

BIOACCUMULATION: AN EVALUATION OF FEDERAL AND STATE REGULATORY INITIATIVES

Regulatory and Scientific Affairs
Publication Number 4701
May 2000



American Petroleum Institute

Environmental, Health and Safety Mission and Guiding Principles

MISSION

The members of the American Petroleum Institute are dedicated to continuous efforts to improve the compatibility of our operations with the environment while economically developing energy resources and supplying high quality products and services to consumers. We recognize our responsibility to work with the public, the government, and others to develop and to use natural resources in an environmentally sound manner while protecting the health and safety of our employees and the public. To meet these responsibilities, API members pledge to manage our businesses according to the following principles using sound science to prioritize risks and to implement cost-effective management practices:

PRINCIPLES

- To recognize and to respond to community concerns about our raw materials, products and operations.
- To operate our plants and facilities, and to handle our raw materials and products in a manner that protects the environment, and the safety and health of our employees and the public.
- To make safety, health and environmental considerations a priority in our planning, and our development of new products and processes.
- To advise promptly, appropriate officials, employees, customers and the public of information on significant industry-related safety, health and environmental hazards, and to recommend protective measures.
- To counsel customers, transporters and others in the safe use, transportation and disposal of our raw materials, products and waste materials.
- To economically develop and produce natural resources and to conserve those resources by using energy efficiently.
- To extend knowledge by conducting or supporting research on the safety, health and environmental effects of our raw materials, products, processes and waste materials.
- To commit to reduce overall emission and waste generation.
- To work with others to resolve problems created by handling and disposal of hazardous substances from our operations.
- To participate with government and others in creating responsible laws, regulations and standards to safeguard the community, workplace and environment.
- To promote these principles and practices by sharing experiences and offering assistance to others who produce, handle, use, transport or dispose of similar raw materials, petroleum products and wastes.

FOREWORD

API publications necessarily address problems of a general nature. With respect to particular circumstances, local, state, and federal laws and regulations should be reviewed.

API is not undertaking to meet the duties of employers, manufacturers, or suppliers to warn and properly train and equip their employees, and others exposed, concerning health and safety risks and precautions, nor undertaking their obligations under local, state, or federal laws.

Nothing contained in any API publication is to be construed as granting any right, by implication or otherwise, for the manufacture, sale, or use of any method, apparatus, or product covered by letters patent. Neither should anything contained in the publication be construed as insuring anyone against liability for infringement of letters patent.

All rights reserved. No part of this work may be reproduced, stored in a retrieval system, or transmitted by any means, electronic, mechanical, photocopying, recording, or otherwise, without prior written permission from the publisher. Contact the Publisher, API Publishing Services, 1220 L Street, N.W., Washington, D.C. 20005.

Copyright © 2001 American Petroleum Institute

ACKNOWLEDGMENTS

THE FOLLOWING PEOPLE ARE RECOGNIZED FOR THEIR CONTRIBUTIONS OF TIME AND EXPERTISE DURING THIS STUDY AND IN THE PREPARATION OF THIS REPORT:

API STAFF CONTACT

Roger Claff, Regulatory and Scientific Affairs

MEMBERS OF THE CLEAN WATER ISSUES TASK FORCE

Dave Pierce, Chairman, Chevron Research & Technology

Ramachandra Achar, BP Amoco

Pete Beronio, BP Amoco

Terrie Blackburn, Williams Pipeline

Deborah Bolton, Chevron Products Marketing

John Cruze, Phillips Research Center

Philip Dorn, Equilon Enterprise LLC

Janis Farmer, BP Amoco

James Ford, ARCO

Clay Freeberg, Chevron

Rochelle Galiber, Marathon Ashland Petroleum LLC

Robert Goodrich, Exxon Research & Engineering

John D. Harris, BP Amoco

Leanne Kunce, BP Oil Company

David LeBlanc, Texaco E&P Incorporated

Rees Madsen, BP Amoco Whiting Refinery

Jim Mahon, FINA

Arnold Marsden, Jr., Equiva Services LLC

William Martin, ARCO Products Company

Joncile Martin, Equiva Services

Greg Moore, Marathon Ashland Petroleum

Gary Morris, ExxonMobil

Richard Nash, Equilon Enterprises, LLC

Michael Parker, Exxon Company USA

Patricia Richards, USX Corporation

Ileana A.L. Rhodes, Equilon Enterprises, LLC

Renae Schmidt, CITGO, Inc.

James Scialabba, Marathon Oil Company

Gerald Sheely, Marathon Ashland Petroleum LLC

Murl Smith, Exxon Company, USA

Paul Sun, Equilon Enterprises, LLC

Joey Tarasiewicz, Conoco Incorporated

Peter Velez, Shell Offshore Companies

Russell White, Chevron Research & Tech Company

Bill Yancy, ARCO

Greg Young, Phillips Petroleum Company

Norman Zieser, Chevron Corporation

Executive Summary	ES-1
1. Introduction	1
2. Science of Bioaccumulation.....	2
2.1 Definitions.....	2
2.2 When Are Chemicals Considered Bioaccumulative?.....	4
2.2.1 Physical and Chemical Properties	5
2.2.2 Environmental Variables	6
2.2.3 Organism-Related Variables	6
2.2.4 Food Chain-Related Factors.....	8
2.3 Why Are Bioaccumulative Chemicals of Concern to Federal and State Regulators?.....	9
3. Chemical-Specific Issues	10
3.1 Arsenic.....	10
3.2 Mercury	13
3.3 Nickel.....	14
3.4 Selenium.....	15
3.5 Dioxins	16
3.6 Polycyclic Aromatic Hydrocarbons (PAHs).....	17
4. Regulatory Applications of Bioaccumulation.....	18
4.1 Federal Regulations	19
4.1.1 Fish Consumption Advisories	19
4.1.2 Great Lakes Water Quality Initiative.....	22
4.1.3 Persistent, Bioaccumulative, and Toxic (PBT) Strategy	27
4.1.4 Great Lakes Binational Toxics Strategy.....	33
4.1.5 Draft Revisions to the Ambient Water Quality Criteria Methodology.....	34
4.2 State Initiatives	36
4.2.1 Louisiana.....	37
4.2.2 Texas	39
4.2.3 Indiana.....	40
4.2.4 New York.....	41
4.2.5 Washington	42
5. References.....	43

Appendices

A. Fish Consumption Advisory Calculations.....A-1

B. Data Requirements for Bioaccumulation Factors in GLI..... B-1

C. Calculation of Human Health and Wildlife BAFs..... C-1

D. Calculation of Human Health and Wildlife Criteria.....D-1

Tables

4-1. Bioaccumulative Chemicals of Concern as Identified by Regulatory Program.....20

4-2. Chemical Properties for Categorizing PBT Chemicals Under TSCA.....30

4-3. Toxic Release Inventory Reporting Thresholds for PBT Chemicals
for Protection32

D-1 Exposure Parameters for the 5 Representative Species Identified for Protection...D-5

Figures

2-1. Simplified Aquatic Food Chain11

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.

