Sediment Criteria Development

Contributions from Environmental Geochemistry to Water Quality Management

ULRICH FÖRSTNER, WOLFGANG AHLF, WOLFGANG CALMANO, and MICHAEL KERSTEN[1]

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[1] Arbeitsbereich Umweltschutztechnik, Technische Universität Hamburg-Harburg. Eißendorferstr. 40, D-2100 Hamburg 90, FRG

Abstract

The role of sediments as carriers and potential sources of contaminants is reviewed. A program of sediment studies will normally consist of a series of objectives of increasing complexity, each drawing part of its information from the preceding data base. The study of dated sediment cores has proven particulary useful as it provides a historical record of the various influences on the aquatic system by indicating both the natural background levels and the man-induced accumulation of pollutants over an extended period of time. Since adsorption of pollutants onto particles is a primary factor in determining the transport, deposition, reactivity, and potential toxicity of these materials, analytical methods should be related to the chemistry of the particle's surface and/or to the pollutant species highly enriched on the surface.

New objectives regarding the improvement of water quality as well as problems with the resuspension and land deposition of dredged materials require a standardized assessment of sediment quality. Biological criteria integrate sediment characteristics and pollutant loads, while generally not indicating the cause of effects. With respect to chemical-numerical criteria immediate indications on biological effects are lacking; major advantages lie in their easy application and amendment to modeling approaches. Numerical approaches, on the one hand, are based on (1) accumulation; (2) pore water concentrations; (3) solid/liquid equilibrium partition (sediment/water and organism/water); and (4) elution properties of contaminants. The second component in an assessment scheme would include characteristics of the solid substrate, in particular, buffer capacity against pH-depression. At the present stage of criteria development we propose that the substrate properties should be classified on the basis of the carbonate and sulfide inventory, whereas the pollutant load is advantageously assessed by the accumulation rate multiplied with a toxicity factor for the respective substance.

1 Introduction

Sediments are both carriers and potential sources of contaminants in aquatic systems, and these materials may also affect groundwater quality and agricultural products when disposed on land (Förstner and Müller 1974). Contaminants are not necessarily fixed permanently by the sediment, but may be recycled via biological and chemical agents both within the sedimentary compartment and the water column. Bioaccumulation and food chain transfer may be strongly affected by sediment-associated proportions of pollutants. Benthic organism, in particular, have direct contact with sediment, and the contaminant level in the sediment may have greater impact on their survival than do aqueous concentrations.

In modern sediment research on contaminants four aspects are discussed, which in an overlapping succession also reflect the development of knowledge in particle-associated pollutants during the past 25 years: (1) Identification of sources and distribution; (2) evaluation of solid/solution relations; (3) study of transfer mechanism to biological systems, and (4) assessment of environmental impact. In practice, aspects (1) and (4) are of particular relevance, and recent developments will be treated in the present review.

2 Identification of Sources and Temporal Developments

A program of sediment studies will normally consist of a series of objectives of increasing complexity, each drawing part of its information from the preceding data base (Golterman et al. 1983):

a) *Preliminary site characterization*: Low density sampling with limited analytical requirements, to provide a general characterization of an area for which little or no previous information exists.

b) *Identification of anomalies*: More detailed sampling and analyses, designed to etablish the presence and extent of anomalies.

c) *Establishment of references*: To create reference points, in the form of some measured parameters, for future comparison.

d) *Identification of time changes*: To show trends in variations of sediment data over time, by use of sediment cores or other repeated sediment samplings.

e) *Calculation of mass balances*: To account for the addition and subtraction of sediment-related components with an aquatic environment (a complex study), by means of accurate and representative sampling and analysis.

f) *Process studies*: Specialized sampling to improve state of knowledge about aquatic systems, e. g. by supplementary laboratory experiments.

The principal relationships between *sampling objectives* and *type of activities* for water-related studies are summarized in Table 1.

Program objectives largely control the type, density, and frequency of sediment sampling and associated analyses; whereas the type of environment (rivers, lakes, estuaries, etc.) largely controls the locations and logistics of sampling. Logistic factors include (Golterman et al. 1983):

1. Local availability of sampling platform or vessel;
2. Time available;
3. Access to sampling region;
4. Suitability of survey system to locate sample position;
5. Availability of trained personnel and supportive staff;
6. Availability of equipment;

Table 1. Sampling objectives and type of activities for water-related studies

Type of activity (UNESCO-WHO 1978)	GEMS water objectives (WHO 1978)	Sediment objectives (categories in text)
Monitor		
Continuous standard measurement and observation	Cultural impact on water quality, suitability of water quality for future use	Establish reference point(s); category (c)
Surveillance		
Continuous, specific observation and measurement relative to control and management	Observe sources and pathways of specified hazardous substances	Trace sources (spatial)
Survey		
Series of finite duration; intensive, detailed programs for specific purposes	Determine quality of natural waters	Identify anomalies (category b); calculate mass balances (category e); study process (f)

7. Storage and security;
8. Transport systems;
9. Follow-up capability.

For complex surveys, there are numerous types of sampling patterns from which to choose, e.g., spot samples, square grids (including nested and rotated grids), parallel line grids and traverse line grids (with equal or non-equal sampling), and ray grids or concentric arc sampling, each of which offers some particular advantage (Golterman et a. 1983, pp 76–79).

The suitability of corers and bottom samplers has been tested during equipment trials by Sly (1969). For sources reconnaissance analysis, fine- to medium-grained bottom deposits from a depth of 15–20 cm can be collected, for example, with an Ekman grab sampler. In environments with a relatively uniform sedimentation, for example, in lakes and in marine coastal basins, where the deposits are fine-grained and occur at a rate of 1 to 5 mm/yr, a more favorable procedure involves the taking of vertical profiles with a gravity or valve corer (Jenne et al. 1980).

The study of dated sediment cores has proven particularly useful as it provides a historical record of the various influences on the aquatic system by indicating both the natural background levels and the man-induced accumulation of elements over an extended period of time. Various approaches to the dating of sedimentary profiles have been used but the isotopic techniques, using ^{210}Pb, ^{137}Cs, and $^{239+240}Pu$, have produced the more unambiguous results and therefore have been the most successful. Major contributions to the "Historical Monitoring" by sediment studies (Alderton

1985) have been given by German Müller (1977a, b, 1979, 1981, 1983, 1985) and German Müller et al. (1890) in different parts of the world.

