3.2

Sediments

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3.2.1 INTRODUCTION

In the context of testing of environmental chemicals, 'sediment' is the common name given to the soil/mud layer at the bottom of a water body resulting from the settling of suspended solids transported in that water body. Sediment composition is exceedingly variable depending on origin of the suspended matter, the flow rate and its fluctuations as well as inputs from human activities. Benthic material is characterized in general by an interphase water/mud layer of fine particles including organic matter in which the water/solids ratio can be as high as 9 to 1, and a more solid sediment bed (van der Harst, 1979).

The occurrence of chemicals of anthropogenic origin in sediments and suspended solids in rivers, lakes, lagoons, and the sea has been reported in numerous publications; therefore, only some examples of references are given here. The chemicals detected include radionuclides, heavy metals, nitrogen and phosphorous compounds, paraffins, polycyclic aromatic hydrocarbons, pesticides, polychlorinated biphenyls, plasticizers, and other man-made chemicals (e.g., Duke et al., 1970; Leland et al., 1973; Frank, 1977;
Miles, 1977; Müller et al., 1977; Müller, 1977a–c; Botello and Mandelli, 1978; Balkas et al., 1978; Tsai et al., 1978; Giam et al., 1978; Müller, 1979a and b; Puccetti and Leoni, 1980; Müller et al., 1980; Giam and Atlas, 1980; Bastürk et al., 1980; Villeneuve et al., 1980; Salihoglu et al., 1980; Murray et al., 1981a and b; Amico et al., 1982; Pimpl and Schüttelkopf, 1982; Geyer et al., 1984). In order to develop models and tests to predict the behaviour of these chemicals in sediments, physical and chemical processes in the sediments, as well as interactions of the sediment with water and aquatic organisms should be understood. The following sections, therefore, deal with physical properties and chemical composition of sediments and the physical and chemical processes involved.

### 3.2.2 PHYSICAL PROPERTIES AND CHEMICAL COMPOSITION OF SEDIMENTS

The particle size of sediments resulting from the settling of solids transported in a suspended form usually is below 0.05 mm (0.063–0.002 mm: ‘silty sediment; 0.002 mm: ‘clay’ sediment). By contrast, particles transported at the bottom of a river by rolling generally have sizes of 0.063–2.00 mm (‘sand’) or more (‘gravel’). Due to their relatively low specific surface, these materials play only a minor role in adsorption and degradation of environmental chemicals (Müller, 1981).

There is a continuous interrelationship between the sediments at the bottom of a water body and suspended solid matter, and, as a consequence of changes in particle size due to various physical or biological influences including water movement or other environmental factors, particles may be transported between both phases. Therefore, when considering the behaviour of chemicals in sediments, water-suspended solid matter must be considered.

The weathering of rock produces individual clay- and silt-sized mineral grains which agglomerate into composite sedimentary particles during transport and deposition in lakes, rivers, estuaries, and oceans. Agglomeration is an important prerequisite for the deposition of clay- and silt-sized mineral grains, especially for suspended matter for which settling velocity is exceeded by the upward vertical velocity of waters. The following abiotic and biological mechanisms may affect agglomeration of suspended sediments in situ.

Electrochemical flocculation, a chemical phenomenon, is the agglomeration produced when salt is added to a fresh-water suspension of clay minerals. Flocculation of suspended sediments occurs principally in estuaries. A second abiotic mechanism is coagulation or sediment agglomeration by dissolved molecules which are sorbed on to immersed mineral surfaces. A mechanism of biological agglomeration is the pelletization of fine-grained sediments by filter-feeding planktonic and
benthic organisms. Finally, growth of microbes on suspended sediments and the associated secretion of sticky mucal substances which bind suspended sediments together, is another mechanism for agglomeration. Diatoms have also been observed to agglomerate suspended sediments in two South Carolina estuaries. Examples of the mode of grain attachment, attributable to fecal pelletization and to abiotic mechanisms of agglomeration, including electrochemical flocculation, have been given for a bay estuary (Zabawa, 1978).

The chemical composition of sediments varies widely, depending on geographical location and origin. Fossil pelitic sediments contain far less than 1% of organic matter. A calculation of the composition of the mineral fraction of pelits on a world-wide scale gave 59% clay minerals, 20% quartz, 8% feldspar, 7% carbonates, 3% iron oxides, and 3% ‘others’ (Yaalon, 1962). When the clay minerals are classified according to their layer structure, illites are most abundant on a global scale. Recent pelitic sediments exhibit a higher fraction of organic matter (range: 1–6%; estimated mean value: 3%) than fossil pelitic sediments. In water bodies with a higher degree of eutrophication, the organic fraction probably is much higher and often exceeds 10%. The composition of the mineral fraction probably does not differ significantly from that of fossil sediments (Müller, 1981). The mineral fraction of suspended particulate matter, in principle, has a similar composition; in coastal waters, quartz, feldspar, calcite, chlorite, kaolinite, and illite are common constituents. The composition of minerals varies with distance offshore, suggesting contributions from land sources and from biogenic sources in the offshore areas (Chan and Chen, 1977).

The organic fractions of sediments and suspended particulate matter have been studied and compared with those of humus from terrestrial environments. Visser (1982) investigated the equivalent weights and the number of carboxyl and phenolic hydroxyl groups of molecular weight fractions of fulvic and humic acids sampled at various locations in a watershed. He compared the results with data reported for humic material from other aquatic and terrestrial environments. This comparison showed that although aquatic humic compounds have several properties quite distinct from soil humus, in their acidic functional groups, aquatic humic compounds differ very little from humus of terrestrial origin. The only dissimilarity observed was that aquatic humic acids normally contain more COOH and fewer phenolic OH groups than their terrestrial counterparts.

Since fulvic acids are defined by their solubility behaviour in alkaline and acidic media rather than by chemical characterization, the ‘fulvic acid’ fraction obtained by standard fractionation procedures may contain considerable portions of non-humic substances; thus, in the ‘fulvic acid’ fraction of marine sediments, polysaccharides containing uronic acids are dominant components (Hatcher et al., 1980).
Suspended particulate matter in marine water has been shown to contain, after hydrolysis, amino acids whose nitrogen content could often account for 100% of the total particulate organic nitrogen content (Siezen and Mague, 1978). Chlorophyll is another important organic constituent of marine suspended matter, and can be used to estimate the concentration of suspended matter in sea surface layers via the measurement of the spectral distribution of the sea radiance coefficient (Pelevin, 1978). Finally, the particulate matter in continuous films on the sea surface consists of lipids containing fatty acids and other surface-active substances (Kattner and Brockmann, 1978).

