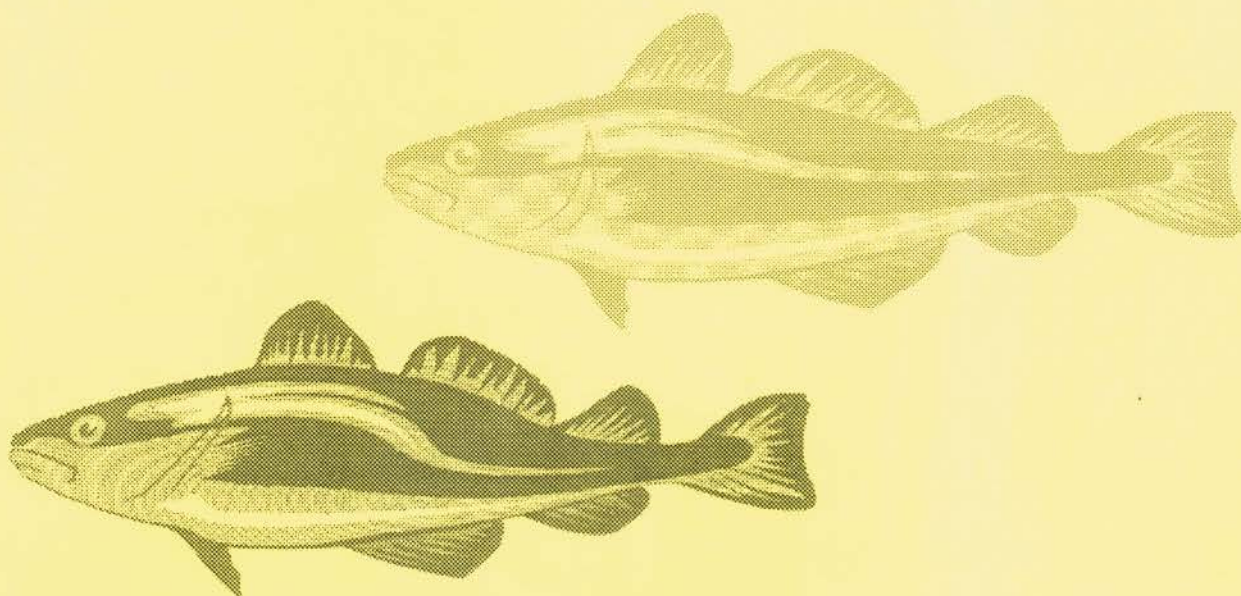

BIOACCUMULATION: HOW CHEMICALS MOVE FROM THE WATER INTO FISH AND OTHER AQUATIC ORGANISMS

Health and Environmental Sciences Department
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Bioaccumulation: How Chemicals Move from the Water into Fish and Other Aquatic Organisms

Health and Environmental Sciences Department

API PUBLICATION NUMBER 4656

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ABSTRACT

The purpose of this work is to provide an intermediate-level primer on *why* and *how* chemicals are accumulated by aquatic organisms (bioaccumulation). This is an important issue because of the potential effects of bioaccumulated chemicals on fish, wildlife, and ultimately, on humans. The chemicals emphasized in this primer are the polycyclic aromatic hydrocarbons (PAHs) and in particular the sixteen priority pollutant PAHs (selected by the U.S. EPA). Aquatic organisms are emphasized, but much of this information applies to terrestrial organisms as well. Key factors governing bioaccumulation are described to facilitate an understanding of this complex phenomenon. The factors include those related to the properties of the contaminant, the characteristics of the exposure media (environment), the organisms, and the supporting food chains. Several draft EPA approaches for assessing bioaccumulative substances are critically reviewed. Also, other potential assessment options such as use of transplanted sentinel organisms and lipid-containing semipermeable membrane devices (SPMDs) are examined. This report shows that although considerable information exists on the bioaccumulation phenomenon, there is a critical need for improved methods of assessing the presence of bioaccumulative chemicals. Of the bioaccumulation assessment methods examined for PAHs, the use of SPMDs offers the most potential. Finally, this work suggests that the likelihood for PAHs to have large bioaccumulation factors is relatively low.

