# **Workshop Sediment Quality**

(Karlsruhe 1992)

5th International Symposium on River Sedimentation

Edited by P. Larsen & N. Eisenhauer

Technical Documents in Hydrology



International Hydrological Programme United Nations Educational, Scientific and Cultural Organization

UNESCO Paris, 1993



# INTERNATIONAL HYDROLOGICAL PROGRAMME



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# PREFACE

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# PREFACE

The Fifth International Symposium on River Sedimentation was held at the University of Karlsruhe, Germany, in April of 1992. In connection with the Symposium UNESCO sponsored a Workshop on Sediment Quality. Under the direction of Professor Ulrich Förstner, University of Hamburg-Harburg, the "Effects of resuspension of River Sediments" was focussed on as being a timely and highly environmentally relevant topic. This publication contains Prof. Förstner's summary of the Workshop activities including Recommendations and a paper by Prof. Förstner et al.: "Sediment Quality Criteria - General Aspects and International State of Discussion". In addition the papers addressing sediment quality problems that were accepted for the Symposium proceedings have been included.

In conclusion the Workshop on Sediment Quality was a worthwhile undertaking as evidenced by the number of participants taking part and by the relevance of the conclusions and the recommendations forwarded by renown experts.

Karlsruhe in December, 1992.

Files Leven

(Prof.Dr.Techn. Peter Larsen) Chairman of the Organizing Committee.

# Workshop on Sediment Quality - Report The Activation of Chemical Processes in Contaminated Sediments Due to Resuspension of the River Bed

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# 1.MOTIVATION AND OBJECTIVES

In modern sediment research on contaminants four aspects are discussed, which in an overlapping succession also reflect the development of knowledge in particleassociated pollutants during the past twentyfive years: (i) Identification of sources and distribtuion; (ii) evaluation of solid/solution relations; (iii) study of transfer mechanisms to biological systems, and (iv) assessment of environmental impact. In practice, aspects (i) and (iv) are of particular relevance. Recent developments with special emphasis on the effects arising from resuspension of the river sediments have been treated in the present workshop.

## 2. INTRODUCTION

The role of sediments as carriers and potential sources of contaminants has been discussed following an introductory overview. Major topics were:

- Relation to water quality objectives (UNESCO/GEMS/WHO);

- logistic factors of sediment sampling;

- methods for reducing grain size effects;

- evaluation of lateral and vertical (sediment core) distributions - source detection and historical developments.

# 3. SEDIMENT QUALITY CRITERIA DEVELOPMENT

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 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.

In the context of the workshop theme, porewater seems to be a particularly interesting medium, since contaminants can be released with the interstitual waters subsequent to resuspension of the sediments. While the direct and analysis of water-borne recovery constituents can be seen as a major advantage approach, this there are several of disadvantages, particularly arising from the sampling and sample preparation, which are not yet routine procedures, and are usually involving 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 porewaters from Neckar and Elbe River sediments.

# 4. EFFECTS DURING RESUSPENSION OF CONTAMINATED SEDIMENTS

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

# 5. DISCUSSION AND CONCLUSIONS

## 5.1. Effects on biota from pollutant releases

The greatest potential from impact with solid material is expected on benthic or epibenthic organisms. Relatively simple and implementable liquid, suspended particle and solidphase bioassays have been carried out for assessing the short-term impact of dredging and disposal operations. Standardized tests are characterized by their lack of variability, but essential information (e.g. lethality, alteration of growth rate) can only be obtained with such single species test. For biomonitoring, in-situ bioassays should involve at least three different trophic levels; combination with laboratory ecosystems is useful. In general, the bioassay results must be interpreted in relation to the field situations and site-specific data.

5.2. Reliability of solution/solid equilibrium approach

Development of sediment quality criteria will decisively be influenced by the progress of discussions on equilibrium apporaches ( $K_D$ -approach), on which actual efforts are focussed in the U.S.A. (Shea, D., 1988: Developing national sediment quality critaria-equilibrium partitioning of contaminants as a means of evaluating sediment quality criteria. Environ: Sci. Technol. 22: 1256-1261). While sufficient knowledge is already available regarding nonpolar organic compounds, such as PCB, DDT, and PAH, there are still many questions open with respect to the parameters needed for equilibrium calculations involving trace elements and their major substrates. A

general objection against the  $K_D$ -approach is, that dissolved and particulate constituents originate from independent sources, exhibiting different "histories".

5.3. Conclusions: Significance of sedimentrelated quality criteria

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 toxicological relevant standards. It still seems problematic to relate sediment and porewater data to the relevant "primary" standards for food and water quality. Sediment data, however, can be used to select critical sites for intensive measurements on these primary media.

The approaches of the second group, consisting of the "elution" and "background" approaches, will, nonregarding their numerical character, primarly only provide qualitative indications on a certain status of the extent of sediment pollution. However, it seems to be advantageous to have such a relatively simple initial assessment, which may then be extented, with more complicated procedures, including biological criteria, into an integrated ecological evaluation.

Efforts should be untertaken for improving the methods for the detailed description of individual components of suspended matter and sediments, as well as the assessment of their potential behaviour under typical environmental conditions. With regard to the latter implications, and since oxidation processes play a critical role in the resuspension of polluted sediments, we propose that the factor of the acid producing potential should be included as a primary parameter in sedimentoriented quality criteria.

# Sediment Quality Criteria -General Aspects and International State of Discussion

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ABSTRACT: In the actual discussion of sediment quality criteria there are both pragmatic approaches emphasizing short-term practicability (e.g., background and in in-situ-precontamination approach), and those which are more oriented to basic science (e.g. related to sediment/water and sediment/biota equilibria). The latter approaches, where a number of questions is still open and which involve considerable effort to be performed, have to rely on the content of pollutants in the water phase, with particular emphasis on the "active" components, which are predominantly biologically available. Simultaneously, the "pool" of critical compounds in the solid phases which may be transfered into solution in a middle- of long-term period, has to be considered.

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 being assessed by the accumulation rate multiplied with a toxicity factor for the respective substance.

# 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. 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 food chain transfer may he and strongly affected by sediment-associated proportions of pollutants. Benthic organisms, 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 twenty-five years: (i) Identification of sources and distribution; (ii) evaluation of solid/solution relations; (iii) study of transfer mechanisms to biological systems, and (iv) assessment of environmental impact. In practice, aspects (i) and (iv) are of particular relevance, and recent developments will be treated in the present review.

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) *Identify anomalies* - More detailed sampling and analyses, designed to establish the presence and extent of anomalies.

c) Establish references - To create reference points, in the form of some measured parameters, for future comparison.

d) Identify time changes - To show trends and variations of sediment data over time, be use of sediment cores or other repeated sediment samplings.

e) Calculate 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 as follows

Type of Activity (UNESCO-WHO, 1978)	GEMS Water Objectives (WHO-Geneva, 1978)	Sediment Objectives (Categories in Text)		
Monitor				
Continous standard measurement and ob- observation	Cultural impact on water quality, suita- bility of water qua- lity for future use	Establish reference point(s) - Cat. (c)		
Surveillance				
Continous specific observation and mea- surement relative to control & management	Observe sources and pathways of speci- fied hazardous sub- stances	Trace sources (spa- tial)		
Survey				
Series of finite duration; intensive, detailed programs for spec. purposes	Determine quality of natural waters	Identify anomalies (category "b") Calculate mass balan- ces (category "e") Study processes (f)		

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

- local availability of sampling platform or vessel
- time available
- access to sampling region
- suitability of survey system to locate sample position
- availability of trained personel and support staff
- availability of equipment
- storage and security
- transport systems
- follow-up capability

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

The suitability of corers and bottom samplers has been tested during equipment trials by Sly (1969). For souces 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 favourable 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.

# Sediment Quality Criteria

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

- 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;

- long-term perspectives in water resource management involve "*integrated strategies*", in which sedimentassociated pollutants have to be considered;

- waste water 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 be the United States Environmental Protection Agency to develop standard procedures and criteria for the assessment of environmental impact of sediment-associated pollutants. Initial discussions (Anon., 1984, 1985) suggested five methodological approaches which merit closer consideration: (i) "background approach", (ii) "water quality/pore water approach", (iii) sediment/water equilibrium partitioning approach", (iv) "sediment/organism equilibrium" approach, and (v) "bioassay" approach. Further discussions led to the differentiation of biological and chemical-numerical approaches (Chapman et al. 1987):

# Biological Criteria

Biological criteria have been developed and are already applied in various areas (Anderson et al. 1987, Chapman et al. 1987): - Field biological surveys - conduct on-site studies of biota to evaluate possible impact at site (biological response pass/fail)

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

- Tissue action level - link 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).

- 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 separatedly in any case. Bioassays as well as field surveys are empirical considerations which cannot provide numerical criteria to be transferred on 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 lethality, (e.g., 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 sedicontaminants and organisms ment 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 "triad" by Chapman (1986) quality 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 terms (in of positive or negative results) provide the strongest data for determin numerical sediment criteria.

# Chemical-Numerical Approaches

## Background Approach

## (a) 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 for disposal of contaminated sediment on land - the pollutant concentrations are normalized to a standard

sediment ("underwater soil") consisting of 10% organic matter and 24% clay content (particle size < 2 micrometers). The level for the target value is based on field observations of sediments in surface waters not affected 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 1. Integration of standards for terrestrial and aquatic soils is under discussion and could be of great importance in, for example, the case of disposal of contaminated sediments on land.

Table 1 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

## (b) Pollution Indices

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

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

C<sub>n</sub> is the measured concentration of the element "n" in the pelitic sediment fraction (< 2 micrometer) and  $B_n$ is the geochemical background value fossil argillaceous in 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 7 grades, whereby the highest grade (6) reflects 100-fold enrichment above background values  $(2^6 = 64.1, 5)$ . In Table 2 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 2 - no further consideration is given to the ecological relevance of the values.

# (c) 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 before-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. saying that there exists a proportionality and rarity, and between toxicity "sink-effect", i.e. their to their affinity to solid substrates. After a normalization process the "sedimentological toxic factor" is calculated

in the following sequence:
2n = 1 < Cr = 2 < Cu = Pb = 5 < As =
10 < Cd = 30 < Hg = PCB = 40.
The "toxic response factor", as for-
mulated by Hakanson (1980) from a
complex matix of assumptions, can
possible defined much easier from di-
rect measurements of the relative to-
xicity of typical pollutants in aqua-
tic 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.

Table 2 Comparison of IAWR water quality indices (based on biochemical data) and Index of Geoaccumulation (I<sub>geo</sub>) of trace metals in sediments of the Rhine River (after Müller 1979)

IAWR Index	IAWR water quality (pollution intensity)	Sediment accumulation (I <sub>geo</sub> )	I <sub>geo</sub> - class	Metal exa Upper Rhine	amples 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 mod.poll.	>0-1	1	Cu	Cr, Co
1	practically unpolluted	<0	0	Cr, Co	·

### Pore Water Approach

The compsition 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 hours of collection. Insitu methods are considered more pro-

mising 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 non-degradable dialysis membrane or by a polysulphonate membrane filter sheet (Carignan, 1984) and displaced into the sediment 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 water-borne constituents can be seen as a major advantage of this approach, there are several disadvantages, particularly arising from the sampling and sample preparation, which are not yet routine procedures, and are usually involving conside-

rable 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 porewaters from Elbe River sediments (Figure 1):



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

There are strong gradients for redoxsensitive 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.

#### Sediment/Water Equilibrium Partitioning

This approach is related to a relative broad toxicological basis of water quality data. The distribution coefficient K<sub>D</sub>, 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

evide	enced	fro	om v	rario	us	refe	rences
(Tabl	.e 3)	- sh	ould	clea	urly	be i	ndica-
ted.	Nonet	hele	ss, i	it se	ems	that	sedi-
ment	qual:	ity	crit	eria	of	the	U.S.

Environmental Protection Agency will preferentially be based on these approaches.

Table	3	Factors and mechanisms influencing distribution of pollutants betwee
		solid and dissolved phases

Factor/mechanism	Example	Reference
Sample preparation (e.g. drying)	metals *	Duursma (1984)
Separation (filtration/centrifugation)	metals *	Calmano (1979)
Grain size distribution	metals *	Duursma (1984)
Suspended matter concentration	DDT/Kepone	Connor and Connolly (1980)
Kinetics of sorption/desorption	metals *	Schoer and Förstner (1984)
Non-reversibily of sorption	metals PCBs	Lion et al. (1982) DiToro and Horzempa (1982)
	chloro- phenols	Isaaacson and Frink (1984)
Effect of bioconcentration	1,4-DCB	Oliver and Charlton (1982)

\* Experiments with artificial readionuclides

In practice, three categories of compounds can be distinguished:

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

- K<sub>D</sub>-values of *metals* are not only correlated to organic substances but also with other sorption-active surfaces. Toxicological effects oftenly are 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.

- Polar organic substances (e.g. phenols, polymers with functional groups, tensids) are widely unexperienced with respect to their specific "sorption" behaviour. 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<sub>D</sub>-approach at present cannot be taken into consideration.

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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  $K_{R}$  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<sub>R</sub> and  $K_{octanol/water}$  is expected ( $K_B = 0.048 K_{OW}$ ). This correlation must be used with discretion, particularly for very low  ${\rm K}_{\rm B}^{},$  where the amount of solute in non-lipid phases may be appreciable, and for high-K<sub>OW</sub> compounds (e.g. mirex, octachlorosterene, and higher chlorinated biphenyls).

# Elution Approach

- Solvent leaching - apart from the characterization of the reactivity of specific metals - can provide information on the be haviour of polluunder typical environmental tants 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).

In practice, the effect of lowering pH-values, either from acid Iprecipitation 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 non-polluted soils indicate that typical mobilisation patterns

are obtained for the different elements. Beside 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. 1979) 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 asleaching short-term 50 sess (< years). In the cascade test the same quantity of material es extracted several times with fresh demineralized water (pH = 4) to get an impression medium-term leaching of behaviour (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. 1987). Recent improvements of this methods 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, private 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 significative intensivation of the relevant parameters pH-value, redox potential and temperature, combined with an extrapolation on the potentially mobilizable "pools", which are esti-

mated from sequential chemical extraction before and after treatment of the solid material. An experimental scheme, which has originally been 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 each (Schoer and Förstner 1987). The system can be modified for different intensities of contact between solid and solution, by using materials shakes (e.g., erosion of the depot by rivers) or dialysis bags (flow-by conditions).

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) and residual fractions (Engler et al. 1977). Despite of clear advantages 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 contamined 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 co-workers (1979) has been modified by various authors (Table 4).

Table 4	Sequential extract	ion scheme for	partitioning sediments	
	(Calmano and Först	ner 1983; Kerst	en and Förstner 1986, 198	(7)

Fraction	Extractant	Extracted Component
• • • • • • • • • • • • • • • • • • •		
Exchangeable	1 M NH <sub>4</sub> OAc, pH 7	Exchangeable ions
Carbonatic	1 M NaOAc, pH 5 w/ HOAc	Carbonates
Easily reducible	0.01 <i>M</i> NH <sub>2</sub> OH HC1 w/ 0.01 <u>M</u> HNO <sub>3</sub>	Mn-oxides
Moderately reduc.	0.1 <i>M</i> oxalate buffer pH 3	Amorphous Fe-oxides
Sulfidic/organic	30 H <sub>2</sub> H <sub>2</sub> w/ 0.02 HNO <sub>3</sub> pH 2 extr. w/ 1 M NH <sub>4</sub> OAc-67 HNO <sub>3</sub>	Sulfides together with organic matter
Residual	hot HNO <sub>3</sub> conc.	lithogenic crystall.

# 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 for the prognosis of middle- and long-term processes of mobilization, in particular, of toxic chemicals in a cer-

## tain milieu.

Evaluation of pH-effects can done relatively easily by titration with acid solutions. For quantifying pHproperties and for better comparison of sediment samples it is proposed to use the term pH, which is characterized by the difference of pH-values of 10-percent sludge suspensions in distilled water  $(pH_0)$  and in 0.1 N sulfuric acid after 1 h shaking time (Calmano et al. 1986). Three categories of pH-values can be established ranging from pH < 2 (strongly buffered), pH 2-4 (intermediate) to pH > 4 (poorly buffered).

Evaluation of the pH-changes resulting from the oxidation of anxic 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. As greater is this difference, as higher is the shortterm 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.

For a classification of sludge 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 4). In anoxic, sulfide-containing sediments the two elements were selectively releaduring anaerobic experimental sed 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 one mole of iron sulfide will produce 3 [H<sup>+</sup>]-ions; by reaction with one mole of carbonate 2 [H<sup>+</sup>]-ions are buffered. For an initial estimation, one may compare total calcium and sulfur concentrations in the sediment sample.

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

Examples are given of two potential approaches, which could provide di-

rect 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, section 8.4 will give examples of the different behaviour 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 Chapter 7).

# Index of Geoaccumulation (Müller, 1979)

The "Igeo-approach" of Müller advantageously compares with similar procedures, based on background concentrations, in that it constantly keeps on 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 well be compared. From the examples given in Table 5 the sediment sample from lower Rhine River (collected from the deeper part of the sediment pile) exhibits highest overall metal accumulation relative to the background concentrations, followed by the sample from the Elbe River (Hamburg harbour); in both examples, mercury and cadmium are typically influencing the overall factor of enrichment. The sediment samples from the rivers Weser, Main, and Neckar are by far less contaminated than the before-mentioned materials; however, there is still considerable enrichment of cadmium in sediments of both the Weser River and Neckar River. From the latter example it is demonstrated, that even with a significant recovery there are still characteristic indications from sediment samples on former situations of extreme pollution.

	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

Table 5 Index of geoaccumulation (Müller 1979) for sediments from five examples of rivers.  $I_{Geo} = \log_2 A_n/B_n \times 1.5$ 

Incorporation of "Toxic Effects" into Accumulation Factors

The somewhat unsatisfying situation regarding the comparison of enrichment factors of elements, which exhibit strongly different impact 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 6, 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 emissions from chlorine alkali plants - could significantly contribute to the improvement of the overall sediquality; for example, ment with available technology and reasonable costs the concentrations of mercury in the Elbe River could be reduced to an extent, that the overall sediment quality would be comparable to the sample from the Weser River at least.

		Neckar	Main	Rhine	Elbe	Weser
Lead	(x 1)	2	4	4	б	4
Copper	(x 5)	7	10	17	22	6
Zinc	(x 5)	10	15	55	70	30
Cadmium	(x 10)	62	53	500	340	360
Mercury	(x 35)	46	98	805	2520	81
Total		127	180	1381	2958	481

Table 6 Factor of enrichment x toxicity factor ("Microtox")

### Summary and Outlook

Requirements for water quality criteria include (Höpner, 1989): (i) The system should be simple; (ii) methods should be practicable; (iii) criteria should exhibit ability for registration of temporal changes; (iv) criteria should assess the ecological status of the system in comparison to other situations or sites; (v) the system should sound the alarm at critical situations; and (vi) ecological status should be described. These requirements have been arranged from more simple ones to the most complex systems, i.e. the description of ecological conditions, which rarely can be covered by an easily practicable approach.

