Solid Waste: Assessment, Monitoring and Remediation
Twardowska, Allen, Kettrup and Lacy (Editors)

III.5

Dredged material

Wolfgang Calmano and Ulrich Förstner

III.5.1. Introduction

On a worldwide scale rivers transport eroded material as suspended solids to the coastal areas. Deltas, estuaries and their associated wetlands are natural sinks for this material. In the 1980s, the International Association of Ports and Harbors estimated about 350 million tons of maintenance dredging and 230 million tons of average annual new construction dredging. In the harbors around the North Sea, approximately 100 million m^3 of sediment has to be dredged annually – about 10 times the average annual sediment discharge of the Rhine river. Typical problems with these sediments are:

- increasing volumes of dredged materials and
- high concentrations of toxic substances.

These problems have been concentrated mainly at the mouth of large rivers and in coastal areas.

In Rotterdam harbor, at the mouth of the Rhine river, the volume of sediment, which has to be dredged annually, increased from less than 1 million m^3 in 1920 to more than 10 million m^3 in 1980. The possibilities of disposal of these enormous quantities of material are severely limited because of the pollutants present in the dredged material.

Due to the economic implications, there is increasing worldwide interest in the development of dredging and disposal technologies. Among the authorities particularly dealing with the subject of contaminants in dredged materials, the U.S. Army Corps of Engineers Waterways Experiment Station at Vicksburg, MS, has played a leading role. In the early eighties, the Environmental Laboratory of this institution together with United States Environmental Protection Agency (USEPA) initiated a "Decision-Making Framework for Management of Dredged Material Disposal", which includes test procedures on physical–chemical conditions, aquatic bioaccumulation, and water column effects both at the site of dredging operations and disposal of dredged materials. Further intensification of coordinated research was performed by the Assessment and Remediation of Contaminated Sediments (ARCS) Group of USEPA, which has been focusing on the Great Lakes Areas of Concern (1990–1993); an "Integrated Contaminated Sediments Assessment Approach" (Anonymous, 1994) includes six topics "sampling design and quality control", "sample collection", "chemical analysis", "toxicity testing", "benthic community structure and survey", and "tumors and abnormalities". In addition, the ARCS program was charged with assessing and demonstrating remedial options for contaminated sediment problems in the Great Lakes; laboratory tests were conducted utilizing 13 processes, and pilot-scale (field-based) demonstration of bioremediation, particle size separation, solvent extraction and low-temperature thermal desorption were conducted.

It seems that sufficient data have been assembled by these and other organizations with respect to both risk assessment methods and remediation procedures for contaminated sediments, which should allow developing more integrative perspectives in this subject. The present geochemical approach is emphasizing on the interactive nature of chemical parameters and is focusing on the long-term effects of pollutant release from disposed sediments.

III.5.2. Geochemical concepts for contaminated sediments

Inclusion of the time factor moves beyond the civil engineering approach in waste management, which usually devotes little attention to long-term emissions from waste disposal sites. "Because we have become accustomed to considering the filling period as the most important phase in landfill operation, we have forgotten that subsequent to the active working period there is the infinitely long time in which the site has to function as a depository for all materials unwanted in the biosphere" (Stief, 1987).

Apart from the traditional approach of contaminant loss prediction, concepts are developed by biogeochemical disciplines, emphasizing the interaction of chemical cycles. This approach refers to non-linear and time-delayed responses in contaminated sediments (so-called "chemical time bomb" processes), which at present cannot be predicted, modeled or even estimated to a satisfactory extent. The underlying concepts are:

- *Chemical gradients*: long-term prognosis, in particular, of the behavior of contaminants at critical sites requires both knowledge of interactions of pollutants species in solid matter and solution, and an estimation of future borderline (particularly "worst case") conditions in a dynamically evolving medium (Förstner, 1993). In sediments, typical driving forces for intensified matrix/element-interactions are strong chemical gradients of redox conditions, pH values and organic ligand concentrations, all three factors mainly being induced by degradation of organic matter (Salomons, 1993).
- *Storage capacity controlling properties* (Stigliani, 1993) form the link between geochemical cycles comprising driving forces such as organic matter and cycles of mobilizable pollutants. They are the key aspects in the framework of chemical time bombs concept (Stigliani, 1991). It is useful to distinguish between two different mechanisms: the first is direct saturation, by which the capacity of sediment for toxic chemicals becomes exhausted. The second way to "trigger" a time bomb is through a fundamental change in a chemical property of the solid matrix that reduces its capacity to adsorb (or keep adsorbed) toxic materials. Methodologies should be designed for assessing effects related to processes of "early diagenesis", i.e. mechanisms and effects by which solids are changed in their chemical form, involving new equilibrium between solid and their dissolved species.
- *Mobility concept*: at the target site, distribution between dissolved and particle-bound micropollutants is affected by accelerating and demobilizing factors. The former, for

example, comprise the effects of pH lowering, redox changes, organic complexation, and microbially mediated species transformations such as biomethylation. Within the spectrum of "barriers", physical processes include sorption, sedimentation, and filtration; chemical barriers comprise mechanisms such as precipitation. Biological barriers are often associated with membrane processes, which can limit translocation of micropollutants such as trace metals (e.g. from plant roots to the shoots and fruits).