EXECUTIVE SUMMARY

Chemicals that have a propensity to concentrate in aquatic life to levels higher than those found in the ambient environment (water) are characterized as bioconcentratable or bioaccumulative substances. Bioaccumulation includes the uptake of chemicals from both water and diet whereas bioconcentration represents uptake from water alone. Even though many contaminants are often present in the environment only at trace [less than a part-per-million (ppm)] or ultra trace [less than a part-per-trillion (ppt)] levels, they can accumulate to toxicologically significant levels in the fatty tissues of exposed organisms. The driving force behind this bioaccumulation phenomenon is the propensity of many chemicals to have much higher solubilities in organism lipid (fat) than in the ambient water. Another way to view the bioaccumulation phenomenon is that lipid-loving (lipophilic) contaminants have much lower escaping tendencies (fugacities) from fatty tissues than from water.

Many industrial processes generate wastes with low levels of chemicals that may bioaccumulate. Because of the potential for trace concentrations of these chemicals to adversely affect ecosystems and human health, the U.S. Environmental Protection Agency (EPA) is in the process of drafting methods for the assessment of bioaccumulative substances in industrial effluents. To ensure that bioaccumulative chemicals are not present at unacceptable levels in industrial outfalls or effluents, industry needs to be knowledgeable on the physical-chemical properties that are characteristic of these types of chemicals, how they interact with the environment, and the potential approaches available for their assessment.

This primer on bioaccumulation, prepared under the direction of API's Biomonitoring Task Force, is written for personnel with technical or scientific training, but without specific expertise in the subject matter. Although bioaccumulation is a complex subject, the authors have attempted to explain key aspects without using highly technical

treatment of details. A glossary is included to provide the reader with definitions of important terms related to bioaccumulation. Because several terms are defined only in the glossary and some variability exists in their use in the literature, reading the glossary is recommended. For example, in some literature bioaccumulation and bioconcentration are used interchangeably.

Several classes of organic chemicals have the potential to bioconcentrate or bioaccumulate. Also, certain organometal complexes may bioconcentrate. The focus of this work is on the polycyclic aromatic hydrocarbons (PAHs), and in particular, the EPA "priority pollutant" PAHs. Energy production and use appear to be the primary sources of low levels of PAHs in the environment. The properties of a number of chlorinated hydrocarbons are also examined for comparative purposes. The organisms emphasized are aquatic but much of the information presented also applies to terrestrial life.

The body of this report is divided into two parts: factors affecting bioaccumulation and approaches for assessing bioaccumulative substances. The reader should be aware that the classification of these factors into separate subsections is operational and does not necessarily imply that they are independent of each other.

FACTORS AFFECTING BIOACCUMULATION

Four types of variables affect bioaccumulation—physical-chemical properties of the contaminant molecules, environmental conditions, characteristics of the exposed organism, and the organism's food chain. These factors may act in concert or in opposition resulting in a range of bioaccumulation potentials.

Chemical Related Factors

Physical-chemical properties of the contaminant molecule play a central role in the bioaccumulation process. Features of chemicals that confer the tendency to

bioaccumulate include (1) lipophilicity or fat loving, which is directly related to the magnitude of a chemical's solubility in octanol, and characterized by the magnitude of the octanol-water partition coefficient (K_{ow}); (2) low water solubility or hydrophobicity due to the lack of polar functional groups; and (3) structural stability resulting in environmental persistence (years instead of days). Finally, chemicals of moderate molecular weight and size (i.e., molecular weight of about 350 and molecular breadth of less than 10 Angstroms), and lacking ionizable functional groups have a greater tendency to bioaccumulate.

