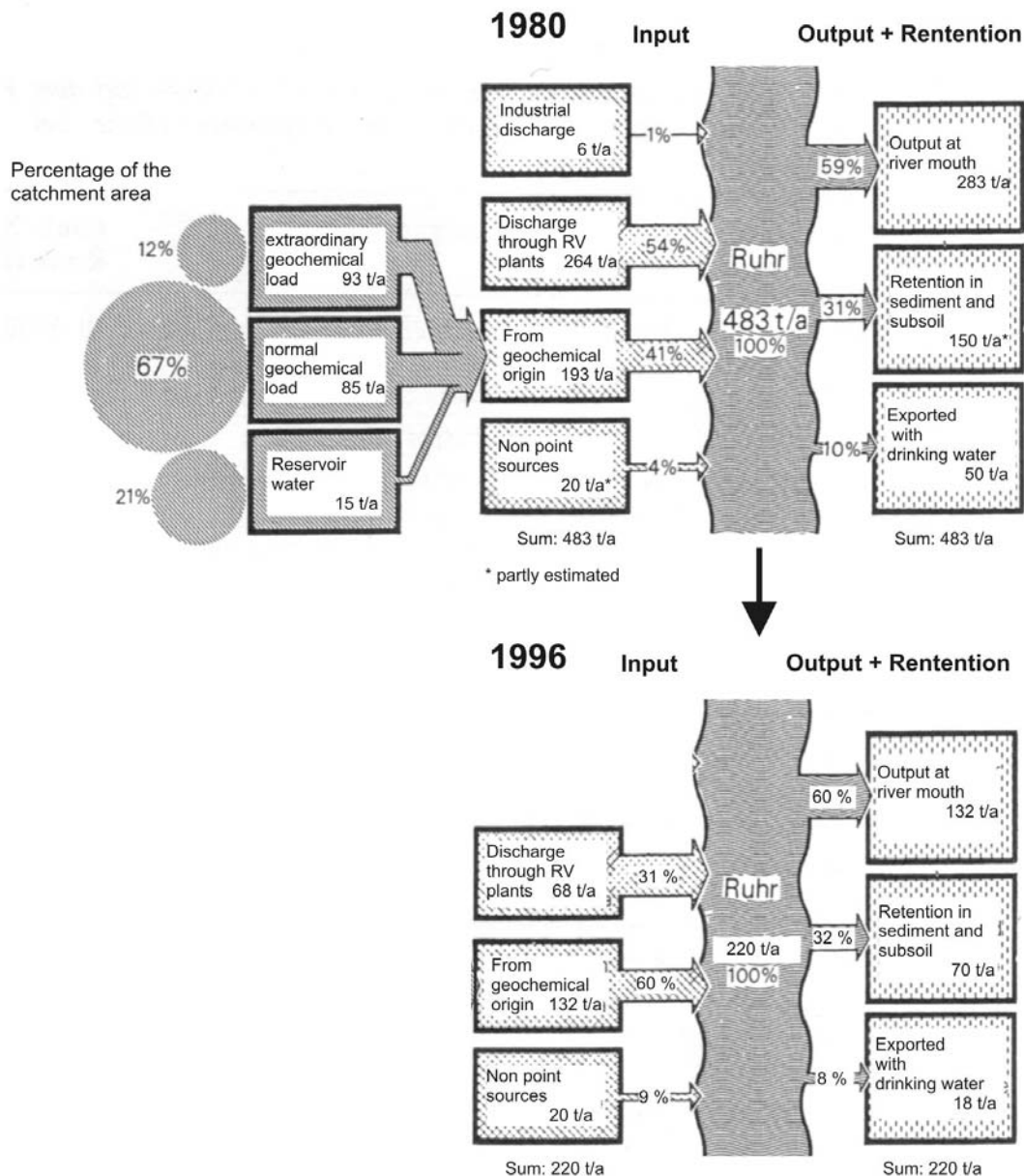


Figure 4. 13 Balance of heavy metal load in the Ruhr River catchment area in 1980 (Top) (Imhoff et al. 1980) and in 1996 (Bottom) (Imhoff et al. 1996)

This development is representative for most tributaries from the Rhine catchment area as the relative percentage of natural and diffuse sources on the whole heavy metal load grew with successful reduction of point sources. The relative output to the river mouth, to the sediment and with drinking water stayed the same.

At the beginning of the 20th century not all wastewater effluents in the Ruhr catchment were adequately purified in wastewater treatment plants. At that time treatment was restricted to mechanical processes only. To keep the Ruhr clean enough for drinking water production, it soon became evident that impounding lakes could serve as 'natural wastewater treatment plants'. Due to reduced flow velocity and prolonged residence time in the reservoirs most particulate substances were deposited and removed from the water body. Currently there are 5 impounded lakes that were built between 1929 and 1950 (Figure 4.14)

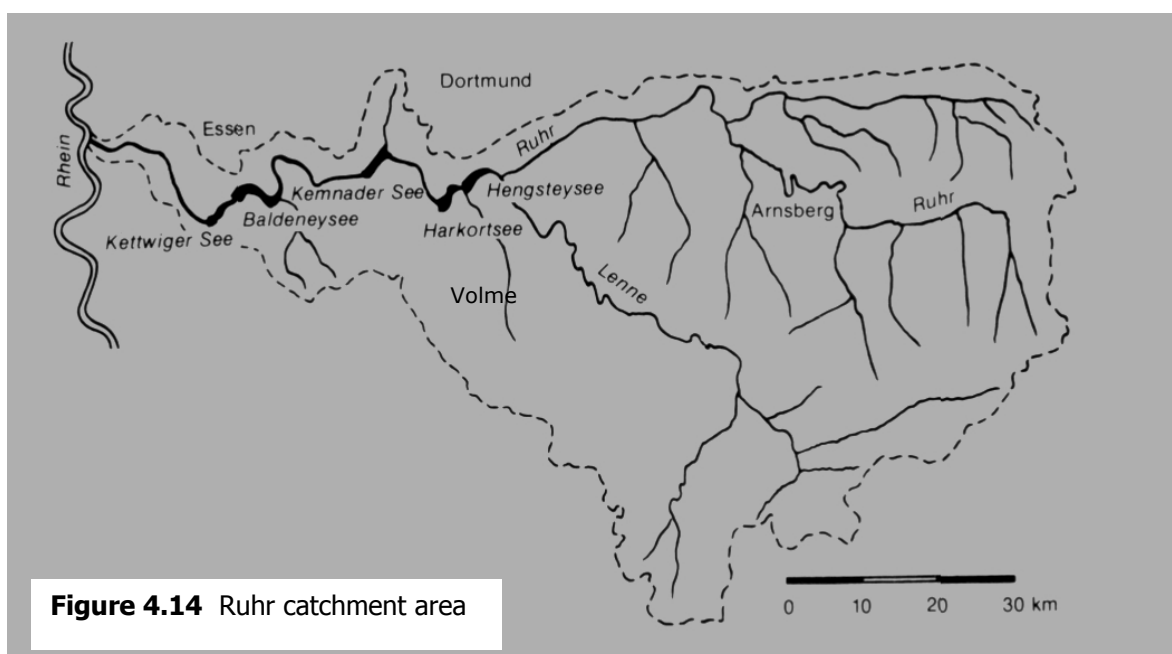


Figure 4.14 Ruhr catchment area

The largest of these lakes, the Baldeneysee, annually retains 540 kg cadmium and 6000 kg chromium. At discharges larger than 1000 m³/s, remobilization of the lake sediments can take place (Imhoff 1990). A discharge of 800 m³/s corresponds with a high water with a return period of 4 years (HQ₄).

An investigation from Klopp and Kornatzki for the Baldeneysee (Klopp & Kornatzki, 1981) shows that at discharges larger than 200 m³/s, three times the mean water discharge, bed sediment is eroded and delivered to the lake as suspended matter, of which only 50 % remained in the lake. With further increasing discharge the quality of the suspended material changes: the percentage of coarse material increases and accordingly the heavy metal load of the suspended material decreases.

In 1999 Rosenbaum-Mertens investigated sediment of the impounded lake "Harkortsee" (Rosenbaum-Mertens, 2003). An analyses of heavy metal contents is reported in Figure 4.15. The highest contamination of heavy metals was found in a sediment layer, which was deposited between the years 1965 and 1967. Anthropogenic origin was assumed because of its still elevated mobility of

heavy metals bound on manganese oxides and organic matter. The pollution input has been attributed to emissions from foundries, battery factories, wastewater treatment plants and steel works upstream. Many of those were located in the catchment area of the tributary "Volme".

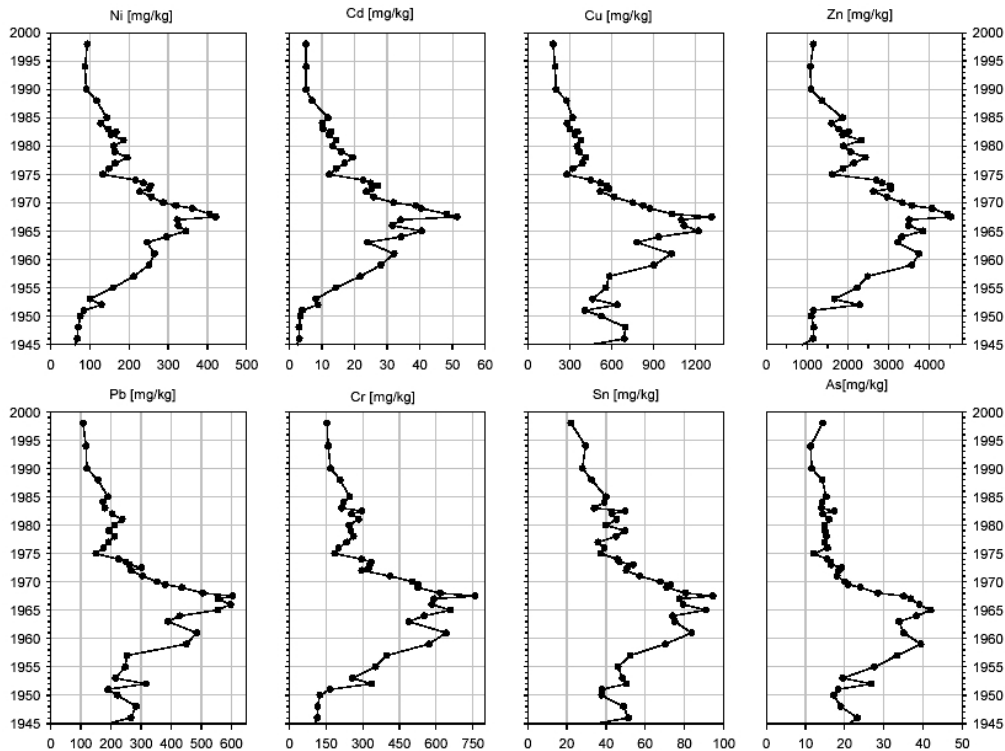


Figure 4.15 Heavy metal concentrations in sediments of the Harkortsee. Sediment depth is dated from 1945 to 1998 (Rosenbaum-Mertens, 2003).

Only a small part of the heavy metal load produced in the factories wastewater was removed in the wastewater treatment plant "Vorhalle", which had a direct pipeline to the Harkortsee. As an example Figure 4.16 shows the annual input/output balance of the Harkortsee for the metal Zn for the years 1965 and 1980.

The Zn input to the Harkortsee was reduced to almost half between 1965 and 1980. This was due to 27% less absolute load that was transported by the Ruhr to the lake, and to 53 % less load by the tributary Volme. The strongest reduction was observed in the effluents of the wastewater plant "Vorhalle" (from 230 to 51 t/a). The relative percentage of sediment input and outflow of Zn from the Harkortsee stayed almost the same - both were considerably reduced. However, two thirds of the Zn that comes in to the lake flows through again.

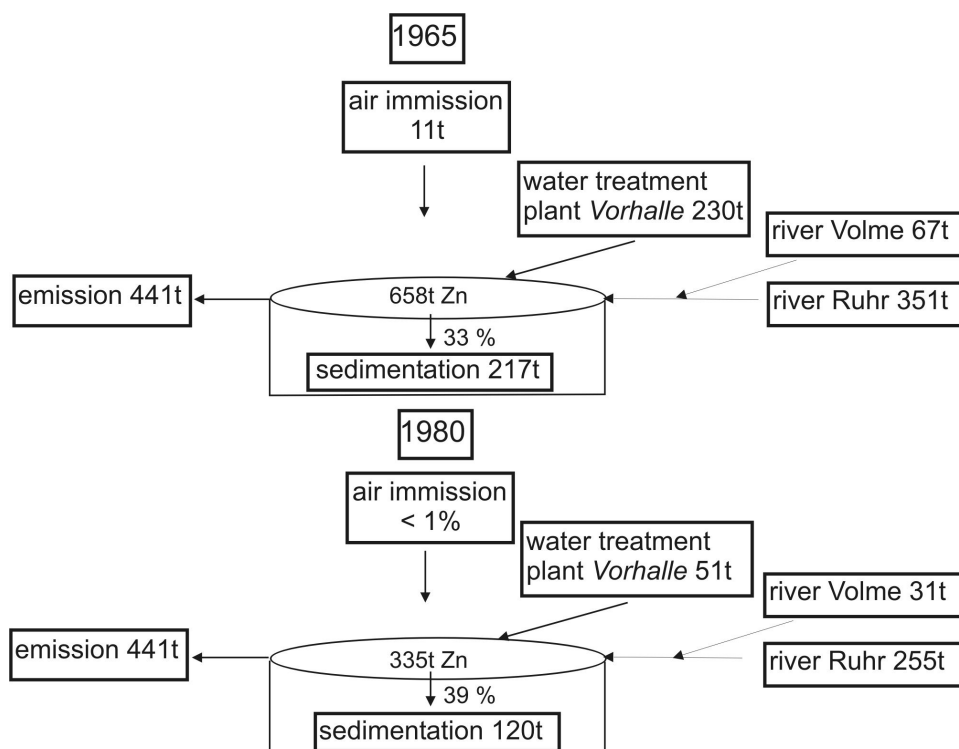


Figure 4.16 Zinc input/output balance of the Harkortsee 1965 and 1980.

Accumulation over the years nevertheless led to a very high contamination in lake sediments with regard to heavy metals and PAHs (e.g.: Cd 28,2 mg/kg, Zn: 3124 mg/kg, Cu 829 mg/kg and PAHs 54 mg/kg, ATV-DVWK, 2003). The accumulated sediment has to be dredged at times and is flushed out on land along the lake. Between 1999 and 2003 ca. 300000 m³ fine sediment were deposited on land (Staatliches Umweltamt).

Although this way, a large quantity of contaminated material is taken out of the system, contamination is still high and the risk of remobilization through flood events considerable. The *Ruhrverband*, one of the large water economy leagues in Nordrhein-Westfalen, reported increased concentrations of lead, cadmium and zinc at higher discharges (e.g. increase in lead in the water phase in 2001 from 1-2µg/l to 13 µg/l at a discharge of 309 m³/s in Hatting).

This is demonstrated in fig. 4.17, which depicts progress lines and frequency distribution of discharge, cadmium and lead at the monitoring station Essen for the hydrological year 2001. A comparison of discharge with contaminants' concentration shows a significant increase of lead and cadmium when flood events take place – like in January, February and March (discharge between 280-290 m³).

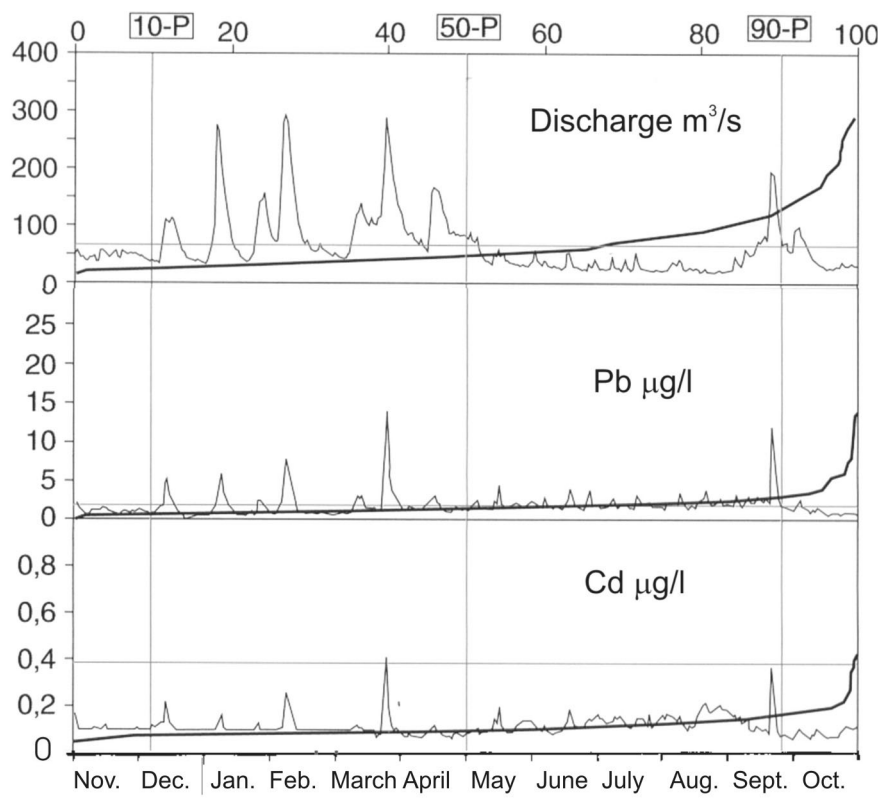


Figure 4.17 Progress lines (bottom x-achsis) and frequency distribution (upper x-achsis) of discharge, Cd and Pb concentration for 2001 (Ruhrverband 2002: Annual report 2001)

4.6 Special case area 2: HCB in the River Rhine¹

4.6.1 Introduction

The upper part of River Rhine (from Lake Constance which is Rhine-km 0 up to Rhine-km 300) (see Figure 4.18) has been heavily contaminated in the seventies and early eighties with hexachlorobenzene (HCB), mainly by discharges of a chemical site in Rheinfelden (see green mark in Figure 4.18) at Rhine-km 148.3 (about 20 km before Basel).

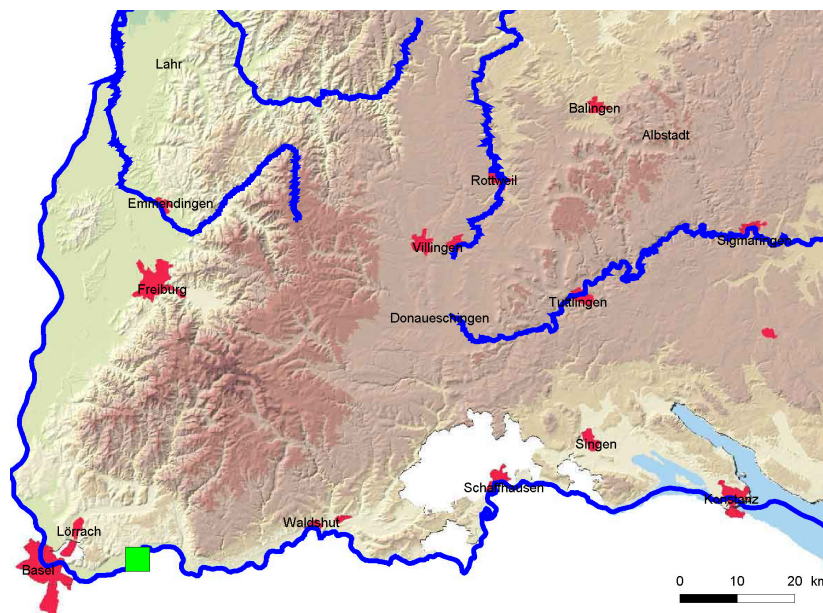


Figure 4.18 The upper part of River Rhine, beginning at Lake Constance

This contribution explains the history of this highly adverse pollution and its consequences. HCB still represents a severe problem as the sediments are still contaminated with this non-biodegradable and extremely bioaccumulative micropollutant. In addition, still, HCB is present in suspended solids and other sources, other than the one described here which is no more existing. Other sources are assumed but could not be identified yet.

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4.6.2 Identification of the HCB source in the seventies

In 1975, a first study of fish from River Rhine for chlorinated aromatic hydrocarbons by competent authorities indicated high HCB contamination. Values up to 150 mg HCB/ kg fat had been detected. The *Industrielle Werke Basel*, the enterprise that is responsible for the energy- and water supply of the city of Basel, confirmed these findings when they analysed filtrated Rhine water, taken at Rhine km 163.9 close to Basel. HCB values up to 100 ng/l have been determined (Figure 4.19). The wastewater discharges of a company in Rheinfelden at Rhine-km 148.3 had been identified as the source of this HCB pollution. Since the sixties this company operated a plant for the production of pentachlorophenol (PCP) and its sodium salt (PCP-Na). At that time this company used so-called "Tetraoil" and trichlorobenzene as raw materials which were highly contaminated with polychlorinated dibenzo-p-dioxin and furans (PCDD/F) as well; values for 2,3,7,8-tetrachloro dibenzo-p-dioxin (the so-called Seveso-dioxin) up to 95 µg/kg have been determined. Finally, the production of PCP-Na has been stopped in 1985 and of PCP in 1986. The PCP/PCP-Na was the major source of HCB also. According to the first wastewater inventory in the year 1981, the emission was in the order of 10 kg HCB/day, which is considered to be very high. The wastewater had to be treated and the emissions could be drastically reduced.

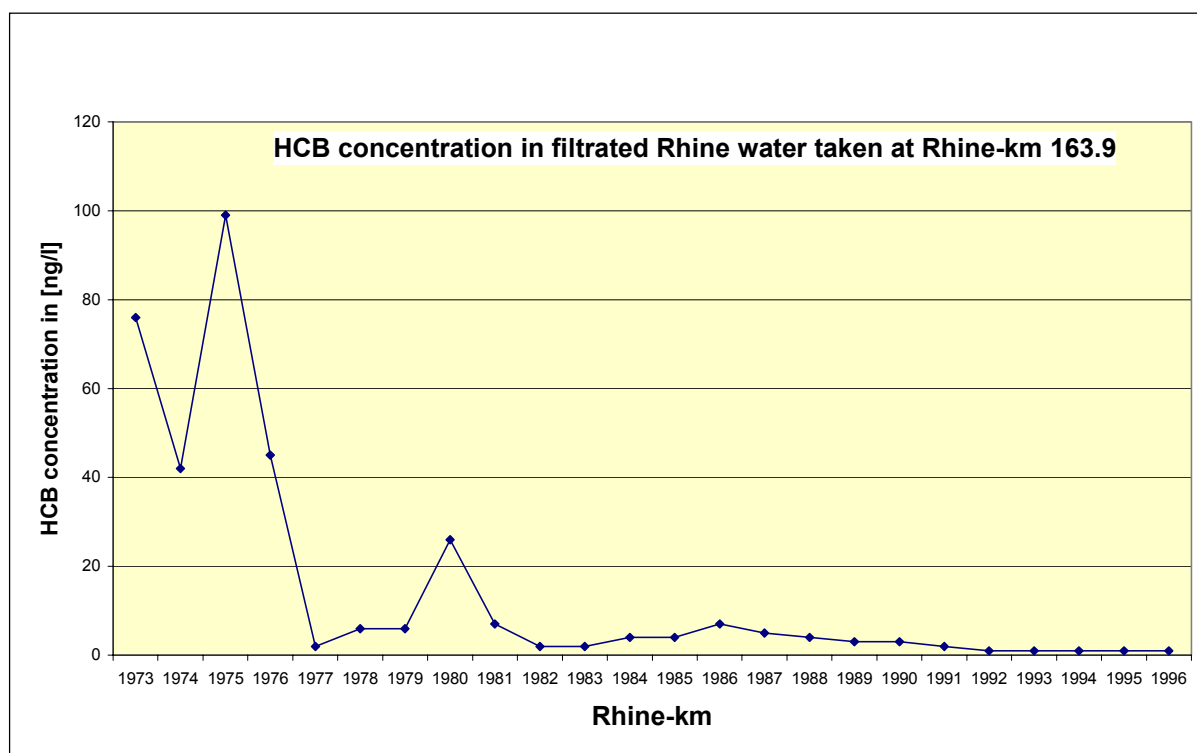


Figure 4.19 HCB in filtrated Rhine water taken at Rhine-km 163.9 which is very close to Basel; from 1992 onwards the values are below the detection limit (1 ng/l)

As a consequence of the shutdown of the PCP/PCP-Na production it has been expected that the HCB would completely disappear. However this was not the case. From figure 4.19 it can be seen that the

HCB values in Rhine water could be drastically reduced but not to practically zero. The same development can be demonstrated with the fish analysis. Figure 4.20 shows the HCB contamination of eels between Rhine km 57 and 307 in the years 1979 - 2000.

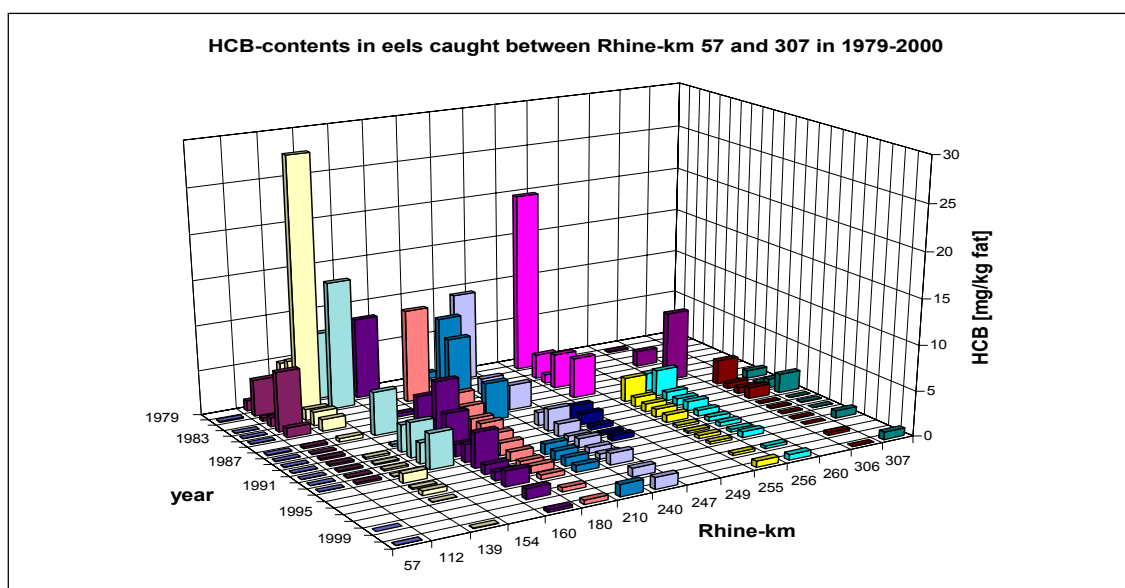


Figure 4.20 HCB contamination of eels in River Rhine caught between Rhine-km 53 and 307 in the years 1979-2000

The plants for the production of chlorosilanes were suspected when looking for sources of the remaining HCB discharges. A company that has been producing these compounds since 1957 significantly increased the production of chlorosilanes which are tetrachlorosilane (SiCl_4) and trichlorosilane (HSiCl_3) as compensation for the closed PCP/PCP-Na production. A big new plant went in operation in 1987.

4.6.3 Manufacturing of chlorosilanes and the formation of HCB

As the synthesis of chlorosilanes is exclusively inorganic chemistry, at first, the formation of HCB and other chlorinated aromatic hydrocarbons as unintentionally formed by-products could not be understood. The flow chart of the production is illustrated in Figure 4.21.

The reaction is carried out at temperatures around 1000°C . The raw material is not pure silicon but contains some weight-% of aluminium, iron, titanium and also traces of inorganic carbon. The second main raw material is hydrochloric acid gas which results from the synthesis of other compounds and is reused for chlorosilanes synthesis. It is contaminated with various compounds such as chloromethane, tetrachloromethane, vinyl chloride, methanol and others, which may serve as precursors for HCB. In addition the temperature may allow radical reactions also and the mentioned metals may function as catalysts. At any rate, during hydrochlorination of silicon, HCB is unintentionally formed to a relevant extend. Therefore the production of chlorosilanes falls under the Stockholm Convention on Persistent

Organic Pollutants (POPs) (Stockholm Convention on Persistent Organic Pollutants (POPs), May 22, 2001).

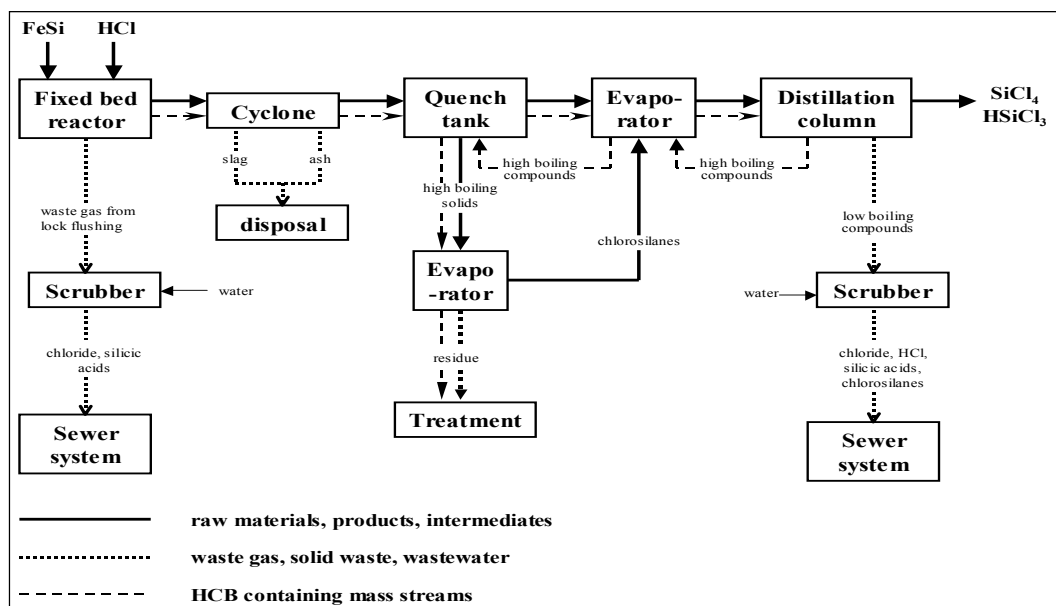


Figure 4.21 Flow chart for the production of chlorosilanes; the mass streams containing HCB are indicated

Until 1986, the residues from chlorosilanes production have been hydrolysed with plenty of water and have been discharged to the River Rhine without any treatment. The residue consists of high boiling solids such as metal chlorides, silicon containing by-products and chlorinated aromatic hydrocarbons, mainly HCB but also pentachlorobenzene, octachloronaphthalene, decachlorobiphenyl and octachlorostyrene. Since 1987, the residues are treated to create a solid residue, which can be disposed off or reused. The scheme for the treatment is illustrated in Figure 4.22.

However the new company continued to discharge untreated rinsing and cleaning water, which caused exceedance of the emission limit value for HCB load which has been prosecuted in 1994 (Landtag von Baden-Württemberg, 1996) .

