# Introduction

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#### 1.1 Sediment Quantity and Quality Issues in River Basins

#### 1.1.1 Introduction

Sediment is an integral and dynamic part of aquatic systems and it plays a major role in the hydrological, geomorphological and ecological functioning of river basins, defined here to include lakes, reservoirs, estuaries and the coastal zone. In natural and agricultural systems, sediment originates from the weathering of rocks, the mobilization and erosion of soils and river banks, and mass movements such as landslides and debris flows. In most river basins there are also important contributions to the sediment load of organic-rich material from a range of sources such as riparian trees, macrophytes and fish. This inorganic and organic material is susceptible to transportation downstream by flowing water, from headwaters and other source areas towards the outlet of the river basin. Flow rates decline in lowland areas (and areas where flow is reduced) where transported material settles in slack-zones and on the bed of the river, and on river floodplains during overbank events. At the end of the river much of the sediment is deposited in the estuary and on the seabed of the coastal zone.

Sediment provides the substrate for organisms and through interaction with the overlying waters (e.g., nutrient cycling) plays an essential role within aquatic ecosystems. In addition, after flooding, fine-grained sediments are left as a deposit on flood-plains, creating fertile soils that are often highly suited for agricultural production. On the other hand, the removal of sediments from harbors, navigation channels, locks, floodplains and river stretches is a high capital cost for authorities and agencies responsible for their maintenance and water quality.

In the 1970s and 1980s, anthropogenic emissions of excessive metals, nutrients, organic pollutants, radionuclides and other substances caused a rapid deterioration of sediment quality. In addition, the hydrodynamic conditions of many rivers were altered: either directly by the construction of hydraulic constructions, such as dykes, dams, seawalls, and drainage; or indirectly by changes in land use, such as deforestation and urbanization. Apart from seasonal flooding of polder areas and floodplains, in recent years there have also been catastrophic events due to extreme rainfall and the failure of dams; examples include the breaching of tailing dams in highly contaminated areas such as the mining districts of Spain (1998) and Romania (2000), which caused considerable and immediate hazards (Hudson-Edwards et al. 2003; Macklin et al. 2003).

Most large river basins throughout the world are highly populated and/or modified by human activities and thus there are many users and uses of sediment within a basin



Fig. 1.1. Schematic representation of some of the main influences and impacts on sediment within a river basin (Owens et al. 2004)

(Fig. 1.1). This means that site-specific interventions will have impacts that will likely affect other users and uses of sediment (Owens 2005a), and it is, therefore, necessary to develop ways to consider and evaluate these needs, including involving stakeholders in the decision-making process (Gerrits and Edelenbos 2004).

The river basin represents an appropriate scale for management because in many cases source control will be the optimal long-term solution: environmentally, socially and economically. In particular, the controlling of diffuse sources of sediment and associated contaminants necessitates a river basin approach in order: (*i*) to identify all or most of the sources of the sediment and contaminants; (*ii*) for conducting meaning-ful risk assessment and evaluation; and (*iii*) to be able to implement remediation and mitigation options that are appropriate for controlling diffuse sources spread over a large area, for example, implementing appropriate land use and land management measures (Owens 2005a). Having extolled the virtues of considering sediment management at the river basin scale, the following sections briefly consider some of the main sediment quantity and quality issues in river basins, and consider some options and future requirements for sediment management at the river basin scale.

# 1.1.2 Sediment Quantity Issues

Rates and patterns of sediment supply (including soil erosion, bank erosion and mass movements) and sediment transport are a function of three, broad inter-connected groups of factors. First, there are factors that control the inherent susceptibility of the landscape to erode and transport sediment. Factors that control this include the resistance of geology and surficial material, soil type, topography (slope steepness and complexity), and drainage network. Second, there are driving factors that facilitate the physical movement of sediment from source to receptor (such as a river or water body). Factors that control this include the type, amount and intensity of precipitation, and snowmelt. Third, there are anthropogenic factors that modify the inherent susceptibility of the landscape to: (*i*) erode, and this includes land use and management (such as deforestation, cultivation, over-grazing, artificial drainage etc.); and (*ii*) transport sediment, and this includes river use and management (such as channelization, building dams etc.).

Given the large variation in these controlling factors, there is considerable spatial variation in sediment mobilization, sediment supply and sediment transport, both within river basins (especially large basins like the Danube, Yangtze, Mississippi and Amazon) and between river basins. Furthermore, due to temporal variations in the forces that drive sediment production and supply (e.g., rainfall events) there is also considerable temporal variability in sediment movement in river basins. It is these temporal and spatial variations, particularly in terms of the extremes in both maximum and minimum fluxes, that are often of concern for sediment management. At this stage it is important to recognize that sediment quantity issues as part of sediment management tend to apply to specific requirements for society. Large volumes of sediment - both coarse and fine - naturally move through river systems, and it is only when such sediment impinges or impacts on how society uses river basins (see Fig. 1.1) that it becomes an issue and requires some form of management. The following sections consider some of the main issues of sediment quantity that require management. It is convenient to consider the issues of too much and too little sediment, before considering relevant sediment management options and requirements, and also the possible effects of global environmental change.

#### **Too Much Sediment**

In most river basins, the main "quantity" issue is too much sediment. Areas within a river basin where there is too much sediment, from a societal perspective, are locations where either the concentration of sediment is too high, such as the intakes of turbines at hydro-electric power plants, and/or where the volume of deposited sediment is too large. In the case of the latter, problem areas include canals, upstream of dams and impoundments, ports and harbors. The specific management options associated with each location vary. In many situations, dredging and subsequent treatment and/or disposal are the preferred management options, especially for canals, ports and harbors (Netzband et al. 2002). For reservoirs, dredging may be an option in some cases, but more often sediment removal by hydraulic flushing, by-passing, or settling ponds are more cost-effective and sustainable (Owens et al. 2005). Too much sediment, especially fine-grained sediment (i.e. clay-, silt- and fine sand-sized particles), can also be a problem for sensitive aquatic habitats such as fish-spawning gravels as the fine sediment blocks the gravels, reducing oxygen supply and increasing fish egg and larval mortality. Unlike canals, ports and harbors, where the amount of sediment requiring dredging can be 1 000s of m<sup>3</sup>, the amount of sediment needed to detrimentally influence aquatic habitats can be fairly insignificant, and it is often the type (i.e. fine-grained) and timing (i.e. during important reproductive times) that are important. This underlines that it is not just the amount of sediment that is important but also the timing of sediment transport and storage that are important.

There are numerous examples of the amounts and costs involved with removing sediment. One of the best documented examples is the port of Hamburg, Germany, which spends of the order of 30 million Euros each year to dredge and treat between 2 and  $5 \times 10^6$  m<sup>3</sup> of sediment, much of which is contaminated thereby increasing the costs (Netzband et al. 2002). Hamer et al. (2005) state that The Netherlands and Germany dredge between 30 and  $50 \times 10^6$  m<sup>3</sup> of sediment annually. These figures compare to estimates of the annual sediment flux to the estuaries and coastal zones of Europe of  $300-700 \times 10^6$  t yr<sup>-1</sup>, depending of the geographic area of concern (Owens and Batalla, in prep.).

### **Too Little Sediment**

While a significant amount of attention and resources are given to dealing with the removal and treatment/disposal of excessive amounts of sediment, in many situations there are problems associated with too little sediment. Again, it is important to recognize that it is too little from the perspective of society, although in many cases the consequences of too little sediment impact on geomorphological and ecological functioning (Owens et al. 2005). It is also important to note that issues of too much sediment and too little sediment often occur in the same river basin, albeit at different locations. One of the major causes of problems associated with a dramatic reduction in sediment fluxes is the construction of dams and impoundments which reduce the supply of sediment to downstream reaches of a river. The natural supply and flow of sediment along a river system are interrupted and sediment that would normally move through a river network is deposited upstream of the impoundment, often causing problems associated with excessive sedimentation such as the reduction in the lifespan of reservoirs and increased operating costs. Downstream of the impoundment there can be problems due to a dramatic reduction in sediment supply which often leads to "hungry waters" whereby the river compensates for the reduced sediment load by downcutting and lateral erosion (Kondolf 1997). This can result in pronounced changes in the hydromorphology of a river system.