3 Assessment of Critical Pools of Pollutants in Sediments

Since adsorption of pollutants onto air- and waterborne particles is a primary factor in determining the transport, deposition, reactivity, and potential toxicity of these materials, analytical methods should be related to the chemistry of the particle's surface and/or to the metal species highly enriched on the surface. Basically there are three methodological concepts for determining the distribution of an element within or among small particles (Keyser et al. 1978):

1. *Analysis of single particles* by X-ray fluorescence using either a scanning electron microscope (SEM) or an electron microprobe can identify differences in the matrix composition between individual particles. The total concentration of the element can be determined as a function of particle size. Other physical fractionation and preconcentration methods include density and magnetic separations.

2. The *surface of the particles* can be studied directly by the use of electron microprobe X-ray emission spectrometry (EMP), electron spectroscopy for chemical analysis (ESCA), Auger electron spectroscopy (AES), and secondary ion-mass spectrometry. Depth-profile analysis determines the variation of chemical composition below the original surface.

3. *Solvent leaching* – apart from the characterization of the reactivity of specific metals – can provide information on the behaviour of pollutants under typical environmental conditions. Common single reagent leachate tests, e.g. U.S. EPA, ASTM, IAEA and ICES use either distilled water or acetic acid (Theis and Padgett 1983). A large number of test procedures have been designed particularly for soil studies; these partly used organic chelators such as EDTA and DTPA (Sauerbeck and Styperek 1985).
Laboratory techniques for generating leachate from solid materials are generally grouped into batch and column extraction methods. The batch extraction method offers advantages through its greater reproducibility and simplistic design, while the column method is more realistic in simulating leaching processes which occur under field conditions (Jackson et al. 1984). For batch studies best results with respect to the estimation of short-term effects can be attained by "cascade" test procedures at variable solid/solution ratios.

In connection with the problems arising from the disposal of solid wastes, particularly of dredged materials, extraction sequences have been applied which are designed to differentiate between the exchangeable, carbonatic, reducible (hydrous Fe/Mn oxides), oxidizable (sulfides and organic phases),

Table 2. Sequential extraction scheme for partitioning sediments (Calmano and Förstner 1983; Kersten and Förstner 1986, 1987)

Fraction	Extraction	Extracted component
Exchangeable	1 *M* NH_4OAc, pH 7	Exchangeable ions
Carbonatic	1 *M* NaOAc, pH 5 with HOAc	Carbonates
Easily reducible	0.01 *M* NH_2OH HCl with 0.01 *M* HNO_3	Mn-oxides
Moderately reducible	0.1 *M* oxalate buffer pH 3	Amorphous Fe-oxides
Sulfidic/organic	30% H_2H_2 with 0.02 HNO_3 pH 2; extracted with 1 *M* NH_4OAc-6% HNO_3	Sulfides together with organic matter
Residual	Hot concentrated HNO_3	Lithogenic crystalline

and residual fractions (Engler et al. 1977). Despite clear advantage of a differentiated analysis over investigations of total sample – sequential chemical extraction is probably the most useful tool for predicting long-term adverse effects from contaminated solid material – it has become obvious that there are many problems associated with these procedures (Kersten et al. 1985). One of the more widely applied extraction sequences of Tessier and coworkers (1979) has been modified by various authors (Table 2).

4 Sediment Quality Criteria

Three major reasons have been given for the establishment of sediment quality criteria:

1. In contrast to the strong temporal and spatial variability in the aqueous concentrations of contaminants, sediments integrate contaminant concentrations over time, and can, therefore, reduce the *number of samples* in monitoring, surveillance, and survey activities;
2. Long-term perspectives in water resources management involve *integrated strategies*, in which sediment-associated pollutants have to be considered;
3. Wastewater plans will increasingly be based on the *assimilative capacity* of a certain receiving system, which requires knowledge of properties of sedimentary components as the major sink.

Efforts have been undertaken mainly by the United States Environmental Protection Agency to develop standard procedures and criteria for the assessment of environmental impact of sediment-associated pollutants. Initial discussions (US Environmental Protection Agency 1984; Anonymous 1985) suggested five methodological approaches which merit closer consideration: (1) background approach; (2) water quality/pore water approach; (3) sediment/water equilibrium partitioning approach; (4) sediment/organism equi-

librium approach; and (5) bioassay approach. Further discussions led to the differentiation of biological and chemical-numerical approaches (G. Chapman et al. 1987):

Biological criteria		*Chemical-numerical criteria*
– Field biological surveys		– Background approach
– Bioassay on original sediments	Sediment-quality-"triad"	– Pore water approach
– Bioassay on spiked sediments		– Sediment/water-equilibrium
		– Sediment/organism-equilibrium
		– Elution tests
		– Substrate composition

4.1 Biological Criteria

Biological criteria have been developed and are already applied in various areas (Anderson et a. 1987; G. Chapman et al. 1987):

1. *Field biological surveys* conduct on-site studies of biota to evaluate possible impact at site (biological response pass/fail).

2. *Bioassay of spiked sediment* estimates effect/no effect sediment concentration for a specific chemical (numerical criterion). May be desired in clearance of new chemicals.

3. *Tissue action level* links sediment concentration to safe tissue concentration (e. g., FDA action level or body burden-response data) through application of equilibrium or kinetic models (numerical criterion).

4. *Aqueous toxicity data* apply toxicity data from typical water-column bioassays to sediments through direct measurement of pore water concentration or estimation of pore water from sediment concentrations through application of equilibrium models. May be desired in evaluation of new chemicals.

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 to different situations.

Generally, it is difficult to establish clear cause-and-effect relationships between acute or chronic toxic effects on biota and the occurrence of specific pollutants in sediments. One major limitation is that not all sediment-

associated chemicals can presently be identified; thus, unidentified compounds cannot be ruled out as principal etiological factors.

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 a 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 1987).

With restriction to the effects on benthic communities, the sediment quality "triad" by P.M. Chapman (1986) combines chemistry and sediment bioassay measurements with in-situ studies: Chemistry and bioassay estimates are based on laboratory measurements with field-collected sediments. In-situ studies may include, but are not limited to, measures of resident organism histopathology, benthic community structure, and bioaccumulation/metabolism. Areas where the three facets of the triad show the greatest overlap (in terms of positive or negative results) provide the strongest data for determining numerical sediment criteria.