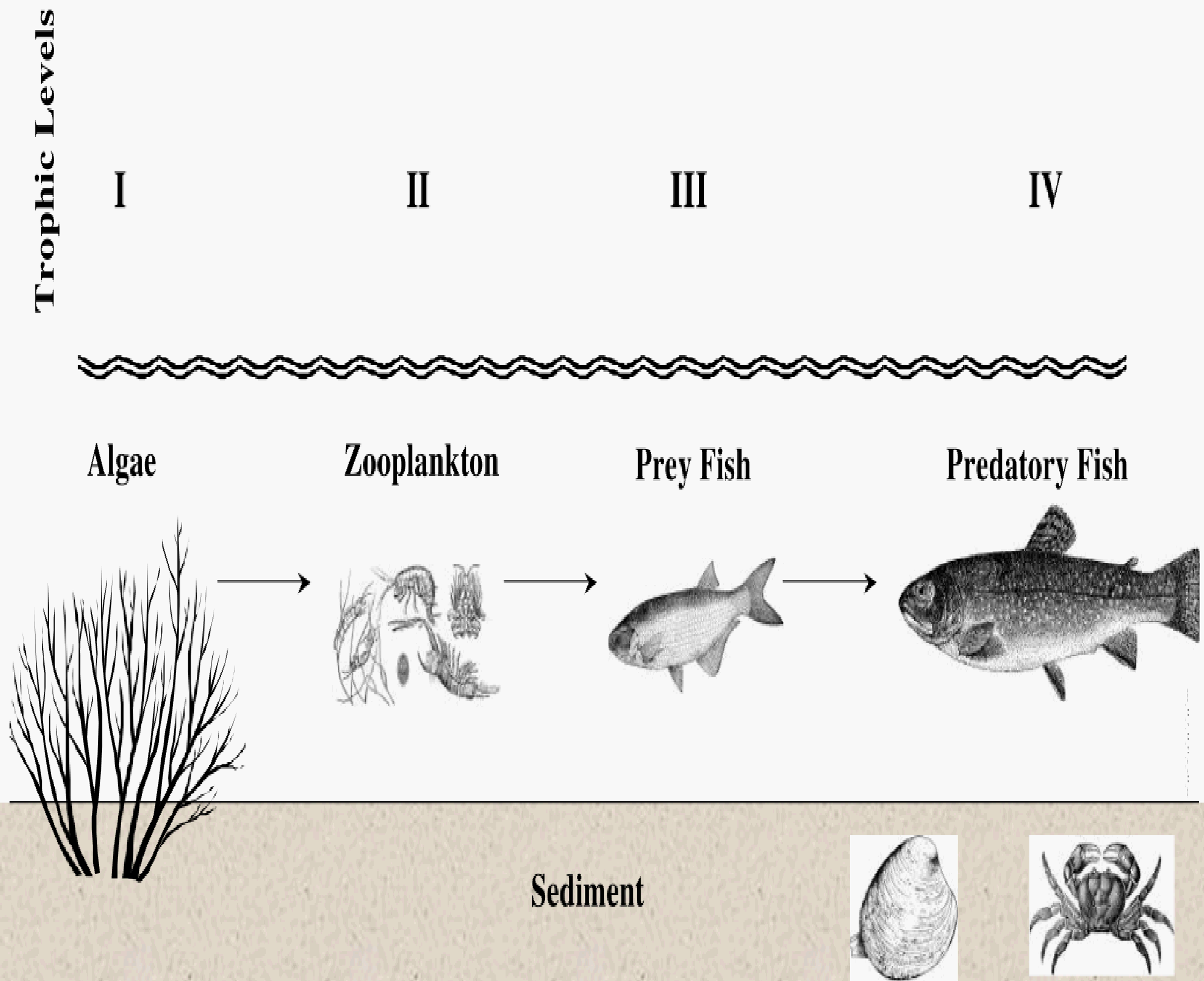
3. Chemical-Specific Issues

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,

including humans, and can produce death or defects in offspring (Eisler, 1988).

Bioconcentration factors compiled by USEPA (1985a) for freshwater organisms are quite low for both inorganic and organic forms of arsenic, ranging from zero to 17 (API, 1998). Few studies provide marine BCFs (USEPA, 1985a); however, because arsenic is present in higher marine organisms in a nontoxic form (i.e., arsenobetaine), it is of less concern in the marine environment. A recent review of metal bioaccumulation by aquatic macro-invertebrates identified arsenic bioaccumulation from sediments as a data gap in the scientific literature, as only a small number of studies have addressed this topic (Goodyear and McNeill, 1999). Additional information on arsenic toxicity and bioaccumulation can be found in API (1998) Publication Number 4676: *Arsenic: Chemistry, Fate, Toxicity, and Wastewater Treatment Options*.

3.2 Mercury

Mercury is found in the environment as elemental mercury vapor (Hg^0), inorganic mercury salts (including Hg^{+1} and Hg^{+2}), and organic mercury (mostly as mono- or dimethylmercury). Much of the mercury in the aquatic environment is from atmospheric deposition and enters the aquatic system as Hg^{+2} (Jonnalagadda and Rao, 1993; Westcott and Kalff, 1996). Methylation of mercury occurs primarily through the action of sulfate-reducing bacteria, although other mechanisms of methylation also exist (Gilmour and Henry, 1991).

Methylmercury is much more bioaccumulative than inorganic mercury. Methylmercury bioaccumulates quickly because it becomes protein bound and cannot be efficiently eliminated. It is biomagnified up the food chain, potentially resulting in concentrations in predatory fish that are thousands to millions of times greater than in the surrounding water (e.g., Bloom, 1992; Jonnalagadda and Rao, 1993). Under normal exposure conditions, human exposure to methylmercury occurs almost exclusively through fish and shellfish ingestion. Because of its biomagnification potential, water quality criteria for mercury are generally calculated using bioaccumulation factors to protect human and wildlife consumers of fish, rather than aquatic organisms (which are affected by mercury toxicity only at higher water concentrations).

The bioaccumulative potential of mercury is site-specific, because the extent of mercury methylation depends on the interaction of numerous environmental factors. Factors that favor the activity of sulfate-reducing bacteria increase methylation up to a point, but higher levels of sulfate reduction produce sulfide levels that inhibit methylation. In addition to sulfide, factors that affect mercury methylation include organic carbon, sulfate, nutrients, group VI anions, pH, salinity, and temperature (Beckvar et al., 1996; Gilmour and Henry, 1991). Specific environmental conditions that tend to increase mercury methylation and bioaccumulation include flooding of soils, such as during the creation of reservoirs, and acidification of lakes and rivers (Westcott and Kalff, 1996).