Practical applicability of sediment quality criteria has been proceeding to 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 pre-

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sent level of knowledge. There are already several examples of statewide water quality evaluations, which use the "I<sub>geo</sub>"-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", whatever will be the underlying test system to be 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).

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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5th International Symposium on River Sedimentation Karlsruhe 1992

# Sediment Quality Criteria -Role of Redox-Sensitive Components

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ABSTRACT: 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 for the prognosis of middle- and long-term processes of mobilization, in particular, of toxic chemicals in a certain milieu.

## Introduction

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 sediment characteristics integrate and pollutant loads, while generally not indicating the cause of effects. With respect to chemical-numerical indications criteria immediate 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.

Both pH and redox potential in a sediment/water system are significant parameters in the mobilization and transformation of metals (Stumm & Morgan, 1981; Hong & Wang, 1984). Many investigations have shown that the pH value declines during the oxidation of sediments (e.g., Calmano, 1989). In practice, therefore, characterization of sediment substrates with respect to their buffer capacity is a first step for the prognosis of middle- and long-term processes of mobilization, in particular, of toxic chemicals in a certain milieu.

# Evaluation of pH-Changes

The acidification problem of a sediment/water system arises after hydrogen ions are generated during the oxidation, e.g., during dredging or resuspension mainly of fine grained material containing less carbonate than needed for long-term neutralization (Drever, 1982; Breemen et al., 1984). 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; summary is given by Ferguson & a Erickson, 1988). Our findings on the effects of perrodical redox processes on both APP and metal mobility in estuarine sediments (Kersten et al., 1985 Kersten & Förstner, 1991) have further enhanced research interest in this field. Because of the manifold implications with dredging activities and other sectors of river quality management a number of typical effects will be described here.

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 pHdifference between the original sample and oxidized material. As greater is this difference, as 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 har-Figure 1 bour is presented in (Calmano et al., 1992).

Results from titration experiments using 1 molar nitric acid on sediment suspensions of 100 g/l are presented in Figure 2. The titration curve of the Rhine River sediment exhibits a small plateau in the pH-range of 5.5 and 6, probably due to a certain fraction of carbonate, which is consumed by addition of 80 mmol of acidity. On contrary, the titration curves of both Elbe River sediments are continously decreasing as a result of the low contents of carbonate in these samples. The sediment from the inland harbor basin of Harburg, originally sulfide-rich material which has 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. Respective lowering of pH has been found from upland disposal sites of dredged sediments from Hamburg harbor (Tent 1982).



Figure 1. Influence of redox potential on the pH-value during oxidation of a sludge suspension from Hamburg harbour (Calmano et al., 1992)



Figure 2. Variation of pH-values (titration curves) of suspensions (100 g/L) of sediment samples from the Rhine and Elbe Rivers after addition of 1 M nitric acid (Förstner et al., 1989)

## Effects on Metal Mobility

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 diffethe between rentiate exchangeable, carbonatic, reducible (hydrous Fe/Mn oxides), oxidizable (sulfides and organic phases) and residual fractions. With sequential extraction procedures rearrangements of specific solid "phases" can be evaluated prior to its actual remobilisation. One of the more widely applied extraction sequences of Tessier and co-workers (1979) has been modified by various authors (Kersten & Förstner, 1987)

Partition of metals was determined in a sample of sediment from Hamburg Harborg, which was pretreated in different ways, including: (1) The EPA Standard Elutriate Test, 1:4 sediment/site water for 30 min.; (2) Freeze-dried sample; (3) Oven-drying at 60<sup>0</sup>C. It was observed that oxidation had a great effect on regulating the chemical form of Cd and other trace metals (Fig. 3, Kersten et al. 1985). Compared to the original sample (A), which was extracted under an argon atmosphere, there was a typical change from oxidizable phases, which were mainly Cd-sulfide, to easily reducible application forms upon of the shaking/bubbling test (B). During freeze-drying - which is commonly assumed to present a relative smooth mode of sample pretreatment, transformation to carbonatic and exchangeable forms takes place (C). This effect is further enhanced during ovendrying at  $60^{\circ}C$  (D).



Figure 3. Partitioning of cadmium in anoxic mud from Hamburg harbour in relation to the pretreatment procedures (Kersten et al., 1985)

Applying the before-mentioned extraction scheme, a more reliable prognosis can be made regarding the acid potential of a sediment sample, which can be produced by oxidation of sulfidic components, can be made by using the data of calcium and sulfur from the sequential extraction. 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 one mole of iron sulfide will produce 3 1-ions; by reaction with one mole [H] of carbonate 2 [H<sup>+</sup>]-ions are buffered. 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. Here examples are given for an "elution index" based on the metal concentrations exchangeable with 1 N ammonium acetate at pH 7 (Table 1). These metal fractions are considered to be remobilizable from polluted oxic and anoxic sediments at a relative short term under more

Table 1. Elution-index as determined from exchangeable fractions (1 N ammonium acetate solution at pH 7) related to back-ground values from old sediments from 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	59
Cadmium	30	30	230	30	) _
Total oxid	2 38	40	261	68	3 10
(anoxic	0.5	0	.38	>4	4)

saline conditions, for example, in the estuarine mixing zone. Comparison of the release rates from oxic and anoxic sediments indicates, that the oxidation of samples gives rise to a very significant increase in the overall mobilization of the metals studied. This effect was particularly important for Cd. When proceeding further in the extraction sequence, more long-term effects can be estimated, but generally with a reduction of prognostic accuracy.

The relative low carbonate content of the Elbe River sediments. which is consumed during several months or years, has several practical implications: High concentrations of metals have been measured in pore waters from sedimentation polders in the Hamburg harbour area, in the older, oxidized deposits (Maaß et al., 1985). 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 & Tent, 1982). The situation in the Elbe River estuary is particularly critical since low buffer capacities of the sediments coincide with a relative long residence time of suspended particles (Tent, 1987).

Metal release from tidal Elbe River sediments by a process of "oxidative remobilization" has been described by Kersten (1989). Short (30 cm) sediment cores were taken from a site, where diurnal inundation of the finegrained fluvial deposits takes place; subsamples were analyzed with sequential extraction according to the methods described above. In the upper part of the sediment column, total particulate cadmium content was approximately 10 mg kg<sup>-1</sup>, whereas in the deeper anoxic zone the total particulate concentration of Cd was 20 mg kg 1. The results of the sequential extractions of the core sediment samples separated at 2-cm levels (Figure 4) indicate, that in the anoxic zone 60-80% of the Cd was associated with the sulfidic/organic fraction. In the upper - oxic and transition - zone the association of Cd in the carbonatic and exchangeable fractions simultaneously increase up to 40% of total

Cd. Thus, high proportions of mobile cadmium forms correlate with the reduction in total cadmium contents. This distribution of total and partitioned Cd in the "Heukenlock" sediment profile suggest that the release of metals from particulate phases into the pore water and further transfer into biota is controlled by the frequent downward flux of oxygenated surface water. In the oxic zone, Cd is leached from the labile particulatebinding sites, where the predominant mechanism controlling the availability of Cd is adsorption/desorption. With the downward flux of pore water, the mobilized metal moves into the anoxic environment, where Cd is reprecipitated by the formation of sulfidic associations. From the observed concentrations, it would be expected that longterm transfer of up to 50% of the Cd from the sediment subsurface would take place in the anoxic zone located further below the sediment-water inerface. By this process of "oxidative pumping" (Kersten & Förstner 1987) a maximum downward flux of 0.4 g Cd/m<sup>2</sup> per year can be estimated in the Heukenlock sediments.

### Outlook

Recent investigations by Calmano et al. (1992) show that at identical pH values obviously more metals are mobilized in the oxidized sediment than in the reduced state. But although the pH value is the key factor - in particular if it sinks below 4.5 - the redox conditions may also control the mobilization of certain metals. Consequently, also in well buffered sediments a mobilization of metals during oxidation cannot be excluded.



Figure 4. Total concentrations and partitioning of cadmium in a tidal flat sediment profile in the Heuckenlock area sampled in 1984 and 1988. Sedimentation rates were determined by the  $^{137}$ Cs-method. Cd pore water profile was determined at low tide (Kersten, 1989)

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# Comparison of the Quality of Sediments in Impounded and Unimpounded Sections of the Austrian Danube

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ABSTRACT: The Austrian section of the Danube is nearly completely utilized for hydropower generation. Due to the impoundments the sediment carrying capacity has been changed and in several reservoirs remarkable sedimentation rates, especially of silt and clay, are observed. The quality of sedimenents in reservoirs and in unimpounded sections is compared with sediments in the flood plain area and also with the respective indicators of the suspended material. The emphasis is on the mineralogic analysis and on several heavy metals such as Zn, Cd, Pb, Cu, Cr and Ni. Except the samples taken in the mouth of a tributary downstream of Vienna the sediments can be classified as moderately polluted according to the geo-accumulation index of Müller.

# **1 INTRODUCTION**

The Austrian stretch of the Danube is intensively utilized by hydropower schemes. Recently, nine schemes, of which one is jointly operated by a German and Austrian company, are in operation contributing about 25 % to Austria's hydro-electric power generation. Large sediment deposits - in some of the backwater reaches exceeding a thickness of more than 15 m have been accumulated in the last decades of operation. The quantity of sediments and its temporal development is discussed in detail in /1/.

In two reservoirs the sedimentation rate and the quality of the sediments were investigated in detail /2, 3/. The two reservoirs refer to the hydropower stations Aschach, the most upstream scheme, and Altenwörth, the largest scheme along the Austrian Danube. The location of the reservoirs is given in Fig. 1 and the sedimentation in these two reservoirs is displayed by longitudinal profiles in Fig. 2.



Fig. 1 Hydropower schemes on the Austrian Danube (Published by Österreichische Donaukraft)



Fig. 2 Longitudinal profile of the accumulated sediments (Source: According to /1/)

It can be concluded from regular monitoring of the river bed that during operation from 1965 to 1989 about 20 million  $m^3$  of sediments were deposited in the reservoir of the hydropower scheme Aschach and about 5 million  $m^3$  were sedimented in the time of operation from 1976 to 1989 in the Altenwörth reservoir.

Fine grained sediments are trapped in the reservoirs and the accumulation of pollutants like heavy metal loads gained increasing importance. Data describing quality of Danube sediments are published by /4, 5, 6, 7, 8, 9, 10/ and briefly summarized by /11/. The data refer to different grain size diameters and cannot directly by compared.

The objective of this paper is to describe the sediment quality in the reservoirs, in unimpounded sections, of suspended material and to compare it with data from other sources. During flood events remarkable spills of sediments occur which are partly sedimented in the flooded area downstream. Conclusions are drawn to assess possible adverse environmental impacts.

# 2 QUALITY OF RESERVOIR SEDIMENTS

# 2.1 Grain size distribution

In this study the 20  $\mu$ m fraction was used for all samples. In 1988 three cores exhibiting a diameter of 8 cm were taken from the whole sediment layer in the lower section (1982,2 km, 1984,2 km and 1987,9 km) of the Altenwörth reservoir. The grain size distribution ranges from sandy to clayey silt. A distinct shift towards finer fractions could be observed in cores in the downstream direction.

# 2.2 Mineralogic analysis

The fraction less 20  $\mu$ m abstracted by seiving with nylon seives was used for a mineralogic analysis and for the chemical analysis. Considering possible desorption processes during the seiving procedure vacuum filtration through a screen of the desired mesh size using a conventional Buchner funnel with a little of the overlaying core water to speed the filtering process was applied in /9/. Comparing the results from the two techniques there is some indication that metals were desorbed from the fine particels. Still, the differences are in the range of statistical uncertainty.

In the cores ranging up to 6.5 m thickness of the sediment pillow several distinct layers could be identified referring to ersosion and modified sedimentation processes after flood events. Although the sequence of the layers in the three cores exhibits a similar band like structure an assignment of specific flood events or time periods was not possible. In total, 41 sediment layers were identified and characterized by their gradation curve, water and clay content, and by the amount of organic matter (Fig. 3). The relation between the density, fraction of clay and water content is given in Fig. 4 and 5 together the fitted linear relationship. The water content of the samples ranged from 20 volumetric percent in fine grained sand up to 54 % in clayey silts. The corresponding bulk density varied from 2.0 g/cm<sup>3</sup> to 1.38 g/cm<sup>3</sup>. Based on a statistical analysis a correlation r=0.86 among silt and water content and r=0.73 among density and water content was obtained.

A mineralogical analysis was carried out for subsamples of each layer. The figures of the core taken at 1982.2 km, about 1.8 km upstream of the barrage are given in Tab. 1.

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Table	1.	Minera	logic	anab	2120	nt	reservoir sediments
raute	1.	TATTICI G	ULIU	anar	1010	<b>U</b> 1	reserven seaments

shoet silicates (miss and slav minamls)	10 %
sheet sincales (mica and clay minerals)	47 70
chlorite	6%
quartz	14 %
feldspar	6%
calcite	7%
dolomite	18 %

-27-



Fig. 3 Grain size percentage, water content and bulk density for borehole nr.5 in Altenwörth reservoir



 $LD(q/cm^3)$ 2 1,9 1, 8 1,7 1, 6 1, 5 1,4 30,25 24,75 41.25 46 TS 52,25 35,75 275 22 38.5 33 495 55 WG %

Fig. 4 Sample density versus fraction of clay in various layers taken from samples from the Altenwörth reservoir

# 2.3 Chemical analysis

For chemical analysis of the sediments the 20  $\mu$ m fraction was ground in an agate mortar and 1 g of the powdered sample was mixed in 3 ml aqua dest and subsequently exposed to 15 ml HCl and 5 ml HNO3. After 24 h hours the dilution was heated up to 105 C and kept at this temperature for one hour. Then after coolin, the mixture was diluted by 2 n HNO3 to 100 ml. After filtration

Fig. 5 Sample density versus water content

the heavy metal concentrations were measured by a direct coupled plasma emission spectrometer. Reference samples and repeated measurements confirmed the reliability of the analytical technique. The concentrations of Zn, Cd, Pb, Cu, Cr and Ni were determined for the various layers in the most downstream core in the reservoir. Results are given in Table 2.

Table 2: Sediment quality in the reservoir Altenwörth at location 1982.2 km (fraction <20 $\mu$ m ) S 63 $\mu$ m-2mm, UuT 2 $\mu$ m-63 $\mu$ m, T <2 $\mu$ m

Depth cm	WG %	LD g/cm3	S %	UuT %	T %	Zn	Cd	Pb ppm	Cu	Cr	Ni
41-54	38.6	1.63	39.1	50.3	10.6	278	1	77	65	64	60
80-92	53.0	1.39	13.0	57.2	29.8	469	2	100	64	85	54
96-127	53.6	1.38	4.9	59.0	36.1	668	2	149	70	104	53
132-154	28.1	1.76	16.4	67.7	15.9	463	2	80	59	72	59
194-232	44.3	1.54	2.2	67.5	30.3	308	2	99	52	70	51
251-266	29.9	1.82	48.7	45.1	6.2	364	1	107	78	77	65
291-334	43.2	1.58	4.1	62.3	33.6	501	1	101	56	74	62
334-348	23.3	1.78	62.1	34.1	3.8	390	1	101	85	73	69
400-448	40.5	1.64	7.2	65.9	26.9	557	2	133	69	79	60
448-481	42.9	1.54	5.8	59.3	34.9	988	2	233	85	114	55
500-520	40.3	1.61	3.5	66.6	29.9	420	2	86	57	67	55
527-566	42.4	1.57	1.1	64.5	34.4	577	2	138	62	80	60
585-596	21.5	1.91	83.6	12.3	4.1	704	2	162	78	90	70

A simple statistical analysis yields a correlation between the fraction of sand and concentration of Ni (r=0.83) and Cu (r=0.61). Also, a correlative dependency among Zn, Cr and Pb (r=0.90 - 0.94) can be assumed. The relationship between the depth which is an indication for the age of this layer and the respective heavy metal concentration is rather weak. but a tendency of increasing heavy metal concentations with depth is presumable. The corresponding correlation coefficients for Zn, Pb and Ni have been estimated to r= 0.47, 0.48 and 0.38.

With respect to remobilization processes of heavy metals the redox potential in the sediments was measured in situ in the reservoir /12,13/. The shape of the redox profil is dependent on the grain size and the interrelated biological activity in substrate. Three examples are given in Fig. 6 for different locations in the reservoir. At the most upstream location with coarse and partly sandy sediments an excellent oxygen supply is observable even in deeper layers. Due to the dense colonization of silty sediments by tubificides, which generate a pore like structure in the upper sediment layer, the oxygen supply is even satisfactory in the upper 10 to 15 cm. The maximum observed density of individuals was more than 8 000 per 27 cm<sup>2</sup>. Chemical data referring to total carbon, nitrogen and phosphorous are given in /13/.



Fig. 6 Redox-profile in the sediments at three sites in the reservoir (Source: /12/)

In /14/ environmental isotopes such as  ${}^{3}H$ ,  ${}^{137}Cs$  and  $\delta^{8}$ O were measured in the pore water of a sediment core. Although these data refer to the reservoir Aschach the conclusions hold also for Altenwörth because of the similar technical design of the impoundment, whitch prevents an exchange between groundwater and the impounded river section. Furthermore, in both reservoirs the water content does not significantly decrease with depth. Assuming that the pore water of a certain layer consists of the water from the time of sedimentation, the <sup>3</sup>H content of the water may be used to date the sediments. Some of the layers from the time periods with remarkably increased <sup>3</sup>H rates in precipitation could be quite satisfactory identified. In other layers maior discrepancies were observed, probably due28to a sequence of erosion and sedimentation processes. On

the other side, variations in the <sup>3</sup>H content of the pore water indicate stratigraphic gaps in the sediment column and might help to identify sequences of erosion.

# 3 SEDIMENT QUALITY IN UNIMPOUNDED SECTIONS

From the Altenwörth scheme downstream to the Austro-Tschechoslowakian border 14 sites were selected located on both sides of the river to identify possible impacts of tributaries or waste water effluents. At the right side several small rivers discharge into the Danube and also the treated waste water from the city of Vienna is effluenting on the right river bank. The samples were taken in the vicinity of the river banks with a corer. The samples F2, F4, F6 and F9 refer to sediments of tributaries. Obviously, the sediments in this section are mostly composed of coarse gravel. The cumulative frequency distribution of grains less than 100 µm is in the range of some of the layers found in the reservoir. Again, the 20 µm fraction was used for the chemical analysis of total heavy metal concentrations. The results of the chemical analysis are given in Table 3.

