Pesticide bioavailability in aquatic sediments
– a literature review

by

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Introduction

In our present world, the environment and all living organisms are exposed to many different kinds of chemicals originating from i.e. chemical industry, pharmaceutics, building industry, and the agricultural use of pesticides. In the USA alone, 2.7 trillion kg of industrial chemicals are produced or imported each year, and 72 000 different chemicals circulate through the USA economy (Inform 1995). Pesticides are used to control organisms occurring on agricultural products and crops and serve to protect plants, animals, and humans. World-wide, an estimated 2.3 billion kg of 1600 different pesticides are applied yearly (Pimentel 1995). In Europe, the total agricultural use of pesticides is estimated to be 350 000 tons of active ingredients per year (1996) (Kreuger 1999).

Many pesticides are organic and have hydrophobic properties. These hydrophobic contaminants tend to bind to suspended particulate matter and to accumulate in the bottom sediments of lakes and seas, once entered to the water ecosystems (Leppänen 1995). In this condition contaminants tend to be less degradable. Conversely, more hydrophilic, dissolved organic molecules, are more accessible to light, other dissolved chemicals and microorganisms compared to sorbed molecules, why the latter are degraded slower (Schwarzenbach *et al.* 1993). Organochlorine pesticides have been detected in aquatic sediments and organism tissues many years after a ban and usage stop of that particular pesticide in one country, due to both their persistence as well as dispersal from other countries where these compounds are still in use (Bernes 1998). Currently used pesticides (CUP) should be more readily degradable and less harmful to nontarget organisms and have therefore to a large extent replaced the first generation of persistent halogenated pesticides. Yet, even though bioaccumulation of modern pesticides is lower, these compounds are frequently found in aquatic environments at concentrations at which ecotoxicological effects can be expected (Kylin *et al.* 1998). The extensive use of pesticides as well as their relatively high persistence in aquatic sediments may result in high concentrations of pesticides, especially in intensive agricultural areas.

The hydrophobic properties of the compounds also make them accumulate in aquatic biota, which is more hydrophobic than the surrounding water. Benthic macro-invertebrates may take up environmental pollutants via several different routes, e.g. overlying water, interstitial water and sediment particles (Conrad *et al.* 1999), (Leppänen 1995). Sediment-dwelling animals therefore have a greater risk of accumulating toxic substances than pelagic animals, because they are exposed to all possible accumulation routes (Leppänen 1995). Sharpe and Mackay (2000) estimates that benthic organisms attain about 95% of their accumulated contaminant from the sediment. However, researchers argue about the relative importance of the possible uptake routes, through the gills/epidermis from pore water or via ingestion of contaminated food. Regardless of uptake route, the impact of environmental contaminants on benthic invertebrates is important to assess, since these organisms are functionally important in transferring environmental contaminants to higher trophic levels (fish, waterfowl, humans), and play a key role in sediment energy, nutrient and contaminant fluxes.

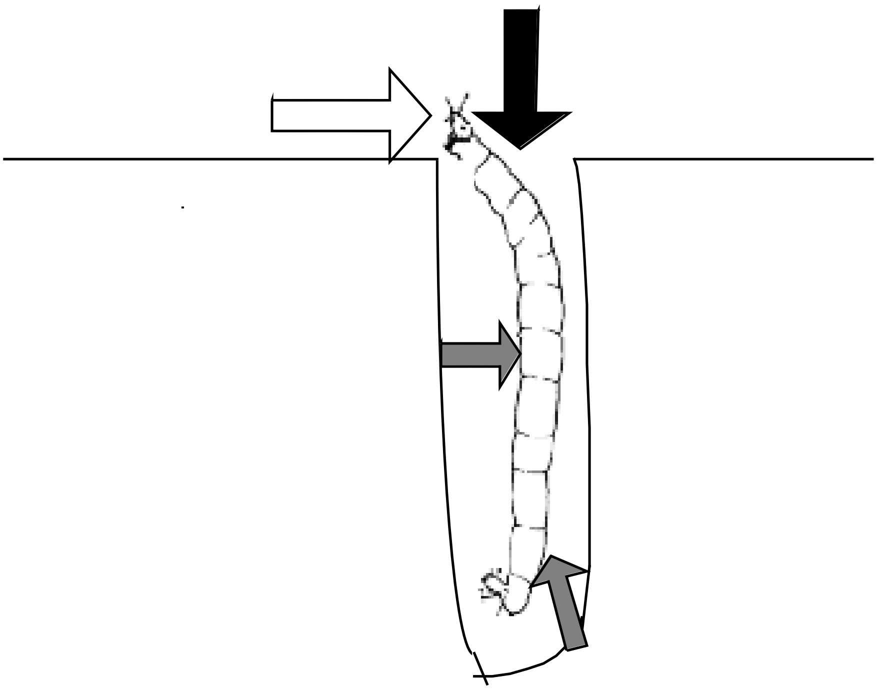

Fig 1. *Chironomid larvae in sediment being exposed to contaminant from three routes; overlaying water (black arrow), pore water (striped arrows) and via ingestion of sediment particles (white arrow).*

High concentrations of toxic compounds in sediments may not necessarily lead to adverse effects on organisms living in the sediment (Burton 1992). Suffet *et al.* (1994) found no relationship between sediment chemical concentration (total dry weight basis) and biological effects. The key to this is bioavailability. Ingested particle-associated contaminants may not be bioavailable due to their tight associations with particles. For example, pesticides associated with humic coatings may be largely unavailable for consumer animals due to the strong binding (Decho and Luoma 1994), (Kukkonen and Oikari 1991), (Freidig *et al.* 1998). Conversely, pesticides associated with easily available food sources (higher digestibility) may be readily incorporated into consumer biomass (Gunnarsson *et al.* 1999a), (Schlekat *et al.* 2000), (Dabrowska *et al.* 1999).

Microbial exopolymers, or EPS (extracellular polymeric substances), are secreted by many microorganisms in aquatic habitats, in the form of e.g. slime or mucus into the surrounding environment (Underwood *et al.* 1995), creating what is commonly known as biofilms. EPS is a comprehensive term used for the different classes of organic macromolecules such as polysaccharides, proteins, nucleic acids, phospholipids and other polymeric compounds, which have been found to occur in the intercellular spaces of microbial aggregates (Wingender *et al.* 1999). The notion that EPS could affect both bioavailability and further transfer of contaminants in the aquatic food chain has recently been recognised (Selck *et al.* 1999), (Schlekat *et al.* 2000). Bacterial communities have been shown to bioconcentrate pesticides (herbicide diclofop methyl, Wolfaardt *et al.* 1994), (chlorinated hydrocarbon insecticides, Grimes and Morrison 1975), (atrazine, Geller 1979) and mucous secretions of other origin (burrow linings of polychaetes) are an ideal sorption matrix for organic contaminants (e.g. TCB) (Gunnarsson *et al.* 1999b). Furthermore, many benthic invertebrates can efficiently use the EPS as a carbon source (Schlekat *et al.* 2000), (Decho and Moriarty 1990), (Baird and Thistle 1986). Considering this, it has therefore been suggested that EPS might act as a vector for contaminant uptake into aquatic food webs. This might be a crucial step for bioaccumulation, because in recent years, several researchers have recognized the importance of trophic transfer for bioaccumulation of contaminants (Landrum and Fisher 1998), (Forbes *et al.* 1998), (Loonen *et al.* 1997) compared to bioconcentration from water which was previously considered to be the dominant pathway (Connell 1988), (Barron 1990). To a first approximation, the bioaccumulation process is seen as a simple partition process between pore water and the benthic fauna (Loonen *et al.* 1997). The mechanisms that govern bioavailability and subsequent bioaccumulation and biomagnification, however, are quite complex.

