1. Characterization of Key Processes

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

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

Table 1.1 Processes Affecting the Cycling of Pollutants in Aquatic Systems

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

1.1. Interaction of Key Processes in Fluvial Systems

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

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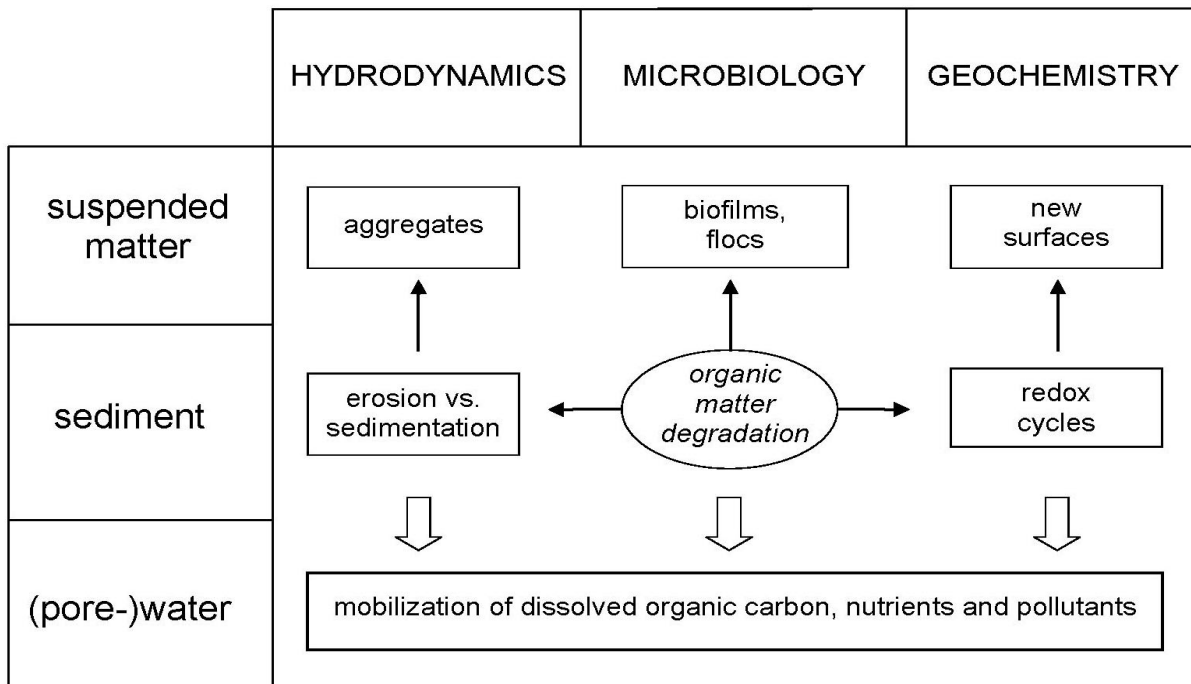

Figure 1.1 Scientific Disciplines and Study Objects in a Coordinated Research Programme of the German Federal Ministry of Education and Research, 2002-2006, on Fine Sediment Dynamics and Pollutant Mobility in Rivers (SEDYMO; Förstner 2001)

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

1.2. Erosion and Transport: From Sediment to Suspended Matter

1.2.1. Beginning and Intensity of Erosion

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

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

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

1.2.2. Sediment Erosion Stability Tests

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

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

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

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

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

1.2.3.   Sediment Depth Profiles

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

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

1.2.4.   Transport of Resuspended Sediments

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

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

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

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

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

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

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

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

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

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

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

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

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

1.3. Mobilization of Sediment-Associated Contaminants

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

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

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

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

- lowering of pH, locally from mining effluents (Salomons and Förstner 1988), regionally from acid precipitation (examples from Rhine catchment area: Stigliani and Jaffe 1993; Stigliani et al. 1994, Stigliani 1995);

- increasing salt concentrations, by the effect of competition on sorption sites on solid surfaces and by the formation of soluble chloro-complexes with some trace metals (Salomons and Mook 1980);

- increasing occurrence of natural and synthetic complexing agents (DTPA, EDTA, NTA), which can form soluble metal complexes with trace metals that are otherwise adsorbed to solid matter (Salo-mons 1983); and

- changing redox conditions, e.g., after land deposition of contaminated anoxic dredged materials (Maass et al. 1985).