### 3.2.3 PHYSICAL, CHEMICAL AND BIOCHEMICAL PROCESSES IN SEDIMENTS

The *spatial distribution of anthropogenic chemicals in sediments* normally depends on their sources and form by which they are transported. Environmental chemicals in sediments originate from various sources, for example from direct emission by waste water, by rainfall, or by surface run-off of soil. They may enter the water in dissolved form as well as adsorbed on particles. The transfer of dissolved chemicals to the sediment is governed by adsorption/desorption processes; the transport of chemicals adsorbed on particles by soil run-off is especially important for agricultural chemicals. The extent of pesticide run-off depends, in addition to the physico-chemical properties of the chemicals, on the intensity and duration of rainfall, soil cover, soil type, and slope (Weber, 1977; Johnson and Baker, 1982). Additionally, the spatial distribution of pesticides from run-off is affected by limnological characteristics of the respective aquatic system.

Upon entry into an aquatic system, pesticides attached to particulates are fractionated according to the size and density of the adsorbent particles; the finer and often less dense particles show greater movements. This process of particle size segregation contributes to a positive correlation between the clay and organic matter contents of lake sediment and the depth of water or distance from shore at which the sediment is sampled. The similarity between the densities of water and organic matter and the association of organic matter mainly with the finer mineral fraction causes the more highly organic particles to settle out in deeper waters. Similarly, a vertical segregation of particles occurs with the coarsest particles being deposited first and the finer ones later. Thus the finest particles tend to constitute the solid phase at the sediment–water interface, although this process is overshadowed where there is substantial mixing at the interface (Browman and Chesters, 1977). Since soil-sorbed pesticides are concentrated on the finer particles (e.g., Richardson and Epstein, 1972), this particle size fractionation results in an uneven distribution of pesticides from soil run-off within the sediments.
The principles of sorption of chemicals to sediments are comparable to those of sorption to soils (see Chapter 5.2). Adsorption data on sediments or suspended particulate matter have been shown to fit Freundlich or Langmuir equations (Reimers and Krenkel, 1974; Harding and Phillips, 1978; Karickhoff and Brown, 1978; Karickhoff et al., 1979; Hiraizumi et al., 1979; Peck et al., 1980; Bibbo and Müller, 1982). As in soils, the adsorption of chemicals to sediments is mainly adsorption to organic matter. This applies to non-ionic organic chemicals but also to some metals (Leland et al., 1973; Herbes, 1977; Kronmayer and Streit, 1978; Karickhoff et al., 1979; Kerndorff et al., 1979; Hiraizumi et al., 1979; Nriagu and Coker, 1980; Peck et al., 1980). A key distinction between soils and sediments in this context is particle size composition. Unlike soils which contain a wide range of particle sizes, sediments within a given compartment may contain a very narrow range of particle sizes. Functional dependence of adsorption on particle size could vary the degree of sorption in different river compartments and produce a non-uniform distribution of sorbed pollutant within the sediment, similar to that of pesticides from soil run-off. For given particle size isolates, the linear partition coefficients for non-ionic organic chemicals were found to be directly related to organic carbon content. Partition coefficients based on the organic carbon content of the sediment fractions ($K_{oc}$-values) showed a bell-shaped dependence on particle size, the maximum being in the medium or fine silt fraction (Karickhoff et al., 1979). The authors concluded that, given the set of sediment-independent $K_{oc}$s, the content of organic carbon and the masses of each size fraction, a composite adsorption constant can be computed for any given sediment.

The $K_{oc}$-values have been reported to be well correlated to $n$-octanol–water partition coefficients. Octanol–water partitioning provides a much better estimator for sediment–water partitioning, than does solubility, because in a molecular sense, the partitioning of a compound between water and either sediment or octanol involves monomer distribution between two phases. On the other hand, saturated aqueous solutions involve the equilibration of primarily dissolved monomers with crystalline compounds. Crystal energy contributes to water solubilities but does not affect the monomer-associated properties of partition and adsorption coefficients. Since the $K_{oc}$s are well correlated to octanol–water partition coefficients, reasonable estimation of the sorption behaviour of hydrophobic pollutants can be made from a knowledge of the particle size distribution and associated organic carbon content of the sediment and the octanol–water partition coefficients of the chemicals (Karickhoff et al., 1979).

For the cationic pesticide paraquat which is sorbed mainly by ion exchange, sorption partition coefficients showed a definite correlation with the cation exchange capacity of individual size fractions (Karickhoff and Brown, 1978).

For metals in general, hydrous oxides of manganese and iron furnish the
principal control on fixation in fresh-water sediments (Jenne, 1968). Some organic chemicals are also adsorbed on Fe(III) oxides and can be coprecipitated by Fe(III) salts from water (Sridharan and Lee, 1972). For mercury (as HgCl), the adsorption on clays, sands and specific organics was negatively influenced by the chloride ion concentration of the water (Reimers and Krenkel, 1974; Kerndorff et al., 1979). The content of the radionuclide plutonium in sediments of the Rhine river was shown to be higher in sediment fractions with lower particle diameter than in larger particles (Pimpl and Schüttelkopf, 1982).

Sediments would be the final sink for adsorbed chemicals if exchange reactions between sediment and water were negligible. However, this assumption is true only for sediments at very deep sites of water bodies. Normally, there exist remobilization processes which result in a continuous release of chemicals into the water and, thus, in their bioavailability and entry into the food chain.

One remobilization process is desorption. Adsorption/desorption equilibria may be disturbed by a decrease of the concentration in the aqueous phase as a result of high water flow rates and/or of volatilization. Uptake of the desorbed chemicals by organisms, including plankton, invertebrates, and fish, which, depending on the properties of the chemical, may be followed by metabolic reactions resulting in degradation or production of metabolites with increased water solubility, also contributes to the mobilization of sediment-associated chemicals. Erosion of sediments is another important mechanism by which chemicals associated to sediments are mobilized and made available for uptake by fish (Olsson, 1978).