- *Selectivity of organic matrices*: the dominant role of organic matrices in the binding of non-polar organic pollutants and metals (as demonstrated in the multi-chamber transfer experiment for copper (Calmano et al., 1988)) is of particular relevance for the transfer of these substances into biological systems. It can be expected that even at relatively small percentages of organic matrices these materials are primarily involved in metabolic processes and thus may constitute the major carriers by which micropollutants are transferred within the food chain. Including these mechanisms of pollutant enrichment on mineral surfaces ("geoaccumulation"; Müller, 1979), organic matrices and, in particular, by organisms, the concept of coupled biogeochemical cycles as originally designed by Salomons (1993) can be extended. Biogeochemical cycles involving redox transformations usually are relatively slow compared to physical–chemical processes such as dissolution or desorption. The influence of mobilizing agents like dissolved organic carbon, salt ions or protons may be reduced by capacity-controlling properties such as cation exchange and pH buffer capacity.
- *Final storage quality* (Baccini, 1989): this approach is one way to develop and control landfills on a conceptual basis. It has been defined by the Swiss Federal Government in 1986: "Landfills with solids of final storage quality need no further treatment of emissions into air and water." Including new experience from impact evaluations related to capacity controlling properties, the mobility concept of environmental geochemistry can be implemented into waste management practice by different ways of optimizing barrier systems. 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 milieu conditions. A common feature of geochemically designed deposits is their tendency to increase stability in time, due to the formation of more stable minerals and closure of pores, thereby reducing water permeation.
- *The biogeochemical concept* of sediment management involves integrated strategies, i.e. the analytical and experimental parameters should always be related to the potential remediation options for a specific sediment problem. In addition to the common predictive techniques for estimating contaminant losses the interactive nature of various parameters has to be recognized. This means, that particular emphasis should be posed on the evaluation of the two data sets "driving force/geochemical gradient" parameters and "capacity controlling properties". Such evaluation includes the type of dissolved/solid interactions, transfer rates of contaminants between various substrates and, in particular, processes in interstitial waters.

Remediation techniques on contaminated sediments generally are much more limited than for most other solid waste materials, since the widely diverse contamination sources in larger catchment areas usually produces a mixture of pollutants, which is more difficult to treat than an industrial waste. Here, "geochemical engineering" (Salomons and Förstner, 1988a,b) emphasize the efforts to use natural resources and processes for reducing negative environmental effects of pollutants, e.g. by immobilizing toxic metals.

III.5.3. Risk assessment of contaminated sediments

During the last 20 years various strategies have been proposed for decision-making on contaminated sediments. One of the earlier schemes of USEPA following identification of problem areas and critical chemicals first decides on priority sources. With ongoing sources, the maximum percentage of possible source control is estimated, as well as the question, if recovery can be accomplished in an acceptable time frame. If the question on ongoing sources is denied, an evaluation takes place on combined sediment remedial action and source control. If the sources have been stopped and recovery cannot be expected in acceptable time frame, then sediment remedial action has to be evaluated.

Beside the costs of the remediation techniques, the major questions relate to the contaminant loss pathways. Contaminant loss can occur through one or more pathways. The example of a confined disposal facility indicates that the potential pathways for contaminant loss include surface runoff, effluent, seepage, leachate, dust and uptake by plants and animals. Predictive techniques for estimating contaminant losses comprise two categories (Meyer et al., 1994):

- *a priori* techniques which are suitable for planning-level assessments, and
- techniques that use pathway-specific test data provide state-of-the-art loss estimates (generally more advanced techniques).

For some remediation components there are no pathway-specific tests and *a priori* techniques for all pathways of all components available. Confidence and accuracy for *a priori* loss estimates from confined disposal facilities are low. For test-based loss estimates they vary with the stage of development of the test. Confidence is high for test-based estimates of leachate losses. Confidence and accuracy are high for estimation of test-based runoff loss.

Typical methods for measuring physical and engineering properties of contaminated sediments – *a priori* techniques – as recommended in the early seventies comprise: particle size distribution, organic content – measured as total volatile solids – solids content, liquid and plastic limit test, void ratio and density.

III.5.3.1. Sediment quality criteria

During the last 20 years, considerable experience has been assembled with pathway-specific test data, in particular with more innovative treatment procedures. However, most important progress in risk assessment of contaminated sediments has been made in the context of sediment quality criteria development, following the experience that long-term perspectives in water management need "integrated strategies", in which sediment-associated pollutants have to be considered as well. In particular, it has been evidenced, that for most cases of surface waters, the contaminant levels in the sediments have greater impact on the survival of benthic organisms than do dissolved concentrations (e.g. BenKinney et al., 2001).

First efforts have been undertaken by the USEPA to develop standard procedures for the assessment of environmental impact of sediment-bound pollutants. Further discussions led to the differentiation of biological and chemical–numerical approaches. Biological criteria integrate sediment characteristics and pollutant loads, but they do not generally indicate the cause of effects. With respect to chemical–numerical criteria, there is no immediate indication on biological effects. Their major advantages lie in their easy application and amendment to modeling approaches.

III.5.3.1.1. Biological criteria

Biological approaches on development and application of sediment quality criteria exhibit a common basis in the study of damaging impacts from contaminated sediments on organisms. The biological parameters "bioaccumulation", "toxicity", and "mutagenity" have to be considered separately in any case. Bioassays as well as field surveys are empirical considerations, which cannot provide numerical criteria to be transferred on different situations.

Bioassays are used to estimate toxic potentials of substances. The application of bioassays for the assessment of sediment or dredged material quality is required/advised by the dredged material management guidelines of international conventions like the Oslo and Paris (OSPAR) and the Helsinki and the London convention. However, both on a national and international level the implementation of bioassays for the purpose of dredged material management is still under development. In the Netherlands, a number of bioassays are evaluated and their implementation is scheduled for 2002.