A good example is the Ebro River basin in Spain, where about 190 dams now impound almost 60% of the annual runoff in the basin. Total annual sedimentation in the reservoirs is estimated at  $15 \times 10^6$  m<sup>3</sup> yr<sup>-1</sup>. As a result of these impoundments, the total annual sediment load to the coastal zone at present is estimated to be only 3% of the sediment load at the start of the 20<sup>th</sup> century, and most of this sediment is now derived from channel sources compared to hillslope sources originally (Batalla 2003; Vericat and Batalla 2006). These reductions in sediment supply to downstream river reaches, estuaries and the coastal zone can result in the loss of important habitats such as wetlands, mud flats and salt marshes, which are particularly sensitive to change (Batalla 2003). Downstream of the Hoover Dam on the Colorado River in USA, the riverbed had degraded by 7.5 m within 13 years of dam closure and this erosion had affected 120 km of the river during that period (Williams and Wolman 1984). Downcutting of

river channels can undermine structures such as buildings, roads and bridges, and in some cases lead to loss of life, as demonstrated by the collapse of a bridge on the Duero River in Portugal (Batalla 2003). Furthermore, Leopold (1997) describes the situation downstream of the Aswan Dam where 15–19% of the habitable land of the Nile delta could be gone within 60 years due to subsidence resulting from a lack of sediment deposition, which in turn could displace 15% of the population of Egypt.

#### **Towards Solutions for Sediment Quantity Issues**

Solutions for the occurrence of excessive amounts of sediment tend to focus on removal/dredging and treatment/disposal/relocation, or on schemes to divert or flush sediments through fluvial systems. The examples described above present information on the amounts of sediment involved and the costs. However, these solutions can be considered as "end-of-pipe" solutions in that they tend to deal with a problem as and when it appears, as opposed to dealing with the root cause. Thus for most situations, controlling the initial mobilization and supply of sediment from various sources (i.e. source control) will often be more sustainable from an ecological, economical and environmental perspective. This requires an assessment of the sources, pathways and fluxes of sediment within a river basin. It also requires an assessment of how much sediment and the type of sediment that are needed in rivers for geomorphological and ecological functioning, and also the timing of sediment fluxes (i.e. not too much at ecologically sensitive times of the year), so that sediment supply can meet geomorphological and ecological requirements. At present we are lacking sufficient information to determine the "requirement" part of the equation.

The sediment budget concept offers considerable potential for sediment management and should form part of the early stages of a river basin plan for sediment management (Owens 2005a). There are a variety of tools that can be used to provide the necessary information needed to establish a sediment budget. Thus, sediment fingerprinting and sediment tracing approaches can be used to identify where sediment originates (Table 1.1) and determine transfer pathways and sediment residence times. Magilligan et al. (2006), for example, used the fallout radionuclide <sup>7</sup>Be as a tracer to estimate the sediment transport velocities in regulated and unregulated streams in the USA, so as to assess the impacts of impoundment on sediment transport.

**Table 1.1.** Load-weighted mean contributions of each source type, derived from agricultural and urban areas of the basin, to the suspended sediment samples collected from two river gauging stations (Beal and Methley) in the downstream reaches of the River Aire basin, UK, during the period November 1997 to January 1999 (from Carter et al. 2003)

Site	Number of samples	Source type contribution (%)					
		Channel bank	Uncultivated topsoil	Cultivated topsoil	Woodland topsoil	Solids from STW <sup>a</sup>	Road dust
Beal	18	33	7	20	0	18	22
Methley	5	18	4	45	0	14	19

<sup>a</sup> STW: Sewage treatment works.

Having identified sources, pathways and fluxes (including the identification and estimation of storage elements) (Owens 2005a), there are several options for management, which apply to both issues of too much sediment and too little sediment. At this point, the two-stage risk assessment procedure of Apitz and White (2003) is useful, and this is discussed further in Sect. 1.1.4. On a river basin or regional level, there are several broadscale options available. One is to implement regional- or basin-scale measures to reduce sediment mobilization and delivery to channels via awareness, education and improved practices. These measures are best achieved voluntarily through realization that benefits are both environmental and economical. A good example is conservation agriculture which has been demonstrated to both reduce adverse environmental impacts, including soil erosion, sediment delivery and diffuse pollution of waters, and also be economically viable (Jones et al. 2006). Another broad-scale approach is through legislation, and national and multi-national policies and agreements such as the Dutch-German Exchange and the International River Protection Commissions. At present, there are fairly limited legislation and policy measures relevant to sediment, particularly from a quantity aspect. A useful review is given in Köthe (2003; see also Salomons and Brils 2004; Owens et al. 2005; Owens and Collins 2006). Two pieces of legislation particularly worthy of mention for sediment quantity for the countries of the EU are the Water Framework Directive (WFD) and the Soil Framework Directive (SFD). The former is discussed further in Sect. 1.1.4, mainly in terms of sediment quality issues, although sediment quantity is also relevant for habitat (i.e. ecology) and hydromorphology goals within the WFD. The SFD is forthcoming legislation that in part will address issues of sediment mobilization and sediment delivery, mainly in the context of reducing soil erosion.

At the basin- or local-scale there are more specific measures that can be used to deal with issues of sediment quantity, many of which are also relevant for sediment quality, that should help to reduce the need for expensive "end-of-pipe" solutions like dredging. Examples include the use of buffering features placed at specific points in the landscape to help reduce sediment delivery to rivers (Owens et al. 2006) and measures to facilitate the more "natural" flow of water and sediments through river channels, which can also have ecological benefits (Batalla et al. 2006). Most of the measures and options identified above agree with the philosophy of the European Sediment Network (SedNet; www.sednet.org).

#### The Impact of Global Environmental Change

It is important to assess the implications of likely future global environmental change on sediment fluxes in rivers and how this may influence some of the sediment quantity issues described above. Global environmental change mainly refers to biogeochemical processes, including water and sediment fluxes, and how they are modified by human activities, and encompasses global climate change. It is important to stress that at present we are not certain what these changes will be and thus how they will influence sediment fluxes. There is still considerable debate and uncertainty about the direction (i.e. positive or negative, increases or decreases), magnitude and timing of global environmental changes in climate (temperature, precipitation and seasonality) and carbon cycles, for example, and we are not clear how land use and management will change under ever-changing policy and guidance on food production and security. Plus, global environmental change is itself part of a wider concept of global change that includes economic, cultural and geopolitical global issues, among others (Slaymaker and Owens 2004).

Some likely or probable effects of climate change and associated responses in soil erosion and sediment fluxes are described in Owens (2005b). These include a likely increase in sediment supply and fluxes in rivers due to the anticipated increase in wildfires in many parts of the world, especially areas of the Mediterranean and similar bioclimatic regions and the boreal forests of North America and Russia. Although changes in sediment fluxes due to likely changes in climate are no doubt important, some believe that changes in land use and management may be equally or more important (Slaymaker 2001).

In order to determine the likely changes in sediment fluxes in rivers, models can be used to simulate the production and transport of sediment through river basins under certain scenarios of climate and/or land use change. For example, Asselman et al. (2003) developed a suite of GIS-embedded models to simulate the production and transport of fine sediment through the 165 000 km<sup>2</sup> basin of the Rhine River. Table 1.2 presents some of the results of this study based on two different scenarios:

- 1. CP present climatic conditions with autonomous changes in land use.
- 2. CPC UK Hadley Centre high-resolution atmospheric general circulation model climate conditions (lower, central and upper estimates) with both autonomous and climate-induced changes in land use.

The effects of climate change on the future sediment load of the Rhine River can be estimated from the differences between the sediment load estimated by the combined climate and land use change scenario (CPC scenario) and that produced by the autonomous land use change scenario (CP scenario). The sediment load is estimated to increase by ca.  $0.15 \times 10^6$  t yr<sup>-1</sup> near the tidal limit. There are, however, considerable spatial variations in sediment fluxes in this large river basin (Asselman et al. 2003). Other studies have modeled the likely effects of changes in climate and land use on contaminated sediment fluxes and storage in the Rhine River (e.g., Thonon et al. 2006).