Table 3: Sediment quality in the unimpounded section downstream of Altenworth (fraction <20µm)

Sample ID km	Loca- tion	Zn	Cd	Pb ppm	Cu	Cr	Ni
F1	1945.9	416	2	123	63	65	64
F2	1935.4	181	1	48	56	47	46
F3	1920.3	356	1	97	71	58	48
F4	1919.6	550	2	193	292	74	54
F5	1917.5	480	1	229	115	84	57
F6	1912.0	1470	3	406	339	867	64
F7	1907.5	264	1	80	78	86	56
F8	1905.0	330	1	108	52	61	51
F9	1899.0	478	2	114	294	79	51
F10	1894.0	360	1	117	81	76	60
F11	1894.0	368	2	113	59	67	57
F12	1887.0	438	2	121	80	76	60
F13	1884.5	683	2	192	78	77	52
F14	1881.0	428	1	97	62	71	52

It is worth to note that sample F6, taken in the mouth of the right side tributary Schwechat, exceeds remarkably the heavy metal concentrations obtained from other sites. The catchment of this river is intensively industrialized and the waste water treatment has been at a rather low standard. These concentrations represent by far the highest loads in this measurement series. Subsequently, the data from this sample will be excluded from averaging sample data.

Although there are no left side tributaries a comparison between left and right bank sampl sites indicates nearly the same average values. Comparing the reservoir samples with Table 3 it can be concluded that Cd, Pb and Ni loads are quite similar. Zn concentrations are in the average about 20 % lower in the unimpounded section. Cu loads show the opposite behaviour downstream the urbanized areas and and indicate the higher contermination of the tributaries.

Additionally, an attempt was made to get older sediment samples taken in the flood plain area at several dephts. The sites were selected such that it could be readily expected that only minor erosion processes had occurred at least in the last century. For comparison, a site A1 at a small island close to the right river bank and exposed to frequent erosion and sedimentation was also included. A detailed description of the location and the corresponding hydrological conditions is given in /15/. Several subsamples were taken from the core and were mixed with samples from similar soil layers Therefore, only a few layers are given in summarized form in Table 4.

Table 4 Heavy metal concentrations in flood plain sediments downstream of Vienna (<20µm)

Sam	ple Depth	Zn	Cd	Pb	Cu	Cr	Ni
		<u> </u>		ррш) 			
A1	0-70	306	1.6	89	68	64	57
	70-170	370	1.9	94	74	71	57
	170-280	391	2.0	120	77	72	55
A2	0-70	121	1.2	46	47	66	63
	70-230	91	1.1	25	37	53	53
A3	0-90	<b>9</b> 8	1.2	33	45	54	54
[	90-100	99	1.1	27	47	55	56
A4	0-70	136	1.4	42	48	60	58
	70-130	116	1.1	27	44	54	54
	130-240	82	1.1	21	41	50	51
	290-340	118	1.0	26	42	58	58
A5	0-40	115	1.2	34	39	55	52
	40-70	<b>99</b>	1.3	30	42	59	56
	310-370	119	1.1	27	38	58	60

It can be concluded that in these sediments the respective concentrations are much lower than in recent sediments. Compared with the Altenwörth data the Zn concentration is only 20%, for Pb 25%, for Cu 63% and Cr 70%. Ni exhibits nearly the same concentrations in reservoir sediments and in the soil layers of the flood plain. The data for site A1 are just in between the concentrations in flood plain sediments and river sediments but closer to the latter.

In Table 5 the arithmetic mean values of the samples from the reservoir, the unimpounded section, the flood plain area and background data from the literature are compiled. The data from sediments in the flood plain are in good agreement with data referring to fossile river sediments in the Rhine /18/.

Table 5: Summary of sectiment quanty of	Table	5: Su	mmary	of	sediment	qual	ity	da
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location	Zn	Cd	Pb ppm	Cu	Cr	Ni
Reservoir						
mean	514.2	1.7	120.4	67.7	80.7	59.4
stdv	191.	0.4	43.	11.0	14.5	5.9
Unimpounde	zd.					
left	404.	1.7	142.	76	. 72.	55.
right	413.	1.9	118.	119.4	70.2	53.6
mean	410.	1.9	125.5	106.2	71.	54.2
Flood plain						
-	112.2	1.2	30.7	42.7	56.5	56.0
Shale /17/	95.	0.3	20.	90.	68.	
Rhine /18/	115.	0.3	30.	51.	. 47.	46.

# 4 QUALITY OF SUSPENDED MATERIAL AND OF WATER

Only a few data are available describing the quality of suspended material in the Danube /6, 9, 19/. Due to high variability in the daily series of suspended load and the time consuming procedure to obtain a representative sample volume, efficient sampling and monitoring techniques for suspended load are tested in a current research program /16/. Samples are taken at different depth by pumping and continuous flow centrifugation at a rate of about 11/min. To accumulate the solid phase the sample is ultracentrifuged and subsequently filtered and dried at 45 C. The gradation curve is obtained by substracting the 40 µm fraction by ultrasonic seiving and by analysing the frequency of smaller particles in a SEDIGRAPH 5000ET. The cumulative distribution function of a samples taken at several locations in the reservoir is given in Fig.7. Profil 3 corresponds to the site where the sediment core has been taken. The variability of the concentration of the suspended materials and thus also of heavy metal concentration can be easily seen in Fig. 8.


Fig. 7 Gradation curve of suspended load in the reservoir Altenworth



Fig. 8 Variation of concentration of suspended material

Chemical data including dissolved heavy metal concentrations in the Danube are given in /6, 9, 15/ and are summarized in Table 6.

Table 6: Dissolved heavy metal concentrations in the water of the Austrian Danube

	Loca tion	Refe rence	Рь	Zn	Cd ug/l	Mn	Fe
	2210	/6/	<1.	6.	<0.1	10.	190
	2138	/6/	<1.	10.	0.3	10.	120.
	2127	/6/	1.	13.	0.1	30.	560.
	2120	/6/	1.	11.	0.1	20.	160.
	2095	/6/	1.	10.	0.1	10.	160.
ļ	2060	/6/	1.	13.	<0.1	10.	140.
	2038	/6/	2.	6.	< 0.1	10.	160.
	1984	/9/	0.2	5.2	0.06	4.5	21.
	1901	/15/	2.	50.	0.1	18.	400.

#### **5 DISCUSSION AND CONCLUSIONS**

Sediments in the reservoir Altenwörth, in the unimpounded downstream section, in the flood plain and also suspended particles were analysed with respect to their gradation curve, their mineralogic composition and their heavy metal concemtrations. A summary of the measurements described by their arithmetic means is given in Table 5. Considering also the measurements at site F6 in Table 3 the following conclusions can be drawn.

By far, the maximum concentrations were observed at the mouth of a tributary downstream of Vienna.

The concentrations in the reservoir Altenworth are slightly above the corresponding values observed in unimpounded stretch of the Danube. the Concentrations of cupper are increased downstream of Vienna and are also above the respective reservoir figures. Although there are no major tributaries or waste water outlets on the left bank of this Danube section the figures are quite similar on both sides. Three cores were taken over the whole thickness of the sediment layer in the reservoir. The analysis indicates an increase with the depth of layer. Other investigations based on isotope techniques show that the pore water of trapped sediments corresponds to the composition of the Danube water during the time when sedimentation of the respective layer has occurred. It can be concluded that the heavy metal concentration in the sediment input into the reservoir decreases slowly.

An analysis of sediments taken in the flood plain region yielded the lowest concentrations during this measurement campaign and were in good agreement with fossil sediments of the Rhine river.

It is beyond the scope of this paper which background data have to be used for the Danube. To be able to compare the results with other data /4, 6, 9/ the shale background data /17/ were used. Utilizing these data as background data to calculate the geo-accumulation index /18/

 $I_{geo} = \log_2 (measured conc./background conc. *1.5)$ 

the mouth of the tributary (sample F6) is to be classified as strongly polluted with  $I_{geo}$  values between 2.2 for Cu and 3.7 for Pb. The reservoir sediments can be classified as moderately polluted.

Although the concentrations are somewhat lower in the unimpounded section they are classified in the same category like the reservoir sediments. In general, the heavy metal load of sediments in the Austrian Danube is low but care has to be taken at the mouth of some tributaries. The  $I_{geo}$  index calculated from the averaged figures of reservoir sediment yields 1.9 (Zn), 1.9 (Cd), 2.1 (Pb), and 0 for Cu, Cr, Ni. According to the index the concentrations of Pb are somewhat increased. Also Hg, not discussed here, yields increased figures corresponding to moderately polluted. The tendency to remobilization was tested in /8/ by sequential leaching /21/. In the upstream reservoir Cu, Cr, As, and Pb are in this order decreasingly leachable with an easy mobilizable fraction from 55 M-% to 11%. Downstream in Vienna Pb and Zn are predominantly leached.

Also, the concentration of dissolved metals along the Austrian Danube can be classified as low. Recently, the effect of heavy metals on the bacterial life has been investigated in the Danube /20/ and levels for the concentrations have been proposed with respect to maintain bacteriological activity. The ideal levels would be accordingly at 5µg/l Cu, 50 µg/l Zn and 20 µg/l Ni. Even doubled figures could be classified as acceptable. The other tested elements like Hg, Pb, Cd and Cr had no effect on the bacterial activity within a reasonable range of concentrations.

In general, the Austrian Danube exhibits a low grade pollution with slightly increased Pb figures. This holds for both the total heavy metal concentrations and also for the values of dissolved metals. At the moment, there are no indications for remobilization of metals in the reservoir sediments. But, due to high spills of sediments during flood events where also deeper sediment layers are exposed to the water body and considering the leaching results attention should be paid to this events.

ACKNOWLEDGEMENT: This paper is partly based on research data from the ecosystems study Altenwörth, funded by the Austrian Ministry of Sciences. Further the support by the Österreichische Verbundgesellschaft, by Donaukraft and by the Wasserstraßendirektion is highly appreciated.

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# Heavy-Metal Pollution from a Former Ore Mine in Sediment of the River Erft

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ABSTRACT: The paper reports on heavy metal problems affecting the Erft, a 110 km long tributary of the Rhine with a catchment area of  $1800 \text{ km}^2$ .

The lower reaches of the Erft have a mean flow rate of  $16 \text{ m}^3$ /s, some  $11 \text{ m}^3$ /s of which originate from the discharge of groundwater to drain lignite open-pit mines. Biological and chemical/physical investigations confirm that the Erft is largely characterized by human influences. The nutrient loading of the Erft through nitrogen and phosphorus presents a problem. Of particular importance are the geogenic heavy metal concentrations introduced into the river from a former ore mining site. The high heavy metal levels from these mine waters significantly influence the composition of the aquatic biocoenoses. There are also increased concentrations of these heavy metals in the Erft sediment. Particularly during floods, intensive displacements of heavy metals occur due to disturbance of the sediment.

The paper describes the impacts of heavy metals on sediment quality in the Erft and reports on laboratory experiments to reduce heavy metal concentrations from the mine waters discharged into the river.

#### 1. INTRODUCTION

The Erft rises south-west of Bonn at an altitude of 540 m above mean sea level. After some 20 km, the river leaves the mountains and continues as a lowland river. The Erft flows mainly northwards over a course of roughly 110 km, with its mouth on the left bank of the Rhine at Düsseldorf. The gradient in the upper course of the river is approximately 5  $^{0}$ /oo. Typically of this region, the middle and lower course have an extremely low gradient of 0,5 to 1  $^{0}$ /oo. The course of the Erft and the surrounding landscape are marked by human influence. Except for short stretches, the Erft is fully developed. Mean precipitation levels

range from 650 to 700 mm/a. The catchment area of the Erft measures 1,800 km<sup>2</sup>. Approximately 600,000 people live in this largely agricultural area. In the middle course of the river, large quantities of groundwater are discharged to the Erft in order to drain open-pit lignite mines. As a result of these measures, there are constant medium high water levels in the lower reaches, with an average flow rate of 16 m<sup>3</sup>. Displacement of the open-pit lignite mines is leading to a significant reduction in discharges in the middle course of the Erft. Biological investigations show a moderate pollution level in the upper reaches and medium levels in the remaining course of the river. Raised nutrient contents in the Erft may be regarded as problematical. Heavy-metal pollution is especially significant. The biocoenosis is severely affected by the abundant heavy metals present in the river.

# 2. HEAVY METAL POLLUTION OF THE ERFT

Results of chemical tests in the superfluous water zone indicate considerable concentrations of numerous heavy metals, for example nickel (see Fig. 1, top). Of spezial interest is the wide dispersion of nickel in the travelling wave of the Erft. It is only through deposition in the sediment and dilution effects due to groundwater discharges from the openpit lignite mines that nickel concentrations are reduced in the lower middle reaches.

The high heavy-metal concentrations stem from the Veybach, a tributary of the Erft. It is apparent from the findings of a biological analysis indicating the totals for quality-grade-assigned organisms (Fig. 1, below), shown here with the totals for representatives of a lagely unpolluted state above the abscissa, and the representatives of increased pollution below it, that the composition of the aquatic biocoenosis of the Erft is significantly influenced below the mouth of the Veybach. The entire range of species is decimated. The cause may be found in toxic impacts of the high heavy-metal contents from the Veybach.



Fig. 1 : Nickel Concentrations and Population of the Erft /1/

Biological studies have also revealed distinct impoverishment of the biocoenoses in the Veybach. Parallel chemical tests clearly identify a gallery used to drain a former lead mine as the source of the toxic loads.

Since the heavy metals found in the superfluous waters may be expected to enrich in the sediment, damaging the aquatic biocoenosis so severely that natuaral self-purification is obstructed and an improvement in water quality becomes more difficult, Erft sediments were analyzed in order to estimate the potential hazard.

#### 3. RESULTS OF THE SEDIMENT STUDIES

In order to achieve a base of comparison for the sediment studies analyses, only the sediment component < 63 u was used as a characteristic grain size fraction. To allow qualitative evaluation of the measured heavy-metal concentrations, sediments were classified in one of seven load categories, according to their heavy-metal content /2/.

From the mouth of the Veybach onwards, zinc contents show severe to excessive loads. The increased loads continue with some fluctuations in the concentration curve until the Erft enters the Rhine. Zinc decisively inhibits the degrading activity of micro-organisms and hence negatively affects natural self-purification. Zinc concentrations are particularly important, as they are known to produce increased toxic effects (synergies) when associated with other heavy metals, e.g. nickel.

From the mouth of the Veybach onwards, the nickel concentration in the sediment significantly exceeds the heavy-metal content for an unaffected sediment. In the case of Nickel, however, the sediment quality in the lower reaches again approaches the geochemical level for unpolluted conditions. Substantially higher nickel levels are measured in the superfluous water. Enrichment of nickel in the sediment and on suspended solids is known to be slight, owing the metal's good solubility in water.

The cadmium contents in the sediment show distinct similarities with the zinc concentrations. The high affinity of these two heavy metals is well known. Geogenic cadmium is almost always associated with cadmium-containing minerals. There are fluctuations in the concentration curve for cadmium from the upper middle reaches of the Erft to its confluence with the Rhine, similar to those for zinc. The measured concentrations in the superfluous water zone do not attain the relevance of the cadmium contents found in the sediment.

As expected, there are extremely high lead concentrations in the sediment (up to 3,3 g/kg), since



Fig. 2 : Heavy Metal Concentrations in the Erft Sediment



Fig. 3 : Cadmium-Loading of Erft Sediments

the water from a gallery of a former lead mine is introduced to the Erft via the Veybach. However, findings in the water body by no means correspond with those in the sediment studies. Severe concentrations cannot be demonstrated in the travelling wave at a belanced flow rate; since from a limnochemical viewpoint the solubility of lead compounds is extremely slight. The mine waters have a high carbonate content, leading to rapid precipitation and immobilization of the lead in the sediment due carbonate precipitation and subsequent deposition in the sediment as relatively insoluble lead carbonate. Heavily lead-contaminated sediments reach the Erft via the Rotbach, another tributary of the Erft, whose catchment area also touches the former mining works, because lead-containing residues from the former benefication and smelting works are being eroded by the stream waters. This adds to the already high lead content in the Erft downstream from the Veybach, resulting in excessive loading. Exceptionally high concentrations are measured in the water body at the mouth of the Rotbach under floodwater conditions. Disturbance of the sediment at high flow rates leads to substantial dispersion of pollutants.

# 4. CAUSES OF HEAVY-METAL ENRICHMENT

The former lead mines are enclosed to the south by the valley of the Veybach and to the north by the valley of the Bleibach (Blei = lead), which flows into the Rotbach. The minable ore deposit is 9 km long and 1 km wide.

Heavy-metal-containing sediments in the streams in this region stem partly from topsoil material transported into the waters by surface-flowing rainwater, especially on the steep slopes typifying the region. It is precisely in these upper soil levels that natural enrichment leads to higher metal contents, resulting in similarly increased metal concentrations in the stream sediments. Erosion of the tips frequently sited in the immediate vicinity of the Bleibach have also lead to transport of the eroded tip material. Lead ore was mined in this region even in Roman times. The considerable shifting and destruction of the surface of the mine over its two-thousand-year history, with numerous small mining operations, intermediate ore tipping and beneficiation works, have been an important factor in the widespread dispersion of pollutants.

In the upper middle reaches of the Veybach, mine water from the catchment area of the former mine is discharged to the stream via a drainage gallery. The gallery is 7.5 km in length. This gallery was used to mine ores from the deeper beds. The primary ore minerals in the deposit are sphalerite and galena. Apart from iron and manganese oxides, partially arseniferous pyrite and bravoite (a mixture of iron, nickel and cobalt sulphides) or their weathering products are present. The cadmium which is also present is bound to sphalerite. Apart from the intensively-mined lead ores, a large zinc deposit was also found. After 1957, the previously important ore mining operation was discontinued, owing to declining metal prices. The lead and zinc deposits nonetheless represent an important raw material reserve for future use. Some of the mine galleries have been preserved. The rock is severely fractured, owing to the former intensive mining activity. As a result, groundwater mobility is greatly increased. The sulphidic ore components erode to sulphate under the influence of the atmospheric oxygen present in pore and cleft spaces and, due to the greater solubility of the sulphate in water, are discharged to the draining gallery through constant groundwater replenishment. In this way, mineral-rich mine water containing significant amounts of heavy metals is washed out and discharged to the Veybach and thence to the Erft. Apart from the soluble fractions, heavy metals are transported as suspended solids. During World War I, nickel and cobalt were extracted from the mine waters by means of lime precipitation, and used commercially. The gallery water concentrations were then quantified at 10 to 14 mg/l for nickel and cobalt /3/. The flow rate at the mouth of the gallery is 330 1/s. The mine water has a high calcium carbonate content. Since the toxicity of the heavy metals varies inversely with the hardness of the water, this tends to diminish toxic effects.