In addition to the above mobilization pathways, sediment-dwelling and deposit-feeding animals (aquatic worms, clams, shrimps) contribute to the mobilization of sediment-associated chemicals by two other mechanisms. The first mechanism is direct uptake of the chemical from the sediment into their body through feeding activities without preceding desorption. Such uptake may be followed by tissue accumulation and thus the entry of the chemical into the food chain. Concentration factors for the uptake of some chemicals from sediment are lower than those from water by several orders of magnitude (Ueda et al., 1976; Roesijadi et al., 1978a; Fowler et al., 1978; Lyes, 1979); nevertheless, sediments may contribute the bulk of lipophilic chemicals to the body burden of worms since sediments represent by far the largest depot for these chemicals in the aquatic systems (Fowler et al., 1978). However, the uptake of chemicals by the two routes, uptake of the desorbed substance in interstitial water and ingestion of solid material with the adsorbed chemical, is not clearly distinguished in most of the experiments reported (Renfro, 1973; Amiard-Triquet, 1974; Beasley and Fowler, 1976; Murray and Renfro, 1976; Courtney and Langston, 1978; Elder et al., 1979; Lyes, 1979; Phelps, 1979; McLeese et al., 1980; Jennings and Fowler, 1980).
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Special experimental techniques are needed for the separate determination of both uptake pathways. In the case of cadmium, it has been shown that uptake through ingestion of sediment is relatively inefficient (Luoma and Jenne, 1976 and 1977). Nevertheless, this pathway may be important for the mobilization of chemicals with low desorption rates.

The accumulation of polychlorinated biphenyls by the Polychaete worm Nereis virens from sandy sediment was shown to be directly related to PCB concentration in sediment and to exposure time and inversely related to worm size; similarly, a relation of accumulation to sediment concentration and animal size was observed for the shrimp Crangon septemspinosa (McLeese et al., 1980). The biological availability of lead in the sediment was shown to be strongly influenced by the level of readily extractable iron (Luoma and Bryan, 1978). There is only limited information on correlations between bioavailability of sediment-associated chemicals and their physical or chemical properties. The availability of sediment-bound metals to the deposit-feeding clam, Macoma balthica, was dependent upon the physico-chemical nature of the metal–sediment association (Luoma and Jenne, 1977). No simple correlation has been observed between the bioavailability of sediment-bound metals and chemical extractability (Luoma and Jenne, 1976; Jennings and Fowler, 1980). For hydrocarbons, it was found that the heavier molecular weight aromatic compounds tended to be more concentrated in tissue and retained for longer periods of time than the lighter compounds (Roesijadi et al., 1978a).

The second mechanism by which deposit-feeders, especially aquatic worms, contribute to the mobilization of adsorbed chemicals is their burrowing activity which can be regarded as 'biological erosion'. Thus, Renfro (1973) reported 3–7 times higher losses of $^{65}$Zn when Polychaete worms were burrowing through the sediment, as compared to losses caused by slowly flowing seawater. For mercury, it is assumed that the benthic macrofauna, e.g., tubificid worms, could be entirely responsible for the clearance of the metal from the bed sediments of flowing water systems (Boddington et al., 1979).

Information on migration of chemicals within sediments is limited. The migration of $^{137}$Cs in sediments with and without benthos has been studied (Robbins et al., 1979). In sediment without benthos, small but measurable migration of $^{137}$Cs occurred with an effective molecular diffusion coefficient of 0.02 cm$^2$/yr. In sediment with the deposit-feeding Oligochaete, Tubifex tubifex, which feeds below 3 cm and defecates on surface sediments, the labelled layer was buried by the animals at a rate of 0.052 ± 0.007 cm/day (20 °C). When labelled particles entered the feeding zone, $^{137}$Cs reappeared in surface sediments creating a bimodal activity profile. In time, the activity tended toward a uniform distribution over the upper 6 cm, decreasing exponentially below this layer to undetectable levels by 9 cm. In sediment with the deposit-feeding Amphipod, Pontoporeia hoyi, which feeds on
near-surface sediment and moves through superficial sediments in a plough-like manner, uniform activity developed rapidly (~17 days) down to a well defined depth (1.5 cm). The mixing of sediments by Pontoporia is described by a simple quantitative model of eddy diffusive mixing of sediment solids. The value of the diffusion coefficient, 4.4 cm²/yr (7 °C), was computed from a least squares fit of theoretical to observed profile broadening over time. Similarly, a redistribution of mercury in sediments was observed under the influence of tubificid worms (Boddington et al., 1979).

Chemical and biochemical processes in sediments are characterized by the aeration profiles of the sediment. Upper sediment layers which are characterized by aerobic microorganisms, by the occurrence of Fe-III-oxides and often by higher aquatic plants, vary greatly in thickness, depending on the oxygen supply from the overlying water. In flowing water bodies, the thickness range is between some decimetres to a few centimetres (Fischer and Baumann, 1976). On the other hand, anaerobic conditions frequently do occur at very shallow depths. Lake sediments have the tendency to become cyclically anaerobic for extended periods. This capacity is related to the size, shape, and productivity of the lake. Changing conditions from aerobic to anaerobic alters significantly the composition of the sediment solid phase (Browman and Chesters, 1977).

Whereas the activity of aerobic microorganisms is characterized mainly by the production of carbon dioxide, in anaerobic environments other gases are formed as metabolic end products. These are mainly hydrogen sulphide resulting from sulphate reduction (Udluft and Weil, 1974; Oremland and Taylor, 1978), methane resulting from bacterial decomposition of organic compounds (Snodgrass, 1976; Oremland and Taylor, 1978), ammonia, and free nitrogen resulting from denitrification processes which have been shown to increase in anaerobic medium (Andersen, 1977).

For the differentiation between aerobic and anaerobic sediment zones, measurements of oxidation-reduction potential (Patrick, Jr., 1966) or of oxygen consumption (Edberg and Hofstein, 1973; Brewer et al., 1977) have been reported. However, it is also possible to determine anaerobic reaction products by chemical oxidation methods, e.g. of readily oxidizable reduced substances. Fischer and Baumann (1976) reported the determination of reduced substances by rapid oxidation with a diluted potassium dichromate/sulphuric acid solution. These values, expressed as meq/100 ml of fresh sample, showed a non-linear, negative correlation with redox potential.

The participation of anthropogenic chemicals in the natural biochemical reactions in the sediment results in a multitude of oxidative, reductive, or hydrolytic metabolic conversion and degradation products and their conjugates, which are not discussed here in detail (see Chapter 4.1; Klein and Scheunert, 1978; Alexander, 1981). In aerobic sediments, oxidative metabolic processes prevail, and carbon dioxide is the final degradation
product of environmental chemicals. Enzymes produced by sediment-dwelling invertebrates (Lee et al., 1979; Gardner et al., 1979) and higher plants (Moza et al., 1974) rooted in sediment contribute to conversion and degradation of organic xenobiotics. Since anaerobic conditions probably prevail in sediments, their influence on the degradation and conversion of environmental chemicals will be important. The information available today on such conversions has been obtained in experiments not only with sediments but also with other anaerobic material maintained in the laboratory, e.g., flooded soil, anaerobic sewage sludge, etc.