The USEPA's *Mercury Study Report to Congress* (USEPA, 1997b) contains a comprehensive review of mercury bioaccumulation from water. While the report concludes that site-specific measurements of mercury bioaccumulation are preferred, a range of BAFs is developed from the published literature for use where site-specific data are not available. For fish that eat zooplankton (trophic level 3), BAFs for methylmercury generally range from 461,000 to 5,410,000, with a median of 1,580,000. For fish that eat other fish (trophic level 4), methylmercury BAFs generally range from 3,260,000 to 14,200,000, with a median of 6,810,000. These BAFs are higher than the values used to develop water quality criteria as part of the GLI (USEPA, 1995b) and earlier national water quality criteria (USEPA, 1985b).

3.3 Nickel

Nickel (Ni) is most commonly found in aquatic environments as Ni^{+2} . Nickel can be found dissolved as the free ion, sorbed to minerals, or bound to organic carbon (USEPA, 1986a). In seawater, Ni^{+2} forms complexes with chloride and sulfate ions. The acute toxicity of nickel decreases with increasing water hardness and total organic carbon, indicating that it is the dissolved, free ion that is toxic to aquatic organisms (Babukutty and Chacko, 1995). Freshwater invertebrates, daphnids, and salt water mysid shrimp appear to be the most sensitive aquatic species (USEPA, 1986a).

In general, nickel does not accumulate to a high degree in aquatic organisms. Bioconcentration factors and bioaccumulation factors compiled by USEPA (1986a) range from less than ten to approximately 700, depending on the type of organism. Nickel concentrations in edible fish tissue (muscle) may actually be lower than nickel concentrations in the surrounding water (USEPA, 1986a). For comparison, the GLI does not consider chemicals having BAF values below 1000 to be of concern with regard to bioaccumulation. Nickel bioaccumulation from sediment has not been extensively studied, although a small number of studies are available (Goodyear and McNeill, 1999).

3.4 Selenium

Selenium is predominantly found in three valence states in aquatic systems: Se^{+6} (e.g., selenate, SeO_4^{-2}), Se^{+4} (e.g., selenite, SeO_3^{-2}), and Se^{-2} (selenide). Selenate and selenite are the predominant species in water and can be toxic to aquatic organisms (Canton and Van Derveer, 1997; USEPA, 1998a). Selenide can be found in either organic or inorganic forms. Inorganic selenides precipitate readily and show minimal toxicity to aquatic organisms. In contrast, organic selenides, particularly selenomethionine, are of primary importance because of their bioaccumulation potential and toxicity to fish and wildlife (Canton and Van Derveer, 1997; USEPA, 1987; 1998a). Selenomethionine is produced by phytoplankton from inorganic forms of selenium, especially selenite (USEPA, 1998a), by substituting selenium for sulfur in the essential amino acid methionine.

Aquatic organisms are mainly exposed to selenium through the diet, rather than through water, because of low solubility and the tendency of organic selenides to bioaccumulate in tissues. Generally, selenium is likely to initially enter the aquatic food chain through organisms that have contact with sediments or detritus (Canton and Van Derveer, 1997). The potential for bioaccumulation is also greater in standing water than in flowing systems, as flowing systems do not readily convert selenate and selenite to more toxic organo-selenium forms (Adams et al., 1997, Lemly, 1998). Similar to mercury, the bioaccumulation potential of selenium is strongly site-specific. In some cases, reproductive effects have been seen in fish and birds due to biomagnification, even with selenium concentrations in the water below chronic ambient water quality criteria

(AWQC). In other cases, concentrations exceeding the AWQC produce no adverse effects (Lemly, 1998). As with aquatic organisms, humans are exposed to selenium primarily through the diet. Seafood, particularly predatory fish, can contribute significantly to selenium exposure (ATSDR, 1996).

Conditions that favor selenium bioaccumulation can result in BAFs for fish on the order of thousands (Peterson and Nebeker, 1992), but much lower bioaccumulation is frequently observed. Due to the difficulty of predicting ecological effects from selenium concentrations in water, it has been suggested that tissue-based or sediment-based criteria be adopted (Canton and Van Derveer, 1997; Lemly, 1998; USEPA, 1998a). Water-based criteria for use in regulating selenium discharges would be developed from the tissue or sediment-based criteria as needed based on site-specific bioaccumulation data.

3.5 Dioxins

Chlorinated dibenzo-para-dioxins (“dioxins”) are a group of 75 congeners consisting of two benzene rings fused to the para-dioxin ring, with varying numbers of chlorine atoms attached to the benzene rings. The more toxic dioxin congeners have chlorine atoms in the 2, 3, 7, and 8 positions, possibly with chlorine atoms in other positions as well. 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) is the most toxic form of dioxin. The toxicity of other dioxin congeners is described relative to 2,3,7,8-TCDD using toxicity equivalency factors (TEFs), in which 2,3,7,8-TCDD is assigned a value of 1.0. As an example, a dioxin congener that is one-tenth as toxic as 2,3,7,8-TCDD would be assigned a TEF of 0.1. The TEFs developed for dioxins other than 2,3,7,8-TCDD range from 0.5 – 0.00001 (Van den Berg et al., 1998).

Dioxins have very low water solubility, a high affinity for organic carbon, and tend to remain bound to sediment particles in aquatic environments. Chlorine atoms protect the molecules from common environmental degradation processes such as hydrolysis and bacterial degradation (Eisler, 1986; ATSDR, 1998). Increased chlorination is associated with increased hydrophobicity and lipophilicity, and an increased ability to bind to organic matter (Cook et al., 1991). In general, these factors contribute to increased bioaccumulation with increased chlorination.

However, highly chlorinated dioxins are less bioaccumulative due to their large molecular size and reduced ability to penetrate biological membranes (Cook et al., 1991).

A review of dioxin bioaccumulation (USEPA, 1993) indicates that dioxin concentrations tend to be lower in benthic invertebrates than in sediment, and lower in fish than in invertebrates. Dioxin bioaccumulation is usually measured using BSAFs because dioxins are very hydrophobic, and concentrations in water are typically extremely low (below typical detection limits). For Lake Ontario fish, BSAF values range from 0.03 to 0.2 (USEPA, 1993). While these values are lower than typical BSAFs for many other organic chemicals, bioaccumulation of dioxins is of concern due to the sensitivity of fish and fish consumers (humans and wildlife) to these compounds. Based on the large differences observed between dioxin concentrations in sediment and water, bioaccumulation may be primarily sediment-related; however, BAFs can be calculated from measured BSAFs for the purpose of regulating dioxin discharges to the water column. BAFs for dioxins, which account for bioaccumulation from both sediment and water, range from the thousands to hundreds of thousands (Loonen et al., 1996; USEPA, 1995).