A comparison of heavy metal emissions from the gallery with those from domestic and industrial polluters throughout the Erft catchment area clearly indicates the relevance of heavy metal pollution from the mine waters.



Fig. 4 : Heavy Metal Discharges in the Erft Catchment Area

#### 5. ELIMINATIONS OF HEAVY METALS

Attempts to eliminate heavy metals from the waters of the gallery by precipitation with lime slurry have achieved extremely good results. Precipitation with lime slurry enables the heavy metals to be stabilized in extremely stable compounds as a sedimentable precipitate. Under optimum conditions, heavy metal concentrations in the superfluous water can virtually be eliminated. The fact that a number of heavy metals occur in association in the mine waters has a favourable effect on precipitation performance. The Erft River Board is attempting to ensure future treatment of the heavy-metal-containing mine waters in an elimination plant.

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# Determination of Heavy Metals Contamination in River Sediment

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ABSTRACT: Researches on the content of heavy metals in river sediment form an important basis for the investigation of river hydrochemistry, contaminants sources and regional water environmental pollution. In China heavy metals in sediment in Changjiang River, Xiangjiang River, the Second Songhuajiang River, Zhujiang River and the Grand Canal (artificially excavated river) have been studied so that the distribution, accumulation, transport features and contamination level of heavy metals can be determined. Summing up these research results, some important and interesting problems are proposed and discussed so as to come into notice.

#### 1 INTRODUCTION

River sediment has its own natural and geological condition and the chemical elements (including heavy metals) in sediment form a certain background content. Intervention of human activities, however, has caused the destruction of the equilibrium. Researches on the content of heavy metals in river sediment can provide important basis for historical development of regional water environmental pollution. In China from 1976 on, the investigation and study of heavy metals in sediment have been successively made in Changjiang River (Zang, 1986; Yu and others, 1987), Xiangjiang River(Jin and others, 1986), the Second Songhuajiang River (Wu and others, 1985), Zhujiang River (Yan, 1987) and the Grand Canal (Wang, 1987; Wu, 1987). The distribution, transport and accumulation of heavy metals in sediment are approached from the angle of environmental science. A large number of research data are accumulated by the study from the Second Songhuajiang River in North China to Zhujiang River in South China. The existing of the problems in the researches, of course,

is in affirmative, especially in the determination of heavy metals contamination in river sediment. These problems are proposed in the paper in order to come into notice.

2 DISTRIBUTION OF HEAVY METALS AND SAM-PLING OF SEDIMENT

Industrial waste water and residue containing heavy metals are discharged into water body through different ways. Heavy metals compounds that have poor solubleness deposit very rapidly near the discharge opening (point). A part of soluble heavy metals compounds are adsorbed by suspended substance in water and then transport with the flowing of water in ionic state. In the process of transport the suspended substance gradually subside and stand still on the bottom of river when the load of the suspended substance exceeds the motive power of transport. Because the size of suspended substance, the flow capacity and velocity and the discharge time of pollution sources are different, the content of heavy metals in river sediment shows the law of hori-

zontal and vertical distribution. In order to understand the law of contaminant transport and deposition, the samples in different depth of one section must be taken meanwhile besides sampling in every section of river. The significance of research in such a way is remarkable. Vertical accumulation capacity of heavy metals in sediment has relation to discharge capacity of industrial waste water and residue, time length of discharge, distance from pollution sources, flow capacity and velocity. The thickness of polluted sediment indicates that the longer the discharge time of contaminants, the more the discharge capacity (Wang and others, 1987). The researches on heavy metals of sediment in Suzhou section of the Grand Canal can be seen in Table 1 that waste water and residue

Table 1: Vertical accumulation capacity (mg/kg) of heavy metals

depth (cm)	Cu	Zn	Pb	Cd
0–15	1894.9	3679.5	7735.3	44.56
100–125	164.1	952.5	561.2	5.28
125–150	82.82	651.9	319.1	3.50
0–15	70.31	436.3	286.7	4.11
40–50	57.42	672.3	206.2	2.38
80–90	74.94	909.5	351.3	1.80
0–15	18.73	79.47	21.38	0.075
15–30	19.49	75.97	22.47	0.117
30–45	16.92	<u>98.80</u>	22.72	0.096

increase progressively with the increase of production of factories which discharge contaminants and the content of heavy metals in sediment increases by a big margin from deep layer to surface one. For example, the content of Cu, Zn, Pb and Cd in sediment with the depth of 150cm in the first group of Table 1 exceeds the standards (SSB, 1984) and the depth of polluted sediment in this section is estimated above 2.5m. Vertical accumulation capacity of heavy metals in sediment in this section without discharge of heavy metals wastewater, however, is basically unchangeable in the third group of Table 1. Therefore, the depth of polluted sediment of river can be determined. Actual condition is that the sediment in Suzhou section of the Grand Canal has been polluted by waste water and residue of factories and city along the banks of the Canal.

3 ADSORPTION OF HEAVY METALS ON SEDIMENT

Sediment's composition, surface area, system state (dynamic or static state), temperature, coexisting substance (chloride ion, humic acid and sulphide ion) have effect in varying degree on the adsorbability of heavy metals.

3.1 The adsorbability of the same-type sediment in different sections

Actual researches indicate that the adsorbability of Cu, Pb, and Cd on the same-type sediment in different river sections is different due to different composition and structure of the sediment. Figure 1 shows the adsorbability of Cu, Pb and Cd on sediment in different sections  $(A \longrightarrow H)$  of the Second Songhuajang River. It can be seen that the adsorbability in dynamic state is larger than



Fig.l The adsorbability of Cu, Pb and Cd on sediment in different sections

that in static state. This is advantageous to the transport of the sediment into suspended substance when the flow velocity of river water increases, thus increasing the adsorption capacity and speeding up the transport of heavy metal. The difference of the adsorbability of Cu, Pb and Cd on sandy and powdered-sandy sediment in different river sections also exists obviously (Figure 2). The ratio of the dynamic and static adsorbability of Cu, Pb and Cd individually is: 2.0, 2.4 and 1.3. This indicates that



Fig. 2 The adsorbability of Cu, Pb and Cd on sandy and powdered-sandy sediment in different river sections

sandy and powdered-sandy sediment with a larger subsiding velocity can speed up the adsorption and subsidence of Pb. Cu second. Adsorbability of Cd in dynamic state is slightly higher than that in static state, which indicates that the effect of sediment on the adsorption capacity of Cd in the process of water flow is small and Cd is easy to transport.The result is in keeping with the law of heavy metals contamination of sediment in the Second Songhuajiang River.

Sediment involved in Figure 1 is composed of sapropel on which the adsorbability of Cu, Pb and Cd is larger than that on sandy and powdered-sandy sediment. The reason is that specific surface area of sapropel sediment far exceeds that of sandy and powdered-sandy sediment. Sapropel sediment contains much organic matter on which hydroxyl and carboxyl group have a better complexing or chelation action on heavy metals ions. Therefore the adsorbability of heavy metals on sapropel sediment is large.

3.2 Effect of sediment's specific surface area and size on the adsorbability

Experiment made by Wu and others (1987) indicates that when sediment surface area increases by 100 percent the adsorbability of Cu, Pb and Cd all increases obviously among which the increase of adsorbability of Cd is the most obvious. Therefore the bigger the contact surface between sediment and heavy metals ions in water, the higher the adsorbability. Specific surface area is one of important factors.

When the size of sediment decreases the adsorbability of Cu, Pb and Cd on sediment increases due to the increase of specific surface area (Table 2). Although the smaller the size the larger the

				door bubit	<u>+ e j</u>			
he me	heavy	aveter	size					
	netals	system	<0.5mm	<0.05mm	<0.5mm			
	Cu	dynamic static	24.9 15.4	26.4 24.1	47.6 38.3			
	Pb	dynamic static	36.5 30.6	41.2 34.1	51.8 45.3			
	Cd	dynamic static	49.3 44.2	57.8 53.9	74.9 65.8			

Table	2:	Effect	of :	sediment	of	different
		size o	n th	e adsorb	abi]	lity

specific surface area, experimental result indicates that if the sediment with the size below 0.5mm is scattered in water the adsorbability of Cu, Pb and Cd on sediment of this size is larger than that on sediment with the size below 0.05mm. Sediment with the size below 0.05mm has a large specific surface area but when the sediment stand still in water the contact surface area is only 11.34cm<sup>2</sup> which is far smaller than the liguid-solid contact surface area of the sediment with the size below 0.5mm in the form of scattering. Thus it can be seen that although the specific surface area of sediment is an important factor affecting the adsorbability of heavy metals ions, the liquid-solid contact surface is a key factor.

3.3 Effect of coexisting substance on the adsorbability

When 1,000ppm chloride ion, l0ppm humic acid(HA), fulvic acid (FA) and sulphide ion are added into river water, the adsorbability of Cu on powdered-sandy sediment, whether in dynamic state or in static state, presents the tendency of decrease. Particularly, chelate is formed due to the action of Cu ion and humic and fulvic acid containing in water, thus increasing the stabability of Cu ion and reducing its adsorbability 50 percent. This is advantageous to the transport of Cu ion with the diffusion of river water.

Adsorption of Pb on powdered-sandy sediment is similar to Cu. The increase of adsorbability of Pb is favourable to the transport of Cd with the suspended substance. 10ppm humic acid, however, will reduce the adsorbability of Cd.

In brief, the adsorbability of different heavy metals ions on the surface of sediment is closely related to coexisting substance.

#### 4 CONTAMINATION STANDARDS OF HEAVY METAL IN ARTIFICIALLY EXCAVATED RIVER

Background value of river sediment is affected by geological maternal substance and soil type along the banks of river. Ordinary way of studying heavy metals contamination in river sediment is to measure the content of heavy metals in columnar samples taken from enough depth. Sediment in artificially excavated river is shallow. If taking the content of heavy metals in deep sediment as background value, the content is on the low side and the assessment of heavy metals contamination is on the high side. Actual conditions in Suzhou section of the Grand Canal is that the thickness of bottom mud is less than one meter (Wang and others, 1987). When determining original value and evaluating contamination degree of heavy metals in sediment of

artificially excavated river, the following practice is preferable to the ordinary way. That is, three kind of samples, sediment beneath bottom mud, soil along the banks of river and unpolluted or slightly polluted bottom mud, are taken to individually analyse the content of heavy metals. The sum of average value of heavy metals content of these samples and two-time standard deviation can be regarded as original value of contamination accumulation and contamination standard of sediment (Table 3).

lable	3:	Cor	itam	inatio	on s	standard	1s	(mg/	kg)
		of	sed:	iment	in	Suzhou	se	ctio	n
		of	the	Cron					

	<u>of the</u>	<u>Grand</u> Canal	
heavy metals	average values $(\bar{x})$	standard deviation (s)	standards (x+2s)
Cu	21.39	2.66	26.71
Zn	70.53	8.29	87.11
РЬ	24.24	4.28	32.80
Cd	0.09	0.05	0.21
Ni	34.56	7.05	48.66
Со	18.54	10.78	40.10
Hg	0.16	0.04	0.24
Cr	49.33	12.87	75.07

# 5 PROBLEMS OF RESEARCHES ON ACTUAL RIVER SYSTEM

In a specific river the content of heavy metals in aqueous part is not large and in general is in ppb degree. Many researches on the adsorption of heavy metals are made in laboratary, laying particular emphasis on high-concentration range (ppm degree) (Tang, 1984). The limitations in the application of experimental study are caused owing to large difference between experimental conditions and actual water environment.

Tang (1984) and Jin (1986) respectively made the the study of Xiangjiang River system. An example of the adsorption feature of Cd is given here to illustrate the difference between experimental and actual study. Concrete comparison can be

Table	4:Adso	orption	of Cd	in two	conditions

	initial	adsorption	
medium	concentration	capacity	
	<u>(ug/1)</u>	(ug/g)	
river	60 1 10/1 2	1165 5	
water	00.1-1941.5		
ion-rem	ove 1000-10000	8880	
water	1000-10000		

seen in Table 4. A large difference in the adsorption capacity of Cd on suspended sediment exists between actual Xiangjiang River system and ion-removing water system. The adsorption capacity of Cd in ion-removing water is large than that in actual Xiangjiang River water. Therefore the adsorption researches by using natural water is rather necessary, thus obtaining the result relatively closing to actual water body.

#### 6 CONCLUSION

In order to master the law of contaminants' transport and deposition, the sample in different depth of one section must be taken besides sampling in every section of river.

Adsorption of heavy metals on sediment is very complicated. Adsorbability of Cu, Pb, Cd on the same-type sediment is very different in different sections of river due to different sediment composition, structure, specific surface area, system state, coexisting substance and so on.

When determining original value and evaluating contamination degree of heavy metals in sediment of artificially excavated river, the sum of average value of heavy metals content of three kinds of samples and two-time standard deviation can be regarded as original value of contaminant accumulation and pollution standards of sediment.

Actual researches on river system must be carried out so as to reflect the adsorption feature of heavy metals on sediment much better. It is suitable to use lower content range of heavy metals.

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# Particle Bound Transport of Environmental Pollutants in Flowing Waters

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#### ABSTRACT

Concentrations of dissolved pollutants, suspended particle properties and the sources of hydrophobic pollutants are supposed to be responsible for the transport of particle associated pollutants. All statistical relationships between dissolved and suspended solids could be explained in terms of hydrological processes. Suspended particles are supply controlled. Their properties reflect mainly their sources. The same holds true for hydrophobic pollutants. The partition coefficient Kd seems to be responsible for short range movements within the catchment leading to local enrichment of pollutants.

#### 1. INTRODUCTION

According to the literature that deals with the fate of environmental pollutants it can be assumed that the transport of particle associated pollutants is controlled by three groups of factors 1. The chemical properties of pollutants, and the chemical exchange between pollutants in dissolved and suspended form.

2. The properties of transporting particles such as particle size, metallic or organic coatings, or the amount of organic carbon. 3. The sources of particles and pollutants, time and circumstances of their activiation, and the flow paths of water and particles to the river.

In order to evaluate these groups of factors due to their relative importance, the data of several investigations on water quality in rivers of the Eifel mountains were used. Between 1972 and 1978 nutrients and major ions (W.Symader 1976), pesticides (H.H.Rump, 1976), heavy metals (W.Symader 1984) and cyanides (H.Krutz 1979) were investigated in 24, 22, 31 and 30 catchments, respectively, of the northern Eifel mountains and the Lower Rhine area. In all these investigations a multivariate approach was used to analyze dominant patterns of the temporal and spatial variation in the solids under investigaton.

In 1988 a project was started that focused on individual flood waves and their importance to the transport of environmental pollutants. This study was restricted to two catchments near Trier. One is situated in a triassic limestone area (N.Strunk i.pr.; N.Strunk & W.Symader 1991), the bedrock of the second catchment is devonian shist.

2. DISSOLVED AND SUSPENDED POLLUTANTS If the change from the dissolved to the suspended forms or vice versa is an important or even dominant process for the behaviour of micropollutants, then relationships between the concentrations of dissolved and suspended pollutants should be evident.

For some catchments the senior author found sporadically statistical relationships between dissolved and suspended heavy metals. But more often such relationships were weak or non existing, what is in good agreement with the results of E.E. Angino et al (1974) and the experience of several other colleagues (e.g. Ellis, 1977). Most of these experiences have not been published, however, because they have been regarded as failures, as poor understanding of the system or as an inadequate approach. But they were discussed on conferences and during work shops. So it is interesting to have a closer look at those cases, where relationships are found.

In rivers highly polluted by waste water effluents high amounts of heavy metals can be found in solution as well as associated to suspended particles. But the close relationship between dissolved and suspended heavy metals goes back to the heterogenity of the statistical sample. It becomes much weaker, if only waste water events are considered.

A second possibility is the remobilisation of highly polluted fluvial sediments. Heavy metals have been enriched in the interstitial water during low flow periods and are released into the river water during flood conditions. It is the sediment, where important chemical reactions take place. In the river water the process of dilution dominates. If the pollution is caused by industrial waste waters all heavy metals can be involved. Domestic sewage causes only an increase in zinc, iron and manganese. Most efficient are small summer floods after extended dry periods.

The remobilisation of fluvial sediments has also an effect in catchments where ore deposits are of importance. In this case the situation is more complicated. Again the sediments are rich in heavy metals, but probably due to a lack of organic carbon in the sediment the concentrations in the interstitial water are low. The dissolved heavy metals must come from a different source, In these catchment winter floods show the strongest effects. Winter floods contain a high proportion of groundwater. The ground water table rises to zones of soil and bedrock, which are rich in oxygen. Under these conditions ZnS together with other heavy metal

compounds can be dissolved. In this case the relationship between dissolved and suspended heavy metals can be explained by the common occurrence of two different processes, the remobilisation of heavy metal bearing sediments by flood waves and the contribution of groundwater, which is rich in heavy metals, to the generation of runoff.

In none of these examples chemical interactions could be made responsible for the observed relationships between dissolved and suspended heavy metals. If chemical reactions are involved, they occur in the soil, the sediment, the waste water plant or the atmosphere, but its influence in the flowing water is dominated by hydrological processes. This could be shown by D.P.H. Laxen et al. (1984) in detail for manganese.

As only a limited amount of data of both dissolved and suspended organic pollutants are available (R.Bierl, 1988b), the possibility that chemical processes play an important role for these solids cannot be totally excluded. but the chemographs of adsorbed and dissolved fluoranthen and benzo(a)pyren for a flood wave of the River Rotmain differ widely indicating that the situation is similar.

#### 3. PROPERTIES OF SUSPENDED PARTICLES

The significance of suspended particle characteristics is better understood. From theoretical reasoning an inverse relationship between particle size and the concentration of suspended pollutants can be expected. It is the specific surface which is responsible for this relationship by controlling the adsorption capacity or the organo-metallic coatings (E.A.Jenne 1968). S.W.Karickhoff (1979,1984) could show that the sorption of hydrophobic pollutants can be directly related to the organic carbon content of the sorbent.

Investigations on suspended pollutants under field conditions, however, could not confirm these results. A distinct preference for smaller particles was found only for suspended iron (W.Symader 1985; N.Strunk in press).

R.Bierl (1988a) and G.Umlauf and R.Bierl (1987) investigated PAHs and chlorinated hydrocarbons in flood waves of the river Rotmain and found no relationship between particle size or organic carbon and the concentration of organic pollutants. The highest concentrations were found in the coarse fraction of the medium silt class and there is still considerable debate in our working group whether these findings go back to the high erodibility of silty soils or to a relationship between the different affinity of groups of humic substances to different particle size fractions.