Under anaerobic conditions, chemicals such as chlorinated hydrocarbons, which are normally persistent, may have short lifetimes (Hill and McCarty, 1967). This probably is due to the fact that the first degradation step for these substances, reductive dechlorination, easily occurs in anaerobic media and is not exclusively a biotic process. A typical example is the reductive dechlorination of DDT to DDD in sediments (Leland et al., 1973; Miles, 1977). Glass (1972) reported the reductive dechlorination of DDT to DDD by an iron redox system in vitro and proposed a mechanism for the degradation of DDT in anaerobic soils. Electrons furnished by the reduced organic substrate are transferred to the DDT molecules via the Fe²⁺-ions thus initiating a free radical reaction in the absence of oxygen. Zoro et al. (1974) achieved only a very slow reaction under these conditions. They concluded that this reductive process is mediated by reduced iron porphyrins and is not a essential part of cell metabolism. This finding has considerable environmental significance since most living material contains iron porphyrins bound with proteins which, under the reducing conditions in an anaerobic environment characteristic of dead and decaying matter, would catalyse rapid conversion of DDT to DDD and other products.

Toxaphene degradation in anoxic estuarine sediments is another example of reductive reactions in sediments (Williams and Bidleman, 1978). Reduction occurs in sterile as well as non-sterile sediments and also in sand—Fe²⁺—Fe³⁺—system, but not in a sand system that does not contain the iron redox complex couple.

The simulation of metabolic conversions of environmental chemicals by simple chemical laboratory reactions is in general problematic because of the stereospecificity of the enzymes involved. However, since it is evident that abiotic factors can act upon environmental chemicals in sediments, simulated reactions in the laboratory may be useful to replace complicated tests. Thus, the anaerobic conversion of DDT to DDD and of DTE (1,1,1,2-tetrachloro-2,2-bis-[p-chlorophenyl]ethane) to DDE (Beland et al., 1974) can be performed electrochemically (Rosenthal and Lacoste, 1959). The complete reductive dechlorination of lindane in anaerobic sewage sludge and soil, resulting in formation of benzene, can be simulated by an electrochemical reduction (Beland et al., 1976). The authors reported the
predictability of anaerobic degradation products of organohalogen compounds in the environment by electrochemical reduction. Based on their results, they proposed tentatively, that compounds with an $E_{2d}$ more positive than $-1.521$ V (versus saturated calomel electrode) in dimethylsulphoxide will be anaerobically degraded and compounds with an $E_{2d}$ more negative than $-1.757$ V will not be anaerobically reduced ($E_{2d}$ is the interrupt potential determined by the zero crossing of the second derivative curve; Farwell et al., 1975).

Contrary to the elimination of chlorine atoms bound to non-aromatic carbon, elimination of aromatic chlorine of the herbicide diuron was shown to be an exclusively biotic process and was performed only by adapted microorganisms (Attaway et al., 1982a and b).

Reduction reactions other than dechlorination are also common in anaerobic media, e.g. the reduction of the nitro group of pentachloronitrobenzene in anaerobic soil (Murthy and Kaufman, 1978) and of parathion in sediments (Wahid and Sethunathan, 1979).

As the final degradation product, carbon dioxide is formed also under anaerobic conditions. When identical degradation studies of 14 environmental chemicals were carried out with identical soil/water suspensions under aerobic and anaerobic conditions, the amount of carbon dioxide formed from the chemical under anaerobic conditions did not greatly differ from that produced under aerobic conditions (Korte et al., 1983).

The formation of the other degradation products like methane, sulphide, or nitrogen from xenobiotics has been investigated thus far only to a very limited extent. Methodology is available to determine methane as a metabolic end product for natural compounds such as acetate (Winfrey and Zeikus, 1979).

There exists also the possibility of secondary reactions of environmental chemicals with these natural end products, especially with hydrogen sulphide. Heavy metals are immobilized as sulphides. The involvement of hydrogen sulphide in the dealkylation of aminoparathion has been demonstrated by Wahid and Sethunathan (1979).

Covalent binding of organic chemicals, like anilines or phenols, to humic acid precursors and their incorporation into humic acid macromolecules in soils, similarly could occur in sediments. This would imply an immobilization of the compound and its slow remobilization by microbial degradation of the humic acids (Hsu and Bartha, 1976; Klein and Scheunert, 1982).

Interactions between sorptive effects and chemical processes have been demonstrated by several authors. Fischer and Baumann (1980) reported a positive effect of oxidation on the sorption of phosphate. During intensive reduction by sodium dithionite, phosphate sorbing river sediments showed a pronounced desorption of phosphate. Reoxidation by air caused an increase in phosphate sorption up to five times the original value, the level of sorption being linearly related to the ferric oxide content of the sample. A possible
explanation for this phenomenon is the oxidative precipitation of iron(III) oxides which have a high surface area and are very active in phosphate adsorption. Fe(III) oxides have been shown to be also important adsorbers for heavy metals (Jenne, 1968) and for some organic chemicals which are coprecipitated from water by Fe(III) salts (Sridharan and Lee, 1972). Thus, a higher aeration state of the sediment and, consequently, a higher content of Fe(III) oxides result in lower bioavailability of heavy metals to deposit-feeders (Luoma and Jenne, 1977); a similar behaviour is to be expected for some organic chemicals.

A positive effect of adsorbing surfaces on biodegradation has been reported for chlorinated phenols (Boyle et al., 1980; Blades-Fillmore et al., 1982), for the herbicide 2,4-D (Watson, 1977) and for the other organochlorine compounds (Lee and Ryan, 1979). An indirect influence of surfaces on the biological degradation via effects on microorganism growth was reported for experiments with 2,4,6-trichlorophenol in water in the presence of various sediments as well as inorganic surfaces (Blades-Fillmore et al., 1982). The authors demonstrated the role of colonizable surfaces in providing optimum conditions for the biodegradation of 2,4,6-trichlorophenol. While the positive effect of the presence of sediments has been known for a while, often sediments were thought to be sources of specific metabolizing bacteria; this work showed that 2,4,6-TCP degrading bacteria were available in the water, but surfaces for bacterial attachment were important in the water self-purification process.

