2. Requirements on Sediment Data Quality

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

2.1. Strategies for Water Quality Assessment: Particulate Matter¹

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

2.1.1. Types of Assessment Programmes

The implementation of the assessment programme objectives may focus on the spatial distribution of quality (great number of stations), on trends (high frequency of sampling) or on pollutants (in-depth inventories). Full coverage of all three requirements is virtually impossible, or very costly². Table 2.1 summarizes some common types of water quality assessments in relation to their main objectives. In the past, many countries or water authorities have installed multi-purpose or multi-objective monitoring programmes without conducting the necessary preliminary surveys. Critical scrutiny of results after several years of operation has led to a second generation of programmes with more differentiated objectives such as impact assessment, trend analysis or operational management decisions.

2.1.2. Water Quality Assessment using Particulate Matter Data

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

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

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

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

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

Table 2.1	Objectives and	aims of water	quality	assessment o	perations (Meyb	beck et al.	1992)
								/

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

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

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

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

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

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

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

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

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

2.1.3. Strategy of the Present Study

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

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

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



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

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

2.2. Quality Control of Field and Laboratory Chemical Data

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

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

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

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

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

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

Assessment step	Operation	Possible source of error	Appropriate actions
Monitoring design	Site selection	 station not representative (e.g., poor mixing in rivers) 	Preliminary surveys
	Frequency determination	 sample not representative (e.g., variations betw.samples) 	
Field operations	Sampling	 sample contamination (micropollutant monitoring) 	Decontamination of samp- ling equipment, containers
	Filtration	contamination or loss	Running field blanks
	Field measurement	 uncalibrated operations (pH, conduct., temperature) 	Field calibrations Replicate sampling
		 inadequate understanding of hydrological regime 	Hydrological survey
Sample	Sample con-	• error in chemical conservation	Field spiking
shipments to	servation and	lack of cooling	
Laboratory	identification	• error in biological conservation	Appropriate field
		• error and loss of label	Pre-treatment
		break of container	Field operator training
Laboratory	Preconcentration	contamination or loss	Decontamination of labora- tory equipment and facilities
	Analysis	contamination	Quality control of laboratory air, equipment and water
		lack of sensitivity	Quality assurance tests
		lack of calibration	(analysis of control sample or standards)
		• error in data reports	Check internal consistency of data (e.g., with adjacent sample, ionic balance etc.)

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

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

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

Water Framework Directive (WFD) and Priority [Hazardous] Substances (PS/PHS) Environmental objectives (WFD Article 4)

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

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

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

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

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

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

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

Other requirements of the Water Framework Directive

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

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

Strategies against pollution of water (WFD article 16)

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

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

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

Timetable of the WFD

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

Initial steps for implementing measures under the WFD are:

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

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

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

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

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

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

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

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Spatial Monitoring

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

Metal Background Reference Concentrations (BRCs)

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

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

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

Study of Dated Sediment Cores

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

Analysis and Monitoring of Solid Matrices under the Water Framework Directive (Report of the Expert Group on Analysis and Monitoring of Priority Substances¹) <u>Sediment and biota</u>

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

Relevant matrix

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

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

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

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

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

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

Analysis and Monitoring of Solid Matrices (continued) Analytical perspective of compliance checking of SPM, sediment and biota EQS

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

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

Waters with high SPM contents

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

Design of monitoring programmes for sediments and biota

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

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

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

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

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

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

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

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

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

Priority Substance	Sediment	Biota	
Anthracene	Р	0	
Brominated diphenyl ethers a)	Р	Р	
C10-13-chloroalkanes	Р	Р	
Fluoranthene	Р	0	
Hexachlorobenzene	Р	Р	
Hexachlorocyclohexane ^{b)}	0	Р	
Pentachlorobenzene	Р	0	
Polyaromatic Hydrocarbons ^{c)}	Р	O ^{d)}	
Tributyltin compounds	P ^{e)}	P ^{e)}	
DDT (including DDE, DDD)	Р	Р	

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

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

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

^{d)} preferable in mussels;

e) marine environment

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

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

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

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



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

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

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

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

- Sampling and sample preparation. Project planning, sampling stations, sampling devices, handling and storage, and quality control are not standardised, but well documented in all aspects (Mudroch and Azcue 1995).

- Analytical. Reference sediment materials are commercially available. While direct species analysis is still limited, standardised extraction schemes for metals and phosphorus in sediments as well as certified reference materials for comparisons were developed under the auspices of BCR/IRMM (Quevauviller 2002).

