6. Summary and Conclusions

6.1. Identification of areas of risk in the Rhine catchment area and its tributaries for the Port of Rotterdam due to historic contamination

After extensive reduction of emissions by point sources (industrial and municipal) along the Rhine as a consequence of the Action Program "Rhine" of the ICPR and other initiatives like the Rhine Research Project of the Port of Rotterdam, those sediments now gain in importance, which had been contaminated in the past and accumulated in areas of low water current. The relative contribution of these sediments to the exceedence of regulatory concentration limits for relocation will increase. Non-compliance with the required chemical criteria demands expensive disposal options. The concern with regard to historical contaminated sites is, that their contribution to port sediment contamination may continue on an undetermined time frame: Their exact location and extent is often unknown and once found the sites have to be managed, unless consolidation processes prevent resuspension effectively.

In the present report, the risk for the Port of Rotterdam due to those historical contaminated sites is assessed. This risk addresses the probability that sediment in the Eastern part of the port may be contaminated above current sea/Slufter threshold values, regulated by the Dutch "Chemistry –Toxicity Tests (CTT)-levels", due to resuspension processes upstream. Exceedance of the CTT-values not only increases the ecological risk, but leads to cost-intensive actions as this material has to be disposed in a contained disposal facility (the Slufter) rather than be relocated at the North Sea.

A three step approach with a classification after each step was used to approach this risk:

6.1.1 Identification and classification of SUBSTANCES OF CONCERN

Substances of concern in this report	Hazard classes
Cadmium (Cd)	2
Chromium (Cr)	1
Copper (Cu)	1
Mercury (Hg)	2
Nickel (Ni)	1
Lead (Pb)	1
Zinc (Zn)	1
DDT+DDD+DDE (SUM)	2
Dioxins and Furans	2
Hexaclorobenzene	2
Polycyclic aromatic hydrocarbons	2
Polychlorinated biphenyls	2
Tributyltin	1

Table 6.1 Substances of concern

Table 6.1 depicts those substances, which were addressed in this study, and the hazard classes that were assigned to them depending on their chemical persistence, their partitioning to sediment and their environmental risk.

Heavy metals, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), DDT and its metabolic products DDD and DDE, as well as hexaclorobenzene (HCB) were discussed in this study because they frequently exceed the Dutch "Chemistry –Toxicity Tests (CTT)-concentrations" in suspended matter, measured in Brienenoord at the entrance to the Port of Rotterdam. The organic substances were assigned to hazard class 2 because of their strong partitioning to sediment and their long half-lives of more than 10 years in sediment. Of the heavy metals, cadmium and mercury were assigned to hazard class 2 because of their high toxicity and bioaccumulative potential.

Tributyltin (TBT) was chosen because the world's largest TBT producing company is located in the Rhine catchment area. TBT was classified as hazard class 1, because it shows a shorter half life (less than 10 years) and lower affinity to sediments compared to the other organic contaminants.

Dioxins and furans are not intentionally manufactured but are produced as by-products in combustion processes. They are not addressed in the CTT-list so far, but would be if the dioxin-specific bioassay "DR-calux assay" were integrated which is under discussion. Dioxins and furans adsorb strongly to sediment and show very low rates of degradation or transformation. Accordingly, they were assigned as hazard class 2.

<u>The following substances were discussed for inclusion but eventually omitted:</u>

Insecticides like γ-HCH, aldrine, dieldrine, and endrine, which were part of the former *Uniform Content Test* list, are not part of the CTT list anymore because of their permanently low sediment concentrations. Due to their effect on insect metabolism they may also affect the amphipod test (*Corophium volutator*) that has been discussed as one of the bioassays that may be included in 2 years time. However, no data on concentration of these compounds were available and, hence, no areas of concern identifiable. EDTA/NTA were discussed and omitted, because studies confirm that under environmental conditions, no significantly enhanced remobilization of heavy metals from sediments occurs due to these kind of substances.

6.1.2 Identification and classification of AREAS OF CONCERN

Areas were defined to be of concern, if surface sediment data exceeded the CTT levels for sediment in Rotterdam. The classification into four classes, differing in the extent of risk and the degree of uncertainty, was based on

- the confidence in the sediment data for the specific area (e.g. only one sample taken as compared to frequent sampling over years),
- the extent of contamination and
- the hazard class of those substances that exceeded the CTT thresholds.

Information on known historical emissions was then used to validate and check the data for comprehensiveness.

The classification resulted in

Class 0 – low hazard or no hazard identified

Class 1 – there is indication for a potential hazard

Class 2 – there is indication for a potentially high hazard

Class 3 – there is high certainty that a high hazard is present.