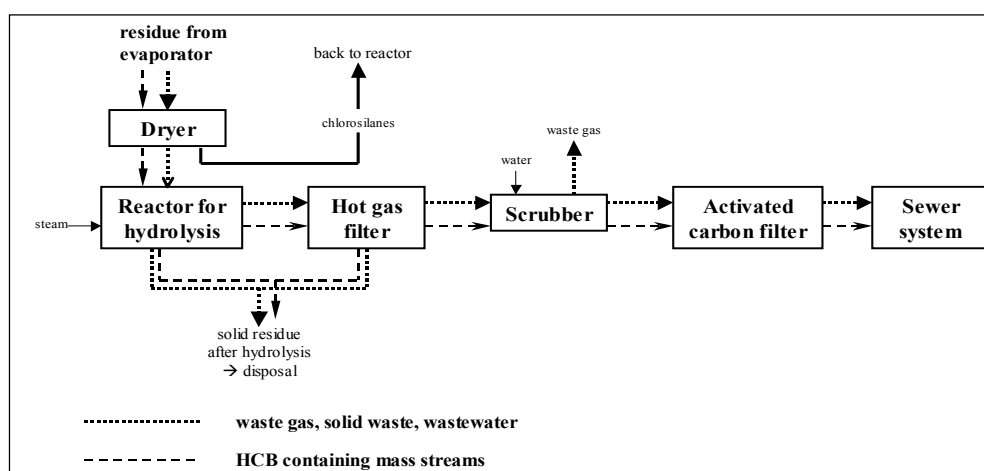


Figure 4.22 Treatment of the residue from the synthesis of chlorosilanes

4.6.4 Development of HCB emissions and of the immission situation

After the reduction of HCB from PCP/PCP-Na production the remaining HCB load originated from chlorosilane production. However, the company had to invest a lot of efforts to reduce the severe environmental impact. The most important issue was the prevention of the direct discharge of the above-mentioned residues. Since 1993 no residues are discharged to the River Rhine any more. This development can be seen from Figure 4.23. The discharged load could be decreased steadily. It was important to treat the HCB containing waste gas from residue treatment as well as rinsing and cleaning waters. In addition the hydrochloric acid gas has been purified by low temperature condensation.

The responsible company had to analyze the discharged wastewater for HCB every day from flow proportional taken 24-h-composite samples.

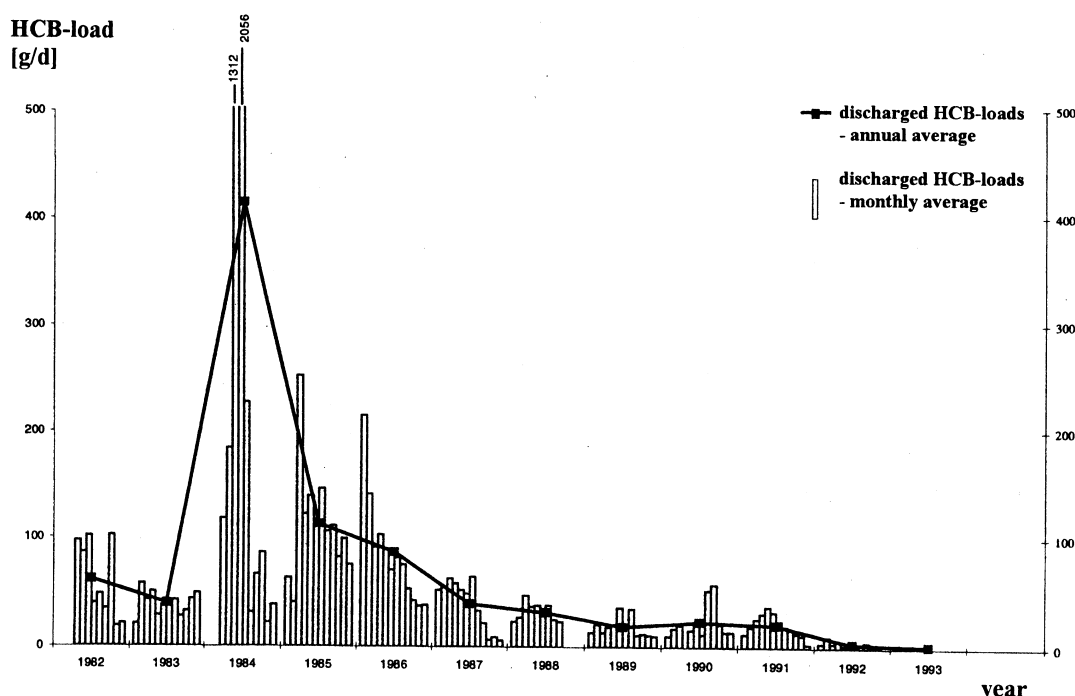


Figure 4.23: Discharged HCB-loads to River Rhine by a company in Rheinfelden from 1982 – 1993; from discharged water a flow proportional taken 24-h-composite sample has been daily analysed

Figure 4.24 confirms this development showing the frequency distribution of the discharged HCB-loads (daily samples). From 1994 onwards the discharged HCB-load is practically zero (<0.1 g/d). The significant reduction of discharged HCB-loads is reflected in the HCB concentration of the River Rhine water (Figure 4.19) and in fish also (Figure 4.20). The same is valid for the contamination of the sediments. Figure 4.25 illustrates the results of the sediment samples, which have been taken from 1982 – 1998 between Rhine-km 3 and 359. This profile also shows that the contamination sharply increased after the discharge point at Rhine-km 148.3 but drastically decreased after the implementation of the described measures. However the profile also indicates that there another HCB source could be present between Rhine-km 180 and 300, which could not be detected yet.

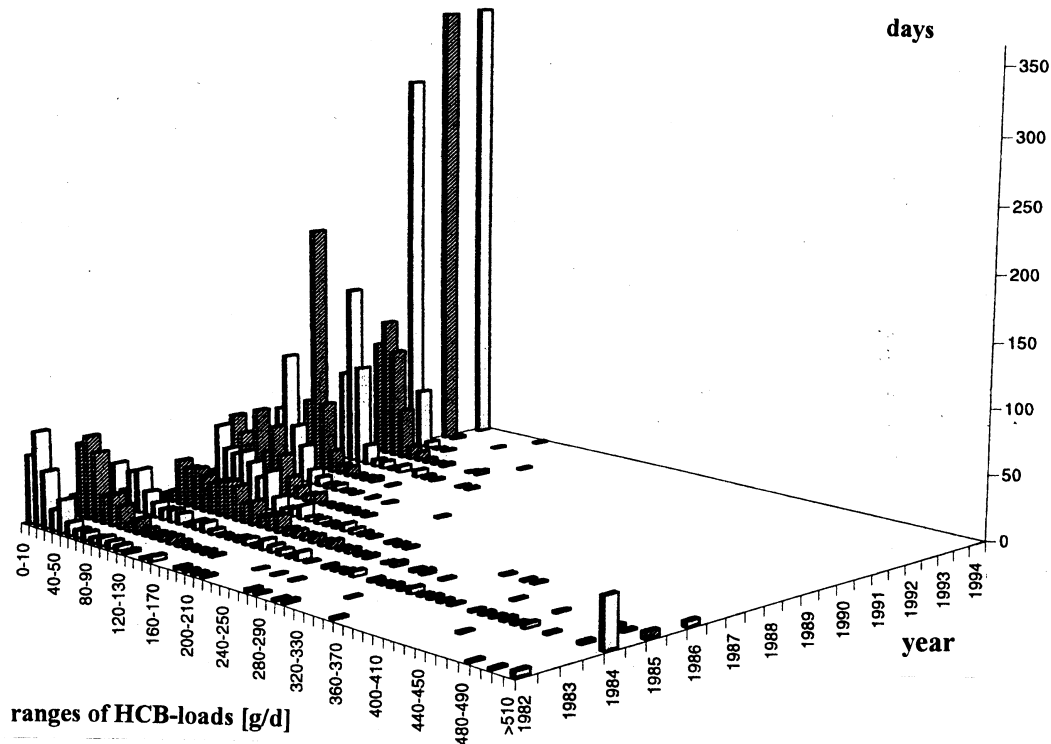


Figure 4.24: Frequency distribution of discharged HCB-loads from daily 24-h-composite samples, which have been taken and analyzed by a company in Rheinfelden

The significant reduction of discharged HCB-loads is reflected in the HCB concentration of the River Rhine water (Figure 4.19) and in fish also (Figure 4.20). The same is valid for the contamination of the sediments. Figure 4.25 illustrates the results of the sediment samples, which have been taken from 1982 – 1998 between Rhine-km 3 and 359. This profile also shows that the contamination sharply increased after the discharge point at Rhine-km 148.3 but drastically decreased after the implementation of the described measures. However the profile also indicates that there another HCB source could be present between Rhine-km 180 and 300, which could not be detected yet.

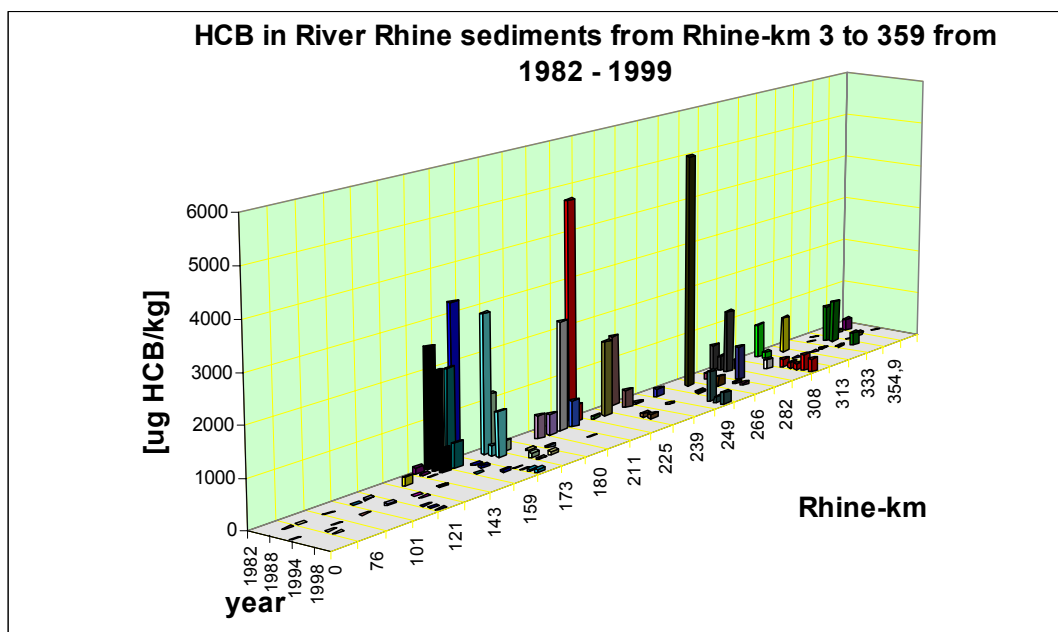


Figure 4.25 Results of sediment samples in the River Rhine taken between Rhine-km 3 and 359 in the period 1982-1998.

The sediment can be considered as the memory of contamination of a river. However it is subject to permanent change because of steady sediment mobilisation and relocation. In contrast, at average or low flow of the river, the suspended matter reflects the actual contamination situation. Regularly taken samples of suspended matter at Rhine-km 173 which is shortly after the Rhine knee at Basel (see Figure 4.25) confirm that the former HCB discharge at Rheinfelden is no longer existing. At Rhine-km 173, the HCB load of suspended matter is less than 5 µg/kg. After this point, the HCB concentration is steadily increasing. Even in 2003, HCB values in suspended matter up to 400 µg/kg have been determined. However the concentrations found at five different points vary a lot and do not show a consistent profile. Because of this findings one or more HCB sources are assumed to be still existing. Thus, in 2004 the search for their possible location has been intensified again.

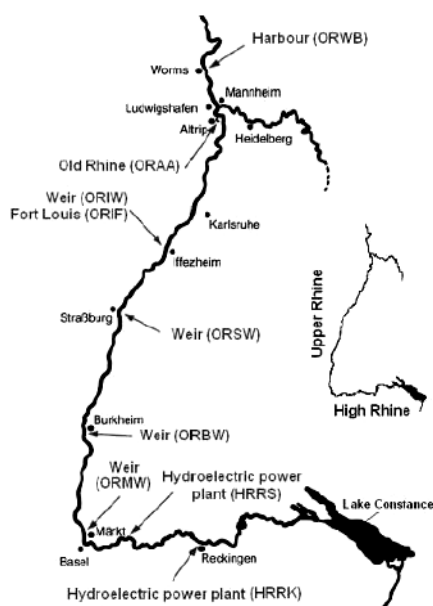
4.6 Ecotoxicological assessments along the River Rhine

Extensive ecotoxicological surveys along the River Rhine have been carried out by the Federal Institute of Hydrology (BfG, Koblenz), the University of Heidelberg, the institute for environmental protection in Baden-Württemberg (*Landesamt für Umweltschutz*, LfU), by the ecotoxicological working group of the Technical University Hamburg Harburg (TU HH, Hamburg) and by the International Graduate School in Zittau.

An extensive ecotoxicological survey covering **the whole Rhine area** with 37 locations, as well as 11 other German rivers (including Ruhr, Mosel, and Saar) was carried out by the International Graduate School in Zittau on behalf of the Environment Agency (Duft *et al.*, 2002). For an ecotoxicological assessment only 2 biotests were applied which led to different conclusions: The nematode test showed that sediments from the Main, Rhine, Ruhr and Weser were the most toxic among the 12, while the chironomide test assigned sediments from the Elbe, Ems, Mosel and Ruhr as the most effective ones. Both tests identified the **Ruhr** sediment as a highly toxic.

The LfU investigated in the years 1998 and 1999 58 sites **along the High and Upper Rhine** in Baden-Württemberg and the Neckar River, comprising surface and partly also core samples. Porewater and elutriates were investigated with 3 test systems (test with algae, daphnia and bioluminescence test with *Vibrio fischeri*), chironomides were used for whole sediment tests. In addition to these organism tests, assays to assess genotoxicity and estrogenicity were applied. A classification into 4 categories was mainly carried out on the basis of elutriate and porewater tests. Both in the Rhine and in the Neckar, most sediments were classified as “moderately toxic” (category 3 out of 4). And 33 % of the sediment samples from the Rhine gave a “critical toxic effect” (category 4), while only 21% of the Neckar locations were assigned to this class. Only one sample showed

genotoxicity in the Rhine survey (site “Vogelgrün”, km 223,7) and also two samples in the Neckar survey (Zipperle & Deventer, 2003).



Samples from **9 locations at the High and Upper Rhine** were investigated by the University of Heidelberg, the Federal Institute of Hydrology (BfG) and the Technical University Hamburg Harburg in 2001, on behalf of the BfG (Fig. 4.26).

Figure 4.26 Sampling stations of the BfG survey along the High and Upper Rhine river in 2001

The University of Heidelberg and the Federal Institute of Hydrology detected significant genotoxicity in sediment extracts of the Rhine River in contrary to the River Neckar, where less samples had previously shown genotoxic effects (Kosmehl *et al.*, 2004).

A bacterial sediment contact assay was used to test the sediment-related toxicity in surface and core samples at the Technical University Hamburg Harburg (Heise & Ahlf, unpublished). Only the highest applied sediment concentration is shown in fig. 4.27. Toxicity showed an increasing trend in surface (0-5 cm) and core samples (1-150 cm) towards Iffezheim (ORIF1) which continued to be high at the weir (ORIW) and downstream in the Old Rhine at Altrip (ORAA). The dilution series (data not shown) indicates that the quality of the effective contamination changes towards Iffezheim.

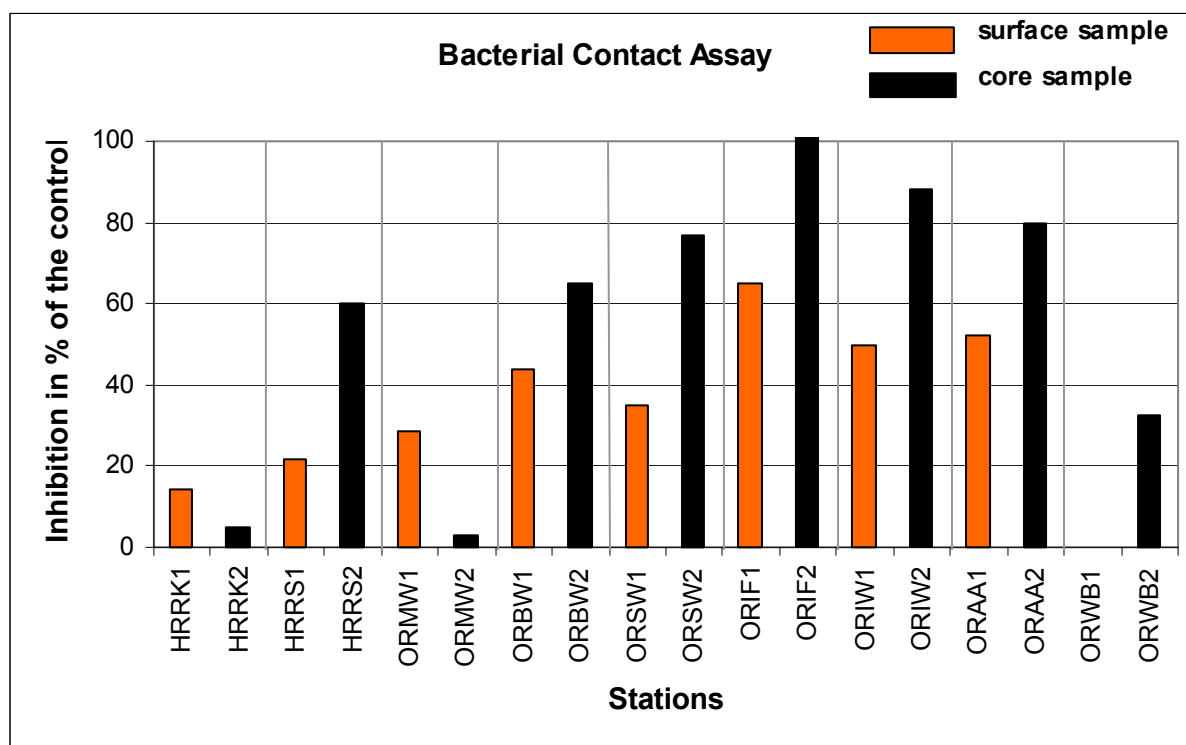


Figure 4.27 Toxicity in bacterial contact assay with *Bacillus cereus* measured in surface and core sediments along the High and Upper Rhine in 2001

Figure 4.28 shows the results of a survey of surface sediments along **the Middle and Lower Rhine** from 1996 that covered 14 locations (Ahlf & Gratzer, 1999). In the survey 5 bioassays addressing different exposure pathways (sediment contact test with the bacterium *Bacillus cereus* and nematodes; elutriate tests with algae and bioluminescence inhibition tests with *Vibrio fischeri* on elutriates and on methanol extracts) were carried out and the results were classified into 5 classes with increasing hazard from 1 to 5 according to a fuzzy-based classification system. This classification takes the results of all applied biotests into account and derives the final toxicity assessment from this response pattern (Heise *et al.*, 2000).



Figure 4.28 Toxicity classes for sediments of the Middle and Lower Rhine, sampled in 1996, based on 5 bioassays and an integrated assessment of the response pattern

Figure 4.28 and table 4.7 indicate that the highest toxicity class was assigned to the harbour Oberwinter, Hitdorf Harbour, the Duisburg harbours Rheinpreussen and Eisenbahnhafen, and the next two locations downstream: the flooded quarry Rheinberg and the harbour Wesel. This corresponds to a large extent well with the identified areas of concern with the exception of the harbour Oberwinter, for which solely an exceedance of HCB has been noted.

The harbour Hitdorf has been described as an area of concern. The northern Duisburg harbour basins Rheinpreussen and Eisenbahnhafen are located downstream of the Ruhr and of the Duisburg industrial area. As the sites upstream are classified as 3 and 4 on both sides of the Rhine, the toxic effects seem to originate at the Duisburg (or Ruhr) area which also influences the next stations downstream.

Rhine km	location	Rhine side	Toxicity classes
639,1	Oberwinter	left	5
695,6	Köln-Niehl	left	4
706,9	Hitdorf Harbour	right	5
735,8	Neuss Gnadenthal	left	4
764,1	Krefeld	left	3
773,6	Duisburg-Rheinhausen	left	4
776,6	Duisburg-Aussenhafen	right	4
781,1	Duis.-Rheinpreußen	left	5
781,1	Duis.-Eisenbahnhafen	right	5
807,2	flooded quarry Rheinberg	left	5
814,6	Wesel	right	5
830	flooded quarry Lohrwardt	right	4
853,8	Hüthumermeer	right	4
863,8	Altrhein Keeken-Bimmen	left	4

Table 4.7 Toxicity classes at different sampling locations in the Middle and Lower Rhine in 1996

4.7 Summary

Areas of concern in Germany have been identified so far with regard to a potential resuspension of historic contamination to a concentration that exceeds the CTT values. This is being done so far without consideration of the final risk for the port of Rotterdam, as the transport estimations will be included in the next chapter.

12 areas of concern have been identified:

- 1) **Sediments in the High and Upper Rhine area:** The accumulated sediments of the reservoirs of the Upper Rhine are contaminated with increased concentrations of mercury (e.g. Marckolsheim, Strassbourg), PCB (Kehl), DDT (Gamsheim) and HCB.
- 2) **Harbours in the Upper and Middle Rhine:** Harbours like Loreley and Worms Bauhafen accumulate a lot of sediment and partly reflect (with the exception of PCB) the contamination pattern of the reservoirs: they show elevated levels of mercury, and DDT+DDD+DDE
- 3) **Mosel:** Unfortunately, only few sediment data of the Mosel are available. However, on the basis of monitoring data from the station "Koblenz/Mosel" this tributary could be identified as a significant contributor of especially PCB, nickel, copper, lead and zinc into the Rhine river. As no emitters of these heavy metals are currently known to be located at the Mosel, historic contaminated sites along this river are likely to be the source. Potential origin of heavy metals as well as PCB-contamination is suspected to be the mining sites along the tributary Saar.
- 4) **Neckar:** The Neckar shows a high contamination of especially cadmium in older sediments, PCBs and copper also partly in fresh sediments. The risk of these sediments depends on the remobilization risk of sediments during high waters.
- 5) **Main:** In the Eddersheim barrage, high concentrations of mercury and cadmium of up to 60 mg/kg were found.
- 6) **Wupper:** This river still shows a complex contamination pattern. Production sites for dyes, pharmaka and pesticides determined for a long time its colour by their emissions, a history which is still reflected in the sediments. Beside various heavy metals (chromium, copper, mercury, nickel, lead and zinc (and arsenic)), main organic pollutants were esters of (thio)phosphoric acid, triazolfungicides, aniline- and pyridine-derivates. No measures have been planned for hazard reduction in this area.
- 7) **Lower Rhine - Small harbours near Leverkusen (Hitdorf, 706.9 km, right side) and the Ruhr area:** One of main emitters of HCB and PCB, zinc, copper, mercury, cadmium, nickel and chromium was located near Hitdorf harbour which is also influenced by the Wupper effluents. As changes in the flood regime of the Rhine generally affect smaller harbours more strongly than large industry ports, potentially leading to a removal of new and an exposure of old sediments, the accumulated legacy at Hitdorf presents a potential area of concern. A legacy of the industrial

productions at this site is the high PCB contamination in the sediment which has been shown to be exposed during floods. In addition, an old disposal site leaks di- and trichlorobenzene through the groundwater into the Rhine. Other harbours like the Neuss-Hafenbecken may be influenced by emissions from the Ruhr area and / or the Erft effluents and show peaks in cadmium, lead and HCB.

- 8) **Duisburg and the Ruhr area:** The Ruhr area is the European area with the highest density of industries. Most of the steel-industry and mining industry was located here and about half of the German coking plants, emitting heavy metals and organic substances. Monitoring data near Duisburg showed especially at the Aussenhafen-station and in the Diergard Harbour still high concentrations of cadmium, chromium, zinc and lead, that did not decrease between 1988 and 1994 but settled on concentration levels, that significantly exceeded the CTT-values. An extremely high contamination of Diergard Harbour sediments with Dioxins will need special attention.
- 9) **Erft:** The Erft was highly influenced by an industrial plant for metallic soap (zinc and cadmium emitter) and by intensive exploitation of zinc and lead. Although industrial emissions have decreased, weathering of the damaged ground which is a consequence of the intensive mining activities, leads to a continuous emission of heavy metals due to mine waters.
- 10) **Ruhr:** The sediment quality of the Ruhr river is low due to high concentrations of cadmium, lead, copper, PCB, partly PAH. The Ruhr flows through the highest densely industrialized area in Europe and is therewith subject to emissions from industry as well as communal effluents. Especially the impounding reservoirs which are known to store a large amount of heavy metals, will have to be in the focus of the risk assessment procedure of chapter 5.
- 11) **Emscher:** The 3 rivers Ruhr, Emscher and Lippe are in close proximity to each other. Their environmental fate was determined about a hundred years ago, when Lippe and Emscher were "sacrificed" for the sake of the Ruhr which was supposed to deliver drinking water. The Emscher is still considered to be one of the highest contaminated rivers in the Federal Republic considering its concentration of contaminants and nutrients. Known historic contaminated sources, which continue to pollute the river are in the region of an old fertilizer plant and a former coking plant, from which apart from nutrients PAHs, heavy metals, cyanide and coking plant typical organic compounds (PCB) are emitted into the water. As the monitoring station Lobith is still in the trail of the Emscher (and Bimmen is not), continuously higher concentrations in Lobith than in Bimmen point to an influence of the Emscher effluent.
- 12) **Lippe:** In the vicinity of the river Lippe, the only producer of TBT in Germany and the largest one in the world is located. Due to insufficient wastewater treatment, large amounts of organotin compounds reached the Lippe via the small river Seseke and contaminated its sediments for years. The implementation of a new treatment unit in the production process, that is suitable to treat the specific wastewaters of this company, was planned for the near future. In addition, the sediments of the Lippe are usually slightly increased in HCB concentration. The company that produces chlorosilane released - usually small - concentrations of HCB into the Lippe.

Table 4.8 Areas of concern and their main contaminating compounds in sediments ( no measurements or only single data on organic substances)

	High and Upper Rhine	Upper and Middle Rhine	Lower Rhine		Tributaries							
	Barrages	Harbours e.g. Loreley	Duisburg, Ruhr area	Harbours Flooded quarries	Neckar	Main	Mosel	Emscher ²	Wupper	Ruhr	Erft	Lippe
Cd												
Cr												
Cu												
Hg												
Ni												
Pb												
Zn												
Aldrin												
DDT+DDD +DDE												
Dioxins + Furans												
HCB												
γ-HCH												
PAH												
PCB												
TBT												

² As no sediments are available for the Emscher, these data are based on suspended matter concentrations upstream of the last waste water treatment plant (Dinslaken) before the confluence into the Rhine

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5 Quantification of the Risk for the Port of Rotterdam

5.1 Introduction to the approach of risk quantification

The risks that are going to be quantified in this report do not primarily concern environmental or human health issues, i.e. regarding the potential for adverse environmental effects to organisms or drinking water quality at the port of Rotterdam, but rather the additional costs caused by the fact, that exceeding the CTT could make it necessary to dispose the sediments in a contained depot rather than relocate them at the North Sea.

The material from historical contaminated sites has to be resuspended and transported, before it will become an issue for the Port of Rotterdam in the above-mentioned respect. This can be a quite complex issue: Less contaminated sediment can cover the deeper deposits, but during stronger currents, deeper layers can be eroded as well. Sediment may be mobilized by erosion in still water zones, river banks and flood plains, and parts of the mobilized sediments can be contaminated with quite a large spectrum of concentrations of various contaminants (Chapter 1.2).

Even surface sediments are sometimes highly contaminated as has been shown in chapter 4:

- a) There is still a consisting contaminant source that keeps the immissions at high levels. This can be either a primary source, such as industrial emissions like they have been observed for TBT and only recently stopped in the Lippe area (chapter 4) or it can be a secondary source, called historic contamination such as the HCB contaminated material in the High and Upper Rhine, which is intermittently transported downstream, mixing with and thus contaminating previously clean sediments on its way.
- b) Exceptionally high current velocities remove freshly deposited, clean surface material during flood events. Unexpectedly, historic contaminations may suddenly be exposed. This may be the reason, why at the High Rhine barrage "Augst" HCB concentrations of 2500 µg/kg¹ were measured in surface sediment during a survey in July 1999 (Zipperle & Deventer, 2003), while previous sampling surveys had only shown low concentrations (M. Keller, BfG, personal communication). In May 1999 the High Rhine experienced a flood with a return period of about 100 years, which probably caused significant erosion along the Rhine (see below) and may have swept away the uncontaminated material on top of the contaminated material.

Despite the uncertainties with sources and processes, there is clear evidence from sediment profiles in Ketelmeer, that contaminated material is transported from historic sites downstream on a short time scale: After the flood event in May 1999, highest concentrations of HCB were measured in the top sediment layer at a sand pit near the mouth of the river IJssel.

¹ several sediment samples were taken with a van-Veen grab (up to 15 cm depth) and homogenized

Whether historical contaminated sediments can be eroded, and subsequent hazards arising from particle-associated contaminants for the downstream regions must be considered depends on processes such as mechanical consolidation and chemical diagenesis. The latter process generally leads to a reduction of the reactivity of solid matrices and of the bioavailability of contaminants (sections 1.4 and 1.5.1). As yet, however, the data base for calculations on the erodibility of sediments is still limited (although significant advancement has been made by the group of Westrich in this field; see section 1.2) and even less information is available for the estimation of overall “ageing” effects, i.e., the reduction of mobility and toxicity of particle-bound contaminants.

As these data are missing, a reasonable way to come to conclusions on the risk for the port of Rotterdam, is the following:

- Assessment of those areas of concern that would have a sufficiently high contaminant level to presumably raise the concentration in the port above CTT level, despite dilution processes that might occur during transport downstream.
- Gathering evidences for actually or potentially occurring resuspension events. Erosion criteria thresholds will be included in the assessment wherever they can be quantified. Increases in loads and concentration of suspended particulate contaminants is another indication of resuspension events.
- From the relationship between concentration in suspended particulate matter (SPM) and water discharge, information can be drawn on the influence of diffuse sources. If the eroded suspended matter is generally contaminated, the concentration does not change with discharge (Figure 5.2, PCB). This indicates diffuses sources.
- If, however only uncontaminated material (surface run-off and bed erosion) is eroded, the contaminant concentration in suspension decreases, due to mixing with the uncontaminated material (Figure 5.1, HCB).
- In the case of erosion at contaminated sites (point source), the contaminant particle concentration is constant or increases with discharge.

