
BIOACCUMULATION: AN EVALUATION OF FEDERAL AND STATE REGULATORY INITIATIVES

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American Petroleum Institute Environmental, Health and Safety Mission and Guiding Principles

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Executive Summary

The objective of this Primer is to describe the science of bioaccumulation in the aquatic environment as it relates to federal and state regulatory activities facing the petroleum industry. As chemicals that accumulate in organisms have come under increased scrutiny, both federal and state agencies have begun to implement additional regulations that limit chemical releases, and reduce exposure to humans and wildlife. These regulations affect the levels of chemicals that may be discharged to the environment, discharge reporting requirements, and responses to existing environmental contamination.

Scientific issues regarding bioaccumulation are discussed in detail in American Petroleum Institute (API) publication number 4656, *Bioaccumulation: How Chemicals Move from the Water into Fish and Other Aquatic Organisms* (API, 1997). This Primer provides a brief overview of these issues, and an expanded discussion of selected chemicals, including arsenic, mercury, nickel, selenium, dioxins, and polycyclic aromatic hydrocarbons (PAHs). Among these, mercury, selenium, and dioxins have faced particular scrutiny due to their potential to accumulate in fish at concentrations that may be harmful to wildlife and humans.

Federal regulations that have been developed to reduce exposures to these and many other bioaccumulative chemicals include: fish consumption advisories, the Great Lakes Water Quality Initiative (GLI), the Persistent, Bioaccumulative, and Toxic (PBT) strategy, and the Binational Strategy. These regulations and selected state initiatives are summarized below.

Fish Consumption Advisories

Between 1993 and 1997 the number of fish consumption advisories in the US increased 80 percent, mostly due to an increased focus on elevated concentrations of mercury, PCBs, chlordane, dioxins, and DDT in fish. In 1997, the US Environmental Protection Agency (USEPA) released risk-based consumption limits for 25 chemicals, including mercury, selenium, PAHs, and dioxins. Chemicals were selected for evaluation based on their bioaccumulation potential. For these 25

chemicals, USEPA has developed fish consumption advisories based on the concentration in fish tissue, the meal size eaten, and the population of concern. Fish consumption advisories have provided an impetus for other regulations aimed at controlling the sources of bioaccumulative chemicals to the environment.

Great Lakes Water Quality Initiative

On March 23, 1995, USEPA finalized the Water Quality Guidance for the Great Lakes System, otherwise known as the GLI. Implementation of the GLI began two years later in the states surrounding the Great Lakes. The GLI sets three types of water quality standards for (1) the protection of aquatic life; (2) the protection of human health; and (3) the protection of wildlife. Although the GLI only finalized water quality criteria for a handful of chemicals, the guidance sets forth the process for determining additional criteria for many more chemicals. Bioaccumulation is a critical consideration in the derivation of both human health and wildlife criteria.

Protection of Human Health. The GLI contains human health criteria, known as human cancer values and human noncancer values, for 18 pollutants, as well as methodologies to derive criteria for additional chemicals. Separate methodologies are provided for chemicals that meet minimum data requirements (Tier I), and chemicals for which less information is available (Tier II). In all cases, bioaccumulation factors are used to derive water quality criteria to protect individuals from adverse health effects (including an increased cancer risk of 1 in 100,000 or 1×10^{-5}) due to consumption of aquatic organisms and water, including incidental ingestion of water during recreational activities.

Protection of Wildlife. The GLI contains criteria for the protection of wildlife for four chemicals (DDT and its metabolites, mercury, PCBs, and 2,3,7,8-tetrachlorodibenzo-p-dioxin) and a methodology to derive criteria for all other bioaccumulative chemicals of concern. The wildlife criteria are designed to protect mammals and birds from adverse effects due to consumption of food and/or water from the Great Lakes system. Unlike criteria for human health, the wildlife criteria focus on endpoints related to reproduction and population survival, rather than effects on individuals. The wildlife species selected for evaluation in the GLI include those

species in the Great Lakes Basin expected to have the highest exposures to bioaccumulative chemicals through the aquatic food web: bald eagle, herring gull, belted kingfisher, mink, and river otter.