Studies have been performed in the Puget Sound, Washington by Long and Chapman (1986). In the sediment three dominant and representative chemical groups were distinguished in the analyses and were selected for further study: high molecular weight combustion polyaromatic hydrocarbons (CPAHs), polychlorinated biphenyls (PCBs), and lead. Three types of sediment bioassays were considered: the amphipod *Rhepoxynius abronius* acute lethality test, the oligochaete *Monopylephorus cuticulatus* respiration effects test, and the fish cell anaphase aberration test. Bottom fish histopathology was based on the frequency of selected liver lesions in English sole (*Parophrys vetulus*) from different areas of Puget Sound; liver lesions have been considered most likely to be related to chemical contaminant exposures (Malins et al. 1984). A summary comparison of the data based on effects frequencies of sediment bioassays and in-situ studies (i.e., bottom fish histopathology) indicates that roughly similar sediment contaminant concentrations produce both types of biological responses (Table 3). Bioassay data are divided into those frequencies of effects that contain all rural areas, and those that contain only urban, industrialized areas. Bottom fish histopathology data are divided into frequencies of occurrence of up to 5% and those that are greater than 5%.

The general question, how the borderline concentrations ($\geqq$ 130 mg/kg Pb, $\geqq$ 6.8 mg/kg PAHs, $\geqq$ 0.8 mg/kg PCBs) are related to biological effects, has been studied by G. Chapman et al. (1987) from independent experiments; results from these investigations indicate remarkable coincidence with the

Table 3. Summary comparison of biological effects frequencies with sediment concentrations of selected chemical contaminants in different areas of Puget Sound, Washington (Chapman 1986)

Effects frequency (%)	Chemical contaminants[a] (μg/g)		
	Pb	CPAHs	Total PCBs
Sediment bioassays			
15–50	20– 50	0.2– 5.0	0.01–0.10
55–80	90–800	3.8–24.0	0.10–0.90
Bottom fish histopathology			
0– 5	20– 90	0.2– 3.8	0.01–0.20
6–40	130–800	6.8–24.0	0.80–0.90

[a] Borderline concentrations are underlined.

"triad" data. The obvious similarity of results from different areas may be explained by the experience that the spectrum of pollutants in sediments is widely comparable due to the inputs from common sources, such as from atmospheric emissions from combustion of fossil fuels, where PAH and metals exhibit typical associations (Müller 1977).

4.2 Chemical-Numerical Approaches

4.2.1 Background Approach

4.2.1.1 Standard Values. An example of standard values for sediment quality criteria is given by the Dutch sediment quality draft (van Veen and Stortelder 1988). Dutch environmental pollution standards have traditionally been based on contaminant concentrations. The advantages, particularly for monitoring this type of standard, are simplicity and absence of ambiguity. The lack of consideration of the ecological impact is a disadvantage. In a draft for developing sediment standards – aimed at disposal of contaminated sediment on land – the pollution concentrations are normalized to a standard sediment ("underwater soil") consisting of 10% organic matter and 24% clay content (particle size < 2 μm). The level for the target value is based on field observations of sediments in surface waters unaffected by industrial or other discharges. The level for the standard value is based on observations of sediments which are slightly contaminated but with no known ecological effect. The levels for the limit value do not have any ecological background; they are based on existing standardization in the Rotterdam area. These three levels are defined for many toxic compounds, some of which are given in Table 4. Integration of standards for terrestrial and aquatic soils is under discussion and could be of great importance, for example, in the case of disposal of contaminated sediments on land.

Table 4. Draft standards for contaminated sediments (van Veen and Stortelder 1988). Data in mg/kg, except PCB and PAH (μg/kg)

	Cr	Cu	Zn	Cd	Hg	Pb	As	EOX	Oil	PCB	PAH
Target value	100	25	180	0.8	0.3	50	25	–	–	1	50
Standard value	125	70	750	4	1	125	40	5	2000	10	500
Limit value	600	400	2500	30	15	700	100	20	5000	100	3500

4.2.1.2 Pollution Indices. A quantitative measure of metal pollution in aquatic sediments has been introduced by Müller (1979), which is called the Index of Geoaccumulation:

$$I_{geo} = \log_2 C_n/1.5 \times B_n,$$

where C_n is the measured concentration of the element n in the pelitic sediment fraction ($< 2\,\mu m$) and B_n is the geochemical background value in fossil argillaceous sediment ("average shale"); the factor 1.5 is used because of possible variations of the background data due to lithogenic effects. The Index of Geoaccumulation consists of seven grades, whereby the highest grade (6) reflects 100-fold enrichment above background values ($2^6 = 64 \times 1.5$). In Table 5 an example is given for the River Rhine; and a comparison of these sediment indices with the water quality classification of the International Association of Waterworks in the Rhine Catchment (IAWR) has been made. It should be mentioned that – similar to the sediment standards in Table 5 – no further consideration is given to the ecological relevance of the values.

Table 5. Comparison of IAWR water quality indices (based on biochemical data) and Index of Geoaccumulation (I_{geo}) of trace metals in sediments of the Rhine River. (After Müller 1979)

IAWR Index	IAWR water quality (pollution intensity)	Sediment accumulation (I_{geo})	I_{geo}-class	Metal examples	
				Upper Rhine	Lower Rhine
4	Very strong pollution	>5	6		Cd
3–4	Strong to very strong	>4–5	5		
3	Strongly polluted	>3–4	4		Pb, Zn
2–3	Moderately to strongly	>2–3	3	Cd, Pb	Hg
2	Moderately polluted	>1–2	2	Zn, Hg	Cu
1–2	Unpolluted to moderately polluted	>0–1	1	Cu	Cr, Co
1	Practically unpolluted	<0	0	Cr, Co	

4.2.1.3 Ecological Risk Indices Derived from Enrichment Factors. A sedimentological approach for an "ecological risk index" was introduced by Hakanson (1980) and tested on 15 Swedish lakes representing a wide range in term of size, pollution status, trophic status, etc. These estimations are based on four "requirements", which are determined in a relatively rapid, inexpensive, and standardized manner from a limited number of sediment samples. Contrary to the afore mentioned approaches, a special term is introduced for estimating the ecotoxicological significance of the individual contaminants. The toxic requirement differentiates the various contaminants according to an "abundance principle", i.e. assuming that a proportionality between toxicity and rarity, and to their "sink effect" exists, i.e. their affinity to solid substrates. After a normalization process the "sedimentological toxic factor" is calculated in the following sequences: $Zn = 1 < Cr = 2 < Cu = Pb = 5 < As = 10 < Cd = 30 < Hg = PCB = 40$.