In this paper I review the current state of knowledge on organic contaminant bioavailability in sediments. In particular, the role of microbial exopolymers as a vector for contaminants to enter the aquatic food webs is addressed. Since more work has been done on bioavailability and bioaccumulation of substances in water compared to in sediments, some general mechanisms and principles are described from the latter area. These processes are comparable to contaminant uptake from pore water, which is important in sediment exposures. In addition, since most pesticides are organic molecules I will refer to them in the more general term "organic contaminants" to avoid misinterpretations.

Accumulation processes

The uptake routes of pollutants in aquatic organisms are through the epidermis, through the gill epithelium and through the gastrointestinal tract, following ingestion (Swartz and Lee 1980). In all these cases, pollutants must pass through a number of biological membranes to become assimilated. The properties of both membranes and the toxic compounds are important factors controlling the uptake. Some compounds, mainly small and lipid-soluble, are taken up by passive diffusion, which does not require any energy from the organism. Distribution systems within the organism (body fluids) help to maintain the concentration gradient across biological membranes until all compartments (e.g. brain, liver and muscle tissue) within the organism are at steady state. The term fugacity is used to describe the concept of compounds moving between compartments, down chemical activity gradients until the chemical activities are equal. This concept has been used to estimate contaminant concentration in different compartments and to explain processes such as biomagnification (will be discussed later) in aquatic food webs (Campfens and MacKay 1997). Accumulation of compounds by passive diffusion is often proportional to the rate of metabolism and is affected by nutritional state, size, and age of the animal, as well as the temperature of the surrounding water. Some metals and organic molecules, such as glucose, require a carrier molecule, but are still passively transported across membranes. In this case, rates of accumulation typically exhibit saturation kinetics, because of limited numbers of carrier molecules. Other substances, e.g. heavy metals, are actively transported into the organism, which is an energy requiring process.

Bioavailability, bioconcentration, bioaccumulation and biomagnification

The **bioavailable** fraction of a compound is the part of the total amount of a particular compound in a medium that is available to be taken up and become incorporated into living tissue. In sediments, typically between 16-50% of the contaminant is bioavailable depending on the compound, characteristics of the sediment, and which deposit-feeding invertebrate that is used in the study (Lamoureux and Brownawell 1999). Factors influencing contaminant bioavailability are discussed later.

Bioconcentration is the accumulation of freely dissolved contaminant in water by aquatic organisms through nondietary routes (Bacci 1994). In water-only exposures, the primary route of uptake of dissolved contaminants in fish is across the gill epithelium, but depending on the compound and animal body size, a substantial part of the body burden (25-40%) may penetrate across the epidermis (Landrum *et al.* 1996). In many cases, the toxicokinetic behaviour of organic contaminants in aquatic organisms can be described by a first-order, one-compartment model. The degree of bioconcentration at steady state, represented by the bioconcentration factor (BCF), depend both on the rate of absorption and the rate of elimination:

$$BCF= k_1/k_2=C_a/C_w$$

where k_1 is the uptake clearance (e.g. ml/(g organism*h)), k_2 is the elimination rate constant for the compound (e.g. l/h), C_a is the concentration in the organism at steady state, and C_w is the concentration in water at steady state. Using the freely dissolved water concentration and assuming no biotransformation, this BCF represents the relative solubility of the compound in water versus the organism’s tissue. Biotransformation processes and active elimination can reduce the BCF. The steady state condition represents the maximal accumulation that can be attained for a given set of exposure conditions (Landrum *et al.* 1996). However, conditions may change so rapidly that steady state may not be attained except under controlled conditions, a problem that makes actual bioconcentration difficult to predict. The mechanism of bioconcentration from water is comparable to the uptake mechanisms of contaminants from pore water, why this mechanism is relevant also for sediment exposures.

Partition coefficients are used to describe the distribution of nonpolar organic compounds between water and natural solids (e.g. soils, sediments, and suspended particles) or organisms. It can be viewed as a partitioning process between the aqueous phase and the bulk organic matter present in natural solids or in biota (Schwarzenbach *et al.* 1993). The premise behind the use of equilibrium models is that accumulation of compounds is dominated by their relative solubility in water and the solid phases, respectively. Equilibrium models therefore, rely on the following assumptions (Landrum *et al.* 1996);

- the compounds are not actively biotransformed or degraded,
- there are no active (energy-requiring) processes dominating the distribution,
- the conditions are sufficiently stable for a quasi-equilibrium to occur,
- environmental factors, such as temperature, do not change sufficiently to alter the equilibrium conditions and
- organism and/or organic matter composition is not sufficiently variable to alter the distribution .

A commonly used partition coefficient is the 1-octanol/water partition coefficient, K_{ow}, which is the ratio of a chemical's concentration in 1-octanol to its concentration in water at equilibrium in a closed system composed of octanol and water (Bacci 1994). The 1-octanol is chosen to mimic biological lipids. For organic chemicals, log K_{ow} ranges from –3 to 7. When log K_{ow} exceeds 2, substances are considered hydrophobic (Elzerman and Coates 1987). The K_{ow} partition coefficient has been extensively used as an estimate of the bioconcentration factor (BCF). According to Paasivirta (1991) the BCF can be calculated by the use of:

$$BCF=0.048*K_{ow}$$

but this equation can vary depending on the species used. The relationship between log K_{ow} and BCF can be viewed by a linear regression analysis (fig 2). These regressions show a clear relationship for many compounds and over a broad range of log K_{ow}, but there are also several discrepancies. In general, there is a good linear relation between log BCF and log K_{ow} for low or moderately hydrophobic compounds (log K_{ow} 3-6) but this relation breaks down for strongly hydrophobic compounds (log K_{ow} >6) (Hawker and Connell 1986), (Landrum *et al.* 1996). Hawker and Connell (1986) argue that the lack of linear relationship for these strongly hydrophobic compounds depends on the fact that the time needed to reach equilibrium is generally longer than the exposure time.