Persistent, Bioaccumulative, and Toxic (PBT) Strategy

The objective of the USEPA's PBT strategy is to reduce risks to human and ecological health by reducing exposure to PBT pollutants. PBT chemicals are defined by USEPA as those chemicals that are resistant to degradation in the environment, remain in the environment a long time, and may travel long distances (persistent); accumulate in fish and other organisms (bioaccumulative); and have been demonstrated to cause adverse effects in humans or wildlife (toxic). To date, USEPA has identified 12 PBT chemicals, including mercury, dioxins, and one PAH (benzo(a)pyrene).

USEPA's program is designed to address issues on an Agency-wide basis. Over the last year, several program offices have developed strategies to manage PBT chemicals and meet the PBT goals, as described below.

Toxic Substances Control Act (TSCA). To prevent the introduction of new PBT chemicals, USEPA has revised the pre-manufacture notice process under TSCA to include a new category of PBT chemical substances or mixtures. The new PBT chemical category under TSCA includes chemicals that have half-lives of greater than two months and bioaccumulation factors greater than 1000. These chemicals will be subjected to additional testing requirements before their manufacture is permitted.

Resource Conservation and Recovery Act (RCRA). The recently developed Draft RCRA Waste Minimization PBT Chemical List of 53 chemicals was developed by screening for persistence, bioaccumulation, and toxicity. The 53 chemicals on the RCRA List will be used by USEPA to: (1) measure progress toward the national goal to reduce generation of PBT chemicals by 50 percent by the year 2005; (2) report national progress on a periodic basis; (3) identify and acknowledge industrial sectors that contribute to national progress; and (4) promote a

coordinated waste minimization program among federal, state, and local agencies.

Emergency Planning and Community Right-to-Know Act of 1986 (EPCRA) - Toxic Release Inventory. USEPA has proposed to increase the reporting requirements of certain chemicals on the Toxic Release Inventory. EPA's proposal reduces the reporting thresholds for the manufacture, process, and use of certain bioaccumulative chemicals depending on the chemical's half-life and bioconcentration factor (BCF). USEPA proposes to reduce reporting thresholds as follows: (a) 100 pounds for chemicals with half-lives of two to six months and BCFs of 1,000 to 5,000, and (b) 10 pounds for chemicals with half-lives greater than six months and BCFs greater than 5,000.

Binational Strategy

Environment Canada and USEPA have developed the Great Lakes Binational Toxics strategy with the goal of virtually eliminating from the Great Lakes Basin toxic chemicals that result from human activity, particularly those chemicals that bioaccumulate or may affect the Great Lakes ecosystem. The Binational strategy focuses on an initial list of 12 priority chemicals (the same chemicals identified in USEPA's PBT Strategy).

The Binational Strategy includes eight challenges to be completed by 2006. Those of potential interest to the petroleum industry include:

- A challenge to seek a 50 percent reduction in the deliberate use and release of mercury nationally, and
- A 75 percent reduction in releases of dioxins, furans, hexachlorobenzene, and benzo(a)pyrene from sources associated with human activity.

These goals apply both to aggregate air releases nationwide, and to releases to water within the Great Lakes Basin.

State Programs

State initiatives regarding bioaccumulation are most often related to determination of water quality standards. Under the Clean Water Act, USEPA develops criteria for water quality. States may either (1) adopt the recommended criteria as developed by USEPA; (2) modify the criteria to reflect site-specific conditions; or (3) adopt criteria derived using other scientifically defensible methods.

This Primer describes the water quality programs in specific states of interest to the petroleum industry: Louisiana, Texas, Indiana, New York, and Washington. In most cases, these states have implemented the basic provisions of the water quality standards as promulgated by USEPA. Both New York and Indiana have adopted the recently developed GLI provisions, as required by the regulation. The human health criteria adopted by New York are more restrictive than those derived by USEPA, however, due to the use of a lower acceptable level of cancer risk, and a higher estimate of the amount of fish consumed.

1. Introduction

The objective of this Primer is to describe the science of bioaccumulation in the aquatic environment as it relates to federal and state regulatory activities facing the petroleum industry. The scientific issues regarding bioaccumulation have already been discussed in detail in American Petroleum Institute (API) publication number 4656; *Bioaccumulation: How Chemicals Move from the Water into Fish and Other Aquatic Organisms* (API, 1997).