Bioassays seem a promising tool addressing explicitly two issues:

- The implementation of bioassays as additional criteria for the quality of sediments/-dredged material might cover chemicals with different modes of action, otherwise overseen relying on a limited set of chemical criteria.
- An integrated approach, combining bioassays and chemical analysis (toxicity identification evaluation, TIE) can identify harmful chemicals.

The first can complement the chemical monitoring in a cost-effective manner by investigating integrated toxic effect potentials of the "cocktail" of substances present in the aquatic environment. The latter not only detects effect potentials but also can link them to individual chemicals, which could serve as a basis for more detailed studies and subsequently enable the implementation of specific measures at the source.

Selection of the optimal methods for assessing aquatic ecosystem degradation and potential risks from contaminated sediments will depend on the study objectives, resources, and the characterization of the methods. In particular, this is valid for biological test procedures, which increasingly form the key aspect in an integrated approach, characterizing the physical–chemical conditions (including habitat and contaminant patterns), indigenous biological communities, and toxicity. The sediment quality triad (Chapman, 1986) is an integrated procedure, which uses empirical evidence that is observation, not being based on theories. Such procedures seem to be particularly promising, since each component of the system is contributing to the interpretation of the other components.

Currently, there are not many standardized sediment toxicity tests. ASTM (1994) procedure for risk assessment is performed with use of freshwater invertebrates: insects, oligochaete and amphipods as test organisms (*Chironomus* sp., *Hexagenia* sp., *Tubifex tubifex*, *Hyalella azteca* and *Diporeia* sp.) at total duration of 28–30 days. The draft OECD TG 218 (2000) test recommends *Chironomus* sp. as an assay, with use of spiked sediments. The EU Technical Guidance Documents (TGD, 1996) based on the equilibrium partitioning method (EPM) does not provide detailed assessment procedure for sediments; besides, EPM has been found insufficient for highly sorptive or binding substances. This gave rise to the revision of TGD and to development of the newly proposed EU risk assessment concept based on whole-sediment long-term tests with bioassays that represent all possible routes of exposure. Besides benthic invertebrate species, also primary producers (rooted plant) have been considered as assays for a sediment test battery. This concept is now still under development, though already has proven to be valuable in long-term risk assessment for the river sediments (Riedhammer and Schwarz-Schulz, 2001).

Relatively simple and implementable liquid, suspended particulate and solid-phase bioassays have been carried out for assessing the short-term impact of dredging and disposal operations on aquatic organisms (Ahlf and Munawar, 1988). Standardized tests are characterized by their lack of variability, but essential information (e.g. lethality, alterations of growth rate) can only be obtained with such single species test. The influence of the main environmental variables on the interaction of suspended particulates or *in situ* sediment contaminants and organisms should also be determined under simulated field conditions. In particular, benthic bioassay procedures, due to recent developments, are important in evaluating the relationship between laboratory and field impacts (Reynoldson et al., 1987).

The concept of Ahlf et al. (1992) for the assessment of sediment-bound pollutants is mainly based on microbial toxicity tests, using bacteria and algae. An overall biological assessment scheme includes:

- field description of benthic communities,
- benthos bioassay on total sediment,
- sediment contact bioassay with luminescent bacteria,
- porewater bioassay (bacteria, Chromotest), and
- elutriate bioassay (algae, bacteria, Chromotest).

In addition, tests can be performed on fractions of the sediment, which have been extracted or treated with a co-solvent. For example, a non-polar surfactant has been applied, which is commercially used to solubilize hydrocarbons from contaminated soil. On the other hand, the concept can be modified according to users requests, in that only parts of this structure may be needed for a site-specific problem.

In practice, the following question have been posed for test procedures—in particular biotests—on contaminated dredged sediments:

- What are the most toxic sites?
- Where should remediation start?
- What technique has to be used, in accordance with the site-specific pollutant load?

- Is there a difference in the toxicity of sediments, which are resuspended into the water phase and those, which are buried in deeper layers?
- What is the minimum number of assays for non-redundant information?
- What is the relation between different assays and chemical data?

The last two questions are closely related to the costs of such investigations. At present the management of dredged materials comprises hazard assessment of the sediments. Despite the inherent difficulties of conducting risk assessments at the disposal site, it should be integrated in future approaches for decision-making frameworks. Further research is needed before implementation.

For the sake of cost-effectiveness, hazard assessment should be carried out in a multi-level approach.

- *Level I*: limited chemical criteria, limited test battery with bioassays.
- *Level II*: application of an extended battery of bioassays as well as case studies in order to identify the culprit chemicals.

Level II should only be applied for toxic or highly toxic materials where the toxicity cannot be explained by the presence of the investigated chemicals. TIE-like procedures can be used to establish links between effect potentials and causative chemicals as well as to distinguish between toxic potentials from man-made and natural compounds (e.g. phytoestrogens) (Gandrass and Salomons, 2000).

Open questions relate to the implications of anoxic sediments, mainly with respect to the effect of toxic metals. In sulfidic anoxic sediment, even if it is strongly polluted by metals, organisms are considered to be still safe due to the strong fixation of metal ions by S^{2-} or HS^- as source of acid volatile sulfide. Such polluted sediments, however, can behave as a time bomb, which is triggered by only one factor: redox increases to a critical point, i.e. by exposure to oxygen-rich overlying water or directly to air. Once this situation occurs (a possible pathway also is oxygen transfer via plant roots), toxic metals in the sediments will be released to the water phase or transformed into more bioavailable species.