All together 12 areas of concern were identified as potentially hazardous. Table 6.2 lists the "areas of concern" together with the hazard classes (HC) that characterized the locations. If the sediment samples from an area, such as a tributary, were assigned mostly to one class, this one is depicted as the dominant class in that area in table 6.2. If locations were classified differently, the range (e.g. 1-3) is indicated.

Table 6.2 Areas of concern and their main contaminating compounds in sediments
(no measurements or only single data on organic substances)

Areas of concern		HC	Cd	Cr	Cu	Hg	Ni	Pb	Zn	DDT DDD DDE	Sum Dioxin Furan	HCB	Sum PAH	Sum PCB	TBT
High and Upper Rhine	Barrages	3													
Upper and Middle Rhine	Harbors e.g. Loreley	1-3													
Lower Rhine	Duisburg harbours	1-3													
	Harbors, flooded quarries	3													
Tributaries	Neckar	1													
	Main	3													
	Mosel	2-3													
	Emsch.	3													
	Wupp.	3													
	Ruhr	3													
	Erft	3													
	Lippe	2													

The contaminant pattern that derives from table 6.2 depends on:

a) the historical emissions, and

b) the dynamic of the system, and

c) the amount of data, that forms the basis of these results.

Similar contamination patterns in unconnected tributaries can be caused by similar economical situations, such as similar industries influencing the sediment quality. Comparing the Mosel, Wupper and the Erft, which are all areas under direct (Erft, Wupper) or indirect (Mosel via Saar) influence of the mining industry, all sediments are contaminated with nickel, lead and zinc. Exceptions are Ruhr and Neckar which show a similar pattern, having cadmium, copper and PCBs accumulated in the sediments despite differing industrial activities in these areas.

Similar patterns are also caused by transport of contaminants with sediment or suspended matter downstream, as it is the case with the locations from the barrages at the High Rhine till the harbors in the Middle Rhine such as Loreley and Worms Bauhafen. All show mercury, DDT and hexachlorobenzene contamination.

Also the Wupper and the harbors in the Lower Rhine, like Hitdorf and the Duisburg harbors, share a similar pattern. The harbors are all located downstream of the confluence of the Wupper and especially Hitdorf is known to be affected by the tributary's effluents.

6.1.3 Identification and classification of AREAS OF RISK

The risk assessment for the Rotterdam port sediments due to those "substances of concern" that could derive from the identified "areas of concern" required estimating resuspension, transport probabilities and determination of transported quantities. Business as Usual (BAU) conditions were considered, when discharges are average and no anthropogenic activities cause suspension of sediments. As floods frequently occur in the main river and its tributaries, the final assessment of "areas of risk" also had to take into account the impact of increasing discharge levels. These are characterized according to the frequency of their occurrence: An average annual flood is described as HQ1, whereby a high water situation, which occurs statistically only once in a hundred years, is called HQ100 (Table 6.3).

The different aspects were regarded as separate lines of evidence, from which at the end the final conclusions were drawn, depicted in Table 6.3.

According to the amount of evidence that was seen, the areas of concern were categorized as follows:

no evidence of risk

presence of risks can not exluded

evidence for risk

evidence for high risk

Table 6.3 Areas of Risk in the Rhine basin and its tributaries

areas of concern	Flood scenario	Areas of risk
chapter 4		***chapter 5***
Higher and Upper Rhine/ barrages	BAU	
	>HQ1	
Upper and Middle Rhine / harbours e.g. Loreley	BAU	
	>HQ50	
Lower Rhine / Duisburg and Ruhr area	BAU	
	>HQ?	
Lower Rhine / Harbours and Flooded quarries	BAU	
	>HQ?	
Neckar	BAU	
	>HQ1	
Main	BAU	
	>HQ50	
Mosel	BAU	
	>HQ10	
Emscher	BAU	
	>HQ100	
Wupper	BAU	
	>HQ10	
Ruhr	BAU	
	>HQ10	
	>HQ100	
Erft	BAU	
	>HQ10	
Lippe	BAU	
	HQ10	

<u>Areas presenting a high risk with high certainty</u>:

Barrages in the Higher and Upper Rhine with respect to HCB. There are indications that even under business as usual conditions, when there is normal discharge and no management activity, HCB is transported downstream from Iffezheim at concentrations, that may already have an effect on the sediment quality in Rotterdam.

The Ruhr River. The sediment in the Ruhr is relatively easy to resuspend, leading to a potential transport of PAHs and cadmium downstream.

