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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 Bril (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 ($\text{Mn}^{4+} \rightarrow \text{Mn}^{2+}$; $\text{Cr}^{6+} \rightarrow \text{Cr}^{3+}$),
- the sulphate reduction zone ($\text{Fe}^{3+} \rightarrow \text{Fe}^{2+}$; $\text{Cu}^{2+} \rightarrow \text{Cu}^{1+}$),
- 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).

D. FATE OF CHEMICALS IN SEDIMENTS

1. INTRODUCTION

The high level of biological activity in sediments makes them an important compartment of the aquatic environment. Sediments may concentrate certain organic compounds by direct partitioning from the overlying aquatic phase or indirectly by sorption onto suspended matter which subsequently deposits. The constant presence of chemicals in the sediment may suggest that they are persistent. This presence may also reflect a steady state concentration as a result of a balance between continuous input and degradation. The main properties of both compound and sediment that influence the fate of the chemical in the sediment are listed in Table 1. These properties relate to two types of phenomena, namely, the exchange processes between dissolved and sorbed state and the degradation pathways.

2. ASSOCIATION OF CHEMICALS WITH SEDIMENTS

Sorption processes proceed via various intermolecular interactions such as hydrogen bonding, Van der Waals interactions and ion and ligand exchange.

Experimental studies have shown that sorption of chemicals onto sediments can be modelled by a number of classic adsorption isotherms. Kinniburgh (1986) has reviewed the existing models and concludes that the linear model is a satisfactory simplification in many cases:

$$S = K_d \cdot C$$

where: S is the concentration of the chemical in the sediment in ug/g;
K_d is the partition coefficient in ml/g.
C is the concentration of the chemical in the water phase in ug/ml;

The sorption process is greatly influenced by the nature of the chemical and the characteristics of the sediment. In particular, it is necessary to distinguish between non-ionisable and ionisable organic compounds (inorganic chemicals are outside the scope of this report).

2.1. Non-Ionisable Organic Compounds

The organic matter (OM) content of the sediment is most important for non-ionisable organics although several other characteristics have been shown to influence the extent of the sorption process (van Bladel and Moreale, 1982). A linear correlation between the partition coefficient and the organic matter content (% OM) which defines the organic matter partition coefficient has been established (Sherburne and Freed, 1954; Lambert et al., 1985):

$$K_{om} = K_d / OM$$

For comparative reasons, the partition coefficient was then adjusted with respect to organic carbon (OC) and as such an organic carbon partition coefficient is defined :

$$K_{oc} = K_d / OC$$

This coefficient which is now widely used, is approximately linearly related to the organic matter partition coefficient since organic carbon is about 60% of the organic matter (see section 3.1).

$$K_{oc} = K_{om} / 0.6$$

The clay fraction would only play an important role in the case of a sediment with an organic carbon content below 0.1 % (Calvet et al., 1980; Banerjee et al., 1985).

Several attempts have been made to predict sorption by sediments relating the organic carbon (or matter) coefficient with some other physico-chemical properties of the compound. Several molecular

descriptors such as the parachor and free energy substituent constants have been used but are not applicable to a wide range of chemical structures (Lambert, 1967; Sabljic, 1987).

Sorption of neutral non-ionisable organic compounds can be predicted from the n-octanol/water partition coefficient and the organic carbon content of the sediment (Zierath et al., 1980; Schellenberg et al., 1984). Among other published correlations the one by Briggs (1981) which is based on the largest number of chemicals is probably the most accurate :

$$\text{Log } K_{om} = 0.52 \text{ Log } K_{ow} + 0.64 \quad (n=105; r=0.95)$$

For many organic compounds, the octanol-water coefficient is inversely correlated with the aqueous solubility (S_o). It is therefore not surprising that several correlations between this latter property and the organic matter (or carbon) partition coefficient have been reported. For instance, Karickhoff et al. (1979) published the relationship:

$$\text{Log } K_{oc} = - 0.54 \text{ Log } S_o + 0.44 \quad (n=10; r=0.97)$$

(S_o is expressed in mole/litre).

The linear partitioning model discussed above is rather simple. Three observations challenge it.

- First, there are some cases where a Freundlich isotherm with an exponent "n" different from unity, or the relationship proposed by Langmuir (a is a constant), may be more appropriate than a linear isotherm (e.g. Lotse et al., 1968; Hiraizumi et al., 1979; Griffin and Chou, 1981) :

$$S = K_d \cdot C^n \quad \text{or} \quad S = K_d \cdot C / (1 + a \cdot C)$$

- Secondly, the results of several studies show that the sorption coefficient decreases with an increase of the sediment to water volume ratio (O'Connor and Connolly, 1980; Voice et al., 1983; Voice and Weber, 1985). This raises difficulties in extrapolating laboratory determined partition coefficients in well-mixed systems to bottom sediments where the sediment to water ratio is higher.
- Thirdly, sorption is not always a completely reversible process. Partition coefficients determined in sorption studies are different from those determined in desorption studies suggesting hysteresis may occur (Di Toro and Horzempa, 1982; Curl and Keoleian, 1984).

Many investigators have tried to gain understanding of these phenomena (MacKay and Powers, 1987). One explanation could be the presence of a third phase which is not eliminated when separating the solid from the liquid phase. This phase consists of either very fine materials or dissolved macromolecular substances which are able to bind the chemical irreversibly. The presence of this phase increases the concentration of the chemical in the aqueous phase which is expressed as a decrease of partition coefficient (Gschwend and Wu, 1985). The removal of this type of fine non-settling materials is a very difficult experimental problem and the hypothesis proposed by Gschwend and Wu is not universally accepted (MacKay and Powers, 1987; Lande, 1988).

2.2. Ionisable Organic Compounds

The sorption of ionisable organic compounds is, in general, strongly dependent on the pH of the solution. Furthermore, there is a need to consider both ionised and non-ionised forms. The proportion of the acid form can be determined knowing the dissociation constant of the compound. One problem may arise from the fact that the pH at the adsorbent surface is not well known (cf. Chapter C). pH units of 2 - 4 below the pH of the solution have been reported (Carringer et al., 1975).

For ionised organic compounds, anions generally have a small affinity for sediments owing to their negative charge (Carringer et al., 1975), whereas the adsorption of cations is much more important and has been related to the properties of the adsorbent. Although the surface area and inter-molecular reactions of the sediment play some role, the most relevant property is the cation exchange capacity of the sediment (Swanson and Dutt, 1973; Weiss, 1982; Zachara et al., 1986).

The composition of the aqueous phase must also be taken into account as an increase in ionic strength may decrease the amount of sorbed organic chemical. Indeed, an excess of a mineral cation may displace the organic cation from the sediment surface.

No practical quantitative models have been identified to describe the ion exchange of ionised organic molecules in the context of sediment studies.

2.3 Sorption Kinetics

The kinetics of exchange processes for chemicals between water and sediment are not yet fully understood since they are complicated by several interactions. The exchange may be direct between the water body and the bottom sediments, or indirect via sedimentation of suspended matter. The exchange between the water body and the bottom sediments proceeds via at least two steps, namely transport of the chemical through the pore water and the exchange between the sediment particle and its surrounding pore water.