III.5.3.1.2. Chemical numerical criteria

Numerical approaches for the assessment of environmental impact of sediment-associated metals are based on:

- accumulation,
- porewater concentrations,
- solid/liquid equilibrium partition (both sediment/water and organism/water), and
- elution properties of contaminants.

Background approach: compares the actual data with sites comprising natural or insignificant pollutant concentrations. Particularly useful are samples from deeper layers of the sediment sequence at a given site, for example, from drill holes, since this material is derived from the same catchment area and usually similar in its substrate composition. Nonetheless, standardization with respect to grain size distribution is indispensable.

Porewater approach: based on the experience, that the composition of interstitial waters is the most sensitive indicator of the reactions that take place between pollutants on particles and the aqueous phase, which contacts them. There is the advantage of a direct recovery and analysis of water-borne constituents. But there are several disadvantages, mainly arising from the sampling and sample preparation, which need considerable precaution, such as for exclusion of oxygen.

Equilibrium approaches: these approaches are related to the broad toxicological basis of food and water quality data – a very important advantage. On the other hand, there are the effects of sample preparation (e.g. the drying procedures) and separation techniques (e.g. filtration or centrifugation). There are also strong effects of grain size composition and the influence of suspended matter concentration in the aquatic system, which is even more important, if the kinetics of sorption and desorption are too slow for equilibrium to be achieved in a given time of interactions. Unlike non-ionic organic chemicals, K_D-values of metals are not only correlated to organic substances but also to other sorption-active surfaces. Therefore, the equilibrium partition approach exhibits strong limitations for metals.

Remobilization: short-term effects may be studied from water/sediment-suspensions, medium-term effects from experiments using tanks, and long-term effects by applying chemical extractions, either single or in sequence. Field observations often do not show clear effects, as has been demonstrated for the release of metals from anoxic sediments during oxidation. Such implications for future criteria development, particularly important for dredging and management of dredged material, will be discussed on the basis of experience from metal speciation studies on soils and sediments.

III.5.3.2. Long-term effects, particularly of redox processes

Reliability of long-term prognoses on the impact of metal-contaminated sediments is particularly restricted due to the dominance of non-linear and delayed processes in redox- and pH-controlled systems. Acidity is perhaps the most serious long-term threat from metal-bearing wastes. For decades, water seeping from mine refuse has delivered increased metal concentrations into receiving waters. The threat is especially great in waters with little buffer capacity. The acidity production can develop many years after disposal, once the neutralizing or buffering capacity in a pyrite-containing waste is exceeded.

The major processes (see Equations (III.5.1)–(III.5.3)) affecting the lowering of pH values (pH – from 3 to 2) are the exposure of pyrite (FeS_2) and other sulfidic minerals to atmospheric oxygen and moisture, whereby the sulfidic component is oxidized to sulfate. Bacterial action can assist the oxidation of $Fe^{2+}_{(aq)}$ in the presence of dissolved oxygen. Nitrification also results in proton liberation.

$$4\,FeS + 9\,O_2 + 10\,H_2O \rightarrow 4\,Fe(OH)_3 + 4\,SO_4^{2-} + 8\,H^+ \tag{III.5.1}$$

$$4\,FeS_2 + 15\,O_2 + 14\,H_2O \rightarrow 4\,Fe(OH)_3 + 8\,SO_4^{2-} + 16\,H^+ \tag{III.5.2}$$

$$2\,NH_4^+ + 3\,O_2 \rightarrow 2\,NO_2^- + 2\,H_2O + 4\,H^+ \tag{III.5.3}$$

The acidification of a sediment/water system begins after hydrogen ions are generated during the oxidation (e.g. during dredging or resuspension of mainly fine-grained material containing less carbonates than needed for long-term neutralization). Primary emissions containing high metal concentration issue from waste rocks and mine tailings, while tailing ponds are primarily responsible for secondary effects on groundwater. Important and long-term sources of metals are the sediments reworked from the floodplain, mainly by repeated oxidation and reduction processes.

High concentration factors were found in inland waters affected by acidic mine effluents. The concept of acid-producing potential (APP) was initially developed in the prediction and calculation of acid mine drainage and waste tailings management (Anonymous, 1979) as summarized by Ferguson and Erickson (1988). Our findings on the effects of periodical redox processes on both APP and metal mobility in estuarine sediments (Kersten et al., 1985; Kersten and Förstner, 1991) have further enhanced research interest in this field.

Periodical redox processes can induce an increase or decrease in APP or pH in a sediment/water system. In a closed system, periodical redox processes can lead to the change or transfer between APP(s) and APP(aq) but the total APP of the system does not change. The processes are reversible. The hydrogen ions produced during oxidation will be consumed by the following reduction. Contrarily, in an open system, the total APP of the system will change depending on the properties of the system and the reaction processes. Under certain conditions total APP in the system increases, while under other conditions total APP in the system decreases. Some processes are irreversible. The components producing or consuming H^+ ions leave the system and cause the change in APP(s), APP(aq) and permanent acid neutralizing capacity (ANC).

Figure III.5.1 gives the example of "split of sulfate" (van Breemen, 1987). The first reaction is characterized by the reduction of sulfates, e.g. in tidal flats. At the same time organic matter is degraded. Most of the sulfide formed is fixed in the sediment as FeS or FeS_2. Whereas the acid producing potential APP(s) is fixed in the sediment, the ANC in the form of hydrogen carbonate is mobile and can be flushed away. After the next aeration and oxidation extreme acidification of the system can take place.