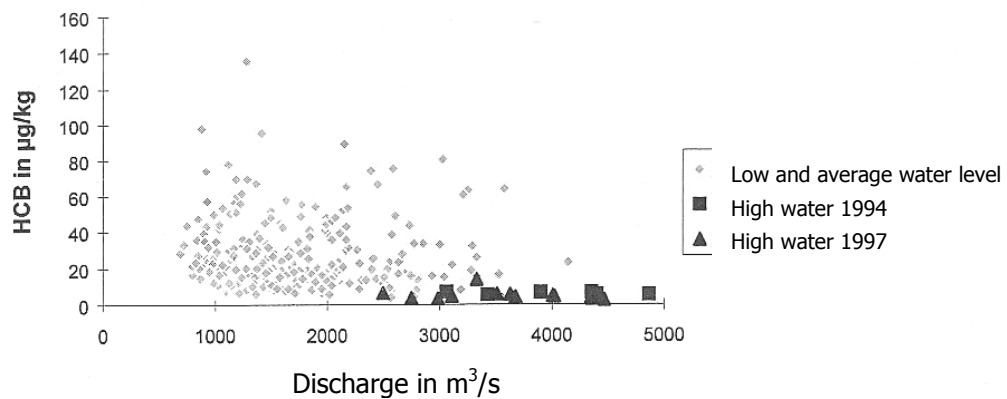


Figure 5.1 HCB concentration of suspended matter at Koblenz / Rhine between 1991 and 1997 (BfG, 1997)

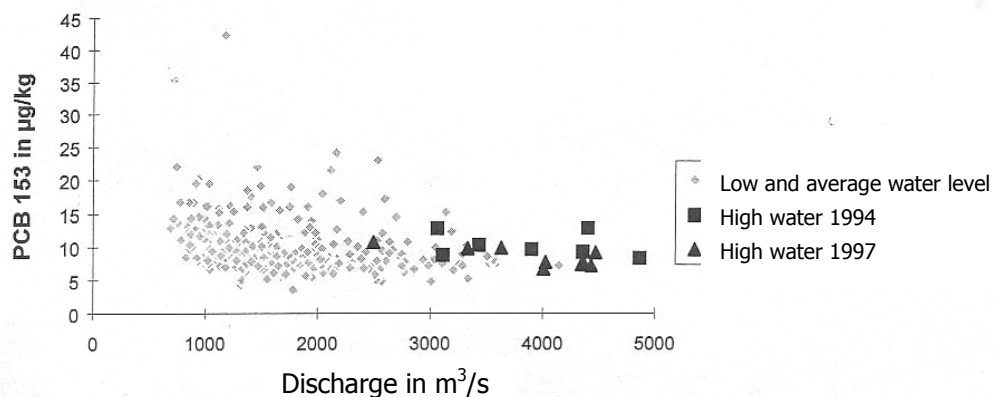


Figure 5.2 PCB concentration of suspended matter at Koblenz / Rhine between 1991 and 1997 (BfG, 1997)

However, the connection between flood events and concentration of contaminants on suspended matter is not simple as the resuspension of large amounts of relatively uncontaminated material obstruct the detection of eroded, heavily contaminated sites. Whether deeper sediments are eroded depends on the shear stresses that are applied by the water current, on the consolidation of the material, but also on the availability of sediment. Under high discharge conditions in winter, erosion of previously (fresh) deposited sediment can occur and the amount of temporarily stored sediment will decrease (Asselman, 1999). In a series of flood events, one following quickly after the other, this can lead first to an exposure of older layers followed by erosion processes. Accordingly, a case by case consultation of flood event data may sometimes be helpful, as is shown in Figure 5.3, where the copper load of suspended matter was increased at the last flood event of a sequence of high waters in 1995. Hence, interpretation of SPM and its contaminant concentration needs consideration of the hydrological regime, flood events and preferably erosion thresholds.

The risk for the Port of Rotterdam is highest, if the concentration in the suspended matter increases due to resuspension of heavily contaminated material, **and** the load of this contaminated SPM is high.

Not only the quality but also the quantity of material is important to assess whether a risk exists: Low amounts of highly contaminated material will be diluted due to mixing processes in the port itself, whereby concentrations from several sites that are below the CTT thresholds may accumulate and add up above the CTT threshold value.

The determination and interpretation of loads transported with suspended matter has to be done carefully as a number of uncertainties in sampling and analytical methods decrease the accuracy.

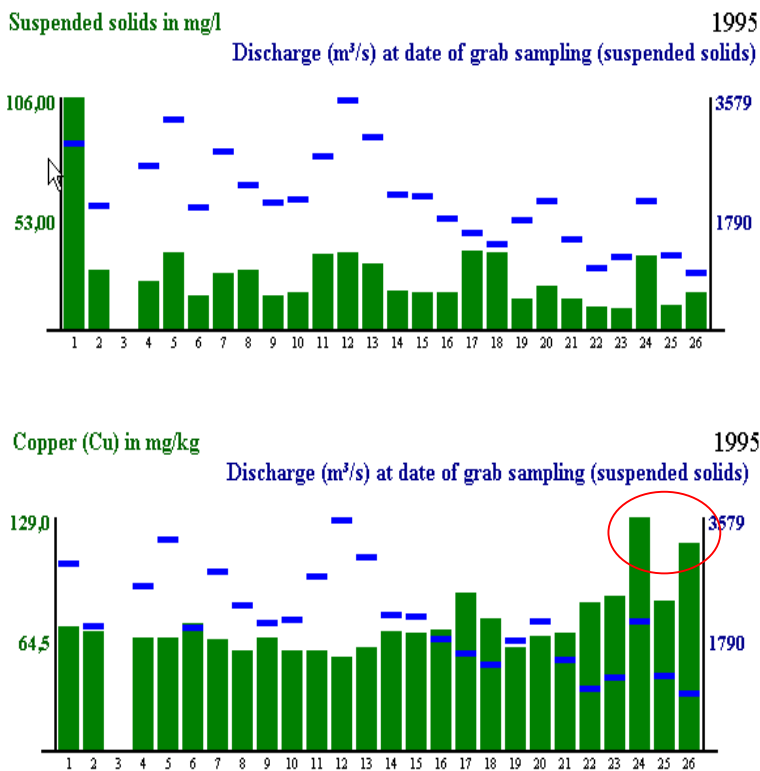


Figure 5.3 Suspended solids and copper concentrations on suspended solids at monitoring station Koblenz/Rhein in 1995, compared to the discharge at the time of sampling. The red circle indicates increased copper concentrations at low SPM at the 3rd high water.

5.2 The hydrological regime, flood events, and sediment dynamics of the Rhine catchment area

5.2.1 The hydrological regime and flood events

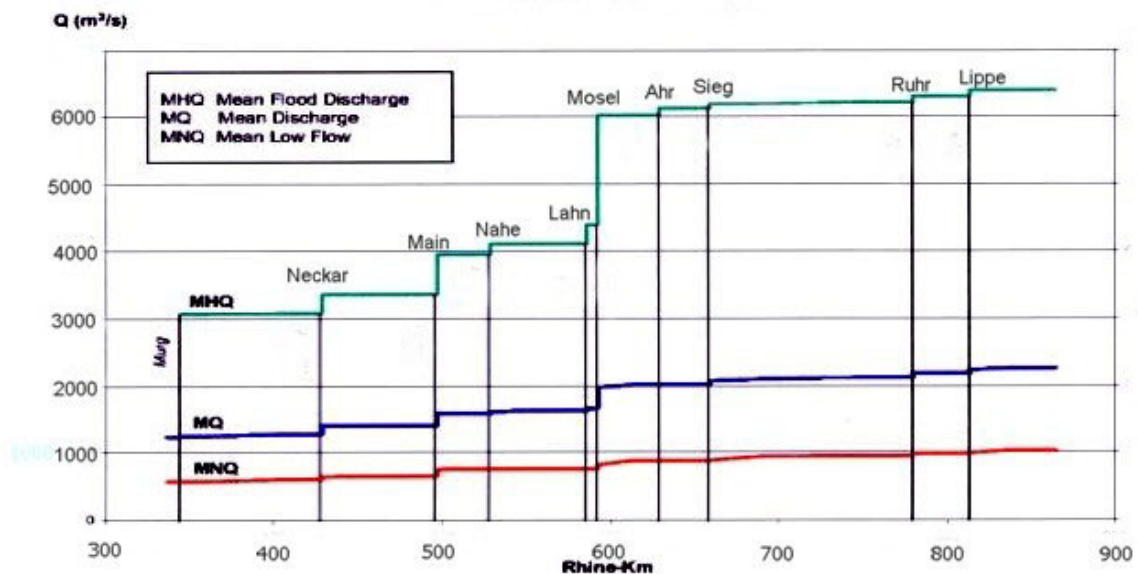


Figure 5. 4 River Rhine discharges

(Deutsches Gewässerkundliches Jahrbuch 1994, time series 31/93)

The Rhine is the largest river in Western Europe. Its drainage basin upstream of Rees is about 165000 km². Figure 5.4 shows the mean low flow (MNQ), mean discharge (MQ), and mean flood discharge (MHQ) as averaged values calculated from the time series 1931 up to 1993 (see Box 5.1.). The strong influence that the large tributaries Neckar, Main and Mosel can have on the Rhine water regime during high waters becomes obvious. However, due to the heterogeneity of the catchment area and its meteorological conditions, building up of high waters and their impacts show strong regional differences and no high flood is alike another one (BfG, 1996; Engel, 1999). Therewith the shown figure has to be seen as showing average, hence theoretical values for the flood discharge and not a typical hydrological event.

The discharge of the River Rhine is strongly influenced by the amount and timing of precipitation, snow storage and snowmelt in the Alps, the evapotranspiration during the summer period, and changes in groundwater and soil water storage. Storage of precipitation in the snow cover in winter, and its melting in spring and summer, together with summer rains, lead to pronounced runoff maxima in summer in the High and Southern Upper Rhine. Between Worms and Mainz, along the Northern Upper Rhine, precipitation starts dominating the discharge regime. Accordingly high waters mainly occur during winter in the Lower Rhine area. Usually, the floods in spring and summer in the Southern

Rhine catchment have no influence on the Lower Rhine (LUA, 2002). An exception was the spring flood in January/February of 1999 when high discharges were experienced in the whole Rhine catchment area.

Box 5.1 Abbreviations of water discharge levels

MNQ	mean low discharge
MQ	mean water discharge
MHQ	mean flood discharge
HHQ	highest experienced discharge
HQ_x	flood return period. X indicates the frequency in years, with which such a high water is expected

The high water of 1995

The exceptional highwater of 1995 was triggered by strong rainfalls in the montaineous regions of the Alps in January which filled the soil pores and lead to increased water runoff. While at the Upper Rhine, the discharges only increased to a high water situation for one day (4000 m³/s at Maxau corresponding to an HQ₁₅), the catchment areas of the tributaries Sauer, Saar, Mosel, Nahe, and Main were strongly impacted by the precipitation between January 25th and February 4th. At the confluence of the Main, the extreme water flow in this tributary increased the discharge of the Rhine River up to 6000 m³/s (Engel, 1999) (Figure 5.5). Regional, extreme rainfalls in the catchment areas of Ruhr and Lippe on January 29th 1995 added to the Rhine discharge and resulted in an HQ₁₀₀-situation, when the water finally reached the last German water level measuring post in Emmerich.

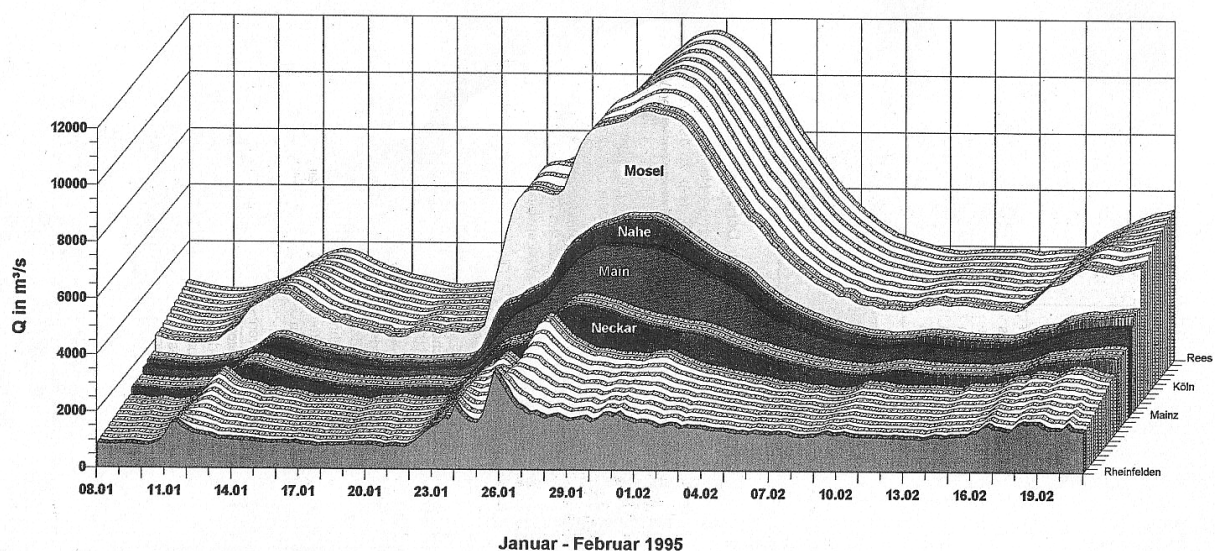


Figure 5.5 Flood wave along the Rhine during the high water event in spring 1995 (BfG, 1996)

The high waters in 1999

Three flooding events are recognizable in 1999: In February, in June and in December (Figure 5.6)

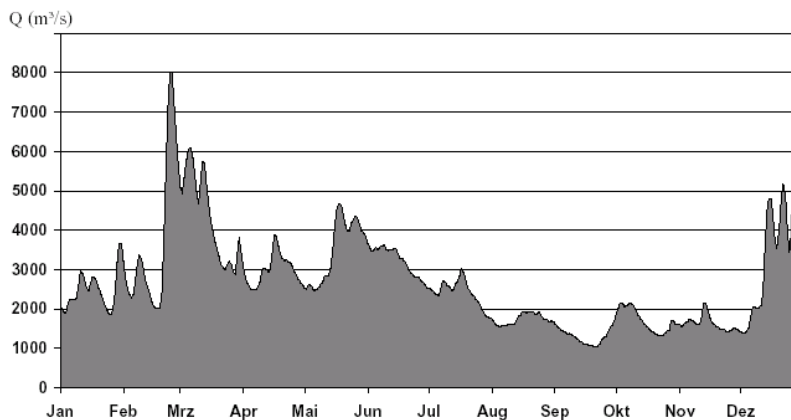


Figure 5.6 Change of discharge with time at the Lower Rhine during 1999 (gauging station Köln/Rhein), based on daily discharge measurements of the BfG.

February 1999: Strong snow falls in the Alpine area resulted in a flood return period of HQ_5 to HQ_{10} in the High and Upper Rhine. The elevated water levels from upstream were amplified by high discharges in the Middle Rhine tributaries, which were a consequence of sustained strong precipitation in that region of the catchment area due to a very mild winter in 1998/1999. As is shown by Figure 5.7, especially the rivers Neckar, Main (gauging station Mainz) and Mosel (gauging station Bonn) contributed to the high water which still affected the Lower Rhine. For the gauging station Worms (Neckar) and Kaub (Main) the discharges reached the level of flood return periods between HQ_{10} and HQ_{25} (table 5.1). The combination of the high discharges in the Southern Rhine area and in the Middle Rhine in this spring led to an extraordinary flood event because it impacted the whole river Rhine.

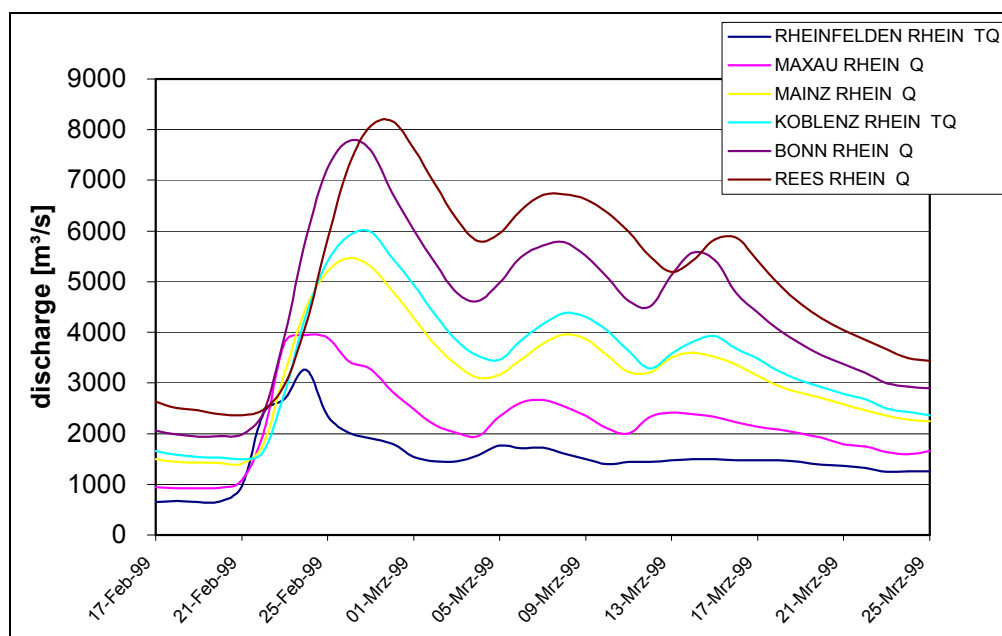


Figure 5.7 Hydrographs from the Rhine monitoring stations during the February flood in 1999

Although the flood ebbed away to a two-years flood downstream, it had a flood return period of more than 5 years in the Upper and Middle Rhine and in the Southern tributaries Neckar and Nahe. Also the flood in the Ruhr was high with an HQ₄ (table 5.1)

Table 5.1 Hydrological data of gauging stations along the Rhine River and selected tributaries.

gauging station	river km	discharge [m ³ /s]	date 1999	flood return period
Rheinfelden	148,3	3470	22.2	HQ10
Maxau	362,3	4160	22.2	>HQ5
Speyer	400,6	4160	23.2	>HQ5
mouth Neckar	428,5	1690	21.2	>HQ5<HQ10
Worms	443,4	4770	23.2	>HQ10<HQ25
mouth Main	496,8	934	24.2.	>HQ1
Mainz	498,3	5500	24.2	>HQ5
mouth Nahe		256	21.2	<MHQ
Kaub	546,2	5930	24.2	>HQ10<HQ25
mouth Lahn		216	23.2	<MHQ
mouth Mosel	592,5	2040	23.2	>HQ1<HQ5
Andernach	613,8	7770	24.2	>HQ2<HQ5
mouth Sieg	659,x	391	02.3.	<MHQ
Köln	688,8	8100	24.2	>HQ2<HQ5
mouth Wupper		71,9	02.3.	<MHQ
mouth Erft		25,1	03.3.	<MHQ
Düsseldorf	744,2	8040	25.2	>HQ2<HQ5
mouth Ruhr	780	755	03.3.	HQ4
mouth Lippe	814	256	04.3.	>MHQ
Rees	837,4	8260	26.2	>HQ2<HQ5

May 1999: Extensive thaw in spring and summer amplified by sustained precipitation in the catchment areas of the Alpine Rhine led to an extreme flood event in the Lake of Constance which is considered a centennial flood (HQ₁₀₀) (Figure 5.8). At the measuring station Cologne ("Köln"), however, this event was only classified by a less than 2-years flood return period (ca. 4600 m³/s), which was half the discharge of the high water in Cologne in February (table 5.1). This extreme flood in the High Rhine may explain the exceptionally high HCB concentrations that were measured in Augst during a sampling survey of the LFU Baden-Württemberg in Juli 1999: High water currents had probably removed younger and less consolidated material, in which case they may have exposed the deeper layers with higher HCB contamination.

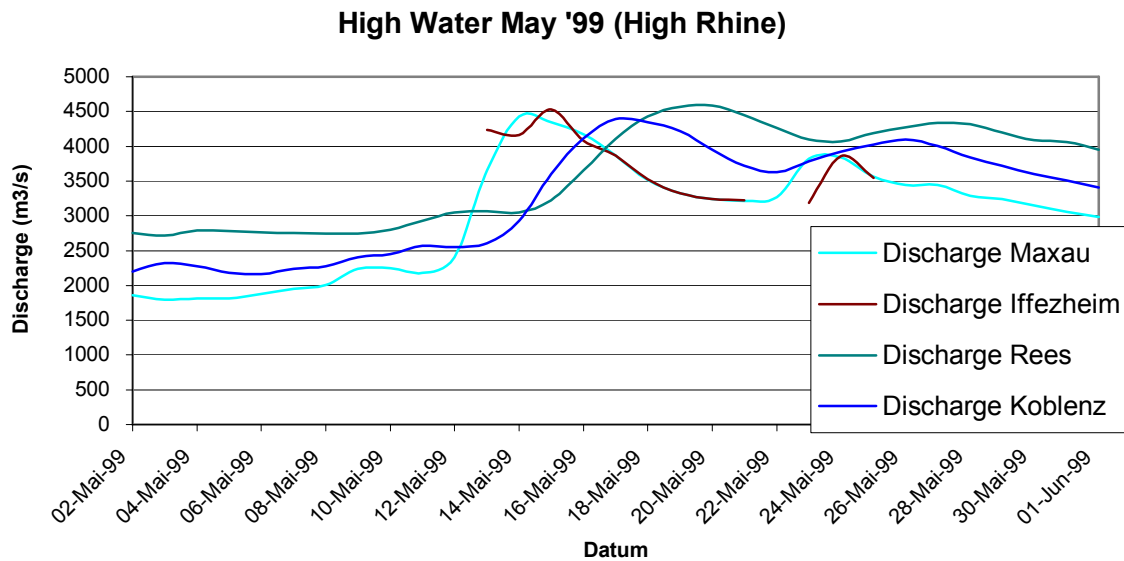


Figure 5.8 Flood event in May 1999: Discharges at different monitoring stations

December 1999: The winter 1999/2000 was again very mild and resulted in high precipitation, leading to elevated water discharges in the Middle Rhine and a high water period in the Lower Rhine at the end of 1999.

5.2.2 Sediment dynamics

Under present climate and land-use conditions, the total annual sediment supply from the hill slopes into the channels in the entire Rhine basin is estimated to be about 3 to 7 million tons (Asselman, 1999; Asselman *et al.*, 2003). From transport measurements that have been carried out by the BfG it was concluded that only about 27% of this amount reaches the German-Dutch border and the remainder is deposited at intermediate locations. In the Alpine rivers, most sediment is deposited in lakes, such as the Lake of Constance ("Bodensee"). In the German tributaries, much sediment is stored in low water zones, e.g. behind weirs. In the Rhine downstream of Andernach, floodplain sedimentation plays an important role in storage of suspended sediment (Asselman *et al.*, 2003). Analyses of suspended sediment concentrations measured in the downstream part of the River Rhine at Andernach and Rees indicate that sediment depletion occurs during a hydrological year and during individual floods. Apparently, sediment is deposited under low flow conditions during summer. During winter floods, part of the temporary stored sediment is eroded and the amount of available sediment decreases (Asselman, 1999).

The suspended matter load in the Rhine and its tributaries has decreased since the 70s mainly due to communal and industrial wastewater treatment plants, but also through accumulation in storage basins. Therewith less material that could be resuspended is available (IKSR, ???). Whether this

situation significantly adds to the sediment depletion and increases the erodibility of sediments needs to be investigated.

The suspended matter concentration varies strongly depending on the discharge and flood situation.

Figure 5.9 depicts the average suspended matter concentrations at the monitoring station Koblenz at the Rhine and at the Mosel (source: ICPR). The very high suspended matter concentration in the year of the high flooding events 1999 are clearly indicated.

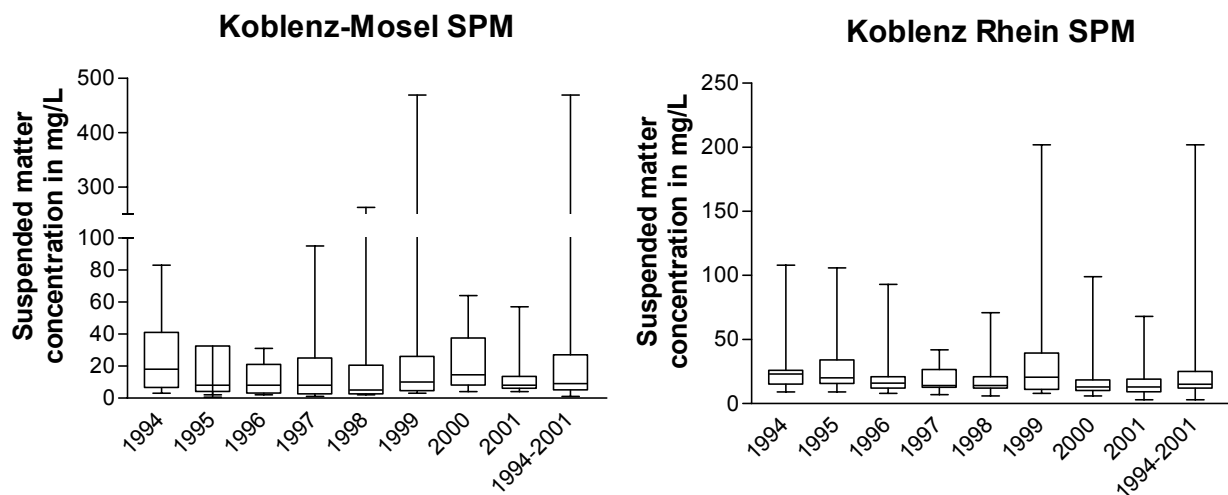


Figure 5.9 Suspended matter concentration from 1994 to 2001 at the monitoring station Koblenz at the Rhine (right) and at the Mosel (left)

Figure 5.10 shows the SPM concentration in the Rhine and its lowland tributaries during normal discharges (Source: LUA) (periods of high water are not considered). The median in all shown tributaries is in the magnitude of 10 to 20 mg/L. The number of data that have been available for this graph are small (5 to 10) for the tributaries and give only an indication, whereby the data basis for the Rhine was large with more than 1000 data points.

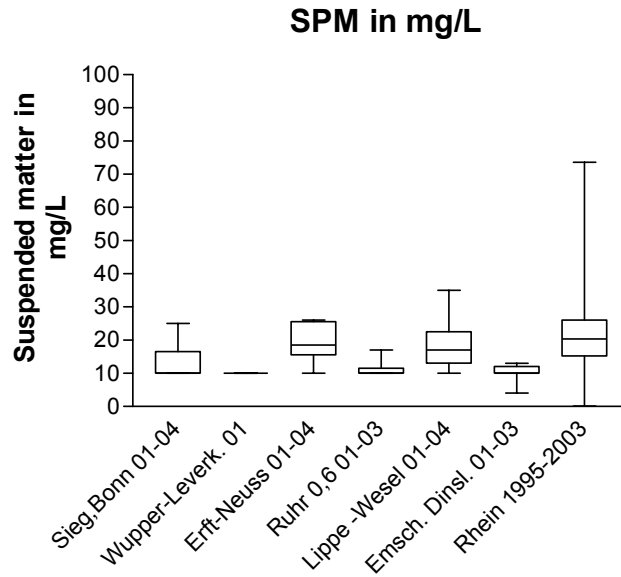


Figure 5.10 Suspended matter concentration in mg/L in the Rhine and its lowland tributaries (source: LUA)

The suspended matter load is difficult to assess, due to a number of reasons: while the data on discharges are relatively accurate due to the continuous data recording at the water-level measurement points, and well known relationships between water levels and discharges, the determination of concentrations and especially where suspended matter is involved, show a high uncertainty because of analytical variations, but more so because of the inhomogeneity in the distribution of suspended matter in the cross-section of a river. The Federal Institute for Hydrology recommends load determination on the basis of composite samples, which are automatically gathered at short time intervals and then mixed at a certain time frame (e.g. every two weeks) to increase the accuracy of yearly load estimations. Conservation of samples for that time period in a way, that allows the differentiation between suspended matter and dissolved fractions, has not been achieved yet. Therefore the current estimations of suspended matter load in the literature as well as in this report have to be regarded cautiously and while being aware, that the calculated data can be prone to errors of more than 100% (Hilden, 2003). Nevertheless, figure 5.11 gives an impression on the roughly estimated suspended matter load during the high water event between January 22nd and February 12th 1995 with the extreme contributions of the rivers Main and Mosel.

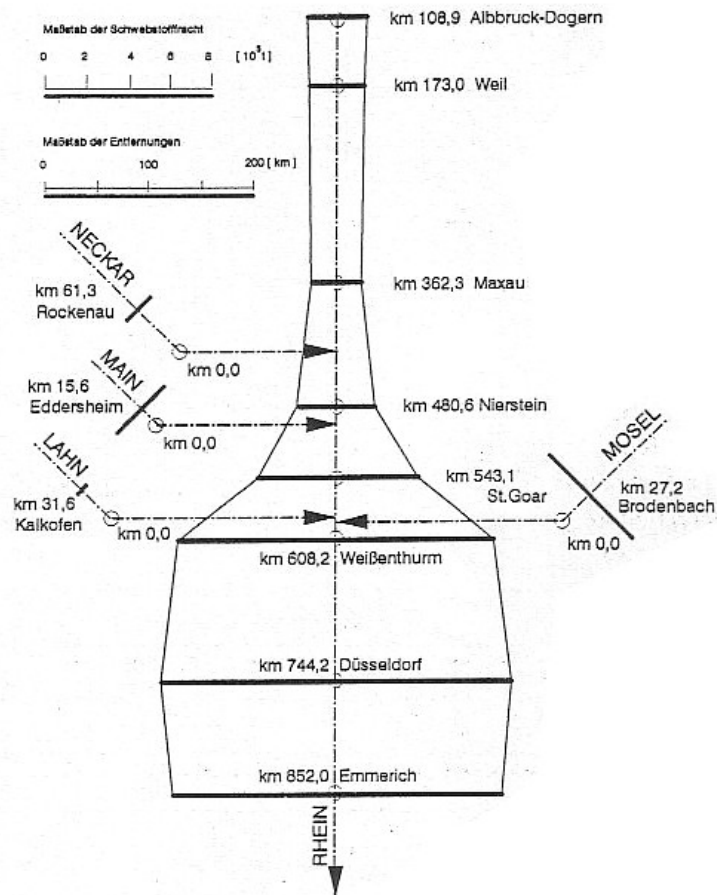


Figure 5.11 Loads of suspended matter in Rhine, Neckar, Main, Lahn and Mosel during high water between January 22nd and February 12th 1995 (from (BfG, 1996))

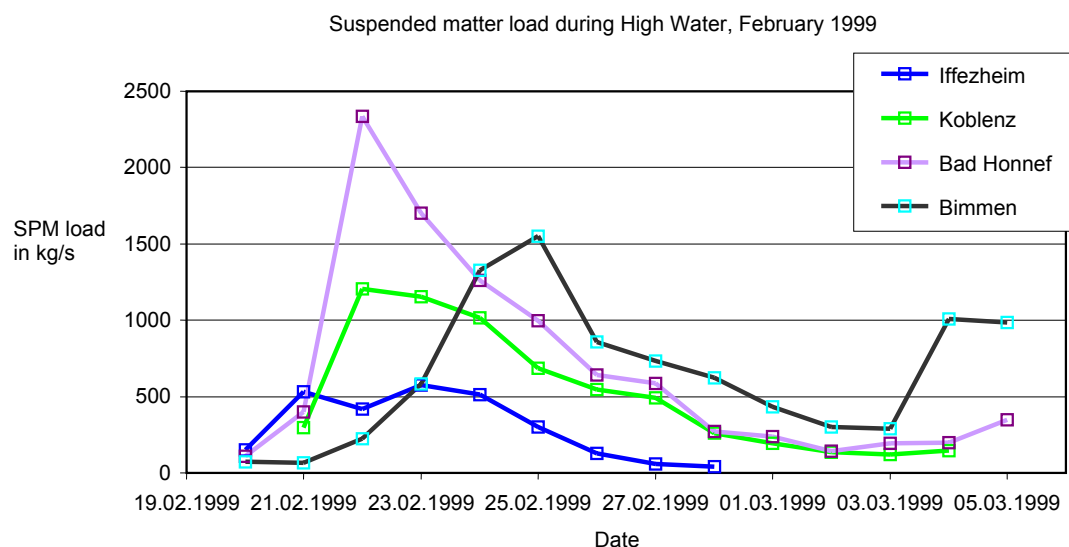


Figure 5.12 Suspended matter load along the Rhine during High Water in February 1999

Figure 5.12 indicates the transport of suspended matter downstream the Rhine during the flood event in 1999. The high increase in load between Koblenz and Bad Honnef could indicate the influence of the Mosel tributary, which - like in 1995 - largely added to the overall SPM load.