Transport of the chemical through the pore water can simply be a diffusive process or facilitated by the water flow through the sediment. Furthermore, there is the possibility of sediment particle transport via bioturbation (Karickhoff and Morris, 1985). At present, the quantitative aspects of these phenomena have not been extensively investigated.

Equations have been developed to simulate the kinetics of the sorption process. The simplest approach considers the process as instantaneous; this is acceptable if the time required to reach the equilibrium is short compared with the residence time in the receiving environment. The equation is a first-order function of concentration difference between the sorbent and the solution. Unfortunately, this model does not provide a good fit with the experimental data. Sorption kinetic data generally show a very rapid initial uptake followed by a slow approach to equilibrium which may be over several weeks (Shea, 1988). Difficulties are commonly encountered in extracting chemicals from sediments showing that a significant portion of the chemical is often very difficult to desorb and this can be related to the observation of hysteresis in the desorption curve. Variations to the first-order equation have been suggested (Hendricks and Kuratti, 1982).

In a second approach, the sorbent is divided into two compartments, one easily accessible and the other not. This type of model fits the data quite well, but unfortunately, requires knowledge of three independent parameters: an adsorption constant for each compartment and an equilibrium constant between the two compartments (Di Toro and Horzempa, 1982).

A more theoretical approach based on molecular diffusion gives satisfactory results. The intra-particulate diffusibility is the only required parameter; it is a function of chemical and particle properties (Gschwend and Wu, 1985). The mathematical description is complex, especially if the particle size distribution is taken into account.

2.4. Estimation of Sorption/Desorption of Chemicals in Sediments

For non-ionic substances calculated or experimentally determined octanol/water partition coefficients can be used to provide a first estimate of the sorption potential of chemicals in sediments (ECETOC, 1983).

There are two widely used guidelines for the measurement of sorption/desorption of chemicals on soils which can be used for sediments.

The OECD (1981) published Test Guideline N° 106. The experimental procedure measures the decrease in concentration of a chemical substance in aqueous solutions brought in contact with three different soil types at room temperature. The aqueous solvent phase is a 0.01M CaCl_2 solution. This method is applicable to non-ionic and ionic chemicals which are soluble in water to an extent which can be measured analytically. It is not applicable to compounds which are unstable over the time scale of the test (about 16 hours). If there is an sorption equilibrium showing at least 25 % sorption, a two step desorption test is performed.

Similar test procedures have been described by US-EPA (1982) (Pesticide assessment guidelines) and by the EEC (1979) (Notification of new chemicals).

3. DEGRADATION OF CHEMICALS IN SEDIMENTS

3.1. Fundamentals

Since sediments are a location for intensive microbial activity (Bauer and Capone, 1985) biodegradation is considered to be the most important degradation process. Sediments possess the capacity to degrade a wide range of chemical types because of the wide variety and number of microbes present.

Biodegradation should not be considered as the only degradation process, since many abiotic reactions may also occur. Variations in pH, or the presence of oxygen, oxygenated species or radicals, and other reactants generated in situ (e.g. H_2S) may transform molecules and subsequently make them more or less amenable to biodegradation. Phototransformation is only important for shallow sediment systems.

The biodegradation rate of organic compounds (mg/l/day) in sediments will be determined primarily by the numbers of effective organisms and/or by the concentration of the bioavailable compound. Depending upon the oxygen content of the sediment, biodegradation can be aerobic or anaerobic. Generally, aerobic conditions prevail near the surface, while anaerobic conditions prevail in the deeper layers. Bioturbation often plays an important role in the transport of oxygen in the superficial layers of the sediment.

The microbial population of an environment is determined by the characteristics of that environment and the nature and quantity of the various inputs. It is known, that significant physico-chemical and biological changes occur within short horizontal and vertical distances (Mac Farlane et al., 1984). These will have a determining influence on the microbial population present in the different layers of the sediment.

Biodegradation may also be inhibited by higher concentrations of the chemical. The degree of inhibition may be assessed in a manner similar to that used for aquatic and biodegradation soil systems (Reynolds et al., 1987). One can measure the degradation rate of a known degradable substance using radiolabeled material (e.g. sodium ^{14}C -benzoate or ^{14}C -glucose) in the presence and absence of test substance at the appropriate concentration.

There is a paucity of information on biodegradability in anaerobic environments. There are reports on the biodegradation of natural inputs of detrital organic carbon in sediments (Nedwell, 1984) but little is known of the rates, metabolic pathways and microbial populations involved in the anaerobic biodegradation of xenobiotic compounds (Holliger et al., 1988).

From the above it can be concluded that compounds which are readily biodegradable in laboratory tests may persist in the sediment environment because of limiting conditions in that environment (e.g. compounds requiring molecular oxygen for their biodegradation will

persist in anaerobic environments). It follows that persistence is not an inherent property of a substance but is also a function of its environment (i.e. microbiological and physico-chemical properties of the sediment).

3.2. Assessment of Biodegradation in Sediment Systems

In devising methods for assessing the biodegradability of compounds in sediments, the interactions and factors outlined above should be considered. Except for complex in situ experiments, the degree of environmental relevance will be limited. Thus, classical biodegradation tests that include sediment as another dispersed phase will be a poor mimic of the natural environment, but intact ecocore systems with continuous flow will cover all the interactions and develop the gradients representative of natural sediments. The former test will be practically simple such as shake flask experiments in which the sediment is suspended and constant aeration takes place. The test is essentially aerobic and provides data that assesses the maximum potential aerobic degradation for that sediment. The ecocore studies use conditions which are more relevant to the natural environment but are experimentally more difficult. They provide data on the likely degradation rates allowing anaerobic communities to participate in the degradation sequences. The degradation rates also reflect the influence of diffusion processes within the experimental system.

These types of studies are usually limited to specific compounds where a comprehensive research programme can be justified. A prerequisite is the availability of specific analytical methods and/or radiolabeled test substances. When such conditions are met, three types of test may be considered:

- i. a biodegradation test with suspended sediment,
- ii. a static ecocore system or laboratory gradient system,
- iii. a continuous flow ecocore system.

More details about these tests are given in Appendix 2.

4. FATE MODELS

By combining the rate of input of the chemical in the aquatic environment with the sorption and degradation data it is possible, in principle, to model the fate. This will provide data on how long, where and at what concentration a chemical is present. For new chemicals, mathematical models are a useful tool in the estimation of the exposure. For existing chemicals for which specific analytical methods are available, the measurement of environmental concentrations has often proven to be a more simple and accurate approach.

Models dealing with the fate of a chemical in an aquatic environment can be classified using the following criteria:

- number of compartments (water, sediments, suspended solids, biota,...),
- whether or not degradation has been taken into account,
- achievement of thermodynamic equilibrium between the different compartments,
- steady state situation (based on a constant input or none at all),
- subdivision into general or site-specific models.

From these criteria, four types of models with increased complexity were defined by MacKay and Paterson (1981) and MacKay et al. (1983, a, b). This classification, which can be applied to either general models or site-specific models, is illustrated in Appendix 3.

In principle, it is possible from a knowledge of chemical inputs, sorption/desorption and degradation kinetics to predict the concentration of a particular chemical in a sediment. In practice, even if the input

is known with some accuracy, the difficulties in describing the receiving environment make such predictions at best only semi-quantitative.

