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Review article

BIOACCUMULATION OF LIPID — SOLUBLE POLLUTANTS IN AQUATIC SYSTEMS

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Summary

One of the major problems of water pollution is the capability of pollutants to concentrate in aquatic organisms. Bioaccumulation and bioconcentration of such chemicals in fish render it unsuitable for human consumption. Bioconcentration of water pollutants through algae, zooplankton and other organisms, can lead to their accumulation through food–chain, with the fish at the top of the pelagic food web. The occurrence of elevated residue levels of various xenobiotics with increasing trophic level has been demonstrated in a variety of aquatic environments and organisms. The increased bioconcentration occurs with increasing trophic level. The tendency of a chemical to bioconcentrate has been shown to be strongly related to its lipophilicity. Trophic–level differences in bioconcentration are due largely to increased lipid content and decreased chemical elimination efficiency of organisms occupying increasing trophic levels. The accumulation of pollutant is expressed as the bioconcentration factor (BCF), which is determined as the rate of its uptake to the organism and its elimination from it plus the organism growth rate. Chemical uptake efficiency from water, excretion rate, and chemical assimilation efficiency are variable as a function of the octanol–water partition coefficient (K_{OW}).

Key words: bioaccumulation, bioconcentration, biomagnification, lipids, pollutants, water

INTRODUCTION

A life in water requires that gills and other body, surfaces be designed for the efficient exchange of oxygen and other essential molecules. Unfortunately, the same physiological designs that make aquatic life so successful also lead to the efficient uptake of many other nonessential chemicals. Thus, aquatic

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organisms are well known for their ability to absorb a variety of chemicals from water. Some chemicals may be found only at low levels in various tissues, whereas others may build up to significant concentrations (Spacie et al., 1995). Bioconcentration and bioaccumulation of contaminants in fish sometimes make it unsuitable for human consumpiton.

The phenomenon of a chemical's transfer through the food chain, resulting in its elevated concentrations with increasing trophic level, was called *biomagnification* (Leblanc, 1995). Biomagnification was first described in the sixties (Woodwell et al., 1967), when the researches considering accumulation of dichlorodiphenyldichloroethane (DDT) in organisms demonstrated that if the total amount of DDT contained at one trophic level is efficiently transferred to the next, and this next trophic level has less biomass associated with it, then the concentration (but not the total amount) of DDT associated with this trophic level will be greater than that present in the previous trophic level.

The concept of *bioconcentration* is defined as the uptake of a chemical by an organism directly from the environment, resulting in a concentration of chemical in the organism that is higher than the environmental concentration (Leblanc 1995; Strunjak–Perović, 1995). Bioconcentration is a specific term reserved for describing accumulation from water alone (Spacie et al., 1995).

Bioaccumulation is defined as the uptake of a chemical by an organism directly from the abiotic and/or biotic environment due to the direct (percutaneous) contact with surrounding medium, respiratory contact and consumption of contaminated food. Bioaccumulation is the general term describing the net uptake of chemical from the environment by any or all of the possible routes from any source in the aquatic environment where chemicals are present (i. e. water, dissolved, colloidal or particulate organic carbon, sediment, other organisms) (Spacie et al., 1995). The concentration of chemical attained in the organism may or may not exceed the concentration in the source (Leblanc, 1995).

Contaminate residues in fish are a result of direct uptake of the chemicals from water and/or uptake from consumption of contaminated food (Thomann and Connolly, 1984; Oliver and Niimi, 1985).

Although the concentration of many conatminants in water bodies is low, ussually in the nanogram per liter range, due to the large volume of water processed by the gills (10–100 l/day depending on fish size), significant concentrations of contaminants, like polychlorinated biphenyls (PCBs), can be accumulated by this route (Thomann and Connolly, 1984; Oliver and Niimi, 1985). The bioconcentration of chemicals from water by algae, zooplankton, etc. can lead to food chain accumulation in fish at the top of the pelagic food chain. The uptake of chemicals by macroinvertebrates such as oligochaete worms from contaminated sediments and detritus can lead to food chain accumulation in fish at the top of the benthic food chain (Oliver and Niimi, 1985).