<u>Areas with evidence of risk:</u>

The Neckar may represent a risk. High cadmium concentrations, especially in Lauffen, have frequently been reported. Whether this material can be transported downstream into the Rhine is not clear, as the measuring station in Feudenheim did not gather data during flood events. However, load calculations point to a considerable Cadmium input from the Neckar to the Rhine.

The Wupper shows a wide spectrum of contaminants, which is reflected by the small harbors downstream of the confluence. Although no data on resuspension of material is available, this is taken as a potential risky area during flood conditions.

The Lippe shows an increased level of HCB in sediments, which may not be able to contribute substantially to the contaminant load in Rotterdam if the flood waves merge. If the crest of the Lippe wave reaches the mouth of the river earlier, there will be a risk, due to the relatively short distance between the Lippe and the Port of Rotterdam.

Most other tributaries (**Mosel, Main, Erft**) are difficult to assess due to lack of data. Mostly the erosion threshold values are missing, which are needed for these kinds of assessments. These values would help verifying whether the sediment **from harbors along the (Upper, Middle and Lower) Rhine including the harbour basins in Duisburg** only act as sink, as is suspected, or under what circumstances these sediments can be resuspended into the River.

The only certain water body with no risk is the **Emscher**, of which the water is completely treated in a river treatment plant before release into the Rhine.

6.1.4 Risk influencing dynamic processes

In most cases flood events lead to resuspension of historical contaminated sites, as they are usually covered by younger and mostly less contaminated material. There is no proportional relationship between the discharge and remobilisation of historic contamination, as sometimes the top layer has to be swept away before the newly exposed, older material can become resuspended. Occurrence of suspended particulate matter at relatively low quantities with at the same time high contamination at the end of a series of flood waves can hence be considered a good indication that here a historic site has contributed to the contaminant load of the river.

The highest risk for the Port of Rotterdam derives from those sites, which lead to an increase in contaminant concentration in suspended particulate matter (above CTT) **and** in the transported load, meaning that a large amount of suspended matter is transported downstream and will (partly) settle in the Eastern part of the port **and** the concentration is high enough to exceed the sea/Slufter threshold. This risk decreases with the distance from the Port and if the site is located within a tributary – both due to dilution effects.

However, dilution effects depend very much on the interaction between the different flood waves that flow down the Rhine and its tributaries:

- <u>The risk increases, if the flood wave of a tributary, transporting contaminated material, reaches the confluence to the main river before the flood wave of the Rhine does.</u> If, additionally, the distance to the Port is short, contaminants can be carried along the Lower and Delta Rhine at high concentrations. This is probably the reason for the high hexachlorobenzene (HCB) and cadmium concentrations that were measured in Kleve Bimmen at relatively low total Rhine discharge: Possibly flood waves of the Ruhr (cadmium) and of the Lippe (HCB) had discharged into the Rhine and experienced relatively low dilution effects due to a late Rhine flood wave.
- <u>The risk increases, if the flood wave is restricted to the limited area upstream, and hence normal discharges in the tributaries downstream do not lead to dilution of the upstream resuspended material</u>. This situation can take place during spring and early summer, when snow melting increases the discharge of the Higher and Upper Rhine and exposes HCB contaminated material in the barrages. Like in May 1999, contaminants in the Southern Part of the Rhine become transported downstream without much mixing with incoming flood waves from the tributaries. Consequently, an increase in HCB concentration in suspended matter, that exceeded the sea/Slufter-values three times, was observed at Lobith subsequently to the high water in May 1999.
- <u>The highest risk exists, if the concentration in suspended matter is increased without any dilution by a flood wave.</u> Any anthropogenic resuspension by e.g. dredging activities, that erodes contaminated material extensively without the immediate dilution of a flood wave will raise the risk that the CTT values in the Eastern Part of the Port of Rotterdam will become too high and the sediment will not be suited for relocation into the North Sea anymore.

6.2. Requirements on Sediment Data Quality

The use of particulate matter as an assessment medium has several advantages, at least compared to the water phase, mainly due to the high sensitivity to low levels of contamination and the medium to low sample contamination risk. However, considering the complex system of a large river basin and the novelty of the present approach, a closer look was necessary both with respect to state-of-the-art of quality control and quality assurance in these water quality assessment procedures and specifically to quality requirements in relation to chemical, biological and hydraulic sediment data.

For both erosion risk and chemical mobilization risk studies the chains of comparison are broken at early stages of sampling and sample preparation (traceability concept). Sampling of flood-plain soils and sediments is affected by strong granulometric and compositional heterogeneities arising from the wide spectrum of flow velocities at which the sediments were eroded, transported and deposited. These heterogeneities can be reduced by subsequent normalization procedures; however, the overall comparability of the samples will be significantly lower than in the applications for surveillance and monitoring tasks, respectively.