As site-specific models generally involve a more precise description of the environment, they are more accurate than general models. Indeed, a major difficulty in modelling the fate of chemicals in sediments is the great heterogeneity of this compartment. In the estimation of chemical concentrations using models, it is generally assumed (especially for general models) that the sediment is a single homogeneous compartment of a well defined size. This does not correspond with the observed heterogeneity of environmental sediments.

In specific situations, the interpretation of monitoring data with the help of an adequate exposure model, may give some insight into the disappearance of a chemical due to biodegradation in sediments.

5. CONCLUSIONS

The fate of a chemical in a sediment is a function of its sorption properties and persistence. Although the mechanisms of sorption for different types of chemicals are not fully elucidated, satisfactory sorption/desorption test protocols are commonly used.

Biodegradability test protocols using sediments (including anaerobic sediments) are described in the literature; they are not generally used and have not reached a level of international standardisation. A valuable screening test (aqueous only) to anticipate biodegradability in anaerobic sediments is described by ECETOC (1988) and by Birch et al. (1989). Sediment biodegradation tests and fate models are recommended areas for further research.

For new chemicals, estimations of concentrations in sediments can be made semi-quantitatively with fate models currently described in the literature. Only site-specific models have any degree of precision. The resulting estimates of exposure concentrations are necessary for the justification of further benthic toxicity testing.

For existing chemicals, it is suggested that, when justified by possible ecotoxicological hazard, the levels of chemicals in sediments to which organisms may be exposed should be directly assessed by analytical measurements. Sediment samples should be taken from locations where xenobiotic chemicals are known to be discharged.

E. BIOAVAILABILITY AND TOXICITY OF CHEMICALS IN SEDIMENTS

1. INTRODUCTION

This chapter is concerned with the bioavailability and toxicity of sorbed chemicals to aquatic organisms. Of major interest is whether or not the availability of chemicals to these organisms (particularly benthic) is modified by the presence of sediments. Bioavailability relates to the degree and route of chemical exposure to the aquatic organism. The toxic effects induced by a chemical in organisms depend on its inherent toxicity and effective exposure concentration, i.e. the fraction of the concentration that is bioavailable.

When a chemical is strongly sorbed to sediments, free swimming organisms may be exposed to lower concentrations than benthic organisms which may have their food and habitat contaminated with higher concentrations. For benthic organisms in particular, the transfer of a chemical may follow different routes e.g. via the interstitial water, via direct uptake of the sediment and desorption in the digestive tract, and via uptake of sediment and its digestive destruction. For chemicals likely to be present in sediments, it may be appropriate to include toxicity tests with benthic species in the hazard assessment programme.

Bioaccumulation of chemicals by aquatic organisms is determined by rates of uptake, depuration and metabolism. Relevant factors include the lipid content of the organism and lipophilicity of the chemical. For chemicals with log Kow (Kow octanol/water partition coefficient) between 3 and 6, the bioconcentration factor (BCF) is often directly proportional to log Kow and may therefore be predicted from specific empirically derived equations (Veith et al., 1980; MacKay, 1982; Isnard and Lambert, 1988). When using such relationships to predict BCFs for benthic organisms, it may be necessary to include sediment/water partition coefficients so that BCFs may be related to sediment concentrations (ECETOC, 1983; Bruggeman

et al., 1985). Chemicals which are most likely to bioaccumulate are also those which show the highest sorption to sediments.

The test assays discussed below relate primarily to the testing of specific chemicals in laboratory sediment systems rather than to the field testing of contaminated sediments sampled in polluted environments. In principle three approaches may be taken to design methods to address the biological effects of chemicals associated with sediments.

The first approach is to assume that the chemical can only cause an effect in the non-sorbed state and that toxic effects which are observed are due to the equilibrium concentration of the chemical in the interstitial water (Ziegenfuss et al., 1986). The bioassay procedure can then be reduced to a determination of toxicity in that single phase, i.e. water containing the chemical at a concentration assumed to be that in interstitial water. The results are interpreted in terms of sediment concentration either by testing the actual aqueous phase from a sediment which has been dosed with a known level of the chemical, or by calculation using an experimentally determined sediment/water partition coefficient. In such bioassays the particular species tested may be nektonic or benthic.

The second approach is to assume that the chemical may exert a toxic effect in both the sorbed and non-sorbed state. Dietary uptake of sediment particles may result in additional exposure to chemicals with high Kow (10^5 - 10^7). In this case, the bioassay procedure necessarily involves an experiment with a two-phase system of sediment and interstitial water. Either uncontaminated natural sediments or artificial defined sediments dosed in the laboratory with the chemical under investigation are assessed by an appropriate bioassay procedure in which the test animal lives in or on and ingests the sediment.

The third and most complex approach is environmental monitoring of sediments which are known to be contaminated with specific chemicals. For an existing chemical, this approach could provide the most convincing evidence that at a particular level it does not affect the ability of

that sediment to support the expected animal population. The approach is complicated because there may be many reasons why a contaminated sediment does not host the expected animal community. It may also be difficult to obtain a suitable sediment containing a significant quantity of the chemical under consideration. For these reasons, environmental monitoring cannot be regarded as a generally applicable approach for assessing the bioavailability and effects of chemicals in sediments on benthic organisms. This approach will not receive further consideration in this report.

2. IMPORTANT TEST PARAMETERS

The first two approaches described above may be used either in tests designed to assess the toxicity of chemicals in the presence of uncontaminated sediments or to assess the hazard of contaminated samples collected from the field.

As indicated above, the bioassays may be classified into single-phase (water only) or two-phase (water and sediment) systems. A further classification into freshwater and marine/estuarine systems may also be made. Apart from these rather broad classifications, a number of experimental variables need definition as part of any useful bioassay method.

2.1. Sediment

The characterisation of sediments and the factors which influence the association of chemicals with sediments are considered in detail in chapters C and D. It is evident from these chapters that for lipophilic chemicals, the organic carbon content of the sediment plays a major role in the partitioning behaviour, whereas for ionic materials it is the mineral type/ion exchange capacity of the sediment which is dominant.

Although artificial sediments have been described (e.g. Lee, 1986) on balance it seems preferable to use a natural sediment, possibly after

some degree of treatment before use (e.g. removal of fauna). Since natural sediments are variable in composition, no precise specification can be made but the sediment should be characterised (particle size range, % sand, silt and clay, organic carbon content, water content and cation exchange capacity). Where a number of sediments is used to assess chemical effects on organisms it may be appropriate to correct, for example, for varying organic carbon content. A standard sediment with 5% OC has been used as a reference for this purpose in the Netherlands (Van de Guchte and Maas-Diepeveen, 1987).

It is preferable to use freshly collected sediments rather than sediments which have been stored for long periods. Both freezing and drying alter the micro-biological and sorption capacity of sediments.

2.2. Water

The water to be used may be either a natural or reconstituted water, fresh or marine. In the use of natural waters, their source and any treatment (e.g. filtration or elutriation of pore water) should be indicated along with parameters such as hardness, salinity, pH, dissolved oxygen, temperature etc. For reconstituted water the make-up of the water should also be described.