In recent years, many chemicals that bioaccumulate have been under increased scrutiny by federal and state agencies. As a result, these agencies have started to implement additional regulations that limit chemical releases and reduce exposure to humans, aquatic life and wildlife. For example, the number of fish consumption advisories continues to increase as regulatory agencies consider the fish consumption pathway an important source of exposure to certain bioaccumulative chemicals. To reduce exposure via this route, limits have been placed on consumption of fish from some waters. Increasingly, water quality standards are being revised by states to consider bioaccumulation of chemicals.

This Primer is organized into three major sections. Section 2 briefly describes the science of bioaccumulation, including how bioaccumulation is defined by regulatory agencies, and why certain bioaccumulative chemicals have been the focus of regulatory attention. Section 3 addresses chemical-specific bioaccumulation issues for the most important chemicals to the petroleum industry. Finally, Section 4 provides information on federal and state initiatives to regulate bioaccumulative chemicals. Regulations specifically discussed include fish consumption advisories; the Great Lakes Water Quality Initiative (GLI); the Persistent, Bioaccumulative, and Toxic (PBT) Strategy; and the Binational Strategy. For each regulatory initiative, this Section describes how bioaccumulation factors are used to identify chemicals of concern, to set standards, and/or to further reduce chemical releases.

2. Science of Bioaccumulation

Section 2.0 provides a brief description of the science of bioaccumulation, including definitions of key terms and the identification of those physical/chemical and biological factors that influence the bioaccumulation potential of a chemical. As described earlier, some of this information has been drawn from API publication number 4656, *Bioaccumulation: How Chemicals Move from the Water into Fish and Other Aquatic Organisms*. This section concludes with a discussion on why regulatory agencies are concerned about bioaccumulative chemicals.

2.1 Definitions

Bioconcentration of a substance is defined as an aquatic organism's passive uptake directly from water through respiratory membranes, such as gills or other body surfaces. Accumulation from other environmental media, such as sediment, or from food is not considered. A **bioconcentration factor** (BCF) is the ratio of the chemical concentration in an organism to the concentration in water, assuming no exposure by food sources (see Text Box 2.1). The concentration in water should be calculated from a controlled laboratory experiment where the only source of the chemical is from water, and bioaccumulation is at steady state (uptake equals elimination).

In contrast to bioconcentration, **bioaccumulation** of a substance refers to an organism's general uptake and retention from water, and from ingested materials, such as sediment or food. The **bioaccumulation factor** (BAF) represents the ratio of the concentration in an organism to the concentration in water, including both the organism and food sources exposed to the chemical. Unlike the BCF, the BAF is generally derived from a field concentration rather than from laboratory experiments.

The main distinction between bioaccumulation and bioconcentration is the role of ingested sediment and food. For aquatic organisms such as phytoplankton, uptake of chemicals mainly occurs through the water column and can be expressed by a BCF. However, a BAF should be used when food chain transfer or uptake from ingested sediment becomes more important. Unfortunately, the terms BAF and BCF have sometimes been used interchangeably by federal and state agencies. Because of this confusion, federal and state agencies now often specify how BCFs and BAFs should be determined (e.g., field-measured, estimated from laboratory data) before being used as part of a standard calculation. Although this standardization will reduce the variation in the BAF or BCF selected, often the use of estimated values, in lieu of measured values, has a significant effect on the final outcome.

In addition to BAFs and BCFs, federal and state agencies also use a **biota-sediment accumulation factor** (BSAF) to predict organic chemical accumulation by aquatic organisms. For organic chemicals, the BSAF refers to the ratio of a chemical's lipid-normalized tissue concentration in an aquatic organism to its organic carbon-normalized (OC) concentration in surface sediment. Lipid (i.e., fat or fat-like tissue) and organic carbon levels are key factors that cause bioaccumulation levels to differ among organisms and among sediments (see Section 2.2). As described in the GLI, BSAFs can be used to calculate BAFs for use in setting organic chemical water quality standards. For metals, BSAFs may be measured on a site-specific basis, but typically are not normalized to lipid and organic carbon concentrations.