3.6 Polycyclic Aromatic Hydrocarbons (PAHs)

Polycyclic aromatic hydrocarbons (or polynuclear aromatic hydrocarbons) are a large group of chemicals characterized by two or more fused benzene rings, with or without substituted groups attached to the rings. The characteristics of PAHs are influenced primarily by their molecular weight. Major sources of total PAHs to the aquatic environment include natural oil seeps, oil spills and petroleum industrial operations, atmospheric deposition of combustion products, and municipal runoff (NRC, 1985).

As a group, PAHs include hundreds of compounds that range in molecular weight from 128 g/mol (naphthalene, a two-ring structure) to 300 g/mol (coronene, a seven-ring structure). PAHs are commonly divided into two groups: light and heavy. Generally, light PAHs contain two to three rings, are acutely toxic to aquatic organisms, but do not cause tumors. Common light PAHs include acenaphthylene, acenaphthene, fluorene, phenanthrene, and anthracene. PAHs with

higher molecular weights are relatively immobile and insoluble, and have very low volatility (Neff, 1985). Heavy PAHs contain four to seven rings, are less acutely toxic, but can cause tumors or defects in offspring (Eisler, 1987). Common heavy PAHs include fluoranthene, pyrene, benz(a)anthracene, benzo(a)pyrene, ideno(1,2,3-cd)pyrene, and benzo(g,h,i)perylene.

Light PAHs are generally available for microbial degradation in sediments, while heavy PAHs are not. Rates of degradation depend on PAH structure, sediment redox potential, sediment temperature, nutrients present, and the number and type of microbes present, although the products of biodegradation are not necessarily less toxic than the parent compound (Shuttleworth and Cerniglia, 1995). PAHs do not biomagnify in most organisms because of degradation through mixed-function oxygenase (MFO) enzymes. In addition, higher animals have low intestinal absorption of PAHs. In fish and mammals, the degradation of some PAHs (i.e., benzo(a)pyrene) results in reactive metabolites, which are potentially carcinogenic (Neff, 1985). Invertebrates, however, do not have as highly developed MFO as mammals, and as a result, PAHs will bioaccumulate in these species (Van der Oost et al., 1991).

Bioaccumulation factors for fish generally are not available and would not be meaningful, because fish metabolize PAHs. For invertebrates, BSAFs are available and may be used to calculate BAFs. Tracey and Hansen (1996) provide a comprehensive review of BSAFs for benthic invertebrates exposed to PAHs in sediments. These authors identified a median BSAF of 0.29 from a distribution of BSAFs based on the published literature, indicating that PAH concentrations in invertebrates tend to be lower than the concentrations in sediment (on a lipid and organic carbon normalized basis).

4. Regulatory Applications of Bioaccumulation

In response to increasing public concern regarding exposure to chemicals in the environment, USEPA and state agencies have begun to focus their regulatory agenda on those chemicals that are considered bioaccumulative. This section reviews several USEPA initiatives, including fish consumption advisories; the Great Lakes Water Quality Initiative (GLI); the Persistent, Bioaccumulative, and Toxic (PBT)

Strategy; and the Binational Toxics Strategy. For each initiative, the initiative's overall intent, the selection of bioaccumulative chemicals of concern, and the initiative's implications for the petroleum industry are discussed. In Section 4.2, the use of bioaccumulation in state water quality programs is reviewed.

4.1 Federal Regulations

4.1.1 Fish Consumption Advisories

In total, USEPA (1997c) has identified 25 target chemicals or chemical groups, including PCBs, chlordane, dioxins, DDT (including DDE and DDD), mercury, selenium, and PAHs, as presenting a potential health risk due to bioaccumulation in fish (see Table 1). For most inorganic chemicals (except methylmercury), USEPA does not distinguish between the different species and only regulates based on the total chemical concentration.

Depending on their chemical structure, some chemicals will accumulate in fat tissue, while other chemicals tend to accumulate in muscle tissue. Lipophilic chemicals such as dioxins and PCBs tend to accumulate in the fatty tissues of fish. Other chemicals, such as mercury, tend to accumulate in the muscle tissue. Several studies have shown that chemicals in fat tissue can be reduced through trimming and cooking of fish (Zabik et al., 1995, Zabik et al., 1996), while chemicals in muscle cannot.

In response to concerns about increased risk of carcinogenic and noncarcinogenic health effects from the consumption of contaminated fish, USEPA (1997c) developed risk-based consumption limits for the 25 chemicals in its target list. Consumption limits are based on the concentration in fish tissue, the meal size eaten, and the population of concern. USEPA's consumption limits generally apply to recreationally- and subsistence-caught freshwater, estuarine, and marine fish. Separate risk-based consumption limits are calculated for the general population, pregnant or nursing women, and children. Subsistence fishermen can also be of concern in certain areas.

Table 4-1. Bioaccumulative Chemicals of Concern as Identified by Regulatory Program

Chemical	Regulatory Program							
	GLI ¹	PBT ^{2,13}	RCRA ³	TRI ⁴	Fish Consumption ⁵	Binational Strategy Level I ¹³	Binational Strategy Level II	POP
Acenaphthene			√					
Acenaphthylene			√					
Aldrin		√		√		√		√
Alkyl-lead		√				√		
alpha-Endosulfan			√					
Anthracene			√				√	
Antimony			√					
Arsenic			√		√ ⁷			
Benzo(a)anthracene							√	
Benzo(a)pyrene		√				√		
Benzo(ghi)perylene			√	√			√	
Beryllium			√					
beta-Endosulfan			√					
Bis-(2-ethylhexyl)phthalate			√					
4-Bromophenyl phenyl ether			√					
Butylbenzyl phthalate			√					
Cadmium			√		√		√ ⁸	
Chlordane	√	√		√	√	√		√
Chloroform			√					
Chlorpyrifos					√			
Chromium			√					
Copper			√					
Cyanide			√					
DDT	√	√			√	√		√
DDD	√	√			√	√		
DDE	√	√			√	√		
Diazinon					√			
Dibutyl phthalate			√					
1,2-Dichlorobenzene			√					
1,3-Dichlorobenzene			√					
1,4-Dichlorobenzene			√				√	
3,3'-Dichlorobenzidine							√	
1,1-Dichloroethane			√					
Dieldrin	√	√			√	√		√
Dicofol				√	√			
Dinitropyrene							√	
Dioxins	√	√	√	√	√	√		√
Endosulfan					√ ⁹			
Endrin					√		√	√
Ethion					√			
Fluoranthene			√					
Fluorene			√					
Furans		√	√		√	√		√
gamma-Hexachlorocyclohexane (Lindane)	√		√		√			
Heptachlor			√	√			√	√
Heptachlor epoxide			√		√			
Hexachlorobenzene	√	√	√	√	√	√		√
Hexachlorobutadiene	√		√				√	
Hexachlorocyclohexanes	√ ¹⁰						√	
Isodrin				√				
Lead			√					