#### Table 1.2.

Expected per cent change in average annual sediment loads under scenario climate and land use conditions in different parts of the River Rhine basin (ranging from Diepoldsau in the headwaters to Rees near the coast) by the year 2100 (from Asselman et al. 2003)

Area	СР	СРС		
		Lower	Central	Upper
Diepoldsau	220	240	257	284
Rheinfelden	112	132	145	167
Maxau	31	31	37	52
Worms	7	5	11	31
Kaub	-16	-17	-12	8
Andernach	-17	-19	-13	8
Rees	-17	-19	-13	9

The effects of global environmental change on sediment fluxes in river basins are at the center of numerous research programs and initiatives, including the International Sediment Initiative (ISI), that has been launched by the United Nations Educational, Scientific, and Cultural Organization (UNESCO), as a major activity of the International Hydrological Programme (IHP; www.unesco.org/water/ihp).

#### 1.1.3 Contaminated Sediments

The perception of aquatic sediments as a very valuable material for humans (e.g., for agriculture) and nature (e.g., as a habitat) rapidly and drastically changed into one of viewing sediments as a legacy of industrialization and related mass consumption, leaving an immense problem for water quality managers and other stakeholders to deal with (Anon. 2002). In fact, the value of today's aquatic sediments is concealed by several negative factors (Förstner 2004a).

Firstly, even without direct and hard dumps, sediments function as a sink for ongoing releases from many sources; these include wet and dry fallout from air emissions, runoff from farms, solid and dissolved inputs from mines, and discharges from landfills, industrial plants, and sewage-treatment plants. Restoration of the quasi-natural state will be a long-lasting process.

Secondly, subsequent to the natural erosive processes described in Sect. 1.1.1, sediment-bound contaminants are dispersed, in an unpredictable manner, on floodplains,



Fig. 1.2. Pathways and processes for the transport of historic contamination downstream (Heise et al. 2004)

dike foreshores, and polder areas. Even moderately polluted solids and pore waters are secondary sources of toxic chemicals, and further accumulation of these substances can then take place in the food chain. Therefore, monitoring and assessment of adverse effects will persist as a priority task in sediment management in the coming decades.

#### Transport of Historic Contamination Downstream

Today, relatively unpolluted recent sediment surface layers cover older contaminated sediments deposited in areas of low flow in river corridors, such as floodplains, river slack-zones and channel beds, reservoirs, and groyne fields. Nevertheless, there is an increasing risk of the resuspension of old contaminated sediment layers and the transport of the particle-bound pollutants downstream in river systems due to the potential for increasing water discharge associated with both anthropogenic activities (i.e. increased runoff to rivers due to land use changes) and climate change (i.e. increased precipitation). Contaminated material can also be introduced to river systems from contaminated soil and other diffuse sources during surface runoff or erosion events (Fig. 1.2).

The requirements for a river basin-wide sediment management concept will include inventories of interim depots within the catchment area (underground and surficial mining residues, river-dams, lock-reservoirs), integrated studies on hydromechanical, biological and geochemical processes, risk assessments on sedimentary biocoenoses and, last but not least, development of decision tools for sustainable technical measures on a river basin scale including sediment aspects.

# Solutions for Contaminated Sediment Problems

Remediation techniques for contaminated sediments are generally much more limited than for most other solid waste materials. The widely diverse sources of contaminants and sediments in large basin areas usually produce a highly complex mixture of pollutants. For most of the sediment derived from maintenance dredging, there are more arguments in support of disposal compared to treatment. Considering the energy input which is needed for the separation of contaminants from their valuable matrices and for the purification of the various gaseous, liquid and solid emissions, then sediment conditioning for reuse – as pushed by waste legislation – will rarely conform to the principles of sustainability. In addition, dubious modes of utilization, such as filling of depressions etc., are often justified by data from test procedures which do not relate to characteristic sediment properties such as the content of redox-sensitive compounds (Förstner 2004a).

At this point, there is an emerging science-based technology for the final storage of sediments, called 'sub-aquatic depot'. The EU Landfill Directive (Anon. 1999) 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 milieu to guarantee extremely low solubility of metals; and (*ii*) base layers of compacted fine-grained sediments which prevent the advective transport of contaminants to the groundwater (Anon. 2002b). Together with advanced geochemical and transport modeling, such

deposits offer the most cost-effective and sustainable problem solutions for dredged sediments.

In the wake of this technology – of which the flagship is the Dutch 'De Slufter' depot – innovative sediment-specific applications can be developed, for example, techniques for active capping to safeguard both depot and in-situ contamination against pollutant release into the overlying surface waters.

Different from the management of dredged sediments, problem solutions for largescale, complex contamination of floodplains are still in the early stages of development. In the 'intrinsic barrier' concept – presumably one of the very few realistic approaches to deal with contaminated soils and sediments on floodplains – soil and sediment components not only act as substrates ('habitats') for organisms to biodegrade substances, but also as media for supporting chemical and mechanical stability ('geochemical engineering approaches'; Förstner 2003).

#### 1.1.4 Risk Assessment at the River Basin Scale

Many of the sediment issues and problems described above are mostly located at the mouth of the large rivers, such as deposition of sediment in harbors and ports, and the problem owners, such as the port authorities, are in a rather uncomfortable situation as they have to pay the costs for all former, actual and future shortcomings in the emission control within their catchment area. According to available information, there should be many more 'interim owners' of sediment problems in the upstream river basin. Many of them, however, ignore their problems or claim to follow a procedure called 'sediment relocation'. In the case of the latter, management problems and costs for the 'end owners' can be exacerbated further (Förstner 2002). In fact, it is not really a relocation or transfer of contaminated sediment to its original site, but rather a downlocating (as re-cycling of waste materials mostly is a down-cycling), and with the dispersion of pollutants there is an unecological increase of entropy. Although the largescale effect of natural and technical resuspension processes is well-known - for example, in the Elbe basin typical patterns of dioxin congeners from the Bitterfeld area can be detected in the sediments of the Port of Hamburg more than 300 km downstream (Götz et al. 1998) - sediment problems in river basins are still regulated locally, sometimes by means of dubious threshold values.

#### Sediments and the EU Water Framework Directive

Here, a clear deficiency of the European Water Framework Directive (WFD) becomes evident. The WFD aims at achieving a good ecological potential and good surface water chemical status in European river basins by the year 2015, using a combined approach of emission and pollutant standards. These consider priority pollutants from diffuse and point sources, but neglect the role of sediments as a long-term secondary source of contaminants. Such a lack of information may easily lead to unreliable risk analyses with respect to the, apparent, 'good status' of waters.

The WFD monitoring objectives require compliance checking with Environmental Quality Standards (EQS) but also require the progressive reduction of pollution. However, *compliance monitoring for sediment* is not yet appropriate because of: a lack of definition of valid Environmental Quality Standards for sediment (EQS<sub>Sediment</sub>) in a European context; analytical limitations; and the anticipated high costs required to obtain full spatial coverage. Sediment *trend monitoring* may be both spatial and temporal, and may be related to the chemical and ecological status of a water body. Sediment monitoring may also play a part in *risk-assessment*, for example in cases where the good-ecological-status/potential is not met or where water quality is adversely affected by the channel bed and/or resuspended sediment, and also in order to prioritize sites where actions can take place, and/or where monitoring should be intensified with respect to its effects along the river basin (Anon. 2004).

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 in chemical sediment analysis (see Sect. 10.1, Förstner 2004b).