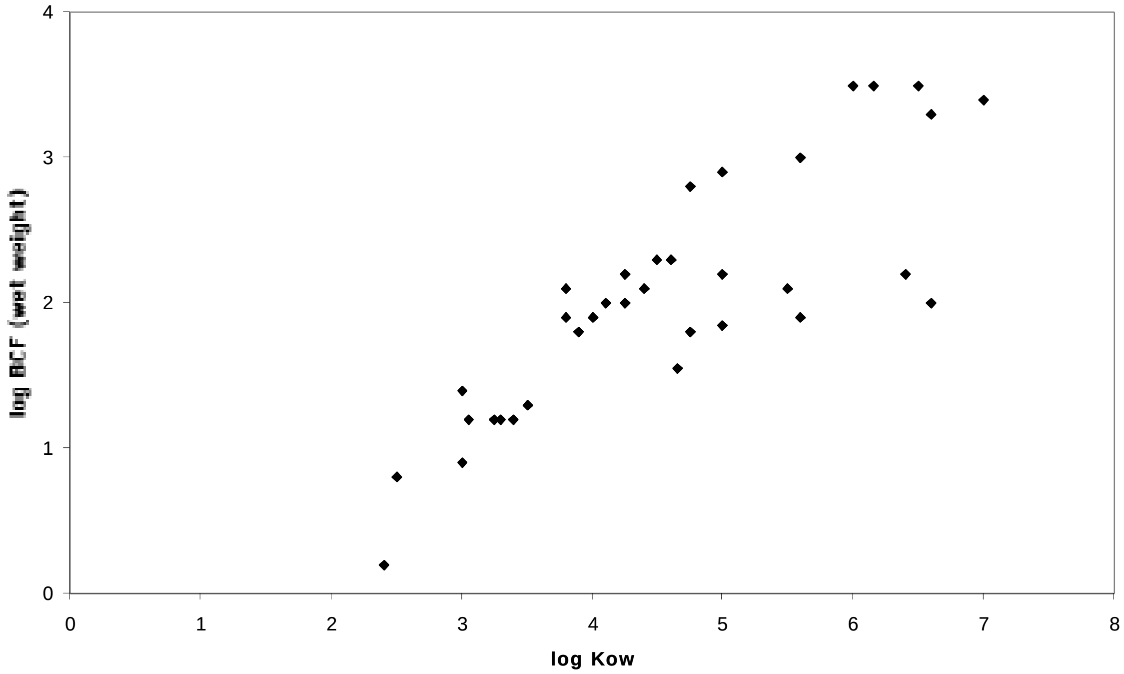

Fig 2. *Plots of log BCF- versus log K_{ow}-values, showing the lack of linear relationship for very hydrophobic compounds. Modified from de Wolf et al. (1992) and Barron (1990).*

The maximal observed value for log BCF is acquired for compounds having a log K_{ow} between 5 and 6 (Landrum 1989, Landrum 1996). Recently even a negative linear relationship between BSAF (biota-sediment accumulation factor) and log K_{ow} was demonstrated for very hydrophobic PCBs (log K_{ow}>6.7) (Maruya and Lee 1998) (fig. 3). This negative relationship is thought to be due to difficulty of the relatively large molecules to penetrate membranes because of diffusion and blood flow rate limitations. In addition, it has become evident that 1-octanol is not an ideal solvent for larger molecules (Landrum and Fisher 1998). The equilibration model has been criticised for its fundamental assumptions of negligible metabolism, lack of steric hindrance, and ignorance of the importance of blood flow in controlling uptake, distribution, and elimination. The factor determining uptake of some compounds appears to be molecular size, rather than molecular weight, why steric hindrance might be of importance for the transfer between water and organism (Barron 1990), (Landrum *et al.* 1996).

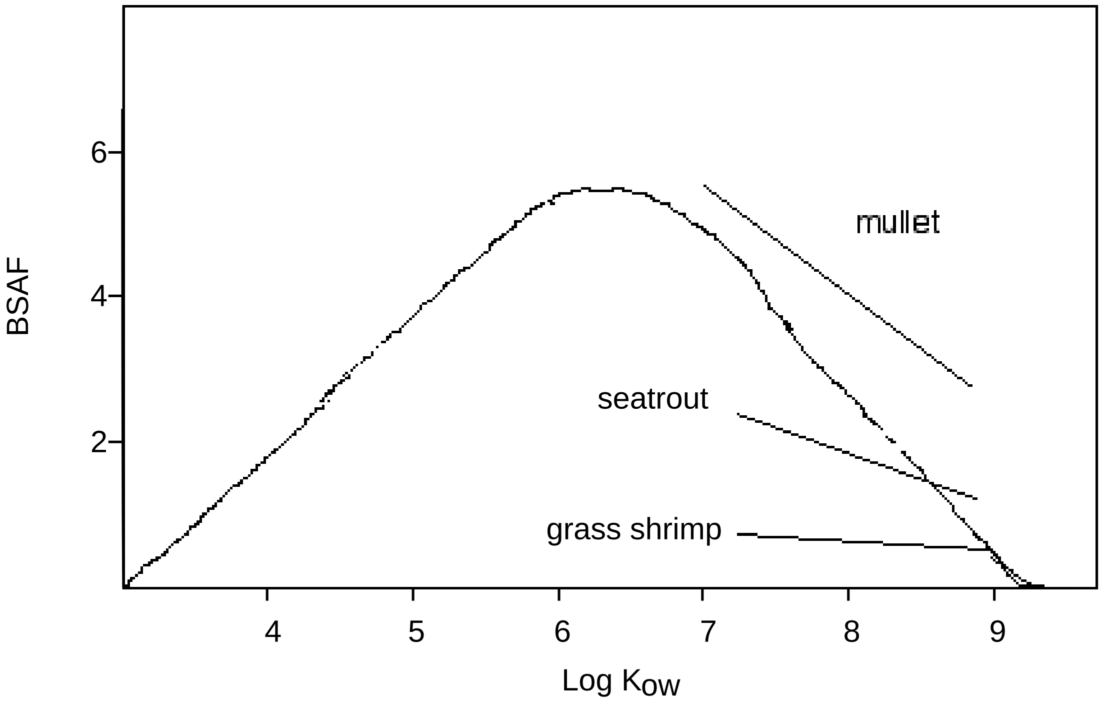

Fig 3. *Schematic presentation of the relationship between log* K_{ow} *and biota-sediment accumulation factor (BSAF) for some very hydrophobic PCBs. The curved line indicates model predictions from other studies, and the straight lines indicate data from a few model organisms. Modified from Maruya and Lee (1998).*

Bioaccumulation means the uptake of a chemical (e.g. pesticide) by a living organism by means of all possible routes, for example contact, respiratory surfaces, and ingestion (Bacci 1994). A persistent compound is accumulated in the organism tissue if the degradation and elimination processes are slower than the uptake rate, and the concentration in the tissue thus becomes higher than in the surrounding media. The term **biomagnification** refers to an increase in the concentration of a substance along the food chain, i.e. predators have higher tissue levels of the contaminant than their prey. Hence, biomagnification can be considered a special case of trophic transfer. The issue of biomagnification has been controversial for many years and some researchers claim that what is misinterpreted as biomagnification is, in fact, simply bioconcentration (Leblanc 1995). Other researchers argue that biomagnification only occurs in air-breathing organisms (such as birds and seals), that feed on aquatic organisms, but have no direct contact through their respiratory surfaces with the water mass and therefore can not be subject to bioconcentration (Connell 1988). Personally, I agree with other researchers that have found that biomagnification actually exist in some systems with special properties. In a review of hundreds of studies on biomagnification, Suedel *et al.* (1994) concluded that biomagnification is possible with a small, but important group of highly hydrophobic (log Kow>5) nonmetabolized contaminants that include DDT, DDE, PCBs, toxaphene, and organic forms of mercury and arsenic. Suedel (1994) points out that data on the potential for thousands of organic contaminants to biomagnify in aquatic systems are lacking, especially for those compounds that are not hypothesized to readily biomagnify. Therefore, conclusions regarding their potential to biomagnify cannot be drawn until such data are available.