STUDIES ON MECHANISMS ATTRIBUTED TO TROPHIC — LEVEL DIFFERENCES IN BIOCONCENTRATION

Through the last 25 years numerous investigations were performed, concerning accumulation and elimination of pollutants in organisms, using laboratory field models (Canton et al., 1975; Thomann and Connolly, 1984; Hawker and Connell, 1989; Markwell et al., 1989; Thomann, 1989; Tsezos and Bell, 1989; Clark et al., 1990). In those studies organisms of different trophic levels were exposed to several concentrations of the test substances during various amount of time. The processes of accumulation and elimination were studied then, in the separate organisms, as well as through the organisms of a food–chain. Such experiments were conducted with the most used pesticides, insecticides, and other pollutants, like alpha–hexachlorocyclohexane (alpha–HCH) (Canton et al., 1975), gamma–hexachlorocyclohexane (gamma–HCH) (Tsezos and Bell, 1989), PCBs (Thomann and Connolly, 1984; Markwell et al., 1989; Thomann, 1989; Tsezos and Bell, 1989; Clark et al., 1990), chlorobenzene (Hawker and Connell, 1989; Markwell et al., 1989; Thomann, 1989), DDT (Thomann, 1989), pentrachlorophenol, diazinon (Tsezos and Bell, 1989), etc. Those models mostly prove biomagnification through food–chain, although the uptake of alpha–HCH by the organisms directly from contaminated water, described by Canton et al., in 1975, appears to be much more important than the uptake from contaminated food.

Similar experiments were performed with food–chain organisms collected from the localities proven to be contaminated by certain pollutants (Pierce et al., 1981; Hidaka et al., 1984; Flegal, 1985; El–Rayis, 1986). The idea was to determine in what concentrations are the pollutants in the organisms of various trophic levels. Bioaccumulation potentials of pollutants in separate water organisms were also determined through laboratory and field reseraches (Hansen et al., 1971; Nimmo et al., 1974; Southworth et al., 1978).

The accumulation of pollutants is expressed as the bioconcentration factor (BCF) (Hawker and Connell, 1989), which is determined as the ratio of the steady–state concentration of a chemical in the organism (or part of it) to that in the water or food (cit. Strunjak–Perović, 1995). It is the ratio of the uptake rate to the excretion rate plus the organism growth rate (Thomann, 1989). Since the bioconcentration in aquatic organisms occurs largely through passive partitioning of the chemical between the organism and the environment, the bioconcentration factor is directly associated with the chemical's octanol–water partition coefficient (K_{ow}) (Chiou et al., 1977; Chiou, 1985; Hawker and Connell, 1989; Clark et al., 1990; Leblanc, 1995).

For a chemical to biomagnify, it must have a bioconcentration factor of >114000 (Leblanc, 1995). Few chemicals (i. e. DDT, some PCBs) have been experimentally shown to have BCFs>114000.

To better understand the effect of lipids in bioconcentration, Chiou (1985) studied the partition characteristics of organic compounds in lipid–water systems. He selected triolein (glyceryl trioleate) as the model lipid because of its abundance and its structural similarity to other triglycerides in organisms and because it is a liquid at room temperature. Determining triolein–water partition coefficients (K_{tw}), the author noticed discrepancies between bioconcentration factors (BCF) and K_{tw} (or K_{ow}). Compounds that are unstable in water or that are readily metabolized by organisms, give anomalous BCF values because of the inability of the system to reach true equilibrium state. BCF values obtained with short exposure times before steady–state concentrations in both biotic and water phases are reached, may be expected to differ greatly from equilibrium values. The author concluded that BCF values from laboratory experiments should be considered to be somewhat idealized.

The partition coefficients of three PCBs and 12 organophosphates were determined by the method developed by Chiou et al. (1977) using n–octanol. The utility of the lipophilic storage–partition coefficient correlation has been demonstrated in the treatment of several cases of human poisoning involving organophosphates. It was postulated that fat deposition with the resultant slow release into the circulatory system was the probable cause of the prolonged toxic manifestations.