Our investigations on PCBs in the small triassic catchment near Trier show striking differences between individual flood waves (fig. 1 and 2), but no relationship to particle size or suspended organic carbon.

Again all these findings seem to show that the characteristics of suspended particles and the variations of the concentrations of hydrophobic pollutants are controlled by different processes. In order to understand these processes the internal structure of flood waves was studied by using the hydrograph, the chemographs dissolved solids and the variations in suspended sediment concentrations and in turbidity. Even homogenous looking flood waves consist of a succession of waters of different origin (N.Strunk in press). In some cases these different waters could be synchronized with suspended material from different sources such as material from the rural pathway system, waste water remobilized sediment, soil surface material and subsoil material. The change of suspended particle

Fig. 1:

Particle Size and Concentrations of PCB in High Flood Samples, 18.02.89 and 19.12.88, Kartelbornsbach



Fig 2:

Organic Carbon and Concentrations of PCB in High Flood Samples, 18.02.89 and 19.12.88, Kartelbornsbach



characteristics can be explained in terms of changing particle sources (W.Symader and N.Strunk 1991)

#### 4. THE SOURCES OF PARTICLE ASSOCIATED POLLUTANTS

It stands to reason to assume that the transport of hydrophobic pollutants is supply and source controlled as it is in the case of suspended particles, but this assumption is hard to prove.

In the figure 3 a short summer flood in a small tributary of the shist catchment near Trier is shown. This single peaked flood wave causes two peaks of suspended particle concentration linked by a plateau. The comparison of concentration and turbidity reveals that the material of the first peak is coarser than that of the second one.

The second sample at the beginning of the wave contains mostly resuspended sediment and increased concentrations of dissolved iron and manganese probably from interstitial water. The high concentrations of suspended particles in samples 4 to 8 go back to soil surface material from two different areas and are characterized by slightly increased amounts of phosphate and potassium. The high

concentrations of dissolved manganese can be explained by the influence of ore deposits, but it must be stated that a second wave, sampled on the 4th of july, 1989 showed much lower concentrations of manganese.

The graph of Acenaphten, Fluoranthen and Benzo(a)anthracen could be synchronized with the three assumed particle sources, what supports the hypothesis of a supply controlled transport of hydrophobic pollutants. There seems to exist a relationsship between the partition coefficient of the PAHs and the transport behaviour. The smaller molecules show a reaction to the flood wave that is more distinct. One possible explanation is that the smaller molecules are transported partly in dissolved conditions in the catchment and therefore can be enriched in some parts near the river or in the river itself, whereas the large molecules are more evenly distributed.

#### 5. CONCLUSIONS

The concentration of dissolved pollutants does not have a significant effect on the transport of particle associated pollutants. This finding may have some consequences on approaches of water quality monitoring that depend on fluvial sediments. If the same

Fig. 3:



results could be obtained for the relationship between the concentrations in solution and sediment, then the pollution of sediments comes from sedimented particles and hydraulic conditions are more important than chemical interactions.

The characteristics of suspended particles reflect mainly their sources. A direct influence on the transport of hydrophobic pollutants could not be found in the rivers. If the properties of suspended particles are important, their importance is restricted to the sources of particles and pollutants.

The transport of hydrophobic pollutants seems to be supply controlled as well. PAHs with a high partition coefficient show a less distinct temporal pattern than PAHs with a lower coefficient do. A possible explanation is that the Kd coefficient determines short range processes of transport within the catchment leading to marked differences between different sources.

For the time being the knowledge of the transport of hydrophobic pollutants is limited due to a general lack of data and the poor understanding of the internal structure of flood waves in varying hydrologic environments.

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# Sediment-Phosphorus Relationships in Watersheds

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ABSTRACT: Sediment and particulate phosphorus (PP) load relationships and their dependence on land use (grassed, cultivated and gullies) and watershed scale (1 to 2\*10<sup>6</sup> ha) are investigated for the Washita River Basin, Oklahoma, USA. Sediment and PP loads are directly related (mean  $r^{2} = 0.86$ ) for the three land uses and watershed scales considered in the study. The data consistently brought out two distinct relationships: one for gullied, cultivated and grassed source areas, and another for stream gages at various watershed scales. The relations reflect differences between the sediment and PP producing source areas, and the channels, the environment in which sediment and PP are transported downstream. Also, sediment and PP loads are strongly dependent on land use and associated soil erodibility with loads increasing in the order of grassed, cultivated and gullied areas (1.3 to 65.5 mt/ha and 0.6 to 7.0 kg/ha for sediment and PP, respectively). Sediment and PP concentrations were inversely related (mean  $r^2 = 0.56$ ) and decreased in the order of gullied, cultivated and grassed areas, due to sediment size sorting and downstream enrichment. Sediment and PP data varied greatly due to variability of watershed and precipitation characteristics, and seasonality of soil cover, soil erodibility and biological phosphorus (P) uptake. Problems relating to data availability and consistency for large watersheds, as well as limitations of integrated data to interpret cause-effect relations, suggest the complementary use of field data and physically-based numerical modeling of sediment and P transport. The results of this study indicate that a PP transport model for large watersheds must rely not only on chemical P transformations during transport, but also on a detailed sediment production, transport and accounting model.

# 1 INTRODUCTION

An increased public awareness of the role of agriculture in nonpoint source pollution, has identified a need to obtain information on the impact of current and proposed agricultural management practices on surface water quality (US EPA, 1984; Crowder and Young, 1988). The transport of phosphorus (P) to surface waters can lead to accelerated eutrophication of these waters, which limits their use for fisheries, recreation, industry, or drinking. Phosphorus is transported in soluble (SP) and particulate (PP) forms. While SP is

immediately available for algal uptake (Numberg and Peters, 1984), PP which includes P sorbed by soil particles and organic matter during runoff, may provide a long-term source of P for algal growth (Carignan and Kalff, 1980). As P is strongly sorbed by clay particles and organic matter contains relatively high levels of P, PP constitutes the major portion of P transported in runoff from cultivated land (Sharpley and Menzel, 1987). In runoff from grassland, with little erosion, SP is the dominant form transported (Burwell et al., 1975).

Most studies of land use and P transport in runoff have been conducted on small plots and at field scales (0.1 to 10 ha) with limited climatic, soil, topographic, and management variability (Ryden et al., 1973; Johnson et al., 1976; Sharpley and Menzel, 1987). Limited information is available on the transport of P as a function of sediment at several scales within a given watershed, from source areas to watershed output several miles downstream. This paper presents an investigation of sediment versus PP relationships as a function of scale and sediment-phosphorus watershed production/transport environment using measured data over a 10-year period from watersheds of different size and land use, but within the same geographic and geologic setting. will determine future The results data acquisition needs and guide the development of a P transport model for large watersheds to assess the economic and environmental benefits of improved agricultural management practices on surface water quality.

# 2 STUDY AREA

The investigation was conducted on the Washita River Basin in southwestern Oklahoma, USA (Fig. 1). Three different watershed scales are considered (Table 1):

- large scale: Washita River Basin; single gage; 1'865'300 ha;
- intermediate scale: Little Washita River Watershed; three gages; 58'793, 53'794 and 16'025 ha, respectively;
- and, small scale: Source Areas; 10 sites; 0.6 to 4.2 ha; land use: grassed, cultivated, and gullied.

Average annual precipitation for the Washita River Basin is about 550 mm and 850 mm on the western and eastern edge, respectively. For the Little Washita River Watershed it averages 750 mm. Most of the precipitation occurs in spring and fall. In the Washita River Basin, the Land Resource Areas which define predominant soil and natural vegetation types are primarily Western Rolling Red Plains, Cross Timbers and Central Reddish Prairie. Land use is approximately 25% cultivation, 65% range and 10% miscellaneous uses such as timber,

rock, urban areas, and reservoirs (USDA-ARS, 1983).

# 3 DATA COLLECTION

Data consist of water runoff, suspended sediment and PP data collected at stations identified in Table 1 and Fig. 1. Data for the stream gage locations represent mean daily values, whereas those at the source areas represent daily event values. All available data, regardless of season during which they were collected, are used in this study.

The data on the Washita River near Dickson were measured every few months throughout the year by the US Geological Survey (USGS 1980-1989). The stream gage data on the Little Washita River were measured throughout the year during and between runoff events by the USDA Agricultural Research Service (ARS). Daily mean discharge was computed from mean daily stage and suspended sediment determined from samples collected using depth-integrating Data from the source areas were samplers. measured for about 80% of all runoff events by the USDA-ARS. Break point runoff and total sediment were measured at the drainage outlet using Chickasha samplers (Allen et al., 1976). From these measurements daily water and sediment yield were computed.

Dissolved and total P were determined after acid digestion on filtered (0.45  $\mu$ m) and unfiltered samples, respectively. The samples from the source areas and the stream gaging stations on the Little Washita River were digested with perchloric acid (O'Connors and Syers, 1975), and for the Washita River Basin with acidifical (USGS data) ammonium persulfate (Gales et al., 1968). For all samples, colorimetrically P was measured by the molybdate-blue method (Murphy and Riley, Particulate P was calculated as the 1962). difference between dissolved and total P.

# 4. ANALYSIS AND RESULTS

Sediment and PP loads and concentrations are analyzed for all land uses and watershed scales together, and also as a function of land use and watershed scale separately.

# 4.1 Load relationships

Particulate P increases with sediment load for all watershed scales and land uses (Fig. 2). The data show two distinct relationships: one for source areas (dashed line), and another for stream gages (solid line). The data for the source areas include all three land uses with the gullied areas producing higher sediment and PP values than the grassed and cultivated areas. The stream gage data cover several watershed scales with minor differences between the three gages on the Little Washita River and the one of the Washita River. However, the stream flow versus source area relationship is: (i) shifted towards higher sediment and PP loads; and, (ii) offset by about one order of magnitude upward on the PP-load scale (Fig. 2).

The increase in sediment and PP load at the stream gages is clearly attributed to the greater water, sediment and phosphorus yield resulting from larger upstream drainage areas than for the source areas. However, the reasons for the vertical offset are more ambiguous and could be the result of one or several of the following downstream enrichment of factors: fine sediment due to sediment sorting; in-channel chemical transformations; biological P uptake; sediment delivery ratio; or a bias in the sediment sampling method. At the source area level there are no channels, and, by necessity, sediment is collected, whereas only total suspended sediment is collected at the stream gages. This may also explain why there is not a significant offset between stream gages even though drainage area changes several orders of magnitude between the Little Washita River and the Washita Basin. Clearly, detailed information on processes controlling PP transport and transformations is required to explain the offset between the two relationships.

The wide range of sediment and PP load values results from the variability in transport capacity of the flow. The sediment and PP load varies at a given station due to discharge variability with upstream rainfall amounts, and, in a downstream direction due to increasing discharge with increasing upstream drainage area. Both these dependences must be normalized to bring out true sediment-PP relationships.

# 4.2 Unit area relationships

The dependence of sediment and PP load on upstream drainage area is removed by expressing the variables on a unit area basis (Fig. 3). Two distinct sediment-PP relationships for source areas and stream gages still exists, but over a much smaller range of sediment and PP values. In addition, the shift and offset of the stream gage data is reversed (Fig. 3). The reversal in the shift, with smaller sediment and PP values at stream gages, is brought about by spatial extent and variability of precipitation over large areas, leading to lower runoff values per unit area. Reversal in offset of the stream gage data which now appears below the source area data, is brought about by the rescaling of the data with respect to drainage area.

The data in Fig. 3 also shows that at low sediment loads for the Little Washita River, PP load is below the linear relationship. This trend was also present in Fig.2, but was masked by the source area data. The lower PP loads are believed to be the result of water and sediment retention by reservoirs for small runoff events (Menzel et al., 1986). Portions of the washload high P content with never reach the downstream gages, and the PP values in the low sediment range for the Little Washita River would be higher if it were not for the reservoirs. Therefore, the slope of the solid regression line for stream gages would be closer to the one of the dashed regression line for the source areas.

# 4.3 Unit area and runoff relationships

Normalizing sediment and PP loads with respect to drainage area and runoff depth, reduces the range of values further. The remaining sediment and PP variability is attributed to varying rainfall intensities with storm, and seasonal changes in soil erodibility and plant cover. The two sediment-PP relationships for source areas and stream gages are again apparent (Fig. 4). In general, gullied source areas have highest sediment and PP loads, grassed areas lowest, and stream gage are intermediate. There no longer is a pronounced shift between the source area and stream gaging



Fig. 1 Geographic setting and location of gages.

Table 1. Watershed characteris
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Watershed Identification	Drainage Area (ha)	Sampling Period	Number of Samples	Land use
Source areas				
5201	3.7	1980-1989	94	Eroded gullies, native grass land, no management
5202	5.7	1980-1989	101	1980-1983 as 5201; 1984-1989 rehabilitated, native grass land
5215	0.5	1980-1985	27	Road side gully
5227	3.2	1980-1983	28	Road side gully
5233	2.3	1980-1982	9	Native pasture land, overgrazed
5234	1.2	1980-1982	11	Native pasture land, moderately grazed
5268	3.1	1980-1985	39	Bermuda grass pasture
5269	4.2	1980-1985	57	Wheat
5275	0,6	1980-1985	43	Wheat, conventional tillage
5276	0.6	1980-1985	44	Stubble mulch wheat, low tillage
Little Washita	a Watershed	s *		
526	16'025	1979-1983	34	66% Range
522	53'872	1979-1983	56 >	18% Cultivation
520	58'793	1979-1982	17 J	16% Miscellaneous
Washita Rive	r Basin			
3310 1	'865'300	1980-1989	54	Mixed

\* Land use assumed the same above each stream gage station.



Fig. 2 PP versus sediment load.



Fig. 3 PP versus sediment load per unit area.



Fig. 4 PP versus sediment load per unit area and runoff depth.



Fig 5 PP versus sediment concentration

station data, even though the sediment load for the latter appears lower. However, the slight difference in slope and the vertical offset between the sediment-PP relationships persists. The causes of the latter remain unanswered given the limited information on individual processes controlling the sediment and PP interactions during downstream transport.

In summary, the data presented in Figures 2, 3, and 4 consistently show a strong direct relation between sediment and PP loads (mean  $r^2 =$ 0.86). A different relationship is obtained for the source areas (all land uses) and stream gages (all watershed scales) with the slope approximately the same for both the land use and the stream gage relationships. This suggests that a PP transport model must first be sensitive to sediment and PP production versus transportation, and that land use and watershed scale effects can be treated within this framework.

# 4.4 Concentration relationships

Particulate P concentration decreases with an increase in sediment concentration for all land uses and watershed scales (Fig. 5). This inverse relationship is most likely related to sediment size composition. For large runoff events, with higher sediment concentration, the percentage of coarser particles increases. These coarser particles add to the weight of the sediment, but are of relatively low P content and sorptivity compared to finer clay-sized material (Sharpley et al., 1981), thus resulting in the inverse relation.

The slope of the relationships for sediment and PP concentration for source area and stream gages may be closer than shown in Fig. 5, if it were not for the effect of the reservoirs, as previously explained. Also, the vertical offset of the sediment-PP concentration relationship may be the result of a lower phosphorus concentration in the stream environment due to the input of P deficient bed and bank material, desorption of P with the input of subsurface flow low in SP concentration, or biological P uptake in the stream environment. In addition, the differential sampling of total sediment load on the source areas and suspended sediment in

the streams, may cause some displacement of the relationships. However, these interpretations are weak given the low coefficient of determination ( $r^2 = 0.32$ ) for the stream gage data (Fig. 5).

4.5 Land use and scale relationships

Sediment and PP loads are summarized in Table 2 by measurement site, land use and watershed scale. Land use summaries (Table 3) are weighted by the number of years of record to emphasize the more reliable long-term records. Sediment and PP loss from gullied and cultivated areas is up to 10- and 2-fold larger than from grassed areas. This is a reflection of the soil disturbance, erodibility and erosion. The ratios of PP versus sediment load (0.11, 0.43 and 0.47 for gullied, cultivated and grassed areas, respectively) are similar despite large differences in sediment and PP loads between the three land uses. The lower PP/sediment ratio for the gullied areas is primarily the result of the lower P content of source material (subsurface soils) compared to P-fertilized grassed and cultivated surface soils. Also. larger particles are directly eroded into the stream channel from gullied areas due to a lesser size sorting than occurs in overland flow from the cultivated and grassed areas. The ratios and the trends in sediment and PP load (Table 3) clearly show that P loss in runoff is strongly related to sediment erosion and transport, with variations due to sediment size composition, seasonality in soil cover and erodibility, and agricultural activity.

Finally, on a watershed scale, sediment load decreases in a downstream direction (Table 3). The only single value that does not follow this general trend is the sediment runoff per unit area and runoff depth for the Little Washita River Watershed. However, the deviation from the general trend is not significant because the range of the particular sediment loads over all and three scales is relatively narrow. fluctuations due to precipitation intensity, seasonality and/or sediment supply from channel instability can easily account for the discrepancy.

The trends for the PP load are somewhat less

Land use	Runoff depth ' [cm]	Sediment ' [mt/ha]	Sediment/ runoff ' (mt/ha/cm)	Sediment concentration [ppm] <sup>2</sup>	Particulale ' phosphorus ' [kg/ha]	Particulate phosphorus/ runoff ' [kg/ha/cm]	Particulate phosphorus concentration [ppm] <sup>3</sup>
				7014.02		0.705	102.2
GL	7.742	65.532	6.865	70.139	6.987	0,796	193.2
CL	12,773	3.607	0.267	2'202	1.435	0.123	1'301 3
GR	8.046	1.305	0 139	1'545	0.621	0 064	2'052 1
Watershed Scale							
Source areas 4	8.866	8.142	0.835	8'703	1.404	0.148	1*731.1
Little Washita Watersheds	1.10	1.487	1.209	4'901	0.316	0.292	393 3
Washita River Basin	0.12	0.067	0.33	1'366	0.010	0.050	948.0

# Table 3. Water, sediment and phosphorus runoff characteristics by land use and watershed scale

GL: gullied field and road side gully; GR: grass or range land; CL: cultivated field.

1: Data for sampled events only; 2: ppm by weight of water; >: ppm by weight of sediment.

\* : Estimated 10% GL, 72% GR and 18% CL.