However, if degradation is determined only by measurement of the loss of parent compound, adsorbing material containing humic substances can irreversibly bind and incorporate the substance into humic acid macromolecules, which may be misinterpreted as degradation. The compound 2,4,6-trichlorophenol used in the study of Blades-Fillmore et al. (1982) shows a marked tendency to form such humic acid complexes in soil (Fragiadakis, 1980). The same applies to studies on the biodegradation of 2,4-D with and without sediment (Watson, 1977); 2,4-D forms considerable amounts of bound residues in soil (Smith and Muir, 1980). Boyle et al. (1980) showed, using 14C-labelled pentachlorophenol, that the addition of sediment to the water decreased the half-life of pentachlorophenol but not the total amount of 14C recovered in the system. Nevertheless, since positive effects of surfaces on residue losses have been observed for inorganic surfaces, and since such effects have been found in degradation studies with 14C-labelled chemicals by measuring 14CO₂ (Lee and Ryan, 1979), it may be concluded that biodegradation occurs most readily at the sediment/water interphase.

Catalytic reactions similar to those affecting the total degradation of chemicals adsorbed on dry surfaces (Bahadir et al., 1978) do not occur in the aquatic environment; however, *indirect influences of suspended sediments on photolysis* have been reported. If suspended particles do not absorb light to a
significant extent, then the rates of direct photolysis can be enhanced in turbid water compared to clear water because of the increased diffusiveness of light (Miller and Zepp, 1979). If the suspended particles do absorb light, then direct photolysis decreases (Oliver et al., 1979); this decrease, however, may be offset by an increase in the rates of photosensitized reactions (Bedding et al., 1983).

### 3.2.4 LABORATORY TESTS TO DETERMINE SINGLE FACTORS AFFECTING THE FATE OF CHEMICALS IN SEDIMENTS

Numerous laboratory tests have been reported to determine single factors such as adsorption/desorption processes, remobilization and accumulation by aquatic organisms, and chemical and biochemical reactions, affecting the fate of chemicals in sediments. In laboratory model ecosystems and in field tests mostly natural sediments are used, whereas, in single factor laboratory tests, which often are used for comparative evaluation of chemicals, other materials have been tested since natural sediments cannot be standardized. Müller (1981) proposed, as a standard artificial sediment mixture, the average of the mineral composition of sediments from four German rivers (illite, 50%; kaolinite, 11%; chlorite, 5%; quartz, 19% feldspar, 8%; carbonate, 6%); 8% organic matter is added but the difficulties involved in its standardization have not been solved. The same problems of standardization arise when water-logged soil or natural soil or sediment fractions are used instead of intact natural sediment samples. Therefore, synthetic materials have also been used to simulate the respective component of the natural sediment, which is primarily responsible for the specific fate process investigated. In Table 3.2.1, examples for laboratory tests are listed, and the materials used are included.

For adsorption/desorption of organic chemicals, an OECD test guideline is available for soils (OECD Chemicals Testing Programme, 1981), which may be used also for natural sediments, sediment particle fractions, or other materials (see Chapter 5.2). After equilibration of the dissolved chemical between soil and water, the adsorption coefficient is determined as a physico-chemical substance property characteristic of the distribution behaviour of the chemical between soil/sediment and water. It is anticipated that within the shaking time (16 hours) an equilibrium between both phases is reached and that no significant biodegradation occurs during this time. For metals, in principle the same method is used; the equilibration time may be very short (Kerndorff et al., 1979; Amiard-Triquet, 1974). Since organic matter is the most important constituent of sediment particles for the adsorption of non-ionic organic chemicals, for these compounds it might be useful to carry out adsorption tests only with organic adsorbents, e.g. autoclaved yeast cells (Herbes, 1977) or dehydrated plankton (Hiraizumi et al., 1979).
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<td>Adsorption-redox interactions</td>
<td>Reduction/oxidation of sediment and adsorbable chemicals</td>
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<td>Determination of chemical in flowing water over sediment</td>
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Table 3.2.1 (continued)

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<tr>
<td>Uptake of chemicals from particulates by organisms via water</td>
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<td>Luoma and Jenne, 1976 and 1977</td>
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<td>Humic acid, bentonite, protein</td>
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<td>Separate determination of uptake of adsorbed or</td>
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<td>desorbed chemical</td>
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<td>Natural sediments, amorphous Fe- and Mn-oxides</td>
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References:
- see Chapter 5.3 (e.g., principle of Klöpffer et al., 1982)
- Laube et al., 1979
- Harding, Jr., and Phillips, Jr., 1978
- Kobylinski and Livingston, 1975
- Courtney and Langston, 1980
- Elder et al., 1979
- Renfro, 1973
- Lyes, 1979
- Phelps, 1979
- Murray and Renfro, 1976
- McLeece et al., 1980
- Courtney and Langston, 1978
- Beasley and Fowler, 1976
- Jennings and Fowler, 1980
- Amiard-Triquet, 1974
- Roesijadi et al., 1978a and b
- Ueda et al., 1976
- Fowler et al., 1978
- Roesijadi et al., 1978a and b
- Phelps, 1979
- Luoma and Jenne, 1976 and 1977
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<td>Accumulation of chemicals from sediment in food chains</td>
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<td>Natural sediments</td>
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<td>Conversion reactions in sediments</td>
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<td>Ward and Matsumura, 1978</td>
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<td>Anaerobic sewage sludge</td>
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<td>Experiments with organisms</td>
<td>Miyazaki <em>et al.</em>, 1975</td>
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<td>Culture media with microorganisms</td>
<td>Clark and Matsumura, 1979</td>
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<td>Sediment-dwelling worms</td>
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<td>Boyle <em>et al.</em>, 1980</td>
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<td>Williams and Bidleman, 1978</td>
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<td>Miyazaki <em>et al.</em>, 1975</td>
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<td>Beland <em>et al.</em>, 1976</td>
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*Notes: The table lists various activities related to the accumulation, migration, and conversion of chemicals in sediments, along with the organisms or environments used in these activities. The references are cited for each activity, providing further details on the methods and results. The table also includes references for similar activities in sediment columns and sludge systems, highlighting the diversity of approaches used in ecological and environmental studies.*
<table>
<thead>
<tr>
<th>Factor investigated</th>
<th>Principle of test</th>
<th>Material used</th>
<th>References (examples)</th>
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<td>Degradation of chemicals in sediments</td>
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<td>Nelson and Zeikus, 1974</td>
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<tr>
<td>Reactions of chemicals with gases from natural anaerobic processes</td>
<td>Reaction with H$_2$S</td>
<td>H$_2$S</td>
<td>Wahid and Sethunathan, 1979</td>
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</table>
The dependence of adsorption/desorption processes on the state of aeration of the sediment may be tested by reduction of the adsorbing mixture with sodium dithionite and by reoxidation with air (Fischer and Baumann, 1980).