Uncertainties of Load estimations

Load estimations are prone to a number of potential sampling or measuring errors, which directly affect the total value of SPM and contaminant concentration:

Different sampling techniques: A campaign for comparing the different sediment sampling devices that are used at in the Rhine riparian states was performed by the International Commission for the Hydrology of the Rhine basin (IKHR). The results showed a difference of up to 30 percent depending on the sampling technique.

Inhomogeneous SPM distribution in the water body: Incomplete mixing of tributaries and Rhine at the measuring station like e.g. at the Station Bad Honnef (right Rhine bank located) where Mosel and Rhine are not completely mixed, sampling can result in inadequate calculation of the SPM concentration.

Insufficient sampling frequency: Annual load calculation must rely on regular measurements. When sampling flood events, the sampling frequency must be proportional to the discharge, otherwise the load can not be calculated properly. A sufficient number of samples must be taken at the rising and falling stage.

Analytical Errors: Laboratory analysis of SPM and contaminant concentration usually exhibits an error up to 30 % (Keller, BfG, pers. communication). (See also chapter 2.2: Quality Control of Field and Laboratory Data).

5.3 Erosion thresholds in reservoirs of Rhine, Main and Neckar

The International Commission for the protection of the Rhine (ICPR) recently commissioned an investigation on the resuspension risk of sediments in the upper river Rhine. All together 6 headwaters where investigated in the upper Rhine namely Markolsheim, Gerstheim, Strasbourg, Gamsheim. Furthermore, sediment sampling and field investigations were conducted in the Dutch portion of the river Rhine at Amerongen and Hollandsch Diep. In addition, sediment cores were taken and erosion stability tests were performed with samples from the headwater of Eddersheim in the tributary Main and in the headwater of the weir Ruhrwehr Duisburg in the tributary Ruhr. The ICPR study was performed from the year 2000 to 2003 for all the above mentioned weirs except Rheinau which was investigated in 1999. Unfortunately, the ICPR report is not yet finished. However, the essential results and conclusions are presented below:

Knowing the critical erosion shear stress the remobilization risk for the investigated sites was attributed to a hydrologic scenario (e.g. the flood event in January 1999 ~100 year flood). The sediment stability was investigated by the SETEG-System at the University of Stuttgart to detect the depth dependent critical erosion shear stress. With a 2D hydraulic model the actual bed shear stress was calculated for different hydrological discharge scenarios specified by their statistical return period resulting in Q_{10} , Q_{20} , Q_{50} , Q_{100} .

Table 5.2 Sediment stability in the headwaters of the Upper Rhine and major tributaries

Weir / River	River station [km]	Critical shear stress [Pa] min/max	Calculated discharge [m³/s] with associated shear stress [Pa]		
			HQ ₁₀	HQ ₅₀	HQ ₁₀₀
Gerstheim/ Rhine	~268,5	1-5	no numerical calculation		
Strasbourg/ Rhine	~283,9	0,5-6	4500 3,5-4,5	4700 4,5-5	
Marckolsheim/ Rhine	~234	0,5-8	see Point 3.1		
Gamsheim/ Rhine	~309,0	0,5-8	3240 0,4-0,8	4700 0,9-1,8	5100 0,9-1,8
Iffezheim/ Rhine	~333,9	0,5-3	4800 1->3	5200 2,7->3	
Eddersheim/ Main	~15,7	0,5-9	972 (HQ) 7-9	2280 (Q ₅₀) 7-10	2580(Q ₁₀₀) 7-11
Ruhrwehr Duisburg/ Ruhr	~4,3	0,5-9			1500 (Q ₁₀₀) 7-9
Amerongen/ Rhine		1,05-7	6570/ 1-5	11765 (Q ₅₀) 3-4	12675 (Q ₁₀₀) 3-4
Hollandsch Diep/ Rhine		< 1 (Sand) 2-7 (cohesive material)	no numerical calculation		

Table 5.3 Erosion risk in reservoirs along the Rhine

Reservoir/River	
Gerstheim/ Rhine	No numerical calculation
Strasbourg/ Rhine	Small erosion risk, due to flow direction and higher stability of the upper sediment layer (20 cm)
Gambsheim/ Rhine	At a discharge of 3240 m ³ /s there is no remarkable erosion. At a discharge of 4700 m ³ /s and 5100 m ³ /s the critical shear stress is exceeded and erosion takes place
Iffezheim/ Rhine	Both numerical calculations shows a significant excess critical shear stress -> high erosion risk
Eddersheim/ Main	Small erosion risk, due to the cohesive material. Only the upper sandy sediment layer (10 cm) on the left side are mobil. Due to the higher shear stress no fine material is found on the right bank.
Ruhrwehr Duisburg/ Ruhr	High erosion risk of the upper less stable layers (0-10 cm and 10-40 cm). Stable conditions below 40 cm.
Hollandsch Diep/ Rhine	no numerical calculation

In 14 of all together 27 Neckar reservoirs the major part - 1.3 Million tons - of sediments are accumulated. The sediment contamination is most severe upstream of the weir Lauffen. The investigation shows that the sediment bound Cadmium concentration between 1980 and 1996 is reduced from about 7 mg/kg less than 1 mg/kg. Nevertheless, there is a remobilization risk for discharges beyond 1100 m³/s.

To estimate the risk of contaminated sediment erosion, the University of Stuttgart made an investigation on the sediments with the SETEG-System followed by a pollutant transport modeling for the navigation portion of the river Neckar (160 km) between Plochingen and Mannheim (river mouth) with the COSMOS Model (Haag et. al 1997, 1999 & 2002). On the average the critical shear stress of mass erosion of the fine-grained bed sediment for the reservoir Lauffen is 4.6 N/m². The erosion resistance of the sediment in the other reservoirs is likely to be in the same range. The model was calibrated on the cadmium load measured at the point of confluence near the city Mannheim by the LfU Karlsruhe. Thereafter, a numerical simulation was performed to predict the future trend of cadmium input to the river Rhine. The results show a distinct future decrease of annual cadmium load to the river Rhine.

An investigation of the flood in January 1995 showed an increase of particulate heavy metal concentration in the river flow direction with the maximum measured in Lauffen (LfU 1996).

5.4 Estimated risk to the Port of Rotterdam due to substances of concern

5.4.1 Introduction to the approach

In this chapter, those areas will be identified that show a high enough contaminant concentration in sediments that they would theoretically be able to exceed the CTT levels at the Port of Rotterdam, if this material became resuspended and transported downstream under the assumption of worst case conditions.

This can only be a rough assessment due to a number of constraints such as:

- o lack of those data that would allow a consistent and reliable simulation of suspended matter within the Rhine under the influence of its tributaries.
- o lack of information about erosion/sedimentation patterns in the Rhine.
- o the heterogeneity of high water situations: Depending on kind and location of origin, high waters are usually limited to certain river drainage areas, such as the high water from 1995, which was most pronounced in the Mosel area, as opposite to the flood in January/February 1999, which affected the whole Rhine basin.
- o The concentration of suspended material does usually not correlate with the peak in high water flow, although this will be assumed under the present scenarios.

In the following scenarios, the existing data on contaminant concentration in surface sediments that were available for this study and which were the basis for the classification of the areas of concern in chapter 4, will be compared with the minimal concentrations that would be necessary to exceed the CTT values in the Port under consideration of dilution effects by non-contaminated suspended material during transport downstream (see figure 5.13) and making a number of assumptions:

In order to take into account situations at normal water flow (MQ), at average high water flow (MHQ), and at exceptionally high water flow (HHQ) the assumptions for the simulation of risk-relevant concentration data were set as follows (see figure 5.13 for illustration):

- o It is assumed that the suspended matter concentration in all tributaries and in the Rhine are the same and depend on the water flow situation. In order to get an idea of the transported SPM-load, a calculation was done which is depicted in Table 5.4, using average SPM concentrations deduced from the data depicted in figures 5.9 and 5.10:

MQ – 20 mg/L; MHQ – 150 mg/L; HHQ – 250 mg/L.

- o It is assumed that the whole sediment contamination at a specific site is transferred to the water phase and transported as such. Hence, sediment concentration equals the concentration of contaminants in the suspended material. No immediate dilution with suspended matter from upstream is included in the calculation.

- o It is assumed, that the concentration at Kleve-Bimmen will equal the concentration in the Port of Rotterdam. Therewith CTT-values are directly compared with the calculated concentrations.
- o For the initial approach, it will be assumed, that a flood event affects the Rhine and its tributaries at the same time, which is usually not the case. An exception here was the high flood in January/February 1999, which impacted the whole river basin. As consecutive flood events in the tributaries increase the probability of risk rather than reduce it with regard to the necessary concentrations to exceed the CTT values, these situations will be discussed exemplarily.

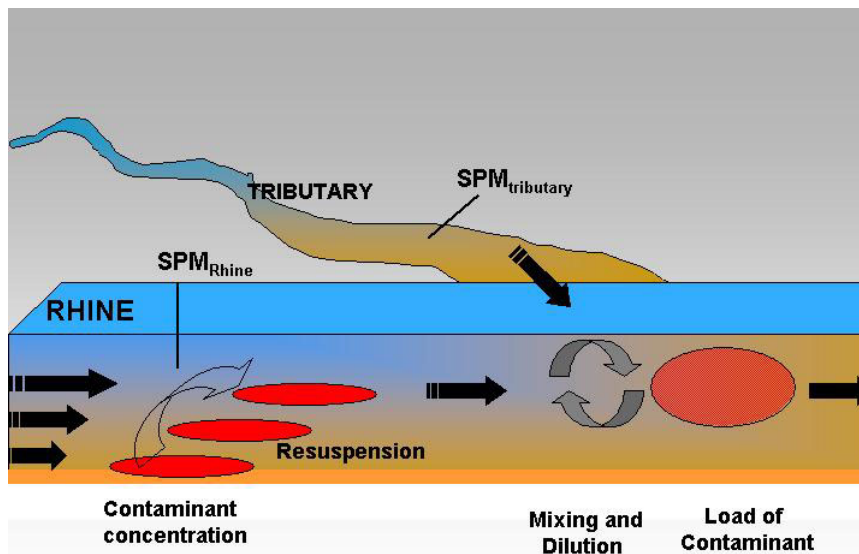


Figure 5.13

Assumptions of the case study to assess the risk for the port that is represented by substances of concern.

For generalisation purposes, mean values for the discharges at the different scenarios MQ, MHQ and HHQ, published at the “Deutsches Gewässerkundliches Jahrbuch”, which summarizes the hydrological data per year, and based on data of the time period between 1931 and 1993 were used for the calculations (see fig. 5.1).

The flow budget of the River Rhine was calculated from the data in Table 5.4. A factor, which accounts for the dilution by the Rhine water and its SPM concentration was determined for the different tributaries and areas in the Rhine basin.

In tables 5.4 to 5.7, those sediment or rather SPM-concentrations were calculated which would – given the assumptions that we made – could lead to an increase in contaminant concentration in the port under a given scenario.

Calculation of the minimal concentration at location A, that could lead to an exceedance of the CTT value in the Port of Rotterdam, if it becomes resuspended and transported downstream, being diluted by suspended matter originating mainly from the tributaries.

Formula:
$$X_A = X * Q_{KB} / Q_A$$

X_A : The concentration at location A which would be needed for the respective CTT value at Rotterdam to be exceeded.

X : CTT-value for the respective substance

Q_{KB} : suspended matter load at Kleve-Bimmen

Q_A : suspended matter load at location A

Table 5.4 Flow rates of the Rhine and its tributaries at three different flood scenarios. Assigned are theoretical SPM concentrations in order to calculate the suspended matter load in the Rhine basin.

	Stream- km	MQ m³/s	SPM µg/kg	Load		Addition	MHQ m³/s	SPM µg/kg	Load kg/s	Addition		HHQ m³/s	SPM		Load kg/s	Addition
				kg/s	kg/s					kg/s	kg/s		Extreme			
Maxau/Iffezheim	362,3	1260	20	25,2	25,2	25,2	3190	150	479	478,5	4550	250	1138	1137,5		
Neckar	428,5	135	20	3,4	28,6	28,6	1230	150	185	663,0	2690	250	673	1810,0		
Main	496,8	192	20	3,8	32,4	32,4	975	150	146	809,3	2010	250	503	2312,5		
Lahn Leun-Neu	25,1	32,5	20	0,7	33,1	33,1	287	150	43	852,3	746	250	187	2499,0		
Mdg.Mosel	592,5	313	20	6,3	39,4	39,4	2110	150	317	1168,8	4179	250	1045	3543,8		
Andemach	613,8	2020	20	40,4	40,4	40,4	6340	150	951	951,0	10600	250	2650	2650,0		
Mdg. Sieg	659	52,4	20	1,0	41,4	41,4	561	150	84	1035,2	1053	250	263	2913,3		
Mdg. Wupper		14,5	20	0,3	41,7	41,7	110	150	17	1051,7	181	250	45	2958,5		
Mdg. Erft		18,2	20	0,4	42,1	42,1	32,4	150	5	1056,5	47,1	250	12	2970,3		
Düsseldorf	744,2	2140	20	42,8	42,8	42,8	6540	150	981	981,0	10800	250	2700	2700,0		
Mdg. Ruhr	780	69,9	20	1,4	43,5	43,5	557	150	84	1140,1	907	250	227	3197,0		
Mdg. Lippe	814	42,6	20	0,9	44,4	44,4	242	150	36	1176,4	396	250	99	3296,0		
Rees	837,4	2270	20	45,4			6770	150	1016		11800	250	2950			
Kleve Bimmen	865		24	55,1			6600	170	1122			329	3882			

Table 5.5 Target concentrations above which a potential increase in the sediment concentration in the Port of Rotterdam occurs under conditions of MQ

MQ	CTT HCB, DDT (µg/kg)	PCB (µg/kg)	PAH (mg/kg)	Zn (mg/kg)	Ni (mg/kg)	Pb	Hg	Cu	Cr	Cd
CTT-Values	20	100	8	365	45	110	1,2	60	120	4
Maxau/lfezheim	44	219	17	798	98	241	3	131	262	9
Neckar	324	1621	130	5915	729	1783	19	972	1945	65
Main	287	1435	115	5237	646	1578	17	861	1722	57
Lahn Leun-Neu	1695	8477	678	30941	3815	9325	102	5086	10172	339
Mdg.Mosel	176	880	70	3213	396	968	11	528	1056	35
Andernach	27	136	11	498	61	150	2	82	164	5
Mdg. Sieg	1052	5258	421	19190	2366	5783	63	3155	6309	210
Mdg. Wupper	3800	19000	1520	69350	8550	20900	228	11400	22800	760
Mdg. Ertf	3027	15137	1211	55251	6812	16651	182	9082	18165	605
Düsseldorf	26	129	10	470	58	142	2	77	154	5
Mdg. Ruhr	788	3941	315	14386	1774	4335	47	2365	4730	158
Mdg. Lippe	1293	6467	517	23605	2910	7114	78	3880	7761	259
Rees	24	121	10	443	55	134	1	73	146	5
Kleve Bimmen	20	100	8	365	45	110	1	60	120	4

Table 5.6 Target concentrations above which a potential increase in the sediment concentration in Port of Rotterdam occurs under conditions of HMQ

HMQ	HCB, DDT (µg/kg)	PCB (µg/kg)	PAH (mg/kg)	Zn (mg/kg)	Ni (mg/kg)	Pb	Hg	Cu	Cr	Cd
CTT-Values	20	100	8	365	45	110	1,2	60	120	4
Maxau/lfezheim	47	234	19	856	106	258	3	141	281	9
Neckar	122	608	49	2220	274	669	7	365	730	24
Main	153	767	61	2800	345	844	9	460	921	31
Lahn Leun-Neu	521	2606	209	9513	1173	2867	31	1564	3128	104
Mdg.Mosel	71	355	28	1294	160	390	4	213	425	14
Andernach	24	118	9	431	53	130	1	71	142	5
Mdg. Sieg	267	1333	107	4867	600	1467	16	800	1600	53
Mdg. Wupper	1360	6800	544	24820	3060	7480	82	4080	8160	272
Mdg. Erft	4617	23086	1847	84265	10389	25395	277	13852	27704	923
Düsseldorf	23	114	9	417	51	126	1	69	137	5
Mdg. Ruhr	269	1343	107	4902	604	1477	16	806	1611	54
Mdg. Lippe	618	3091	247	11282	1391	3400	37	1855	3709	124
Rees	22	110	9	403	50	122	1	66	133	4
Kleve Bimmen	20	100	8	365	45	110	1	60	120	4

Table 5.7 Target concentrations above which a potential increase in the sediment concentration in PoR occurs under conditions of HHQ

HHQ	CTT HCB, DDT (µg/kg)	PCB (µg/kg)	PAH (mg/kg)	Zn (mg/kg)	Ni (mg/kg)	Pb	Hg	Cu	Cr	Cd
CTT-Values	20	100	8	365	45	110	1,2	60	120	4
Maxau/lffezheim	68	341	27	1246	154	375	4	205	410	14
Neckar	115	577	46	2107	260	635	7	346	693	23
Main	155	773	62	2820	348	850	9	464	927	31
Lahn Leun-Neu	416	2082	167	7598	937	2290	25	1249	2498	83
Mdg.Mosel	74	372	30	1356	167	409	4	223	446	15
Andernach	29	146	12	535	66	161	2	88	176	6
Mdg. Sieg	295	1475	118	5383	664	1622	18	885	1770	59
Mdg. Wupper	1716	8579	686	31315	3861	9437	103	5148	10295	343
Mdg. Erft	6594	32970	2638	120340	14836	36267	396	19782	39564	1319
Düsseldorf	29	144	12	525	65	158	2	86	173	6
Mdg. Ruhr	342	1712	137	6249	770	1883	21	1027	2055	68
Mdg. Lippe	784	3921	314	14313	1765	4314	47	2353	4706	157
Rees	26	132	11	480	59	145	2	79	158	5
Kleve Bimmen	20	100	8	365	45	110	1	60	120	4

5.4.2 Indication of risk by simulation of sediment transport from contaminated sites

In this chapter, the following different situations are assessed:

- 1) "business as usual", meaning normal discharge (MQ) and no management measures like dredging activities are carried out. As we assume, that the whole sediment is transferred to the water column and former sediment concentrations are not the concentrations in the suspended matter, this scenario is a worst case scenario, because it neglects dilution with suspended matter from upstream.
- 2) HQ – average high water discharges and HHQ – exceptionally high water charges. The latter addresses a flood with a return period of 50 to 100 years.

Calculations for these scenarios are not done on worst case assumptions, as it is assumed that all rivers experience flood events at the same time, and, hence, the dilution in this simulation is higher, than if the crest of a flood wave in a tributary arrives at its mouth before the high water of the Rhine. The different influence of this timing will be addressed exemplarily at the end of this paragraph for the Lippe River.

Hexachlorobenzene: In our worst case scenario under "business as usual" conditions (BAU), and under the assumption, that remobilized sediment does not settle along the Rhine, a concentration above 44 µg/kg of HCB in the sediment of the barrage Iffezheim is sufficient to exceed the CTT-value when transported to the Port of Rotterdam (table 5.5). Measured HCB concentration in Iffezheim-sediments exceed the concentration of either of the flood scenarios (44 to 68 µg/kg) by far with an average HCB concentration of 140 µg/kg and elevated concentrations of 400 to 600 µg/kg in the upper sediment layers (Witt *et al.*, 2003). Concentrations of more than 2000 µg/kg were found in 20 to 30 cm depth in 1994 (Keller, 1994). In opposite to the sediment in Marckolsheim, the next barrage upstream of Iffezheim, where up to 4000 µg/kg HCB was found in consolidated layers in 40 and 100 cm depth (Witt *et al.*, 2003), the upper layer in Iffezheim is likely to be resuspended at water flow rates of more than 3000 m³/s (Witt *et al.*, 2003). This corresponds to our 2nd scenario ("MHQ"). The concentrations, needed under the first two scenarios conditions to surpass CTT-levels are not very different for the Upper Rhine (44 and 47 µg/kg) (table 5.5 and 5.6). The elevated levels of 68 µg/kg that are necessary under HHQ conditions are due to the higher dilution in this situation and are equally easy exceeded.

It can therewith be stated, that on the basis of our worst case scenario: a concentration at Iffezheim of more than 44 µg/kg poses a risk for the Port of Rotterdam in terms of CTT-exceedance.

Downstream of the barrages, mainly in small harbour basins, high HCB concentration are found up to 96 µg/kg in the Baggerloch Müllerhof in the Lower Rhine, Loreley (106 µg/kg) and Speyer Floßhafen (109 µg/kg) in the Middle Rhine. These small Rhine harbours and basins with elevated HCB-concentrations could theoretically add a significant amount to the HCB load if their sediment of an approximate area of 20000 m² were remobilized, following our worst case assumptions.

High HCB concentrations that have been measured at the mouth of the Lippe (436 µg/kg) will according to our calculation not present a risk for the Port of Rotterdam under MQ conditions (calculated minimal value: >1200 µg/kg) due to the high dilution effect with downflowing suspended material. This, however, presumes, that mixing is total (which it isn't between Lippe and Bimmen, according to Dr. Vogt, LUA, personal communication), and that no additional HCB-contaminated suspended matter comes from upstream.

Under HQ and HHQ conditions, the minimally necessary concentration level decreases and approaches the range of actually measured HCB levels. If a more realistic view were adapted and assumed that the Lippe wave crest enters the Rhine while the main river does not show an increased water discharge yet, the risk would increase considerably, as will be shown below.

Polychlorinated Biphenyls: According to the results shown in tables 5.5. till 5.7, no elevated PCB concentrations from tributary sediments can increase the concentrations in the Port of Rotterdam above CTT level, not even the high PCB concentrations in the River Ruhr (up to 462 µg/kg). The highest risk with regard to PCB that can be deduced from the present sediment data is located again at small Rhine harbours (e.g. Loreley with 211 µg/kg) and at the flooded quarry Müllerhof at river km 848 with PCB-concentrations of 332 µg/kg near the Dutch-German border.

Polycyclic Aromatic Hydrocarbons: Areas of concern with regard to PAHs are the small harbor Wanheimer Süd with concentrations of more 69 mg/kg and 107 µg/kg (compared to a calculated minimal concentration of 10 to 11 mg/kg) and the other small harbor basins in Duisburg, which could increase the CTT concentrations. The Ruhr showed PAH concentrations in the upper sediment layer of more than 2500 µg/kg in 1994 10 km from the mouth of the tributary, but much lower values 3 years later (18 µg/kg). If the older material were resuspended, the Ruhr could significantly contribute to the PAH risk because its concentration would clearly exceed the minimal concentrations of 315 mg/kg (MQ), 107 mg/kg (MHQ) and 137 (HHQ). As our calculations indicate that the dilution effect is highest for the Ruhr-material at normal flow conditions, this risk is present at all times and increased during "business as usual conditions".

DDT: In some sediment samples from the Upper Rhine (Kehl, Bellenkrappen) and in the harbor "Loreley" elevated DDT levels up to 113 µg/kg were found which are above the calculated level for exceeding the CTT level under any flow condition.

Zinc, copper, chromium: Only the Rhine harbor basins would have a high enough concentration to increase the CTT at Rotterdam.

Nickel: No concentrations that would be high enough to cause an increase at the Port of Rotterdam were recorded

Lead: No concentrations that would be high enough to cause an increase at the Port of Rotterdam were recorded

Mercury: areas where the threshold value can be exceeded, are small harbors upstream like Loreley and harbors in the Duisburg area (Aussenhafen, Diergardt harbor) with more than 2 mg/kg.

Cadmium: On the basis of the available data, the only concentrations which could lead to an increase above CTT-level would be the extremely high concentrations in the Neckar (Gundelsheim: 36 µg/kg) under conditions of high water flow (MHQ: 24 µg Cd/kg; HHQ: 23 µg/kg).

On the basis of the very rough model that we used, and the sediment data, that were available, we can conclude on the following “areas of risk”:

With regard to HCB, the upper Rhine barrages and sediments, small Rhine harbors and basins downstream can lead to an exceedance of CTT levels in the Port of Rotterdam – according to our worst-case assumption for BAU conditions. PCB concentrations at the Loreley harbor and the basin “Müllerhof” may present a risk. The Ruhr with regard to PAH, the Duisburg area and here the harbour Wanheimerort Süd with respect to PAH and copper and Duisburg-Diergaardt with respect to Dioxins show values above our calculated safe levels. Also the Aussenhafen Duisburg with regard to mercury can - according to our worst-case assumption - become a risk for the Port of Rotterdam.

Although this is a very simple approach and the assumptions are coarse, there are some statements that are illustrated by it: Comparing the outcomes of the HMQ and the HHQ scenario, the higher suspended matter load is partially compensated by the higher discharges. Concentrations in tributaries, calculated for the MQ scenario differ from the HMQ by a factor of about 2 to 4 – according to the increase in discharges. Mostly the sediment concentrations in the tributaries differ by a number of magnitudes from the data that were calculated here as being necessary to exceed CTT levels.

Restrictions with regard to the used approach

It has to be emphasized, however, that the flood waves from the tributaries often reach the Rhine and travel down the river before the high water discharge from the main river itself reaches their mouth. A confluence of flood waves from main river and tributaries that would amplify the whole flood situation, as it is simulated here, occurs rather seldom, for the Wupper e.g. with a less than 100 yrs probability (LUA, 2002). The influence high water discharge in tributaries have for the risk situation, if they do not merge with the flood wave of the Rhine, are more pronounced the lower the water level in the Rhine (and hence the dilution) and the shorter the distance to the Port of Rotterdam. Exemplarily, two situations are compared: (A) the situation when a flood wave of the Lippe representing a medium

high water (MHQ) of the Lippe enters the Rhine which also carries high water (MHQ), and (B) the situation when the main river still shows normal flow conditions (MQ) at the mouth of the tributary, while this is transporting elevated loads towards the river (B). Situation (A) equals the case that has been shown in table 5.6. Table 5.8 depicts the concentration thresholds of the substances of concern under the different situations, taking into account the different dilution factors. (A) repeats the concentrations that were calculated in table 5.6 as those at the Lippe that could lead to exceedance of the CTT levels in Rotterdam under MHQ conditions. Under (B) those concentration values are given that account for the lower dilution of the Lippe suspended sediment if the Rhine discharges are still normal. Comparing those concentrations that were measured along the Lippe – the highest value measured in Lippe sediments and those at the mouth – a conclusion can be drawn, whether these sediments could lead to an exceedance at the Port of Rotterdam, given the conditions described here.

Table 5.8 Comparison of calculated concentration thresholds for exceedance of the CTT at the Port of Rotterdam at two high water scenarios A and B with the sediment surface concentrations that were measured at the Lippe tributary.

S.o.C	Threshold concentrations at the Lippe above which a risk for the port could exist		Real concentrations in Lippe sediments	
	scenario A	scenario B	Lippe, mouth	Lippe (max)
HCB (µg/kg)	618	34	42	140
PCB (µg/kg)	3091	170	81	222
TBT (µg/kg)	3091	170	20 (2003) 278 (1994)	112 (2003)
PAH (mg/kg)	247	14		15
Zn (mg/kg)	11282	620	468	603
Ni (mg/kg)	1391	76		
Pb (mg/kg)	3400	187	67	96
Hg (mg/kg)	37	2	1,3	1,8
Cu (mg/kg)	1855	102	70	137
Cr (mg/kg)	3709	204		
Cd (mg/kg)	124	7		

Under these conditions, the Lippe may be able to substantially transport contaminants towards the Port of Rotterdam at concentrations that may exceed the CTT level. Due to the high HCB concentrations in the Lippe at its mouth, these will probably represent the highest risk, whereby along the river also other substances exceed the critical thresholds (HCB, PCBs, PAHs, mercury, copper and possible TBT if old sediments become resuspended).

The risk that is represented by the tributaries has therewith be regarded with great care, as – depending on the water discharge of the Rhine at the time of flood event in the tributary – it can be much higher than has been shown by the calculations above.

5.5 Indications for resuspension and transport of contaminants in suspended matter – exemplarily described for Cadmium and HCB

5.5.1 Introduction

In this chapter, indications are discussed that point to potential resuspension processes and transport of contaminants downstream. Comparisons of concentrations in suspended matter at different locations and in dependence of the discharges are carried out, and loads are calculated for different monitoring stations in order to identify where and under what circumstances re-introduction of contaminated material into the sediment cycle occurs. Although load estimations have a high uncertainty, they are used here as one line of evidence in the chain of argumentation and as an indication of the quantity of material that might impact the port's sediment.

To estimate concentration and load at the monitoring stations along the river Rhine and the tributaries (Neckar, Main Mosel, Ruhr) for normal discharge and flood returning periods, an evaluation of data from routine measuring programs (performed by the BfG, LfU, LUA, Ruhrverband, HLUG) and, if available, additionally data from flood events, gained at the selected monitoring stations, were used.

Data sheets and databases usually contain the concentration of contaminants in mg/kg or µg/kg so the load [mass/s] was calculated using the following formula:

$$\text{Load [mass/s]} = \text{Concentration contaminant [mass/kg}_{\text{SPM}}] * \text{SPM concentration [mg/l]} * \text{Discharge [m}^3\text{/s]} * \text{correction factor for units}$$

The monitoring stations do not record discharge values, so the discharge data had to be taken from the closest gauging station. In the annex "recording data" the recording data from the different monitoring and gauging stations, the time measuring period for the routine measuring program and the available flood event data are listed.

All parts of information are used as lines of evidence in the final analyses of potential areas of risk for the Port of Rotterdam.

The substances of concern **cadmium** and **hexachlorobenzene** are chosen as examples because

- they are routinely measured in monitoring programmes
- they are known to have different distribution patterns: cadmium has been emitted mainly in the Upper Rhine, North of Karlsruhe, comprising Neckar, Main and the industrial area of Ludwigshafen, and in the Ruhr area, while HCB has been introduced into the environment essentially at two sites: At Rheinfelden in the Higher Rhine and in the Lippe catchment area of the Lower Rhine (Chapter 4).
- In the Rhine they are mostly (Cd) or almost exclusively (HCB) adsorbed to suspended matter.

5.5.2 Evidence for cadmium-resuspension

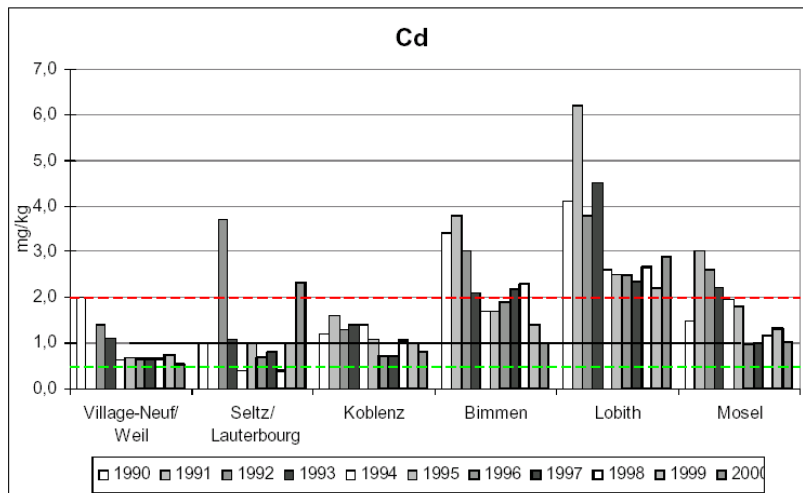


Figure 5.14 Average annual concentration in mg/kg suspended matter at different monitoring stations and ICPR target value (1 mg/kg).