Oliver and Niimi (1985) made an attempt to use the laboratory–derived BCFs to predict residue levels in field rainbow trout from Lake Ontario for chemicals that were detected in the lake. They described the uptake and elimination of chemicals by fish by the classical equation.

$$dC_F/dt = k_1 C_w - k_2 C_F$$

where C_F and C_w are the chemical concentration in fish and water and k_1 and k_2 are the uptake and elimination rate constants, respectively.

At steady stade $dC_F/dt = 0$,

and the bioconcentration factor is

$$BCF = C_F/C_w = k_1/k_2$$

The BCF can thus be estimated by measuring the chemical concentration in fish at steady state after exposing the fish for the appropriate length of time to a constant chemical concentration in the water. The shorter the chemical's half–life in the fish, the more rapidly the equilibrium concentration in the fish is established. The longer the chemical's half–life the larger the discrepancy between the BCFs. The above authors have showed that the steady–state BCF procedure is not reliable for chemicals that are eliminated slowly by fish.

Bioaccumulation and environmental beheaviour of DDTs, PCBs and chlordane compounds were studied in the Antarctic marine ecosystem under the fast ice (Hidaka et al., 1984). Samples of seawater, benthic invertebrates, fishes, Weddell seal etc., were collected at points where pollution by human activity is unlikely and at points where some pollution is likely because of research activities. In seawater, the concentration of PCBs (sum of several tens of individual chlorinated biphenyls) was higher than that of Sigma DDT, but reverse in organisms. Sigma Chlordane (sum of several chlordane compounds and metabolites) concentrations were midway between PCBs and Sigma DDT in both seawater and organisms. In higher throphic level organisms, the bioconcentration factors increased, and variable compositions of PCBs and chloradne compounds were found.

Suothwoth et al. (1978) tried to evaluate the extent and rate at which polycyclic aromatic hydrocarbons (PAH) in aquatic environments are removed from solution and accumulated by the zooplankter, *Daphnia pulex*, a representative component of freshwater aquatic food webs. All PAH studied were rapidly taken up by *Daphnia* and concentrated by several orders of magnitude above ambient aqueous PAH concentrations. The concentration factor (concentration of PAH in *Daphnia*/concentration PAH in water) increased with time until approaching an apparent equilibrium sometime within 24 hours.

The uptake of Aroclor 1254 in estuarine fishes, in flowing water bioassays, was performed also by Hansen et al. (1971). They discovered that the liver concentrated the greatest relative amount of this PCB, followed in decreasing order by the gills, whole fish, heart, brain, and muscle.

Results of several experiments indicate that aquatic invertebrates accumulate total body concentrations of polychlorinated biphenyls (PCB) thousands of times greater than that of the surrounding water. Nimmo et al. (1974) proved that shrimp obtained more of the chemical from the water by absorption through the gills, rather than from ingestion of contaminated detritus. The shrimp were not fed during the experiment.

According to Pierce et al. (1981), trophic transfer of heavy metals and organic contaminants from dredged sediments and other potential sources appears to be negligible in the marine environment. They have concluded that the primary source of PCB residues in marine animals is direct uptake through equilibrium partitioning and not from food or through the food–chain.

Through an age–dependent food–chain model that considers species bioenergetics and toxicant exposure through water and food, Thomann and Connoly (1984) using a dissolved PCB concentration in the water, showed that for the top predator lake trout, PCB exposure through the food–chain can account for greater than 99% of the observed concentration.

Thoman (1989) developed a model for calculating the concentration of organic chemicals in a simple generic aquatic food–chain. Chemical uptake efficiency from water, excretion rate, and chemical assimilation efficiency are variable as a function of the octanol–water partition coefficient, K_{OW}. This model indicates the significance of the growth rate and variable efficiency of uptake in the calculation of the bioconcentration factor under field conditions. For log K_{OW} of 5–7, calculated and observed field concentration factors in top predators indicate significant elevations above calculated field BCF values. Above log $K_{OW}=7$, foodchain effects are sensitive to the chemical assimilation efficiency and phytoplankton BCF.