Remobilization of chemicals from sediments by increased desorption following volatilization of aqueous concentrations, may be tested by an experimental set-up including sediment, water, and physical conditions such as movement of water or air or both, promoting volatilization from the aqueous solution. Kobylinski and Livingston (1975) reported the disappearance of mirex from a system including mirex-containing sand and flowing water. About 40% of the initial mirex concentration was lost from the sediment under constant flow conditions within 4 weeks whereas no loss occurred in a reference static test. Volatilization of particle-associated chemicals via the aqueous phase, in principle, could be determined also in apparatus for the determination of volatility from aqueous solutions (see Chapter 5.3). The method of Klöpfer et al. (1982), for example, could be varied by adding particulate matter with the adsorbed chemical to the water; volatilization is promoted by stirring and by drawing air over the water surface.

Mobilization of chemicals from sediments through desorption into the aqueous phase and uptake by organisms is determined by adding, e.g., algae (Harding, Jr., and Phillips, Jr., 1978; Laube et al., 1979) or fish (Courtney and Langston, 1980; Kobylinski and Livingston, 1975) to water with sediment or particulate matter containing the chemical. If the chemical is added to water containing both sediment and algae or bacteria, sediment and organisms compete for the adsorbable chemical. The distribution of the chemical between water, sediment and organisms can be examined by means of a curve analysis of the distribution pattern of a three compartment model (Nakamura et al., 1977; Ramamoorthy et al., 1977).

The uptake of chemicals from sediments by deposit-feeding invertebrates (aquatic worms, clams, shrimps) normally is tested by keeping the animals in sediments or other materials under water according to their natural living conditions. The kind of adsorbing material has an important influence on the uptake of the chemicals by the animals. Normally, this kind of experiment does not differentiate between uptake of desorbed chemical via interstitial water in the sediment and uptake of adsorbed chemical via ingestion of sediment. However this differentiation may be important for the estimation of remobilization of chemicals with high adsorption and low desorption coefficients. Therefore, a method has been reported by Luoma and Jenne (1976 and 1977) to assess the uptake via ingestion of sediment. This is performed by comparing the amount taken up by normal-living animals with that taken up by animals living in sediment in dialysis bags.

If, in experiments with deposit-feeding worms, the chemical concentration in the sediment is monitored, the influence of the burrowing activity of worms on chemical losses from the sediment may also be recorded.
By feeding fish with cockles contaminated by sediment-associated chemical, a crude examination of biomagnification of sediment-borne chemicals in aquatic food chains has been made (Courtney and Langston, 1980). Complete food chain experiments, however, are feasible only in laboratory ecosystems or in more complex experimental designs with the different trophic levels kept separate (see Section 3.2.5 and Chapter 4).

For determining the distribution and migration of chemicals within the sediment, methods have been reported for radio-labelled metals by Robbins et al. (1979) and Boddington et al. (1979). In both cases the migration through a sediment column was recorded by radioactivity measurement techniques.

Numerous experiments have been carried out to investigate conversion reactions in sediments. Normally, sediments, water, and the chemical in question are incubated and then the aqueous solution is extracted and analysed for conversion products. The portion of unextractable residues which are detectable only when radio-labelled chemicals are used, should be included into the metabolic fraction. In contrast to soils, for which many data are available on unextractable residues (Klein and Schenunert, 1982), only a very limited number of publications have dealt with this problem in sediments (e.g., Miyazaki et al., 1975; Herbes and Schwall, 1978).

The maintenance of aerobic or anaerobic conditions is not well distinguished in some of the conversion tests reported. In general, undisturbed sediment samples flooded with water are regarded as anaerobic, and samples shaken or stirred throughout the incubation period are regarded as aerobic. In order to ensure anaerobic conditions, the samples are kept under nitrogen or a 95% N₂/5% CO₂ mixture. Similarly, for tests carried out with culture media of microorganisms from sediments, if anaerobic conditions are required, culture media are reduced with sodium dithionite (Zoro et al., 1974) or cysteine-HCl (Attaway et al., 1982a and b) and kept under nitrogen.

Abiotic reductions in sediment may be simulated by laboratory reactions of the chemical with iron redox systems (Glass, 1972; Williams and Bidleman, 1978) or reduced hematin (Zoro et al., 1974); this has been achieved for DDT and toxaphene reductions. Electrochemical reduction has been proposed as another method to simulate the reduction of chemicals, e.g., lindane, DDT, or DTE (1,1,1,2-tetrachloro-2,2-bis [p-chlorophenyl]ethane) and to predict anaerobic degradability of chemicals in sediments (Beland et al., 1976). However, these simulation tests have been applied thus far, only to a few substances and are still far from being suitable as standard tests for organic chemicals in general.

Degradation tests may be divided into those determining only the disappearance of the parent compound and those determining complete degradation by measuring carbon dioxide, methane, or other low-molecular fragments of the chemical in question.
If the former group of tests is employed, caution should be used to avoid misinterpretations due to the volatilized, chemically altered, or unextractable portions of the test substance (e.g., Watson, 1977; Sudhakar-Barik and Sethunathan, 1978a; Ward and Matsumura, 1978; Clark and Matsumura, 1979; Boyle et al., 1980; Blades-Fillmore et al., 1982). Standardized tests based on disappearance of the parent compound, as well as those based on oxygen consumption, have been developed for water (see Chapter 4.2).