Text Box 2.1: Bioaccumulation Definitions

(1) Bioconcentration Factor (BCF)

$$BCF = C_o/C_w$$

where:

C_o = concentration in the organism at steady state ($\mu\text{g/g}$)

C_w = concentration in water ($\mu\text{g/L}$) as measured in a controlled laboratory experiment

(2) Bioaccumulation Factor (BAF)

$$BAF = C_o/C_w$$

where:

C_w = concentration in water ($\mu\text{g/L}$) as measured in a field experiment or estimated as a field concentration

(3) Biota-Sediment Accumulation Factor (BSAF)

$$BSAF = (C_o/L)/(C_s/OC)$$

where:

L = lipid concentration ($\text{g}_{\text{lipid}}/\text{g}_{\text{tissue}}$)

C_s = concentration in sediment ($\mu\text{g/g}$)

OC = total organic carbon concentration ($\text{g}_{\text{lipid}}/\text{g}_{\text{sediment}}$)

Once a chemical enters the food chain, **biomagnification** may occur as the chemical moves from one trophic level to another. Biomagnification is defined as an increase in tissue concentrations in an organism, as a result of a series of predator-prey associations, primarily through the mechanism of dietary uptake (Berends et al., 1997; USEPA, 1995). Chemicals that have a tendency to biomagnify are typically highly lipophilic, have low water solubilities, and are resistant to metabolism by organisms.

2.2 When Are Chemicals Considered Bioaccumulative?

Most bioaccumulative chemicals are lipophilic organic chemicals; however, certain metals, such as mercury, that can form organo-metallic complexes can also be bioaccumulative. Many factors have been shown to influence bioaccumulation of chemicals in aquatic organisms, including the physical and chemical properties of the chemicals, environmental variables, organism-related variables, and food-chain-related factors. Generally, bioaccumulation of a chemical becomes ecologically significant when the chemical's BAF is greater than 1000. Above this threshold, depending on the chemical, bioaccumulation may cause adverse effects in humans or wildlife that consume aquatic organisms. In the GLI, EPA uses a BAF greater than 1000 to identify bioaccumulative chemicals of concern. As described in Section 4.1.3, a BAF threshold of 1000 is currently being used by EPA in regulatory decisionmaking.

2.2.1 Physical and Chemical Properties

For organic chemicals, the factors that influence chemical uptake by aquatic organisms include molecular weight, chemical structure, molecular dimensions, log of the octanol-water partition coefficient ($\log K_{ow}$), water solubility, and degree of ionization. Of these factors, regulatory agencies often rely on a chemical's $\log K_{ow}$ (See Text Box 2.2), and half-life or persistence in the environment in predicting bioaccumulation potential (e.g., GLI, PBT strategy). In general, bioaccumulation increases for chemicals with a $\log K_{ow}$ between one and six (McKim et al., 1985; Opperhuizen et al., 1985). As $\log K_{ow}$ increases above six, other factors such as water solubility, molecular weight, and chemical structure begin to play a much larger role in predicting bioaccumulation, and bioaccumulation often decreases (Connell, 1989). Although $\log K_{ow}$ can be both measured or estimated, significant limitations exist with the use of estimated values, especially as $\log K_{ow}$ increases above six. EPA's current methodology for $\log K_{ow}$ (Karickhoff and Long, 1995) relies on a compilation of both estimated and measured values; however, the estimated values are only used to identify outliers in the measured data results. Although Lyman et al. (1990) indicates that $\log K_{ow}$ can be significantly overestimated at values over six using the fragment constant method, several other methods may not share this bias and may underestimate $\log K_{ow}$ for very insoluble chemicals.

For metals, chemical speciation rather than $\log K_{ow}$ can be particularly important in determining bioaccumulation potential. For example, mercury may occur in either inorganic or organically complexed forms (i.e., methylmercury) (see Section 3.2). Methylmercury's affinity for sulfhydryl groups leads to accumulation in the proteinaceous tissue (muscle) of fish, whereas inorganic mercury is much less bioaccumulative. Typically, bioaccumulation of metals is evaluated by regulatory agencies based on chemical-specific empirical data, and is not predicted from physical or chemical properties.

