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 ($HC_c^{13}1 < HC_c^{2}$), which refer to the magnitude of <u>potential</u> 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 <u>a possibility</u> that these sediments, if transferred directly to the Port of Rotterdam lead to an <u>exceedance</u> of the local CTT-values
- (2) A potentially high hazard, meaning that there is <u>a possibility</u> that these sediments, if directly transferred to the Port of Rotterdam would lead to a <u>significant exceedance</u> of the local CTT-values
- (3) High hazard with high certainty, meaning that there is a <u>high certainty</u> that these sediments, if directly transferred to the Port of Rotterdam lead to a <u>significant exceedance</u> of the local CTTvalues

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.

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

<u>Secondly</u>, 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.

<u>Thirdly</u>, 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:

- 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 %.
- 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)
- 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 µg/L. Similar sensitivity has been reported for Aldrin (*Crangon septemspinosa*: EC₅₀: 8 µg/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 promejas,* 24 hour test (Cooper, 1989)) but toxicity data are scarce. Because of very similar modes of action, dioxins, dibenzofurans, and dioxinlike 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.

| SUBSTANCES OF CONCERN | | TARGET VALUES |
|------------------------------|--------------------------|------------------------------|
| SUBSTANCES OF CONCERN | LIMIT VALUES ACC. LO CIT | 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 |
| DCD | 0,1 mg/kg DW | 0,0001 µg/L ¹⁷ |
| РСВ | sum PCBs ¹⁶ | each substance |
| Sum PAHs | 8 mg/kg DW ¹⁸ | 0,1 µg/L ^{17, 19} |
| | | 0,001 µg/L ¹⁷ |
| | 0,02 mg/kg DW | each substance |
| НСВ | 0,02 mg/kg DW | 0,001 μg/L ¹⁷ |
| ү-НСН | - | 0,002 μg/L |
| Aldrin Dioldrin and Endrin | | 0,001 µg/L ¹⁷ |
| Aldrin, Dieldrin, and Endrin | - | each substance |
| Dioxins | - | - |
| ТВТ | 100 – 250 µg Sn/kg DW | 0,001 µg/L ^{,17,20} |

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).

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, Phenantrene, Anthracene, Fluoranthene, Chysene, 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(1,2,3cd)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 <u>hazardous</u> 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 hazar- dous 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)diphenylam | | | | |
| in (6PPD) | | | | |
| I riphenyl Phosphine | | | | |
| Hexamethyldisiloxane (HMDS) | | | | |
| Dicofol | | | | |
| Endosulphan | | | | |
| | | | | |
| PCP (Pentachlorophenol) | | | | |
| | | | | |
| | | | | |
| 2,4,6-tri-tert-Butyiphenol | | | | |
| | | | | |
| | | | | |
| musk xylene | | | | |
| snort chained chiorinated | | | | |
| parattilis | | | | L |

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 partioning 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 programms, 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:

- a) 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.
- b) Cadmium and mercury are known to be highly toxic and bioaccumulative.
- c) 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.
- d) 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 nonyphenol 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).

| Substance of concern | persistence 1 : half life < 1 yr | log K _{ow} | Remarks | Hazard Class (Comp.) |
|------------------------------------|-------------------------------------|---------------------|--|----------------------------|
| | 3: half life > 10 vrs | | | HCc |
| 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 |
| НСВ | 3 ²⁶ | 5,91 | РОР | 2 |
| ү-НСН | 1 ²⁷ | 3,66 | Creation of (toxic) metabolites during degradation | 1 |
| Aldrine (Dieldrine, Endrine) | 3 | 5,59 | РОР | 2 |
| Dioxins | 3 | 6,78 | POP | 2 |
| ТВТ | 2 ²⁸ | 3,59 | | 1 |
| Nonyl-phenol compounds | 2 ²⁹ | 3,28 | | 1 |

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

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 μ m fraction. Data on grain size distribution are not available for every sediment sample. Median values of the percentage of the <40 μ m 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 μ m 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 ecotoxicologial 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 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

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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
- $n \ge 3$; 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 μ g/kg in surface sediments in Augst (Zipperle & Deventer, 2003), and 3000 μ g/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 regard as hazardous because of PCB concentrations of 341 μ g/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 μ g/kg) than those of class 3 (180 up to 900 μ g/kg in Germersheim).

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 μ g/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 μ g/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 μ g/kg were measured in this class 3-area. HCB content in the sediment was higher than 40 μ g/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-Eisenbahnhafen, 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 μ g/kg and HCB reaches 96 μ g/kg.

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

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 μ g/kg) and also PAH values (up to 15 mg/kg). Very high HCB concentrations are found near the mouth of the river (436 μ g/kg) and downstream of Hüls (140 μ g/kg). Increased levels are found up to river km 46.

Potential sources for contamination 4.4

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.