2.3. Test System

As discussed above, two distinct test types may be adopted, namely, testing in the aqueous phase only or testing using the two phased sediment/water system.

- 2.3.1 Aqueous phase test. There are two approaches which may be taken to testing in the aqueous phase. One approach is to prepare a dosed sediment, to equilibrate this with water (typical volume ratios range from 1:1 to 1:4 sediment:water) and to separate off that water for the test using either a static procedure (e.g. sedimentation, pressure filtration or centrifugation) or a flow-through system by

percolating the water through a sediment bed. The use of a range of sediment organic carbon contents achieved, for example, by adding appropriate organic solids (e.g. activated sludge solids) to a natural sediment, will provide a basis for assessing the correlation between organic carbon content and the bioavailability of the non-ionised chemical (Lee, 1986).

Chemical analysis after physical separation of water and sediment will not necessarily provide a measure of the bioavailable fraction as colloidal and complexed forms present in the water may not be available to the organism. This will result in a maximum estimate of bioavailability. Changes in sediment redox potential, for example, may result in a greater degree of ionic chemicals scavenging by metal complexes. The physical agitation of the sediments during the mixing procedure may reduce the bioavailability of the chemical as a result of increased contact between the test chemical and organic matter from deeper fractions of the sediment. There is thus a need for a careful selection of the method to separate pore water from the sediments (Lee and Jones, 1987).

The other approach is to measure the partition coefficient of the test substance between the sediment solids and water (preferably over a range of dose levels in the sediment) and then in a completely separate experiment to determine the toxicity of the test substance in water. The results from the toxicity experiment may then be related to a sediment concentration using the sediment partition coefficient. There are several studies which indicate that for neutral hydrophobic chemicals ($\log P_{ow} = 3.5 - 7$) the exposure concentration or bioavailability to aquatic organisms can be predicted from equilibrium partition coefficients, total chemical concentration in the sediment and the organic carbon content of the sediment. Toxicity responses obtained with chemicals added directly to water may however not be comparable with toxicity responses of equal concentrations in test liquors released by predosed sediments. Complexation phenomena with sediment components and selective adsorption/desorption of certain fractions of technical products

affecting bioavailability, can usually explain the observed discrepancies (Anderson et al., 1987, Lee and Jones, 1987).

The choice of test species for aqueous phase bioassays is not critical particularly if, as a first approximation, the assumption is made that the sensitivity for nektonic organisms is likely to be similar or slightly higher to that for the benthic fauna (Marshall, 1988). On this basis, for freshwater situations organisms such as fish or Daphnia may be selected and for marine situations fish or mysid shrimps. Such water column organisms are useful in the preliminary evaluation of chemical toxicity, i.e. before selection of specific water/sediment tests. The use of a benthic organism in a preliminary aqueous phase test might be preferable as a screening test before the water/sediment test which would follow with the same benthic species. Such procedures are well documented in standard methods (e.g. OECD, 1981) and will not be discussed further. If benthic organisms are required, then one of the species suitable for the water/sediment tests (see below) may be selected.

- 2.3.2 Two phase water/sediment tests. Procedures for assessing the effects of chemicals associated with sediments are less well standardised than those for aqueous phase tests. For these studies experimental procedures and choice of suitable test organisms are far less well developed than for tests in a solely aqueous phase. The species are selected on the basis of their relative sensitivity to sediment contaminants, their position in the food chain (detritivore, food organism), the anatomic structure and physiology of the animals, their contact with the sediment (e.g. burrowing, filtering, feeding behaviour) and their amenability to laboratory rearing.

For marine acute tests, the use of Phoxocephalid amphipods or Ampeliscid amphipods have been described. Oligochaete worms and bivalve molluscs have been recommended for chronic tests (behaviour, reproduction etc) (Anderson et al., 1987).

For freshwater tests, there is less distinction between species selected for use in acute or chronic tests. Several chironomid species have been used to assess both acute and chronic effects of contaminated sediments (Lee et al., 1980; Lee, 1986).

Some of the organisms used to determine the effects of chemicals sorbed by sediments are listed in Table 2. At present, no single test species is specifically recommended for the reasons defined above and more experience is required with a range of tests currently at the developmental stage.

In acute tests, food is not supplied, but in chronic tests, a suitable supply is essential. If the supply does not come from the sediment organic matter then a problem arises in that additional carbon and sorption sites are added to the system and this may influence the distribution of the chemicals. Food additions must therefore be carefully controlled and taken into account in the interpretation of results.

Long term (chronic) water/sediment tests may include the effects of bioturbation. This process may directly affect the species causing the mixing and also indirectly affect epibenthic or nektonic species, if present, as a result of increased release or complexation of the chemical (Malueg et al., 1984).

3. PROCEDURES FOR TOXICITY TESTING IN SEDIMENTS

3.1. Method of Introducing the Test Chemical

For water soluble chemicals, there is relatively little problem in preparing a homogenous mixture of the chemical with the sediment as it can be introduced using a small volume of aqueous medium. For substances of low water solubility there may be considerably greater problems. One approach is to dissolve the test substance in a volatile organic solvent and to mix this with a portion of the air dried sediment in a rotary evaporator flask. The organic solvent can then be

removed by evaporation and the dosed sediment portion mixed into the total sediment sample required for the test.

An alternative method is based on a combination of two procedures described in two publications by Opperhuizen et al. (1988) and Schrap and Opperhuizen (1989). An adsorbent (Chromosorb) is saturated with the test substance dissolved in an organic solvent. The solvent is removed by evaporation. Then water is circulated over the adsorbent and over or through the sediment. In this way the sediment is homogeneously loaded with the test substance stripped from the adsorbent.

Whatever the procedure used, the method should be clearly documented. If possible, aliquots of the dosed sediment should be analysed to confirm uniform dispersion and the mean level of the substance. The time required for the establishment of a long term equilibrium should be considered. This can take more than one month (Shea, 1988). Dosing of sediments may not achieve equilibrium. Thus, the incubation period after dosing should be described in the report.

It must also be realised that it is not feasible to maintain constant exposure levels in these assays with readily biodegradable test substances. This limits the value of these tests to persistent chemicals.

3.2. Test Systems

In both marine and freshwater systems, there are a variety of methods for assessing the toxicity of contaminated sediments or single chemicals in more defined sediments (i.e. spiked sediment bioassays). For both contaminated sediments and single chemicals, test methods differ mostly in the source and preparation of sediments. Many of the biological procedures and response criteria are applicable to both cases, especially where laboratory tests are concerned.

Methods for assessing the toxicity of contaminated sediments usually involve collection of sediments with site water using appropriate dredges or core samplers. The sediment may be sieved to remove large particles and, if not used immediately, stored (cf Appendix 1). If aerobic conditions prevail at the site, the overlying water is aerated; if the overlying water is anaerobic, it may be sparged with nitrogen. Control sediments are either obtained from a nominally clean site where the test organism of choice is found, or substitute sediments are used, for example acid washed sand or sand plus kaolin (Lee et al., 1980).

