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**Fate, Behaviour and Toxicity
of Organic Chemicals Associated
with Sediments**

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SUMMARY

Sediments constitute an important compartment of aquatic ecosystems. Where a substance, by virtue of its known chemical and toxicological properties and mode of use is likely to be found in sediments at harmful levels, a hazard assessment addressing its fate and effects on benthic organisms should be performed. This should consider particularly the association of the chemical with sediments, the degradation of the chemical in sediments and the toxicity of the substance to benthic organisms

Important methodological elements are discussed which are necessary for the sampling and characterisation of sediments. Various forms of association of chemicals with sediments are reviewed.

Published biodegradation test methods for chemicals in sediments range from simple shake-flask tests with sediment slurries to complex flow-through "ecocore" systems. The purpose of these tests is not to establish the biodegradability of chemicals (for which other tests in water or sludge are more convenient) but to assess their biodegradation in conditions which simulate the environmental sediments. Such tests, currently used for research investigations, would only need to be run for large volume chemicals for which there is concern about their potential persistence and toxicity to benthic life. From a knowledge of the input and of the biodegradation rate, estimates of sediment concentrations may be made.

The principles of assessing the toxicity of chemicals associated with sediments are discussed with reference to the source of exposure (i.e. from sediments or interstitial water). Although there is no internationally agreed method to assess the toxicity of chemicals in sediments, methods to measure the toxicity of contaminated sediments samples from the environment have been described. These methods are usually not routine and have the objective of detecting the toxicity of polluted sediments rather than predicting the toxicity of chemicals to benthic organisms. Many of these

methods are nevertheless directly applicable to the hazard assessment of chemicals and constitute the main references in this report for the recommended acute and chronic toxicity tests with benthic organisms. Acceptable protocols established by the OECD and EPA for sorption studies on soils may be applicable.

When a substance is likely to be sorbed at harmful levels in sediments the toxicity to benthic organisms should be considered. As it is not possible to recommend any single test it is suggested that a tier approach be followed. This will start with an acute test in water followed by chronic tests in a sediment system.

For more investigative studies, it is recommended that experience be gained with the wide range of tests currently described in the literature and still often at the development stage, with the view to deriving a more comprehensive "tier type" strategy appropriate to the chemical under scrutiny.

A. INTRODUCTION

The current approach to determining the hazard of chemicals in aquatic systems is based on relating biological effects to chemical exposure. The impact of the chemical is assessed against representatives of primary producers (algae, e.g. Selenastrum), primary consumers (invertebrates, e.g. Daphnia) and top predators (fish, e.g. Salmo gairdneri). This approach does not take into account the full structure and complexity of the aquatic ecosystem. It is known that sediments can have an important influence on the fate and effects of chemicals. Many chemicals are sorbed* by sediments to give higher concentrations on solids than in the aqueous phase. The benthic community is a vital component of aquatic ecosystems and has a major role in the breakdown of detritus and the flow of energy through the ecosystem. The community is highly structured and adapted and constitutes a food web with many complex interactions.

The European Chemical Industry Ecology and Toxicology Centre (ECETOC) recognised the need to improve understanding of the fate of chemicals in sediments and to assess the potential hazards these might pose. A workshop on this subject (ECETOC, 1987) confirmed its importance to the chemical industry and stressed the need for relevant methods to assess biodegradation and toxicity in benthic situations. Accordingly, an ECETOC Task Force was constituted with the following terms of reference:

- describe and characterise types of sediments,
- recommend predictive methods for describing the degree of association of chemicals with sediments,

** The processes by which chemicals are associated with the solid phase in sediments are often complex and not fully understood. They include truly surface processes (adsorption) as well as other forms of association.*

- make recommendations for assays to assess the degradation of chemicals in sediments under realistic conditions to facilitate the prediction of their persistence and consequent environmental hazards,
- make recommendations for bioassays to measure the availability and toxicity of organic chemicals in sediments, including the test system and the most suitable benthic species.