Table 4-1. Bioaccumulative Chemicals of Concern as Identified by Regulatory Program

Chemical	Regulatory Program							
	GLI ¹	PBT ^{2,13}	RCRA ³	TRI ⁴	Fish Consumption ⁵	Binational Strategy Level I ¹³	Binational Strategy Level II	POP
Mercury	√	√ ¹¹	√	√ ¹¹	√ ¹²	√ ¹¹		
Methoxychlor			√	√				
4,4'-Methylenebis(2-chloroaniline)							√	
2-Methylnaphthalene			√					
Mirex	√	√			√	√		√
Naphthalene			√					
Nickel			√					
Nitrobenzene			√					
Octachlorostyrene	√	√	√	√		√		
Oxyfluorfen					√			
Pendimethalin				√				
Pentachlorobenzene	√		√	√			√	
Pentachloronitrobenzene			√					
Pentachlorophenol			√				√	
Perylene							√	
Phenanthrene			√				√	
Phenol			√					
Photomirex	√							
Polycyclic aromatic hydrocarbons (PAHs)			√	√	√		√	
Polychlorinated biphenyls (PCBs)	√	√		√	√	√		√
Pyrene			√					
Selenium			√		√			
Terbufos					√			
1,2,3,4-Tetrachlorobenzene	√						√	
1,2,4,5-Tetrachlorobenzene	√		√				√	
Tetrabromobisphenol A				√				
Toxaphene	√	√		√	√	√		√
Tributyltin					√		√	
1,2,4-Trichlorobenzene			√					
1,1,1-Trichloroethane			√					
2,4,5-Trichlorophenol			√					
Trifluralin				√				
2,4,6-tris-(1,1-Dimethylethyl)phenol			√					
Zinc			√					

Notes:

1. Based on Final Water Quality Guidelines for Great Lakes System (60 FR 15365).
2. Based on USEPA's Strategy for Persistent, Bioaccumulative and Toxic (PBT) Chemicals.
3. Based on USEPA's Draft RCRA Waste Minimization PBT Chemical List (63 FR 60332).
4. Based on USEPA's proposed rule (64 FR 687) to increase the reporting requirements for PBT chemicals.
5. Based on USEPA (1997) Guidance for Assessing Chemical Contamination Data for Use in Fish Advisories.
6. Based on United Nations Environmental Program
7. Inorganic arsenic
8. Includes cadmium compounds
9. Endosulfan I and II
10. Includes alpha-BHC, beta-BHC, and delta-BHC
11. Includes mercury compounds
12. Methylmercury
13. USEPA's list considers aldrin/dieldrin, DDD/DDE/DDT, and dioxins/furans as one group

The specific equations used by USEPA to calculate fish consumption advisories are presented in Appendix A. These equations may be modified to calculate overall daily consumption limits based on exposure to single chemicals in a multiple species diet or to use site-specific body weights or meal sizes (USEPA, 1997c). It is important to note that the equations do not use a BCF or BAF as part of the calculation of acceptable consumption levels. Bioaccumulation potential is only used as a means to identify chemicals of concern.

Using the equations in Appendix A, USEPA has calculated monthly consumption limits for the 25 chemicals identified in the target analyte list. For each chemical, USEPA provides an estimate of the acceptable number of meals assuming a 4 oz., 8 oz., 12 oz., or 16 oz. meal size and a risk level of 1×10^{-4} , 1×10^{-5} , or 1×10^{-6} . For example, assuming an 8 oz. meal size, individuals in the population could be exposed to 1 mg/kg selenium in fish tissue without adverse noncancer health effects (assuming one fish meal per day). At 2 mg/kg, the recommended monthly fish consumption rate drops to 23 meals/month (USEPA, 1997c).

As bioaccumulation becomes of greater concern to regulatory agencies, it is likely that the number of fish consumption advisories will continue to increase. Although USEPA is currently targeting an initial list of 25 analytes, as other chemicals are identified as bioaccumulative (see Table 4-1), it is likely that fish consumption advisories will address additional chemicals in the future.

4.1.2 Great Lakes Water Quality Initiative

On March 23, 1995, USEPA finalized the Water Quality Guidance for the Great Lakes System (60 FR 15365), known as the Great Lakes Water Quality Initiative (GLI). The GLI represents the results of over six years of work by individuals representing the Great Lakes States' environmental agencies, USEPA National and Regional offices, US Fish and Wildlife Service, and the National Park Service. Amendments to the Clean Water Act in 1990 were made to ensure that the GLI was consistent with the Great Lakes Water Quality Agreement (GLWQA) signed between the United States and Canada. After final promulgation of the GLI, Illinois, Indiana, Michigan, Minnesota, New York, Ohio, Pennsylvania, and Wisconsin were required to adopt GLI provisions into water quality

standards and National Pollutant Discharge Elimination System (NPDES) permit programs by March 23, 1997.

The GLI was partly a response to the detection of hundreds of contaminants in the Great Lakes System. Of the chemicals detected, approximately one-third have been reported to cause adverse effects in either humans or wildlife (60 FR 15365). Although direct contact with water or sediment containing these chemicals may be a concern, consumption of Great Lakes fish is associated with the greatest risks. USEPA has calculated excess health risks to recreational and subsistence populations consuming Great Lakes fish for eight bioaccumulative chemicals of concern (BCCs): chlordane, DDT, dieldrin, hexachlorobenzene, mercury, PCBs, 2,3,7,8-TCDD, and toxaphene. In addition to human health concerns, studies have documented adverse effects in aquatic life and wildlife living in the Great Lakes Basin (Weseloh et al., 1983; Giesy et al., 1994; Fox et al., 1991), with fish-consuming birds and mammals often at the greatest risk.

To address these potential risks, the GLI sets water quality standards for: (1) the protection of aquatic life; (2) the protection of human health; and (3) the protection of wildlife. Of these standards, bioaccumulation is a critical factor in the derivation of both human health and wildlife criteria. The GLI identifies a specific methodology for identifying and selecting BAFs, as described below. Following the description of the BAF methodology is an explanation of each of the water quality criteria. Although the GLI only finalized water quality criteria for a few chemicals, the guidance sets forth the process for determining additional criteria for many more chemicals.