	•	
Table 2.	Water, sediment and phosphorus runoff characteristics b	y station

Watershed Identification	Land Use	Number Years	Runoff depth ' [cm]	Sediment ' [mt/ha]	Sediment/ runoff <sup>1</sup> c [mt/ha/cm]	Sediment concentration <sup>2</sup> {ppm] <sup>2</sup>	Particulate phosphorus ' [kg/ha]	Particulate phosphorus/ runoff ' [kg/ha/cm]	Particulate phosphorus concentration ' [ppm] <sup>3</sup>
Source are	as								
5201	GLF	10	5.64	20.68	4,15	37 250	2.859	0.597	178
5202A	GLF	4	6,62	56.86	10,54	100'077	5.741	0.851	214
52028	GR	4	15.69	4.31	0.30	4'125	1.943 *	0.128	595
5215	GLR	6	13.26	172.30	10.65	126'900	15.67	1.045	168
5227	GLR	4	5.84	26.18	4,30	37'280	5.530	0.865	248
5233	GR	3	0.49	0.043	0.10	866	0.018	0.046	1'995
5234	GR	з	1.32	0.21	0.16	1'265	0.113	0,066	838
5268	GR	6	10.09	0,48	0.04	305	0.294	0.028	3.629
5269	CL	6	15.63	7.57	0.49	3'585	2.157	0.160	771
5275	CL	6	11.43	1.83	0.16	1'575	1.203	0.107	1'524
5276	CL	6	11.26	1.42	0.15	1'446	0.945	0.102	1.609
Little Wash	ilta W	atershe	ds						
526	MX1	5	1.31	1.29	0.73	2'973	0.189	0.142	449
522	MX1	5	1.12	1.70	1.33	5'669	0.385	0.324	368
520	MX1	4	0.63	1,18	1.77	6'229	0.340	0.486	365
Washita Ri	ver B	asin							
3310	MX2	10	0.12	0.067	0.33	1*366	0.0097	0.0496	948

GLF = gullied field; GLA = road side gully; GR = grass or range land; CL = cultivated field.

MX1: About 66% range, 18% cultivation, 16% miscellaneous.

MX2: Mixed land use.

': Data for sampled events only: ': ppm by weight of water; '' ; ppm by weight of sediment.

4 : Fertilized

clear, but overall the data do show a decrease with watershed scale (Table 3), similar to the one for sediment. The exception is PP per unit area and runoff depth for the Little Washita River Watershed. The deviation from the trend is most probably related to the one for sediment, as noted in the previous paragraph. Again, the PP/sediment ratios are all within a narrow range (0.18, 0.15 and 0.22 for source area, Little Washita River and Washita River, respectively), even though individual sediment and PP values vary greatly.

### 5. CONCLUSIONS

The relationship between sediment and PP load was investigated as a function of land use and watershed scale using data from the Washita River Basin, Oklahoma, USA. The study showed that PP load is directly related to sediment load regardless of land use and scale. Sediment PP watershed and concentrations produce an inverse relationship which is primarily attributed to changes in sediment size composition with sediment concentration. Distinct differences in sediment-PP relationships between source areas and stream gages are apparent. These differences do not appear to be related to watershed scale, but reflect differences in sediment and P production environment versus a transport environment.

With respect to land use, the amount of sediment and phosphorus load are closely related to soil disturbance and erodibility. Increasing amounts of sediment and PP are transported from grassed, cultivated and gullied areas. The proportionality between sediment and PP load is further demonstrated by similar values for PP/sediment-load ratios even though loads varied over a wide range. The PP concentration values show an opposite trend than those for sediment and PP load, increasing from gullied to cultivated to grassed areas. Sediment size sorting and PP enrichment are the main reasons for this inverse trend. Gullied areas produce and transport a higher amount of coarse sediment particles with low P content, whereas grassed areas trap coarse sediment and runoff is enriched with fine material of high P content.

With respect to watershed scale, data trends are land as for use. not pronounced as Nevertheless, the small source areas produce higher unit area and unit runoff depth loads However, this is not than at stream gages. necessarily related to sediment and PP load, but to the effect of spatial extent and variability of sediment and PP runoff with increasing watershed size. The delivery ratio may also contribute to this trend.

In general, the sediment and PP data display significant variability due to spatially variable watershed characteristics and precipitations input, seasonality of soil cover, erodibility, and agricultural activity, and annual variability in runoff. The data also represent the integration effects and do not of all upstream lend themselves disaggregation into to and explanation of individual cause-effect relations. This, with the limited availability of consistent sediment and P data over extended areas, narrows the use of large watershed data analysis to the determination of broad trends, as accomplished in this study. Detailed causeeffect interpretations can be established bv complementing field data with physically-based numerical modeling.

To this end, the close relationship between sediment and PP, as demonstrated in this study, suggest that sediment production and transport are key elements of a PP transport model for large watersheds. Such a sediment model must be sensitive to the influx of high P content washload, changes in sediment size distribution during transport, low P content bed and bank sediment supply, and sediment accounting by source. Chemical transformations and uptake of P, even though biological not addressed explicitly in this study, account for They should include more subtle changes. dilution effects by subsurface return flow, PP, partitioning between SP and and sorption/desorption of P with changing water and sediment characteristics in downstream direction. Future data collection efforts should include sediment size distribution of suspended sediment samples and determination of P content by size fraction.

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# Sediment Quality Downstream of Dams in Extremely Arid Areas

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**ABSTRACT:** Real data from an arid area were used to study the sources and spatial variations of nutrients, ions, and trace metals along ephemeral channels downstream of annual-storage dams. The concentration of the investigated pollutants varies with distance downstream of dam, and is influenced by characteristics of drainage basin and rainstorm.

#### **1 INTRODUCTION**

Climate in arid areas has distinguished features. Temperature and precipitation are characterised by high seasonal and daily variability. Levels of atmospheric and soils humidity are much lower than those in humid areas. Floods are flashy with hydrographs having steep rise and rapid exponential decay. The extreme daily fluctuations in temperature and the violent solar action normally cause breakdown of rocks and disintegration of soils, which furnish the short- duration- high- intensity rainfall with large amounts of solids to be carried with flash floods to downstream sites. The larger portion of these solids is fine grain fractions which normally transport in suspension (2, 3, 4, 13).

Once the floods flow to the reservoir of a dam a large percentage of its transported sediments is trapped. Downstream of the dam, the flow of water is controllable according to the operations strategy of the dam, and the sediments released from the dam are much less in amounts than and different in grain size composition from the sediments supplied with the floods to the reservoir (16). However, because natural channels often adjust their dimension and pattern to maintain balance between sediments and hydraulic conditions (12), the relatively pure released flow tends to erode the boundary of the channel downstream of the dam, resulting in continuous increase in the concentrations of suspended sediments (10). Till the state of balance between sediments and hydraulic conditions is reached, the eroded materials and, accordingly, the concentrations of suspended sediments vary along the channel downstream of dam. As reported elsewhere (17, 18, 19), such transported sediment, under specific environmental conditions, may be responsible in removing some types of pollutions from water or in releasing another types of pollutions in water. It acts as am important agent which transfers pollutions from one place to another. This strong interaction between sediment grains and pollutions conveyed by water makes the determination of the chemical and physical properties of sediments is of fundamental importance in any problem of water quality control.

Previous investigations have resulted in identifying the chemical properties of rainwater and floods under various conditions of climate and drainage basin (17), and in identifying the physical properties of transported sediments to and from dams in arid areas (16). The present work is an extension to such previous investigations. Its main objective is to identify the types and the spatial variation of pollutions transferred with sediments along channels downstream of dams in arid areas.

To reach the above objectives, real data from 12 different drainage basins and from channels downstream of annual-storage dams were collected and analysed. The data covers a wide range of climate

Data <sup>.</sup>	<u>Dam Number (*)</u>											
	1	2	3	4	_5	6	7	8	9	10	11_	12
Drainage basin:												
А	1100	930	1018	902	906	100	58 _	17	20	72	65	67
S	19.4	8.15	19.80	27.75	29.10	20.1	27.15	20.80	23.17	19.80	15 <i>.5</i> 0	21.70
v	Bare	Pastur	e Bare	Pastur	e Bare	Bare	Pas	ture	Past	ure	Pas	ture
SS	Sai	ndstone	Sand-	-clay Sa	ndsto	nc	Sa	nd - c	i a y	Clay	Clay	' Clay
I,	88.10	67.00	83.90	70.10	72.30	90.20	86.00	70_50	74.15	67.00	75.15	55.00
I,	00.21	00.15	00.25	00.25	00.27	00.25	00.30	00.25	00.27	00.35	00.29	00.23
I I	32.50	25.00	30.50	27.10	25.90	31.50	22.50	25.15	29.00	25.50	35.00	20.50
DS	11.80	17.80	12.50	19.60	20.25	12.50	10.80	12.70	11.45	10.50	13.70	10.00
n	00.27	00.29	00.30	00.30	00.27	00.30	00.19	00.22	00.29	00.31	00.36	00.19
Rainstorm events:												
N_	118	103	193	115	154	122	145	90	117	53	92	77
d r	62.7	59.4	62.5	58.3	60.3	57.9	81.6	21.0	49.3	50.0	52.7	48_5
D	37	41	36	35	38	42	78	47	52	28	62	65
Р	72	67	81	<b>7</b> 9	83	77	78	63	69	119	108	45
Runoff hydrograph:							·					
Q_	1008	589	848	873	1046	551	1309	714	257	513	371	415
t	1.05	1.52	1.50	1.95	2.50	1.19	2.96	1.75	0.81	1.72	2.55	2.06
Ď	12.07	23.35	10.45	15.50	20.50	19.28	19.05	16.25	14.23	7.93	7.35	12.50
Reservoir:												
с	71	62	53	49	18.3	15	24	60	18	15	19	15
R <sub>1</sub>	0.78	0.85	0.92	0.81	0.62	0.87	1.03	1.20	1.00	0.93	1.25	1.00
Purpose of dam	Fι	000	i	Cor	ntr	o 1	Water	Supply	Grou	ıd Wa	ter	Recharge
(*) name of numbered dams:	1 = Jiza		2 = Na	igran	3 = Kat	ecf	4 = Nar	nman	5 = Sad	a	6=Ma	imaa
	7= <b>A</b> b	ba	8 = Wa	ajj	9 = Bat	ham	10 = H1	reiml	11 <b>=</b> Ar	nanyl	12 = N	assim

Table 1: Main characteristics of data utilised for the study

and drainage basin characteristics. A summary of these characteristics is shown in Table 1.

## **2 THE STUDY AREA**

The study area is located in the southwest region of Saudi Arabia, between latitudes 16 30 00 N and 22 00 00 N and longitudes 39 30 00 E and 46 00 00 E. The climate of this area is arid, with characteristics covering a wide range (3). Temperature ranges from 2 to 53 C, with a yearly mean of 27 C. The annual relative humidity has an average value of 62%, with maximum and minimum values of about 96% and 17%, respectively. Rainfall are characterised by short duration and high intensity. The mean number of yearly rainstorms is about 7 throughout the region. Rainfall depth has an annual average of 850 mm, with an average maximum up to 1500 mm and an average minimum of about 300 mm. Details of the rainfall characteristics are reported elsewhere (8). The annual runoff coefficients fluctuate between 0.133 and 0.185 resulting in an overall average of 0.158. Runoff are characterised by spates which generally last on average 12 hours from start to finish. Flow hydrographs are characterised by steep rise and rapid recession. The period of the greatest total rise varies from 35 to 90 minutes. The total period of rise, i. e. up to the start of recession, varies from a minimum of 45 minutes to a maximum of 5 hours. More information on the runoff can be found elsewhere (9).

The average total sediment transport rate to the reservoirs in this region is about 1600 gm/s/m, the average reservoir deposition rate is about 120,000  $m^3/km^2$  of drainage basin, and the average trap efficiency of the reservoirs is about 0.86. The average percentage of clay, silt, and sand in the deposits of the reservoirs are approximately 25%, 35%, and 40%, respectively. The suspended sediments observed immediately downstream of the dams consist of clay (about 70%) and silt (about 25%). The mean concentration of such suspended sediment varies between 8.20 and 17.50 gpl. More information on the characteristics of sediment to and from the reservoirs are given elsewhere (16).

# **3 THE SAMPLING TECHNIQUES**

Two types, namely soils and suspended sediment, of samples were collected. The soil samples were collected from the surface of 12 drainage basins (see Table 1), whereas the suspended sediment samples were collected at the centre-line of specific cross sections along the channels downstream of the dams.

In collecting the surface soil samples, consideration was given to the range of land use, geology, and topography. The distance between two samples was in the order of one kilometre. The suspended sediment samples were collected during flows of a wide range in the channels.

At selected distances (0.50, 2.00, 5.00, 10.00, and 18.00 m) downstream of dams, suspended sediment and flow measurements were made. These include suspended sediment concentration, particle size, specific gravity of suspended sediment, temperature of water-sediment mixture, water discharge, distribution of flow in the stream cross section, bed materials, and water surface elevation measurements. Sediment concentrations were determined from pump samples collected from nozzles fixed to two masts and positioned at various heights above the stream bed. The concentrations of sediment determined by this method were compared with those determined using a calibrated automatic sampling

equipment at selected verticals. The comparison resulted in a correction factor which should be applied to the concentrations from the pump samples to obtain corrected concentrations for the samples. Water discharge and flow distribution in the cross section were determined from velocity and depth observations at properly spaced stream verticals. Data on particle size distribution were obtained from samples selected to be representative of a range of sediment discharge and runoff conditions. The average bed material size grading was derived from nine surface layer samples collected near the bed. A recently developed procedures (10, 11), suiting this particular channel and flow conditions, were then used to estimate the transported rate of suspended sediment and bed load.

# **4 METHOD OF ANALYSIS**

Previous investigations have indicated that the concentrations of transferred pollutions are influenced by the nature of climate (5, 6, 7, 15) and by the grain size distribution of transported suspended sediment (1). In addition, properties of sediments, which are influenced by both drainage basin and rainstorm characteristics (2, 3), may affect both flow and channel properties (12, 14). Therefore, to have a clear picture on the way by which pollutions transfer along channels downstream of dams, the available data were sorted into groups according to each of these hydrologic factors. Further, the data of each group, i. e. each of the suspended sediment and soil samples, was separated into divisions of specific grain size ranges. In this regard, divisions containing particle size diameters of the following ranges were considered; smaller than 0.01 mm, 0.01 mm - 0.025 mm, 0.025 mm - 0.05 mm, and larger than 0.05 mm. The data of each division of diameter range were then analysed for selected nutrients, ions, and trace metals using the standard methods of testing (20, 21).

# **5** RESULTS AND DISCUSSIONS

# 5.1 Physical properties of sediment

As mentioned earlier, the released water from a dam erodes the channel boundary during the process of maintaining balance between sediments and hydraulic conditions. The rate of such erosion decreases with the increase in suspended sediment concentrations as the distance downstream of the dam increases. This is indicated by the results shown in Table 2. In addition, it can be seen that the percent-

Table 2: Average variation of suspended sediment with distance downstream of dam

Data	Distance (km) downstream of dam											
	0.00	0.50	2.00	5.00	10.00	18.00						
Mean concentration [gpl]	13.20	18.40	31.60	42.00	54.60	62.18						
Percentage of clay	70.15	64.30	54.25	43.00	30.50	26.15						
Percentage of silt	24.00	30.40	31.00	36.50	36.27	43.07						
Percentage of sand	1.05	2.55	6.14	14.33	20.00	26.00						

age of transported clay decreases but the percentages of both silt and sand increase with the increase of distance downstream of dam.

To show the relationship between the physical and the chemical properties of transported sediment downstream of dams, the results of analyses of two sets of data having different ranges of particle size diameters are presented in Table 3. The first range of diameters ( $D \le 0.01 \text{ mm}$ ) mainly includes transported clay and fine silt, whereas the second range of diameters ( $D \ge 0.05 \text{ mm}$ ) mainly includes transported course silt and sand.

Table 3: Effect of sediment grain size on sediment quality downstream of dam number 1

Constituent		distance (km) downstream of dam -[D < 0.01 mm]							distance (km) downstream of dam -[D>0.05 mm]					
		0.50	2.00	5.00	10.00	18.00	CAT 1	0.50	2.00	5.00	10.00	18.00	CAT 1	
NUTRIENTS:														
Nitrate Nitrite	NO <sub>2</sub> /NO <sub>3</sub>	00.46	00.83	01.16	01.94	02.08	01.54	00.18	00.31	00.55	00.71	00.87	00.68	
Ammonia	NH	00.42	00.63	01.19	01.41	01.46	00.98	00.13	00.19	00.29	00.41	00.65	00.58	
Total Kieldahl N	TKN	00.52	00.51	00.87	00.91	01.23	00.98	00.20	00.62	00.69	00.76	00.93	00.69	
Dissolved Carbon	DC	00.79	02.44	05.33	07.65	07.92	05.54	00.39	00.92	02.74	06.28	06.50	03.67	
Total Phosphorus	ТР	00.09	00.18	00.36	00.48	00.55	00.32	00.02	00.08	00.17	00.21	00.26	00.18	
IONS:														
Calcium	Ca	13.05	18.24	27.05	32.14	39.89	31.45	09.15	09.81	11.78	19.65	21.55	18.36	
Magnesium	Mg	00.82	01.05	03.37	05.67	07.08	04.18	00.37	00.81	01.05	01.98	02.84	03.67	
Sodium	Na	01.17	02.98	04.05	04.17	04.87	03.25	01.37	03.19	03.15	03.90	04.01	03.15	
Potassium	К	00.27	00.39	00.71	00.92	00.96	00.71	00.21	00.19	00.28	00.37	00.39	00.29	
Sulphate	SO	15.29	17.29	24.78	31.72	39.30	32.18	12.25	14.33	19.10	19.98	21.29	21.25	
Chloride	cı T	00.19	01.20	02.05	03.29	04.89	03.55	00.25	00.92	01.74	02.51	03.45	02.95	
METALS:											• • • • •			
Barium	Ba	0.089	0.129	0.155	0.192	0.218	0.188	0.053	0.072	0.103	0.132	0.155	0.142	
Cadmium	Cd	0.009	0.016	0.028	0.028	0.031	0.019	0.003	0.010	0.012	0.015	0.021	0.018	
Chromium	Cr	0.010	0.013	0.027	0.038	0.041	0.033	0.006	0.009	0.012	0.016	0.018	0.015	
Copper	Cu	0.017	0.026	0.031	0.038	0.057	0.027	0.012	0.016	0.018	0.022	0.027	0.019	
Lead	РЬ	0.019	0.084	0.107	0.187	0.192	0.155	0.006	0.010	0.016	0.016	0.028	0.019	
Nickel	Ni	0.016	0.028	0.030	0.038	0.042	0.035	0.007	0.015	0.017	0.028	0.031	0.023	
Zinc	Ze	0.032	0.036	0.041	0.055	0.059	0.041	0.017	0.029	0.029	0.033	0.036	0.021	
Iron	Fe	0.558	0.921	3.775	5.148	8.155	6.055	0.320	0.911	1.493	4.286	4.901	3.900	
Constituent		distance (km) downstream of dam number 1						distance (km) downstream of dam number 6						
------------------	------------	--	-------	-------	-------	-------	-------------	--	-------	-------	-------	-------	-------	
		0.50	2.00	5.00	10.00	18.00	CAT 1	0.50	2.00	5.00	10.00	18.00	CAT 6	
NUTRIENTS:														
Nitrate Nitrite	NO2/NO3	00.23	00.61	00.95	01.08	01.18	01.42	00.19	00.43	00.74	00.97	01.17	01.32	
Ammonia	NH	00.29	00.41	00.68	00.93	01.15	00.86	00.17	00.19	00.23	00.29	00.35	00.78	
Total Kieldahl N	TKN	00.41	00.47	00.69	00.74	00.91	00.71	00.33	00.46	00.60	00.64	00.69	00.65	
Dissolved Carbon	DC	00.43	0.89	01.45	02.69	04.88	04.67	00.39	00.67	01.55	02.05	02.95	05.41	
Total Phosphorus	ТР	00.04	00.12	00.29	00.32	00.41	00.26	00.01	00.05	00.11	00.19	00.28	00.28	
IONS:														
Calcium	Ca	09.14	11.36	18.05	25.06	29.67	28.17	05.18	08.28	12.33	17.16	23.05	27.45	
Magnesium	Mg	00.42	00.78	00.93	01.45	03.89	03.55	00.27	00.45	00.72	00.96	01.95	0285	
Sodium	Na	00.86	00.97	01.67	02.55	03.87	03.02	00.33	00.49	00.89	01.78	02.53	02.83	
Potassium	К	00.19	00.25	00.33	00.57	00.89	00.85	00.09	00.17	00.19	00.27	00.31	00.72	
Sulphate	SOA	13.24	14.89	20.00	23.55	27_58	26.45	09.22	09.69	11.67	15.33	16.67	25.95	
Chloride	<b>ต</b> ์	00.12	00.92	01.46	02.82	03.05	03.15	00.07	00.53	00.96	01.87	02.07	02.95	
METALS:							· · · · · ·							
Barium	Ba	0.055	0.098	0.120	0.152	0.195	0.192	0.021	0.036	0.097	0.123	0.131	0.167	
Cadmium	Cd	0.003	0.010	0.014	0.027	0.029	0.015	0.001	0.005	0.009	0.013	0.015	0.015	
Chromium	Cr	0.006	0.009	0.015	0.021	0.027	0.030	0.002	0.003	0.008	0.013	0.019	0.024	
Copper	Cu	0.009	0.014	0.021	0.029	0.036	0.021	0.005	0.008	0.015	0.023	0.028	0.018	
Lead	Рь	0.012	0.055	0.076	0.093	0.145	0.149	0.009	0.037	0.053	0.072	0.105	0.135	
Nickel	Ni	0.014	0.019	0.028	0.032	0.039	0.032	0.008	0.011	0.019	0.027	0.029	0.026	
Zinc	Ze	0.025	0.028	0.035	0.042	0.047	0.043	0.018	0.021	0.023	0.027	0.031	0.037	
Iron	Fe	0.354	0.589	1.559	3.702	5.180	4.055	0.277	0.505	1.039	2.781	3.132	3.955	