Text Box 2.2: $\log K_{ow}$

$\log K_{ow}$ is the logarithm of the ratio of a chemical's concentration in n-octanol to its equilibrium concentration in water contacting the n-octanol. $\log K_{ow}$ is an indicator of a chemical's tendency to leave the water column and accumulate in the lipid (fat tissues) of an organism.

As a chemical's $\log K_{ow}$ increases (up to about six), its tendency to accumulate in aquatic organisms increases.

Chemicals with high $\log K_{ow}$ are considered hydrophobic and lipophilic. In other words, they tend to partition to organic carbon and lipids rather than water.

2.2.2 Environmental Variables

Environmental conditions also play a key role in determining a chemical's potential to bioaccumulate in aquatic organisms. In particular, the amount of organic carbon in sediment and dissolved in the water column is typically the most important factor influencing the amount of chemical available for uptake. Because sediment organic carbon (or sediment organic matter) is a large sink for lipophilic chemicals, the higher the organic carbon content the lower the fraction of chemical available for uptake by aquatic organisms.

In addition to organic carbon content, other factors such as sulfide, pH, salinity, biological activity (environmental degradation processes), and water clarity also play a role in bioaccumulation of chemicals. The level of sulfide in sediment is a particularly important factor influencing the bioaccumulation of certain metals. Changes in pH may also affect chemical speciation, resulting in either increases or decreases in bioavailability and bioaccumulation. For example, naphthenic acids in refining effluent become more water soluble and less bioaccumulative as pH increases. Similarly, biological activity and other environmental degradation processes that reduce concentrations of the parent compound, such as polycyclic aromatic hydrocarbons (PAHs), can lead to reductions in bioaccumulation, although such processes can result in the formation of more toxic breakdown products. In the case of PAHs, photolytic breakdown and metabolism by higher trophic level organisms (i.e., fish) will reduce environmental concentrations; however, some bioaccumulation will occur due to the ongoing releases of these chemicals to aquatic systems (API, 1997).

2.2.3 Organism-Related Variables

Aquatic organisms accumulate chemicals through diet and direct uptake from water. If the rate of intake is greater than the rate of elimination, then bioaccumulation occurs. Organism-related factors that affect bioaccumulation rates include lipid content, species-specific differences in chemical uptake and elimination rates, ability to metabolize certain types of chemicals, and gender, as described below.

Within organisms, hydrophobic organic chemicals tend to partition into lipid stores (i.e., fat). For this reason, organisms that contain higher lipid levels tend to accumulate higher levels of hydrophobic organic chemicals. Differences in lipid content among fish species are one of the factors used in the GLI to estimate bioaccumulation levels for fish of different trophic levels.

Factors that affect chemical uptake rates depend on whether uptake occurs directly from water or via the diet. For many aquatic organisms, direct uptake from water across the gills is the major route of exposure to chemicals (Spacie and Hamelink, 1982). Even very lipophilic materials for which food chain transfer is important are accumulated through water as well. McKim et al. (1985) reported gill uptake efficiencies for 14 organic chemicals from five chemical classes ranging from seven percent to over 60 percent, depending on the chemical's $\log K_{ow}$. Consistent with other studies on $\log K_{ow}$ (Opperhuizen et al., 1985), uptake efficiencies were greatest for chemicals with $\log K_{ow}$ between one and six. Although $\log K_{ow}$ is more influential in predicting uptake, differences in gill structure from species to species may affect uptake to some extent.

Similar to uptake from water, dietary uptake of chemicals is variable and depends both on the chemical and the organism. If ingested materials are mostly comprised of nondigestible materials (e.g., sediments), gut assimilation of chemicals will be limited by the desorption of the chemical from organic matter (API, 1997). Different species also have different gut uptake efficiencies for the same chemicals. For example, the efficiency of PAH uptake by fish, crustaceans, and marine worms ranges from less than ten percent to greater than 70 percent. Part of the reason for this variability may be species differences in the ability to breakdown ingested organic matter (API, 1997). Finally, when chemicals are moved through gastrointestinal membranes, a molecular size limitation (circa 9.5 Å) appears to hold true. Above this size limitation, absorption of chemicals through the gastrointestinal tract will be limited.