Bioaccumulation Methodology. A critical part of the water quality criteria derivation for human health and wildlife is the calculation of BAFs. Unlike earlier water quality criteria calculations, the GLI uses a baseline BAF that takes into account uptake from sediment and the food chain, as well as water (see Text Box 4.1). The baseline BAF is specific to the GLI and is developed using available BAF and BCF data. Calculation of the baseline BAF is presented in

Text Box 4.1 Great Lakes Initiative BAF Definitions

Baseline BAF: For organic chemicals, a BAF is based on the concentration of freely dissolved chemical in the ambient water, and that accounts for partitioning of the chemical within the organism (lipid-normalized); for inorganic chemicals, a BAF is based on the wet weight of the tissue (not lipid-normalized).

Food Chain Multiplier (FCM): The ratio of a BAF to an appropriate BCF. FCMs are used to account for biomagnification of chemicals up the food chain.

Appendix C, Section C-2. The GLI provides four methods for deriving a baseline BAF for organic and inorganic chemicals in order of preference (60 FR 15402). Please note that only methods 1 and 3 may be used for inorganic chemicals:

1. A measured baseline organic or inorganic chemical BAF derived from a field study of acceptable quality;
2. A predicted baseline organic chemical BAF derived using field-measured BSAFs of acceptable quality;
3. A predicted baseline organic or inorganic chemical BAF derived from a laboratory-measured BCF and a food chain multiplier (FCM); or
4. A predicted baseline organic chemical BAF derived from a log K_{ow} and a FCM.

The specific data requirements for obtaining an acceptable baseline BAF are identified in Appendix B. When a baseline BAF for organic chemicals cannot be calculated using Method 1 or 2 above, the GLI provides FCMs. FCMs are based on Log K_{ow} and are used to calculate a baseline BAF for trophic levels 3 and 4 in the absence of a field-measured BAF or an acceptable BSAF or BCF value. Most organic chemicals with a Log K_{ow} greater than four have a FCM greater than 1.0. For inorganic chemicals, the baseline BAF for trophic levels 3 and 4 are assumed to be equal to a BCF measured using fish. In other words, the FCM is assumed to be equal to one. The only exception to this rule is for inorganic chemicals, such as methylmercury, which may biomagnify up the food chain.

Baseline BAFs are used in the calculation of cancer and noncancer human health criteria values assuming an acceptable cancer risk of 1×10^{-5} and a noncancer hazard quotient of 1.0 (i.e., exposure is set equal to a noncancer no-effect level). In order to be used to derive human health criteria, the baseline BAF for organic chemicals must first be converted into a BAF^{HH}_{TL3} (human health BAF for trophic level 3) or a BAF^{HH}_{TL4} (human health BAF for trophic level 4). This ensures that water quality criteria are protective for individuals that consume trophic level 3 or 4

fish. Detailed equations to calculate BAF^{HH}_{TL3} or BAF^{HH}_{TL4} for organic chemicals are presented in Appendix C, Section C-1.

Wildlife criteria values for the 22 bioaccumulative chemicals of concern (BCC) are also calculated using BAFs (see Table 4-1). Similar to human health, a baseline BAF for organic chemicals must first be converted to a BAF^{WL}_{TL3} (wildlife BAF for trophic level 3) or a BAF^{WL}_{TL4} (wildlife BAF for trophic level 4). Calculations are presented in Appendix C.

Protection of Aquatic Life. The GLI contains, for 15 chemicals, water quality criteria to protect aquatic life. A two-tiered methodology (Tier I criteria and Tier II values) is also included to allow the calculation of water quality criteria for additional chemicals. The two-tiered system is designed to allow states to derive total maximum daily loads (TMDL) and NPDES permit limits from narrative criteria. Using the Tier I methodology, criteria are calculated from laboratory toxicity data. To set Tier I criteria, acute or chronic data must be available for at least one species of freshwater animal in at least eight different families. If sufficient data are available, a Final Acute Value (FAV) or a Final Chronic Value (FCV) can be calculated. This procedure is similar to that used by USEPA to determine national ambient water quality criteria (AWQC). In contrast, by applying uncertainty factors the Tier II methodology allows calculation of criteria using less data. As a result, to compensate for the lack of sufficient data, the Tier II methodology generally results in more stringent standards.

Unlike the human health and wildlife criteria described below, the GLI criteria for the protection of aquatic life are calculated without using any data on bioaccumulation. Instead, these values are estimated based solely on available toxicity data through the calculation of a Genus Mean Acute Value (GMAV) and Genus Mean Chronic Value (GMCV). The FAV and FCV represent the concentrations at which 95 percent of the genera have a higher GMAV and GMCV. In the case of an important species, the Species Mean Acute Value (SMAV) or Species Mean Chronic Value (SMCV) may be substituted for the FAV or FCV, if the SMAV or SMCV is lower.

Protection of Human Health. The GLI contains human health criteria - human cancer values (HCV) and human noncancer values (HNV) - for 18

pollutants, as well as Tier I and II methodologies for deriving cancer and non-cancer criteria for additional chemicals. Similar to aquatic criteria, Tier I criteria are to be derived for chemicals that meet minimum data requirements, while Tier II criteria are derived when less data are available. In all cases, the human health criteria have been derived to protect individuals from adverse health effects (including cancer, an acceptable incremental cancer risk of 1×10^{-5} is specified) due to consumption of aquatic organisms and water, including incidental water consumption during recreational activities.

Detailed calculations for deriving Tier I and Tier II criteria are presented in Appendix D. A critical component of the HCV and HNV calculation is bioaccumulation. To be used in the calculation, BAFs must be calculated using one of the four methods described above. In addition, the BAF used must account for trophic level transfers (see Appendix C). HCV and HNV calculations also assume that an individual consumes 15 g/day of recreationally caught fish and two liters/day of water. For water bodies that are not used for drinking water, consumption can be reduced to 0.01 liters/day.

Protection of Wildlife. The GLI contains criteria for the protection of wildlife for four chemicals (DDT and metabolites, mercury including methylmercury, PCBs, and 2,3,7,8-TCDD) and a methodology to derive Tier I criteria for all other BCCs (see Appendix D). 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. Tier 1 wildlife criteria are limited to BCCs, since these chemicals are likely of greatest concern to wildlife species. Tier II criteria may be calculated for other nonbioaccumulative chemicals using the same methodology.

Appendix D presents the calculations for wildlife values (WVs). WVs are used to calculate Great Lakes Water Quality Wildlife Criteria (GLWC). It is important to note that USEPA uses the terms Tier I wildlife criterion and GLWC interchangeably. Similar to the human health criteria, bioaccumulation is a critical component in the calculation.