The "toxic response factor", as formulated by Hakanson (1980) from a complex matrix of assumptions, can possibly be defined much easier from direct measurements of the relative toxicity of typical pollutants in aquatic systems, e.g. from bioassays on water samples. We propose a toxicity factor based on the standardized "Microtox test system", where the individual concentrations are determined from comparable EC_{50} values. According to Walker (1988), the following factors could be used for metallic elements: $Pb = 1$; $Zn = 5$; $Cu = 5$; $Cd = 10$; $Hg = 35$.

4.2.2 Pore Water Approach

The composition of interstitial waters is the most sensitive indicator of the types and the extent of reactions that take place between pollutants on waste particles and the aqueous phase which contacts them. Particularly for fine-grained material the large surface area related to the small volume of its entrapped interstitial water ensures that minor reactions with the solid phases will be indicated by major changes in the composition of the aqueous phase (Förstner and Kersten 1988).

Interstitial waters are recovered from sediments by dialysis, centrifugation, or squeezing. Oxidation must be prevented during these procedures. Watson et al. (1985) showed that sediments stored prior to the separation of interstitial water yield significant changes on chemical composition compared to samples processed within 24 h of collection. In-situ methods are considered more promising because of their inherent simplicity, and appear to be well adapted to the study of trace metals at the sediment-water interface under field conditions. An in-situ sampler for close-interval pore water studies as presented by Hesslein (1976) can be made from a clear acrylic plastic panel with small compartments predrilled in 1-cm steps or less. This panel can be covered by a nondegradable dialysis membrane or by a polysulfonate membrane filter sheet (Carignan 1984) and displaced into the sedi-

ment allowing equilibrium to take place over a period of some days to weeks. An improved sampler of this type has been decribed by Schwedhelm et al. (1988).

While the direct recovery and analysis of waterborne constituents can be seen as a major advantage of this approach, there are several disadvantages.

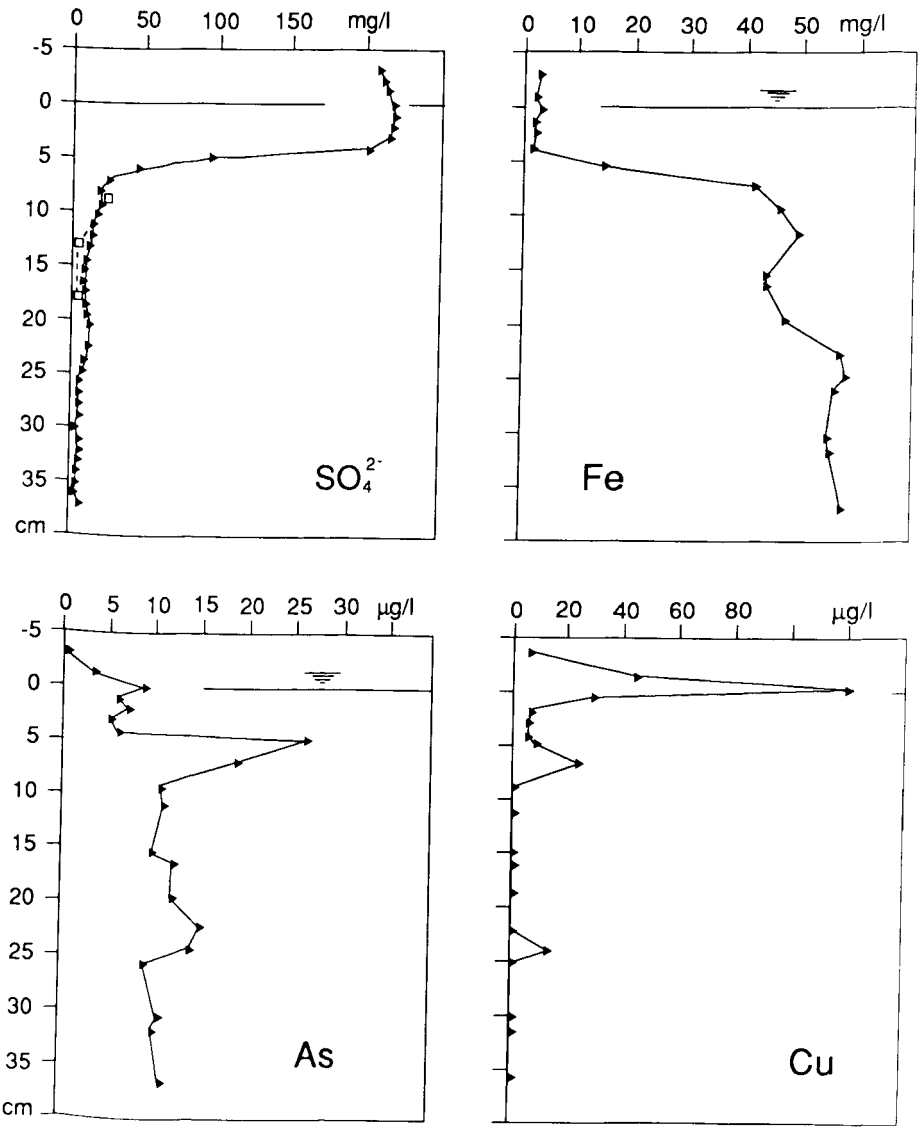

Fig. 1. Pore water profiles in Elbe River sediments (after Schwedhelm et al. 1988). 0-cm-depth contour line reflects the sediment/water interface

particularly arising from the sampling and sample preparation, which are not yet routine procedures, and usually involve considerable precautionary measures such as exclusion of oxygen. In addition, interpretation of profile data may be difficult, as demonstrated from the examples of depth profiles of typical constituents in pore waters from Elbe River sediments (Fig. 1): There are strong gradients for redox-sensitive constituents, such as iron, arsenic, and sulfate; the question is which position in the core profile is the most typical with respect to the uptake by benthic organisms. In this context, the characteristic enrichment of copper at the sediment/water interface, probably due to complexation by organic ligands from degrading organic matter, seems to be particularly relevant.

4.2.3 Sediment/Water Equilibrium Partitioning

This approach is related to a relative broad toxicological basis of water quality data. The distribution coefficient K_D, which is determined from laboratory experiments, is defined as the quotient of equilibrium concentration of a certain compound in sediment (C_s^x, e.g. in mg/kg) and in the aqueous phase (C_w^x; e.g. in mg/l). Since, in particular, water quality management is requesting such simple calculation bases, the problematic nature of these relations – as evidenced from various references (Table 6) – should clearly be indicated. Nonetheless, it seems that sediment quality criteria of the U.S. Environmental Protection Agency will preferentially be based on these approaches.