Figure 5.14 depicts the average annual cadmium concentration in SPM, measured at the different ICPR monitoring stations from 1990 to 2000. According to these average data, no annual cadmium_{SPM}-concentration has been measured that exceeded the CTT-level of 4 mg/kg since 1993. The comparatively higher values at Lobith are assumed to derive from the Ruhr-Area (IKSR, 2002).

Single peak-concentrations exceeded the CTT value in 1998 at Bimmen/Lobith (12 mg/kg) and 2000 in Lauterbourg (7,3 mg/kg) (ICPR-monitoring data). The increased values at Bimmen/Lobith in 1998 were measured at the end of the year after a high flood in Nordrhein-Westfalen. This points to an input from the tributaries Erft and Ruhr where high concentrations of cadmium have been measured.

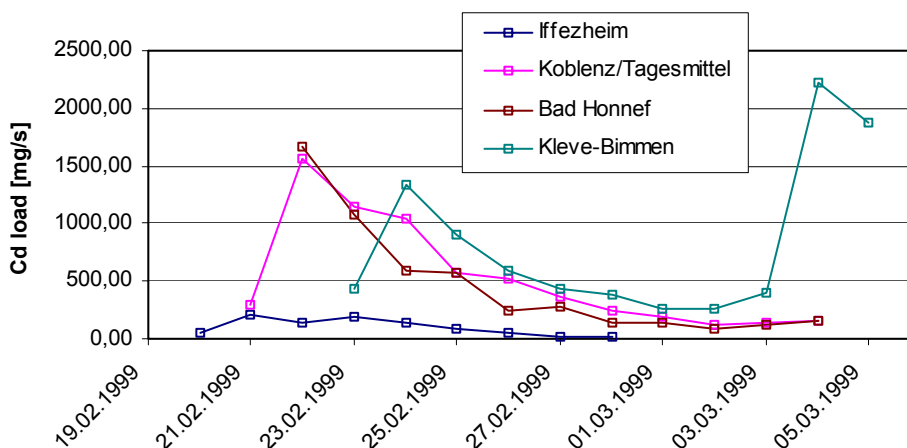


Figure 5.15 Cd load at monitoring stations along the river the Rhine

This observation, that some cadmium input may derive from the Ruhr Area tributaries during floods, is supported by data from a measuring campaign that was executed by the State Institute for Environmental Protection Baden-Württemberg [LfU] (station Iffezheim), The Federal Institute of Hydrology [BfG] (station Koblenz) and North Rhine-Westphalia State Environment Agency [LUA] during the flood event in February/March 1999 (Figure 5.15): A strong increase of the cadmium-load

was calculated for March at the Station Kleve–Bimmen. With an estimated transport time of suspended matter between Bad Honnef and Kleve-Bimmen of roughly 1 or 2 days, there should have been some indication of increased levels, if the material came downstream with the Rhine. As no corresponding peak was reported, the second cadmium-load peak in March 1999 was likely to derive from the Ruhr Area.

Figure 5.16, depicting the discharge and the cadmium concentration of the River Ruhr, shows the corresponding peaks of the discharge at Hattingen and the total Cadmium concentration in the water. This increase can be due to erosion of groynefields and other still water zones (Nusch, Ruhrverband). The critical discharge for sediment erosion in the River Ruhr is about $200 \text{ m}^3/\text{s}$, which – together with the high erosion risk of the upper 40 cm at the Ruhr weir ("Ruhrwerk") in Duisburg at the confluence of the rivers (Table 5.3) may lead to increased discharge of cadmium-loaded suspended matter into the Rhine. According to Klopp and Kornatzki (1981) an increase of cadmium concentrations through surface runoff can be excluded.

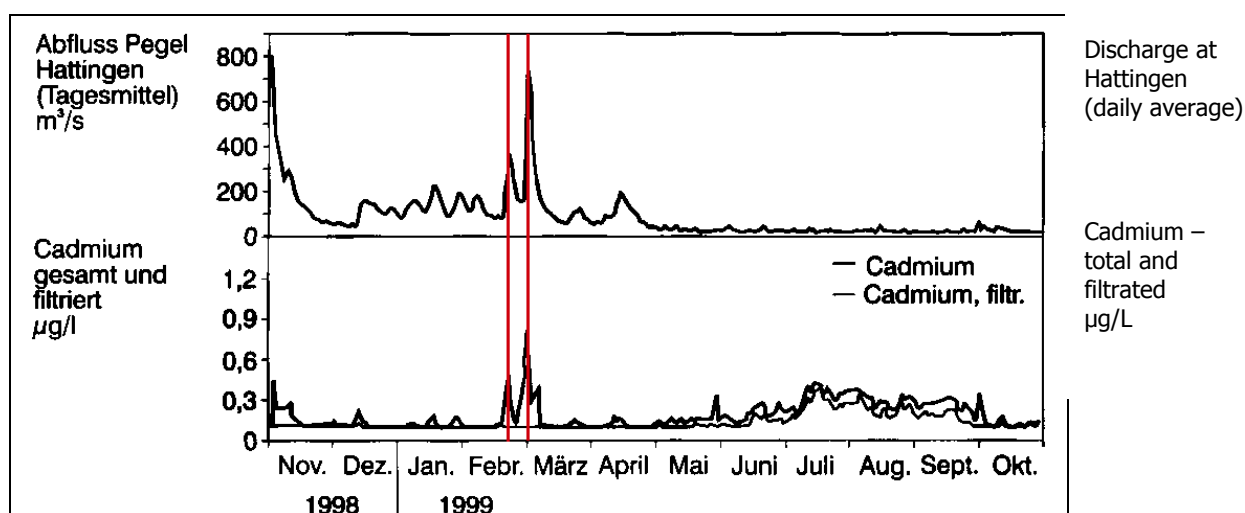


Figure 5.16 Discharge and cadmium concentration for the hydrological year 1999 (from Ruhrverband 2000).

Figure 5.17 shows cadmium concentrations and cadmium loads with discharges, measured between 1994 and 2003 at the Ruhr (top graph) and at Kleve-Bimmen (bottom graph). The peak concentration of 55 mg/kg in the Ruhr is exceptionally high when compared with monitoring stations at Iffezheim ($<1 \text{ mg/kg}$), Koblenz (2 mg/kg), and Bad-Honnef ($<3 \text{ mg/kg}$). The decrease with increasing water flow indicates, that point sources are responsible for the initial high concentrations (see chapter 5.1). Concentrations at Kleve-Bimmen ($<7 \text{ mg/kg}$) (Fig. 5.17) are much lower than in the Ruhr due to dilution (and/or deposition). However, it still frequently shows concentrations $> 2 \text{ mg/kg}$ that are higher than those of most other stations and tributaries, and this may be considered as a strong indication of the influence of the Ruhr.

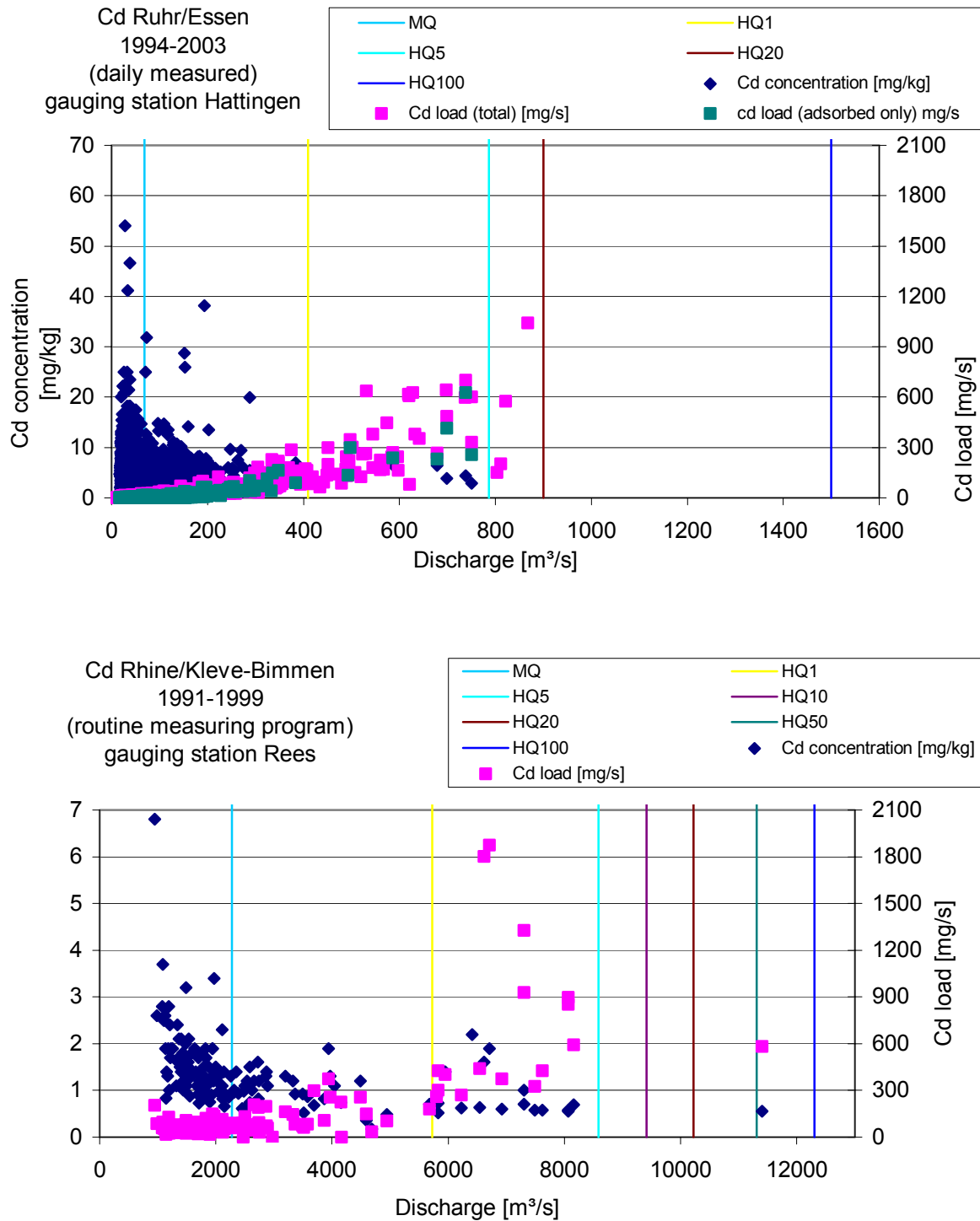


Figure 5.17 cadmium concentrations and loads at the routine measuring stations Hattingen and Rees, depicted depending on the discharge. Vertically, the different flood return periods are indicated.

Apart from strong evidence, that some Cadmium resuspension and transport takes place from the Ruhr towards the Rhine, the cadmium-load peaks that are shown in Fig. 5.15 for Koblenz and Bad Honnef at the end of February must have originated from the area North of the Upper Rhine barrages, as the load at Iffezheim is comparatively small.

Areas of concern with regard to cadmium in the Upper and Middle Rhine between Iffezheim and Koblenz are the Main and Neckar. Although a company at Ludwigshafen near Mannheim has been known to emit Cadmium to the Rhine, no data were available that point to any still persisting historic contaminated site with regard to cadmium in this area.

The increase in load could be attributed to the River Neckar, unfortunately during this flood event no measurements in the Neckar were executed (Storck, LfU). Investigation by Haag et. al showed, that the critical discharge for erosion of highly contaminated sediments in the head water at the power station Lauffen amounts to about 1100 m³/s. In February 1999 the discharge in Lauffen reached 1100 m³/s, so it can be assumed, that erosion of cadmium-contaminated sediment really happened. The contribution of the river Main to the total cadmium load in Koblenz cannot be specified, because no measuring campaign was performed during flood events (Seel, HLUG). However, it has been shown, that the accumulated material at the barrage of Eddersheim near the mouth of the Main only has a small erosion risk (table 5.3). Hence, input from the Main may be limited.

5.5.3 Evidence for HCB-resuspension

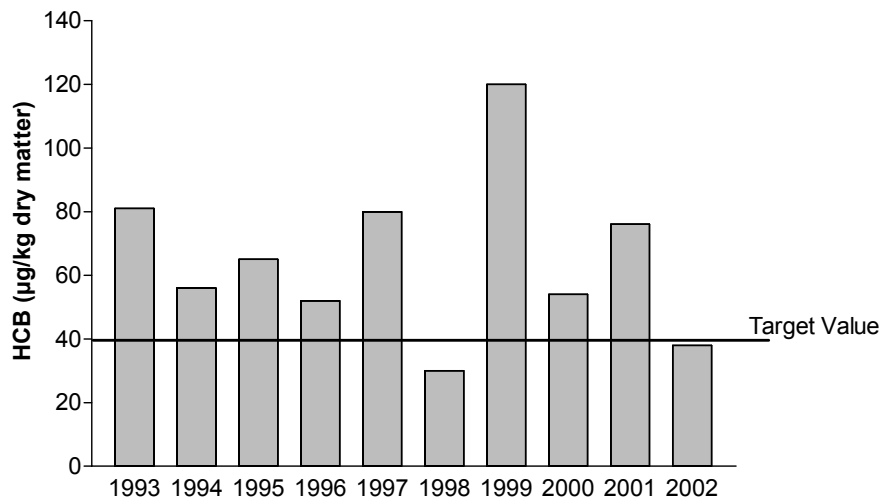


Figure 5.18 HCB-concentrations in suspended matter of the Rhine near Iffezheim (90% percentile) between 1993 and 2002 (Source: LfU 2003)

As depicted in figure 5.18, the suspended matter in Iffezheim in 1999 showed concentrations of up to 120 µg/kg pointing to a strong resuspension of contaminated material at this barrage during that year's flood event. Figure 5.19 shows the time dependency of the HCB transport rate during the flood. For Iffezheim with increasing discharge (20.2. – 2500 m³/s; 21.2. – 4100 m³/s) an increase of the HCB load up to 3000 µg/s could be observed. This is primarily due to the erosion of HCB contaminated sediments in the five lower barrages in the Upper Rhine and is in good agreement with investigations of Witt et. al. (2003) who found that release of HCB occurs at flow rates more than 3000 m³/s.

Between Iffezheim and Koblenz almost no change of HCB load can be detected (Figure 5.19).

At Bad Honnef an increase to 70000 $\mu\text{g/s}$ was measured. Between Koblenz and Bad Honnef only the river Mosel (no HCB contamination known; Breitung, BfG 2003) discharges into the Rhine. This increase could point to a resuspension of HCB contaminated sediments from still water zones (groyne fields) and possibly from small harbours along the Rhine that effect the HCB load. As there was an almost full bank flow with relatively high flow velocities, contaminated sediments in the groynefields are likely to be resuspended, resulting in an increase of the contaminant load as indicated in the diagram. However, due to the previously described uncertainties and high variances of suspended matter load estimations (chapter 5.2.2), no sound evidence can be assigned to these relatively small and on few data points relying differences in load transport. The same is true for the increase in load between Bad Honnef und Kleve-Bimmen from ca. 70000 $\mu\text{g/s}$ to ca. 90000 $\mu\text{g/s}$. It could be explained by HCB input from the Lippe, but, again, these differences are too small and too little reliable to be seen as evidence.

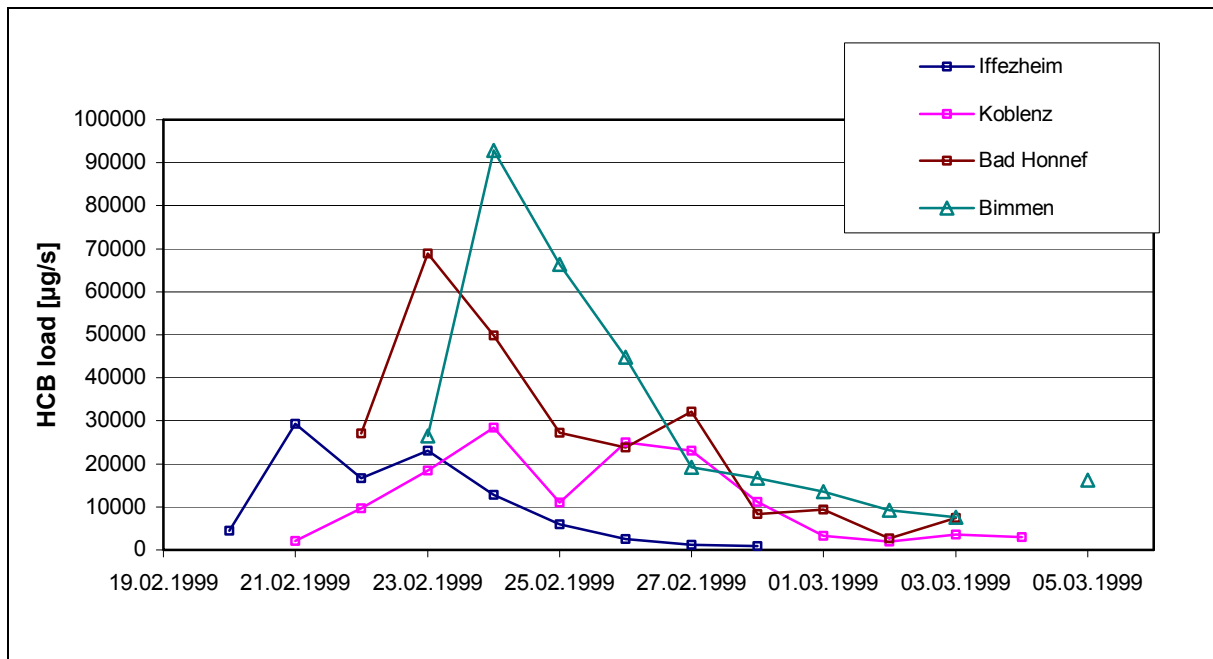


Figure 5.19 HCB load at monitoring stations along the river the Rhine during the flood event in 1999

Figure 5.20 shows HCB concentrations and loads in Iffezheim in relation to water discharges at the gauging station Maxau, downstream of Iffezheim. First resuspension occurs already at an HQ_1 , which leads to HCB concentrations up to 270 $\mu\text{g/kg}$. These increase even further (~ 340 $\mu\text{g/kg}$), when an HQ_{10} is surpassed.

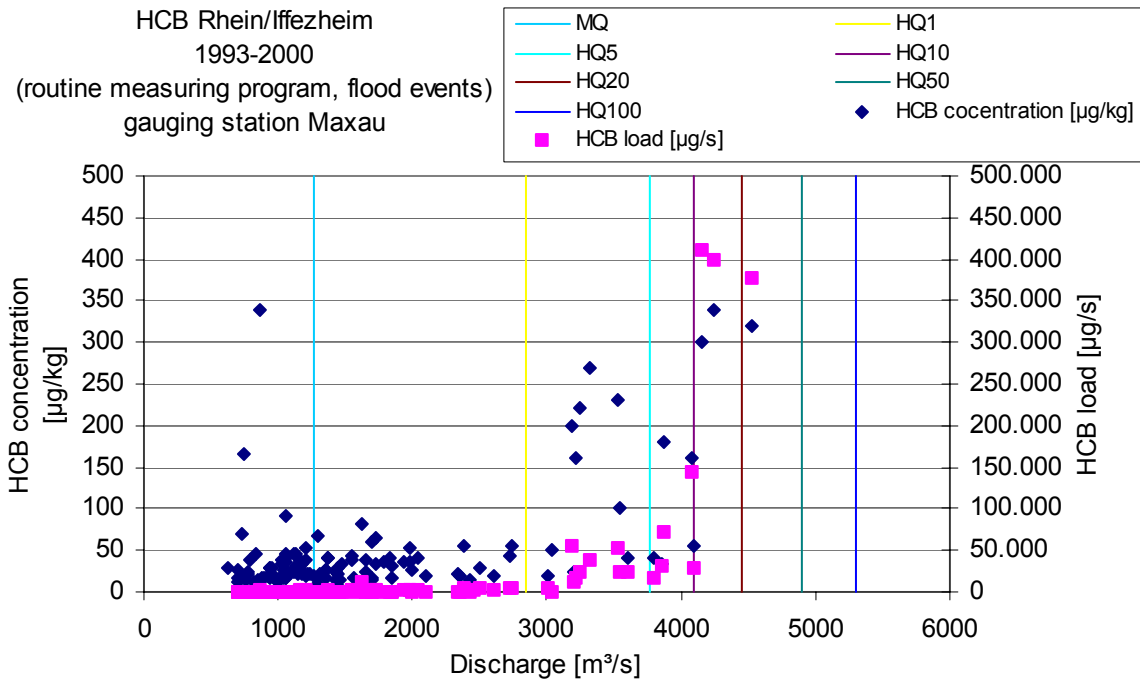


Figure 5.20 HCB concentrations in suspended matter and loads at the routine measuring station Maxau depicted depending on the discharge. Vertically, the different flood return periods are indicated.

Figure 5.21 shows the HCB concentrations in SPM during the May flood in 1999 in Iffezheim and between January and August 1999 in Lobith, compared with the discharges. During the May flood, which was considered a 100 years flood in the High Rhine, HCB concentration in suspended matter increased to almost 350 $\mu\text{g/kg}$ at Iffezheim. And 5 days later, HCB concentrations increased at Lobith at the Dutch-German border: Here the concentrations of 68 $\mu\text{g/kg}$ still exceed the CTT value three times (Data were made available by Doreen ten Hulscher, RIZA).

Either the HCB became resuspended in Iffezheim and transported down the river, or another HCB source is responsible for the increased values at Lobith. There are indications, that the HCB contaminated sediment in the Lippe can be resuspended (see below). However, the flood in May 1999 mainly affected the High and Upper Rhine and had little impact on discharges of the Lower Rhine tributaries. In addition, the variation of the HCB concentration in Lobith corresponds very well with the discharges at Maxau.

Therewith, these data support strongly the assumption, that HCB contaminated material that becomes resuspended in Iffezheim can be transported within a few days to Lobith and is diluted only by a factor 5 during this process.

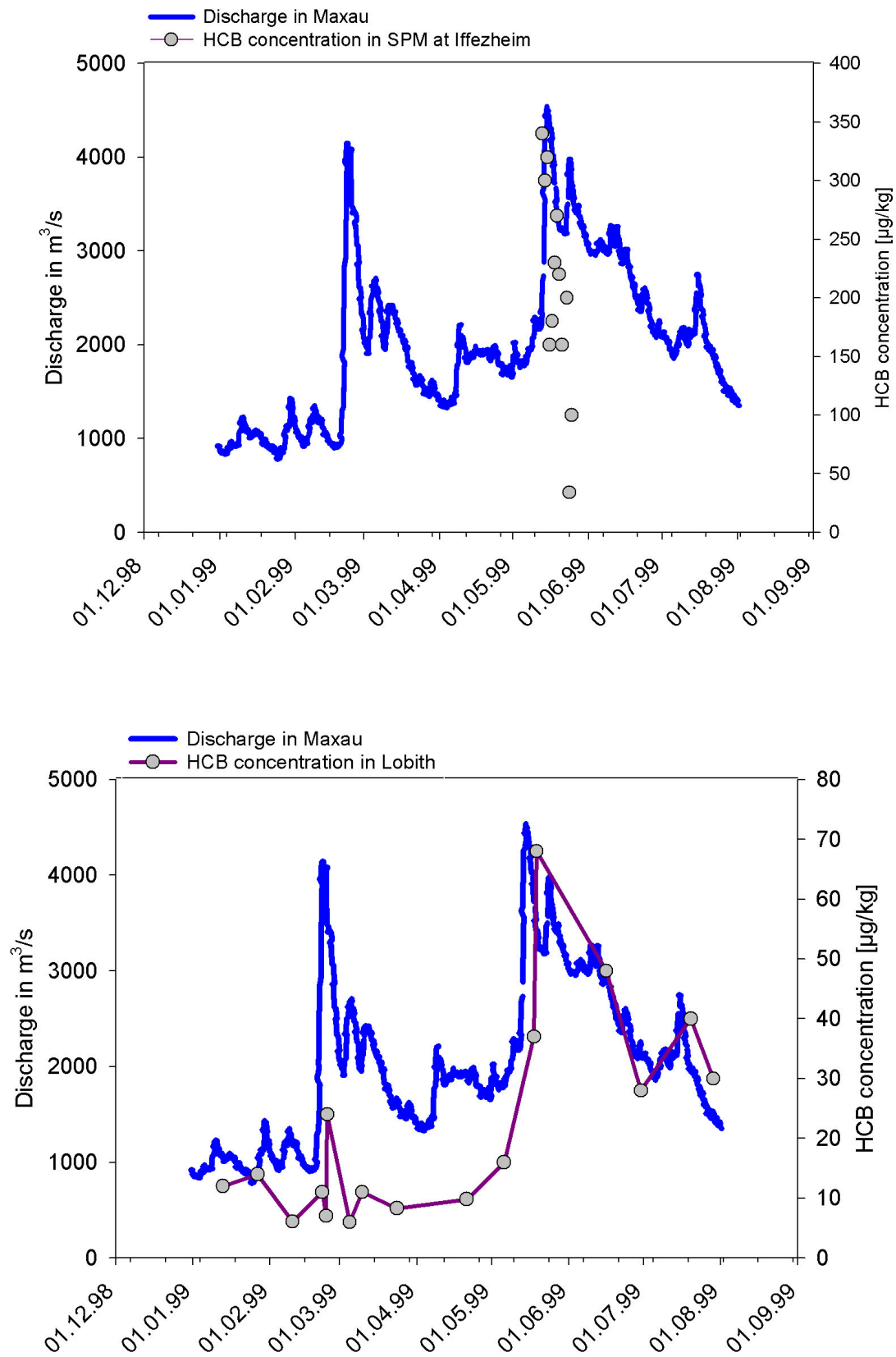


Figure 5.21 HCB concentrations in suspended matter at monitoring stations Lobith and Iffezheim and discharge during the flood event in May 99.

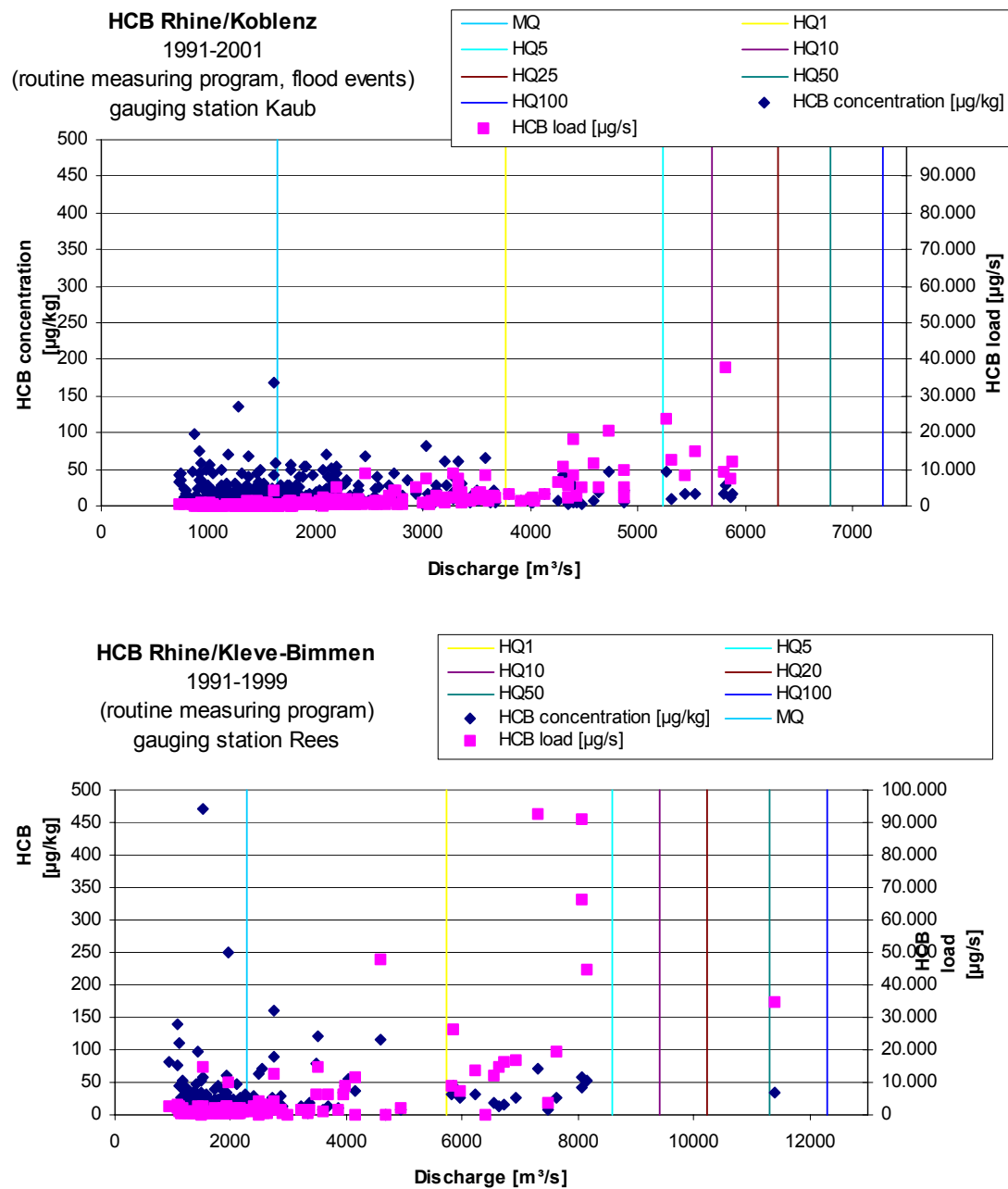


Figure 5.22 HCB concentrations in suspended matter and loads in Koblenz (upper graph, 1990 – 2001) and Kleve Bimmen (lower graph, 1990 – 1999) in relation to discharges measured at the nearest gauging stations

A comparison of load and concentration at the Rhine station in Koblenz and at Kleve-Bimmen is carried out to look for evidences that the tributary Lippe contributes to the HCB load at all (Fig. 5.22). Concentrations at Koblenz rise up to 170 $\mu\text{g/kg}$, but are usually found to stay below 100 $\mu\text{g/kg}$. At Kleve-Bimmen, however, concentrations of more than 100 $\mu\text{g/kg}$ with a peak of more than 460 $\mu\text{g/kg}$ have been frequently measured. Two explanations are possible for these high levels, which are not reflected by correspondingly high values in Koblenz: Either no measurements were carried out at Koblenz during high flood events, or the Lippe area, which is the only other substantial HCB source between Koblenz and Kleve-Bimmen, apart from smaller harbors in that region, contributes to the HCB load.