This report reviews available methods in the areas of:

- characterisation of sediments,
- measurement of sorption-desorption properties of organic chemicals,
- measurement of biodegradability of organic chemicals in sediment systems,
- assessment of bioavailability or toxicity of organic chemicals to benthic organisms.

The report proposes guidelines and criteria to justify the need for testing effects of organic chemicals on sediment ecosystems (benthos). It also makes recommendations concerning the interpretation of benthic test results and the hazard assessment of chemicals which enter sediments as contaminants.

B. BACKGROUND

The scientific literature describes many procedures to evaluate the toxicity of aquatic pollutants to water column (nektonic) organisms. Such tests are important to predict the effect of chemicals in the aquatic environment. In contrast, fewer test procedures using sediment dwelling (benthic) organisms have been described for the predictive environmental safety assessment of chemicals. Benthic organisms constitute an important link in aquatic food chains. For chemicals which could become associated with sediments and which are persistent, there is thus a need to consider toxicity tests with benthic organisms.

Most of the currently described test methods with benthic organisms relate to measuring the degree of pollution of sediments and also to deciding on disposal practices for dredged material (Dickson et al., 1987). The expertise developed in this area is valuable for the design of methods assessing the potential toxicity of candidate chemicals.

The consideration of potential exposure and adverse effects to benthic organisms and the implementation of appropriate testing strategies are necessary elements of a complete environmental safety assessment for chemicals which could enter sediments. Benthic organisms may have a different sensitivity compared to water-column (nektonic) organisms and chemicals sorbed on sediments will have a modified bioavailability (i.e. modified levels and routes of exposure to the biota).

The need to conduct benthic testing for certain materials, in addition to testing with standard water column organisms, derives from three considerations:

1. Concentrations of organic chemicals in sediments can be significantly greater than those in the overlying water.

Chemicals reaching water may partition in favour of the water column or the sediment. In the latter case, the equilibrium concentration in the sediment and the associated interstitial (pore) water will be higher than in the water column. The partitioning between water column, sediment and interstitial water depends on the molecular properties of the chemical and the nature of the sediment.

2. Benthic organisms form an ecologically important community which via their food and habitat may undergo exposure to sediment-sorbed materials.

The organisms of the benthos are taxonomically, physiologically and ecologically very diverse. The various characteristics of benthic species lead to different types of exposure. For example, some organisms occupy the sediment-water interface (e.g. many aquatic insects, larvae), others burrow (e.g. clams and aquatic worms) and some do both (e.g. amphipods). Feeding modes vary amongst benthic fauna, and include filter feeders (e.g. clams), collector-gatherers (e.g. midge larvae), sediment-ingestors (e.g. amphipods, aquatic worms) and omnivores (e.g. crayfish). Thus routes of exposure and the sensitivity of benthic organisms to organic chemicals may differ significantly from those of fish and daphnids.

The activity of benthic organisms is very important for the mixing of the sediments (bioturbation) and for the metabolic processes mediated by sediment microorganisms. The latter are both numerous and diverse within the sediment system.

3. Little is known about routes of exposure and sensitivities of benthic species to organic chemicals.

Extrapolations from tests with "standard" water-column organisms have not been validated. At present benthic bioassays in sediment-water test systems are considered to be the best means to determine the no-effect concentrations of organic chemicals. In this respect, a better understanding of the bioavailability of sediment-sorbed

chemicals is required, that is the relationship between the overall concentration in the sediment and the fraction available to benthic organisms. Bioavailability is also likely to play an important role in biodegradation processes in sediments. The apparent persistence of a chemical may reflect its lack of bioavailability rather than lack of inherent biodegradability.

The design of test systems to determine the toxicity of chemicals to benthic organisms needs, inter alii, to take account of how the test chemical is introduced and equilibrated. It must also address the sediment characteristics, the habitat, the physiology and the feeding modes of the test organisms.