Environmental Related Factors

As suggested earlier, the environmental presence of chemicals that meet most of the aforementioned criteria does not always lead to high degrees of bioaccumulation. This attenuation of bioaccumulation is often due to low residue bioavailability. For bioaccumulation to occur, a molecule must make contact with a biomembrane and move through the membrane to lipid-rich storage sites. The amount of chemical making contact with an organism's absorbing membranes is dependent not only on its environmental concentration in the bulk water phase (includes particulates), but also on the fractional amount that is available for uptake (i.e., the bioavailable fraction). This bioavailable fraction usually corresponds with the fraction of chemical that is truly dissolved in water.

Lipophilic or bioaccumulative chemicals also have high affinities for particulate organic carbon in suspended and bed sediments because the organic carbon associated with sediments has some of the same chemical characteristics as lipid. Most of the mass of a highly lipophilic contaminant in an aquatic system is usually not dissolved in the water but rather is sorbed on particulate organic carbon. The desorptive release of a lipophilic residue from sediment organic carbon can be very slow, thus significantly reducing the amount of chemical available for bioaccumulation. However, the slow release of sediment-sorbed contaminants in areas where contaminant inputs have declined is often the major source of trace levels of bioconcentratable compounds.

Another factor that greatly affects the potential of a compound to bioaccumulate is its environmental stability or persistence. The effects of environmental degradation processes (e.g., hydrolysis, photolysis and microbial degradation) on contaminant molecules typically result in more hydrophilic (water-loving) or polar products, which have lower bioaccumulation potentials than did the parent compounds. Some exceptions to this outcome do exist, especially under conditions of low oxygen. However, the overall effect of these degradation processes is to reduce parent compound concentrations and organism exposure time, thereby decreasing the amounts of residues bioaccumulated.

Organism Related Factors

Lipophilic contaminants are accumulated by aquatic organisms from water via respiration, and from ingested food or sediments. Bioconcentration (uptake from water) is generally viewed as the predominant route of uptake for most chemicals (including most PAHs) by aquatic organisms. Because liters of water per day are ventilated across the gill membranes of fish, the gill is generally the principal point of contaminant entry into an aquatic organism. The assimilation efficiencies of a variety of lipophilic compounds by this route range from about 20 to 90% of the contaminant residues present in ventilated water.

Diet is more likely to be the major route of uptake when chemicals are persistent and have high K_{ow} (i.e., greater than 10^5). This is especially true for the top predators (aquatic and terrestrial) of a food chain. The assimilation efficiency of lipophilic chemicals across the gut is dependent on the quality of the ingested materials. If ingested materials are largely nondigestible, such as most natural sediment organic carbon, then the likelihood of gastrointestinal uptake is diminished. Gut assimilation efficiencies for a series of lipophilic chemicals, from high quality fish food (e.g., animal or plant tissues), have been shown to range from about 50 to 85%. Note that lipid content of the consumer organism has little or no effect on dietary and respiratory uptake rates of chemicals but it does affect the ultimate capacity of an organism to accumulate a chemical.

Bioaccumulation occurs only if the rate of a chemical's uptake exceeds the rate of its elimination. In aquatic organisms, depuration of many lipophilic chemicals occurs passively across the gills. This route of elimination appears to be most important for nonpolar compounds that are not biotransformed. The rates of elimination for these compounds are generally inversely related to their K_{ow} .

In many organisms (especially mammals, birds, and aquatic vertebrates), both the enzyme system known as the cytochrome mixed-function monooxygenase (MFO) system, and the aryl hydrocarbon hydroxylase system are responsible for the biotransformation of a variety of lipophilic compounds, especially the PAHs. Remember that biotransformation products are typically more hydrophilic and have much more rapid elimination rates than their parent compounds. In fish, birds, and mammals, most MFO activity is localized in the liver and the route of elimination of the more hydrophilic metabolites is by the bile. Although the MFO system effectively detoxifies and reduces the bioaccumulation of many contaminants, certain PAHs and alkanes can be transformed to intermediates that are more toxic (including carcinogenic) than the parent compounds.