Direct assessment of the pH-changes resulting from the oxidation of anoxic sediment constituents can be performed by ventilation of sediment suspensions with air or oxygen and subsequent determination of the pH-difference between the original sample and

aerobic	**conditions**			**anaerobic conditions**		
4 $MeSO_4$	+	Fe_2O_3	$\xrightarrow{\text{"CH}_2\text{O"}}$	$2FeS_2$	+	4 $Me(HCO_3)_2$
4 H_2SO_4	+	Fe_2O_3	$\xleftarrow{O_2}$	acid producing potential(APP)		acid neutralization potential (ANC)
solid			$\longrightarrow$	*dissolved*		

Figure III.5.1. "Split" of sulfate in the redox cycle (after van Breemen, 1987).

oxidized material. The greater this difference the higher is the short-term mobilization potential of metals, e.g. during dredging, resuspension and other processes, by which anoxic sediments get into contact with oxygenated water or—following land deposition of dredged material—with atmospheric oxygen. A typical example demonstrating the temporal development of redox and pH-values in a sludge suspension from Hamburg harbor is presented in Figure III.5.2.

Porewater data from dredged material from Hamburg harbor indicate typical differences in the kinetics of proton release from sulfidic and organic sources (Maaß and Miehlich, 1988). Recent deposits are characterized by low concentrations of nitrate, cadmium and zinc. When these low-buffered sediments are oxidized during a time period of a few months to years, the concentrations of ammonia and iron in the porewater typically decrease, whereas those of cadmium and zinc increase (with the result that these metals are easily transferred into agricultural crops). Of the two major release processes, the first—oxidation of sulfides—can be predicted to some extent, whereas the implications of long-term degradation of organic matter on the release of less mobile elements such as copper and lead as yet cannot be described satisfactorily. Here, as with the effects of these interactions on the cycles of anionic metal compounds such as arsenate, further research is needed.

Experimental approaches for calculating APC and ACC for sulfidic mining residues have been summarized by Ferguson and Erickson (1988). A test described by Sobek et al. (1978) involves the analysis of total pyritic sulfur. Potential acidity is then subtracted from neutralizing potential, which can be obtained by adding a known amount of HCl, heating the sample and titrating with standardized NaOH to pH 7. Bruynesteyn and Hackl (1984) calculated APC from total sulfur analysis; here, acid-producing capacity was then subtracted from acid-consuming capacity, obtained by titration with standardized sulfuric

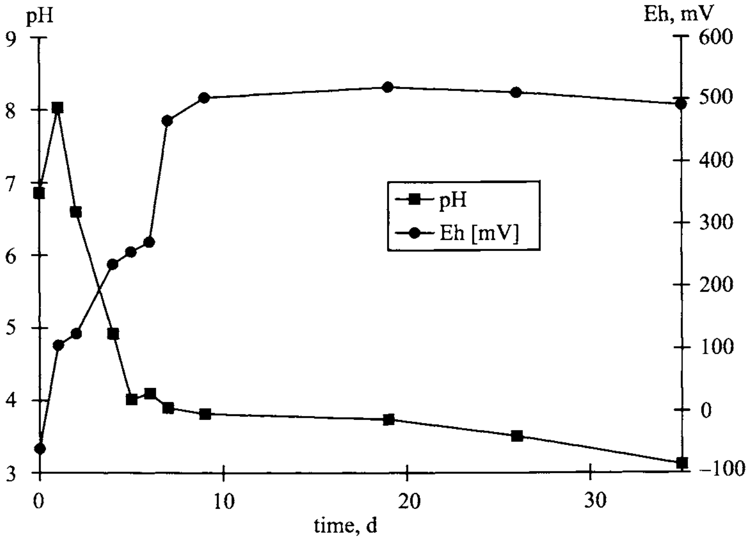

Figure III.5.2. Development of redox potential and pH during the oxidation of a low-buffered dredged mud suspension from Hamburg harbor (Calmano et al., 1992).

acid to pH 3.5. The APC relationships of sediments are more complex than that in sulfidic ores because the APC from organic matter must be considered.

The most efficient *fixation process* within anoxic sediments for trace metals is production of free sulfide during degradation of organic matter and reduction of sulfate. Study of heavy metal associations with sulfides and carbonates in anoxic sediments, therefore, provides insight into early diagenetic processes (Berner, 1981; Morse and Mackenzie, 1990).

Whereas the ability of the sediment to produce free sulfide is determined by the sulfate reduction rates, the ability to remove all produced free HS^- is given by the reactive metal—predominantly reducible Fe^{3+} concentrations—available to form sulfide minerals (available sulfide capacity (ASC): Williamson and Bella, 1980). Simultaneous application of standard sequential leaching techniques on critical trace elements and matrix components can be used for geochemical characterization of anoxic, sulfide-bearing sediments in relation to the potential mobility of critical trace metals (Kersten and Förstner, 1991). For determining the acid-producing capacity ("maximum APC") in anoxic sediments, both the FeS pool ("actual" APC) and the maximum ferrous sulfide (worst case: pyrite)-producing capacity upon disposal has to be taken into consideration.