Bioaccumulation of chemicals only occurs if the rate of chemical uptake exceeds the rate of elimination. For many nonpolar chemicals, elimination occurs primarily via the gills. Elimination rates for these chemicals are generally inversely related to $\log K_{ow}$ (Spacie and

Hamelink, 1985). For some chemicals, such as PAHs, metabolism is the major route of elimination. Metabolites of PAHs and other chemicals are formed in the liver and transported to the gall bladder, where they are discharged with bile (API, 1997). Two other processes that result in elimination of chemicals include egg deposition in fish, birds, and invertebrates, and lactation and reproduction in mammals. In both these cases, females can significantly reduce their chemical body burdens, although this may result in an increased body burden in their offspring.

2.2.4 Food Chain-Related Factors

As described in API (1997), biomagnification of organic chemicals occurs when prey tissues are digested. As the tissues are broken down into more polar constituents, the nonpolar lipophilic contaminants are more likely to migrate and dissolve in the fatty tissues in the predator. With the consumption of additional prey items, the rate of active uptake from the diet can exceed the rate of passive elimination into water. Biomagnification is typically more pronounced in organic chemicals that are highly lipophilic, have low water solubilities, and are resistant to metabolism. Certain metals, notably mercury and selenium, can also exhibit biomagnification.

As discussed in Section 4.1.2., to account for bioaccumulation through the food chain, USEPA has developed food chain multipliers (FCM) as part of the Great Lakes Water Quality Initiative (see Text Box 4.1). These FCM are designed to ensure that water quality criteria are protective of wildlife and humans who may consume fish at trophic levels 3 and 4. Trophic level is defined based on an organism's diet, with primary producers at the lowest trophic level of the food chain and carnivores at the highest level. Figure 1 presents a simplified aquatic food web showing trophic levels 1 through 4. As defined in the GLI, trophic level 3 fish include freshwater drum, alewife, smelt, killifish, and darter. Trophic level 4 fish include lake trout, coho salmon, and rainbow trout.

2.3 Why Are Bioaccumulative Chemicals of Concern to Federal and State Regulators?

Bioaccumulation is of concern both for its possible effects on aquatic organisms and for the contamination of higher trophic levels, including humans, through the food chain. Because chemicals that bioaccumulate tend to persist in the environment and move between and within aquatic and terrestrial systems, exposure to these chemicals is potentially greater than other chemical exposures. As chemical exposure increases, so does the potential for adverse human health, wildlife, and environmental effects. Regulatory agencies tasked to protect public health, therefore, have begun to target bioaccumulative chemicals.

One mechanism used by regulatory agencies to control chemical exposures is through fish consumption advisories. The number of fish consumption advisories in the US increased 80 percent between 1993 and 1997, mostly due to an increased focus on elevated concentrations of mercury, PCBs, chlordane, dioxins, and DDT (including DDE and DDD) in fish (USEPA, 1997a). As the result of increased monitoring of chemical contamination in fish, many states have instituted state-wide consumption bans for all lakes or rivers. Although most of these fish consumption bans are focused on recreational fisheries, in a small number of cases, limits have been placed on commercial fishing operations (USEPA, 1997a).

USEPA has predicted that human exposure to chemicals in fish tissue may lead to a variety of cancer and noncancer health effects. Risk levels in the range of 1×10^{-4} to 1×10^{-6} are generally recognized as acceptable, depending on specific conditions. The GLI currently estimates that fish consumption by Native Americans in the Great Lakes results in an excess cancer risk ranging from 1.2×10^{-2} to 1.8×10^{-3} . For

Text Box 2.3. A Case Study of a Bioaccumulative Chemical

DDT was extensively used as an agricultural pesticide and to control for vector-borne diseases between 1920 and 1970. DDT is highly lipid soluble ($\log K_{ow}$ 6.19), has an extremely long half-life, and therefore, tends to bioaccumulate. In 1972, DDT was banned because of concerns regarding bioaccumulation in the environment and resulting adverse health effects in humans and wildlife (e.g., raptor eggshell thinning in Great Lakes region and the potential for induction of cancer in humans).