The ability to eliminate accumulated PAH residues by all processes varies among species according to the following general trend: mammals > fishes > crustaceans > bivalve molluscs. The typically low elimination rates of PAH and other contaminant residues by bivalves, which leads to high bioaccumulation, accounts in part for their popularity as sentinel or biomonitoring organisms.

Food Chain Related Factors

Biomagnification is the increase in the bioaccumulation factors (BAFs) of certain chemicals in organisms occupying sequentially higher trophic positions in a food chain. This phenomenon occurs because of the following sequence of events. As lipids of contaminated prey are digested in the gut of predators, the capacity of the digestate

(due to its increased polarity) to retain nonmetabolized lipophilic contaminants is reduced, resulting in the net transfer of these chemicals to the predator's lipid-rich tissues. Then, assuming that the predator continues to consume numerous prey, the rates of uptake by the diet can exceed the rate of elimination, resulting in contaminant concentrations higher than those that would be found in the predator's fatty tissues at equilibrium. If this animal is, in turn, consumed by a predator of higher trophic level, a further magnification in residue concentrations can occur. In cases where the predators are fish-eating birds and mammals having high consumption rates of contaminated fatty prey and limited elimination pathways, biomagnification can result in residue concentrations that are 100-fold higher than the equilibrium values.

BIOACCUMULATION ASSESSMENT

Three approaches are being considered by EPA to assess the presence of bioconcentratable or bioaccumulative substances (not covered by water quality criteria) in surface waters and effluents. These approaches are the tissue residue measurement option, effluent measurement option, and sediment assessment option. In this primer, only the salient features of these options are covered and an evaluation of each is provided. Also, the use of transplanted bivalve molluscs and lipid-containing semipermeable membrane devices (SPMDs) is examined as alternative options for the determination of bioaccumulative chemicals.

Tissue Residue Option

The tissue residue approach involves measuring the concentrations of contaminants in tissue samples of indigenous organisms from receiving water sites and comparing these values with those in similar organisms collected from relatively uncontaminated control sites. The tissue residue measurement approach is environmentally realistic. However, the same or similar species may not be collectible at the test and reference/control sites, there are potential differences in the residence time of the test organisms at the sites, there are differences in the abilities of different organisms to

eliminate contaminants, and costs of tissue collection and analysis are high. These factors limit the certainty and practicality of the tissue residue option.

Effluent Option

This approach involves the collection of samples of effluent water, the extraction of the organic chemicals from the water, and the separation and analysis of the bioconcentratable chemicals in the extracts. The effluent separation procedure is designed to sort the results of the initial screening analysis in order to determine which of the contaminants pose a hazard. The bioconcentration factors (BCFs) of those compounds identified in the effluent that appear to pose a hazard are estimated from $\log K_{ow}$ -log BCF relationships or obtained from measured values of BCFs in the literature that followed accepted standards for fishes and saltwater bivalve molluscs.

The effluent assessment option does not allow detection of all bioconcentratable chemicals that may be present in aquatic organisms. The approach is fairly robust for chlorinated hydrocarbons but may fail to detect many PAHs because of the likelihood of acid-mediated PAH degradation during sample cleanup. Other limitations include analytical interferences from the hydrocarbons often present in refinery effluents, lack of sensitivity of the analytical method, and the probable lack of reliably measured BCFs and/or BAFs for detected bioaccumulative substances.

Sediment Assessment Option

In some receiving waters, sediments may be a significant source of bioaccumulative chemicals. Since sediments can accumulate pollutants over relatively long periods of time and can be preferential sorption sites, contaminant residues are generally present at greater concentrations in sediments than in the overlying water. This characteristic can facilitate detection of contaminants that are only present in an effluent or other source at very low concentrations or that are only released periodically. Because of the sample cleanup procedures used by EPA, this option is useful only for acid-stable

compounds. Other limitations include potential interferences in sediment samples that can reduce analytical sensitivity and preclude analysis, and lack of reliable organic carbon partition coefficient (K_{oc}) and BCF values for many bioaccumulative substances. However, unlike the tissue residue option, it should be possible to detect a broader spectrum of potentially bioconcentratable chemicals.