In practice, three categories of compounds can be distinguished:

1. *Nonpolar organic compounds*, which are dominantly correlated to the content of organic carbon in the sediment sample. The partition coefficient K_D

Table 6. Factors and mechanisms influencing the distribution of pollutants between solid and dissolved phases

Factor/mechanism	Example[a]	References
Sample preparation (e.g. drying)	Metals[a]	Duursma (1984)
Separation (filtration/centrifugation)	Metals[a]	Calmano (1979)
Grain size distribution	Metals[a]	Duursma (1984)
Suspended matter concentration	DDT/Kepone	Connor and Connolly (1980)
	PCBs	Voice et al. (1983)
Kinetics of sorption/desorption	Metals[a]	Schoer and Förstner (1984)
Nonreversibility of sorption	Metals	Lion et al. (1982)
	PCBs	DiToro and Horzempa (1982)
	Chlorophenols	Isaaacson and Frink (1984)
Effect of bioconcentration	1,4-DCB	Oliver and Nicol (1982)

[a] Experiments with artificial radionuclides.

can be normalized from this parameter and the octanol/water coefficient (K_{OW}): $K_D = 0.63\ K_{OW}$/content of organic carbon in total dry sediment (0.63 is an empirical value). For these substances, such as PCB, DDT, and PAH reliable and applicable data can be expected with respect to the development of sediment quality criteria.

2. *K_D-values of metals* are not only correlated to organic substances but also with other sorption-active surfaces. Toxicological effects are often inversely correlated with parameters such as iron oxyhydrate. Quantification of competing effects is difficult, and thus the equilibrium partition approach for sediment quality assessment of metals still exhibits strong limitations.

3. *Polar organic substances* (e.g. phenols, polymers with functional groups, tensids) are widely unexperienced with respect to their specific "sorption" behavior. Partition coefficients are influenced by anion and cation exchange capacity and surface-charge density as a function of pH and other complex properties, so that the K_D-approach at present cannot be taken into consideration.

4.2.4 Sediment/Biota Equilibrium Partitioning

A very important aspect of the assessment of the environmental fate of chemicals is the prediction of the extent to which these substances will achieve concentrations in biotic phases. For organic chemicals, it has been suggested by Mackay (1982) that the bioconcentration factor K_B can be regarded simply as a partition coefficient between an organism consisting of a multiphase system and water; if the dominant concentrating phase is a lipid that has similar solute interaction characteristic to octanol, a proportional relationship between bioconcentration factor K_B and $K_{octanol/water}$ is expected ($K_B = 0.048\ K_{OW}$). This correlation must be used with discretion, particularly for very low K_B, where the amount of solute in nonlipid phases may be appreciable, and for high-K_{OW} compounds (e.g. mirex, octachlorosterene, and higher chlorinated biphenyls). In fact, Oliver (1984) found characteristic dependencies of bioconcentration of oligochaete worms in sediments from K_{OW}-values of the chemicals, where a slow linear increase in bioconcentration factors with K_{OW} is observed for chemicals with K_{OW}'s less than 10^5, and a rapid decrease in bioconcentration occurs for chemicals with very high partition coefficients ($>10^6$). The decrease may be caused by difficulties in chemical transport across worm membranes due to large molecular size or may be affected by strong binding of these chemicals to the sediments making them less bioavailable.

Similar to aqueous equilibria this approach is based on relatively broad experience with food quality data. Here, too, the three categories of compounds – nonpolar organic substances, metals, and polar organic substances – can be distinguished; in practice, again, only for the nonpolar organic com-

pounds sufficient experience is available for developing quality criteria from equilibrium data. As outlined, hydrophobic organic substances show a strong correlation between the bioconcentration factor K_B and the octanol/water coefficient, indicating that the lipid content of the organism constitutes the major concentrating phase in the system water/organism. Simple steady-state correlative models have been used in laboratory studies to predict the bioconcentration from water of organic compounds by fish, mussels, and other aquatic organisms. One major difficulty is that these models were developed from steady-state concentrations and laboratory systems lacking suspended particulate material, and thus cannot deal with the varying concentrations and forms of pollutants found in many environments (Lake et al. 1987). Inclusion of solid particulate matter considers bioaccumulation as a redistribution of contaminants between sources (organic carbon of waste materials) and sinks (dissolved phase and lipids of organisms). For conditions in which the aqueous phase is not important as a sink, e.g. for high solid aqueous partition coefficients, the bioaccumulation factor will depend on the concentration (C_i = concentration of component i) in the source (oc = organic carbon) and sink (lipids of organisms). Partition factors (PFs) between sediments and organisms have been defined as (Lake et al. 1987):

$$PF = \frac{C_i/\text{g sediment (dry wt)}/\text{g oc}/\text{g sediment (dry wt)}}{C_i/\text{g organism (dry wt)}/\text{g lipid}/\text{g organism (dry wt)}}.$$

PF-values for chlorinated compounds from experiments where exposure concentrations were constant and could be established (i.e., concentrations in sediment were used for infauna; concentrations in suspended particulate matter in dosing systems were used for mussels) were similar to the partition factor of approximately 0.5, which has been calculated by McFarland (1984) from $K_{oc}/BCF_{(lipid)}$ under various assumptions. These findings indicate that modeling bioaccumulation as a redistribution of contaminants between organic carbon of sediments and lipids of organisms is justified for at least some nonpolar, chlorinated organics, organisms, and exposures.