Because DDT is highly persistent and bioaccumulative, elevated levels of DDT can still be found in soils, sediment, and other environmental compartments, including fish. Although DDT is no longer used or produced in the United States, due to its persistence, it is still targeted by regulatory agencies today.

sport anglers, these risks are estimated to range from 4.5×10^{-3} to 9.7×10^{-4} (60 FR 15367). Often of most concern to regulatory agencies is consumption of fish by pregnant or nursing women, or by children. These populations are predicted to be more sensitive to potential adverse effects from consumption of contaminated fish tissue.

In addition to potential human exposures, wildlife (especially fish-eating birds and mammals) may also be exposed to chemicals in fish tissue. Similar to human exposure, these species often consume fish at trophic levels 3 and 4 (see Figure 2-1). In the Great Lakes in particular, adverse health effects in bird populations have been documented starting with DDT in the 1970s (see Text Box 2.3) (Weseloh et al., 1983; Giesy et al., 1994; Fox et al., 1991).

In an attempt to protect public health, USEPA continues to promulgate regulations that attempt to reduce exposure of humans and wildlife to contaminants in the environment. As described in detail in Section 4.0, these regulations may impact the petroleum industry.

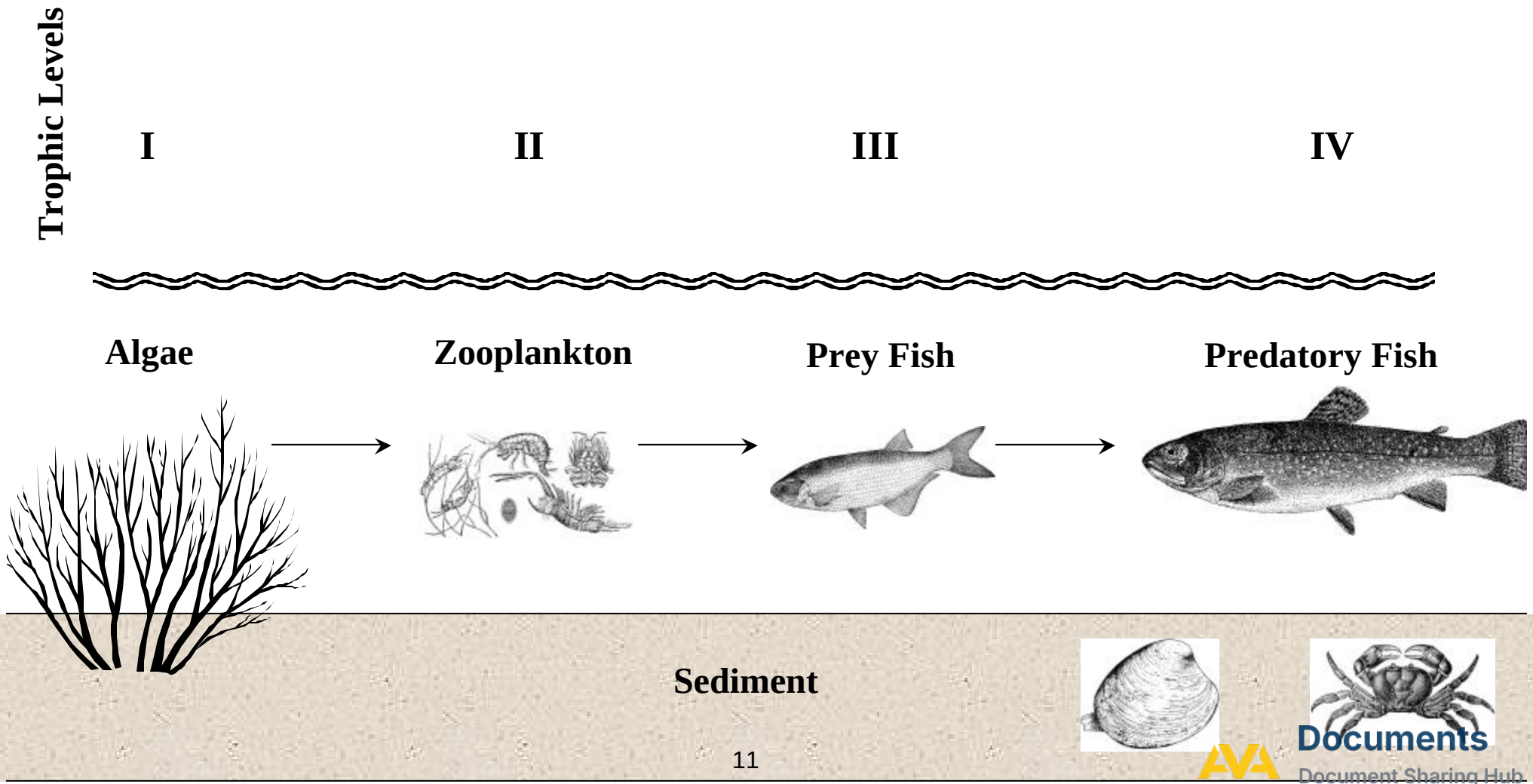
3. Chemical-Specific Issues

Section 3 discusses bioaccumulation issues for selected chemicals that are of particular interest to the petroleum industry. Some of these chemicals have low bioaccumulation potential (e.g., nickel), whereas others are highly bioaccumulative (e.g., dioxin and mercury). For each chemical, the Primer discusses the chemical form or valence state that has the greatest potential to bioaccumulate in aquatic systems, and what factors influence its formation.

3.1 Arsenic

Arsenic (As) is found in four valence states: As^0 (elemental), As^{+5} (e.g., arsenate, AsO_4^{-3}), As^{+3} (e.g., arsenite, AsO_2^-), and As^{-3} (arsenide), although arsenate and arsenite are the most important forms in aquatic systems. Inorganic arsenic compounds (As^{+5} , As^{+3} , and their salts) are more mobile and toxic than organic compounds. Of the inorganic compounds, arsenite is more toxic than arsenate.

Figure 1. Simplified Aquatic Food Chain