The distribution of contaminants in the aquatic environment depends on their characteristics, i.e. water solubility, molecular size and persistence. This will determine the bioavailability of the contaminant and depends on the characteristics of the interactions between the organism and phases into which the contaminant is distributed. The accumulation of a contaminant in an organism depends on the rate of exposure, the rate of distribution within the organism, and the characteristics of the tissues (e.g. lipid content) and is balanced by biotransformation and elimination processes to yield the net accumulation.

Lipid content of aquatic organisms is an important factor determining the bioaccumulation of organic contaminants (Landrum and Fisher 1998). Once a contaminant has entered an organism it can have many different fates. If a contaminant enters the body by passive diffusion, it can diffuse back to the water and thus become eliminated. It can also be metabolised by the organism and then be eliminated through the normal excretion routes. If the organic contaminant is not eliminated, it is transported by the blood or lymph system to eventually become deposited in lipid-rich organs, such as the liver. Highly hydrophobic toxic substances can be sequestered in lipid stores for a long time without harming the organisms, since they are kept away from receptors that mediate the toxic action. However, if the organism is suffering from stress and starvation, the lipid storage might be utilised and the contaminants are released back to the general circulation. The size and also composition of the lipid stores can dictate the accumulation capacities by different species and organisms. Organisms with a high lipid content exhibit slower elimination rates than leaner ones (Landrum and Fisher 1998), (Dabrowska *et al.* 1999), which could explain higher contaminant concentrations in older and larger organisms. Lipids have also been suggested to be the driving force behind trophic transfer of hydrophobic contaminants (Gobas *et al.* 1989). The mechanisms for this are outlined by Landrum and Fisher (1998) in the following way. When contaminated food is ingested by an organism, the contaminant moves into the gastrointestinal tract in association with lipids. Once in the gut, digestion begins. Lipids are dissociated from the bulk of ingested material and transported across the gut wall via specific lipoprotein carriers. Two hypotheses for contaminant transfer can be formulated: (1) the contaminants may stay associated with the lipid material and move actively with them, and (2) the contaminants are left behind while the lipids are digested and absorbed. The latter alternative has two important consequences: (1) there is a smaller food volume remaining in the gut, which momentarily increases the contaminant concentration, and (2) the food remaining in the gut has lost part of the lipid component that sequestered contaminants. This in turn increases the fugacity of the contaminant in the food relative to the organism and the contaminant can diffuse passively across the gut wall into the organism. Thus, net transfer of the contaminant between predator and prey becomes possible, although they appear to be at equal fugacity with respect to the contaminant.

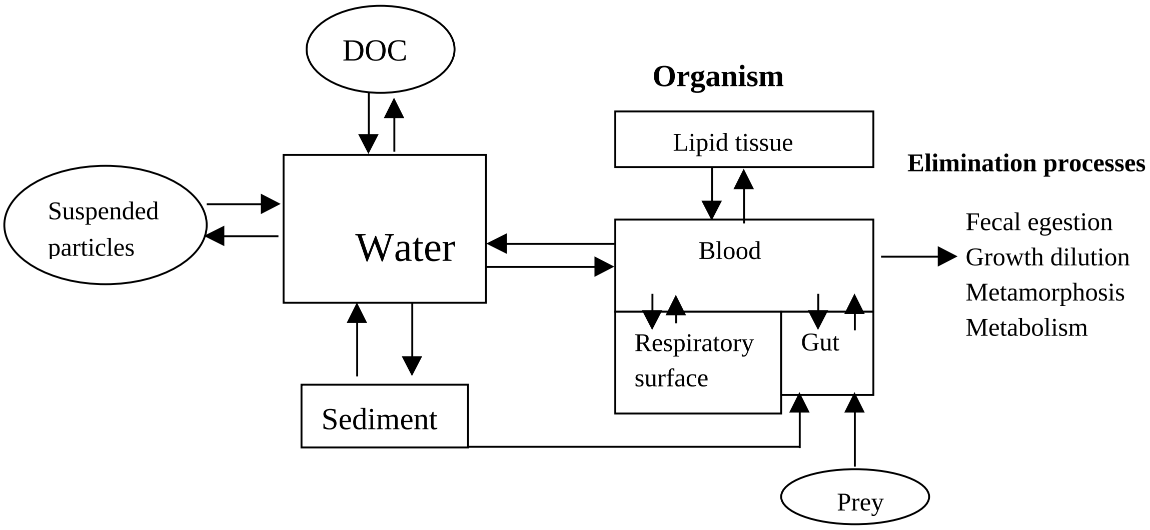

Fig 4. *Schematic illustration of contaminant distribution in the aquatic environment and uptake and elimination in aquatic organisms (modified from Landrum,1998).*

Differences in bioavailability between water and sediment exposures

Factors affecting the uptake of pesticides/contaminants from sediments and water are shown in table 1.

Table 1. *Factors affecting bioavailability of organic contaminants in aquatic systems (from Landrum et al. 1996).*

Factors affecting bioavailability in aqueous exposures	Factors affecting bioavailability in sediment exposures
Dissolved organic material (DOM): Concentration of DOM Molecular structure of DOM	Total organic carbon (TOC): Concentration of TOC TOC composition
pH of exposure media	Sediment particle-size distribution
pKa of contaminant	Organism lipid content
Co-contaminants	Sorption/desorption from particles
Temperature	DOM and colloid conc. in interstitial water
Organism elimination processes	Organism feeding behaviour and life history
	Contaminant physical/chemical characteristics Octanol/water solubility Contaminant concentration

In sediments, a number of physical, chemical and biological factors affect the bioavailability of organic contaminants associated with sediments. Consequently, the exposure and bioavailability of organic contaminants in sediment is difficult to predict. The variability in prediction of contaminant accumulation, using log K_{ow}, is markedly higher for exposure via sediment than for aqueous exposure (Landrum and Fisher 1998). The reason for this is that the organic matrix of the sediment is competing with the organisms lipids for the relative solubility of the contaminant. To overcome this uncertainty in prediction, a model using biota-sediment accumulation factors (BSAF) has been developed. In this model, the lipid-normalised contaminant concentration in the organism is divided by the carbon-normalised concentration in the sediment resulting in a BSAF that is independent of the compound's log K_{ow}. In their review Landrum and Fisher (1998) report of studies that have quantified BSAF among organisms and sediments, in which the variance can exceed 100-fold between the lowest and highest values even for the same contaminant. Spacie (1994) showed that equilibration time between contaminant and sediment particles increases with increasing log K_{ow} and particle size, and may take considerable time in some conditions. Therefore there might probably be a lack of true equilibrium or steady state in any experiment, which obstructs the interpretation of the obtained accumulation factors.