Evaluation of EPA Assessment Options

Recently, fifteen laboratories participated in a round-robin study on the three options proposed by EPA for assessment of bioconcentratable contaminants (not covered by water quality criteria) in effluents and receiving waters. The data obtained by five participating laboratories have been critically reviewed and are the subject of a peer-reviewed journal article (Wong *et al.*, 1997). In general the proposed multi-step procedures for each matrix were found to be complex, prone to loss of the chemicals of interest, and unnecessarily time-consuming.

Other potential options

Two additional approaches for the assessment of bioconcentratable chemicals are examined in this work. These are the use of transplanted sentinel organisms and semipermeable membrane devices (SPMDs). The use of transplanted organisms is essentially a modification of EPA's tissue residue option; the potential of selecting a sentinel species having minimal capability to metabolize analytes of interest and maximal probability to survive at the sample sites is a significant improvement. Unfortunately, sentinel organisms with very low contaminant backgrounds are often unavailable. Also, sentinel organisms are not exempt from a variety of factors (e.g., health, water quality, etc.) known to influence the bioaccumulation of contaminants by aquatic organisms. Finally, the cost of applying this modification of the tissue residue option can be even greater than any of EPA's other options.

Lipid-containing SPMDs represent a new technology, and are designed to mimic the bioconcentration of bioavailable organic contaminants by aquatic organisms without

many of the variables associated with the use of live animals. Conceptually, SPMDs represent a bridge between EPA's tissue residue and effluent options. The devices can be used to estimate the concentrations of bioavailable (dissolved residues; values which are directly comparable to water quality criteria) aqueous contaminants (effluent option) as well as the bioconcentration potentials of chemicals (tissue residue option). SPMDs function well in all environmental water qualities. Data on the SPMD sampling rates (needed for water concentration estimation) for the priority pollutant PAHs have been generated. Uniform devices with extremely low contaminant levels are commercially available. Also, the cost of an SPMD study is considerably less than any of the other options discussed herein. As is true of EPA's effluent and sediment options, SPMDs do not provide data on the dietary uptake of chemicals or on their potential to biomagnify up the food chain. However, the major route of PAH uptake by aquatic organisms appears to be via water. Overall, SPMDs show considerable promise as a new tool for the assessment of bioaccumulative substances, whether used in conjunction with other methods or as a stand-alone approach.

SUMMARY

In this work, certain structural features of chemicals that increase the probability of bioaccumulation in aquatic organisms are delineated. Also, several environmental variables are highlighted that can enhance or reduce the magnitude of a chemical's bioaccumulation in organisms. The roles of organism physiology and diet are shown to be key factors in the bioaccumulation of some chemicals. In particular, differences in the abilities of aquatic species to eliminate the same chemical are shown to greatly affect the magnitude of bioaccumulation. Current and potential approaches for assessing bioaccumulative substances in water are reviewed and evaluated.

For those interested in additional information on this subject, references (Connell, 1990) and (Burkhard *et al.*, 1991) are key sources. In addition, Volume 2 of the "Illustrated Handbook of Physical-Chemical Properties and Environmental Fate for Chemicals"

(Mackay *et al.*, 1992) contains an excellent compilation of data directly and indirectly related to the BAFs of PAHs and other aromatic hydrocarbons.

Section 1

INTRODUCTION

The lipids or fats of fish and wildlife, and humans as well, act as a natural sink for certain types of chemicals. Chemicals that have a propensity to accumulate in aquatic organisms to levels higher than those found in water are called bioconcentratable or bioaccumulatable. Although bioconcentration and bioaccumulation are often used interchangeably in the literature, bioconcentration refers to chemical uptake from water or air, whereas bioaccumulation refers to chemical uptake from water or air and ingested food and/or sediment. Environmental contaminants that bioaccumulate are hydrophobic (water-hating) and lipophilic (lipid-loving) in nature. Most contaminants are transported across biological membranes by passive diffusion. The mechanism by which these contaminants concentrate in an organism's lipid can be expressed by a basic rule of thumb in chemistry, i.e., "like dissolves like." The level of a chemical in fatty tissues reflects the difference in its solubility in the lipid and the surrounding water, which is best described as liquid-liquid partitioning. The magnitude of a chemical's lipid-water partition coefficient generally corresponds to its octanol-water partition coefficient (K_{ow} , see glossary).