4.2.5 Elution Approach

In Section 3 the significance of surface speciation was indicated with respect to the assessment of the reactivity, mobility, and bioavailability of pollutants in aquatic systems. In practice, the effect of lowering pH-values, either from acid precipitation or from oxidation of sulfidic minerals, plays a dominant role in the mobilization of trace elements from sediments, soils, and solid waste materials. A "mobility test" procedure for soils based on variations of pH-values has been proposed by Kiekens and Cottenie (1985). Application to a large number of polluted and nonpolluted soils indicates that typical

mobilization patterns are obtained for the different elements. Besides the nature of the element, the pH-curves reveal typical textural features of different soil substrates. Best results with respect to the estimation of middle-term effects can be attained by cascade test procedures at variable solid/solution ratios: A procedure of the U.S. EPA (Ham et al. 1980) designed for studies on the leachability of waste products consists of a mixture of sodium acetate, acetic acid, glycine, pyrogallol, and iron sulfate. For the study of combustion residues a standard leaching test has been developed by the Netherland Energy Research Centre (van der Sloot et al. 1984). In the column test the material under investigation is percolated by acidulated demineralized water (pH 4; for evaluating most relevant effects of acid precipitation) to assess short-term leaching (< 50 years). In the cascade test the same quantity of material is extracted several times with fresh demineralized water (pH 4) to get an impression of medium-term leaching behavior (50–500 years). As a time scale the liquid/solid ratio (L/S) is used; the maximum leachability is assessed by a shaking experiment at L/S ratio of 100 under mild acid conditions (De Groot et al. 1978). Recent improvements of this method have been achieved by comparing the L/S curves for an individual element with its stability in a wider pH-spectrum; in some cases direct mineralogical evidence can be given for a distinct metal compound (Van der Sloot, personal communication).

Single-extractant procedures are restricted with regard to prediction of long-term effects, e.g. of highly contaminated dredged materials, since these concepts neither involve mechanistic nor kinetic considerations and, therefore, do not allow calculations of release periods. This lack can be avoided by controlled intensification of the relevant parameters, i.e., pH-value, redox potential, and temperature, combined with an extrapolation of the potentially mobilizable "pools", which are estimated from sequential chemical extraction before and after treatment of the solid material. An experimental scheme, which was originally used by Patrick et al. (1973) and Herms and Brümmer (1978) for the study of soil suspensions and municipal waste materials, was modified by inclusion of an ion-exchanger system for extracting the metals released within a certain period of time (Schoer and Förstner 1987). The system can be modified for different intensities of contact between solid materials and solution, by using shakes (e.g., erosion of the depot by rivers) or dialysis bags (flow-by conditions).

4.2.6 Biological and Chemical Approaches: A Comparison

Biological criteria exhibit major advantages in that they integrate effects of multiple factors including sediment characteristics and complex or unknown wastes, and, with respect to field surveys, they are site-specific, requiring minimum extrapolations. On the other hand, field surveys are costly and bioassay organisms may hot represent sensitivity of the natural species assemblage (Anderson et al. 1987).

Major advantages of numerical criteria lie in their easy application and amendment to modeling approaches. However, if criteria do not exist for the chemicals concerned, a biological test may still be required. In addition, some equilibrium modeling approaches will fail if tissue concentration and toxicity are independent (G. Chapman et al. 1987).

5 Modeling of Sediment Data

One of the greatest challenges of environmental chemistry has been to describe the behavior of trace elements in natural aquatic systems based solely on the knowledge of their fundamental physicochemical properties. Initial efforts in applying quantitative models were undertaken for the prediction of metal speciation in solution (Baham 1984). The theoretical foundations for solving the problem of chemical speciation, which is usually not solvable by using experimental analysis, are based upon a model that relates the equilibrium activities of metals and ligands to the formation of complexes in solution. Ionic speciation in multicomponent aqueous systems with hundreds of competing equilibrium reactions can be estimated by computer solution of such geochemical equilibrium models like WATEQB (Arikan 1988). A significant reason for using the geochemical models is that these models yield an estimate of the activity of the metal in solution rather than its total concentration. This is compatible with modern toxicity philosophy because it is the thermodynamic activity of one or more of the aqueous species of the mobile metal in aquatic and terrestrial environments that determines toxicity and bioaccumulation, not the total dissolved concentrations of the metal. These models are also being used increasingly to predict the mobilizable fraction of metals in the sediment (Baes and Sharp 1983) and the transport of toxic metals and radionuclides in ground-waters (Lewis et al. 1987), to assess pollution potential to the ecosystem in general (Luoma and Davis, 1983), and to develop sediment quality criteria (Jenne et al. 1986).

Equilibrium models are, in turn, useful heuristic devices for probing our understanding of the basic physicochemical nature of processes determining metal behavior in natural systems. However, with respect to the modeling of metal partitioning between dissolved and particulate phases in a natural system, e.g. for estuarine sediments (Luoma and Davis 1983), there are still restrictions due to various reasons: (1) adsorption characteristics are related not only to the system conditions (i.e., solid types, concentrations, and adsorbing species), but also to changes in the net system surface properties resulting from particle/particle interactions such as coagulation; (2) the influences of organic ligands in the aqueous phase can rarely be predicted as yet; (3) effects of competition between various sorption sites; and (4) reaction kinetics of the individual constituents cannot be evaluated in a mixture of sedimentary components. These restrictions have been recently discussed in detail by Honeyman and Santschi (1988), who stated that even for aquatic

environments of low particle concentration "the non-deterministic and interactive effects described above generally influence the estimation of an apparent partitioning coefficient by 1 to 3 orders of magnitude in either direction". With respect to environments of moderate to high particle concentration such as in soils and sediments they concluded that these theoretical approaches have failed thus far to provide a sound basis for the prediction of trace-element behavior and fate.

6 Characterization of Sediment Milieu – Acid-Producing Potential

Regarding the potential release of contaminants from sediments, changing of pH and redox conditions are of prime importance. In practice, therefore, characterization of sediment substrates with respect to their buffer capacity is a first step in the prognosis of middle- and long-term processes of mobilization, in particular, of toxic chemicals in a certain milieu.

Evaluation of pH-effects can be done relatively easily by titration with acid solutions. For quantifying pH-properties and for better comparison of sediment samples, it is proposed to use the term Δ pH, which is characterized by the difference of pH-values of 10% sludge suspensions in distilled water (pH_o) and 0.1 N sulfuric acid after 1 h shaking time (Calmano et al. 1986). Three categories of Δ pH-values can be established, ranging from Δ pH < 2 (strongly buffered), Δ pH 2–4 (intermediate) to Δ pH > 4 (poorly buffered).

Evaluation 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 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 contact oxygenated water or – following land deposition of dredged material – atmospheric oxygen.

For a classification of sludges regarding their acid potential, which can be produced by oxidation of sulfidic components, one can preferentially use the data of calcium and sulfur from the sequential extraction scheme as proposed, for example, by Tessier et al. (1979; see Table 2). In anoxic, sulfide-containing sediments the two elements were selectively released during anaerobic experimental procedures (argon or nitrogen atmosphere in glove box) by the Na-acetate step (Ca from carbonates) and peroxide step (S from oxidizable sulfides, mainly iron sulfide). Reaction of oxygen with 1 mol of iron sulfide will produce three $[H^+]$-ions; by reaction with 1 mol of carbonate, two $[H^+]$-ions are buffered. For an initial estimation, one may compare total calcium and sulfur concentrations in the sediment sample.