3.3. Assessing long-term mobility of metals in sediments by titration experiments

With regard to prediction of long-term effects of sediment-bound metals, chemical extraction procedures are of limited value because they usually involve neither reaction-mechanistic nor kinetic considerations. This lack can be avoided, e.g. by an experimental approach, originally used by Patrick et al. (1973) and Herms and Brümmer (1978), where sediments can be treated in a circulation system under controlled intensification of significant release parameters such as pH-value, redox-potential, and temperature. Our experimental design (Schoer and Förstner, 1987) includes an ion-exchange system for extracting and analyzing the released metals at an adequate frequency, and compares sequential extraction results before and after treatment of the sample in the circulation apparatus. Individual metal species are released at different time intervals. Taking into account both element contents released during the 10-week experiments (equivalent to several thousand years of solid/water interaction) and those extrapolated from extraction "pools", concentrations can be calculated for different scenarios.

While these extrapolations have been made from pH 5 conditions, titration curves from investigations on a wide spectrum of metal-bearing waste materials (Obermann and Cremer, 1992) suggest, that pH 4 may be more appropriate for long-term predictions of potential metal releases from contaminated sediments. In this pragmatic approach the pH is automatically adjusted to 4 during the time period of 24 h. Apart from the release rates of metals, which can be determined from samples taken at different time intervals, the sum curve of acid consumption provides information on the potential changes of the matrix composition during acidification and the availability of buffer capacity at different time scales.

Acid consumption reflects slow long-term metal release from sediments. Because calcite dissolution is fast, the acid consumption in the first stage will increase drastically within a short period of time. Cation release and alumosilicate dissolution are dominant factors consuming acid in the later stage. The reactions can be treated as:

$$\mathrm{SO{=}Me} + 2\,\mathrm{H}^+ \leftrightarrows \mathrm{SO{=}H_2} + \mathrm{Me}^{2+},\ \text{and} \qquad \text{(III.5.4)}$$

$$\mathrm{Al_2O_3} + 6\,\mathrm{H}^+ \leftrightarrows 2\,\mathrm{Al}^{3+} + 3\,\mathrm{H_2O} \qquad \text{(III.5.5)}$$

where SO= and Me are surface groups in solid phase and metal, respectively. The reactions of hydrogen ions with metal and alumosilicate are delayed due to the complex sediment structure and matrix. For example, special penetration of hydrogen ions is required for reaction with cations on clay minerals coated with organic matter or biofilms. Rates of reactions can be estimated by measurements of metal concentrations in solution.

In dredged material management two different target areas for combined matrix/metal criteria can be distinguished:

- sediment resuspension and
- dredged material disposal.

With respect to "resuspension of aquatic sediments", which involves more short-term effects than the disposal of dredged material, special emphasis should be posed on the factor "available metal species". Within certain categories of acid producing and consuming capacities, guideline values for individual metals should be based on elutriate data, preferentially at pH 4, for better comparison with other solid matrices (e.g. Swiss Ordinance for Waste Materials (Anonymous, 1990)). Environmental impact of sediment deposits is influenced by the internal chemical conditions rather than by the concentration and extractability of metals. Therefore, priority should be given to the optimization of long-term chemical stability (geochemical engineering).

At the moment, research on long-term effects of redox variations on metal behavior in sediments is mostly based on thermodynamic considerations. Future research should emphasize studies on the kinetics of metal species transformations, hydrogen ion production and metal release as affected by changing redox conditions. Additional important aspects involve the bridging of the gaps between numerical criteria approaches, as reflected by matrix composition and metal mobility, and biological approaches. It may well be, that for such systems, which are much less disturbed than artificial sediment elutriates, relationships between matrix conditions—as reflected, e.g. by redox indices—and metal species bioavailability may be found, which may serve as a more solid basis for the interpretation of results from bioassays, eventually with respect to chronic toxicity.

A promising tool for incorporating both bioavailability and numerical criteria approaches into generic risk assessment of metals in sediments might provide adaptation for the sediment compartment of the recently developed biotic ligand model (BLM) approach that integrates chemical (speciation, complexation) models with more biologically oriented models for predicting metal toxicity in aquatic ecosystems (Janssen and Heijerick, 2002).

III.5.3.4. Integrated process studies

Management of contaminated sediments, i.e. linking risk assessment and identification of cleanup options, requires implementing information on bioavailability and bioaccumulation of pollutants, as well as on processes controlling their particular hydrological and biogeochemical dynamics into a comprehensive sediment assessment scheme, a set of bioassays being a powerful supplement to assess sediment quality. The final development of optimum management strategy, besides economic and social factors, involves engineering elements such as technical feasibility, contaminant reduction, permanence of remedial options like containments and capping, disposal facilities, *in situ* treatment and long-term monitoring concepts. Both for establishing sediment-related quality objectives and for developing adequate remediation procedures and technical problems solutions, a linking set of integrated process studies is needed that comprises a wide range of simulation techniques and models in different spatial and temporal scales (Fig. III.5.3).

The integrated process studies on erosion risks and pollutant mobility in river sediments have been addressed in detail in a series of review papers by Förstner (2001a,b). The major factors, which influence solution/solid equilibrium conditions and the net release of dissolved organic carbon (DOC), nutrients and pollutants from the sediments, include changes of pH and redox conditions, the competitions of dissolved ions and the complexation by organic substances. Special study targets are the formation of new surfaces for the readsorption of dissolved pollutants, or contrariwise, the potential reduction of sorption sites on minerals and the degradation of organic matter, which affects both hydrodynamic processes (erosion vs. sedimentation) and geochemical redox cycles.