Even though bioconcentratable chemicals are often only present in water or air at trace [less than a part-per-million (ppm)] or ultra trace [less than a part per trillion (ppt)] levels, they can accumulate to toxicologically significant levels in the fatty tissues of exposed organisms. Because of this concentration process, the fatty tissues and organs of some exposed organisms can have residue levels many thousands of times higher than those found in the ambient environment (water or air). In some cases, contaminants can reach harmful concentrations in tissues of aquatic organisms even though standard analytical procedures may fail to detect residues of the chemicals in samples of the exposure water. This problem arises because analysis of water samples generally involves extraction of less than 4 liters of water at one point in time

(grab sample), whereas, for some bioconcentratable chemicals, each gram of an aquatic organism's tissue may have effectively extracted the chemical from 50 liters of water over a period of weeks or months, before reaching steady state with the exposure water. Thus, the amount of chemical residue sequestered by 10 g of fish or shellfish tissue (a typical sample size) may be 125 times greater than that found in extracts of a 4-liter water sample. Also, the composition of the chemical residues in the tissue sample may differ markedly from that found in the water sample because of possible periodic or episodic changes in water residue composition and the ability of organisms to depurate or eliminate contaminant residues.

In this primer, the basic principles of bioaccumulation are examined, the reader is familiarized with terminology related to the subject, and key factors governing bioaccumulation are described, which include chemical properties, and characteristics of the environment, the organisms, and the food chains. Also, several assessment options, including SPMDs, are described for testing for the presence of bioaccumulative substances. The focus of this primer is primarily on aquatic organisms; however, much of this information applies to terrestrial organisms as well. The chemicals emphasized in this work are the polycyclic aromatic hydrocarbons (PAHs), and in particular, the priority pollutant PAHs. The priority pollutant PAHs are sixteen compounds selected by EPA as representative of the large PAH chemical class. The selection criteria used by EPA were based on toxicity, availability of chemical standards, frequency of environmental occurrence, and chemical production data.

Section 2

FACTORS AFFECTING BIOACCUMULATION

Four major interrelated factors affect the bioaccumulation of chemicals by aquatic organisms. These include the physical-chemical properties of the contaminant, environmental conditions, and characteristics of the exposed organism and its food chain. It is important that the reader is aware that the separation of these factors is for descriptive purposes only and is not meant to imply that they are independent of each other. Also, it should be emphasized that, regardless of how low a chemical's water solubility is and how large its affinity is for sediments, there is always some exchange with other environmental compartments (e.g., water and biota), i.e., contaminant residues should be viewed as dynamic and not "fixed" even when the residence time in a compartment is great.

PHYSICAL-CHEMICAL PROPERTIES

The nature of individual atoms and the chemical bonds in organic molecules (i.e., chemical structure) confers properties of nonpolarity, lipophilicity, environmental bioavailability and mobility, and resistance to degradation. Note that in the following discussions, it is assumed that a chemical must be dissolved in water before it can be bioconcentrated by aquatic organisms.

Polarity

The presence of one or more polar functional groups (see glossary) in molecules, such as those in free acids and phenols, increases the water solubility of a compound, but reduces its K_{ow} or lipophilicity (Figure 2-1). On the other hand, the lack of polar functional groups, or the state of nonpolarity, decreases the water solubility of a chemical, and increases the lipophilicity. Also, decreasing the water solubility of a chemical enhances its escaping tendency (fugacity) from water by volatilization, unless the molecular weight is relatively high (> 350 daltons). Note that large molecules are