Experimental approaches for prognosis of the "acid-producing potential" of sulfidic mining residues have been summarized by Ferguson and Erickson (1988). A test described by Sobek et al. (1978) involves the analysis

of total or pyritic sulfur; neutralization potential is obtained by adding a known amount of HCl, heating the sample, and titrating with standardized NaOH to pH 7. Potential acidity is subtracted from the neutralization potential; a negative value below 5 t $CaCO_3$/1000 t of rock indicates a potential acid producer. Bruynesteyn and Hackl (1984) calculated acid-producing potential from total sulfur analysis; acid-consuming ability is obtained by titration with standardized sulfuric acid to pH 3.5 (Bruynestein and Duncan 1979). Acid-producing potential is subtracted from acid-consuming ability; a negative value indicates a potential acid producer.

7 Application of Different Criteria Approaches on Sediment Samples from Large Rivers in the Federal Republic of Germany

In the present section examples are given of three potential approaches which could provide direct numerical evaluations of the pollution potential in aquatic sediments; these examples are based on metal data from sediments from five large rivers in the Federal Republic of Germany. In addition, Sect 7.4 will give examples of the different behaviors of sediment substrates with respect to the acid-producing potential, which is a major factor controlling the potential release of critical elements under changing redox conditions (see Sect 6).

7.1 Index of Geoaccumulation (Müller 1979)

The "I_{geo}-approach" of Müller compares advantageously with similar procedures, based on background concentrations, in that it constantly maintains a logarithmic scale. Subsequent to normalization with respect to grain size (which is not discussed here), therefore, pollutant or nutrient concentration data from sediment samples taken from different aquatic systems can be compared. From the examples given in Table 7 the sediment sample from the lower Rhine River (collected from the deeper part of the sediment

Table 7. Index of geoaccumulation (Müller 1979) for sediments from five examples of rivers. ($I_{Geo} = \log_2 A_n/B_n \times 1.5$)

	Neckar	Main	Rhine	Elbe	Weser
Copper	0	1	2	2	0
Lead	1	2	2	2	2
Zinc	1	2	3	4	2
Cadmium	3	2	6	4	4
Mercury	0	1	4	6	1
Average	1.0	1.6	3.4	3.3	1.8

pile) exhibits the highest overall metal accumulation relative to the background concentrations, followed by the sample from the Elbe River (Hamburg harbor); in both examples, mercury and cadmium typically influence the overall factor of enrichment. The sediment samples from the rivers Weser, Main, and Neckar are by far less contaminated than the afore mentioned materials; however, there is still considerable enrichment of cadmium in sediments of both the Weser and Neckar Rivers. From the latter example, it is demonstrated that even with significant recovery, there are still characteristic indications from sediment samples of former situations of extreme pollution (Cd-poisoning of fish in the early 1970s; Müller and Förstner 1973).

7.2 *Incorporation of "Toxic Effects" into Accumulation Factors*

The somewhat unsatisfying situation regarding the comparison of enrichment factors of elements, which exhibit strongly different impacts on ecosystems, could be overcome by introducing a factor for the relative toxicity of the respective element or compound. As discussed above, this approach again will be controversial, as such arrangements can only consider the relative impact of water constituents at a specific trophic level. Nonetheless, as demonstrated in Table 8, the combination of enrichment factors with a factor of toxicity is advantageous, as such indices more clearly point to the critical compounds in the overall mixture of potential contaminants, and may thus stimulate setting priorities for control and rehabilitation measures. In the case of the extreme mercury pollution of the Elbe River, reduction of a specific source, i.e. emissions from chlorine alkali plants, could significantly contribute to the improvement of the overall sediment quality; for example, with available technology and reasonable costs the concentrations of mercury in the Elbe River could be reduced to such an extent that the overall sediment quality would be at least comparable to the sample from the Weser River.

7.3 *Numerical Evaluation of the Factor "Element Mobility"*

Without going into detailed discussions, it should be mentioned that there is a possibility for standardizing the data from elution experiments with respect to numerical evaluation. In Table 9 examples are given for an "elution index" based on the metal concentrations exchangeable with 1 N ammonium acetate at pH 7; these metal fractions are considered to be remobilizable from polluted sediments at a relatively short term under more saline conditions, for example, in the estuarine mixing zone. Comparison of the release rates from oxic and anoxic sediments clearly indicates that the oxidation of samples gives rise to a very significant increase of the overall mobilization of the ele-

Table 8. Factor of enrichment × toxicity factor ("Microtox")

		Neckar	Main	Rhine	Elbe	Weser
Lead	(× 1)	2	4	4	6	4
Copper	(× 5)	7	10	17	22	6
Zinc	(× 5)	10	15	35	70	30
Cadmium	(× 10)	62	53	500	340	360
Mercury	(× 35)	46	98	805	2520	81
Total		127	180	1381	2958	481

Table 9. Elution index as determined from exchangeable fractions (1 N ammonium acetate solution at pH 7) related to background values from old sediments from the Rhine River: Cu = 51 mg/kg, Pb = 30 mg kg, Zn = 115 mg/kg, Cd = 0.3 mg/kg (values multiplied by factor 100)

	Neckar	Main	Rhine	Elbe	Weser
Copper	0.2	–	1	1	–
Lead	1	1	2	1	1
Zinc	7	9	28	36	9
Cadmium	30	30	230	30	–
Total oxic	38	40	261	68	10
(Anoxic)	0.5	0.3	8	> 4	4

ment studied here; this effect is particularly important for cadmium. When proceeding further in the extraction sequence, more long-term effects could be estimated (generally with a respective reduction of prognostic accuracy). A major disadvantage of the present approach, however, is that the critical element, mercury, is not yet included in this scheme.