Before deciding on the need for evaluation of the toxicity of a chemical to benthic organisms, it is important to understand the variables which govern its fate. These are principally: volume of use, discharge pathways, physico-chemical characteristics (essentially solubility and sorption) as well as abiotic and biotic degradability. The exposure concentration of the chemical to benthic organisms will be a function of all these parameters. The concentration in sediment will be affected by the input rate to and the disappearance rate from sediment. These rates will be influenced by the sorption-desorption and the biodegradation of the chemical in sediment systems.

For chemicals already present in sediments, concentrations may be directly measured by environmental monitoring.

C. SAMPLING AND CHARACTERISATION OF SEDIMENTS

Sediments are complex mixtures arising from particles of rocks and organic detritus transported by water and deposited on underlying geological substrates. There are wide varieties of sediments differing in their physical and chemical characteristics which have major effects on the fate and bioavailability of chemicals. It is important that the sediment is characterised before their use in a study. Details of the sediment characterisation should be given in each benthic toxicity report.

1. SAMPLING OF SEDIMENTS

The aim of sampling is to obtain material of representative composition for subsequent characterisation and study. Full details of experimental methods for sampling and characterising sediments are given in Appendix 1.

Before sampling, the use to which the sample is to be put should be considered. It is important to ensure that the sample is representative of the location although this may be difficult because of local variations in water velocity which cause differences in the thickness and composition of the sediment layers. In choosing the sample site, local factors such as topography, geological type and biological environment have to be taken into account and documented.

For the more realistic type of tests it is advisable that undisturbed core samples are obtained. Samples should be stored under conditions which minimise biological activity (e.g. low temperature storage or use of preservatives when only chemical analysis is required).

2. PHYSICAL CHARACTERISTICS

Physical characteristics of the sediment, such as porosity and permeability, will affect the movement of dissolved chemicals. The

particle size distribution and the surface area are basic characteristics of the sediment which are related, though not in a simple manner, with sediment hydrology and with sorption/desorption processes.

2.1. Specific Gravity, Porosity and Permeability.

Specific gravity is the weight of a unit volume of sediment expressed in g/cm^3 . Distinction must be made between wet measurements and dry measurements of bulk density (including pore space).

Porosity is the percentage volume of pore space in the total volume of sediment. It is expressed in m^3/m^3 . In a sediment it equates with the volume occupied by the interstitial water.

Permeability is the rate, in m/s , at which water passes through a unit area of sediment core under a constant pressure.

2.2. Particle Size Distribution and Surface Area.

The basic classification used for particle sizes is the Wentworth scale which classifies sediments into a range of 11 sizes. In most cases, only three categories are used: clay, silt and sand, with sand sometimes subdivided into fine and coarse sand. At present, there is no internationally agreed definition for the three main categories.

The following definitions of the sieve sizes in micrometers are representative.

	clay	silt	fine sand	coarse sand
Wentworth	< 3.9	3.9 -62		62-2000
Germany (DIN, 1977)	0-2	2-63		63-2000
France (NF, 1983)	0-2	2-50	50-200	200-2000

The surface area of a sediment is the sum of the surfaces of all particles of the sediment for a given volume in m^2/m^3 or m^2/kg . It is related to the particle size distribution, the finest fractions having

a greater surface area per unit weight (specific surface). For example, 10^6 spherical particles with a radius of 0.1 mm, which could be contained in a volume of 4 cm^3 , have a total surface of 1260 cm^2 . Although the surface area is an important property for adsorption, it is usually not measured in the context of benthic toxicity investigations. Particle size distribution, which is related to the surface area, is the preferred parameter usually measured.

3. CHEMICAL CHARACTERISTICS

Several chemical characteristics of a sediment affect the sorption process. The organic carbon content is the most important parameter for the sorption of neutral organic compounds, whilst the cation exchange capacity is of primary importance for the sorption of cationic substances. The pH determines the degree of ionisation of salts of weak acids or bases and the redox potential the state of oxidation of oxidisable substances.

3.1. Organic Carbon Content (OC).

The organic carbon in sediments originates from the decomposition of plant and animal tissues and newly synthesised bioproducts. An important fraction of this organic material comprises refractory humic substances which are polymers with aliphatic and/or aromatic structures containing acidic functional groups.