More sophisticated physiologically based pharmacokinetic (toxokinetic) models have been developed to describe chemical uptake and subsequent disposition within fish, a few examples of which are reported by Kulkarni and Karara (1990), Michel et al. (1990), Nichols et al. (1990) and Law et al. (1991).

CONCLUSION

A major problem in environmental contamination by pollutants is thus the extent that these pollutants may concentrate from water into aquatic organisms such as fish.

To resume: the tendency of a chemical to concentrate in the organism relates closely to its lipophilicity (Thomann and Connolly, 1984; Oliver and Niimi, 1985; Leblanc, 1995). Since the lipid content of organism increases with increasing trophic level, most bioconcentration measurements have been shown to correlate well with octanol/water partition coefficients, where octanol is the most commonly used lipid surrogate. Chemical uptake efficiency from water, excretion rate, and chemical assimilation efficiency are variable as a function of the K_{OW} (Thomann and Connolly, 1984; Thomann, 1989).

As the bioconcentration of a chemical is determined by the rate of its uptake to the organism and its elimination from it (Canton et al., 1975; Clark et al., 1990), passive diffusion is likely the primary mode of uptake and elimination of lipophilic environmental chemicals by unicellular organisms (i. e. phytoplankton). In fish, liver cells (hepatocytes) contain specialized membranes rich in trasnport proteins, which conjugate xenobiotics, and are tranported into the bile duct for elimination (Leblanc, 1995). Because of the sequestration of lipophilic xenobiotics in compartments distant from the site of elimination and the reduced ratio of elimination sites/body mass, elimination rates for lipophilic xenobiotics would be expected to decrease with increasing body mass (Oliver and Niimi, 1985; Clark et al., 1990; Leblanc, 1995).

The results of studying the distribution of contaminants show that the biomagnification of lipophilic compounds is the most important factor of accumulation of these compounds in higher trophic level organisms. Since the lipids are the major sites of accumulation of lipophilic chemicals, biomagnification would not occur if the lipid content of some organism and its predator would be alike. Residual PCB varies greatly in different fish tissues, mostly, because of their diverse lipid content (Leblanc, 1995).

The increased bioconcentration can be attributed to increased lipid concreation and decreased chemical elimination efficiency associated with organisms occupying increasing trophic levels, for depuration rates of lipophilic chemicals decrease with increasing organism size.

Still a lot of work has to be accomplished using organisms representing a variety of trophic levels and compounds of varying lipophilicities. The tests carried out up to now could strengthen ecological risk assessment of chemicals for which limited experimentally determined bioconcentration data are available.

Sažetak

BIOAKUMULACIJA LIPOSOLUBILNIH ONEČIŠĆIVAČA U VODENIM SUSTAVIMA

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Jedan od najvećih problema onečišćenja vode raznim onečišćivačima jest u tome što se oni mogu koncentrirati u vodenim organizmima. Bioakumulacija i biokoncentracija onečišćivača u ribi čine takvu ribu nepogodnom za ljudsku prehranu. Biokoncentracija onečišćivača iz vode preko algi, zooplanktona i drugih organizama može dovesti do njihove akumulacije preko prehrambenog lanca, s ribom na vrhu pelagičkoga prehrambenog niza. Pojava povišene razine ksenobiotika uz povišenje trofične razine prisutna je u brojnim vodenim sustavima i organizmima koji žive u vodi. Tendencija neke kemijske tvari prema biokoncentraciji vrlo je usko vezana s njezinom lipofilnošću. Razlike trofičnih razina u biokoncentraciji posljedica su povećanog sadržaja lipida i smanjene sposobnosti kemijske eliminacije organizama viših trofičnih razina. Mogućnost nakupljanja polutanata u organizmu može se odrediti biokoncentracijskim faktorom (BCF), koji je odnos stupnja unosa i stupnja eliminacije određenoga spoja zbrojen sa stupnjem rasta organizma. Djelotvornost unosa

kemijske supstancije iz vode, stupanj izlučivanja, te učinkovitost kemijske asimilacije ovise o kemijskom koeficijentu odnosa oktanola i vode (K_{OW}).

Ključne riječi: bioakumulacija, biokoncentracija, biomagnifikacija, lipidi, onečišćivači, voda

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