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 Most production sites for heavy metals and organic s.o.c. are located in Germany, and here mainly in the Ruhr aria, which had the highest density of 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)

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

 30 Until 1995 untreated waste water release from paper industry in Kaysersberg 31 Will increase in the future due to replacing TBT containing paints

Chapter 4 – Substances and Areas of Concern

| | | | 8 | | | | |
|--------------|----------------------------------|------------------------------|--|-------------------------|---------------------------|-----------------------|--------------------|
| | РАН | PCB | HCB ³² | TBT (and other | DDT+DDD+DDE | Dioxins | Chlororganics |
| | | | | organotin-comp) | | | esp. γ-HCH |
| Source / | coking plant | PCB production ³⁴ | Production of: | Antifouling | Industrial emissions | Production of | Pesticide |
| inductor | Aluminium-industry ³³ | Use in transformers | Pentachlorthiophenol | Fungicides | Insecticides | chlorophenol | PVC-produc. |
| | | use in condensators | - Tetrachlorethylen | (stabilisators for PVC) | | Steel, iron and metal | paper |
| | | as hydraulic oil | - Trichlorethylen | | | working industries | |
| | | in plastics | - Tetrachlorkohlenstoff | | | 1 | |
| | | | - PCNB ³⁵ | | | | |
| | | | Electrode, PVC- prodc. | | | | |
| Diffuse | incineration | Building-material | Tyres | | | Incineration | Disposal sites |
| SOLITCA | | Wood-protection | Seed protection | | | Combustion | |
| 2001 | | Disposal sites | Agriculture | | | | |
| | | | Wood protection | | | | |
| Location of | Duisburg-Hochfeld | Leverkusen (?) | Leverkusen | Seseke (Lippe) | | | Köln |
| nroduction | Linz | Ludwigshafen | Rheinfelden | | | | Mohnheim |
| | | | Arnheim (NL) | | | | Mannheim |
| | | | Rheinberg | | | | currently only one |
| | | | Uerdingen | | | | production site in |
| | | | Dormagen | | | | Europe (located in |
| | | | Hürth | | | | Eastern Europe) |
| | | | Weseling | | | | |
| | | | Ludwigshafen | | | | |
| | | | Frankfurt | | | | |
| | | | Marl (Lippe) | | | | |
| nroduction | | selling and use | | Annlication of TBT- | In most countries | no intentional | Marketing and use |
| production | | prohibited since 1989 | | containing Antifouling | application is forbidden. | production | prohibited under |
| ובאווורובח : | | (Germany) | | paints for ships <25 m | Insecticides widely | _ | Council Directive |
| | | restricted in marketing | | 10.12.89 | restricted under Council | | 79/117/EEC, |
| | | and use by Council | | | Directives 76/769/EEC | | |
| | | Directive 76/769/EEC | | | and 79/117/EEC or not | | |
| | | | | | used in Member States | | |

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

 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 Pentachlornitrobenzol

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:

a) 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.

b) 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:



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

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. 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 Wupppertal, 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 μ m 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 μ m 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 tributaries and its 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 confluences 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.

RHEIN WURPER WURPER

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 loaden 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 III 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 steal 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)

PAHshave 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 transformators 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 <u>annual loss</u> 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 **Moseltributary**, 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 mattler. 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 μ g/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 μ g/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 μ g/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 Chapter4.3 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 μ g/kg in sediments in 1994, and still almost 400 μ g/kg in sediment in 1998 downstream of the 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 μ g/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

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 Diergard 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.

| 0 | D | T 11 1 | A MARKET ALL C |
|------------------------------|----------------------|-------------------|--|
| Source | Potential release to | Likely trends in | Additional notes |
| | land (min. – max.) | release from 1994 | |
| | σ L-TEO (1994) | | |
| | g1-1LQ(1554) | 1 | |
| Pesticide Production | High (no data) | \rightarrow | |
| Chemical Production | High (no data) | \rightarrow | 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) | \rightarrow | |
| Paper & Pulp Production | Medium (8 – 27) | \rightarrow | |
| 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) | \rightarrow | |

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

DDT+DDD+DDE

DDT (dichloro-diphenyl-trichloroethane) was one of the first widely used organochlorine pesticides and

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

was praised for its toxicity to a wide range of insects, its low mammalian toxicity and its persistence in the environment.

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 y-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)



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 Harkotsee. 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 Hartkortsee 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 Hartkotsee 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 (SiCl₄) and trichlorosilane (HSiCl₃) 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 μ g/kg. After this point, the HCB concentration is steadily increasing. Even in 2003, HCB values in suspended matter up to 400 μ g/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 (<u>sediment contact</u> test with the bacterium *Bacillus cereus* and nematodes; <u>elutriate</u> tests with algae and bioluminescence inhibition tests with Vibrio fischeri on elutriates and on <u>methanol extracts</u>) 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 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.

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

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 alsoinfluences 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 | DuisRheinpreußen | left | 5 |
| 781,1 | DuisEisenbahnhafen | 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 classesat different samplinglocations in the Middle andLower 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:

- 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 (Gambsheim) 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.

Chapter 4 – Substances and Areas of Concern

no measurements or only single data on organic

 Table 4.8
 Areas of concern and their main contaminating compounds in sediments substances)

Lippe Ē Ruhr Wupper Tributaries Emscher² Mosel Main Neckar Harbours Flooded quarries Lower Rhine Duisburg, Ruhr area Harbours <u>and</u> Middle Rhine Loreley Upper e.g. High and Barrages Upper Rhine DDT+DDD +DDE Dioxins + Furans Aldrin γ-HCH HCB PCB PAH Zn TBT Нg Ъb S В ïZ Ъ

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

References Chapter 4

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