A less frequently used method is to transport the test organisms to the contaminated sediment and expose them in situ in an appropriate container (Nebeker et al., 1984). This avoids having to disturb the sediment which is difficult to achieve when sampling sediments for use in the laboratory. Whilst a negative response (no effect) indicates that the sediment was not toxic, a positive response may be the result of the toxic sediment or some other stress not necessarily related to the sediment. For this reason such test requires a parallel in situ test with a control sediment. When no adverse effects are observed in the control animals, a positive response in the animals exposed to the contaminated sediment can be assumed to be caused by that sediment.

Methods for assessing the toxicity of single chemicals in defined systems are more applicable to the hazard assessment of new chemicals. Sediments may be collected from uncontaminated sites, particularly sites where the organism of choice is found. After careful characterisation, these sediments may be amended with clay, sand or additional organic carbon. In other methods, the sediment can be constructed from clean laboratory grade materials to mimic the natural sediment. This allows a variety of conditions to be created by varying the organic carbon content, for example, and ensures that the test chemical is the source of any toxic effects. Such procedures require validation to ensure that the test species survives, grows and develops normally through its various life stages in the artificial or amended

sediment. The dilution water is usually also well defined and may be aerated carbon filtered tap water or an artificial medium.

3.3. Exposure and biological responses.

The exposure procedures and biological response criteria range from short term acute tests to long term chronic studies such as the re-colonisation of contaminated sediments. Some of these procedures are described below.

- Acute toxicity tests could be performed using one of the test species listed in Table 2 with methods usually based on those of Prater and Anderson (1977-b), Nebeker et al. (1984) and LeBlanc and Suprenant (1985). Benthic organisms are usually exposed for 10 days and then an assessment of survival is made, but shorter periods are used with nektonic species such as Daphnia (48 hours).
- There are relatively few laboratory methods which allow full life cycle test to be conducted. Many chronic tests omit the mating and egg laying phase. Egg hatching, larval survival, growth and development and maturation or adult emergence are more commonly assessed. Examples of such methods are described by Wentzel et al. (1978), Nebeker et al. (1984), Lee et al. (1980), LeBlanc and Suprenant (1985), Chapman and Fink (1984), Swartz et al. (1985), Nimmo et al. (1982), Hagris et al. (1984), Larsson and Thuren (1987), Birge et al. (1987), Van de Guchte and Maas-Diepeveen (1987) and van Urk and Kerkum (1987). These examples include embryo larval bioassays with fish and amphibians; these are included because the early life stages develop in close contact with the sediment.
- Bioaccumulation studies are usually specifically designed to measure accumulated body burdens. In the same studies chronic toxicity responses may also be usefully monitored (Prater and Anderson, 1977 a,b; Karickhoff et al., 1979; Oliver, 1984; Adams et al., 1985).

- Behavioural responses usually relate to sediment avoidance or the effects on burrowing (Wentzel et al., 1977; Mohlenberg and Kiorboe, 1983; Olla and Bedja, 1983; Keilty et al., 1988).
- Effects on community structure or function are used more often in studies on contaminated sediments than in tests with single chemicals which are added to "clean" sediments. These studies are long term and may be difficult to interpret if seasonal variation is included (Matthiessen and Thain, 1988; Rosemarin, 1988).

4. INTERPRETATION OF RESULTS

From the nominal concentration of a chemical added to a sediment it is possible to calculate the distribution of the chemical between the sediment and the overlying water using the calculated or experimentally determined partition coefficient K_d (cf Chapter D). It is therefore possible, in principle, to relate the toxicity observed in a test to either the concentration of the substance in the sediment or in the water phase. If the toxic threshold corresponds to a water concentration which is similar to the toxic threshold found in a water only system, this indicates that the substance, in its sorbed state, does not significantly contribute to the toxicity and is therefore not bioavailable (cf Chapter D). For inherently toxic chemicals, if the added concentration is very high, and no toxic effects on benthic organisms are observed, this indicates that the material is highly sorbed and not toxic in the sorbed state.

F. HAZARD ASSESSMENT OF CHEMICALS IN SEDIMENTS

1. CRITERIA TO DETERMINE THE NEED FOR BENTHIC TESTING OF NEW CHEMICALS

Benthic toxicity testing is not always relevant or necessary for all chemicals and should be considered only for those which :

- have the potential for significant accumulation in sediments, because of their discharge pattern, volume, sorption/desorption properties and persistence, and
- are at least moderately toxic to water column organisms.

The need and the extent of benthic testing must thus be decided on a chemical-specific basis depending on a preliminary toxicity and exposure assessment.

1.1. Potential to accumulate

Materials which readily sorb to sediments can usually be identified on the basis of the following observations.

- Molecular structure. Structural resemblance of a new compound to existing compounds known to be readily sorbed.
- Intended usage. Chemicals intended to adhere to solid substrates will often sorb well to sediments.
- Water-Octanol Partition Coefficient. The sediment-water partition coefficient corrected for sediment organic carbon content, K_{oc} , can be predicted from the chemical water solubility or from the octanol-water partition coefficient, K_{ow} , or can be determined directly (cf. Appendix 1 and chapter D). When $\log K_{ow}$ is greater than 3, there is

a high probability that the chemical will also have a high adsorptivity to sediments.

- Removal-biodegradation tests results. The fact that a material with low biodegradability shows immediate and substantial removal in treatability tests such as the SCAS (Semi continuous activated sludge) or CAS (Continuous activated sludge) tests without a significant adaptation period is an indication of high adsorptivity to sediments.

1.2. Potential Toxicity

Readily sorbed compounds with at least moderate toxicity to standard test organisms should be considered as having the potential to affect benthic organisms. Data with standard water column (nektonic) organisms should therefore be reviewed in determining the need for benthic testing on sorbed materials. To date, comparisons between standard nektonic test organisms and benthic species indicate that the nektonic organisms are at least as sensitive as the benthic organisms (Marshall, 1988). Nevertheless, sorbed organic chemicals with moderate to high toxicity values (e.g. LC50 values of less than 10 mg/l) have the greatest potential to cause an adverse impact on the benthic community, particularly if they are not rapidly biodegraded.

In summary, if the chemical is significantly sorbed, relatively toxic, poorly biodegradable and significant quantities of the substance are likely to be released with a pattern of discharge which would lead to accumulation in sediments, benthic testing should be considered. Following some period of usage, periodic monitoring of environmental concentrations in sediments and overlying water could be conducted to confirm concentrations or otherwise exposure estimates of the chemical.

2. A TIERED APPROACH TO BENTHIC TOXICITY TESTING

As indicated above, only selected chemicals should be considered for benthic testing and Chapter D outlines some of the considerations in

regard to test design. As with test schemes for assessing the toxicity of dissolved chemicals to nektonic organisms, a tiered approach is recommended for benthic toxicity testing. The outline of such a tier approach is as follows:

Tier 1 : Acute Test in Water.

This preliminary test is carried out with a representative benthic species such as Chironomus, amphipods or oligochaetes (see Table 2). In view of the chronic test (cf. tier 3) chironomids are preferred. The first objective of this test is to confirm that the sensitivity of benthic species is not significantly different from that of nektonic organisms such as Daphnia or fish. The second objective is to compare the toxicity determined in this test with that found in the proposed tier 2 test to decide whether the sorbed test substance is bioavailable (cf. Chapter E).

Tier 2 : Acute Sediment Exposure.