Tests to determine the end products of biological degradation have been long utilized, for example for carbon dioxide production in soil. Carbon dioxide is trapped by alkaline media and determined quantitatively. Blanks are run with material without the chemical in question, and the difference in amount of carbon dioxide produced by treated and untreated soil is a measure of the extent of complete oxidation of the foreign molecule (Bartha and Pramer, 1965). CO₂ can be determined also directly in the gas leaving the test apparatus by gas chromatography; this method is preferred when other gases are to be determined simultaneously. Similarly, in anaerobic degradation tests, the extent of anaerobic degradation is estimated from the formation of anaerobic end products of metabolism; these may be determined by gas chromatography (e.g., methane; Wagner and Bräutigam, 1982) or trapped, e.g. H₂S in 0.1 M CuCl₂ in 0.3 M HCl (Attaway et al., 1982a). However, since in such experiments the origin of the gases formed is not known, the tests do not give accurate quantitative data on the production of the gas exclusively from the chemical in question; furthermore, the methods are not applicable to low chemical concentrations. In order to measure carbon dioxide or methane originating exclusively from the foreign compound as separated from that formed by degradation of normal organic nutrients, labelling with ¹⁴C is indispensable. ¹⁴CO₂ is trapped like unlabelled CO₂ and determined quantitatively by radioactivity counting. However, also in this kind of testing caution in interpretation of results is appropriate since the amount of free ¹⁴CO₂ formed does not always represent the total portion of chemical mineralized as part of the ¹⁴CO₂ formed can be reassimilated to natural mostly high-molecular and unextractable compounds. It is very difficult to distinguish these compounds from other unextractable chemical residues containing the foreign compound molecule or its conversion products. Thus, ¹⁴CO₂ evolved from ¹⁴C-labelled chemicals should be regarded as a minimum estimate of total degradation and as an absolute measure of total degradation only if the portion of unextractable or unidentified ¹⁴C is minimal.

Closed incubation systems have been described in which the radioactive carbon dioxide evolved is trapped within the incubation vessel by cups containing, for example, aqueous alkali (Herbes and Schwall, 1978, Sudhakar-Barik and Sethunathan, 1978b; Herbes, 1981), or by filter paper soaked with aqueous alkali in a centre well (Lee and Ryan, 1979). These methods are suitable only for anaerobic degradation studies since sufficient
oxygen supply cannot be guaranteed for long periods. Furthermore, there is the possibility of adsorption of radioactive volatile organic chemicals in the carbon dioxide trapping liquids, which may be misinterpreted as radioactive carbon dioxide. The use of sterilized blanks is not sufficient to eliminate potential errors of this kind since not only the unchanged parent compound but also volatile metabolites may be absorbed in the carbon dioxide traps. These difficulties may be overcome by using biometer flasks similar to those used for soil by Bartha and Pramer (1965), inserted in an aeration train. Extraction of the aqueous alkali containing $^{14}CO_2$ by n-hexane (MacRae et al., 1967) results in the removal of organic compounds carried over in the air-stream only if they are highly lipophilic and thus partitioned quantitatively into hexane. The best method to determine organic volatiles and carbon dioxide separately is connecting the flask not only to separate traps for carbon dioxide but also to preceding traps for volatile organics. The latter trapping compounds can be Chromosorb W-HP coated with OV-225 (Johnson and Lulves, 1975), toluene (Miyazaki et al., 1975), or ethylene glycol monomethylether (Vockel, 1981); absorbents as used in soil studies may also be suitable (polyurethane foam plugs, Kearney and Kontson, 1976; Murthy and Kaufman, 1978; sulphuric acid and silica gel coated with polyethylene, Süß and Eben, 1978). As absorbents for carbon dioxide, aqueous sodium or potassium hydroxide are most commonly used, but organic bases like monoethanolamine-ethylene glycol (Johnson and Lulves, 1975) or monoethanolamine-2-methoxyethanol (Miyazaki et al., 1975) have been reported to be applicable trapping solutions. If liquid scintillation cocktails are used, their radioactivity can be determined directly without taking aliquots, resulting in much lower limits of detection (Vockel, 1981; reported for soils but suitable also for sediments: Marinucci and Bartha, 1979).

The best method to distinguish clearly between aerobic and anaerobic degradation is to keep the incubating mixtures under air/oxygen or under nitrogen, respectively. In order to facilitate continuous shaking of the mixtures, trapping of volatile organics as well as carbon dioxide is not performed continuously but is accomplished by flushing at appropriate time intervals (Vockel, 1981).

For the determination of $^{14}$C-labelled gaseous anaerobic degradation products, Nelson and Zeikus (1974) have developed a method for the simultaneous analysis of $^{14}$CH$_4$ and $^{14}$CO$_2$. Both gases as well as H$_2$ were separated by a gas chromatographic procedure on a Carbosieve B column and detected by thermal conductivity. Detector effluents were channelled into a gas proportional counter for measurement of radioactivity. This method was more rapid, sensitive, and convenient than gas chromatography-liquid scintillation techniques.

It is surprising that only very limited information is available on the testing of reactions of environmental chemicals with hydrogen sulphide which is
evolved in anaerobic biological systems. Wahid and Sethunathan (1979) bubbled hydrogen sulphide evolved from reactions between sodium sulphide and dilute hydrochloric acid through a solution of aminoparathion in acetone-containing water and then extracted and identified the reaction product. This very simple test procedure should be applied to more environmental chemicals.

Information obtained in all of the single factor laboratory tests discussed here can be confirmed and integrated into the overall patterns of environmental behaviour by studies in laboratory model ecosystems and/or by field tests.

### 3.2.5 LABORATORY MODEL ECOSYSTEMS

Aquatic laboratory model ecosystems are discussed in Sections 3.1 and 4. In this section, only those ecosystems containing sediments will be considered.

Most of the laboratory model ecosystems reported aim at assessing the transfer of chemicals to aquatic organisms; however, in principle, all factors studied in separated laboratory tests, for example adsorption/desorption of chemicals, remobilization and accumulation, distribution within the sediment, chemical and biochemical processes, etc., can be studied in microcosms. The influence of interactions between the members of the ecosystems on these processes therefore would be included in the results. Furthermore, model ecosystem tests point out the importance of the sediments and of the testing of physical and chemical processes in sediments to the understanding of the dynamics of the total system.

In the simpler model ecosystems, the chemical to be tested is adsorbed on soil or sand, added to open aquaria, and flooded with water; aquatic animals of different trophic levels, for example algae, snails, daphnia, and fish are put into the water. The aim of these studies, in general, is to investigate, via desorption phenomena, the transfer and accumulation of sediment-associated chemicals in organisms (Isensee et al., 1976; Kearney et al., 1977; Ambrosi et al., 1978).

A more complex model ecosystem was reported by Titus et al. (1980). In order to assess transport and migration processes in the sediment in more detail, the authors used a stratified sediment bed consisting of sand, potting soil, river mud, potting soil, sand, aquarium gravel and aquarium pebbles. Mercury was introduced in the mud layer, and the time course of its distribution between sediment sites and three animal species—two snails and one fish—was recorded.