Furthermore, bioavailability is not necessarily identical for contaminants of similar hydrophobicity in the same sediment (Landrum and Fisher 1998). One explanation for this could be differences in the distribution of contaminants among the different types of particles in the sediment (Harkey *et al.* 1994). Several researchers have shown that organic contaminants preferentially sorb to small and organic rich particles. For example, Weston *et al.* (2000) found that benzo[a]pyrene (BaP) concentrations in the fine-grained material (<63µm) were 5-8 times higher than in the bulk sediment. Similarly, Kukkonen and Landrum (1996) demonstrated that about 60-70% of the mass of BaP and hexachlorobiphenyl (HCBP) was associated with sediment particles in the 63µm to 31µm range. The results show that the estimation of bioavailability and bioaccumulation of contaminants from sediments is highly complex. The relationship between concentration of contaminants in sediment and bioaccumulation is not linear even when normalised for organic carbon and lipid, and additional factors are probably required to make better predictions.

Factors affecting bioavailability

Bioavailability of sediment-associated contaminants is affected by a number of **physical factors**. Any force that alters the chemical structure, physical properties or concentration of a contaminant might change its bioavailability. For example, UV-light (290-400nm) can penetrate the water column to a depth of many meters and may reach sediment surfaces where it can affect bioavailability (Crosby 1994). Duxbury *et al.* (1997) showed that the BCF values of polycyclic aromatic hydrocarbons (PAHs) to *Lemna gibba* were significantly lower under simulated solar radiation compared to exposures in the dark. This is suggested to be due to a photo-modification of the PAHs that results in more polar and water soluble compounds.

UV energy must be absorbed for chemical change to occur. This absorption can be either "direct" photodegradation, when the energy is absorbed directly by the compound that is degraded, or sensitized, when the energy is first absorbed by another compound, followed by a transfer of energy to the substrate (Crosby 1994). Soluble humic and fulvic acids are among the most important aquatic photo-sensitizers (Crosby 1994), since these large, complex molecules effectively absorb UV-light of a wide range (Frimmel 1994; Schön 1997). It is therefore likely that photo-modification is especially important for bioavailability of contaminants in humic waters. In relation to bioavailability, photodegradation indeed can lower environmental concentrations of both contaminants and natural solutes. However, some photo-degradation products may be even more persistent and toxic than the original compound (Crosby 1994). Meyer *et al.* (1994) showed that in some aquatic systems, photoredox reactions could dominate degradation of xenobiotics within the photic zone and the upper 1 mm of the sediment, especially for pesticides in shallow waters.

Despite the possible significance of photo-degradation for bioavailability, very little work has been reported on sediment photochemistry.

Among the more important **chemical factors** affecting bioavailability, the role of sorption kinetics needs greater attention in the future (Forbes *et al.* 1998). A particle-bound organic contaminant is not available for uptake until it becomes desorbed, either to the water or inside the animal gut. pH of the medium and pK_a of the contaminant strongly affects the toxicity and uptake of ionizable compounds (Landrum *et al.* 1996). For organic acid compounds, the neutral form generally partitions to sedimentary material to a greater extent than the corresponding anion. On the other hand, the cationic form of organic bases generally associates to sediment material to a greater extent than the corresponding neutral form (Suffet *et al.* 1994). Also salinity of the water can affect many chemical fate processes. One of the greatest differences between seawater and freshwater is that the composition and chemical properties of seawater is much more consistent than those of freshwater. Nevertheless, Knezovich (1994) concluded that, in general, marine and freshwater species appear to have the same sensitivity to organic contaminants. Results also indicate that the bioavailability of most contaminants is not appreciably different in seawater compared to freshwater (Knezovich 1994).

The occurrence of oxidizing compounds in the pore water of the sediments and the depth to which oxygen penetrates into the sediment determine the redox conditions within the surficial sediment (Sundby 1994). The redox conditions may affect the bioavailability of contaminants, especially trace metals.

Also the molecular size of a compound affects bioavailability. Some pesticide molecules can be unavailable due to a size that makes them too large for entering biotic membranes or an extreme hydrophobicity that obstructs them from penetrating through gills or the intestinal epithelium (Bernes 1998, Barron, 1990). For example, Pruell *et al.* (2000) demonstrated that highly chlorinated polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDD/Fs) were less bioavailable to polychaetes and lobsters than less chlorinated compounds. They suggested that this was due to stronger binding of PCDD/Fs to the sediment or restrictions of these larger molecules to pass cellular membranes.

The organic carbon content of the sediment influences the bioavailability of organic contaminants. Several studies have reported a trend toward higher bioavailability in sediments of low organic content (Spacie 1994), (Kukkonen and Oikari 1991). In an experiment with extractability of sediment-associated PAHs using digestive fluids from the polychaete *Arenicola* *brasiliensis* Weston and Mayer (1998b) showed that the proportions of solubilized contaminant were inversely related with sediment organic carbon content. However, not only the quantity of organic carbon in the sediment is important, but also its quality (Ewald 1995), (Harkey *et al.* 1994) (Gunnarsson *et al.* 1999a). For example, the bioavailability of organic contaminants is decreased in the presence of humic acids (Freidig *et al.* 1998), (Kukkonen and Oikari 1991) and the bioavailability of PAH is strongly reduced when these compounds are associated with soot particles compared to organic matter of other origin (Gustafsson *et al.* 1997). In addition, the bioavailability of organic contaminants in natural waters is inversely related with concentrations of dissolved organic matter (DOM) (Landrum *et al.* 1996). Suedel *et al.* (1993) found varying bioavailability of fluoranthene in different sediments with approximately the same organic carbon content and attributed this to varying concentrations of dissolved organic carbon (DOC) in the interstitial water. The presence of DOC in interstitial water in the form of dissolved humic and fulvic materials can bind or complex xenobiotic compounds, thereby reducing their bioavailability. It can be hard to distinguish if a material is actually dissolved or is in particular form, but it is nevertheless important for the understanding of future bioavailability and uptake of associated contaminants. Organic matter with an internal diameter of less than 0.1-1µm is considered dissolved or colloidal, while organic matter of larger diameters are referred to as particles (Gobas and Zhang 1994).