In this Tier the species used in Tier 1 is exposed to sediment amended with the test substance, and the concentrations which produce toxic effects are determined. The results of this Tier 2 test are used both as an indicator of the bioavailability of the sorbed substance but primarily to compare with the measured or predicted concentration of the substance in environmental sediments. Three conclusions are possible:

- the predicted environmental concentration of the substance appears to be at or above the acute toxicity level in sediments. Such a conclusion would obviously be of concern and, if validated, would require further investigation and/or appropriate action;
- the predicted environmental level is considerably lower (e.g. over two orders of magnitude) than the effect level: in this case, no further testing would be required;

- the predicted environmental level is slightly to moderately lower than the effect level (e.g. within two orders of magnitude) and the substance is expected to persist at relevant concentrations. In such a case Tier 3 testing should be considered.

Tier 3 : Chronic Study in Sediment.

The purpose of this study is to define acceptable levels of the test substance in the sediment. A lowest observed effect concentration (LOEC) can be determined. As indicated in chapter E, there have been relatively few benthic chronic studies described. On present knowledge the Chironomid study in which the emergence of winged adults is assessed seems to be the most appropriate test method (Lee et al., 1980; Lee, 1986).

3. EXPOSURE ASSESSMENT

For readily sorbed materials with moderate to high toxicity, consideration of the anticipated level of exposure in sediments is required. Ideally, an exposure assessment for benthic communities would contain estimates of concentrations on sediment solids and in interstitial waters.

Unfortunately, current knowledge will not allow highly accurate prediction of chemical concentrations in these compartments. Furthermore, even when the concentration of a chemical in a sediment is measured, its bioavailability to benthic organisms will not be known and depends on:

- the physico-chemical properties of the chemical,
- the characteristics of the water and of the sediments,
- the ecological attributes of the target organism.

Nevertheless, simplified approaches for estimation of concentrations of chemicals in sediments can be used to justify the need for benthic toxicity tests or to interpret their results. These estimations are as approximate as the estimation of the concentrations of chemicals in the water column of surface water systems. Discharge patterns must be reasonably well documented to make these estimates feasible and credible.

Taking the example of a point discharge, where the concentration of the chemical in the effluent is known, one simple approach is to calculate the sediment concentration (C_s) as

$$C_s = C_e \times K_d$$

where C_e is the effluent concentration of the chemical and K_d the partition coefficient between water and sediment solids. However, sediment concentrations are typically overestimated by this technique, due to the particle concentration effect. Specifically, as the concentration of the particles increases (e.g. as suspended solids settle to the substrate), the concentration of a material sorbed to the particles seems to decrease. More complete models are referred to in Appendix 3.

Site specific monitoring involving chemical analysis remains the safest and most reliable approach for estimating the concentration of existing chemicals in sediments.

4. INTERPRETATION OF BENTHIC TEST DATA - HAZARD ASSESSMENT

How do water column, interstitial water and sediment concentrations compare to each other? In some cases, the route of exposure can be predicted from this information.

The interpretation of data from a benthic toxicity testing programme requires incorporation of all available data to allow a decision to be made concerning the overall safety and acceptability of the test material.

Specifically, the benthic test programme will provide data to answer the following questions :

- will benthic species be exposed to higher levels of a material than nektonic species (fish, daphnids)?
- how do benthic species' sensitivities compare with nektonic ones?
- what levels of the material in the sediment cause effects on the test organisms? This would indicate the extent to the material is bioavailable and toxic.
- how do the LC50, NOEC (No Observable Effect Concentration) and LOEC (Lowest Observable Effect Concentration) values compare with predicted or measured concentrations of the material in the environment (PEC)?

On the basis of the benthic toxicity test values obtained and the predicted or measured sediment concentrations of the chemical, its safety factor to benthic populations can be assessed as the ratio EC50:PEC for acute effects or NOEC:PEC for chronic effects.

The more realistic these values are (test conditions close to environmental conditions and chemical monitoring data preferred to calculated PEC), the greater the confidence in the safety factor derived from such risk assessments.

G. CONCLUSIONS

Where the chemical and toxicological properties of a substance and its mode of use make it likely to be found in sediments at harmful levels, a hazard assessment addressing fate in sediments and effects on benthic organisms should be performed.

The hazard assessment should cover:

- the association of the chemical with sediments;
- the degradation of the chemical in sediments;
- the toxicity of the substance to benthic organisms.

In performing such an evaluation, it is important to note :

- that predictive methods should be further developed to measure the association of organic chemicals with sediments, particularly as this applies to ionisable organic substances. The OECD Test Guideline 106 for the measure of adsorption to soil, should be adapted for sediments accordingly.
- that the biodegradation of a substance in sediments should generally be predicted from aerobic or anaerobic test studies, run at an earlier stage and with simpler test matrices than sediments. It is recommended that sediment biodegradation tests, for which ^{14}C labelled materials are normally required, should be reserved for investigative studies aiming at the determination of the rates of these processes.
- that a preliminary estimate of the toxicity of a chemical to benthic organisms should be obtained from the toxicity response to water column (nektonic) organisms (e.g. fish, daphnids). In these tests, bioavailability is usually higher than in tests with sediments and as a first approximation, it is reasonable to consider that water column organisms are at least as sensitive as benthic organisms.

- that toxicity (bioavailability) testing to benthic organisms should only be considered for those substances which are likely to be sorbed at harmful levels on sediments. When these tests are needed, it is not possible to recommend any single test. Among the variety of procedures and organisms described in the literature, a choice must be made on a case by case basis, according to the objective of the study. It is recommended that experience be gained with a range of tests currently described and still often in the development stage, with a view to derive a "tier type" strategy appropriate to the chemical under scrutiny.

A tier approach based on existing methods has been proposed. Further progress on methodology can lead to a further development of the tier approach concept.

For the risk assessment of a chemical to benthic ecosystems a quantitative estimate of the level of the chemical in sediments is needed. Predictive methods and model approaches are available, but the complexity of sediments is such that the results achieved by these methods are semi-quantitative at best. Only in special cases, usually in very site specific situations, can these methods generate more accurate exposure concentrations.

For existing chemicals, analytical monitoring data often gives a better quantitative estimate of exposure levels in sediments than those predicted from exposure models. Analytical data on the level of organic chemicals in sediments should continue to be collected. The selection of substances for which data are required, should be based on a careful consideration of the likelihood that these materials will reach levels which would cause concern for benthic organisms. This requires a review of their production levels, pathways to the aquatic environments, sorption behaviour, potential to persist and inherent toxicity.

TABLE 1

FACTORS DETERMINING THE FATE OF AN ORGANIC COMPOUND IN A SEDIMENT

<u>NATURE OF PROPERTY</u>		<u>PROCESS OR PROPERTY AFFECTED</u>
<u>Compound</u>		
Physical nature	Solid (crystalline/amorphous), liquid or gaseous.	Availability and transport.
Chemical nature	Molecular structure, Chemical reactivity.	Acid/base hydrolysis, Biodegradability, Photoreactivity.
Physico-chemical properties	Density, Solubility, Volatility, Partition coefficient (n-octanol/water), Dissociation constant, Redox potential.	Sorption/ desorption, Distribution/ transport.
<u>Sediment</u>		
Chemical nature	Inorganic matrix, Organic content, Ion exchange capacity.	Sorption/ desorption.
Physical nature	Particle size, Permeability, Porosity, Specific gravity.	Sorption/ desorption, Transport.