For integrating the interdisciplinary study of individual processes and for transferring the results of laboratory experiments to a natural aquatic system, where the processes occur on extremely variable temporal and spatial scales, analytical and numerical models can be applied. Today's models for predicting pollutant transport in rivers are dominated by hydromechanical parameters. A first step for extending these models could involve the consideration of the above-mentioned typical ecosystem factors such as competing ions, complexing agents, redox conditions and—predominantly for metals—pH-values. The next tier 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. The last step, which can be seen so far, would extend the mechanical–chemical

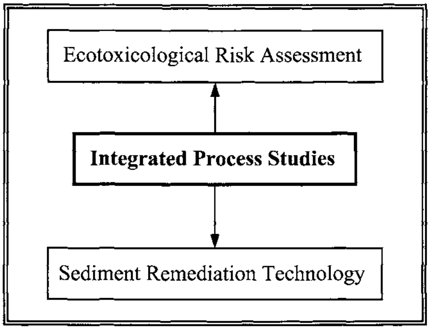

Figure III.5.3. Integrated process studies as a link between ecotoxicological risk assessment and remediation technologies in the management of aquatic sediments and dredged materials (after Förstner, 2001b).

model into biology. According to Kern (1997), such biochemical multi-component models should consider rates of growth and decay of organisms and organic matter.

The thorough characterization of processes, which influence the interaction and transfer of pollutants in sediments and suspended matter, along with development of the relevant models would greatly enhance possibility of contaminant release prevention and control from sediments and optimization of remedial measures.

III.5.4. Remediation procedures

The various types for sediment remediation can be subdivided according to the mode of handling "in place" or "excavation", or in relation to the technologies "containment" or "treatment". Important containment techniques include *in situ* capping (ISC) and "confined disposal facility". Regarding in-place-treatment, biological processes may be applied. Excavated sediments—apart from physical separation—can be treated to immobilize pollutants, mainly metals. An overview on various technology types for sediment remediation is shown in Table III.5.1.

A more general conceptual scheme related to excavated sediment material has been proposed by the 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, etc.

The Dutch Development Program for Treatment Processes for Contaminated Sediments (POSW), starting up in 1989 and running until 1996, was aimed at the development of ecologically sound dredging and processing techniques, to be used in the

Table III.5.1. Technology types for sediment remediation.

Technology	In place	Excavated
Containment	Capping	Beneficial use Capping/confined aquatic disposal Commercial landfills Confined disposal facility
Treatment	Bioremediation Chemical Immobilization	Chemical Biological Extraction Immobilization Physical separation Thermal

remediation and reuse of polluted sediments (Anonymous, 1997; Rulkens, 2001). Technical applicability had to be demonstrated in practice, as part of an integrated remediation chain. Attention was also paid to the economic and environmental consequences of the several types of techniques as part of entire clean-up chains.

Typical research issues of the POSW Stage II (1990–1996) program were (Anonymous, 1997; Rulkens, 2001):

- Separation of sludge into subflows (hydrocyclone separation, upstream separation, settling, flotation, dewatering of fine fractions, practical experience in pilot remediation).
- Thermal and chemical treatment methods (thermal desorption, incineration, wet oxidation, solvent extraction).
- Biological treatment (landfarming, greenhouse farming, slurry treatment in bioreactors).
- Immobilization of pollutants in products (melting, sintering, practical experience in pilot remediation).
- Assessment of the environmental effects of processing chains (based on life-cycle analysis, LCA).
- Scenarios for large-scale processing, varying from "natural" processes in treatment plants (sedimentation, dewatering, landfarming and ripening) to maximum deployment of classifying and polishing methods.

III.5.4.1. Chemical, biological and thermal treatment of dredged sediments

In the following, typical parameters are given for important treatment procedures as well as on the costs of such methods:

Factors affecting immobilization processes: solidification/stabilization is a commonly used term to cover immobilization technologies. The former is related to physical properties, the latter suggests chemical effects. 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.

Factors affecting solvent extraction processes: the primary application of solvent extraction is to remove organic contaminants such as halogenated compounds and petroleum hydrocarbons. 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.

Limitations to biodegradation processes: 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. Often, the request for such procedures is a simple indication of ignorance for sediment pollution problems. Even in optimal cases, there are many limitations to biodegradation processes: Temperature, nutrients, and oxygen, are the most important ones.

Factors affecting costs for treatment technologies: 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. These are mostly well-known examples from industrial waste technology. Typical cost factors for sediments include water quantity, moisture contents, physical and chemical characteristics (e.g. grain size and organic material content).

In a trial to rank the individual technologies, one can follow the proposals in the Draft Remediation Guidance Document prepared by the USEPA Oceans and Coastal Protection Division/Great Lakes National Program. Three criteria have been used:

- *State of development*: is mostly good except for non-removal and treatment alternatives. Such deficiencies should be overcome by intensified research.
- *Potential contaminant loss*: is particularly high for removal. This would favor *in situ* techniques. ISC could be the method of choice for areas, where maintenance dredging is not essential.
- *Costs*: it is already clear at this point, that the cost factor will mostly exclude treatment (in the restricted sense) of large-volume contaminated sediments. The only possibility would be the reduction of the volume by mechanical pretreatment, after that chemical–biological techniques could be used potentially.

It is quite obvious that technological options are more restricted for dredged sediments than for other waste materials in most cases. In particular, remediation techniques in the restricted sense often are economically unacceptable because of the large volume of contaminated sediments.