#### **Catchment-Wide Assessment of Hazards and Risks**

A basin-scale framework for sediment management should be comprised of two main levels of decision-making: the first for basin-scale evaluation (site prioritization) and the second for site-specific assessment (risk ranking) (Apitz and White 2003). Prioritization, among other things, needs the development of appropriate indicators for sediment mobility at a catchment scale and determination of the sediment dynamics and budget in a river basin (Heise 2003; Owens 2005a; Babut et al. 2007). In practice, a catchment-wide assessment of historical contaminated soil and sediment should apply a three-step approach (Heise et al. 2004): (*i*) identification of substances of concern (s.o.c.) and their classification into 'hazard classes of compounds'; (*ii*) identification of areas of concern (a.o.c.) and their classification into 'hazard classes of consideration of erosion and transport processes and their assessment relative to each other with regard to the probability of polluting the sediments in the downstream reaches.

In a study of the historical contaminated sediments of the Rhine River (Heise et al. 2004), the target area was the Port of Rotterdam, with respect to a possible exceedance of those sediment quality criteria (based on the "Chemical Toxicity Test" (CTT) values of key substances) that decide the fate of dredged material: open water or the more expensive upland disposal. The probability of exposure was determined by calculations of erosion thresholds and indications that resuspension occurred. Probability of exposure was the most difficult parameter to quantify, as very little information existed about critical erosion thresholds and shear stresses for different flood situations.

In a catchment scale view, i.e., assessing the risk for downstream areas such as harbors or the coastal zone, inclusion of mechanical effects (e.g., resuspension of contaminated sediments) will significantly increase uncertainties with respect to the interpretation of combined erosion risk and chemical mobilization data, due to the large variability of granulometric and compositional parameters in the hydraulic term (Westrich, in Heise et al. 2004). Modeling pollutant transport on a river-basin scale requires broad information on water volumes, sediment dynamics and processes at the sediment-water interface. Apart from the quantification of anthropogenic activities (e.g., dredging, reservoir flushing) which should be dealt with when addressing advanced watershed management, prediction of the effects of large storm events on flow and the accompanying sediment load – even more pronounced because of its exponential increase – are among the most challenging tasks. In the three-step-approach of the Rhine River study, the hazards of "substances of concern" and of "areas of concern" could be determined with higher certainty than the risks of polluting sediments within the Port of Rotterdam. However, the combined information from critical erosion thresholds and indication that resuspension took place, as well as the differentiation of four risk classes with regard to the exceedance of well-defined target values, provided "evidence for high risk" for the Port of Rotterdam from historical contamination of sediments contained in the barrages of the Higher and Upper Rhine, even at annual flood situations (Heise et al. 2004).

In the future, an increase in the precision and accuracy of the term "indication that resuspension occurred" should significantly increase the weight of evidence for risks on downstream target areas. Here, sediment core profiles merit special attention (Westrich and Förstner 2005). The best locations for such historical records are within or close to the critical target areas (harbor basins, lakes, depressions, lowlands, flood-plain soils and sediments, etc.). Additional information on the source areas of specific pollutants that are analyzed in the target sediment cores can be gained from indicator substances or from typical isotopes (e.g., lead isotopes) and patterns of congeners (e.g., for dioxins/furans; Götz et al. 1998).

#### 1.1.5 Integrated River Basin Strategies

Both for establishing sediment-related quality objectives and for developing and implementing technical problem solutions, practical process-based knowledge is needed that uses a wide range of simulation techniques and models in different spatial and temporal scales (for example see Table 1.2). In practice, specific information on the interactions of hydromechanical, biological and geochemical processes is required for two reasons:

- Sediment quality assessment is considerably more complex than water quality assessment due to the many site-specific parameters that need to be considered, which is not necessarily the case for water. Bioavailability of a contaminant is not only species specific, but also depends on sediment characteristics and sediment deposition and erosion. The methodologies developed to date do not adequately deal with the complex nature of sediments.
- 2. Remediation techniques for contaminated sediments are generally more limited than for other solid waste materials. Considering world-wide dredging activities, only a very small percentage of these materials can undergo "treatment" in the true sense solvent extraction, bioremediation, thermal desorption, etc. Here, geochemical mechanisms such as stabilization and other forms of long-term, self-containing barriers could reduce the mobility and biological availability of critical pollutants.



The position of integrated process studies, for example in the SEDYMO Program (Sect. 1.2), between ecotoxicological risk assessment and remediation technologies in the management of aquatic sediments and dredged materials is presented in Fig. 1.3, which also explains the position of this multidisciplinary research program in the context of the WFD and other integrated river basin strategies. As mentioned above, the WFD, which focuses on the catchment scale, does not consider sediment quality and quantity as a major issue. However, the strategies against chemical pollution of surface waters (WFD article 16) – i.e. implementation of monitoring programs until 2006 and establishment of the program of measures until 2009 – have to consider sediment quality (and quantity) at the catchment scale. With respect to the latter date, the first step – screening of all generic sources that can result in releases of priority substances and priority hazardous substances – will already include an assessment of the specific source/pathway of 'historical pollution from sediment'.

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# 1.2 Sediment- and Pollutant-Related Processes – Interdisciplinary Approach

# 1.2.1 Introduction

Particulate pollutants represent a multi-disciplinary challenge for prediction and strategies to prevent their distribution in the environment. Four aspects, in an overlapping succession, reflect the development of knowledge in particle-associated pollutants during the past thirty years:

- the identification, surveillance, monitoring and control of sources and the resulting pollutant distribution;
- the evaluation of solid/solution relationships for contaminants in surface waters;
- the assessment of the environmental impact of particle-bound contaminants, i.e. the development of sediment quality criteria;
- the study of processes and mechanisms of pollutant transfer in various compartments of aquatic ecosystems.

For simulating real world effects on various temporal and spatial scales, an integrated approach has been developed combining hydrodynamic and chemical/biological factors which influence pollutant mobilization and transfer – the interdisciplinary SEDYMO approach ('SEdiment DYnamics and pollutant MObility in rivers'). The following sections give an overview of process interactions which influence contaminant mobilization in rivers (Sect. 1.2.2); summarizes the state of knowledge in the three major SEDYMO themes: 'experimental techniques', 'processes and properties' and 'development and validation of models' (Sect. 1.2.3), describes three pre-SEDYMO examples for combined hydrodynamic and chemical/biological process studies (Sect. 1.2.4) and, finally, introduces the structure of the SEDYMO program (2002–2006) and its sub-projects (Sect. 1.2.5).

# 1.2.2 Sediment- and Pollutant-Related Processes

In Table 1.3 the major processes influencing the cycling of contaminants in aquatic systems are arranged according to the primary research disciplines involved, and pollutant phase (dissolved or particulate). Sediment bioturbation is a process in which benthic fauna contributes to the mixing and resuspension of different sediment layers. Bioturbation stimulates many of the characteristic interactions between chemistry and biology and between chemistry and photo-degradation. 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 accelerate the settling of particles. There are well-documented effects of reworking and resuspension of sediments by benthic organisms such as tubificid 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, the cycling of pollutants is dominated by the processes of resuspension, settling and the burial of particulate matter.

#### System of Interacting Natural Processes in Rivers

Due to their particular dynamics, three characteristic features of sedimentary processes in rivers should receive special attention:

- The dramatic effects of flood events on particle transport,
- the rapid and far-reaching effects of sulfide oxidation, and
- the biological accumulation and potential release of toxic compounds.

In practice, emphasis has to be put on the role of 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 cause depletion of oxygen and may enhance formation of flocs and biofilms.

Within the system of substrates and processes, three scientific disciplines and three study objects can be discerned from Table 1.3: suspended matter, sediment and porewater/ bulk water; the formation of aggregates in turbulent water, flocs and biofilms from biological transformations; and the formation of new surfaces for re-adsorption of dissolved pollutants. The main focus is on the degradation of organic matter, which affects both hydrodynamic processes – here erosion vs. sedimentation – and (bio)geochemical redox

<b>Table 1.3.</b> Processes affecting the cycling		Aqueous species	Particulate species
of pollutants (organics, metals) in aquatic systems	"Chemical"	Dissolution Desorption Complexation	Precipitation Adsorption Aggregation
		Species transformation	
	"Biological"	Decomposition Sorption, release Cell wall exchange	Food web transfer Filtering, digestion Pellet generation
		Bioturbation	
	"Physical"	Advection Diffusion Colloidal transfer	Resuspension Settling Burial

cycles. The crucial question, after all possible interactions between both existing and newly formed solid and dissolved phases, leads to the net release of dissolved organic carbon (DOC), nutrients and pollutants, including metals, into the open water.