For each BCC, USEPA calculates a WV for each of the Great Lakes representative avian and mammalian species. 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. Because WVs are designed to protect Great Lakes wildlife species from adverse effects related to reproduction and population survival, WVs are not calculated for cancer (as in the human health criteria). Instead, a single WV is calculated by using uncertainty factors to modify either a no observable adverse effect level (NOAEL) or lowest observable adverse effect level (LOAEL) identified from laboratory toxicity studies. The resulting value is considered sufficient to protect the wildlife population from adverse reproductive or other population effects.

The unique nature of the Great Lakes system limits the applicability of the GLI and GLI methodology to other regions; however, it is possible that USEPA and/or states may attempt to adapt the GLI provisions into the development of water quality standards in other ecosystems. A July 1998 USEPA fact sheet (USEPA, 1998b) on revisions to the AWQC reveals the greater role and importance of BAFs in setting water quality standards. However, readers are cautioned that some assumptions made for the Great Lakes (e.g., very long residence times) that drive many of the concerns and approaches in the GLI may not be appropriate in other ecosystems.

More recently (64 FR 53632, 10/4/99), USEPA announced that discharges of BCCs into mixing zones in the Great Lakes will be phased out over the next ten years. In the past, chemical discharges were allowed to mix with receiving waters and dilute, in order to meet standards. Elimination of mixing zones already occurs in Illinois, Indiana, Michigan, Minnesota, and Wisconsin; however, New York, Ohio, and Pennsylvania will now be mandated to also adopt this provision.

4.1.3 Persistent, Bioaccumulative, and Toxic (PBT) Strategy

The objective of the 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 and therefore, may travel for long distances between environmental media (Persistent), accumulate in fish and other organisms in the food chain (Bioaccumulative), and have been demonstrated to cause adverse effects in either humans or wildlife (Toxic). To date, USEPA has identified 12 PBT chemicals and chemical classes (see Table 4-1). Additional chemicals will be added to the PBT list after USEPA obtains comments on the selection methodology.¹

By developing a PBT strategy, USEPA states that it is committing to protect individuals, especially the fetus and child, and wildlife populations from exposure to these chemicals. Because PBT chemicals are found in all environmental media, USEPA's program is designed to cut across offices and address these issues on an Agency-wide basis. USEPA's strategy for PBT chemicals consists of four goals:

- Develop and implement national action plans to reduce priority PBT chemicals;
- Screen and select additional priority PBT chemicals;
- Prevent the introduction of new PBT chemicals; and
- Measure progress by linking activities to environmental results.

Consistent with USEPA's strategy to address PBT chemicals Agency-wide, several program offices have recently developed strategies to manage PBT chemicals and meet the PBT goals. Each of these regulatory strategies is discussed briefly below.

Toxic Substances Control Act (TSCA). As part of the goal to prevent the introduction of new PBT chemicals, USEPA has revised the pre-

¹A parallel initiative is underway in the United Nations Environmental Program (UNEP). The UNEP focuses on persistent organic pollutants (POPs) (see Table 1) and is limited in its regulatory authority to international transport of listed POPs. Additional information on POPs can be found at www.chem.unep/pops/.

manufacture notice (PMN) process under TSCA Section 5(a) to include a new category of PBT chemical substances or mixtures (63 FR 53417). Under the current system, most PMNs contain little data, but instead use computer models and structural or functional analogues as indicators of the potential toxicity and environmental fate of a chemical substance. These predictive methods often estimate the properties of a chemical based on Structure-Activity Relationships (SAR). To date, USEPA has developed 45 categories of chemicals under TSCA, significantly shortening the PMN process and allowing USEPA to target those chemical groups with the greatest potential toxicity. The new PBT chemical category under TSCA includes chemicals with the chemical properties identified in Table 4-2. Chemicals that meet these characteristics are then subject to regulation as either a Significant New Use Rule (SNUR) or a ban pending additional testing.

Chemicals that fall in the “5(e) Order/ SNUR” category will be subjected to increased scrutiny by USEPA, although commercial production will be allowed. Certain restrictions will be imposed such as TRI-type reporting and specific limitations on exposures, releases, and uses by manufacturers, importers, and processors of the PMN substance. Chemicals in the “Ban Pending Testing” category are likely to be subjected to more stringent limitations including a total ban on production or use until the submittal of additional data on chemical toxicity and environmental fate.

Resource Conservation and Recovery Act (RCRA). On November 9, 1998, USEPA’s Office of Solid Waste (OSW) published a Notice of Data Availability (NODA) outlining the Draft RCRA Waste Minimization PBT Chemical List (63 FR 60332). This list was developed as part of the strategy to achieve the goals of USEPA’s (1994a) Waste Minimization National Plan. USEPA screened chemicals based on their persistence in the environment, their bioaccumulative potential, and their toxicity to human and ecological receptors. In addition, USEPA also considered the quantity of chemical in hazardous waste, the presence of the chemical in environmental media, and the degree to which the chemical is of particular concern to the RCRA program using a quantitative ranking system. Using these criteria, USEPA refined its initial list of 694 chemicals and chemical groups to a final list of 53 (see Table 4-1).

Table 4-2. Chemical Properties for Categorizing PBT Chemicals under TSCA

Chemical Properties	TSCA Section 5 Action	
	5(e) Order/Significant New Use Rule (SNUR) ¹	Ban Pending Testing ²
Persistence (or half-life)	> 2 months	> 6 months
Bioaccumulation (BAF or Fish BCF) ³	≥ 1000	≥ 5000
Toxicity	Develop where necessary ⁴	Develop where necessary ⁴

Notes:

1. Exposure/release controls included in order; testing required.
2. Deny commercialization; testing results may justify removing chemical from “high risk concern.”
3. Chemicals must also meet criteria for MW (<1000) and cross-sectional diameter (< 20Å, or < 20x10⁻⁸ cm).
4. May require completion of additional toxicity testing, based upon various factors, including concerns for persistence, bioaccumulation, other physical/chemical factors, and predicted toxicity.

The 53 chemicals and chemical groups on the RCRA priority PBT 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 between federal, state, and local agencies (63 FR 60332). To accomplish these goals, USEPA will rely on voluntary waste minimization mechanisms, recognizing that some voluntary actions will take place in conjunction with a regulatory activity (e.g., implementing pollution prevention measures to meet permit compliance requirements).

Emergency Planning and Community Right-to-Know Act of 1986 (EPCRA) - Toxic Release Inventory. To begin the process of better tracking chemicals identified as being persistent, bioaccumulative, and toxic, USEPA has proposed under Section 313 of EPCRA to increase the reporting requirements of certain chemicals on the Toxic Release Inventory (TRI) (64 FR 687). USEPA's proposal reduces the reporting thresholds for the manufacture, process, and use of certain bioaccumulative chemicals depending on the chemical's half-life and BCF (see Table 4-3). USEPA proposes to reduce reporting thresholds for these chemicals 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. Additionally, USEPA is proposing a separate reporting threshold category for dioxin and dioxin-like compounds.