Table 5.9 Estimations of concentration and load for Cadmium and HCB for the different flood return periods at the monitoring stations of the river Rhine and its tributaries

River	Station		MQ (min/max)	HQ1 (min/max)	HQ5 (min/max)	HQ10 (min/max)	HQ20 (min/max)	HQ 50 (min/max)	HQ100 (min/max)
Rhine	Iffezheim	Cd [mg/kg]	0,25 - 0,9	0,25 - 0,9	0,25 - 0,9	0,25 - 0,9			
		Cd [mg/s]	1,2 - 35	4,0 - 170	10 - ^{*1)}	20 - ^{*1)}			
		HCB [µg/kg]	5,4 - 120 ^{*2)}	10 - 230	30 - 300	55 - 330	70 - 370		
		HCB [µg/s]	130 - 5000	400 - 48000	1600 - 75000	28000 - 420000	40000 - ^{*1)}		
Neckar	Mannheim/ Feudenheim	Cd [mg/kg]	0,43 - 2,6	0,43 - ^{*1)}					
		Cd [mg/s]	1,3 - 35	80 - 450	150 - ^{*1)}				
		HCB [µg/kg]	^{*3)} - 30						
		HCB [µg/s]	^{*3)} - 500						
Main	Bischofsheim	Cd [mg/kg]	0,6 - 1,4	0,5 - 1,1					
		Cd [mg/s]	2,0 - 20	15 - 80					
Mosel	Koblenz	Cd [mg/kg]	0,3 - 2,4	0,3 - 1,5	0,3 - ^{*1)}				
		Cd [mg/s]	0,1 - 20	60 - 200 ^{*2)}	180 - ^{*1)}				
		HCB [µg/kg]	^{*3)} - 8	^{*3)} - 8					
		HCB [µg/s]	^{*3)} - 50	^{*3)} - 400					
Rhine	Koblenz	Cd [mg/kg]	0,18 - 1,9	0,35 - 1,6	0,5 - 1,3	0,6 - 1,2			
		Cd [mg/s]	2,4 - 150	100 - 600	300 - ^{*1)}	400 - ^{*1)}			
		HCB [µg/kg]	2,5 - 170	3 - 70	8 - 50	10 - 45	10 - 45		
		HCB [µg/s]	100 - 4500	1000 - 15000	4000 - 28000	6000 - 36000	8000 - 50000		
Rhine	Bad Honnef	Cd [mg/kg]	0,18 - 2,3	0,25 - 1,7	0,35 - 1,2				
		Cd [mg/s]	3 - 350	100 - 1450	300 - ^{*1)}				
		HCB [µg/kg]	1 - 20	1,2 - 50	1,2 - ^{*1)}	1,2 - ^{*1)}	1,2 - ^{*1)}		
		HCB [µg/s]	^{*3)} - 1000	400 - 22000	1400 - ^{*1)}	17000 - ^{*1)}	1900 - ^{*1)}		
Ruhr	Essen	Cd [mg/kg]	0,44 - 54	2 - 15	2,8 - 8				
		Cd [mg/s] (total load)	1,3 - 30	50 - 320	130 - 950	200 - 1100			
		AOX [mg/kg]	250 - 11000	70 - 750	30 - 200	30 - 120			
		AOX [mg/s]	250 - 2400	1700 - 12500	5000 - ^{*1)}				
Rhine	Kleve-Bimmen	Cd [mg/kg]	0,5 - 4	0,17 - 2,3	0,3 - ^{*1)}				
		Cd [mg/s]	30 - 210	35 - 1500	350 - ^{*1)}				
		HCB [µg/kg]	1 - 250	3 - 100	10 - 60				
		HCB [µg/s]	200 - 15000	200 - 75000	5000 - ^{*1)}				

*1) estimation not possible; *2) neglect of outliers; *3) below detection limit; *4) no flood return period data available

Table 5.9 gives an overview over the ranges of concentrations and loads of HCB and cadmium in relation to the different discharge levels. In some cases it has been difficult or not possible to give exact range values for the corresponding flood return period, due to the low number of flood event measuring campaigns, the complex catchment area of the river Rhine with many tributaries as well as the variability of the flood measurements. Additional uncertainties arise as available flood event data were not measured at all monitoring station.

The available data show, however, that already relatively high concentrations of HCB occur at MQ and increase from 120 µg/kg maximum value to 370 µg/kg at HQ₂₀.

Also the load increases, meaning that the source of the material has to be at Iffezheim, because there is only little dilution and no decrease of concentration with discharge. This results in a situation where a **high quantity** of suspended matter with at the same time **increased HCB concentration** is transported downstream with rising discharge levels.

In Koblenz, the concentration decreases with discharge due to dilution with SPM that has no HCB contamination (see chapter 5.2.2). This again points to the upper barrages as the main source of HCB.

At MQ, the magnitude of load between Iffezheim and Koblenz is the same, and also the concentrations are in the same range, which could mean that there is little dilution effect under normal discharge. At the same time, it means with regard to HCB that the situation may be severe for the Port of Rotterdam under MQ conditions as only little decrease in contaminant concentration occurs along the Upper Rhine at normal, average discharge conditions.

cadmium, as compared to HCB, shows a decrease in concentration with discharge. However, as has been stated before, no measurements were recorded during flood events at Neckar and at the Main and, hence, there are not enough data available to verify the sources of this heavy metal.

Summary: on the basis of HCB and cadmium data, there is a strong indication, that sediment from the barrage Iffezheim, from the River Ruhr and possibly from the River Lippe can be resuspended, partly already at very low discharges (MQ with Iffezheim).

5.5.4 Other evidence for resuspension events

Harbors and Groynes in the Upper Rhine like Loreley, Bauhafen Worms

No data on critical erosion thresholds from the harbors or groynes in the Upper Rhine are available. However, groynes are frequently exposed to higher water currents and probably contribute material towards the suspended matter concentration. As no sediment data from groynes were available, no conclusions can be drawn, whether the exchange of sediment is so frequent, that no historic contamination accumulated or whether these can be regarded as a secondary source of contamination.

Harbours like the Bauhafen Worms and the Loreley harbour from where sediment data were made available by the Federal Institute of Hydrology (BfG), serve as shelters for yachts in case of storms and high waters. Accordingly, they will only be exposed to extreme currents to a limited extent and no contribution of locations to the contaminant load of the SPM in the Rhine can be expected (Keller, BfG, pers. Comm.).

Lower Rhine – Duisburg and Ruhr Area

Also in this area, data on erosion thresholds for the Rhine in the Ruhr Area are lacking. A good indicator for resuspension from Duisburg harbors would be dioxin measurements. These, however, have not been carried out so far.

Figure 5.23 gives an overview over the Duisburg harbour area with the highly contaminated basins "Diergardt" and "Aussenhafen".

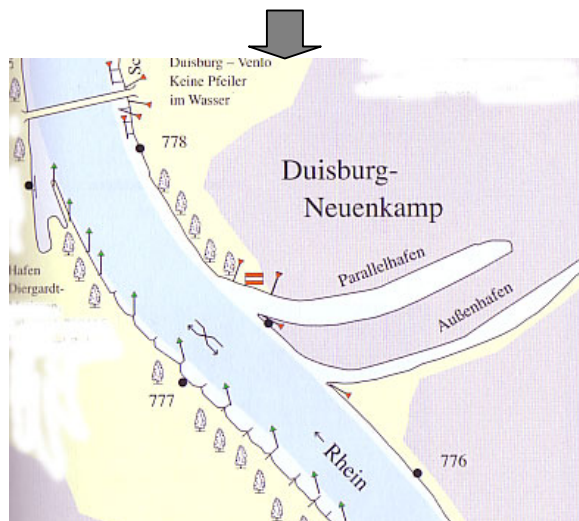
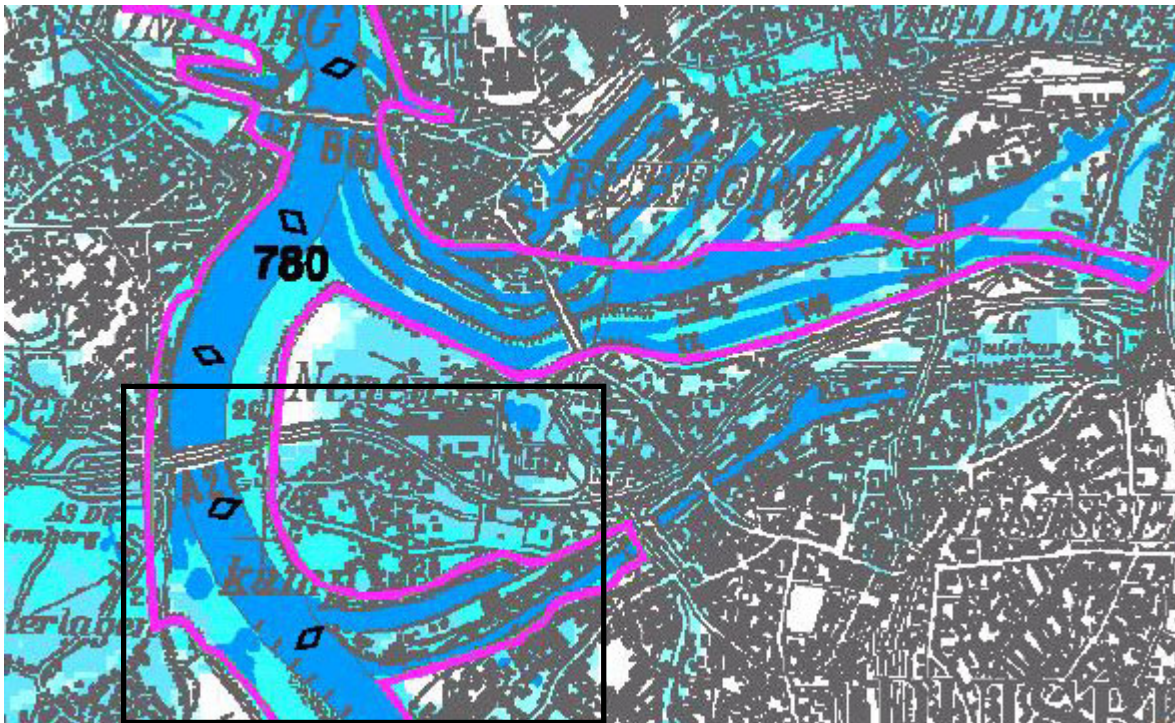


Figure 5.23 Map of Duisburg area with "Hafen Diergardt", "Parallelhafen" and "Außenhafen" (bottom figure, (Fenzl, 2003)) and the borders of the flooded area during an HQ₁₀₀, purple lines, and an HQ₁₀, green lines (ICPR, 2001)

Under high water conditions, all harbours are flooded. Whether these areas then serve exclusively as sinks of material or also as sources of SPM cannot be assessed on the available data base.

Lower Rhine – harbors, flooded quarries

To these belong e.g. Hitdorf harbour (Figure 5.24) at the confluence of the Wupper, the harbor basin Neuss, the quarry "Baggerloch Müllerhof" and others. They show high concentrations of heavy metals, HCB and PCB. Sediment samples that were taken at the Hitdorf station in 1985 during a high water showed extremely high contamination with chromium (855 mg/kg), copper (580 mg/kg), zinc (1610 mg/kg), and lead (525 mg/kg). These concentrations were exceptional, even though Hitdorf is known to be contaminated, and they were explained by the environment agency of Nordrhein-Westfalen to



Der Hafen vor Hitdorf

belong to old contaminated sediment which had been exposed through removal of newly deposited material by the high water before the sampling. (LUA, 1997). As is shown in Figure 5.24, Hitdorf Harbor is exposed to high waters and according to this experience in 1985, sediment can be resuspended.

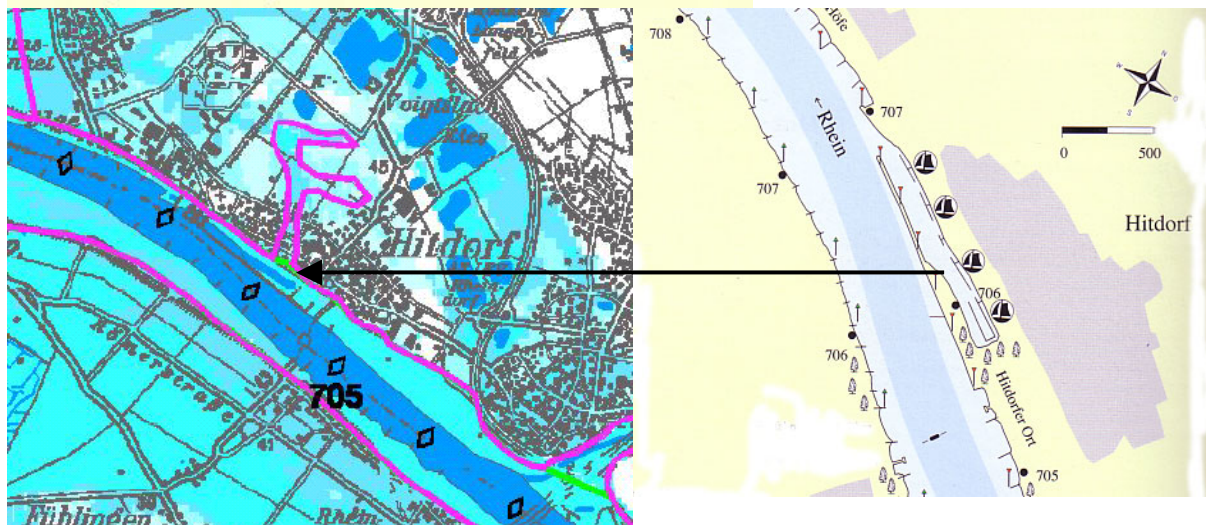


Figure 5.24 Map of Hitdorf harbour (right figure, (Fenzl, 2003)) and the borders of the flooded area during an HQ₁₀₀, purple lines, and an HQ₁₀, green lines. (ICPR, 2001). (reproduction of the maps with kind permission of the ICPR and of the Edition Maritim GmbH)

Although the contaminated basins may contribute towards the total load of contaminants, the volume of material that they could contribute is relatively small, so the risk for the Port will be limited.

Mosel

The Mosel has been shown in this study to be of concern with regard to copper, nickel, lead, zinc and PCB.

Analyzing the average annual concentrations in mg heavy metal/kg suspended matter at different monitoring stations, the high contribution by the Mosel becomes obvious. Although mainly limited to the years before 1994, average annual concentrations of all heavy metals still reached the level of the CTT in 1999 (Pb, Zn) or even exceeded it considerably (Cu and Ni). Due to the importance of diffuse sources for copper and here especially precipitation dependent processes like run-off of houses and vineyards, where copper-based compounds are applied as anti-foulings or pesticides, it is difficult to differentiate between resuspension of historic contaminated sites and increased emission of diffuse sources.

Emscher

The Emscher waters, which are highly contaminated are treated in total. The river water treatment plant has been designed to withstand an HQ₁₀₀, therefore it should be expected that no contaminants on suspended matter are emitted into the Rhine waters to a large extent.

Wupper

A comparison of the contamination pattern of the Wupper with that of the downstream areas of concern like the harbours in the lower Rhine, especially Hitdorf, show that the patterns of heavy metal loads are identical with the exception of cadmium (Table 4.8) which is not considered a substance of concern in the Wupper, but shows elevated concentrations downstream. This can indicate a transport from the Wupper towards the Rhine and its contribution of heavy metal loaded SPM.

Erft

Only few data are available for suspended matter concentration and there is little indication, that the Erft substantially contributes to the Rhine. The relatively high concentration of Cadmium in the Neuss harbour (5.8 mg/kg, total sediment) downstream of the Erft confluence could be an indication of transport of contaminated material along the Erft.

5.2 Summary – areas of risk for Rotterdam

The risk assessment for port sediments due to substances of concern (chapter 4.2) and the areas of concern (chapter 4.3) was done on the basis of information on the quantity of contamination and its resuspension and transport towards Rotterdam. Due to the lack of critical erosion data and information on sediment resuspension, indications were looked for that could hint towards resuspension processes with specific consideration of flooding events. The assessment was done with regard to “business as usual conditions” (BAU) and to different flood scenarios. As floods frequently occur in the Rhine basin and influence resuspension and transport processes, these were of special importance for the conclusions. “BAU” describe situations of average water discharges and without anthropogenic activities that could lead to resuspension of sediment.

Table 5.10 Areas of Risk in the Rhine basin and its tributaries, concluded from evidence of hazard classes of areas of concern, theoretical possibility to exceed the CTT level and indication of resuspension

(+/- no obvious effect; + small effect, ++ significant effect, +++ large effect)

no evidence of risk		risk can not be		evidence for risk		evidence for high risk	
Areas of concern	dominating hazard class	theoretical exceedance of CTT upon resuspension		indication of resuspension			Areas of risk
				hydrological situation	erosion potential	Increase in SPM load Quantity issue	
<i>chapter 4</i>	<i>chapter 4.3.2</i>	<i>chapter 5.3</i>		<i>chapter 5.2</i>	<i>chapter 5.4</i>	<i>chapter 5.4</i>	<i>chapter 5.5.</i>
Higher and Upper Rhine/ barrages	3	HCB Hg	MQ MQ	BAU	+ / -	+	
				>HQ ₁	+	+++	
				>HQ ₁₀	++		
				>HQ ₅₀	+++		
Upper and Middle Rhine / harbours e.g. Loreley	1 - 3	HCB PCB DDT Hg	MQ MQ MQ MQ	BAU	+ / -	+ / -	
				HQ ₅₀	+ / - pers. Comm	+ / - (pers. comm.)	
				HQ ₁₀₀	?	?	
Lower Rhine / Duisburg and Ruhr area	1 - 3	PAH Zn Cu Cr Hg Dioxin	MQ MQ MQ MQ MQ ¹	BAU	+ / -	?	
				HQ _?	?	?	
				HQ ₁₀₀			

¹ Dioxins haven't been considered in table 5.10 because no CTT is assigned to them. Concentrations in the Duisburg area however are high enough to present a risk for the Port of Rotterdam when resuspended.

Lower Rhine / Harbours and Flooded quarries	3	HCB	MQ	BAU	+ / -	?	
		PCB	MQ	HQ ₂	?	?	
		PAH	MQ	HQ ₁₀₀			
		Zn	MQ				
Neckar	1	Cu	MQ				
		Cr	MQ				
		Hg	MQ				
Main	3 (limited data base)			BAU	+ / -	+/-	
				HQ ₅₀	+	+	
				HQ ₁₀₀	++		
Mosel	2 – 3 (limited data base)			BAU			
				HQ ₁₀		+ (HQ1)	
				HQ ₁₀₀			
Emscher	3 (only suspended matter)			BAU	+ / -	River water treatment plant	
				HQ ₁₀			
				HQ ₁₀₀			
Wupper	3			BAU			
				HQ ₁₀		+	
				HQ ₁₀₀		+	
Ruhr	3	PAH	MQ, MHQ, HHQ	BAU	+		
				HQ ₁₀		+ (HQ1)	
				HQ ₁₀₀	+++		
Erft	3			BAU			
				HQ ₁₀			
				HQ ₁₀₀			
Lippe	2			BAU			
				HQ ₁₀		+	
				HQ ₁₀₀		+	

A certain risk was assigned only to 5 areas along the Rhine river basin of which two were assigned to the high risk class (evidence of high risk) under specific discharge conditions: the Upper Rhine area and here specifically to the sediment that has been accumulated in the barrages and the Ruhr river. For Neckar, Wupper and Lippe here was evidence for risk with higher water discharges.

The **barrages in the Upper Rhine** are the only ones, that may already present a risk during business as usual conditions: Already at normal discharges, increased concentrations of HCB have been measured in suspended matter at Iffezheim. With increasing discharges HCB (and possible mercury) becomes resuspended and transported downstream. With the continuous inflow of contaminated sediments from the barrages further South, the existing sediment disposal sites reaching their upper limits, combined with still high HCB concentrations in the sediment and significant gaps in the understanding of its transport processes, this area becomes an important challenge for future sediment management.

The **Neckar** may also represent a risk to the Port of Rotterdam: A resuspension of cadmium in the barrage Lauffen has been predicted due to its low sediment stability, and increases in cadmium

concentration in suspended sediments at this site have been measured. However, whether this load arrives at the Rhine after passing 13 more barrages, is uncertain. Data from the measuring station Feudenheim and Mannheim, the last barrage before the Neckar reaches the Rhine, cannot give any indication as no measurements were done during flood events. There is, however, no cadmium source identified in this report other than the Neckar that could be responsible for cadmium loads of more than 1000 mg/s at stations Koblenz (Rhine) and Bad Honnef, as the concentration and load data from the Main at the confluence with the Rhine are even lower than those of the Neckar.

The **Ruhr** represents a certain risk for the Port of Rotterdam at increased water discharges. High concentrations of PAHs but also of the other substances that are of concern in that river, especially cadmium, are likely to be resuspended and transported downstream. There are a number of management projects that aim at the restoration of the River, which may become of specific importance for the sediment stability and the concentration of suspended matter that is transported along the Ruhr at increased water discharge levels.

There is some indication that the **Lippe** may contribute to the HCB load in the Rhine (chapter 5.4.2) under high water situations. If the crest of the flood wave reaches the Rhine before the flood of the main river arrives, dilution of suspended matter from the Lippe may even be that low, that its contaminated suspended material could lead to an increase in the HCB concentration in the Port of Rotterdam.

The Lippe case clarifies one of the uncertainties that are immanent to this kind of studies: The heterogeneity of the flood regimes along the Rhine basin complicate general statements about risk, as it influences any dilution effects of contaminated and “clean” suspended matter to a large degree. Working with “average data” may simplify the situation to an extent where uncertainties become very high.

The evidence for a risk that originates in the **Wupper** is very indirect and derives mainly from measurements from the Hitdorf-harbour. This small harbour is influenced by Wupper effluents. It is still contaminated (area of concern class 3) and it shows all the substances that are also of concern for the Wupper area. Therefore the Wupper is assigned as an evidence of risk, although this has to be regarded with great caution.

Therefore it cannot be excluded that risks are present in the area the **Erft**, especially so, as the delayed mixing (and therewith retarded dilution) of the suspended matter of tributary and Rhine becomes more effective for the risk to Rotterdam, the nearer the tributaries are to the port.

Additional uncertainties arise from missing information on sediment stabilities e.g. from **the harbor sediments in the Lower Rhine**, and from the lack of analytical data on contaminants in sediments.

Rather than stating that there will be **areas with no risk** for the Port of Rotterdam, the conclusion can be drawn from the present report, that there are two areas, which present a high risk with high certainty: **The sediment in the barrages of the Upper Rhine and the Ruhr.**

5.7 Sediment management at the areas of concern

5.7.1 Institutional framework in water and sediment management

Due to the federal character of Germany, legal as well as administrative powers are clearly divided between the government of the Federal Republic ("Bund") and the Federal States, the "Länder". In the area of water management, the federal government can only enact framework laws, while the *Länder* are free to determine the actual structure and substance of water management within the limits set out in federal legislation (Kampa *et al.*, 2003). Water policy therefore is an area, where the authority of the *Länder* is most pronounced and this is of consequence for the institutional mechanisms for water and sediment management. The main governmental actors in the area of water management in all *Länder* at the state level are the State Ministries of the environment (*Umweltministerien*) and the State Environment Agencies (*Landesumweltämter*). For the Federal waterways, the Federal Ministry of Transport and its subordinated authorities are responsible. Maintenance and development work on Federal waterways are planned and carried out by the Federal Waterways and Shipping Administration (*Wasser-und Schifffahrtsverwaltung des Bundes WSV*). The responsibilities for the Federal Waterways are split up between the subordinate structures of the Administrations: the Waterways and Shipping Direction (*Wasser- und Schifffahrtsdirektion - WSD*) (figure 5.25).

Environmental aspects that concern the Federal Waterways are covered by the Federal Institute of Hydrology (*Bundesanstalt für Gewässerkunde – BfG*) which provides conceptual guidance and project monitoring (Köthe *et al.*, 1998). All other inland waterways are under the responsibility of the *Länder*. The State Environment Agencies carry out monitoring projects, gather data, analyse data with regard to the state of the environment but they seldom initiate sediment management projects (Figure 5.26). For example dredging projects are managed at the municipal or regional level by the competent local or regional authority (Peters & Hagner, 2001) and are not based on a common, coherent German policy, as has been elaborated in chapter 3.2.2.

Contaminated sites are dealt with on the basis of the German Soil Protection Act, which does not expressly address historical contaminated sediments. However, an indication of the efforts undertaken in this field can be seen from the investment in contaminated sites remediation, which is less than 0.03 ‰ of the gross domestic product (GDP) in Germany, whereas the respective Dutch expenditure is 1.5‰ of the GDP (Source: pilot EIONET data flow, January 2002). Handling of dredged material exhibits characteristic differences, in that the German Federal Waterways and Shipping Administration gives preference to sediment relocation (section 3.1.5), while in The Netherlands the actual focus of sediment policy and management is on subaquatic disposal (sections 3.1.6. and 3.2.1).

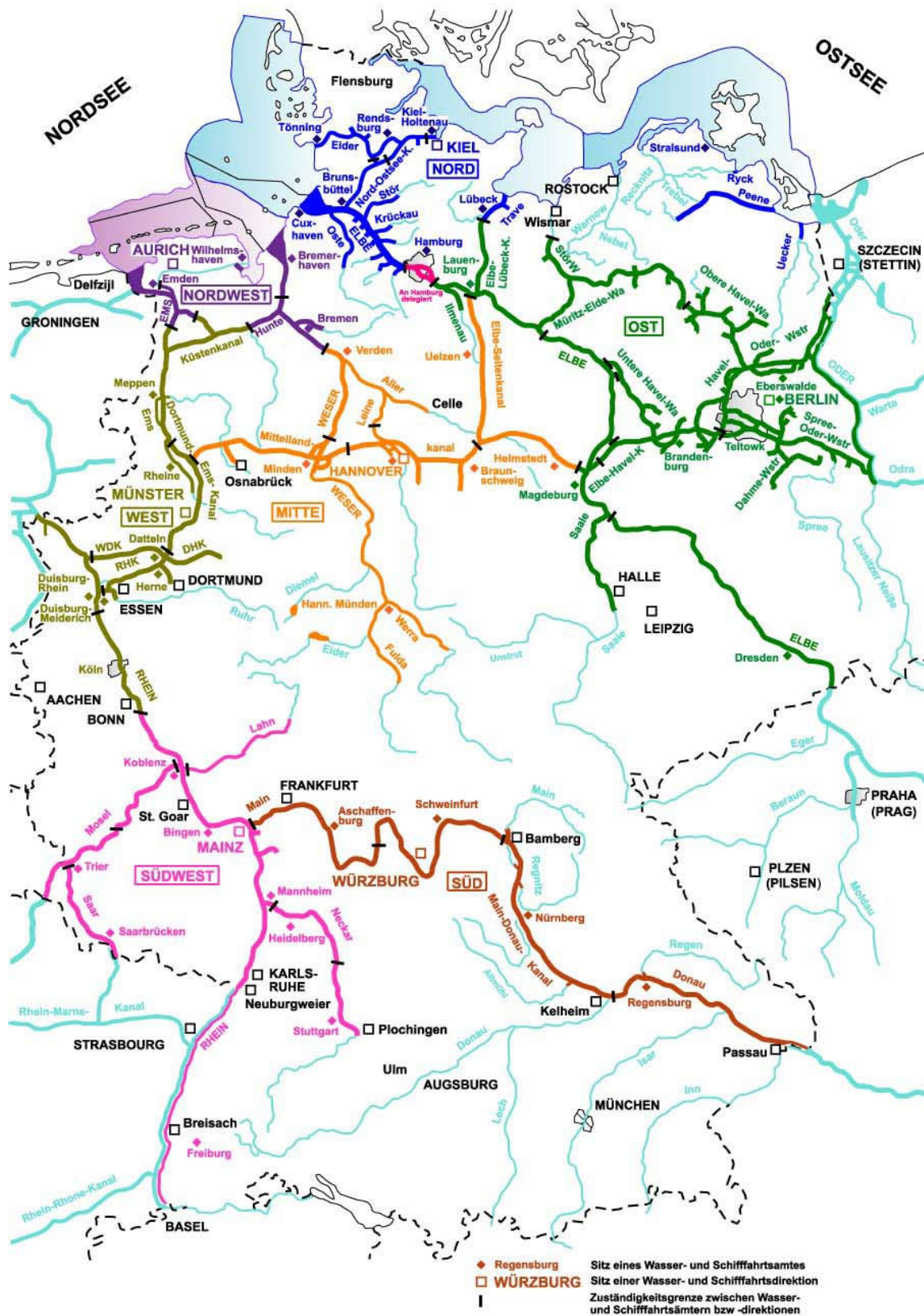


Figure 5.25 “Waterways and Shipping Directions” (WSD □) and “Waterways and Shipping offices” (WSA ◆) along the Federal Waterways in Germany

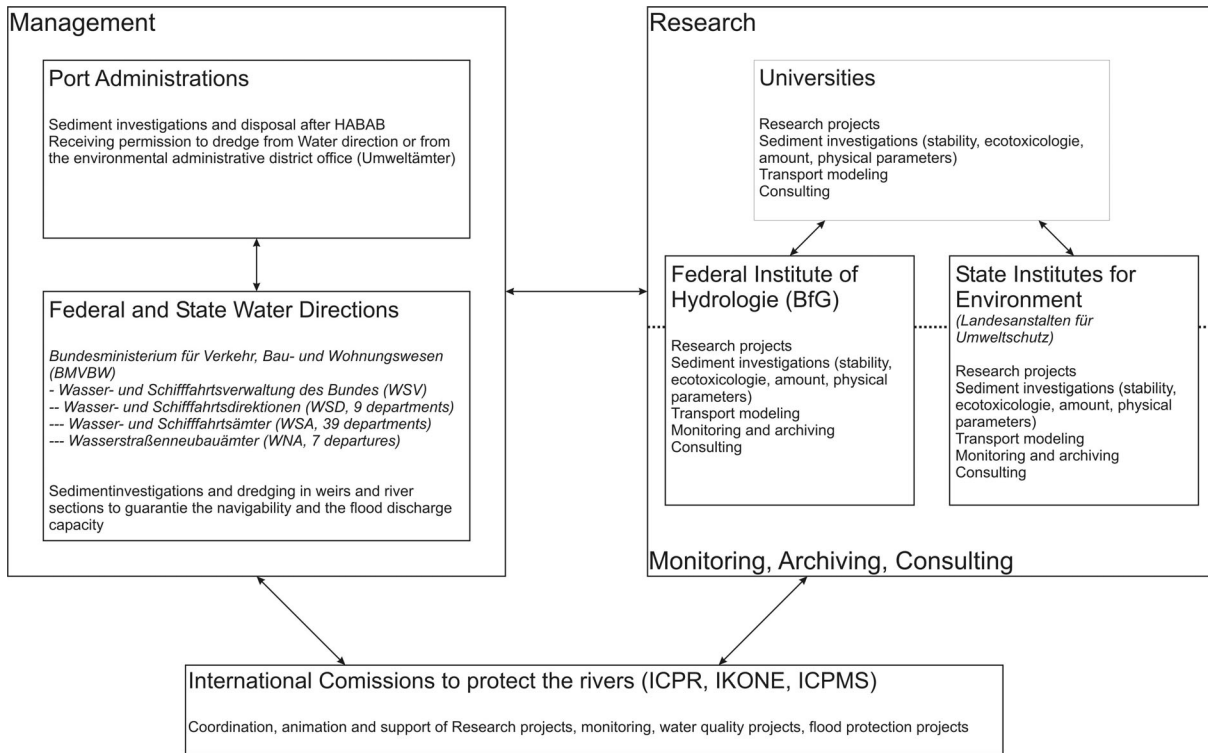


Figure 5.26 Functions and distribution of responsibilities between institutions involved in sediment management issues

5.7.2 Planned and implemented measures for areas of concern

Potential measures to reduce the risk of contaminated sediments fall into the following categories (see also (ATV-DVWK, 2003))):

- a) **reduction of emissions into the aquatic environment**
- b) **removal of contaminated material out of the hydrological cycle.**
- c) **reduction of sediment resuspension and transport of contaminated suspended matter**
- d) **reduction of *in situ* contaminant concentration**

The following will give an overview of what is being done in different areas of concern. Details on measures planned or implemented at the different areas of concern are given in Annex “measures”.

a) reductions of emissions into the aquatic environment

Most activities are done on the basis of further reduction of point sources in order to improve water quality and environmental conditions. Examples are the **Lippe** area and the **Emscher** catchment.