Conversely, mineral organic carbon forms such as coal may not affect chemical sorption and bioavailability in the same way as organic carbon does. Surface area, as well as molecular and physical structure of different forms of organic carbon may influence bioavailability (Suedel *et al.* 1993). Davies *et al.* (1999) concluded that the bioavailability of the biocide 2,4-dichlorophenol to larvae of the midge *Chironomus riparius* was greatest from particles of intermittent adsorption, e.g. particles with a hydrophobic surface that also allowed desorption once in the gut. Also, the lability of the organic matter is of major importance when considering the bioavailability of contaminants bound to sediments. Gunnarsson *et al.* (1999) showed that the accumulation of a PCB by a brittle star (*Amphiura filiformis*) was greatest when treated with the most labile organic substrate tested (green macroalga) and lowest when treated with the most refractory (lignins of terrestrial origin).

The two most important physicochemical factors controlling the deposition of both natural and contaminant organic matter are particle size (and its covariate surface area) and contaminant surface chemistry. The relatively small particles that mainly accumulate in muddy, organic-rich environments have relatively high surface area to volume ratios and thus more specific surface area for contaminant adsorption and/or binding (Forbes *et al.* 1998). Harkey (1994) showed that the 0-10µm- particle-size fraction contained the greatest percentage of total organic carbon (TOC), and also demonstrated that contaminants sorbed to these fine particles were not readily bioavailable. Consequently, there is a need to relate contaminant concentrations to organic carbon content when employing equilibrium partitioning models of bioavailability (Forbes *et al.* 1998).

Biological factors, such as feeding behavior, mobility, and individual differences affect contaminant bioavailability. Feeding, burrowing and irrigation activities of the organisms may strongly influence the total exposure, for example by changing the burrow water concentrations of organic contaminants to more closely resemble that of the overlying water (Forbes *et al.* 1998). The burrow tube itself alters the microenvironment of the organism by enhancing the microbial activity and adsorbing neutral organics (Meyer *et al.* 1994). Activities of benthic organisms can also increase the depth of the oxic zone, change the redox potential, move sequestered substances to the sediment surface, and affect transport of dissolved chemicals (Meyer *et al.* 1994).

There are also intra- and inter-species variations in BCF, which can depend on differences in body size and the body surface/volume-ratio (Barron 1990). The exchange processes between body and environment are relatively fast in small organisms with a low lipid content because of a relatively large surface/volume-ratio and an intensive blood circulation through the skin for oxygen uptake (Loonen *et al.* 1997). Also, early life stages that tend to have higher specific rates of feeding and metabolism in combination with greater specific surface areas, are at greater potential risk when exposed to a contaminant (Forbes *et al.* 1998). Differences between species and organism life-stages regarding the ability to degrade and eliminate substances could influence the degree of bioaccumulation. Bioturbation by sediment-dwelling organisms increases the organic contaminant concentration in interstitial water, which also increases bioavailability (Gunnarsson *et al.* 1999b). This effect is relatively more important at low sediment organic matter levels (10%) than at high (Barron 1990).

Feeding and bioaccumulation

Feeding-related accumulation of particle-bound contaminants and details of particle sorption/desorption kinetics may be important factors controlling the organic contaminant uptake (Forbes *et al.* 1998). Uptake from pore water and overlying water may be the fastest route, but studies have shown that exposure to sediment led to higher concentrations in organisms than predicted from uptake via pore water alone (Loonen *et al.* 1997). Despite a lower uptake rate of contaminants from sediments, the uptake from this medium can be substantial due to the high concentrations found in sediments (Loonen *et al.* 1997). In addition, according to Forbes *et al.* (1998), a number of biotic factors strongly suggest that thermodynamic equilibrium may be a rare occurrence in natural sediments at scales relevant to bioavailability and it would therefore be unwise to uncritically assume that pore-water contaminant is the most bioavailable. Bioaccumulation via the ingestion route depends on feeding rate, assimilation efficiency, gut retention time, and contaminant concentration in the ingested food particles (Harkey *et al.* 1994), (Taghon *et al.* 1978). Contaminant uptake in the gut becomes increasingly important with higher K_{ow} compounds and, according to some researchers, probably dominates for compounds with a log K_{ow} of about 5.5 and above (Landrum *et al.* 1994), (Mackay and Fraser 2000). Weston and Mayer (1998a) claims that the solubilization potential by digestive fluids of deposit-feeders may serve as a good approximation of bioavailability for compounds with high log K_{ow} (>5.5) bound to sediments. Standard methods of chemical analysis of sediments often use a strong extractant that extract all the targeted contaminants, and are thus likely to overestimate the fraction of the contaminant that is actually bioavailable.

Most deposit-feeders selectively ingest the fine, organic-rich and nutritious particles in the available sediment (Lopez and Levinton 1987), (Taghon *et al.* 1978), (Leppänen 1995). They are thereby able to concentrate organic matter through ingestion by a factor that varies among species, but are typically in the order of two or more. If the animals do not discriminate between contaminant and natural organic matter, the concentration of the contaminant within an animal's gut will often be two times or more that of the bulk sediment (Forbes *et al.* 1998). This was demonstrated in a selectivity and assimilation study with *Diporeia* spp. that were fed with different particle-size fractions dosed with one PCB and one PAH (Harkey *et al.* 1994). Accumulation of both these contaminants was greatest when the animals were exposed to a 20-to 63-µm size fraction. Weston *et al.* (2000) showed that the minimal selective abilities of the deposit-feeding polychaete *Abarenicola pacifica* still increased the benzo[a]pyrene (BaP) concentration of ingested sediments by 10-35% relative to that of the bulk sediment.

Deposit-feeders also exhibit extremely high weight-specific sedimentary ingestion rates. These vary markedly among species, with measured values ranging from a few to greater than 100 times their body weights per day (Lopez and Levinton 1987). These values make even very low contaminant absorption efficiencies potentially significant with regard to total exposure (Forbes *et* *al.* 1998). Weston and Mayer (1998b) presented an interesting explanation for bioaccumulation in various animals that appears to be in excess of that predicted by the organic carbon normalized sedimentary concentrations. They suggested that digestive solubilization of many gut volumes of sediment in a relatively stationary gut fluid would increase the fugacity beyond that predicted by a single sediment passage. That is, the concentration of the contaminant in the gut becomes so high that the equilibrium is shifted towards an uptake to the surrounding tissues.

Trophic transfer of contaminants has gained increasing interest during the last few years, because of increasing awareness of particle ingestion as being the dominant uptake pathway of hydrophobic contaminants for deposit-feeding invertebrates in sediment (Forbes *et al.* 1998), (Loonen *et al.* 1997), (Maruya and Lee 1998). Many studies, using both fish and invertebrates as test organisms, have shown that diet is the primary source of contaminant accumulation for highly hydrophobic (log K_{ow}> 5.5) chemicals (Landrum and Fisher 1998), (Mackay and Fraser 2000). Despite the slower transfer processes during accumulation from sediment or from food compared to uptake of dissolved forms from water, these mechanisms could be more relevant to long-term ecosystem dynamics.