A three-phase aquatic microcosm to assess fates and impacts of chemicals in microbial communities was reported by Porcella et al. (1982). The three phases under investigation were sediment, water and gas phase. Mass balances of chemicals introduced can be established with this system as can
the mass balances of critical system-level variables, thus indicating microcosm response to introduced chemicals. Gas dynamics were shown to be most sensitive to stress in this aquatic model ecosystem.

Mixed terrestrial-aquatic model ecosystems have been designed to assess movement, accumulation and degradation, mainly of chemicals applied to crops (Metcalf et al., 1971; Metcalf, 1974; Lichtenstein et al., 1978; Liang and Lichtenstein, 1980; Virtanen et al., 1980). The models include a terrestrial component which is fallow or covered with crop plants, a terrestrial-aquatic interface, and an aquatic portion including water, sediment, aquatic plants, and animals of various trophic levels. Simulated rain delivered occasionally to the terrestrial part results in soil run-off which is channelled into the aquatic compartment with its layer of lake bottom mud and its animal and plant inhabitants (Lichtenstein et al., 1978; Liang and Lichtenstein, 1980). Besides this transport of chemical from the terrestrial to the aquatic part of the system, the transport via food chain interactions (for example, crop plant → insect larvae / algae → snail / diatoms → plankton → mosquito larvae → fish) has also been studied (Metcalf et al., 1971; Metcalf, 1974). In addition to providing a wealth of information on the individual chemicals studied, material balances obtained with these models reveal that soil and sediments may be the main contributors to regulating the fate of the chemical in the model, a fact that may be extrapolated to the real environment (Virtanen et al., 1980).

3.2.6 FIELD TESTS

Only a limited number of field tests for investigating the fate of chemicals in sediments have been reported. Since these are complex and expensive, they cannot be recommended as standard screening procedures for a large number of chemicals, but they are indispensable in evaluating the extrapolation of laboratory test data to predict environmental behaviour. Most information is available on application of chemicals to small ponds. Submerged chambers and enclosures have also been used.

In pond tests, the chemical under investigation is applied to the water. The concentration in sediments is monitored as well as that in water, during a certain time period; bioaccumulation data is included in the analysis. Whereas experiments with unlabelled chemicals (Rice et al., 1974; Mauck et al., 1976; Gasith and Perry, 1980) give information only on the accumulation and persistence of the parent compound and well-known, easily detectable metabolites, experiments with radiotracer chemicals (Salonen and Vaaajakorpi, 1974; Krieger, 1981; Schauerte et al., 1982a) can provide data which will include all conversion products containing the labelled carbon. In such experiments, it was found that radioactive residues, derived from the chemical applied, persist for long time periods in sediments, even when
residues in water are no longer detectable. From this residual source, chemicals are redistributed into organisms where their accumulation shows a time–course curve similar to a damped oscillation (Krieger, 1981; Schauerte et al., 1982a). This is true not only for persistent lipophilic chemicals but even for the hydrophilic biodegradable detergent n-dodecylbenzene sulphonate (Krieger, 1981). This fact confirms the eminent importance of sediments as a depot and source for redistribution of chemicals in the environment, and thus, the importance of development of all kinds of sediment tests. Instead of treating a whole pond with the chemical, PVC-compartments embedded into the pond sediment may be treated with the chemical (Schauerte et al., 1982b). Although such compartments have been used primarily to study effects of chemicals on the aquatic biota, they may be used to study physical, chemical and biochemical reactions in sediments as well. In studies on the fate of chemicals in sediments, it should be considered that persistence in such enclosure is enhanced due to decreased volatilization as a consequence of decreased water turbulence.

Since the physico-chemical as well as ecological situation in small ponds is quite different from that in larger water bodies, the results obtained in small pond tests cannot be extrapolated to lakes or to marine systems. For these water bodies, enclosures have to be used. Sonzogni et al. (1977) used large submerged chambers to measure in situ sediment–water interactions. The cylindrical chamber, sealed at one end, is constructed of opaque PVC material and is embedded in the lake bottom, entrapping about 1.2 m³ of water above 1 m³ of sediment. The chambers were designed to study sediment phosphorous release and would be suitable also to study the behaviour of organic chemicals in sediments.

Polyethylene enclosures were suspended in Saanich Inlet, Canada (Lee et al., 1978). Polycyclic aromatic hydrocarbons dissolved in crude oil were added to the water. Radioactive labelled benzo (a)-pyrene was also applied. Concentrations of aromatics were determined in water, zooplankton, oysters, and bottom sediments. It was shown that sedimentation and photochemical oxidation were primarily responsible for the decrease in concentrations of the higher weight aromatics. Similarly, fibreglass boxes divided into three equal compartments, each with bottoms of fibreglass screens, were inserted into the sediment in the intertidal zone of Sequim Bay (Roesijadi et al., 1978a).

3.2.7 CONCLUSIONS

The results of laboratory tests reported thus far on adsorption/desorption, remobilization and bioaccumulation of chemicals in sediments reveal that sediments play a key role in the distribution of chemicals in the aquatic environment. This key position is confirmed by laboratory model ecosystem data as well as by field test data reported. In view of this importance, the level
of test technology and data interpretation is not appropriate. There exist no standardized and internationally recognized test procedures for any physical or chemical process related to sediments. An OECD adsorption/desorption test designed for soil and OECD biodegradation tests designed for water can, with certain variations, be applied to sediments. The same considerations apply to the testing of volatility of chemicals from sediments via the aqueous phase. Apart from the problem of standardization of test material, which exists also for soils, the test methods for adsorption/desorption and remobilization/bioaccumulation have been better elaborated thus far than those for other parameters. The OECD test for adsorption/desorption and available tests for volatility should be adapted to sediments and then standardized. Similarly, for the accumulation and remobilization of chemicals from sediments due to the activity of organisms such as worms, standard tests should be developed.

For some of the chemical and biochemical processes and interactions in sediments, as discussed in Sections 3.2.3 and 3.2.4, which have enormous importance in determining the final global fate of chemicals, there exist only sporadic experimental data for individual chemicals, which has not been extended to other chemical groups to form generally applicable test methodologies. The relevance of reported test data to predict the environmental behaviour of chemicals in natural sediments has been examined only in a few cases by means of field studies. Therefore, laboratory tests as well as field studies should be improved as a further step towards the understanding of the role of sediments in the environmental behaviour of chemicals.

### 3.2.8 REFERENCES


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