Characterisation data usually include the percentage of organic matter (OM) or organic carbon (OC) on a dry weight basis. The percentage of organic carbon in most biological material is approximately 60 %; the organic carbon may thus be simply related to the organic matter content:

$$\text{OC} = 0.6 \times \text{OM}.$$

Typical values for OC contents in sediments are in the range of 4 to 6 % (MacKay and Paterson, 1981), although a wider range (0.1 to 10 %) is reported by Adams (1986).

3.2. Cation Exchange Capacity (CEC).

Since clays and humic compounds are negatively charged, cations are ionically bonded to them. The latter may subsequently be displaced by other mineral or organic cations. Bonding energy depends on the valence and atomic radius of the cation. For example, Ca^{2+} is more strongly bonded than Mg^{2+} , K^+ and Na^+ . Distinction must be made between the actual quantity of metallic cations sorbed on the sediment and the maximum quantity which can be sorbed. The difference is related to the presence of exchangeable protons.

The CEC is particularly important for the adsorption of organic cations (e.g. cationic surfactants) to suspended solids and sediments. This strong adsorption (largely ionic bonding) was described by Weiss (1982).

The CEC (equivalents/kg dry solid) is defined as the maximum quantity of cations which can be retained and released. The CEC is a function of the organic matter content and the content and nature of the clay fraction of the solid phase. Based on literature data (115 samples) a useful correlation has been derived by Brill (1985):

$$\text{CEC} = 0.019 \times \text{OM} + 0.005 \times \% \text{ clay.}$$

3.3. Redox Potential and pH.

The redox potential, Eh, of a sediment is a quantitative measure of the electron availability as determined by the oxidation state of the ions contained within the sediment. For example the $\text{Fe}^{2+}/\text{Fe}^{3+}$ equilibrium will be displaced to Fe^{2+} in an organic rich anaerobic sediment and to Fe^{3+} in an aerobic sediment. The redox potential is positive in

aerobic sediments and becomes negative in anaerobic sediments (typical range +350 mV to - 300 mV).

Oxidants in the sediment (e.g. oxygen and nitrate) are utilised by micro-organisms and the resulting reducing conditions create horizontal layers in the sediment each with characteristic redox potentials. These reducing conditions are mediated by micro-organisms and are dependent on the presence of ready metabolisable carbon. With increasing depths the following layers are found:

- the oxidised, oxygen containing zone (all metals in oxidised form),
- the nitrate reduction zone ($Mn^{4+} \rightarrow Mn^{2+}$; $Cr^{6+} \rightarrow Cr^{3+}$),
- the sulphate reduction zone ($Fe^{3+} \rightarrow Fe^{2+}$; $Cu^{2+} \rightarrow Cu^{1+}$),
- the methane production zone (all metals in reduced state).

The depth of each zone varies with sediment characteristics. In most sediments the oxidised zone is less than 1 cm thick (Bril, 1985) and may be absent when the overlying water has a high organic load.

As the redox potential of a sediment system changes, so does the pH. For example the microbial reduction of sulphate to sulphide produces hydroxyl ions and consequently an increase in pH. Conversely the oxidation of ammonia to nitrate produces hydrogen ions and a decrease in pH. Biodegradation of organic material in the sediment causes the concentration of CO_2 to increase. Therefore, the pH in aerobic sediments is often lower than in the overlying water (Bril, 1985).

Changes in pH and redox potential may have a considerable effect on the fate and distribution of ionisable organic molecules in the sediment. In anoxic sediments, where the pH is higher, acidic substances such as phenolics, will tend to be more water soluble and hence more mobile and bioavailable. For example Gambrell et al. (1983) noted that

pentachlorophenol was more strongly adsorbed under oxidising than reducing conditions. For basic materials such as amines the converse is true.

There are many examples of the effect of sediment pH and redox potential on the biodegradation of organic chemicals (Gambrell et al., 1983; Muir and Yarechewski, 1984).