III.5.4.2. Geochemical engineering – application to contaminated sediments

Geochemical engineering (Salomons and Förstner, 1988a,b) applies geochemical principles (such as concentration, stabilization, solidification, and other forms of long-term, self-containing barriers) to determine the mobilization and biological availability of critical pollutants.

In modern waste management, the fields of geochemically oriented technology include:

- the study of material fluxes within and between the anthroposphere and "geospheres";
- the optimization of elemental distribution at high-temperature processes;
- the selection of favorable milieu conditions for the deposition of large-volume wastes;
- the selection of additives for the solidification and stabilization of waste materials; and
- the development of test procedures for long-term prognoses of pollutant behavior.

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 milieu conditions. Selection of appropriate environmental conditions predominantly influences 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.

III.5.4.3. Chemical stabilization by additives/storage under permanent anoxic conditions

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 (Malone et al., 1982; Wiedemann, 1982; Goumans et al., 1991).

Laboratory studies on the evaluation and efficiency of stabilization processes 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.

Regarding the various containment strategies it has been argued that upland containment (e.g. on heap-like deposits) could provide a more controlled management than containment in the marine environment. However, contaminants released either gradually from an imperfect impermeable barrier (also to groundwater) or from failure of the barrier could produce substantial damage (Kester et al., 1983). On the other hand, near-shore marine containment (e.g. in capped mound deposits), offers several advantages, particularly regarding the protection of groundwater resources, since the underlying water is saline and inherent chemical processes are favorable for the immobilization or degradation of priority pollutants.

In a review of various marine disposal options, Kester et al. (1983) suggested that the best strategy for disposing of contaminated sediments is to isolate them in a permanently reducing environment. Disposal in capped mound deposits above the prevailing seafloor, disposal in sub-aqueous depressions, and capping deposits in depressions provide procedures for contaminated sediment (Bokuniewicz, 1982). 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 polluted materials are covered with inert sediment became known as “subsediment-deposit”.

Under subsediment 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 milieu 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 (Sahm et al., 1986; Kersten, 1988).

However, if a permanent advective transport through the sediment interface occurs, which may be induced by groundwater seepage, contaminant flux will reappear after a short lag-time following sub-aqueous cap installation. The application of a relatively new method of reactive permeable barriers, i.e. capping layers that consist at least partly of one or more reactive components that are capable of actively demobilizing the contaminants in percolation porewater, may significantly enhance the ISC effect from a safety measure to a full remediation technique provided that the adequately efficient reactive materials for active barrier systems are applied. Highly favorable chemical and physical properties with respect to application in sub-aqueous capping projects, as well as cost-efficiency were found to show natural microporous materials, such as natural zeolites. A field-scale investigation on use of natural zeolite in active barrier systems has been currently conducted in the framework of an Australian–German research project, funded by the German Ministry of Research and Technology (Jacobs and Förstner, 2001).

III.5.4.4. In situ sediment treatment in flood plains

Another type of sediment pollution problems that differs from managing contaminated dredged materials at harbor sites, originate from large-scale dispersion, transport and deposition of contaminants in floodplains and polder areas. In the Spittelwasser Case Study (the upper Elbe river system), a stepwise approach combining different monitoring and remediation techniques has been proposed. These techniques would include point excavations of contaminated material, promotion of plant growth as an element for stabilizing the soil and flood sediments, and the installation of sediment traps. The "diagenetic" effects of natural non-destructive attenuation processes of organic and inorganic contaminants and their temporal development in these sediments and soils will be also studied. Significant reduction of the reactivity of solid matrices due to an enhanced mechanical consolidation of soil and sediment by compaction, loss of water and mineral precipitation in pore space is anticipated there, apart from chemical processes (Förstner, 2001c).

III.5.5. Conclusions

Technological options are more restricted for dredged sediments than for other waste materials in most cases. In particular, remediation techniques in the narrow sense often are economically unacceptable because of the large volume of contaminated sediments. The widely diverse contamination sources in larger catchment areas usually produce a mixture of pollutants, which is more difficult to treat than a specific industrial waste. Even if one has procedures at hand to reduce 9 priority pollutants below the guideline values, number 10, for example for mercury or PCB may render the whole business unrealistic. There is a long retention time for sediments in larger catchment areas. Improvement at the source may need decades to become effective in the sediments at the lower reaches and harbors close to the river mouth. For most sediments from maintenance dredging, there are more arguments in favor of "disposal" rather than "treatment". Final storage conditions would imply, that these materials should be deposited in a favorable chemical environment. At the actual state of knowledge, this could only mean "permanent" anoxic conditions". Such conditions can be made artificially by capping or be selected from natural environments. However, even for these stable geochemical conditions, which are provided, for example, in natural environments such as the Black Sea and fjords, not all potential implications for long-term pollutant release and transformations are known, and therefore, further research is needed. Capping materials usually have been clean sediments, sand or gravel. The protective function of such "non-reactive" barriers, however, is so far restricted to site-specific settings where bioaccumulation of contaminants by benthic infauna, or resuspension and transport by erosive forces, or slow diffusive transport as it may be induced by groundwater seepage are the prevalent mechanisms in contaminant release. The application of reactive barriers, i.e. capping layers that consist at least partly of one or more reactive components that are capable of actively demobilizing the contaminants in percolating porewater, extends the ISC concept in that it is not further subject to this limitation. Thus continuous contaminant loss can be long-term active as well as diffuse transport may be inhibited efficiently by employing reactive barriers.

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