# 1.2.3 Interdisciplinary Approach

Figure 1.4 reflects the basic concept of the coordinated research program "Fine Sediment Dynamics and Pollutant Mobility in Rivers". An interdisciplinary approach has been derived from an evaluation of the state-of-the-art technology with three major themes: "experimental techniques", "processes and properties", and "development and validation of models".

# **Experimental Techniques**

The quantification of flow rates, including the transport of particle aggregates, microorganisms as well as dissolved and adsorbed substances, needs an integration of various experimental and modeling techniques for the determination of hydrodynamical, chemical and (micro)biological parameters. In these fields, research at various institutions has led to new perceptions and a working hypothesis, which allow quantification of the above-mentioned relocation and flocculation/aggregation processes. The development of new systems can be based on the following research work:

- Clarification of the correlation between mineralogical, microbiological and pore water parameters in erosion devices with the precise control of bottom hydrodynamics (Amos et al. 1992; Booij et al. 1994; Wiltshire et al. 1998).
- Determination of the dependence of erosion stability on consolidation and mechanical properties of bottom sediments, including biogenic stabilization by microorganisms (Spork 1997; Tolhurst et al. 2002).
- Studies on the types of aggregates in the water column under (a) turbulent,
   (b) oscillating and (c) slowly cyclic variable (tidal) flow (Perkins et al. 2004).



#### Fig. 1.4.

Scientific disciplines and study areas in a priority research program of the German Federal Ministry of Education and Research, 2002–2006, on sediment dynamics and pollutant mobility in rivers (SEDYMO)

 Investigations of the erosion and deposition behavior of particles and the respective vertical mass fluxes in different hydrodynamic flow field simulators, such as erosion chambers, erosion flumes, differential turbulence columns, etc.(Gust and Müller 1997; Porter et al. 2004)

#### **Processes and Properties**

The second main topic comprises the micro-biological and geochemical studies, which are needed as a basis for the evaluation of priority pollutants relative to quality standards for sediments and suspended matter. The *biological sub-projects* are mainly aimed at investigating the quantity and quality of particulate and dissolved organic substances, their microbial metabolism using various electron acceptors, and the role of biofilms and colloids on the behavior of pollutants in sedimentary systems. The major objectives of the *geochemical sub-projects* are realistic descriptions of nutrient and pollutant transfer from the particulate into dissolved phases (pore water and open water body); the dynamic and subsequent micro-scale heterogeneity of material dispersion within the sediment; and the diffusive transfer of pollutants across the sediment/water interface. Most of the micro- and mesoscale geochemical information will be used in the development of models.

*Riverine flocs* have a complex composition and may be dynamic in both structure and function due to manifold interactive processes which operate between various physical, chemical and biological factors. Most flocculated natural aquatic sediments commonly have a living and active biological component in conjunction with inorganic and non-living biological particles. Flocculation alters the hydrodynamics of particles and therefore influences the fate and effect of sediment-associated contaminants. In a review of these processes, Droppo et al. (1997) suggest that fibrils consisting of extracellular polymers are the dominant agent for both the development and stabilization of flocculated materials. This does not exclude electrochemical flocculation completely, but rather it appears to be less significant than the biological flocculation in natural systems.

#### Biofilms

Biofilms are very heterogenous. They consist of various microorganisms, which develop on various surfaces under multiple conditions (Characklis 1990). In many natural cases, mineral surfaces are at least partially covered by a biofilm. Dissolved substances will thus cross this biofilm first and be possibly sorbed there before they reach the original mineral surface (Chap. 9).

The sorption properties of the insulating layer are, therefore, of importance for the dissolved and the sorbed state of pollutants (Flemming et al. 1995; Flemming and Leis 2002). Active binding occurs through the excretion of binding-, chelating- or precipitation-cell products in response to the presence of the dissolved substance. In addition, active transport systems may allow the uptake of (e.g.,) metal ions into the cytoplasm. Metal binding by bacterial surfaces is considered largely as a passive phenomenon within the process of electrostatic interaction between cationic metals and anionic cell surface groups (Flemming and Leis 2002). In the presence of metabolic activity, however, microorganisms can bring about metal precipitation indirectly through the production of inorganic ligands, such as, sulfide and phosphate among others and directly by changing metal redox state, e.g., oxidation of reduced iron.

#### Colloids

In the transport of pollutants in surface, subsurface and porewater of soils and sediments, the colloidal phase, often defined as particles between 0.001  $\mu$ m and 1  $\mu$ m, can play a major role due to their high specific surface area and high mobility (Buffle and Leppard 1995). From the available data, it appears that sub-micron particles in oxygenated river water mainly consist of organic matter (fulvics, humics, polysaccharides, proteins), silica, iron oxyhydroxides and possibly small clay particles. While representing only a small fraction (<10%) of the total particle mass, their number increases with decreasing particle size (Buffle and Van Leeuwen 1992), and thus represent a considerable portion of the overall surface area available for interaction with pollutants. There are indications that pollutants bound to colloids can increase toxicity in aquatic systems (Vignati et al. 2005).

Key questions are the mobility of colloidal particles and hence their stability against aggregation and capture by larger flocs and the colloid-pollutant interaction, which can significantly differ between different colloidal phases (e.g., iron-oxide colloids and natural organic matter, NOM). Other points of interest are colloidal particle release from sediments and pore water, and generation by aquatic biota. The colloidal part of the NOM seems to play a mayor role in fresh water due to its high mobility. One key observation to understand the behavior of inorganic colloids was reported by Wilkinson et al. (1999) where the aquatic organic matter (mainly polysaccharides) promoted aggregation of inorganic colloids, while soil-derived organic matter stabilized the inorganic colloids against aggregation. Hence not only the general water chemistry as a whole plays a mayor role but also the origin of NOM can change colloidal behavior. Today a thorough quantitative investigation of the role of different colloidal carriers for pollutant transport on the river scale is still rare (Vignati et al. 2005). This is mainly due to the lack of suitable methods to quantify the colloidal particles and the pollutants associated with them. On a routine basis, sequential filtration is often applied to quantify colloidal components and although it is comparably easy to perform it is prone to artifacts (Morrison and Benoit 2004). Also the choice of cut-off diameters and molecular weights seems to be arbitrary and complicates comparisons (Babiarz et al. 2001; Vignati et al. 2005; Rostad and Leenheer 1997; Wen et al. 1999). Studies applying advanced methods for colloid analysis are tedious (Lyven et al. 2003; Lead et al. 2005; Lead and Wilkinson 2006) and therefore limited in their application in terms of temporal and spatial extension. Hence the available data is often only a snapshot, from which it is difficult to derive information about processes. Recently Lyven et al. (2003) identified colloids in the size range between 1 and 10 nm in diameter in a small Swedish creek. While iron (and many other main and trace metals) were found to be associated with carbon-rich colloids (NOM), it was also present with larger colloids (5 nm) of potential inorganic origin. Lead was mainly bound to this second fraction. Investigations of Baalousha et al. (2006) on the river Loire confirmed the absence of lead in the carbon-dominated fraction. Stolpe et al. (2004) sampled the same Swedish creek under different seasonal conditions and the qualitative partitioning of lead seems to be unaffected. This points out the need for investigations which account for the continuum-like size distribution of aquatic colloids, as well as the further development, harmonization and validation of methodologies.

#### Sensor Techniques

Micro-electrodes are useful tools for high spatial resolution assessment of relevant parameter distributions in the immediate vicinity of micro-organisms. For example, the development of a microbial biosensor now allows micro-scale determination of the bio-available fraction of organic carbon in sediments and bio-films (Neudörfer and Meyer-Reil 1997). Considerable progress in the simulation of metabolic processes in sediments has been made possible through the development of particle-oriented sensor techniques, e.g., by the Max Planck Institute for Marine Biology in Bremen (Jørgensen 1994). Apart from glass-based micro-electrodes for measuring oxygen (Glud et al. 1998), hydrogen sulfide (Kühl et al. 1999) and carbon dioxide (De Beer et al. 1997), there are fiber-optical sensors (optodes) for measuring the time-decay of analyte-specific fluorescence receptors of dissolved substances such as oxygen, nitrate, nitrite and ammonia. This allows an analysis on a micro-scale, e.g., at the sediment-water interface (Kühl et al. 1997).