With regard to the biological risk assessment, because of the shortcomings of each assessment technique, the best choice to identify potential impacts towards the environment, would be an integrated approach as suggested by Chapman et al. (1997), in which the information from sediment chemistry, toxicity and resident community alterations are combined and collectively assessed with regard to the overall risk (sediment "Triad" approach).

The applied concept to use hydrological and hydraulic data facilitates to quantify the uncertainty of the eroded sediment mass by statistical terms. When calculating the mass of contaminated sediments released by flood events the spatial variability of the erosion related sediment parameters and the associated particulate concentration of sediments, especially with sediment depth must be taken into account. The variability of both the physical and chemical parameters with depth has shown to be much larger than the horizontal variability. Consequently, the statistical range of results for the resuspension of contaminated sediments will be considerably high in reality. The more processes are involved on the pathway along the river course towards the Port of Rotterdam the higher the variance of the transport quantities involved and the larger the gap between the best and worst case assumption for the sediment management at the downstream end.

6.3. Historical Contaminated Sediments under the European Water Framework Directive

A main objective of the Water Framework Directive (WFD) is to achieve good ecological or good ecological potential and chemical status for each water body. A further objective of the WFD is the "no deterioration" requirement. These objectives need to be taken into account when assessing the different sources/pathways. It is interesting to see that while sediments and dredged materials are not explicitly mentioned in the WFD they will play an important role in the forthcoming steps for the implementation of measures against pollution from priority [hazardous] substances under WFD Article 16 – monitoring programmes to be operational (Article 8, 2006) and establishment of the programme of measures (Article 11, 2009).

In the implementation of measures against priority substances, already in the first phase, "historical contaminated sediments", are listed under "sources/pathway", together with a few substances, including hexachlorobenzene and cadmium, with some indication, that these could end up at category 1 (may lead to a risk of failing to meet the objectives of WFD). More data is needed, particularly with regard to the significance of this source in comparison with traditional sources like sewage effluents. However, specific information for this question can not be expected from "whole water" analyses, the only relevant matrix for compliance checking of the environmental quality standard for the priority substances other than metals.

As recommended by the Scientific Committee on Toxicity, Ecotoxicity and Environment (CSTEE, adopted at the plenary meeting of 28 May 2004) monitoring programmes for lipophilic substances should be focussed on biota (and possible sediment). As the number of chemicals selected as priority substances is very limited, the CSTEE strongly recommend producing the required ecotoxicological information for supporting sound quality standards at least for these substances.

6.4. Sustainable Sediment Management at the Catchment Level

The focus of the present study is directed to potential effects at the catchment level, that could influence the interface between Rhine Catchment Area and North Sea, which has been in the focus of the Rhine Research Project II study. In a wider societal context, the main issue is the "achievement of *'hydro solidarity'* within the basin, i.e. a full upstream/downstream integration of monitoring, stakeholder consultation, models and expert systems that can link basin pressures to transfers, across various administrative and/or political boundaries, and between the various land users, water users and other stakeholders" (Salomons, 2004).

In summary, many studies have dealt with isolated events on sediment transport and this is well described in the literature. However, validated models for the Rhine catchment seem to be lacking let alone an application of these models to isolated contaminated areas in the Rhine catchment. To fill in this gap will require a massive effort, in particular with regard to obtaining field data and monitoring data sufficient for validating this kind of model. In this respect European research is needed, in particular since the phenomenon of the legacy of past contamination in sediments and waste dumps is not restricted to the Rhine catchments but occurs in other European regions as well. As such the "worst care approach" taken in this study appears currently to be the Best Available Technique for a first order risk assessment of contaminated sites in river catchments.

With regard to future risk assessment and communication in the framework of sustainable sediment management (SSM), some of the steps in a site prioritization process have been taken in this report:

The identification of areas of concern in combination with evaluation of resuspension, transport phenomena and the distance of the sites from the Port of Rotterdam results in a site prioritization, that indicates what areas of concern need to be addressed in the first place and where management options should be favored. A risk assessment at the prioritized site could make use again of the hazard classes of compounds, integrating them into the risk ranking. This risk ranking should eventually be undertaken on the basis of chemical, ecotoxicological and ecological aspects in order to identify the minimally disturbing – with regard to the environment - maximally efficient management option. The management option is carried out to fulfill the management objective such as the reduction of the contamination level in the Port of Rotterdam.