Table 4: Effect of size of drainage basin on sediment quality downstream of dam

Inspection of the table indicates that:

(1) the concentrations of the investigated constituents are generally higher with small grain size diameters than with large grain size diameters.

(2) there is a strong correlation between the variation in the concentration of suspended sediment and that of the constituents; both increase with increase of distance downstream of dams. Keeping in mind that the percentage of clay decreases with the increase of distance downstream of dams, it may be concluded that the transported silt and sand are more effective than clay in increasing the concentrations of sediments and the constituents downstream of the dams.

(3) the average concentrations of the constituents in the drainage basins (referred to as CAT 1) is different from that along the ephemeral channel downstream of dam. A distance of about 10.0 km downstream of dam is the distance before which the concentrations in the channels are smaller than those in the drainage basins, but after which the concentrations in the channels become larger than those in the drainage basins. The increase in the concentrations is believed to be due to the increase in suspended sediment concentration, as a result of the boundary erosion of the channels by the released flow. This may indicates that the eroded materials from channel boundary represent an important source of pollutions downstream of the dams.

# 5.2 Characteristics of drainage basin

The effect of different characteristics of drainage basin on the transport of nutrients, ions, and metals in the ephemeral channels downstream of dams has been investigated. These characteristics include size, slope, vegetation, and soil surface of drainage basin.

# 5.2.1 Size of drainage basin

Table 4 summarises the results of drainage basin and dam numbers 1 and 6. The drainage basins are of different sizes but have almost the same other characteristics (see Table 1). Regardless of the fact that

Constituent	distance (km) downstream of dam number 2							distance (km) downstream of dam number 4					
		0.50	2.00	5.00	10.00	18.00	CAT 2	0.50	2.00	5.00	10.00	18.00	CAT 4
NUTRIENTS:													
Nitrate Nitrite	NO,/NO,	00.12	00.37	00.68	00.73	00.98	01.31	00.19	00.55	00.83	00.98	01.07	01.36
Ammonia	NH	00.17	00.35	00.59	00.98	01.12	01.03	00.13	00.15	00.26	00.31	00.32	00.25
Total Kieldahl N	TKN	00.24	00.31	00.37	00.43	00.51	00.48	00.39	00.42	00.59	00.63	00.88	00.69
Dissolved Carbon	DC	00.31	00.67	00.74	00.98	01.59	01.47	00.41	00.79	01.33	02.55	04.98	04.32
Total Phosphorus	ТР	00.01	00.07	00.13	00.21	00.26	00.15	00.03	00.09	00.26	00.30	00.39	00.25
IONS:													
Calcium	Ca	03.44	05.67	10.78	13.67	14.29	12.33	08.14	10.10	16.89	21.55	27.02	25.07
Magnesium	Mg	00.23	00.47	00.56	00.89	01.04	00.97	00.31	00.62	00.81	01.31	02.68	02.17
Sodium	Na	00.36	00.39	00.81	00.94	02.05	01.47	00.71	00.88	01.50	02.63	03.46	03.11
Potassium	ĸ	00.08	00.13	00.25	00.27	00.36	00.21	00.15	00.23	00.29	00.53	00.81	00.73
Sulphate	so,	05.14	09.36	10.59	13.67	17.18	15.33	12.70	13.02	17.69	20.55	25.89	21.17
Chloride	cı <sup>*</sup>	00.04	00.17	00.85	01.59	02.44	01.57	00.09	00.78	01.32	02.58	02.91	02.75
METALS:													
Barium	Ba	0.015	0.052	0.069	0.101	0.116	0.093	0.041	0.077	0.110	0.157	0.163	0.141
Cadmium	Cd	0.001	0.008	0.013	0.018	0.021	0.009	0.002	0.008	0.012	0.024	0.027	0.017
Chromium	Сг	0.002	0.003	0.007	0.015	0.017	0.008	0.003	0.008	0.013	0.019	0.023	0.021
Copper	Cu	0.001	0.005	0.007	0.015	0.024	0.017	0.007	0.012	0.019	0.026	0.031	0.029
Lead	Рь	0.005	0.006	0.009	0.015	0.027	0.019	0.009	0.051	0.065	0.091	0.139	0.119
Nickel	Ni	0.003	0.005	0.015	0.023	0.029	0.014	0.009	0.016	0.021	0.029	0.035	0.024
Zinc	Ze	0.010	0.019	0.024	0.029	0.031	0.023	0.021	0.025	0.030	0.039	0.045	0.034
Iron	Fe	0.067	0.155	0.389	1.022	1.925	1.322	0.276	0.731	1.429	2.903	5.447	4.661

Table 5: Effect of slope of drainage basin on sediment quality downstream of dam

the concentrations of all the constituents are almost the same in both the drainage basins, the table shows remarkable variation between the concentrations along the channels downstream of the dams. The larger the size of the drainage basin the higher are the concentrations of the constituents along the channel downstream of the dam. As size of drainage basin increases the amount of transported sediments and, accordingly, the amount of pollutions transferred from the drainage basin to its damsite with flash floods increases.

# 5.2.2 Slope of drainage basin

The increase in drainage basin slope increases the overland flow velocity, resulting in an increase in the drainage basin erosion and in large amounts of transported sediments to damsite. The results reported in Table 5 shows the effect of drainage basin slope on the concentrations of the constituents downstream of dam numbers 2 and 4. It is apparent that the concentrations in the drainage basins and along the channels downstream of the dams increase as the slope of drainage basin increases. It is believed that such variations in the concentrations are due to the amounts of transported sediments which are larger in steeper slopes (e.g. CAT 4) than in relatively mild slopes (e.g. CAT 2).

# 5.2.3 Vegetation

The effect of vegetation on the concentrations of nutrients, ions, and metals in drainage basins and along ephemeral channels downstream of dams is summarised in Table 6. The table compares the results of a bare drainage basin (CAT 5) with those of a drainage basin with pasture vegetation (CAT 4). It can be seen that the concentrations of the nutrients in CAT 4 and along the downstream channel of its dam are higher than those in CAT 5 and along its channel. Different picture can be seen for the concentrations of both ions and metals. They are higher in CAT 5 and its channel than in CAT 4 and its channel. Such behaviour may be explained by the fact that the concentrations of ions and metals are directly proportional with the amounts of transported

Constituent		distance (km) downstream of dam number 5						distance (km) downstream of dam number 4					
		0.50	2.00	5.00	10.00	18.00	CAT 5	0.50	2.00	5.00	10.00	18.00	CAT 4
NUTRIENTS:													
Nitrate Nitrite	NO2/NO	00.07	00.11	00.23	00.43	00.58	00.55	00.19	00.55	00.83	00.98	01.07	01.36
Ammonia	NH	00.09	00.14	00.32	00.58	00.67	00.64	00.13	00.15	00.26	00.31	00.32	00.25
Total Kieldahl N	TKN	00.13	00.19	00.21	00.25	00.25	00.20	00.39	00.42	00.59	00.63	00.88	00.69
Dissolved Carbon	DC	00.11	00.19	00.21	00.25	00.29	00.27	00.41	00.79	01.33	02.55	04.98	04.32
Total Phosphorus	ТР	00.01	00.03	00.08	00.09	00.12	00.07	00.03	00.09	00.26	00.30	00.39	00.25
IONS:													
Calcium	Ca	09.78	12.57	13.54	25.78	35.87	28.93	08.14	10.10	16.89	21.55	27.02	25.07
Magnesium	Mg	00.56	00.96	01.87	03.47	06.18	03.58	00.31	00.62	00.81	01.31	02.68	02.17
Sodium	Na	01.02	01.97	03.78	03.91	04.88	03.92	00.71	00.88	01.50	02.63	03.46	03.11
Potassium	К	00.23	00.36	00.68	00.89	01.05	00.68	00.15	00.23	00.29	00.53	00.81	00.73
Sulphate	SOA	13.49	15.38	21.67	29.90	37.05	30.03	12.70	13.02	17.69	20.55	25.89	21.17
Chloride	<b>CI</b>	00.15	01.13	01.97	03.11	03.97	03.28	00.09	00.78	01.32	02.58	02.91	02.75
METALS:							· ·						
Barium	Ba	0.066	0.121	0.145	0.171	0.203	0.166	0.041	0.077	0.110	0.157	0.163	0.141
Cadmium	Cd	0.007	0.011	0.021	0.027	0.031	0.019	0.002	0.008	0.012	0.024	0.027	0.017
Chromium	Cr	0.009	0.013	0.023	0.034	0.039	0.028	0.003	0.008	0.013	0.019	0.023	0.021
Copper	Cu	0.015	0.023	0.028	0.039	0.051	0.032	0.007	0.012	0.019	0.026	0.031	0.029
Lead	Ръ	0.017	0.073	0.098	0.163	0.177	0.146	0.009	0.051	0.065	0.091	0.139	0.119
Nickel	Ni	0.013	0.023	0.027	0.035	0.041	0.037	0.009	0.016	0.021	0.029	0.035	0.024
Zinc	Ze	0.033	0.035	0.039	0.048	0.061	0.055	0.021	0.025	0.030	0.039	0.045	0.034
Iron	Fe	0.451	1.879	2.779	4.804	6.033	5.795	0.276	0.731	1.429	2.903	5.447	4.661
1													

Table 6: Effect of vegetation of drainage basin on sediment quality downstream of dam

sediments, which are larger in bare land (CAT 5) than in vegetated land (CAT 4), but those of nutrients are directly proportional with density of vegetation, which is higher in CAT 4 than in CAT 5.

# 5.2.4 Soil surface

Since the concentrations of the constituents are in strong relationship with the amount and physical properties of transported sediments, the soil surface of drainage basin may have an effect on the transport of pollutions downstream of dams. To investigate such an effect, samples collected from the channel of dam number 1 and its drainage basin (CAT 1) were compared with those collected from the channel of dam number 3 and its drainage basin (CAT 3), and the results are summarised in Table 7. It is noticeable that the concentrations of the nutrients metals in CAT 3 and along its channel are higher than those in CAT 1 and along its channel. On the other hand, the concentrations of the ions in CAT 1 and along its channel are higher than those in CAT 3 and its channel.

## 5.3 Characteristics of rainstorms

The effects of rainstorms characteristics; namely, rainfall depth "d", rainfall duration "D", and length of dry period between two successive rainstorms "P" (i.e. rainless period) on the concentrations of the constituents downstream of the dams have been investigated. Samples collected from drainage basin numbers 8 and 9 were used to investigate the effect of "d", from drainage basin numbers 10 and 11 to investigate the effect of "D", and from drainage basin numbers 11 and 12 to investigate the effect of "P" on the concentrations. Due to the limited space available in this paper, only the conclusions from the results are drawn. However, the complete set of results would be available during the presentation in the Symposium.

It has been found that the increase in both "d" or "D" results in negligible increase in the concentrations downstream of the dams. However, the increase in "P" results in significant increase in the concentrations of the ions and metals but slight increase in the concentrations of the nutrients downstream of the

Constituent	distance (km) downstream of dam number 1							distance (km) downstream of dam number 3					
L		0.50	2.00	5.00	10.00	18.00	CAT 1	0.50	2.00	5.00	10.00	18.00	CAT 3
NUTRIENTS:		-											
Nitrate Nitrite	NO,/NO,	00.23	00.61	00.95	01.08	01.18	01.42	00.27	00.81	00.93	00.97	01.29	01.62
Ammonia	NHA	00.29	00.41	00.68	00.93	01.15	00.86	00.32	00.63	00.74	01.06	01.27	00.97
Total Kieldahl N	TKN	00.41	00.47	00.69	00.74	00.91	00.71	00.63	00.94	01.05	01.09	01.13	01.12
Dissolved Carbon	DC	00.43	0.89	01.45	02.69	04.88	04.67	00.49	00.97	01.19	03.11	04.58	04.13
Total Phosphorus	ТР	00.04	00.12	00.29	00.32	00.41	00.26	00.08	00.27	00.39	00.51	00.92	00.41
IONS:													
Calcium	Ca	09.14	11.36	18.05	25.06	29.67	28.17	03.45	05.38	10.14	13.45	19.88	18.05
Magnesium	Mg	00.42	00.78	00.93	01.45	03.89	03.55	00.16	00.31	00.55	00.61	00.93	00.67
Sodium	Na	00.86	00.97	01.67	02.55	03.87	03.02	00.29	00.37	00.74	00.91	01.02	00.83
Potassium	к	00.19	00.25	00.33	00.57	00.89	00.85	00.04	00.11	00.21	00.31	00.33	00.29
Sulphate	SOA	13.24	14.89	20.00	23.55	27.58	26.45	07.55	08.41	12.49	14.70	17.28	14.05
Chloride	cı T	00.12	00.92	01.46	02.82	03.05	03.15	00.02	00.41	00.81	00.96	01.15	01.25
METALS:													
Barium	Ba	0.055	0.098	0.120	0.152	0.195	0.192	0.062	0.129	0.141	0.193	0.244	0.237
Cadmium	Cd	0.003	0.010	0.014	0.027	0.029	0.015	0.007	0.018	0.021	0.037	0.041	0.036
Chromium	Cr	0.006	0.009	0.015	0.021	0.027	0.030	0.001	0.012	0.018	0.027	0.039	0.029
Copper	Cu	0.009	0.014	0.021	0.029	0.036	0.021	0.015	0.023	0.037	0.034	0.037	0.032
Lead	РЪ	0.012	0.055	0.076	0.093	0.145	0.149)	0.014	0.074	0.079	0.119	0.195	0.188
Nickel	Ni	0.014	0.019	0.028	0.032	0.039	0.032	0.019	0.028	0.037	0.043	0.055	0.051
Zinc	Ze	0.025	0.028	0.035	0.042	0.047	0.043	0.032	0.041	0.062	0.078	0.091	0.067
Iron	Fe	0.354	0.589	1.559	3.702	5.180	4.055	0.422	0.910	1.905	4.113	5.415	4.152
}													

Table 7: Effect of soil surface of drainage basin on sediment quality downstream of dam

dams. This may be explained by the fact that the increase in P decreases the soil moisture and, accordingly, destructs the cohesion between soil particles, resulting in large amounts of loose materials which can easily transport with flash floods to the damsite. A large percentage of the transported materials is suspended sediments carrying considerable amounts of ions and metals. As found from the results reported earlier, the concentrations of the constituents downstream of the dam are always directly proportional to those delivered to the damsite and channel by flash floods, and increase as the distance downstream of the dam increases.

# **6** Conclusions

The main conclusions that can be drawn from this study are:

(1) The concentrations of the investigated nutrients, ions, and metals downstream of dams in arid areas vary with drainage basin as well as with rainstorm characteristics. (2) The concentrations of nutrients, ions, and metals along the channel downstream of a dam in an arid area increase with the increase in the amount and concentration of transported suspended sediments.

(3) The concentrations of the nutrients, ions, and metals in the channel downstream of a dam in an arid area are directly proportional to those delivered by flash floods to the damsite.

(4) The concentrations of the nutrients, ions, and metals increases, with decreasing rates, as distance downstream of dam increases. These rates become negligible at a certain distance downstream of dam, when a balance between sediments and hydraulic conditions is achieved.

# ACKNOWLEDGEMENT

This work was supported in part by the King Abdul-Aziz City for Science and Technology, Riyadh, Saudi Arabia; Saudi Arabian National Water Research Project Numbers AR - 2 - 17 and AR - 5 - 62.