A new photo-acoustic sensor was developed for in-situ and online concentration monitoring of aromatic substances in water (Mohacsi et al. 2001). Selective detection is accomplished by transferring the analyte of interest into the gas phase through a permeable membrane. Unlike the conventional approach, where sampling and detection units are separated, here the membrane is inserted directly into the central part of the photo-acoustic resonator, thereby eliminating the need for various gas-handling components and purging gases. In this way, the system becomes simpler, more compact, has a response time of 40 min and a potential for fully automated operation. The use of a near-IR (1.67  $\mu$ m) diode laser coupled to the PA cell by an optical fiber yields detection limits of 350  $\mu$ g (for benzene) and 1.1 mg (for toluene) per liter of water.

When placed directly into water wells or sediments, the proposed sensor can serve as a warning system for long-term automatic observations.

A fiber-optic sensor system for the online detection of heavy metal ions in water was presented by Prestel et al. 2000 and Zhang et al. 2000. This is based on the laserinduced fluorescence spectroscopy of suitable metal-ligand complexes. The sensor system is designed to measure heavy metal ions in the field. Flow injection analysis (FIA) is coupled with the sensor system to overcome problems associated with the slow diffusion rates of heavy metals through the membrane of an in-situ sensor head. First experiments have shown that the new FIA system has good reproducibility, a high sample analysis rate and that one can measure heavy metal ions (Cu(II), Ni(II), Cd(II) and Zn(II)) at the ppb level, if the appropriate ligands are used.

#### **Pore Water Studies**

The composition of pore water is a highly sensitive indicator for reactions between chemicals on solid substrates and the aqueous phase which contacts them. It must be remembered that the chemical composition of the pore water is controlled primarily by microbial processes working at significantly higher spatial resolution. High resolution techniques applied to pore water studies contain among other microsensor studies (see above). Experiments have clearly demonstrated that the surface structure of the sediment plays a key role for the advective oxygen transport (e.g., Huettel et al. 1998).

The turn-over of other redox sensitive elements has turned out to be more difficult to analyze and the results less clear in their interpretation. (Hydr)oxides of iron(III) and manganese(III,IV) are recognized to be very important sinks of pollutants as well as quantitative important electron acceptors in anoxic sediments. The pore water concentration of  $Fe^{2+}$  and  $Mn^{2+}$  correspond to a very small fraction of the total iron and manganese in sediments and extreme analytical care must be taken using traditional analytical approaches. Direct measurements of the transition metals include voltammetric assessment (Nuester and Larsen) and sampling the metals in gels after diffusive equilibrium has been obtained (Davison, see Sect. 8.1).

Given the fact that most processes involving sediment particles and pore water are fast and that the concentrations merely reflects partial equilibria concentrations the concentrations alone tell very little about the actual rates of turn-over in sediments and transport of over the sediment-water interface. Various methods have been developed for the quantification of rates based on radio tracers and stable isotopes (Elsgaard and Jørgensen 1992).

For instance, the rates of sulfate reduction and the turn-over of electron donors like volatile fatty acids can be directly measured using radiotracer techniques. Incubating sediments (e.g., cores or slurries) added radio labeled reactants allow after measuring the partitioning of the radio tracer between product and reactant as well as the reactant concentration a direct quantification of the turn-over rates (Cranfield et al. 1993). Using landers incubation of deep-sea sediments under in-situ conditions is even possible (Greef et al. 1998).

In riverine sediments advective transport plays a large role and the transport regime may in the estuaries change direction and force within few hours. Hence, technology can be transferred from the extensive marine experimental basis but most techniques must be adopted in order to function satisfactorily in rivers (Larsen, Sect. 8.1 in this book).

#### **Development and Validation of Models**

Analytical and numerical models are indispensable for both connecting and integrating the interdisciplinary study of individual processes and for transferring the results of laboratory experiments to natural aquatic systems, where processes take place on extremely variable spatial and temporal scales.

Numerical models can be applied to schematize and simulate physical, chemical and biological processes:

- Transport and reaction modeling, considering advective, dispersive and diffusive transport mechanisms as well as ad- and desorption processes (e.g., CoTReM; Landenberger 1998).
- Hydrodynamic (Johnson and Tezduyar 1997; Boivin et al. 1998; Ling et al. 1998), statistical (Lick et al. 1992) and/or stochastic (Hesse and Tory 1996) models operating on the particle level are best suited for the study of fine-scale aggregation/segregation processes and, in addition, may include biological and chemical processes.
- Macroscale long-term simulation can only be performed using 1- or 2-D model approaches (including particle-tracking models (Wollschläger 1996)) due to limited computing capabilities.
- Three dimensional continuum-models (Le Normant et al. 1998; Malcherek 1995 and 2001) are particularly efficient for locally concentrated emissions and for conducting short to medium-term simulations.

Available material transport models are still restricted mainly to the description of transport and dispersion processes of suspended sediments as well as dissolved and particulate substances. The hydrodynamic interactions between turbulent flow with suspended and bottom sediment are still not totally resolved and process descriptions and numerical simulations of biological and chemical influences on particles and pollutants, especially in the near bottom-zone – are still in an early stage of development.

Diversity and uncertainty complicate the determination and parameterization of bio-chemical parameters affecting binding in heterogeneous systems. Sorption sites have variable affinity for the adsorbents and there is highly variable solubility of the amorphous solid phase. In particular, for describing the transport of inorganic and organic substances, high priority has to be given to the effects of competing adsorption and replacement desorption; here, the influence of dissolved organic matter (DOM) on sorption processes has not adequately been considered as yet. It was shown that DOM can reduce the sorption of hydrophobic organic pollutants due to complex formation (Rebhun et al. 1996), but it seems that the strength of complex binding is substance-specific (Amiri et al. 2005) and therefore of different significance for sorption modeling.

#### Modeling Hydrodynamic and Biogeochemical Data

The calculation of equilibrium speciation in aqueous systems, using computer programs like MINEQL (Westall et al. 1976) or PHREEQC (Parkhurst 1995), requires the exact knowledge of the formation constants of all species under consideration as well as the total mass of some selected components which are derived from chemical analy-

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Numerical description	Components in water body	Solute/solid interaction	Formulation of transport equation
1. Distribution coefficent	Dissolved + particulate	$K_{\rm d}$ = constant	2 coupled linear differ- ential equations
2. Extended K <sub>d</sub> -concept	Dissolved + particulate + milieu factors	$K_{\rm d} = f(pH, pe, complex-ing agents, competingions)$	Additional <i>n</i> linear dif- ferential equations for milieu factors
3. Chemical multi- component model	Chemical individual species	Dissociation and bind- ing constants, solubility products	Coupled differential-, algebraic equation system
4. Biochemical multi- component model	Chemical species + biota	Additional growth and decay rates	Differential algebraic equation system

**Table 1.4.** Development of models coupling hydrodynamic and biogeochemical data for the prediction of pollutant transport in rivers (after Kern 1997)

ses. Imprecision may arise from uncertainties in experimental parameter determination as well as from inconsistencies in published data, sometimes differing by orders of magnitude. These effects are particularly apparent in heterogeneous systems such as sediment and suspended matter.

Models for predicting pollutant transport in rivers are dominated by hydromechanical parameters, including bio-chemical terms using constant distribution coefficients (Table 1.4, Kern 1997). A first step for extending these models involves consideration of typical ecosystem factors such as competing ions, complexing agents, redox conditions and pH values when metals are considered. The next level of sophistication would be the inclusion of binding constants, solubility products and other factors, which can describe solid/solution interactions of critical chemicals in a multi-component system. An quantum step would extend the mechanical-chemical model into biology. Such biochemical multi-component models should at least consider rates of growth and decay of organisms and organic matter.