7.4 pH-Titrations of Selected Sediment Samples

Results from titration experiments using 1 M nitric acid on sediment suspensions of 100 g/l are presented in Fig. 2. The titration curve of the Rhine River sediment exhibits a small plateau in the pH-range 5.5 and 6, probably due to a certain fraction of carbonate, which is consumed by addition of 80 nmol of HCl. In contrast, the titration curves of both Elbe River sediments are continuously decreasing due to the low contents of carbonate in these samples. The sediment from the inland harbor basin of Harburg, originally sulfide-rich material which had been stored for 1 year in a closed bottle, has already reached an initial-pH of 4.3; this is probably due to the consumption of the low residual buffer capacity by oxidation of parts of the sulfide fraction.

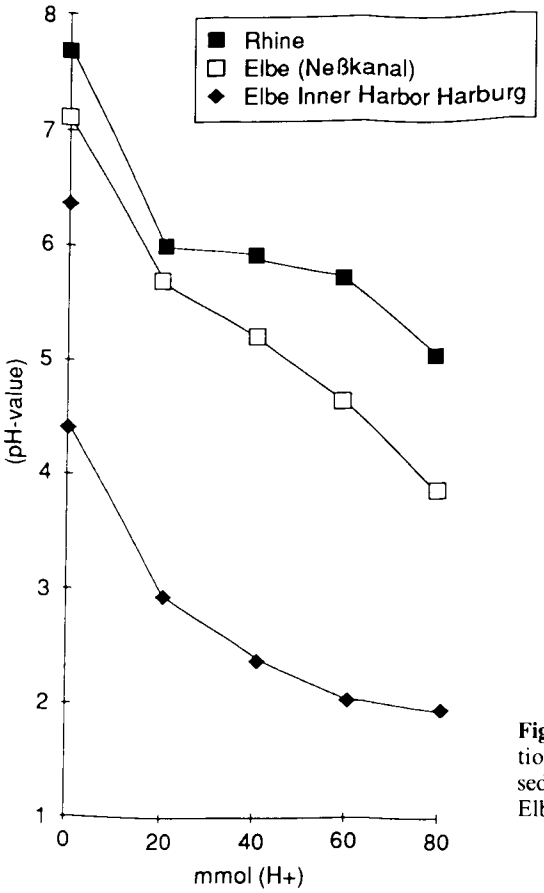

Fig. 2. Variations of pH-values (titration curves) of suspensions (100 g/l) of sediment samples from rivers Rhine and Elbe after addition of 1 M nitric acid

Respective lowering of pH has been found from upland disposal sites of dredged sediments from Hamburg harbor (Tent 1982). Due to the low carbonate content, which is consumed during several months or years, and subsequent lowering of pH, metals are easily transferred to crops, and permissible limits of cadmium have been surpassed in as much as 50% of wheat crops grown on these materials (Herms and Tent 1982). High concentrations of metals have been measured in pore waters from sedimentation polders in the Hamburg harbor area, in the older, oxidized deposits (Maaß et al. 1985). It can be expected that similar effects will occur as well in the aquatic system, particularly in tidal areas affected by periodic drying and wetting (Kersten 1989), and at other high-energy sites exhibiting strong resuspension activities. The situation in the Elbe River estuary is particularly critical since low buffer capacities of the sediments coincide with a relatively long residence time of suspended particles (Müller and Förstner 1975; Tent 1987).

8 Summary and Outlook

Requirements for water quality criteria include (Höpner 1989): (1) The system should be simple; (2) methods should be practicable; (3) criteria should exhibit the ability to register temporal changes; (4) criteria should assess the ecological status of the system in comparison to other situations or sites; (5) the system should sound alarm at critical situations; and (6) ecological status should be described. These requirements reflect a sequence from simpler ones to the most complex systems, i.e. the description of ecological conditions, which can rarely be covered by an easy, practicable approach.

The approaches to sediment quality assessment described so far can be divided into two groups, according to their objectives, i.e., either as a "quality standard" or with regard to an "indicator" function. The first group would comprise, for example, pore water, sediment/water equilibrium, and sediment/organism equilibrium approaches, which are based on toxicologially relevant standards. The approaches of the second group, consisting of the elution and background approaches, will, irregardless of their numerical character, primarily only provide qualitative indications to a certain status of the extent of sediment pollution. However, it seems advantageous to have such a relatively simple initital assessment, which may then be extended, with more complicated procedures, including biological criteria, into an integrated ecological evaluation.

Practical applicability of sediment quality criteria has been proceeding to a different extent. Classifications, on the basis of equilibrium calculations and pore water composition, still seem to require further studies and discussions; on the other hand, interim regulations using modifications of the background approach could well be installed at the present level of knowledge. There are already several examples of statewide water quality evaluations, which use the "I_{geo}"-approach by Müller for the assessment of the pollution status of aquatic sediments. It seems that the next step should be the incorporation of a "toxicity factor", regardless of the underlying test system chosen; there are several initiatives for applying toxicity screening tests, e.g. Microtox, ATP-TOX, and genotoxicity tests, on sediment extracts (e.g. Dutka et al. 1988).

Elution experiments, as demonstrated from the preceding examples, generally confirm the findings of the data from the background approach. However, since elements such as mercury, and organic compounds cannot be incorporated into the presently available scheme, this approach presumably will not be accepted as a primary criterion. On the other hand, recent developments of soil quality criteria should be mentioned, which include a more differentiated approach with respect to metal availability to plants[1].

[1] Annex to article 5 of the Swiss regulation on contaminants in soil from June 9, 1986, includes the following standard values for soluble metal concentrations (0.1 M sodium nitrate; weight ratio of soil sample to solution 1:2.5): Pb = 1.0 µg/g; Cd = 0.03 µg/g; Cu = 0.7 µg/g; Ni = 0.2 µg/g; Zn = 0.5 µg/g.

Another aspect of sediment criteria development has been shown for the first time, namely the estimation of potential changes of substrate properties, in particular by oxidation and subsequent lowering of pH-values. This approach again follows the actual developments in describing the soil "filter system", where assessments are performed with respect to the relative bonding strength of heavy metals and to potential hazards for groundwater pollution, by measuring parameters such as "pH", "organic matter content", and "concentrations of iron oxides". Since oxidation processes play a critical role in sediments, we propose that the factor of the "acid producing potential" should be included as a primary parameter in sediment-oriented quality criteria.

Future development of sediment quality criteria will decisively be influenced by the progress of discussions on equilibrium approaches, on which actual efforts are focussed in the U.S.A. (Shea 1988). While sufficient knowledge is already available regarding nonpolar organic compounds, there are still many questions open with respect to the parameters needed for equilibrium calculations involving trace elements and their major substrates. Further basic research is needed in particular for incorporating kinetic data in such models.

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