Arsenic cycles readily among valence states. The form present in water will depend on several factors (API, 1998). High dissolved oxygen, pH, Eh (a measure of redox potential), and low organic material favor the formation of arsenate, the most common form of arsenic in water. Arsenite and arsenide formation are favored by the reverse of these conditions (API, 1998, Eisler, 1988). In addition, the type and degree of biological activity will also affect the form of arsenic present in the environment and biota. For instance, some anaerobic bacteria, found in soil, sediments and digestive tracts, reduce arsenate to arsenite (Cullen and Reimer, 1989).

Arsenic is primarily introduced into the aquatic food web through uptake of arsenate by phytoplankton. These primary producers can metabolize arsenate into a wide variety of hydrophobic and water soluble derivatives. Commonly, arsenate is reduced to arsenite and subsequently methylated, primarily to methylarsonic acid and dimethylarsinic acid (Phillips, 1990). This process is generally considered a detoxification mechanism. Methylated arsenic can be excreted, reducing toxicity within the organism. The excreted methylated arsenic can cycle back to arsenate in deep waters, most likely through bacterial demethylation (Phillips, 1990).

The most common water-soluble form of arsenic in higher marine organisms is arsenobetaine. Conversion of arsenic to arsenobetaine is also a detoxification mechanism (Phillips, 1990). Under normal conditions, the primary source of arsenic to humans is from seafood as arsenobetaine. While it is readily absorbed in the digestive tract, arsenobetaine is generally excreted without transformation and therefore, poses little toxic hazard (Phillips, 1990; Neff, 1997). Little research has been conducted to determine whether arsenic is present in freshwater higher organisms in a detoxified form; however, betaine is expected to be more prevalent in marine organisms because it is used for osmoregulation.

Inorganic arsenic in mammals, including humans, is metabolized and then excreted. Because of this, chronic toxicity due to low concentrations of arsenic is uncommon. Larger doses can overwhelm the excretion mechanism and cause acute or subacute toxicity. In addition, inorganic arsenic is capable of crossing the placental barrier of many mammals,