Physico-chemical properties	Temperature, pH, Redox potential, Salinity.	Chemical stability, Aerobic/anaerobic activity, Macro-biological activity.
Biological status	Flora and fauna, Microbiology, Metabolic potential.	Mixing/bioturbation, Population growth.
Water-sediment	Nutrient inputs, Organic content, Sedimentation rate, Leaching rates, Continuous water flow, Water currents, Static water column, Water exchange/transport.	Biological activity. Sediment transport.

TABLE 2

EXAMPLES OF ORGANISMS USED TO DETERMINE THE EFFECTS OF
MATERIALS ADSORBED ON SEDIMENTS

<u>Group</u>	<u>Species</u>	<u>Effect</u>	<u>Reference</u>
<u>Freshwater taxa</u>			
Amphibia	<u>Rana Arvalis</u>	h/bi*	Larsson and Thuren, 1987
Fish	<u>Pimephales promelas</u>	l	Prater and Anderson, 1977-b
	<u>Salmo gairdneri</u>	e	Birge et al., 1987
	<u>Brachydanio rerio</u>	e	Van de Guchte and Maas-Diepeveen, 1987
Ephemeroptera	<u>Hexagenia limbata</u>	l	Nebeker et al., 1984 Prater and Anderson, 1977-b Malueg et al., 1983
Chironomid	<u>Chironomus riparius</u>	lc/d	Lee et al., 1980 van Urk and Kerkum, 1987
	<u>Chironomus tentans</u>	g/l	Adams et al., 1985
	<u>Paratanytarsus parthenogenetica</u>	h/em	LeBlanc and Suprenant, 1985
Cladocera	<u>Daphnia magna</u>	l/r	LeBlanc and Suprenant, 1985 Nebeker et al., 1984 Prater and Anderson, 1977-b Malueg et al., 1984
Amphipoda	<u>Gammarus lacustris</u>	l	Nebeker et al., 1984
	<u>Hyalella azteca</u>	l	Nebeker et al., 1984
Mollusca	<u>Corbicula flumiae</u>	l/g	Lomas and Hayton, 1988
Oligochaetes	<u>Tubifex tubifex</u>	bi	Oliver, 1984
	<u>Lumnodrilus sp.</u>	l/g	Wiederholm et al., 1987 Reynoldson, 1987 Keilty et al., 1988

TABLE 2 (cont.)
EXAMPLES OF ORGANISMS USED TO DETERMINE THE EFFECTS OF
MATERIALS ADSORBED ON SEDIMENTS

Group	Species	Effect	Reference
<hr/>			
<u>Marine taxa</u>			
Fish	<u>Leiostomus xanthurus</u>	l	Hagris et al., 1984
	<u>Fundulus heteroclitus</u>	l	Chu-fa et al., 1979
Mysid	<u>Mysidopsis bahia</u>	r	Nimmo et al., 1982
Crustacea	<u>Crangon septemspinosa</u>	l	McLeese and Metcalfe, 1980
	<u>Palaemonetes pugio</u>	l	Clark et al., 1987
	<u>Crangon crangon</u>	l	Lloyd, 1984
Amphipoda	<u>Rhepoxynius sp</u>	l	Swartz et al., 1985
	<u>Urothoe poseidonis</u>	b	Matthiessen and Thain, 1988
	<u>Phoxocephalid sp</u>	b/l	Anderson et al., 1987
	<u>Ampheliscid sp</u>	b/l	Anderson et al., 1987
Mollusca	<u>Mercenaria mercinaria</u>	b	Olla and Bedja, 1983
	<u>Crassostrea sp</u>	s	Chapman and Morgan, 1983
	<u>Mytilus edulis</u>	bi	Calabrese, 1984
Polychaeta	<u>Capitella capitella</u>	lc	Chapman and Fink, 1984
	<u>Nereis virens</u>	l b	McLeese et al., 1982 Mohlenberg and Kiorboe, 1983
	<u>Nereis diversicolor</u>	l/g	Taylor et al., 1985
	<u>Arenicola marina</u>	r l	Bowmer, 1988 Conti, 1987

*b - behaviour, bi - bioaccumulation, d - deformities, e - early life stage development, em - emergence, g - growth, h - hatching, l - lethality, lc - life cycle, r - reproduction, s - settlement

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APPENDICES

APPENDIX 1

EXPERIMENTAL METHODS FOR THE SAMPLING AND CHARACTERISATION OF SEDIMENTS

1. SAMPLING OF SEDIMENTS

There are a number of sampling devices: grabs, spade and bucket, scooping buckets and gravitation-plummet or core sampler.

Grabs are used to take samples of the surface layers of sediments. There are several types varying in the shape of the bite and in the area and size of the sample taken. They have the advantage of being able to take large samples in deep as well as shallow waters but alter the integrity of stratification and may lose some fine material from the surface layers by water movement during the sampling procedure.

Perhaps the simplest device is the spade and bucket which may be used to sample intertidal sediments.

Scooping (or clam shell) buckets are containers with a volume up to 2 litres. They are attached to lines or poles and are appropriate for sampling the surface layers of sediments.

Core samplers, unlike the previous examples, do not take composite samples. These devices (e.g. gravitation plummet) can take undisturbed samples down to a depth of about 3 metres. They are used when it is necessary to maintain the vertical integrity of the sediment. Special closing devices ensure that the sample does not lose any surface material.

The storage of sediment samples will depend on subsequent use. When only physico-chemical parameters are investigated, sediments can be sterilised

and sieved to remove debris and coarse fragments. When samples are to be used for biodegradability or bioavailability/toxicity studies it is best to minimise disturbance and storage time. If storage is necessary, it may be appropriate to store the sample at low temperature (e.g. 4°C) to reduce the rate of microbial growth and chemical processes. Storage under a nitrogen atmosphere is recommended for anoxic grab samples.

2. CHARACTERISATION OF PHYSICAL PROPERTIES

2.1. Porosity and Permeability.

To determine these characteristics, it is essential to obtain undisturbed cores and to avoid compaction during sampling. The determination of porosity involves the measurement of volume (or weight) of water in the wet sediment and the volume of the sediment particles. The weight of water in the sediment can be obtained by drying at e.g. 105°C, and subtracting the dry weight of the sediment from the original weight of wet sediment (Buchanan, 1984).

Permeability (in m/s) can be measured by percolating water through a column of sediment under a constant pressure and measuring the volume of water collected in a certain time (Bonneau and Souchier, 1979; Dawe, 1979).

2.2. Particle Size and Distribution and Surface Area.

Size ranges may be determined by sieving followed by sedimentation (Buchanan, 1984). After drying of the sediment, the sand fractions are determined by appropriate sieving. The organic material in the remaining fraction is destroyed with H_2O_2 in the remaining fraction. After re-suspension with a dispersing agent such as $Na_4P_2O_7$, the clay and silt fractions are determined by measuring the rate of sedimentation based on Stoke's law (NF, 1983).