# 1.2.4 Pre-SEDYMO Integrated Process Studies

First integrated process studies on sediment dynamics and pollutant mobility in river sediments date back to a coordinated research project of the German Research Council "Interactions between abiotic and biotic processes in the tidal Elbe River" (1986–1996; Kausch and Michaelis 1996). This included:

- studies on the temporal and spatial fluctuations of suspended matter discharges via sound ranging, which provide data on the fractioning and remixing of solids in various stages of tidal river flow (Seibt-Winckler and Schirmer 1996);
- model development on the hydrodynamics of suspended matter, allowing simulation of three-dimensional transport (including interstitial scenarios) and variable bottom topographies in the tidal Elbe River (Rolinski 1997);

- studies of the increased enzymatic activities on suspended matter, and the dependence of microbial inhibition on the sediment load (Neumann-Hensel and Ahlf 1995);
- investigations on exopolymeric substances, which both provide highly sorptive matrices for particulate/dissolved substances and may induce stabilization of aggregates (Kies 1995; Humann 1995);
- the mutually influencing groups of variables such as "driving forces" (C-, N-, S-, Fe/Mn-cycles) and capacity controlling properties of the solid matrix – for the redistribution of trace elements (Hong 1995; Förstner 1996; Petersen et al. 1996).

Two experimental devices, the suspension cell, consisting of a thermostatic bioreactor with a 3 liter water volume in a gas cycle, and the LABOratory SImulation Apparatus (LABOSI), where six sediment cores can be inserted and processed at the sedimentwater interface, were developed by the GKSS Research Centre in Geesthacht (Petersen et al. 1995). In his dissertation, Hennies (1997) provided detailed insights on the exchange processes at the sediment/water boundary layer and on the release of previously accumulated individual substances during biological degradation of phytoplankton in the water column. Suspension cell experiments demonstrated the effect of typical estuarine conditions, i.e. light deficiency, increasing salinity, on the decay of limnic algae during a vegetation period. About 30-50% of the particle-bound copper, cadmium, zinc and lead was remobilized, presumably due to interactions with organic matter. Using the LABOSI apparatus in which up to six sediment cores are in contact with laminar water flow in a close water cycle (Schroeder et al. 1992); Hennies (1997) showed that pore water transfer of chemicals in the upper 1 cm sediment layer is controlled by molecular diffusion and benthic activity. In the deeper sediment advection along voids caused by methane gas dominates.

# SETEG Flume Experiments – Hydrodynamic vs. Chemical/Biological Stability in Sediment Core Profiles

Since 1994, a sequence of individual projects was carried out at the Institute of Hydraulic Engineering at the University of Stuttgart, combining channel experiments and field studies on the lock-regulated Neckar River in Southern Germany (Westrich and Kern 1996). At a later stage, the experiments were performed on layered sediments at different flow velocities (Westrich and Kern 1996). Transport equations involving terms for convection and longitudinal dispersion, and information on either sedimentation or erosion were combined with a set of equations including data on adsorption and desorption, pollutant degradation and evaporation. With regard to pollutant transport, the actual model is more or less based on a simple  $K_d$ -approach. This involves the assumption of a uniform distribution coefficient for each pollutant, disregarding the specific conditions of the liquid and solid phases. Further developments are mainly aimed at overcoming the limitations which result from this gross simplification.

Using this model of Westrich and Kern (1996), the hazard potential arising from resuspension of contaminated sediments can be estimated from the product of hydraulic mobilization and chemical mobilization (Fig. 1.5). Mobility is the net result of stabilizing and mobilizing effects in both sectors. For example, hydraulic mobility can be assessed by measuring sediment coverage, critical shear stress and the bottom shear

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Fig. 1.5. Physical and chemical factors for contaminated sediment mobility assessment (after Westrich and Kern 1996)

stress. Geochemical mobility, e.g., for heavy metals, can be estimated from solubility and desorption data, which may, however, be strongly influenced by changes in the chemical milieu. For heavy metals, acidity plays a dominant role, and protons may be produced from the oxidation of metal sulfides.

At this time, major deficiencies were identified in biological information. Boxes in Fig. 1.5 indicate typical examples for biological implications both for stabilizing and mobilizing sediments and their associated pollutants. Biofilms, for example, will stabilize sediment deposits mechanically. However, some of their exopolymers may become effective as complexing agents for the mobilization of heavy metals. With regard to organic pollutants, biological degradation can be considered as a stabilizing effect, when degradation reaches its completion. However, it is possible that metabolic reactions will produce more mobile and toxic intermediates than the original pollutant. In many cases, biofilms will provide a temporary sink for sorbed pollutants which will turn into a source when either the sediment which supports the biofilms is disrupted by high shear forces or if nutrient depletion leads to biofilm decomposition. As a consequence, sorbed substances which are not fully degraded or non-degradable (e.g., metals) will be remobilized.

# Simulating Natural Hydrodynamics and Behavior of Organic Contaminants with a Differential-Turbulence Column

The Differential-Turbulence Column was developed at Cornell University in the framework of a Ph.D. thesis by Brett Brunk (1995) and was initially used to simulate the homogeneous turbulent kinetic energy and sediment-loading profiles for open channel flow (Brunk et al. 1996). The reactor consists of five vertically spaced grids, which oscillate to simulate turbulence in natural hydrodynamic systems. The spatial distribution of turbulence is measured using an acoustic Doppler velocimeter. In-situ sampling can be made by introducing chemicals and monitoring chemical dynamics. Under homogeneous and open channel flow turbulent conditions, sediment profiles obtained in the differential-turbulence column accurately followed conventional theory (Brunk et al. 1996).

Using this device, Brunk et al. (1997) studied the enhancement of sorption of phenanthrene to particles in an estuary, since certain locations had been reported to be sinks for hydrophobic pollutants, and sorption has been commonly considered to be an important mechanism for the observed pollutant trapping. The sorption enhancement caused by 'salinity effects' and dissolved organic matter (DOM) coatings were both measured and modeled. The polycyclic aromatic compound phenathrene, an extracellular polymer from a soil bacterial isolate, and a low organic carbon kaolinite were used respectively as models for the hydrophobic pollutant, DOM, and for suspended sediment. Both salinity effects and DOM coatings induced increased sorption, the former ~50%, the latter ~10%. These experiments showed, that equilibrium sorption of phenanthrene cannot explain the full extent of pollutant trapping in estuaries. It seems that some sediment-bound phenanthrene, perhaps associated with atmospheric soot particles, may not be available for an aqueous phase equilibrium distribution.

# 'Microcosm' Experiments – Metal Transfer during Sediment Resuspension in Rivers and Estuaries

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 for ever. Factors influencing the storage capacity of sediments or the bio-availability of the stored chemical can change and indirectly cause sudden and often unexpected mobilization of chemicals in the environment (Stigliani 1988). From the discussions on the 'Chemical Time Bomb' (CTB) concept during the early 1990s, it became apparent, that it is imperative to know what sediment properties will control the toxicity levels of a chemical and how sensitive the chemical toxicity is to changes of these properties. Acidity, as suggested by Stigliani (1991), is the most important driving force in chemical time bomb effects. In river sediments, acidity can be produced from the process 'split of sulfate' (Van Breemen 1987): During organic degradation, iron sulfide and calcium bicarbonate are formed and the latter is removed with running water. The (solid) acid producing potential can come into action during resuspension and oxidation. With each cycle of deposition and erosion, a certain proportion of buffer capacity in the sediment is consumed. In cases when buffer substance - mainly calcium carbonate - is no longer available, a breakthrough of acidity and heavy metals can be expected (Förstner 1995).