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

- approaching the source of the compound, adhering to the surface and/or changing the hydrophobicity of the cell surface;

- changing their specific affinity to the compound (e.g. by switching the membrane-bound uptake systems);

- by producing detergents that increase solubility of the substance and allow a reduction of the distance to the organic compound (Wick et al., 2001).

1.5. Processes Related to Remediation Measures on Contaminated Sediments

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

1.5.1. Risk Reduction by Ageing Processes

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

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

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

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

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

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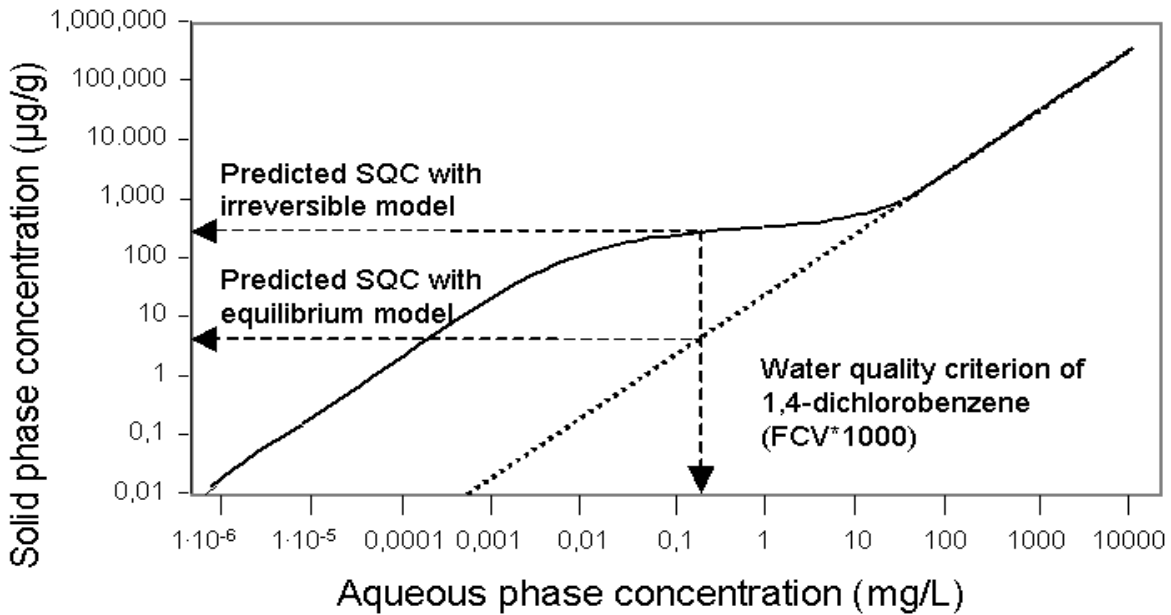

Figure 1.2 Implication of irreversible adsorption on sediment quality criteria (after Chen et al. 2000)

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

1.5.2.   Enhanced In-Situ Stabilization based on Natural Processes

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

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

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

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

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

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

1.5.3.   Processes Underlying Conventional Treatment Techniques

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

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

Table 1.5 Technology types for sediment remediation (Anonymous 1994)

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

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

Classification of Dredged Material

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

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

Solidification/Stabilization

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

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

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

Solvent Extraction

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

Biodegradation and biorestoration

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

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

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

Likelyhood of Success, Costs

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

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

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

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

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

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

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

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

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

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

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