## **9 LIST OF ABBREVIATIONS**

The following abbreviations are used in this text:

Α	[km <sup>2</sup> ]	- size of drainage basin
Ra	$\left[ \frac{mg}{l} \right]$	- average concentration of barium
C	$\{10^{\circ} \text{ m}^3\}$	- storage capacity of dam
Ca	[] [mo/]]	- average concentration of calcium
Cd	[mg/l]	- average concentration of cadmium
CL	$\left[\frac{mg}{l}\right]$	- average concentration of chloride
C.	[mg/1]	- average concentration of chromium
Ci Ci	[mg/1]	average concentration of conper
Cu D	[mg/1]	average duration of rainfall
	[mm] (ma/l]	- average concentration of dissolved
DC	img/ii	- average concentration of dissolved
-		carbon
DS	[mm]	- depression storage of drainage
		basin
Ða	[hours]	- average duration of hydrograph
d'	[mm]	- average depth of rainfall
Fe	[mg/l]	- average concentration of iron
I	[mm/hr	]- constant rate of infiltration
I,	[mm/hr	]- initial rate of infiltration
Ļ	$[\min^{-1}]$	- decay rate of infiltration
Ķ	[mg/l]	- average concentration of potassium
Mg	[mg/l]	- average concentration of
		magnesium
Na	[mg/l]	- average concentration of sodium
N,		- number of rainstorm events
ם' מ		- Manning coefficient
NO2	[mg/l]	- average concentration of nitrate
NO3	[mg/l]	- average concentration of nitrite
NH4	[mg/l]	- average concentration of ammonia
Ni	[mg/l]	- average concentration of nickel
Р	[days]	- average dry period between two
		successive rainstorm events
Pb	[mg/l]	- average concentration of lead
0	$[m^{3}/s]$	- average peak flowrate of
m	[ , ]	hydrograph
R /		- capacity inflow ratio of reservoir
S <sup>C/1</sup>	[%]	- average slope of drainage basin
SS	[/*]	- surface soils of drainage basin
SO4	[mø/]]	- average concentration of sulphate
t	[hours]	- average time to peak flowrate of
٢p	[nouis]	hydrograph
TKN	[mg/]]	- average concentration of total
1111	["""""]	vieldabl N
тр	[ma /]]	- average concentration of total
	[mg/i]	- average concentration or total
v		phosphorus vegetation of drainage basin
۲ 7-	[m ~ /1]	- vegetation of drainage Dasin
Le	img/il	- average concentration of Zinc

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5th International Symposium on River Sedimentation Karlsruhe 1992

# Modelling of Cohesive Sediments and Its Influence on the Oxygen Conditions

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ABSTRACT: A mathematical modelling system for the simulation of cohesive sediments and its interaction with the water quality is described. The system is comprised of a 1D flow model, a 2D description of erosion and deposition, a 3D description of the advection-dispersion and sedimentation processes, and a multi-layer bed model. The sediment model is coupled with a multi-component oxygen demand algorithm for the simulation of the oxygen conditions. Results of application of the modelling system to a hypertidal estuary are presented.

#### 1 INTRODUCTION

The behaviour of cohesive sediment is a key factor for the water quality in many turbid estuaries. Re-suspension of fine cohesive sediment can give rise to oxygen depletion due to the often large organic content and reduced chemical substances and associated sediment oxygen demand. Cohesive sediment also acts as a carrier for heavy metals and other contaminants. Water quality modelling turbid estuaries therefore in requires an understanding and parameterisation of the behaviour of cohesive sediment.

Mathematical modelling of cohesive sediments has become more widespread in recent years. Many processes have influence on erosion, transport and deposition of cohesive sediments. The key processes include advection, vertical mixing, flocculation, fluid mud development and consolidation. The complexity of the processes involved has forced the modeller to adopt a pragmatic approach, and to only include the most important processes. Application of these mathematical models therefore requires detailed field and laboratory data for calibration and validation.

Cohesive sediments often exhibit a cyclic behaviour during both а tidal cycle and during a neapspring cycle. Mathematical modelling of cohesive sediments therefore involves very long simulations, which will often exclude the use of full three dimensional models due to excess computational time. Depth averaged models are therefore often used, with their obvious shortcoming in describing vertical suspended sediment gradients. This paper describes a mathematical modelling system for simulation of cohesive sediments and its influence on the oxygen content in the water, by describing the essential features in two and three dimensions. The modelling system is based on an existing one-dimensional river model,

which has been further developed to include a two-dimensional description of erosion and deposition, and a three-dimensional description of the transport processes and of the bed sediment. The modelling system is described in the following, along with an application of the model.

#### 2 THE MATHEMATICAL MODEL

#### 2.1 Flow and Transport Model

The basis for the cohesive sediment modelling system is MIKE 11, a one-dimensional general river modelling system, developed jointly by the Danish Hydraulic Institute and the Water Quality Institute. The core of MIKE 11 is a fully dynamic flow model, with add-on modules for water quality and sediment transport modelling. It is described in detail in Ref. /1/ and /7/.

The overall flow pattern, in the form of temporal variations of water level and discharge, is calculated with the one-dimensional hydrodynamic model in MIKE 11. A three dimensional description of the flow is obtained by assuming a specific distribution of the flow within each crosssection. In the vertical direction a logarithmic flow variation is assumed, and in the lateral direction the depth averaged flow is assumed to vary according to a friction law. The following procedure is applied: the cross-section is divided into a number of vertical sections with different depths. The flow velocity in each section is assumed to be proportional to the square root of the depth (Chézy's law). i.e.

$$u = U \left(\frac{H}{R}\right)^{1/2} \tag{1}$$

where

u local depth integrated velocity U cross-sectional mean velocity

- H the local depth
- A cross-sectional area
- R the resistance radius defined by

$$\sqrt{R} = \frac{1}{A} \int_{W} H^{1/2} dy$$
 (2)

The (pseudo) three-dimensional flow pattern is subsequently used in a full three-dimensional advection dispersion model for the suspended solids, where erosion and deposition are accounted for via the bed boundary conditions. The vertical mixing coefficient is assumed to be parabolically distributed, which is consistent with the assumed logarithmic velocity profile.

## 2.2 Sediment Processes

The deposited cohesive sediments at the estuary bed will often be strongly non-uniformly distributed. A full three-dimensional description of the bed is therefore implemented in the modelling system. This multi-layer bed model normally only operates with three layers. Each of these layers are associated with different time scales. The layers are:

- \* weak fluid mud
  \* fluid mud
- \* underconsolidated bed

The weak fluid mud is the sediment depositing around flood slack tide. A part of this sediment is re-suspended during ebb flow, and the rest "consolidating" into the fluid mud layer. The time scale associated with weak fluid mud is therefore one tidal period. Fluid mud is the sediment developing at low tidal energies, i.e. around neap tide, and is re-suspended as the tidal energy increases towards spring tide. The underconsolidated bed layer will increase in periods with small spring tides and decrease in period with large spring tides. The period for this will often be 6 months.

Exchange of sediment from one layer to the next is modelled either as constant rates or as first order processes where the rate depends on the total mass above the interface between the layers. Also lateral exchange of sediment is implemented in the multi-layer bed model. The procedure applied is described in Ref. /8/.

The model distinguishes between two settling regimes. For high concentrations (above 10 kg/m<sup>3</sup>) the settling velocity of the sediment will decrease with the concentration due to the so-called hindered settling effect (Ref. /10/ and /11/). In the hindered settling regime the fall velocity is given by:

$$W = W_o (1-c)^{\gamma} \tag{3}$$

where

- W settling velocity
- W<sub>o</sub> settling velocity of individual flocs
- $\gamma$  coefficient (= 3 to 5)
- c volume concentration

For relatively small concentrations (less than 10 kg/m<sup>3</sup>) the settling velocity will increase with the concentration due to flocculation, i.e. the settling velocity will increase with increasing floc size. In suspension, the particles will collide due to turbulence motion and differential settling. Colliding particles will adhere generating larger particles (or flocs). The frequency of collisions will increase with increaconcentration, and sing hence cause an increased particle aggregation. In the model this is formulated as (Ref. /12/):

$$W = k c^m$$

where

k coefficient
m coefficient (= 1 to 2)

Deposition is modelled two-dimensionally. It takes place when the bed shear stress is less than a threshold value, as given by (Ref. /2/):

(4)

$$D = WC_{b} \left( 1 - \frac{\tau_{b}}{\tau_{cd}} \right) \quad for \ \tau_{b} < \tau_{cd}$$
(5)

Deposition in the model always takes place in the top layer of the multi-layer bed model.

The bed will erode when the bed shear stress exceeds a threshold value for erosion of the layer which is exposed to the flow. Two formulations are implemented: in-stantaneous and gradual erosion. In the first case all the sediment in a layer will entrain instantaneously, when the bed shear stress exceeds the critical shear stress for erosion. This corresponds to an instability type of re-entrainment, and normally applies to weak fluid mud. In the second case the sediment will erode with a rate given by a non-linear function of the excess shear stress, i.e.

$$E = E_o \left(\tau_b - \tau_{ce}\right)^N \qquad for \ \tau_b > \tau_{ce} \quad (6)$$

where

E	erosion rate	
E,	erosion coefficient	
ท้	erosion exponent	
T <sub>ce</sub>	critical bed shear	stress
	for erosion	

Traditionally, the erosion function has been assumed to be linear (Ref. /5/), but both field and laboratory data suggest that the erosion function for soft mud may be strongly non-linear.

2.3 Water Quality

The water quality model is primarily aimed at describing the oxygen conditions. It takes the following processes into account:

- \* reaeration
- decay of BOD
- \* nitrification
- biological respiration
- \* photosynthesis
- benthic sediment oxygen demand (BSOD)
- oxygenation of suspended sediment (SSOD)

In turbid estuaries the two latter processes will normally be dominant, and only these will therefore be discussed in this paper. For a detailed description of the model formulations of the other processes reference is made to Ref. /1/ and /7/.

The use of models for describing the BSOD has been widespread for the last 20 years (Ref. /6/). Such models are generally based on a zero or first order formulation of the oxygen demand, i.e. the BSOD is either a constant or linear function of the oxygen concentration. The following formulation is implemented in the present model:

$$\frac{dC[0_2]}{dt} = \frac{-BSOD(20^{\circ})}{H}$$

$$\cdot \theta^{(T-20)} \cdot \frac{C[0_2]^2}{C[0_2]^2 + K_{0_2}}$$
(7)

coefficient for oxygenation of suspended sediment. Dimensionless.

- T is the water temperature [°C]
- $C[0_{2]}$  is the concentration of dissolved oxygen [g  $0_2/m^3$ ]
- $K_{02}$  is the square of the halfsaturation concentration of dissolved oxygen for benthic sediment oxygen demand [(g 0<sub>2</sub>/m<sup>3</sup>)<sup>2</sup>]

The oxygen demand of the suspended sediment is strongly dependent on the time passed since re-suspension occurred (Ref. /4/). Immediately after re-suspension takes place the SSOD rate is high, but within a relatively short period of time the SSOD rate drops to a lower and approximately constant level. This could be explained by initial release of reduced, easily oxidized substances from the pore water and the sediments (e.g. sulfides and ammonia) when resuspension takes place, and sub-sequent slower chemical oxygenation processes and biological activities in the sediment. SSOD has therefore been assumed proportional to the erosion rate (initial high SSOD) and to the suspended sediment concentration. The formulation implemented in the model is:

$$\frac{dC[0_2]}{dt} = -\left(A \cdot C[SS] + B \cdot \frac{E}{H}\right)$$

$$\cdot \theta^{(T-20)} \cdot \frac{C[0_2]^2}{C[0_2]^2 + K_{0_2}}$$
(8)

where

- A is the steady oxygenation rate of suspended sediment at 20°C [g 0<sub>2</sub>/g SS/d]
  - is the initial oxygen demand of suspended sediment at 20°C [g  $0_2$ /g SS]

where

BSOD(20°C) is the benthic sediment oxygen demand at 20°C [g  $0_2/m^2/d$ ]  $\theta$  is the temperature

В

C[SS] is the concentration of suspended sediment [g SS/m<sup>3</sup>]

#### 3 MODEL APPLICATION

The model has been applied in connection with a feasibility for a tidal barrage across the Usk estuary. A traditional model application programme was adopted for the study, i.e. first the model was calibrated on one set of data and subsequently it was validated on an independent set of data before it was used to predict the post barrage conditions.

The calibration of the model was facilitated by field and laboratory parameterisation of many of the sediment and water quality processes. The parameterisation is described in some detail in Ref. /9/. In the sediment model for instance, only the settling velocity and erosion function were not parameterised directly from observations.

The site conditions and some aspects of the model calibration and validation are described below. Further details are given in Ref. /3/ and /8/.

## 3.1 Site conditions

The river Usk rises in South Wales (UK) and flows into the Bristol Channel at Newport. It drains a catchment area of 1,320 km<sup>2</sup>. Its mean discharge is about 30 m<sup>3</sup>/s and the peak flood discharge (1 in 100 years) is about 1,000 m<sup>3</sup>/s. During droughts the discharge can be as low as 2 - 3 m<sup>3</sup>/s. The tidal influence extends about 25 km from the entrance of the river to Newbridge on Usk, see Fig 1. The estuary is hypertidal, with a mean spring tidal range of 11.9 m. Mean neap range is about 6 m.



Fig. 1 Location of the Usk estuary.

The Usk estuary is turbid. In the upper parts of the estuary the bed is covered by gravel and the banks are muddy. In the lower parts of the estuary the bed is covered by permanent mud deposits. The large spring tides generate high flow velocities, which bring considerable amounts of cohesive sediments into suspension. The turbidity maximum is advected between the upper part of the estuary during high water and the lower estuary at low water. During spring tides, the sediment depositing around flood slack is re-eroded early in the ebb flow. During neap tides the sediment deposited at high water in the upper parts of the estuary is re-eroded late in the ebb flow and transported down to the lower estuary, where it settles out at low water and forms a pool of fluid mud. The fluid mud is generally re-eroded a few days

before spring tide rather than during spring tides. Along with the re-erosion of the fluid mud a significant sag in the oxygen content in the water is observed.

#### 3.2 Model Calibration

The calibration of the model was divided into three phases. First the hydrodynamic model was calibrated aqainst observed water levels for both neap and spring tide events. Thereafter, the sediment transport model was calibrated against data on the vertical distribution of suspended solids and on the formation and re-erosion of fluid mud. Finally the water quality model was calibrated against data from a drought period with critical water quality conditions.

The sediment transport model was first calibrated aqainst time series of vertically suspended solids distributions from both spring and neap tide events. These data were primarily used to calibrate the settling velocity and deposition formulations in the model, as the simulation results were relatively insensitive to the erosion formulation in the model. A sample output of observed and simulated vertical suspended solids distributions are shown in Fig. 2.

Depth (m)



Fig. 2 Simulated and observed suspended solid distributions.

The erosion formulation in the model was calibrated against data on fluid mud formation and erosion. Fluid mud surveys in the estuary indicated a pool of fluid mud of approximately 20,000 tonnes. One day later (November 10, the survey 1989) was repeated showing that only 3,000 tonnes of fluid mud was left in the lower estuary. The river discharge beyond the tidal limit and the tidal variation at the seaward boundary is shown in Fig. 3 and 4, respectively.



River discharge beyond tidal limit.



The result of the model simulation in the form of accumulated fluid mud in the estuary is shown in Fig. 5. The frequent small peaks in this figure represent the deposition and re-erosion of weak fluid mud at each flood slack tide. The massive erosion of fluid mud coincided with a peak in the river discharge of approximately 140 m<sup>3</sup>/s, as shown in Fig. 3. However, one day earlier a flood with approximately the same peak discharge did not cause any massive erosion. A close investigation of the simulation results shows that this peak arrived in the lower estuary, where the fluid mud

Fig. 3

pool is located, at high water thus not giving rise to a significant increase of the flow velocities, whereas the second peak arrives around low water. This emphasizes the need for an accurate hydrodynamic description.



# Fig. 5 Simulated and observed fluid mud.

# 3.3 Model Validation

The model calibration has been validated against independent sets of data. These data included suspended solids and dissolved oxygen concentrations. The result of one of these validation simulations, in the form of calculated dissolved oxygen, is depicted in Fig. 6. The simulation covers an entire spring-neap-spring cycle and demonstrates the models longterm stability, i.e. any influence of initial conditions can be ex-The maximum oxygen sag cluded. coinciding with the erosion of fluid mud shortly after spring tide is reproduced by the model.

#### 4 CONCLUSIONS

A mathematical modelling system for simulation of cohesive sediment and its interaction with the water quality is presented.

The system consists of a one-dimensional hydrodynamic model, а two-dimensional description of erosion and deposition, a full three-dimensional description of the advection-dispersion and sedimentation processes and a multilayer bed model. The sediment model is coupled with a multicomponent oxygen demand algorithm for the simulation of the oxygen conditions.

Application of the model to a hyper tidal estuary shows the models' ability to simulate the temporal and spatial distribution of suspended solids and fluid muds as well as the impact of suspended solids concentration on the oxygen contents in the water.

The model simulations, as well as simultaneous measurements of suspended sediment and dissolved oxygen concentrations, indicated that the sediment plays an important role for the oxygen balance in the estuary. The largest concentrations of sediments is observed in the estuary in connection with erosion of the fluid mud pool, which generally occurs a few days before spring tide. These high sediment concentrations coincide with the lowest oxygen concentrations.

The model runs on a standard PC and offers a viable alternative



to two- and three-dimensional models, when application of such models are not feasible due to excessive computation time.

#### **5 ACKNOWLEDGEMENT**

The field data used in Chapter 3 are part of a comprehensive data set collected in connection with a feasibility study for a barrage across the river Usk in Wales, UK. The study was conducted by Rendel, Palmer & Tritton, Newport, Wales, and the field data collected by Blackdown Consultants Ltd., Wellington, Somerset, UK. Their cooperation and permission to use the data is highly appreciated.

#### 6 LIST OF ABBREVIATIONS

С	[-]	volume concentra- tion	/3/	LARSEN, H
u	[m/s]	depth integrated		
A	[m²]	cross-sectional area		Hypertidal Hydraulic
с	[a/m³]	concentration		modelling
Съ	[g/m <sup>3</sup> ]	near bed concen- tration		aries and H of Bradfor
D	[g/m²/s]	deposition rate		
Е	$[g/m^2/s]$	erosion rate	/4/	MURPHY, P.
H	[m]	water depth		
N	[-]	erosion exponent		In-Situ Met
R	[m]	resistance radius		Sediment O
Т	[C°]	temperature		In K.J. H
U	[m/s]	cross sectional mean velocity		Sediment Ox cesses, Mc
W	[m/s]	settling velocity		surement.
w.	[m/s]	settling velocity of individual flocs		University hens, USA, 322.
$\tau_{\rm h}$	[N/m²]	bed shear stress		
$ au_{cd}$	[N/m <sup>2</sup> ]	critical bed shear stress for deposi-	/5/	PARTHENIAD
		tion		Erosion ar
$\tau_{ce}$	[N/m²]	critical bed shear		Cohesive Se
	•	stress for erosion		Journal of Division, A
θ	[-]	temperature co- efficient for		H41, Proc. ary 1965, j
θ	[-]	temperature co- efficient for oxygenation		H41, ary 1

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