In a project funded by the German Research Foundation (Förstner and Gust 1996), resuspension experiments on cohesive harbor sediments at defined shear stress and related parameters was undertaken using an erosion chamber device ('microcosm'). The principle operational settings of the erosion chamber designed by Gust (1991) are

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chosen to generate a spatially homogenous skin friction at the sediment surface. This is achieved (*i*) by the variable rotational speed of a stirring disk placed 8 cm over the sediment-water interface, and (*ii*) by the volume of recirculated suspension sucked concurrently through the rotating axis. The resulting suspension is monitored on-line in the concentration range  $0-20 \text{ g} \text{ l}^{-1}$  by using an infrared two-channel turbidity meter and a mass flow meter. Concentration is indicative of the phase with erosion/deposition cycles. Investigations on the release of trace metals from model sediments by Akkiparambath (1999) revealed four typical effects:

- 1. during the simulation of skin friction velocity over tidal cycles, the initially resuspended particles of organic bottom sediment typically exhibit higher concentrations of copper and cadmium compared to the subsequent resuspension phases.
- 2. an increase in erosion stability was realized in a sequence of resuspension events. As a result, a decrease of metal mobilization by resuspension took place, particularly in organic-rich model sediments.
- 3. during the resuspension experiments with model sediments with close-to-real sediment composition, an increase in inorganic carbon was observed. This was accompanied by a decrease of dissolved calcium. This result suggested that the precipitation of calcium carbonate occurred.
- 4. During oxidation of sulfide components, i.e. during resuspension of anoxic sediments, the carbonate content steadily decreased. Oxidation of ammonia to nitrate during a batch experiment using artificial sediments, induced a drastic pH decrease and resulted in a continuous increase of dissolved cadmium concentrations during three redox cycles.

In Fig. 1.6, results are presented from a microcosm experiment by Fengler et al. (1999) on the release of calcium and cadmium from a poorly buffered harbor sediment from the Elbe River at Hamburg during an erosion period of more than 1 000 hours. There is a significant difference in the metal release at later stages – after approx. 500 hours depending on whether there was bottom sediment or not. In the former situation, there is practically no pH change and no metal release from the resuspended sediment. This can be explained by an ongoing supply of buffer capacity.

The sequence of factors and processes controlling cadmium mobility has been clarified by Peiffer (1997). Cadmium is relatively mobile and is affected by exchange processes with calcium. In the case of a well-buffered neutral sediment, the addition of



oxygen leads to the oxidation of sulfides, ammonia and organic matter. Acidity, in the form of carbonic acid and protons, is then consumed within the system with matrixbound  $Cd^{2+}$  by the dissolution of calcium carbonate and the exchange of released  $Ca^{2+}$  and protons. Further input of protons is provided from the oxidation of Fe(II) to Fe(III), which then mediates further oxidation of iron sulfides. It is important to note that the exchange of calcium (or magnesium) is the major mechanism for the release of cadmium into the water phase in such buffered systems.

At this stage, the cause of observed *delayed* changes in pH and metal release was not fully resolved. Reports of such effects date back as far as the mid-eighties. Interference with microbial activity (Prause et al. 1985) seems to provide more probable explanations than inorganic complexation following slow oxidation (Salomons et al. 1987).

#### 1.2.5 Sedymo Priority Program 2002–2006

The approaches used to understand sediment-contaminant mobility and resuspensiondeposition tend to be either (*i*) detailed laboratory simulation and/or analytical experiments, (*ii*) field-based measurement programs, or (*iii*) numerical and/or GIS-based modeling approaches. The three types of approach offer different but complementary information (Owens and Petticrew 2006).

On the basis of the concept outlined in Sect. 1.2.2, a proposal for an interdisciplinary research project on sediment processes was initiated in 1999. During discussions concerned with the new EU water directive and with sediment removal by hydraulic dredging – a highly controversial issue on a national level – the theme of interacting sediment processes included also practical aspects. The resulting coordinated research program comprising 13 sub-projects is funded by the Federal Ministry of Education and Research (BMBF); the first seven sub-projects (nos. 1/13, 2, 3, 5, 14, 18b in Fig. 1.7; see also Table 1.5) started in May 2002; Phase 2, comprising six projects (7, 8, 10, 11, 15, and 19 in Fig. 1.7) started in May 2004. A short description of the 13 sub-projects was presented in a preconference overview of the International Sedymo Symposium, held at Hamburg University of Technology, March 26–29, 2006 (Förstner and Westrich 2005). Sections representing contributions of SEDYMO sub-projects in the present book are listed in Table 1.5.

In the center of the first phase was the optimization and application of devices for the study of erosion behavior, i.e., sub-project nos. 1, 2 and 3 (Fig. 1.7), and the development and validation of sediment transport models (sub-projects nos. 13 and 14 in Fig. 1.7). The second phase added the sub-projects focusing on chemical and biological parameters that control the mobility and transport of river sediments and their pollutants. Of particular interest were several subjects studying the potential function and influence of biofilms, such as extracellular polymeric substances (EPS), on sediment stability and pollutant mobility. Sub-project 19 aims at a better understanding of the relationship between key bio-chemical processes and bio-availability of contaminants; the toxicity and chemical data of sediment and water samples were studied under different spatial and temporal conditions along the Elbe River (Sect. 10.2).

In the sense of the three types of approaches for understanding sediment-contaminant mobility mentioned above (Owens and Petticrew 2006), the first enables specific controlling factors to be isolated and examined. Typical Sedymo examples are the subprojects no. 1 (SETEG flume) and no. 2 (turbulence column), the latter closely cooperating with sub-project 8, where the main physico-chemical factors determining the resuspension and deposition behavior of fine sediments was studied. Similar cooperation between the sub-projects no. 10 (metal transfer processes) and no. 15 (sorption of hydrophobic organic pollutants) was based on Gust's 'erosion chamber' (sub-project 3).

The second ('ii'), field-based approach provides a more realistic assessment of conditions within a river, often at larger spatial scales; as an example, the combined work of sub-projects no. 3 (erosion chamber plus field devices) and no. 11 (phosphorus re- and immobilization) shows the difference in sediment-associated phosphorus entrainment rates between laboratory experiments and in-situ studies at the Spree River (Sect. 6.4).

With regard to the third ('iii') approach, modeling often uses the information and understanding obtained from the previous two approaches to develop numerical models and to extrapolate over time and space. This is demonstrated through the validation of the numerical model in sub-project 14 with the laboratory data from sub-project 2 and the two sub-projects no. 1 and no. 13 of Westrich's research group. The relative



Fig. 1.7. Structure of the SEDYMO program. 13 sub-projects are involved in the coordinated research project 2002–2006

 Table 1.5. Titles of the SEDYMO sub-projects and location of SEDYMO contributions in the present book

No	SEDYMO project title	Leader	Section
1	Parameters determining the sediment stability/erosion of cohesive riverine sediments	Westrich	3.2
2	Fine sediment dynamics and flocculation unter the influence of turbu- lence/salt stratification	Jirka	3.4
3	Erosion and deposition cycles of cohesive sediments	Gust	3.3
5	Microbial mediated processes on resuspended sediments	Meyer-Reil	3.5
7	Role of biofilms on the mobility of pollutants in rivers	Flemming	9.2
8	Influence of the particle charge on their erosion and deposition behavior	Frimmel	6.2
10	Forecast of contaminant transfer from sediment and suspended mat- ter	Calmano	6.5
11	Microbial re- and immobilisation of phosphorus at alternating envi- ronmental conditions	Hupfer	6.4
13	Numerical modeling of the mobility of pollutants originating from riverine sediments	Westrich	4.2
14	Modeling fine sediment dynamics in tidal harbor basins and harbor entrances with consideration of the fine structure of both the flow and transport process	Zielke, Markofsky	4.3
15	Sorption equilibrium and desorption kinetics of hydrophobic organics	Worch	6.3
18b	Trace metals as indicators for the dynamics of suspended particulate matter in the tidal reach of the River Elbe: Model calculations and measurements	Ackermann, Keller	7.4
19	Evaluation of the toxicity of sediments from different river basins	Ahlf	10.2

close contact to practice of this approach is shown from the involvement of subproject 13 in the Iffezheim barrage case (Sect. 4.3; case study 'Upper Rhine' in Sect. 2.3 and from the cooperation of sub-project 14 with the Hamburg Port Authority (Sect. 4.4).

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