When a contaminant has entered an organism via the diet, it requires desorption from a hydrophobic site in the food into gut fluid and finally to a hydrophobic site in the intestinal membrane, to be accumulated. This process is slower and less predictable than a simple water-lipid partitioning. However, Landrum *et al.* (1998) claim that bioaccumulation from sediment is a dominant process, especially at lower trophic levels, where benthic invertebrates play an ecologically crucial role when remobilizing contaminants into aquatic food webs by sediment ingestion. Weston and Mayer (1998b) showed that digestive fluid of the polychaete *Arenicola brasiliensis* was capable of solubilizing at least twice as much of the particle-bound PAHs than was seawater, indicating that sediment:water partitioning predictions are not applicable to the gut environment of deposit-feeders. In another experiment by Weston and Mayer (1998a) it was demonstrated that the absorption efficiency of PAH solubilized by gut fluids is nearly 100%. This clearly shows that solubilization in the gut is a crucial step determining bioavailability of organic contaminants.

Pruell *et al.* (2000) demonstrated that trophic transfer occurred in a study were PCBs and several chlorinated pesticides were accumulated from the sediment by polychaetes and transferred to lobster. After introduction in the lower food web, the subsequent trophic transfer of contaminants may account for as much as 90-99% of the contaminant load in top predators

(Landrum and Fisher 1998). This new knowledge of the importance of trophic transfer for total accumulation of contaminants in organisms is of major concern for hazard assessments. It is important to understand the uptake routes of contaminants from the sediment to benthic organisms, and what factors that govern the bioavailability of these substances.

Time dependency

The bioavailability of organic contaminants is also a time-dependent process (Loonen *et al.* 1997), (Landrum *et al.* 1996). Conrad *et al.* (1999) found decreased bioavailability of the insecticide permethrin to *Chironomus riparius* very soon after spiking the water column. They attributed this decrease in bioavailability to binding of the pesticide to the sediment and other surfaces. In sediment exposures, storage and aging of the sediment influences the bioavailability. For example, Loonen *et al.* (1997) showed that the bioaccumulation factors (BAFs) of two PCDD´s (TCDD and OCDD) to oligochaetes were 1.5 to 2-fold lower when the sediment had been stored for almost two years (Loonen *et al.* 1997). Bulk sediment concentrations of TCDD and OCDD remained the same, while the levels in overlying and interstitial water was reduced. Also, the concentration of TCDD in sediment pore water was found to be about ten times lower in aged sediment, compared to that of newly spiked sediment (Loonen *et al.* 1997). Landrum *et al.* (1992) concluded that the uptake rate coefficient for both phenanthrene and pyrene decreased when the contact time with the sediment was increased from 3 to 60 days. They attributed this lowered bioavailability to a tighter association of the PAHs with sediment particles with increased contact time, presumably caused by diffusion into the particles rather than surface sorption.

Other studies have shown that the initial accumulation of contaminants in organisms is much faster than later in the experiment, particularly for some water-soluble compounds (Landrum 1989), (Kukkonen and Oikari 1991). This was explained by an initial accumulation primarily from the pore water, which is then rapidly depleted of the contaminant. Further accumulation is governed by desorption from sediment particles and DOM to the water. A compound that is temporarily unavailable can, after desorption or other changes in chemical speciation, become available. From a risk assessment perspective, the total contaminant entering a system should be considered bioavailable, as a worst case scenario, because of temporal changes. The issue is not whether a compound is bioavailable, but on what time scale it will be available (Landrum *et al.* 1996).

Microbial exopolymers and contaminant bioavailability

Microbial exopolymer secretions, or EPS, are high molecular-weight mucous secretions of bacteria and microalgae. Microbial exopolymers are the major component of “biofilms”, which cover all kinds of surfaces in the aquatic environment. In natural environments, exopolymers ubiquitously occur wherever microflora is associated with surfaces and particles. EPS can either form tight capsules, which closely surround and protect cells, or loose-slime matrix associated with aggregates, sediment, detritus and other surfaces (Decho 1990) (fig.5). These secretions serve many functions, which enhance the survival and competitive success of microbial cells under natural conditions (Decho 1990). Since these secretions are easily destroyed, they are not readily observed. Yet, it is estimated that the quantities of exopolymers in sediments are at least equal or even exceed the biomass of the microbial cells that secrete them (Decho and Moriarty 1990).

In microbial cells, EPS create microenvironments around the cell, which allows it to operate, metabolise and reproduce more efficiently. These microhabitats also buffer the cells from quick environmental and ionic changes such as pH, salinity, and desiccation. In nutrient poor conditions, the secretions can also concentrate nutrients, as well as bind heavy metals and other toxins, thus protecting the cell (Decho 1990). Exopolymers are comprised of polysaccharides, mainly six-carbon sugars such as glucose, galactose and mannose (Sutherland 1977). They are hydrophilic, highly hydrated and contain approximately 99% water by weight (Decho 1990). EPS molecules are very “surface active” and possess high binding affinities for many dissolved compounds in water, e.g. dissolved organic matter and metals. Several metals are trapped quite efficiently (Schlekat *et al.* 1998), but EPS also bind organic compounds, of both high and low molecular weight (Decho 1990). Gunnarsson *et al.* (1999b) found higher concentrations of a tetrachlorobiphenyl (TCB) in the thin mucous (EPS-like) layer covering the burrow linings of the polychaete *Neries diversicolor* compared to the bulk sediment. The same observation was made for the linings of disk chamber and arm burrows of the brittle star *Amphiura filiformis* (Gunnarsson *et al.* 1999a). These findings clearly demonstrate the high sorption capacities of EPS and EPS-like substances for organic contaminants.

In recent years, biofilms have also been used, and play an important role, in the functioning of biological wastewater treatment systems. The ability of microbial biomass to adsorb and accumulate contaminants is thereby utilised for human purposes in an efficient way. This accumulation has been termed biosorption (Tsezos and Bell 1989). The mechanism behind this accumulation is very complex, but involves adsorption or absorption into various components of the microbial cell (Tsezos and Bell 1989).