- Grain size as a characteristic sediment feature. Sampling on fine-grained sediment (Horowitz 1991) and grain size normalisation with "conservative elements" such as Cs, Sc, Li and Al (all reflecting clayey material content) is recommended as standard approach (Förstner 1989).

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

Outlook for secondary sources

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

2.3.4. Sampling and Filtration of Suspended Matter

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

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

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

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

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

2.4. Deriving Ecological Risk from Chemical Data

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

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

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

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

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

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

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

² OCP: DDT, Deldrins, HCB, lindane

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

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

Question 3 – Quality standards for sediments and biota

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

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

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

CSTEE Response

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

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

As a general conclusion the CSTEE believes that specific quality standards can and should be developed for sediment and biota. This should be based on direct assessment and monitoring of sediments and biota directly. The reasons for this misfit are manifold and many have been mentioned in this section already: Phases that strongly bind metals in oxic or anoxic sediments, unusual carbon types (soot, ash, black carbon) that do not behave according to equilibrium partitioning models, ageing processes. They all reduce bioavailability and are usually not incorporated into sediment quality guidelines.

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

Because of the shortcomings of each assessment technique, the best choice to identify potential impacts towards the environment, would be an integrated approach as suggested by Chapman et al. (Chapman et al., 1997), in which the information from sediment chemistry, toxicity and resident community alterations are combined and collectively assessed with regard to the overall risk (sediment "Triad" approach, Figure 2.2). Grapentine et al. added a fourth line of evidence (LOE) to this: the bioaccumulation and biomagnification data (Grapentine et al., 2002). The different LOEs are supposed to end up in an overall weight of evidence (WOE) approach to assist in making a decision as to



Fig. 2.2 Sediment "Triad" approach

whether or not contaminated sediment has resulted in biological impairment (Wenning and Ingersoll, 2002).

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

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

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

2.5. Hydraulic Data Quality

2.5.1. Flood and Sediment Transport Parameters

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

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

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

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

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

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

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

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

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

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

2.5.2. Uncertainties and their Origin

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

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

Uncertainty assessment

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





Reduction of	data quality •higher accuracy •larger number of data • representativity
uncertainties	model improvement •concept refinement •physical processes description
Quantification of the	deterministic-stochastic model simulations
uncertainties	statistical evaluation of results

Figure 2.4 Coping with uncertainties

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

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

Case study Neckar

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

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

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

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

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

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

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

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



Figure 2.5 Sampling site at the River Neckar

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

In the following for simplicity two governing parameters are considered as stochastic. One is the hydrograph and the other is the critical shear stress of erosion ($\tau_{c,E}$). The influence of the two variables on the sediment erosion capacity of the flood is estimated by applying a one-dimensional flow and sediment transport model (Kern and Westrich, 1996) to the 11 km lock regulated river portion of the Neckar. The erosion parameters M and n were regarded as constant and set to be 7.5×10^{-4} kg/m²s and 3.2, respectively.

► Data set

- 6 historical hydrographs and the associated SPM concentration
- erosion coefficient: $5,0 \times 10^{-5}$; $7,5 \times 10^{-5}$; $1,0 \times 10^{-4}$ kg/m².s
- erosion exponent: 1,0 ; 1,5 ; 2,0 ; 3,0 ; 4,0
- critical erosion shear stress: 2; 4; 6; 8; 10; 15; 20 N/m²



≻Model

Figure 2.6 Sensitivity analysis (Li and Westrich 2004)

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



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

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

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



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

The impact of the spatial variability of critical shear stress on the erosion process can be demonstrated by the flood in 1998. In comparison to the flood events (c) and (d) in Figure 2.7 which have about the same peak discharge of 1634 and 1635 m³/s, respectively more sediment is eroded by the flood in 1998 even though it had a lower peak discharge of 1055 m³/s. The critical discharge of erosion in this river reservoir turned out to be some 600 m3/s according to the investigation by Kern (1997).

Fifty simulations were carried out for the flood event from 28th Oct. 1998 to 4th Nov. 1998 using the measured discharge hydrograph with a peak flow rate of 1055 m³/s. The value of the critical erosion shear stress was given by a random process for each simulation. The critical erosion shear stress was assumed to be constant both in space and time.



Figure 2.9 Quantile of calculated sediment mass eroded during flood event 1998 with a peak flow rate of 1055 m³/s: (a) $\tau_{c,E}$ spatially constant and (b) $\tau_{c,E}$ spatially varied (Li and Westrich 2004)

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

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

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

Parameter variability with sediment depth

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

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



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

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

Conclusion

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

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