High TBT concentrations, that were introduced into the **Lippe** River via the Seseke as a result of an organotin –production plant with an inappropriate treatment system for its wastewater has improved significantly due to a newly developed effluent-processing system. In the Summer of 2004, the renaturation of the small river Seseke is planned. Then the treated effluents of the plant will be guided directly into the **Lippe**.

The **Emscher** is still considered a sewer of industrial effluents. However, when the subsidence stopped, that had been induced by coal-mining, it became possible to restore the **Emscher** waters by technical means. In addition to 3 large wastewater treatment plants in Dortmund, Bottrop and Dinslaken, another, smaller one was built in 2000, which clears the direct industrial effluents from a company at the Landwehrbach. Up to a discharge of 30 m³/s the whole river water is cleaned at the river water treatment plant in Dinslaken, before being introduced into the River Rhine. The sludge is incinerated totally (Dr. Piegsa, StUA Herten, personal communication). This way, an ecological improvement in the **Emscher** already started, and a long term plan has been set up to support the ecological restoration of the **Emscher** within the next 25 to 30 years (Busch *et al.*, 2001) by decreasing the volume of mine waters (Busch & Büther, 2000) and introducing pre-treatment processes of industrial effluents.

b) removal of contaminated material out of the hydrological cycle

This is the most frequently applied measure to limit the exposure of contaminated sites. Removal of sediment can be initiated by environmental concerns (remediation dredging) or by economical pressures, e.g. if the navigational depth has to be secured or the water discharge of a hydropower

plant has to be guaranteed. Several projects have been realized in the Rhine catchment area, that aim at separating dredged contaminated material from the river regime. The different options that have been applied in sediment management in the River basin are:

Disposal of dredged material in gravel pits:

Knöpp suggested the disposal of sand and silt with consolidating properties in subaqueous gravel pits that have a connection with the river (Knöpp, 1989). Under the premises that after a fast consolidation all water flow within the material stops, anaerobic conditions are facilitated and leaching processes reduced. The subaqueous disposal has the advantage that the material is not exposed to quickly changing environmental conditions like temperature, humidity, acid rain. The measure is comparatively cost-efficient, no land is used and it bears the potential to create wetlands.

Disposal in separated river zones:

At the Hengsteysee at the Ruhr, an area of the impounded lake was blocked off the river by a dam from coarse material. Accumulated fine sediment from the lake was flushed into this area and clogged the pores of the dam within 1 to 2 days. No leaching of heavy metals could be detected. However, no future agricultural usage was recommended (ATV-DVWK, 2003).

Subaquatic disposal in a confined site:

Examples are the IJsseloo project in the Ketelmeer and the "Slufter" in Rotterdam (chapter 3.5.2). In the aqueous surrounding, in case of the IJsseloo project directly inside the Ketelmeer, a ring-shaped dam is constructed from uncontaminated material and filled with dredged material. The water surface inside the pit is kept at a level that is lower than outside in order to prevent efflux of contaminants into the surface or groundwater.

Disposal on terrestrial flushing fields:

Heavy metal and PAH-contaminated sediments from the Hartkortsee in the Ruhr were removed and flushed on two 11 hectares large flushing fields outside of the high water retention areas (Knotte & Brinkmann, 2002).

c) reduction of sediment resuspension and transport of contaminated suspended matter.

The probability of sediment resuspension and its exposure to the environment can be reduced by providing a protective layer on top of the sediment (capping). No evidence of measures that primarily focus on the reduction of sediment resuspension has been gained.

However, measures like restoration of rivers that comprise reduction of flow velocity, realignment of dikes combined with the formation of new retention fields, remediation of flood plains and protective measures against the formation of high flood events, like the "Ruhrauenprogramm", the "Lippeauenprogramm", and the "integrated Rhine programme" of the LfU will all add to reduction of sediment resuspension.

Transport of contaminated suspended matter can be reduced by providing settling basins, in which sediment is trapped and contaminants are kept out of the hydrodynamic cycle, or by storing sediment away from the main current if it has to be removed. Examples for these are the River **Ruhr** with a

number of settling basins (chapter 4.5), which were built with the purpose of self-purification, but which now serve as recreational sites for the Ruhr area. It is planned to classify the Ruhr River as “heavily modified water body” according to the WFD, and to change the hydromorphological regime to achieve a good ecological status. This will comprise reducing the effects of the impounding lakes, increasing the current velocity and during that process to dredge the heavy metal contaminated material from the bottom of the lakes.

Another example is the **barrage Iffezheim**. Fine-grained materials, contaminated predominantly with HCB, accumulate at the barrage. Hydraulic structures (moles) were built that serve as confined aquatic disposal sites and also reduce the aggradation. In near future, however, a problem will arise, because there will be a need for new dredging, but the containment at Iffezheim is almost filled. In parallel to plans for building a new disposal site within the river downstream, *in situ* research activities have been started to study the sediment transport and the behaviour of HCB in sediments and suspended matter (Köthe, 2000).

d) reduction of *in situ* contaminant concentration

In situ remediation is usually restricted to those sediments, that contain a limited number of contaminants which can be specifically targeted by organisms. Hence, only one example for *in situ* contaminant reduction was found: A BMBF funded project dealt with biological and chemical stabilisation of contaminated sediment at the Oberhafen in Frankfurt (Main). The aim was to apply a combination of aeration (venting) using the potential of aerobic degradation of the autochthonous microbes and to introduce an oxidising agent (H_2O_2) for the chemical elimination of more persistent organic substances. All organic parameters showed reduction in the sediment after a remediation period of 12 months. PAHs were reduced by stimulating biological degradation in the sediment (Thomas, C.A.U. GmbH, pers. communication).

Challenges in the remediation of historical contamination:

For example the Wupper: The Wupper still has a high contaminant load, which derives mainly from the urban area of Wuppertal, but also partly from upstream where historic contaminated sediments but probably also new emissions increase the contaminant load. The complex situation of having a variety of small and smaller industrial plants, about 17000 sites which are suspected of being contaminated, and an old canalization system in the city, renders any measures fruitless. Sediments of the 2 impounding reservoirs upstream of Wuppertal are potentially flushed out during high water. The small backwater reservoirs certainly will (Lacombe StUA Düsseldorf, pers. communication). Still no realistic possibility to reduce the immissions in the Rhine by the Wupper is envisaged.

5.8 References Chapter 5

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6. Summary and Conclusions

6.1. Identification of areas of risk in the Rhine catchment area and its tributaries for the Port of Rotterdam due to historic contamination

After extensive reduction of emissions by point sources (industrial and municipal) along the Rhine as a consequence of the Action Program "Rhine" of the ICPR and other initiatives like the Rhine Research Project of the Port of Rotterdam, those sediments now gain in importance, which had been contaminated in the past and accumulated in areas of low water current. The relative contribution of these sediments to the exceedance of regulatory concentration limits for relocation will increase. Non-compliance with the required chemical criteria demands expensive disposal options. The concern with regard to historical contaminated sites is, that their contribution to port sediment contamination may continue on an undetermined time frame: Their exact location and extent is often unknown and once found the sites have to be managed, unless consolidation processes prevent resuspension effectively.

In the present report, the risk for the Port of Rotterdam due to those historical contaminated sites is assessed. This risk addresses the probability that sediment in the Eastern part of the port may be contaminated above current sea/Slufter threshold values, regulated by the Dutch "Chemistry –Toxicity Tests (CTT)-levels", due to resuspension processes upstream. Exceedance of the CTT-values not only increases the ecological risk, but leads to cost-intensive actions as this material has to be disposed in a contained disposal facility (the Slufter) rather than be relocated at the North Sea.

A three step approach with a classification after each step was used to approach this risk:

6.1.1 Identification and classification of SUBSTANCES OF CONCERN

Substances of concern in this report	Hazard classes
Cadmium (Cd)	2
Chromium (Cr)	1
Copper (Cu)	1
Mercury (Hg)	2
Nickel (Ni)	1
Lead (Pb)	1
Zinc (Zn)	1
DDT+DDD+DDE (SUM)	2
Dioxins and Furans	2
Hexachlorobenzene	2
Polycyclic aromatic hydrocarbons	2
Polychlorinated biphenyls	2
Tributyltin	1

Table 6.1 Substances of concern

Table 6.1 depicts those substances, which were addressed in this study, and the hazard classes that were assigned to them depending on their chemical persistence, their partitioning to sediment and their environmental risk.

Heavy metals, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), DDT and its metabolic products DDD and DDE, as well as hexachlorobenzene (HCB) were discussed in this study because they frequently exceed

the Dutch "Chemistry –Toxicity Tests (CTT)-concentrations" in suspended matter, measured in Brieneoord at the entrance to the Port of Rotterdam. The organic substances were assigned to hazard class 2 because of their strong partitioning to sediment and their long half-lives of more than 10 years in sediment. Of the heavy metals, cadmium and mercury were assigned to hazard class 2 because of their high toxicity and bioaccumulative potential.

Tributyltin (TBT) was chosen because the world's largest TBT producing company is located in the Rhine catchment area. TBT was classified as hazard class 1, because it shows a shorter half life (less than 10 years) and lower affinity to sediments compared to the other organic contaminants.

Dioxins and furans are not intentionally manufactured but are produced as by-products in combustion processes. They are not addressed in the CTT-list so far, but would be if the dioxin-specific bioassay "DR-calux assay" were integrated which is under discussion. Dioxins and furans adsorb strongly to sediment and show very low rates of degradation or transformation. Accordingly, they were assigned as hazard class 2.

The following substances were discussed for inclusion but eventually omitted:

Insecticides like γ -HCH, aldrine, dieldrine, and endrine, which were part of the former *Uniform Content Test* list, are not part of the CTT list anymore because of their permanently low sediment concentrations. Due to their effect on insect metabolism they may also affect the amphipod test (*Corophium volutator*) that has been discussed as one of the bioassays that may be included in 2 years time. However, no data on concentration of these compounds were available and, hence, no areas of concern identifiable. EDTA/NTA were discussed and omitted, because studies confirm that under environmental conditions, no significantly enhanced remobilization of heavy metals from sediments occurs due to these kind of substances.

6.1.2 Identification and classification of AREAS OF CONCERN

Areas were defined to be of concern, if surface sediment data exceeded the CTT levels for sediment in Rotterdam. The classification into four classes, differing in the extent of risk and the degree of uncertainty, was based on

- the confidence in the sediment data for the specific area (e.g. only one sample taken as compared to frequent sampling over years),
- the extent of contamination and
- the hazard class of those substances that exceeded the CTT thresholds.

Information on known historical emissions was then used to validate and check the data for comprehensiveness.

The classification resulted in



Class 0 – low hazard or no hazard identified

Class 1 – there is indication for a potential hazard

Class 2 – there is indication for a potentially high hazard

Class 3 – there is high certainty that a high hazard is present.

All together 12 areas of concern were identified as potentially hazardous. Table 6.2 lists the “areas of concern” together with the hazard classes (HC) that characterized the locations. If the sediment samples from an area, such as a tributary, were assigned mostly to one class, this one is depicted as the dominant class in that area in table 6.2. If locations were classified differently, the range (e.g. 1-3) is indicated.

Table 6.2 Areas of concern and their main contaminating compounds in sediments 
( no measurements or only single data on organic substances)

Areas of concern		HC	Cd	Cr	Cu	Hg	Ni	Pb	Zn	DDT DDD DDE	Sum Dioxin Furan	HCB	Sum PAH	Sum PCB	TBT
High and Upper Rhine	Barrages	3													
Upper and Middle Rhine	Harbors e.g. Loreley	1-3													
Lower Rhine	Duisburg harbours	1-3													
	Harbors, flooded quarries	3													
Tributaries	Neckar	1													
	Main	3													
	Mosel	2-3													
	Emsch.	3													
	Wupp.	3													
	Ruhr	3													
	Erft	3													
	Lippe	2													

The contaminant pattern that derives from table 6.2 depends on:

- the historical emissions, and
- the dynamic of the system, and
- the amount of data, that forms the basis of these results.

Similar contamination patterns in unconnected tributaries can be caused by similar economical situations, such as similar industries influencing the sediment quality. Comparing the Mosel, Wupper and the Erft, which are all areas under direct (Erft, Wupper) or indirect (Mosel via Saar) influence of the mining industry, all sediments are contaminated with nickel, lead and zinc. Exceptions are Ruhr

and Neckar which show a similar pattern, having cadmium, copper and PCBs accumulated in the sediments despite differing industrial activities in these areas.

Similar patterns are also caused by transport of contaminants with sediment or suspended matter downstream, as it is the case with the locations from the barrages at the High Rhine till the harbors in the Middle Rhine such as Loreley and Worms Bauhafen. All show mercury, DDT and hexachlorobenzene contamination.

Also the Wupper and the harbors in the Lower Rhine, like Hitdorf and the Duisburg harbors, share a similar pattern. The harbors are all located downstream of the confluence of the Wupper and especially Hitdorf is known to be affected by the tributary's effluents.

6.1.3 Identification and classification of AREAS OF RISK

The risk assessment for the Rotterdam port sediments due to those "substances of concern" that could derive from the identified "areas of concern" required estimating resuspension, transport probabilities and determination of transported quantities. Business as Usual (BAU) conditions were considered, when discharges are average and no anthropogenic activities cause suspension of sediments. As floods frequently occur in the main river and its tributaries, the final assessment of "areas of risk" also had to take into account the impact of increasing discharge levels. These are characterized according to the frequency of their occurrence: An average annual flood is described as HQ1, whereby a high water situation, which occurs statistically only once in a hundred years, is called HQ100 (Table 6.3).

The different aspects were regarded as separate lines of evidence, from which at the end the final conclusions were drawn, depicted in Table 6.3.

According to the amount of evidence that was seen, the areas of concern were categorized as follows:





	no evidence of risk
	presence of risks can not exluded
	evidence for risk
	evidence for high risk

Table 6.3 Areas of Risk in the Rhine basin and its tributaries

areas of concern	Flood scenario	Areas of risk
chapter 4		chapter 5
Higher and Upper Rhine/ barrages	BAU >HQ1	
Upper and Middle Rhine / harbours e.g. Loreley	BAU >HQ50	
Lower Rhine / Duisburg and Ruhr area	BAU >HQ?	
Lower Rhine / Harbours and Flooded quarries	BAU >HQ?	
Neckar	BAU >HQ1	
Main	BAU >HQ50	
Mosel	BAU >HQ10	
Emscher	BAU >HQ100	
Wupper	BAU >HQ10	
Ruhr	BAU >HQ10 >HQ100	
Erft	BAU >HQ10	
Lippe	BAU HQ10	

Areas presenting a high risk with high certainty:

Barrages in the Higher and Upper Rhine with respect to HCB. There are indications that even under business as usual conditions, when there is normal discharge and no management activity, HCB is transported downstream from Iffezheim at concentrations, that may already have an effect on the sediment quality in Rotterdam.

The Ruhr River. The sediment in the Ruhr is relatively easy to resuspend, leading to a potential transport of PAHs and cadmium downstream.

Areas with evidence of risk:

The Neckar may represent a risk. High cadmium concentrations, especially in Lauffen, have frequently been reported. Whether this material can be transported downstream into the Rhine is not clear, as the measuring station in Feudenheim did not gather data during flood events. However, load calculations point to a considerable Cadmium input from the Neckar to the Rhine.

The Wupper shows a wide spectrum of contaminants, which is reflected by the small harbors downstream of the confluence. Although no data on resuspension of material is available, this is taken as a potential risky area during flood conditions.

The Lippe shows an increased level of HCB in sediments, which may not be able to contribute substantially to the contaminant load in Rotterdam if the flood waves merge. If the crest of the Lippe wave reaches the mouth of the river earlier, there will be a risk, due to the relatively short distance between the Lippe and the Port of Rotterdam.

Most other tributaries (**Mosel, Main, Erft**) are difficult to assess due to lack of data. Mostly the erosion threshold values are missing, which are needed for these kinds of assessments. These values would help verifying whether the sediment **from harbors along the (Upper, Middle and Lower) Rhine including the harbour basins in Duisburg** only act as sink, as is suspected, or under what circumstances these sediments can be resuspended into the River.

The only certain water body with no risk is the **Emscher**, of which the water is completely treated in a river treatment plant before release into the Rhine.

6.1.4 Risk influencing dynamic processes

In most cases flood events lead to resuspension of historical contaminated sites, as they are usually covered by younger and mostly less contaminated material. There is no proportional relationship between the discharge and remobilisation of historic contamination, as sometimes the top layer has to be swept away before the newly exposed, older material can become resuspended. Occurrence of suspended particulate matter at relatively low quantities with at the same time high contamination at the end of a series of flood waves can hence be considered a good indication that here a historic site has contributed to the contaminant load of the river.

The highest risk for the Port of Rotterdam derives from those sites, which lead to an increase in contaminant concentration in suspended particulate matter (above CTT) **and** in the transported load, meaning that a large amount of suspended matter is transported downstream and will (partly) settle in the Eastern part of the port **and** the concentration is high enough to exceed the sea/Slufter threshold. This risk decreases with the distance from the Port and if the site is located within a tributary – both due to dilution effects.

However, dilution effects depend very much on the interaction between the different flood waves that flow down the Rhine and its tributaries:

- The risk increases, if the flood wave of a tributary, transporting contaminated material, reaches the confluence to the main river before the flood wave of the Rhine does. If, additionally, the distance to the Port is short, contaminants can be carried along the Lower and Delta Rhine at high concentrations. This is probably the reason for the high hexachlorobenzene (HCB) and cadmium concentrations that were measured in Kleve Bimmen at relatively low total Rhine discharge: Possibly flood waves of the Ruhr (cadmium) and of the Lippe (HCB) had discharged into the Rhine and experienced relatively low dilution effects due to a late Rhine flood wave.
- The risk increases, if the flood wave is restricted to the limited area upstream, and hence normal discharges in the tributaries downstream do not lead to dilution of the upstream resuspended material. This situation can take place during spring and early summer, when snow melting increases the discharge of the Higher and Upper Rhine and exposes HCB contaminated material in the barrages. Like in May 1999, contaminants in the Southern Part of the Rhine become transported downstream without much mixing with incoming flood waves from the tributaries. Consequently, an increase in HCB concentration in suspended matter, that exceeded the sea/Slufter-values three times, was observed at Lobith subsequently to the high water in May 1999.
- The highest risk exists, if the concentration in suspended matter is increased without any dilution by a flood wave. Any anthropogenic resuspension by e.g. dredging activities, that erodes contaminated material extensively without the immediate dilution of a flood wave will raise the risk that the CTT values in the Eastern Part of the Port of Rotterdam will become too high and the sediment will not be suited for relocation into the North Sea anymore.

6.2. Requirements on Sediment Data Quality

The use of particulate matter as an assessment medium has several advantages, at least compared to the water phase, mainly due to the high sensitivity to low levels of contamination and the medium to low sample contamination risk. However, considering the complex system of a large river basin and the novelty of the present approach, a closer look was necessary both with respect to state-of-the-art of quality control and quality assurance in these water quality assessment procedures and specifically to quality requirements in relation to chemical, biological and hydraulic sediment data.

For both erosion risk and chemical mobilization risk studies the chains of comparison are broken at early stages of sampling and sample preparation (traceability concept). Sampling of flood-plain soils and sediments is affected by strong granulometric and compositional heterogeneities arising from the wide spectrum of flow velocities at which the sediments were eroded, transported and deposited. These heterogeneities can be reduced by subsequent normalization procedures; however, the overall comparability of the samples will be significantly lower than in the applications for surveillance and monitoring tasks, respectively.

With regard to the biological risk assessment, because of the shortcomings of each assessment technique, the best choice to identify potential impacts towards the environment, would be an integrated approach as suggested by Chapman et al. (1997), in which the information from sediment chemistry, toxicity and resident community alterations are combined and collectively assessed with regard to the overall risk (sediment "Triad" approach).

The applied concept to use hydrological and hydraulic data facilitates to quantify the uncertainty of the eroded sediment mass by statistical terms. When calculating the mass of contaminated sediments released by flood events the spatial variability of the erosion related sediment parameters and the associated particulate concentration of sediments, especially with sediment depth must be taken into account. The variability of both the physical and chemical parameters with depth has shown to be much larger than the horizontal variability. Consequently, the statistical range of results for the resuspension of contaminated sediments will be considerably high in reality. The more processes are involved on the pathway along the river course towards the Port of Rotterdam the higher the variance of the transport quantities involved and the larger the gap between the best and worst case assumption for the sediment management at the downstream end.

6.3. Historical Contaminated Sediments under the European Water Framework Directive

A main objective of the Water Framework Directive (WFD) is to achieve good ecological or good ecological potential and chemical status for each water body. A further objective of the WFD is the "no deterioration" requirement. These objectives need to be taken into account when assessing the different sources/pathways. It is interesting to see that while sediments and dredged materials are not

explicitly mentioned in the WFD they will play an important role in the forthcoming steps for the implementation of measures against pollution from priority [hazardous] substances under WFD Article 16 – monitoring programmes to be operational (Article 8, 2006) and establishment of the programme of measures (Article 11, 2009).

In the implementation of measures against priority substances, already in the first phase, "historical contaminated sediments", are listed under "sources/pathway", together with a few substances, including hexachlorobenzene and cadmium, with some indication, that these could end up at category 1 (may lead to a risk of failing to meet the objectives of WFD). More data is needed, particularly with regard to the significance of this source in comparison with traditional sources like sewage effluents. However, specific information for this question can not be expected from "whole water" analyses, the only relevant matrix for compliance checking of the environmental quality standard for the priority substances other than metals.

As recommended by the Scientific Committee on Toxicity, Ecotoxicity and Environment (CSTEE, adopted at the plenary meeting of 28 May 2004) monitoring programmes for lipophilic substances should be focussed on biota (and possible sediment). As the number of chemicals selected as priority substances is very limited, the CSTEE strongly recommend producing the required ecotoxicological information for supporting sound quality standards at least for these substances.

6.4. Sustainable Sediment Management at the Catchment Level

The focus of the present study is directed to potential effects at the catchment level, that could influence the interface between Rhine Catchment Area and North Sea, which has been in the focus of the Rhine Research Project II study. In a wider societal context, the main issue is the "achievement of 'hydro solidarity' within the basin, i.e. a full upstream/downstream integration of monitoring, stakeholder consultation, models and expert systems that can link basin pressures to transfers, across various administrative and/or political boundaries, and between the various land users, water users and other stakeholders" (Salomons, 2004).

In summary, many studies have dealt with isolated events on sediment transport and this is well described in the literature. However, validated models for the Rhine catchment seem to be lacking let alone an application of these models to isolated contaminated areas in the Rhine catchment. To fill in this gap will require a massive effort, in particular with regard to obtaining field data and monitoring data sufficient for validating this kind of model. In this respect European research is needed, in particular since the phenomenon of the legacy of past contamination in sediments and waste dumps is not restricted to the Rhine catchments but occurs in other European regions as well. As such the "worst care approach" taken in this study appears currently to be the Best Available Technique for a first order risk assessment of contaminated sites in river catchments.

With regard to future risk assessment and communication in the framework of sustainable sediment management (SSM), some of the steps in a site prioritization process have been taken in this report:

The identification of areas of concern in combination with evaluation of resuspension, transport phenomena and the distance of the sites from the Port of Rotterdam results in a site prioritization, that indicates what areas of concern need to be addressed in the first place and where management options should be favored. A risk assessment at the prioritized site could make use again of the hazard classes of compounds, integrating them into the risk ranking. This risk ranking should eventually be undertaken on the basis of chemical, ecotoxicological and ecological aspects in order to identify the minimally disturbing – with regard to the environment - maximally efficient management option. The management option is carried out to fulfill the management objective such as the reduction of the contamination level in the Port of Rotterdam.

List of abbreviations

AbfKlärV	Ordinance on Sewage Sludge (<i>Klärschlammverordnung</i>)
ABWAG	Waste Water Charges Act (<i>Abwasserabgabengesetz</i>)
AEs	Assimilation Efficiencies
AHP	Analytic Hierarchy Process
ALARA	As Far As Reasonably Achievable
α -HCH	α -Hexachlorocyclohexan
AMPS	Analysis and monitoring of priority substances
a.o.c.	Areas of concern (this report)
a.o.r.	Areas of risk (this report)
AQC	Analytical quality control
ARGE Elbe	Working Group of the Elbe (<i>Arbeitsgemeinschaft zur Reinhaltung der Elbe</i>)
ATV	German Association for Water Pollution Control (<i>Abwassertechnische Vereinigung</i> ; see ATV-DVWK)
AVS/ Σ SEM	Acid Volatile Sulfide/Sum Simultaneously Extractable Metals
BBodSchG	Federal Soil Protection and Contaminated Site Act
BBodSchV	Federal Soil Protection and Contaminated Site Ordinance
BimSchG	Federal Immission Control Act (<i>Bundesimmissionsschutzgesetz</i>)
BCR	Community Bureau of References (EC)
BEBA	Biological effects-based sediment quality assessments
BAT	Best Available Techniques
BfG	Federal Institute of Hydrology (<i>Bundesanstalt für Gewässerkunde</i> , Koblenz)
BLAK QZ	German federal working group on quality targets
BNatSchG	Federal Nature Conservation Act (<i>Bundesnaturschutzgesetz</i>)
BRCs	Background Reference Concentrations
CBM	Conceptual river basin model
CDFs	Confined disposal facilities
CDM	Contaminated Dredged Material
CEDA	Central Dredging Association
CIS	Common Implementation Strategy
COSMOS	Contaminant and Sediment Transport Modelling System
CSS	Combined sewer system
CSTEE	Scientific committee on toxicity, ecotoxicity and the environment
CTM-SUBIEFF	Contamination Transport Module (French Transport Model)
CTT	Chemistry-Toxicity Test (The Netherlands)
CUWVO	Commission for the implementation of the Act on Pollution of surface waters (The Netherlands)
DGE-1	Dutch-German Exchange on Dredged Material, Part 1
DM	Dredged materials
DMAF	Dredged Material Assessment Framework
DOC	Dissolved organic carbon
DVWK	jetzt ATV-DVWK: German Association for Water, Wastewater and Waste
EAF	Expert Advirsoy Forum
ECJ	European Court of Justice
EDA	Effect Directed Analysis
EDTA	Ethylenediaminetetraacetic acid

EPS	Extracellular polymer substances
EQSs	Environmental Quality Standards
ERA	Ecological risk assessment
EROMOB	mobiles Erosionstestgerät
FCV	Final Chronic Value
FIAM	Free-ion activity model
γ -HCH	γ -Hexachlorocyclohexan
HABAB-WSV	Directive for the Handling of Dredged Material on Federal Waterways (Inland)
HABAK-WSV	Directive for the Handling of Dredged Material on Federal Waterways (Coast)
HCB	Hexachlorobenzene
HC _C	Hazard Class of Compounds (this report)
HC _S	Hazard Class of Sites (this report)
HELCON	Convention on the Protection of the Marine Environment of the Baltic Sea Area (Helsinki Convention)
ICES	International Council for the Exploration of the Sea
ICPR	International Commission for the Protection of the Rhine
IKSR	Internationale Kommission zum Schutz des Rheins
IMO	International Maritime Organization
IRMM	Institute for Reference Material and Measurements (EC)
IPPC	Integrated Pollution Prevention Control
IUPAC	International Union of Applied Chemistry
JAMP	Joint Assessment and Monitoring Programme
K _{ow}	Partitioning between n-octanol and water
KrW-/AbfG	Closed Substance Cycle and Waste Management Act (<i>Kreislaufwirtschafts- und Abfallgesetz</i>)
K _{tw}	Partitioning between water and triglycerides in organisms
LAWA	Länder Expert Group on Water (Germany)
LC	London Convention
LCA	Life cycle analysis
LfU	Landesanstalt für Umweltschutz Baden-Württemberg
LOE	Line of evidence
LUA	Landesumweltamt Nordrhein-Westfalen
MCA	Multi criteria analysis
METHA	Mechanical separation of harbour sediments
Metropolis	Metrology in Support of Precautionary Sciences and Sustainable Development Policies
NGO	Non Governmental Organisation
NOEC	No Observable Effect Concentration
NTA	Nitrolotriacetic acid
NW4	Vierde Nota Waterhuishouding; Forth Policy Document on Water Management
OCP1s	Organo Chloro PesticidesDDT, Deldrins, HCB, lindane
OSPARCON	Convention for the Protection of the Marine Environment of the North-East Atlantic (Oslo and Paris Convention)
PAHs	Polycyclic Aromatic Hydrocarbons
PCBs	Polychlorinated Biphenyls
PIANC	Permanent International Navigation Association
POSW	Dutch Development Program for Treatment Processes for Contaminated Sediments

QSAR	Quantitative structure-activity relationships
QsS	Quality Standards
RIKZ	Rijksinstituut voor Kust en Zee; National Institute for Coastal and Marine Management
RIZA	Rijksinstituut voor Integraal Zoetwaterbeheer en Afvalwaterbehandeling; Institute for Inland Water Management and Waste Water Treatment
RM	Reference Material
RWS	Rijkswaterstaat; Directorate General for Public Works and Water
SAR	Structure-activity relationships
SEDCIA	Sediment Erosion Detection by Computer aided Image Analysis
SEDYMO	BMBF-Verbundprogramm: Feinsedimentdynamik und Schadstoffmobilität in Fließgewässern
SETEG	Pressure duct for the study of depth dependant erosion stability of aquatic sediments (<i>Strömungskanal zur Ermittlung der tiefenabhängigen Erosionsstabilität von Gewässersedimenten</i>)
s.o.c.	Substances of concern (this report)
SQGs	Sediment quality guidelines
SPM	Suspended particulate matter
SQC	Sediment quality criteria
ΣHC	Sum hydrocarbons
TA-Abfall	Technical Directive on Waste Disposal
TBT	Tributyltin
TIE	Toxicity Identity Evaluation
TRIAD	Combined Sediment analysis (Sediment chemistry, sediment toxicity, resident community alterations)
TU	Toxic units
UCT	Uniform content test
UBA	Umweltbundesamt; Federal Environmental Agency
UNEP	United Nations Environmental Programme
UNESCO	United Nations
UQC	Uniform Quality Criteria; Uniforme Gehalte Toets (UGT)
US-EPA	Environmental Protection Agency of the United States
VROM	Ministerie van Volkshuisvesting, Ruimtelijke Ordening en Milieubeheer; Ministry of Housing, Spatial Planning and the Environment
WaStrG	Federal Waterway Act (<i>Bundeswasserstraßengesetz</i>)
WBB	Soil Protection Act
WFD	Water Framework Directive
WHG	Water Management Act (<i>Wasserhaushaltsgesetz</i>)
WHO	World Health Organization
WM	Environmental Management Act (NL)
WOE	Weight of evidence
WVO	Pollution of Surface Waters Act Freshwater (NL)
WVZ	Pollution of Surface Waters Act Seawater (NL)
WWTP	Wastewater treatment plant