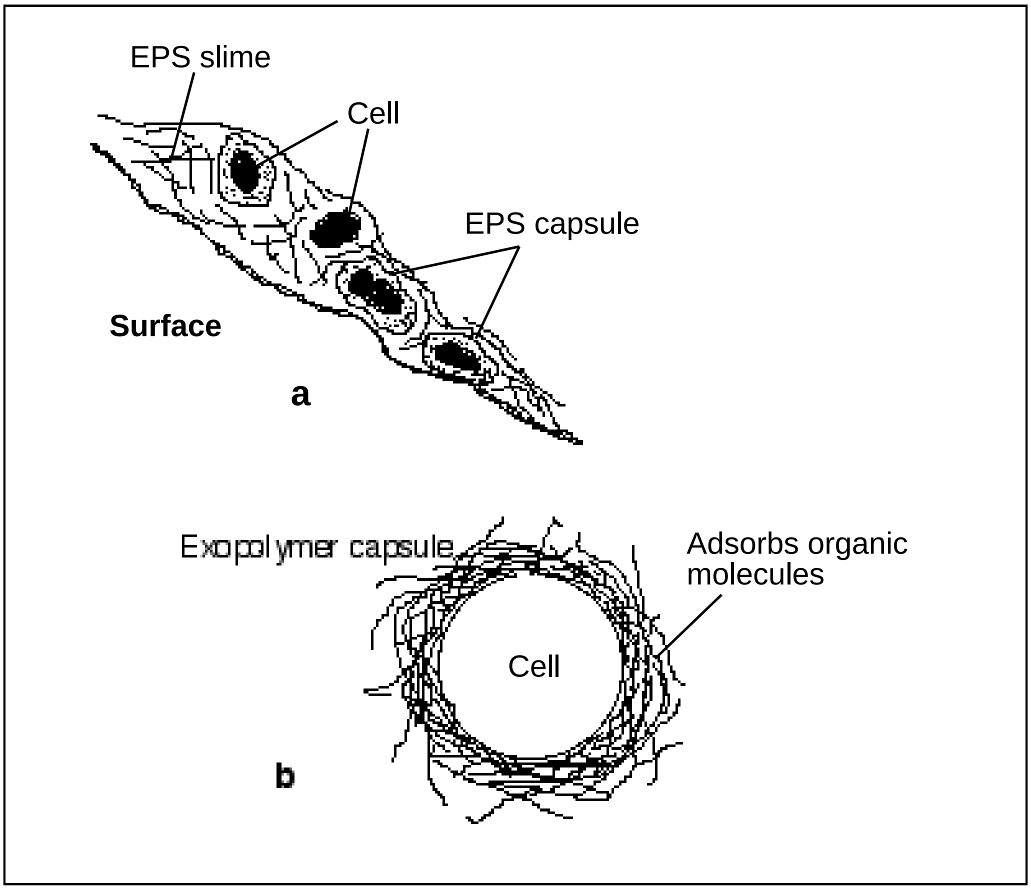

Fig 5. *Schematic diagram showing (a) bacterial cells and secreted exopolymers on the surface of a sediment or detrital particle; and (b) bacterial cells and exopolymer capsule. (Redrawn from Decho 1990)*

Grimes and Morrison (1975) showed that thirteen bacterial species sorbed and bioconcentrated five investigated chlorinated hydrocarbon insecticides. The uptake was found to be rapid, and pH 7 appeared optimal for bioconcentration as examined over the range pH 6 to 8. Wolfaardt *et al.* (1994) showed that most accumulation of the herbicide diclofop methyl occurred in cell capsules and certain regions of the exopolymer matrix. Accumulation of diclofop methyl typically reached maximum levels within 14-21 days, which suggests a saturation of binding sites in the biofilm matrix for this compound. In an earlier study Wolfaardt *et al.* (1994) showed that this particular bacterial consortium formed near steady-state biofilms in 14-21 days. Grimes *et al.* (1975) demonstrated that bioconcentration of different pesticides of various bacterial species increased with increased hydrophobicity of the pesticides. This finding seems contradictory to the hydrophilic properties of the EPS, but the binding occurs mainly through cation exchange processes with water, resulting in loss of "bound water" for organic compounds or metals (Decho 1990). Binding sites are carboxyl and hydroxyl groups of the polysaccharides that act as binding ligands for dissolved compounds (Decho 1990). Unfortunately, Grimes *et al.* (1975) never discussed the influence of EPS on the bioconcentration of pesticides. They suggested that the bacterial lipids provide a hydrophobic material capable of binding chlorinated hydrocarbon insecticides. In addition, however, in this relatively early paper they discussed the potential importance of bacterial cells to act as a vehicle through which toxic substances enter aquatic food chains.

Roles of EPS on trophic transfer of contaminants

Benthic invertebrates, in particular deposit-feeders, can ingest and utilise EPS as a highly labile carbon source (Decho and Moriarty 1990), (Baird and Thistle 1986). In fact, most deposit feeders digest the microbial epigrowth of particles, rather than using nonliving organic matter directly (Taghon *et al.* 1978). Moriarty (1982) estimated that detrital slime, mucus and extracellular exopolymers may comprise more than 50% of the carbon assimilated by a sea cucumber. Additionally, if the EPS adsorbs other labile DOM molecules (amino acids, sugars etc.) it will provide an important pool of both C and N which can be easily utilised by animals after ingestion (Decho 1990). Both Decho and Moriarty (1990) and Taghon (1982) demonstrated that deposit-feeders preferentially ingest sediment particles with an organic coating, e.g. EPS. Taghon (1982) suggested that one reason for this may be that mucus on the pick-up feeding structures results in a stronger adhesion to organic-coated particles compared to uncoated. In recent years, several researchers have suggested that the high affinities of EPS for metals and organic contaminants as well as the high digestibility of EPS, may increase the bioavailability of these contaminants to deposit-feeders and introduce them to the aquatic food web (Wolfaardt *et al.* 1994), (Schlekat *et al.* 2000), (Decho and Moriarty 1990), (Selck *et al.* 1999).

In many aspects, EPS can be considered a highly labile organic substrate. Accordingly, Schlekat *et al.* (2000) found the highest assimilation efficiencies of Ag and Cd by the amphipod *Leptocheirus plumulosus* when fed sediment particles coated with bacterial EPS compared to more refractory organic coatings such as diatoms and amorphous iron oxide. Similarly, in a study by Selck *et al.* (1999) the uptake of Cd by the deposit-feeding polychaete *Capitella* sp. I increased linearly with an increased EPS-layer coating the sediment particles. In one of the few studies examining the bioavailability of organic contaminants from EPS, Wolfaardt *et al.* (1994) observed a variety of protists nonselectively ingesting cell capsules and exopolymers contaminated with diclofop methyl. These grazers were also later observed to have accumulated the contaminant.

Once the EPS is in the gut of consumer animals, the associated substances can be desorbed by a simple pH change, because the binding affinities of EPS are pH-dependent (Decho 1990). Many deposit-feeding invertebrates establish an acidic condition in their digestive tract (Schlekat *et al.* 1998). In a study by Schlekat *et al.* (1998) the sorption of Cd to EPS was only 10% at pH 5, compared to approximately 95% at pH 9. This implies that there is a quick release of the contaminant once in the acidic environment of the animal gut. Another mechanism to release contaminants might be the common presence of carbohydrase enzymes within the digestive tracts of certain sediment-ingesting invertebrates (Schlekat *et al.* 1998). Both these mechanisms liberate the contaminant and thus make them available for assimilation across the gut wall.

There are strong indications that EPS might increase the bioavailability of sorbed substances and play an important role for the entry and subsequent trophic transfer of the contaminants through the aquatic food web. Evidences are; substantial ingestion of EPS by deposit feeders, high sorption affinities of EPS for different compounds, as well as the properties of EPS being a labile food resource, which readily desorbs associated contaminants. However, few studies so far have addressed the role of EPS in organic contaminant bioavailability.

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