Recently a technique of laser-diffraction measurement has been developed which provides a quicker and more detailed analysis with additional differentiation in particle size within the silt/clay fraction (Hart and Shillabeer, 1987).

3. CHARACTERISATION OF CHEMICAL PROPERTIES

3.1. Organic Carbon Content (OC).

The approximate OC content of a dried sediment sample can be roughly determined by measuring the weight loss on ignition. This method is mostly used to make comparisons between sediments rather than to obtain absolute values. To increase the accuracy, the sediment should be acid washed to remove carbonates before ignition. The method can also be improved by combusting the material in a stream of oxygen and monitoring the release of CO_2 .

An alternative approach consists in measuring the chemical oxygen demand (COD) of the sediment by digestion with a chromic-sulphuric acid mixture. The excess of chromic acid which is not reduced by the organic matter is titrated with a standard ferrous salt solution (Bonneau and Souchier, 1979; Buchanan, 1984; NF, 1985-a).

3.2. Cation Exchange Capacity (CEC).

All exchangeable cations are initially replaced by percolation with a Ba or NH_4 salt solution. After this first exchange, the Ba^{2+} or NH_4^+ ions are then replaced by percolating a second salt solution (e.g. Mg^{2+} or Ca^{2+} chloride) and the replaced ions determined by titration or flame photometry. Examples of the procedure are described by Bonneau and Souchier (1979), DIN (1977) and NF (1985-b).

3.3. Redox Potential and pH.

There are considerable practical difficulties in obtaining reliable electrochemical measurements. Weber and Wolfe (1987) have described

the measurement of the redox potential of sediments by placing a Pt electrode on the sediment surface for approximately 2 to 3 hours before a reading is made. Other authors have taken a thermodynamic estimation approach by considering the oxidation states of elements such as Fe, S or N. This rather complex subject has been reviewed by Price (1976) and Morel (1983). The development of micro-electrodes have allowed in situ measurement of redox potential and pH (Fenchel, 1969; Thomas, 1978).

The pH of sediments is normally measured using a sediment/water mixture (1/1). Instead of pure water, a salt solution such as KCl may be used. Values obtained are lower but more stable than those obtained with the previous method using pure water (Bonneau and Souchier, 1979).

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APPENDIX 2

BIODEGRADATION TESTS IN SEDIMENT SYSTEMS

1. TEST WITH SUSPENDED SEDIMENT

Most experimental systems involving complex multiple phases (water and sediment) have used radiolabeled substrates and monitored biodegradation by the evolution of radiolabeled carbon dioxide. The principle of the tests has been to include the sediment in the system as a slurry and to keep this in suspension by shaking or mechanical stirring. The systems are usually run in aerobic conditions and do not reflect anaerobic gradients that occur in natural sediments.

Generally, slurries contain from 0.5 - 5 g/l of sediments suspended in synthetic test media or in the water originally associated with the sediment. Test substances have been applied in concentrations from 10^{-9} g (picograms) to tens of 10^{-3} g (milligrams) per litre. The slurries are prepared in shake flasks and carbon dioxide free air is used to sweep any radiolabeled carbon dioxide into traps. The biodegradability is determined from the cumulative carbon dioxide evolved and the theoretically expected quantity based on total radiolabeled organic carbon added to the system (Larson and Payne, 1981).

These experiments may provide data on the optimum aerobic degradation rate. They do not include significantly anaerobic activities and do not reflect diffusion limitations since it is essentially a completely mixed system.

2. STATIC ECOCORE SYSTEMS

These systems attempt a simple approach to natural systems in that gradients are allowed to develop and only the surface of the sediments may be disturbed. The extent of biodegradation is normally followed by

using radio-labelled substances and monitoring the released carbon dioxide with time. Complications may arise in long term experiments due to incorporation of radio-labelled materials into sediment organic material or biomass. Ideally a full ^{14}C balance should be obtained. The basic system was developed by Pritchard et al. (1979). The sediment core may be produced by settling collected material or preferably by taking cores of sediment with minimal disturbance of the natural system and maintaining those natural gradients of oxygen and redox potential that already exist.

Practical difficulties are encountered for compounds sparingly soluble in water. For intact cores, the surface sediment may be disturbed to incorporate the test substance. Alternatively, the substance may be added to dried sediment either directly or as a solution in an organic solvent which is removed after mixing. This sediment is then added to the surface of the sediment column integrating it with the top four millimetres of the aerobic zone.

The natural gradients that exist can develop even in model systems which differ from the realistic ecocore systems. One such system is the gel-stabilised model sediment developed by Morgan and Watkinson (1989) for studying gradient effects. One advantage of this system is that for chemicals with suitable chromophores, the potential for biodegradation can be assessed by spectrophotometry.

Neither of these systems has developed the methodology for monitoring methane production from the anaerobic components of the system.

These experiments provide data on the extent and likely rate of degradation of test substances and include some of the diffusional barriers inherent to the natural gradients present in the environment.

3. CONTINUOUS FLOW SEDIMENT SYSTEMS

The ecocore has been extended to include a flowing water column over the sediment column. This allows some potential for following the water

column-sediment exchange and transport processes. An early apparatus has been described by Pritchard et al. (1979); Smith and Klug (1987) made the system more experimentally rigorous and capable of monitoring the anaerobic contribution of sediment microbiology.

The biodegradation behaviour of organic inputs in sediment systems can be further investigated in field model ponds, streams and marine sediments. These studies are the most environmentally relevant for the assessment of the fate of organic chemicals in sediments (Crossland et al., 1986).

The above studies may be complemented by in situ monitoring and residue analysis carried out in field trials or end use situations. These monitoring studies do not replace biodegradation studies but allow the validation of fate models for the behaviour of organic compounds entering the environment.

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APPENDIX 3

KEY FEATURES OF ENVIRONMENTAL FATE MODELS

LEVEL 1 models are conservative and equilibrium distribution models which need only a knowledge of the physico-chemical properties of the chemical. The results obtained are estimates of the relative distribution of the chemical over the different environmental "target" compartments (e.g. air, water, soil, sediment). The information obtained will indicate the compartment most exposed and for which further assessment is required (Zitko and McLeese, 1980; MacKay et al., 1983 a, b) .

LEVEL 2 models are equilibrium and non-conservative models and consider a steady-state situation (i.e. a continuous input). Although they take into account biodegradation kinetics, they are in general not used because they do not consider non-equilibrium situations and thus do not give more relevant information than Level 1 models.

LEVEL 3 models are non-equilibrium and non-conservative and consider a steady-state situation (i.e. a continuous input). They require knowledge of the degradation rates, transfer rates between compartments and the input of the chemical in the environment. These models give more information on the concentration and the persistence of the chemical in each compartment when the input is well defined (Neely, 1979; Mackay et al., 1983 a, b).

LEVEL 4 models give the same information as the Level 3 models but deal with simple unsteady-state situations (e.g. an accidental release). Most of them are only able to deal with simple unsteady-state situations (e.g. instantaneous input or instantaneous change from one continuous input to another continuous input) (Neely and Blau, 1977; MacKay et al., 1983 a, b; Yoshida et al., 1987; Basmadjian and Quan, 1987; Schramm et al., 1988).

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APPENDIX 4

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