List of boxes

Bioavailability – Limitations and Empirical Relationships (Dickson et al., 1994).....	14
Processes Controlling the Pollutants Mobility in Sub-Aquatic Depots of Dredged Material.....	23
Water Framework Directive (WFD) and Priority [Hazardous] Substances (PS/PHS).....	33
Analysis and Monitoring of Solid Matrices under the Water Framework Directive (Report of the Expert Group on Analysis and Monitoring of Priority Substances).....	36
Recommendations of the AMPS Drafting Group on Sediment Monitoring (06/2004).....	38
Opinion of the scientific committee on toxicity, ecotoxicity and the environment (CSTEE) on „The Setting of Environmental Quality Standards for the Priority Substances included in Annex X of Directive 2000/60/EC in Accordance with Article 16 thereof“, 28 May 2004.....	45
Differences between Dutch and German Regulations Concerning Sediment Quality.....	62
ICPR - Recommendation to the Criteria for the Relocation of Dredged Material into the Rhine and its Tributaries (Document Ssed 06-04=No. 89=PLEN 40/97).....	65
Priority Substances in Historical Contaminated Sediments as Possible Secondary Sources for Releases to the Aquatic Environment – WFD Article 16 “Measures”.....	87
Recommendations of SedNet WG 5 “Risk Management and Communication”.....	81
Die subaquatische Unterbringung von Baggergut in den Niederlanden (DEPOTEC 2002)	93

List of tables

ES1	Substances of concern and their ranking	II
1.1	Processes Affecting the Cycling of Pollutants in Aquatic Systems.....	5
1.2	Examples for Empirical Relationships in Bioavailability (Dickson et al., 1994).....	14
1.3	Demobilization of Pollutants in Solid Matrices by Natural Factors (Förstner 2003).....	17
1.4	Selected options for in-situ sediment remediation (after Joziasse and Van der Gun 2000; the original version comprises more than 20 technological concepts).....	19
1.5	Technology types for sediment remediation (Anonymous 1994).....	20
2.1	Objectives and aims of water quality assessment operations (Meybeck et al. 1992)....	28
2.2	increasing levels of monitoring sophistication (after Thomas and Meybeck, 1992).....	29
2.3	Some possible sources of errors in the water quality assessment process with special reference to chemical methods (Meybeck et al. 1992).....	32
2.4	for trend monitoring in sediment and or biota. P = preferred matrix over water phase, O= optional matrix).....	38
2.5	Overview on traceability aspects of chemical sediment analysis (Förstner 2004)	39
3.1	Criteria for the decision of relocation according to HABAB-WSV.....	71
3.2	NL-classification of effects in bioassays in the Triad approach 1).....	80
3.3	Ecotoxicological criteria for the CTT test for evaluation of dredged marine sediment....	82
3.4	Examples of Substances for further Assessment on Historically Contaminated Sediments.....	87
4.1	« substances of concern » with limit values according to CTT, and target values according to ICPR.....	109
4.2	Persistent organic pollutants (POPs), priority hazardous substances (WFD), priority substances (OSPAR) are depicted by grey cells. Substances of concern in this report are shown, assigned to different risk classes.	105
4.3	Organic substances of concern with the assigned hazard classes (Hazard Class Compound HC _c) due to their chemical properties.....	110
4.4	Potential industrial sources of heavy metals of concern in the Rhine area from 1985 to 1996.....	118
4.5	Potential industrial sources of organic substances of concern in the Rhine area.....	119
4.6	Estimations of likelihood of dioxin and furan releases to water from certain sources (Quass et al., 2000).....	133
4.7	Toxicity classes at different sampling locations in the Middle and Lower Rhine in 1996	148
4.8	Areas of concern and their main contaminating compounds in sediments	151
5.1	Hydrological data of gauging stations along the Rhine River and selected tributaries ...	162
5.2	Sediment stability in the headwaters of the Upper Rhine and major tributaries.....	168
5.3	Erosion risk in reservoirs along the Rhine.....	169
5.4	Flow rates of the Rhine and its tributaries at three different flood scenarios. Assigned are theoretical SPM concentrations in order to calculate the suspended matter load in the Rhine basin.....	173
5.5	Target concentrations above which a potential increase in the sediment concentration in PoR occurs under conditions of MQ.....	174
5.6	Target concentrations above which a potential increase in the sediment concentration in PoR occurs under conditions of MHQ.....	175
5.7	Target concentrations above which a potential increase in the sediment concentration in PoR occurs under conditions of HHQ.....	176

5.8	Comparison of the calculated concentration thresholds for exceedance of the CTT at the PoR at two high water scenarios A and B with the sediment surface concentrations that were measured at the Lippe.....	180
5.9	Estimations of concentration and load for the different flood return periods at the monitoring stations of the river Rhine and its tributaries.....	191
5.10	Areas of risk in the Rhine basin and its tributaries, concluded from evidence of hazard classes of areas of concern, theoretical possibility to exceed the CTT level, and indication of resuspension.	197
6.1	Substances of concern in this report.....	207
6.2	Areas of concern and their main contaminating compounds	209
6.3	Areas of risk in the Rhine basin and its tributaries.....	211

List of figures

ES.1	Pathways and processes for the transport of historic contamination downstream.	I
1.1	Scientific Disciplines and Study Objects in a Coordinated Research Programme of the German Federal Ministry of Education and Research, 2002-2006, on Fine Sediment Dynamics and Pollutant Mobility in Rivers (SEDYMO; Förstner 2001)	6
1.2	Implication of irreversible adsorption on sediment quality criteria (after Chen et al. 2000)	18
2.1	Sources of pollutants to sediments and the associated appropriate sampling operations for surveys of particulate pollutants (Thomas and Meybeck, 1992)	30
2.2	Sediment „Triad“ approach	46
2.3	Origin and transmission of uncertainties	50
2.4	Coping with uncertainties	51
2.5	Sampling site at the River Neckar	52
2.6	Sensitivity analysis	53
2.7	Calculated sediment mass eroded by historical flood events with variation of critical erosion shear stress from 2 to 10 N/m ²	54
2.8	Hydrograph of two selected historical flood events with different flood volume	55
2.9	Quantile of calculated sediment mass eroded during flood event 1998 with a peak flow rate of 1055 m ³ /s: (a) $\tau_{c,E}$ spatially constant and (b) $\tau_{c,E}$ spatially varied	55
2.10	HCB content of sediment from different sampling sites in the upper river Rhine reservoir Iffezheim (Witt 2004)	57
3.1	Overview over the interactions of national and international regulations (PORII, 2001)	62
3.2	Sources and Pathways of Contaminants in River Basins	95
3.3	Percentage of suspended solids flux discharged in 2% of time (Ms ²) vs log of basin area (km ²). (Meybeck et al. 2004b)	96
4.1	Schematic illustration of redistribution of certain organochlorine compounds based on their partitioning coefficients among air, water, and solids and the influence of temperature (Iwata, 1994)	109
4.2	Hazard classes for the areas of concern along the River Rhine	116
4.3	Cd in the clay fraction of sediments in the Rhine and its main tributaries in Germany (from Förstner & Müller, 1974)	120
4.4	Cadmium concentrations along the right Rhine side in the years 1980, 1985, 1988, and 1994 (LUA, 1997)	122
4.5	Cr in the clay fraction of sediments in the Rhine and its main tributaries in Germany (from Förstner & Müller, 1974)	123
4.6	Cu in the clay fraction of sediments in the Rhine and its main tributaries in Germany (from Förstner & Müller, 1974)	124
4.7	Hg in the clay fraction of sediments in the Rhine and its main tributaries in Germany (from Förstner & Müller, 1974)	125
4.8	Pb and Zn in the clay fraction of sediments in the Rhine and its main tributaries in Germany (from Förstner & Müller, 1974)	126
4.9	Ni in the clay fraction of sediments in the Rhine and its main tributaries in Germany (from Förstner & Müller, 1974)	127
4.10	Average PCB concentration in suspended matter (Busch & Büther, 2000)	129
411	Sum PCB (PCB 28, PCB 52, PCB 101, PCB 118, PCB 138, PCB 153) in the rhine	130

	between Königswinter and Rotterdam in 1995. (modified from ICPR, 1995)	
4.12	TBT concentrations in Lippe sediments between 1994 and 2003 in µg/kg (Data: LUA)	131
4.13	Balance of heavy metal load in the Ruhr River catchment area in 1980 (Imhoff et al. 1980) and in 1996 (Imhoff et al. 1996)	134
4.14	Ruhr catchment area	135
4.15	Heavy metal concentrations in sediments of the Harkortsee. Sediment depth is dated from 1945 to 1998 (Rosenbaum-Mertens, 2003)	136
4.16	Zn input/output balance of the Harkotsee 1965 and 1980	137
4.17	Progress lines and frequency distribution of discharges, Cd, and Pb concentrations for 2001	138
4.18	Upper Part of the River Rhine, beginning at Lake Constance	139
4.19	HCB in filtrated Rhine water taken at Rhine-km 163,9 which is very close to Basel	140
4.20	Contamination of eels in River rhine caught between Rhine-km 53 and 307 in the years 1979-2000	141
4.21	Flow chart for the production of chlorosilanes; the mass streams containing HCB are indicated	142
4.22	Treatment of the residue from the synthesis of chlorosilanes	142
4.23	Discharged HCB loads to River Rhine by a company in D-Rheinfelden from 1982 – 1993; from discharged water a flow proportional taken 24h-composite sample has been daily analysed for HCB	143
4.24	Frequency distribution of discharged HCB-loads from daily 24 h-composite samples which have been taken and analysed by a company in D-Rheinfelden	144
4.25	Results of sediment samples in River Rhine taken between Rhein-km 3 and 359 in the period 1982 - 1998	145
4.26	Sampling stations of the BfG survey along the High and Upper Rhine river in 2001	146
4.27	Toxicity in bacterial contact assay with Bacillus cereus measured in surface and core sediments along the High and Upper Rhine in 2001	147
4.28	Toxicity classes for sediments of the Middle and Lower Rhine, sampled in 1996, based on 5 bioassays and an integrated assessment of the response pattern	148
5.1	HCB concentrations of suspended matter at Koblenz / Rhine between 1991 and 1997 (BfG, 1997)	157
5.2	PCB concentrations of suspended matter at Koblenz / Rhine between 1991 and 1997 (BfG, 1997)	157
5.3	Suspended solids and copper concentrations on SPM at monitoring station Koblenz/Rhine in 1995, compared to the discharge at the time of sampling.	158
5.4	River Rhine discharges	159
5.5	Flood wave along the Rhine during the high water event in spring 1995 (BfG 1996)	160
5.6	change of discharge with time at the Lower Rhine in 1999 (gauging station Köln/Rhine), based on daily discharge measurements of the BfG	161
5.7	Hydrographs from the Rhine monitoring stations during the February flood in 1999	161
5.8	Flood event in May 1999: Discharges at different monitoring stations.	163
5.9	Suspended matter concentration 1994 to 2001 at the monitoring station Koblenz at the Rhine (right) and the Mosel (left) (Data: LUA)	164
5.10	Suspended matter concentration in mg/L in the Rhine and its lowland tributaries (Data: LUA)	165
5.11	Loads of suspended matter in rhine, Neckar, Main, Lahn and Mosel during high water between January 22 nd and February 12 th 1995 (BfG, 1996)	166

5.12	Suspended matter load along the Rhine during High Water in February 1999	166
5.13	Assumptions of the case study to assess the risk for the port that is represented by substances of concern.	171
5.14	Average annual concentration in mg/kg suspended matter at different monitoring stations and ICPR target value (1 mg/kg)	182
5.15	Cd load at monitoring stations along the river Rhine	182
5.16	Discharge and Cd concentration for the hydrological year 1999 (Ruhrverband 2000)	183
5.17	Cd concentrations and loads at the routine measuring stations Hattingen and Rees, depicted depending on the discharge. Vertically, the different flood return periods are indicated.	184
5.18	HCB concentrations in suspended matter of the Rhine near Iffezheim (90 percentile) (source: LUA 2003)	185
5.19	HCB Load at monitoring stations along the river Rhine during the spring flood event in 1999	186
5.20	HCB concentrations and loads at the routine measuring station Maxau depicted depending on the discharge. Vertically, the different flood return periods are indicated.	187
5.21	HCB concentrations at monitoring stations Lobith and Iffezheim after the flood event in May 1999.	188
5.22	HCB concentrations and loads in Koblenz (upper graph 1990-2001) and Kleve Bimmen (lower graph, 1990-1999) in relation to discharges measured at the nearest gauging stations	189
5.23	Map of Duisburg area with "Hafen Diergardt", "Parallelhafen" and "Aussenhafen" (bottom figure) and the borders of the flooded area during an HQ ₁₀₀ , purple lines, and an HQ ₁₀ , green lines (ICPR, 2001).	194
5.24	Map of Hitdorf harbour (right) and the borders of the flooded area during an HQ ₁₀₀ , purple lines, and an HQ ₁₀ , green lines (ICPR, 2001).	195
5.25	Waterways and Shipping Directions and Offices along the German Federal waterways	201
5.26	Functions and distributions of responsibilities between German institutions involved in sediment management	202

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ANNEXE

Annex 1: Assessment framework for relocation of dredged material in marine waters in the Netherlands

Annex 2 Samples, contaminations and assigned hazard classes that were the basis for this report

Annex 3 Industrial sites in the „Ruhrgebiet“ (Ruhr area) in Germany in 1970

Annex 4 Overview over available recording data from the monitoring stations.

Annex 5 Additional information on measures planned or implemented in areas of concern

Annex 1: Assessment framework for relocation of dredged material in marine waters in the Netherlands

Chemistry Toxicity Tests

Substance name	Group	Unit	Criterion ³	Signal value ⁵
Amphipod <i>C. volutator</i>	Combination toxicity	Mortality (%)		50
Microtox SP, Bacteria <i>V. Fisheri</i>	Combination toxicity	Bioluminescence (1/EC ₅₀) ¹		100
DR-CALUX cell-line	Dioxine-type	ng TEQ/kg dw		50
Tributyltin	Organometal	µg Sn/kg dw	100-250 ⁴	
Copper ²	Metal	mg/kg dw	60	
Arsenic ²	Metal	mg/kg dw	29	
Cadmium	Metal	mg/kg dw	4	
Mercury	Metal	mg/kg dw	1.2	
Chromium ²	Metal	mg/kg dw	120	
Zinc ²	Metal	mg/kg dw	365	
Nickel	Metal	mg/kg dw	45	
Lead	Metal	mg/kg dw	110	
Sum 10-PAH	PAH	mg/kg dw	8	
Hexachlorobenzene	Pesticide	µg/kg dw	20	
Sum DDT/DDD/DDE	Pesticide	µg/kg dw	20	
Mineral oil C10-40 ²	Oil	mg/kg dw	1250	
Sum 7-PCB	PCB	µg/kg dw	100	

1. EC₅₀ corrected for fraction of fine silt.

2. On these parameters the 50%-rule applies.

3. The criteria are upper levels, with the exception of the parameters where the 50%-rule applies for which exceedence of the criteria with a maximum of 50% is allowed for one or two parameters.

4. For tributyltin a range in criteria is used. Within this range the actual criterion is determined for individual permits for relocation of dredged material in marine waters.

5. Exceedence of a signal value will not lead to disqualification.

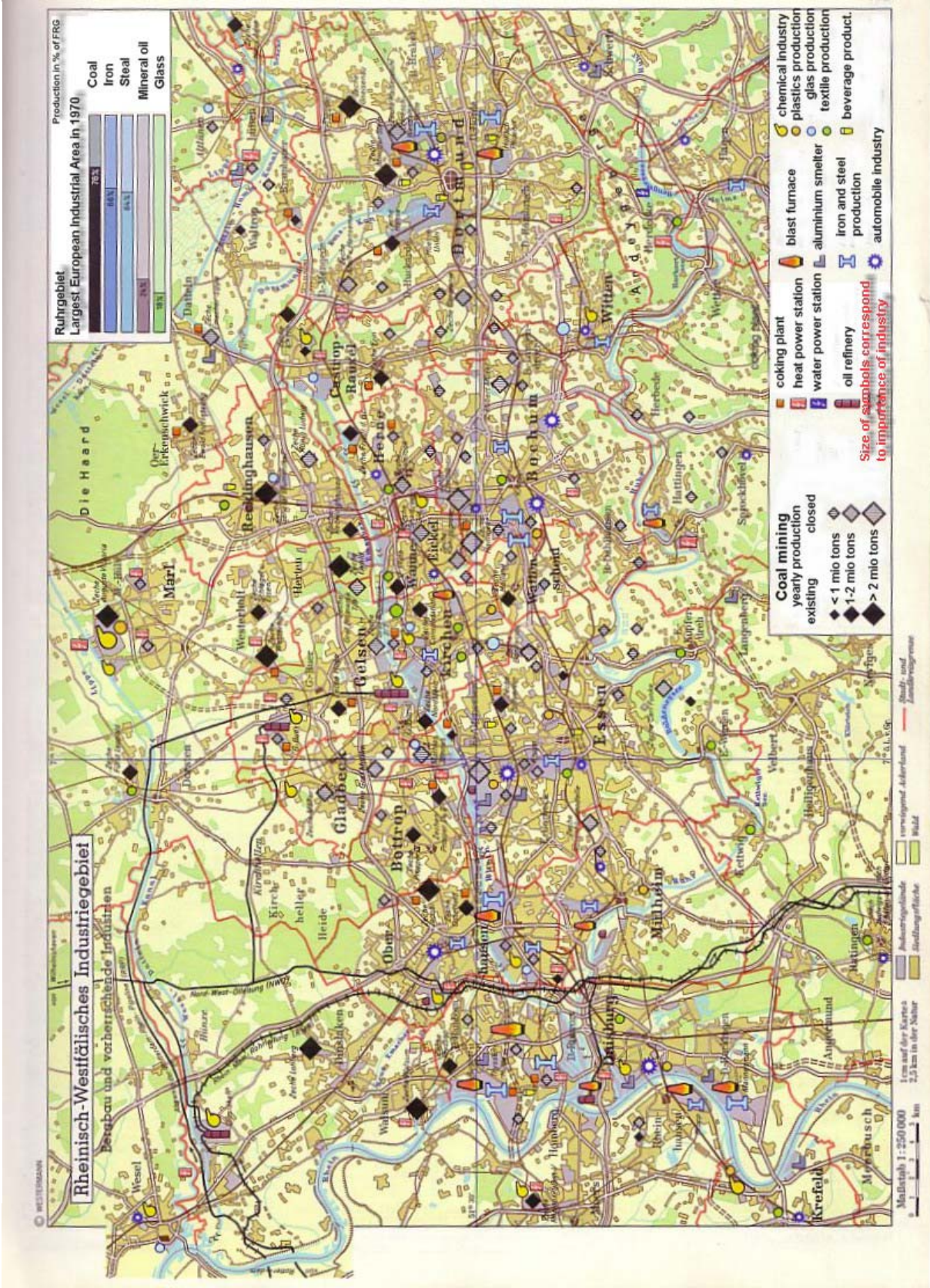
Annex 2 - Samples, contaminations and assigned hazard classes that were the basis for this report

HAZARD	Ort	Mess-stelle	River km	Zn	Cd	Cu	Cr	Hg	Pb	Ni	PCB	PAH	SumDDT+DDD+DDE	HCb	Dieldrin	dioxins
3	Marokolsheim					100		4,2						3000,00		
3	Iffezheim					60				60				600,00		
0	Neckar	Feudenheim, unterer Vorhafen der Schleuse		105,4	1,2452	24,64	41,14			12,1						
1		Kochendorf		217,0		55,18	80,6			32,24						
3		Lauffen, Stauhaltung		709,9	18,3535	193,688	366,289		134,332	63,261	170,7					
3	Rhein	August	155,00											2500,00		
2		Birsfelden	163,00											44,00		
2		Märkt	174,00											106,00		
2		Vogelgrün	223,70											250,00		
2		Burkheim	234,30											82,50		
2		Weisweil	249,00											130,00		
2		Rhinau	256,00							10,58				250,00		
2		Gerstheim	288,00											190,00		
2		Straßburg	283,40											356,00		
3		Kehl	297,30			63,9		1,98	142,416	49,5	341			21,00		
3		Gambsheim	308,00	672,5		70,219							113	470,00		
2		Fort Louis	328,35			40,35								90,00		
2		Iffezheim	333,00			55,106				32,596				180,70		
2		Karlsruhe	359,90			33,158				25,1685				80,00		
3		Germersheim	384,40			27,636				46	110			900,00		
2		Speyer	399,40			59,024				48,552				65,00		
2		Speyer Flosshafen	400,40			34,17				26,52				109,00		
2		Altrip	416,95					1,8145		43,93			69	53,00		
3		Bellenkrappen	422,30			91,68				43,505				370,00		
1		Mannheim (Mündung Neckar)	426,50			60,636				63,57						
2		Worms	443,20													
2		Bauhafen	443,00			30,96		0,612						60,00		
3	Binnenhäfen	Loreley	555,00	448,5	2,82	111,75		3,3225	112,5	46,5	211	9,17	60	460,00		
1		Ehrenbreitstein	591,00	475,0		79,56			94,38	48,36				106,00		
1	Neckar	MA-Feudenheim	8,30			72,303				46,95						
0		Schwabenheim	18,10			26,78										
0		Neckargmünd	30,90			38,124				30,1815						
1		Neckarsteinach	39,70			51,392				38,72						
1		Hirschhorn	48,00			58,646				41,3						
1		Eberbach	56,97			86,13										
1		Rockenau	61,60			58,743										
1		Guttenbach	73,70			60,828										
1		Neckarzimmern	86,10			74				48						
2		Gundelsheim	94,10		36	119				52	212		29			
1		Kochendorf	104,10			83,42				39,56		8,90				
1		Heilbronn	111,45			77,22				37,44						
1		Horkheim	118,00			56,625				36,24						
1		Lauffen	125,50			66,385				39,831						
1		Besigheim	137,05			102,5685				41,622						
1		Hessigheim	143,60			50,481				28,755						
1		Pleidelsheim	150,60			69,048				46,032						
1		Poppenweiler	165,40			98,78										
1		Aldingen	172,30			97				46						
2		Hofen	177,00			75,696				44,688	209					
2		Cannstadt	183,00			92,872		2,679		41,971	99					
1		Untertürkheim	186,90			72				43,2						
1		Obertürkheim	190,00			53,586										
1		Esslingen	195,60			67,536				45,024						

Annex 2 - Samples, contaminations and assigned hazard classes that were the basis for this report

[illegible]

Annex 3: Industrial sites in the „Ruhrgebiet“ (Ruhr area) in Germany in 1970



Annex 4: overview over available recording data from the monitoring stations.

Pollutant		Discharge		Measuring period	Flood event data	Flood return period
Monitoring station	Source	Gauging station	Source			
Iffezheim, Rhine	LfU data base	Maxau	LfU data base Gewässerkundliches Jahrbuch	1993 - 2000	LfU Gütebericht	LfU - Regionalisierung
Mannheim/Feudenheim, Neckar	LfU data base	Rockenau	Gewässerkundliches Jahrbuch	1992 - 2000	LfU Bericht	LfU - Regionalisierung
Bischofsheim, Main	HLUG	Raunheim	BfG HYDABA1 data base	1999 - 2002	-	-
Koblenz, Mosel	BfG - IKSR data base	Cochem	BfG Gewässerkundliches Jahrbuch	1991 - 2001	-	Gewässerkundliches Jahrbuch, BfG Mittelungen Nr. 10
Koblenz, Rhine	BfG - IKSR data base	Kaub	Gewässerkundliches Jahrbuch	1991 - 2001	04/94, 02/97, 2/99	Gewässerkundliches Jahrbuch, BfG Mittelungen Nr. 10
Bad Honnef, Rhine	LUA data base	Andernach	Gewässerkundliches Jahrbuch	1993 - 2003	02/99	LUA - Regionalisierung
Essen, Rhur	Ruhrverband	Hattingen	Ruhrverband	1994 - 2003	daily measured	Ruhrverband
Kleve-Bimmen, Rhine	LUA data base	Rees	Gewässerkundliches Jahrbuch	1991 - 1999	02/99	LUA -Regionalisierung

Annex 5: Additional information on measures planned or implemented in areas of concern

Iffezheim – HCB-contamination

The following methods have been investigated as potential alternatives to the current containment of HCB contaminated material at the Iffezheim barrage (BfG, 2003):

- a) Intermediate storage of dredged material in the existing mole of the barrage or in a hydraulic structure downstream, which would have to be constructed. The idea was to store the material until the HCB concentration became reduced by natural degradation and then flush it into the Rhine current. It was decided, that too many unknown factors like HCB half life and depth-dependency of degradation would make the applicability of this option questionable.
- b) Disposal of dredged material in gravel pits of the vicinity. This measure was assumed to be relatively cheap. The possibility of HCB desorption with consequent groundwater contamination was put into question. Extensive licensing would be required for this measurement with dubious chances of success.
- c) Usage of HCB contaminated material as covering layer of potash spoil dumps. This option was regarded as having an environmental risk due to the unknown extent of remobilisation of HCB and to be very expensive due to high costs of treatment and transport of the material.
- d) Land disposal: existing soil protection values for HCB are much higher than the highest measured concentrations in dredged material in Iffezheim (4000 µg/kg on playing grounds), so that land disposal would be an option, if suitable areas were available. A necessary purchase of grounds would make the process lengthy. Before storage, the dredged material would have to be treated, adding costs of transport and processing to the measure.
- e) As a short-termed solution, 330.000 m³ sediment were dredged from the barrage and flushed into the still water zone below the spur-jetty of the barrage between summer 2000 and March 2001.

Investigations were carried out, whether the HCB concentration in the sediment would prevent extensive flushing of sediment from the barrage into the Rhine. This was primarily not an option, because the HCB concentration in the dredged material in Iffezheim (55 – 1700 µg/kg dw in the dredging area with an average value of 300-350 µg/kg) was much too high to comply with the relocation criteria of the HABAB-WSV and the ICPR values. They do not allow relocation if contaminant concentration in the dredged material exceeds more than three times the concentration in suspended matter in the planned relocation area, which in this case were 35 µg HCB/kg in Lauterbourg and 30 µg HCB/kg in the surface water at Iffezheim. Discussion about this option started when investigations showed, that HCB in Iffezheim does not bind to 90 % to the <20 µm grain size fraction but is enriched in the 60 to 200 µm fraction, leading to modification in the interpretation of the HABAB.

Ruhr River

The Ruhr river provides a good example of integrated water resources management in Germany, facilitated by the "Ruhrverband" (Ruhr River Association for water quality management). The association has been founded 80 years ago by the Prussian State and is nowadays a self-governing public body, controlled by the Ministry of the Environment of the State of North Rhine Westphalia. It has the function to secure and develop a functional water supply and wastewater disposal infrastructure. In total, the wastewater load of 3.6 million population equivalents bein contained in a volume of 400 mio m³/a(?) wastewater is treated in the Ruhrverband's 84 treatment plants. The tasks are divided between the communities and the Ruhrverband. The communities are responsible for the construction and operation of the sewage systems up to a location where a wastewater treatment plant can be constructed. After that, the Ruhrverband takes over. Associates of the Ruhrverband are, by compulsory membership, all those who benefit from the activities of the association, in particular the communities, manufacturers and other enterprises who contribute to the pollution of the Ruhr River and its tributaries, as well as the water works. Unhampered by political borders, the Ruhrverband could set up a system-wide management, which has the potential of balancing and minimizing costs (Bode *et al.*, 2003). In the coming years, a number of wastewater treatment plants, that do not fulfill current technical standards, will be modified and modernized, and partly combined (Essen-Kettwig, Essen-Rellinghausen, Essen-Steele, Essen-Burgaltendorf, (LUA, 2002)). As purification is done by the wastewater treatment plants, the impounded lakes now only have a minor function for removal of heavy metals from the system (Podraza, 2000). In the scope of the WFD, the following objectives for the Ruhr River are discussed which mainly aim at reducing effects of the impoundments on the lower Ruhr River, thus possibly influencing sediment dynamics to a different extent – depending on the eventually chosen scenario (Podraza, 2000)

- a) Increase of flow velocity, and reduction of flow residence time. The flow residence time in the lower Ruhr River is assessed as 7.25 days compared to 2 hours flow time under natural conditions.
- b) Restoration of a continuous stream without back-waters, meaning that impounded lakes would have to be abandoned or their volumes reduced, and weirs would have to be replaced by artificial riffle sections.

Accompanying measures could be the removal by bank fixation, planting of alluvial forest, grove or wood. In her report on the Ruhr River as an example for Heavy Modified Water Bodies in the frame of the WFD, Dr. Podraza emphasizes that removal of heavy metal contaminated dredged material from the river and especially the lakes will be a necessary measure. Remediation dredging in this respect could perhaps compensate for the increased flow velocity, which would also increase the shear stress on the sediment.

GAP and flood protection

Restoration of the Ruhr River is also part of the "Gewässerauenprogramm" of the Ministry of the Environment of Nordrhein-Westfalen (NRW), which has been founded in 1990 and aims at the restoration of larger rivers in Nordrhein-Westfalen from source to mouth. The idea behind it is the support of a natural development of formerly intensively used and modified regions along the rivers. Consequently, usage of areas along the riverbanks will become restricted or even completely terminated (other word).

Due to the usual stabile riverbank constructions, increased discharges lead to strong erosion with depth. Allowing areas next to the river to turn into flood plains will reduce erosion, current velocity and the height of the flood wave that is transported downstream in case of high waters. Therefore the "Gewässerauenprogramm" of NRW is connected with the flood protection programmes that have been initiated republic-wide in Germany.

Lippe River

The following observations were made and consequences of the increased TBT contamination in the Lippe have been drawn (LUA, 2002):

- For the industrial wastewater effluents of the TBT producing company in Bergkamen, a treatment plant specifically for elimination of organotin-compounds is constructed in cooperation with the Technical University Paderborn. With the start of operation in 2002, the requirements of appendix 22 (chemical industry) of the wastewater regulation as well as the regulation for aquatic environments (LAWA: 0,1 ng/L TBT; GewQV NRW: 0,01 µg/l DBT, 0,001 µg/L TTBT) shall be fulfilled.
- Sewage sludge from the Seseke-River water treatment plant will not be applied to agricultural land anymore but incinerated completely.
- No organotin (with the exception of slightly elevated monobutyltin-concentrations) were measured on agricultural land on which sludge from the Lippe area had been applied.
- On flood plain soils, organotin compounds were detected.
- In Kuhbach, Seseke and Lippe, elevated organotin concentrations were measured that can have adverse effects on the aquatic community.

- Fish in the Lippe showed elevated concentrations of dibutyltin and tributyltin, but still below the maximum concentration level for human consumption.

Emscher-PLUS : Emscher Project for the long-time study of the sanitation success

Nearly 80% of the water flux of the Emscher consists of sump water from coal-mining and municipal and industrial wastewater. As it has become possible to restore the Emscher waters by technical means, when the coal-mining induced subsidence stopped, the plan for the ecological restoration of the Emscher system was developed: It aims at the reestablishment of the Emscher's ecological function in 25 to 30 years, which was mainly addressed by:

- building wastewater treatment plants;
- Separation of combined water;
- pretreatment of highly contaminated industrial effluents.

The oxygen conditions along the Emscher have improved significantly since the start of the Emscher PLUS-Programm. Toxicities in the Emscher have decreased due to improvements of chemical quality of the water. Biological re-colonization has been observed in parts of the river. However, there are still peak effluents of industrial processes which can not be removed by the wastewater treatment plants and especially some tributaries are still of bad quality. Due to the chain of treatment plants with the final plant at Dinslaken, that treats the whole River water, ecological restoration of the area downstream Dinslaken has been observed, where the Emscher confluences with the Rhine.

However, historic contamination due to former industrial areas and mining sites, that are introduced into the Emscher by ground- or surface water still represents a major challenge.