USEPA is also proposing to add seven chemicals and one chemical class to the list of chemicals subject to reporting requirements under EPCRA. These chemicals have been identified based on their potential to bioaccumulate, as well as their demonstrated toxicity at low levels: benzo(ghi)perylene, fluoranthene, 3-methylcholanthrene, octachlorostyrene, pentachlorobenzene, tetrabromobisphenol A, vanadium, and dioxin and dioxin-like compounds. Once added to the TRI, any use, production, or releases of these chemicals at the quantities listed in Table 4-3 must be reported to USEPA on a yearly basis. All information in the TRI is then released to the public.

Table 4-3. Toxic Release Inventory Reporting Thresholds for PBT Chemicals^a

Chemical	Reporting Threshold (lbs)
Aldrin	100
Benzo(ghi)perylene	10
Chlordane	10
Dicofol	10
Dioxin and dioxin-like compounds	0.1 grams
Heptachlor	10
Hexachlorobenzene	10
Isodrin	10
Methoxychlor	100
Octachlorostyrene	10
Pendimethalin	100
Pentachlorobenzene	10
Polycyclic aromatic compounds	10
Polychlorinated biphenyl (PCBs)	10
Tetrabromobisphenol A	100
Toxaphene	10
Trifluralin	100
Mercury	10
Mercury compounds	10

a. Proposed rule, January 5, 1997; 64 FR 687.

4.1.4 Great Lakes Binational Toxics Strategy

The objective of the Great Lakes Binational Toxic Strategy (also known as the Canada-United States Strategy for the Virtual Elimination of Persistent Toxic Substances in the Great Lakes Basin) is to obtain reductions in certain PBT chemicals in order to protect the health and integrity of the Great Lakes system. This strategy was developed during 1996 and 1997 and signed by both countries on April 7, 1997. The project is now managed by the Binational Executive Committee (BEC), which is chaired by Environment Canada (EC) and USEPA.

The focus of the Binational strategy is to virtually eliminate from the Great Lakes Basin toxic chemicals resulting from human activity, particularly those chemicals that bioaccumulate or may affect the Great Lakes ecosystem. For those chemicals that are also naturally occurring, the anthropogenic sources will be targeted in order to achieve naturally occurring levels. The goals of the Binational strategy will be achieved through a variety of programs and actions with the primary emphasis on pollution prevention. Because many of the chemicals of concern in the Great Lakes Basin are associated with atmospheric deposition, the Binational strategy will also seek to work on issues associated with long-range transport.

Environment Canada and USEPA have developed a four-step process to work toward the goal of virtual elimination:

- Gather information;
- Analyze current regulations, initiatives, and programs that manage or control substances;
- Identify cost-effective options to achieve further reductions; and
- Implement actions to work toward the goal of virtual elimination.

The Binational strategy focuses on an initial list of 12 Level I priority PBT chemicals and chemical classes (see Table 4-1). These chemicals were selected based on their widespread, long-term adverse effects in wildlife, and their potential to cause adverse health effects on humans due to

bioaccumulation in food items. In addition, these chemicals are targeted for virtual elimination through pollution prevention and other incentive-based actions that over time will phase out their use, generation, or release in a cost-effective manner. To date, USEPA has developed a virtual elimination strategy for PCBs; however, additional strategies are in process for all Level I priority chemicals.

An additional list of Level II substances, including chemicals identified by either the US or Canada based on PBT characteristics, has been compiled but not yet been agreed to by both countries. PAHs as a group are included on this list. Currently, no regulatory action is being taken on the Level II chemicals, although both countries encourage all stakeholders to reduce these chemicals through pollution prevention activities.

Consistent with the four-step process described above, the BEC has developed eight challenges to be completed by 2006. Those of potential interest to the petroleum industry include the following:

- A challenge to seek a 50 percent reduction in the deliberate use and release of mercury nationally. This release challenge applies both to aggregate air releases nationwide and to releases to water within the Great Lakes Basin, and
- A 75 percent reduction in releases of dioxins, furans, hexachlorobenzene, and benzo(a)pyrene from sources associated with human activity. This release challenge applies both to aggregate air releases nationwide, and to releases to water within the Great Lakes Basin.

4.1.5. Draft Revisions to the Ambient Water Quality Criteria Methodology

On August 14, 1998, USEPA published in the *Federal Register* (63 FR 43756) a *Notice of Draft Revisions to the Methodology for Deriving Ambient Water Quality Criteria (AWQC) for the Protection of Human Health*. This notice outlines specific changes in the derivation of water quality criteria since the publication of USEPA's 1980 methodology. Using this revised methodology, USEPA is planning to revise human

health AWQC for chemicals of high priority and national importance, including chemicals that bioaccumulate, such as PCBs, dioxin, and mercury. The methodology does not address changes in criteria for the protection of aquatic life, although changes to the aquatic life methodology are currently underway at USEPA.

Major changes in the methodology for deriving human health AWQC include: (1) use of a BAF instead of a BCF; (2) use of a default fish consumption rate of 17.8 g/d for the general population and 86.3 g/d for subsistence fishers/minority anglers; (3) calculation of a fish concentration in addition to a water concentration for some constituents; and (4) use of a relative source contribution (RSC) to account for exposure from other media. In the case of bioaccumulation, the revised AWQC methodology adopts many of the provisions from the GLI. In particular, EPA recommends the use of the four-method hierarchy for developing BAFs (see Section 4.1.2) as well as the use of food chain multipliers (FCMs). Fish consumption has been significantly increased compared to both the 1980 methodology and the GLI. USEPA recommended a default fish consumption rate of 6.5 g/d in the 1980 AWQC methodology and 15 g/d in the GLI. The changes made in the fish consumption rate lead to the calculation of a lower acceptable AWQC. Finally, USEPA has made some methodological changes not found in either the GLI or the 1980 AWQC methodology. Neither of these regulations allowed for the calculation of a fish concentration instead of, or in addition to, a water concentration, or recommended the use of a RSC. Although the impact of calculating a fish concentration is unclear, the use of a RSC can significantly reduce the resulting AWQC as USEPA attempts to account for other exposures that may contribute to risk.

At the request of USEPA, a peer review of the revised methodology was conducted (USEPA, 1999). In their report, the peer reviewers identified several concerns with the bioaccumulation approach put forth by USEPA. In general, the reviewers agreed with the use of BAFs instead of BCFs; however, there was significant concern that the methodology was not appropriate for implementation on a national level. As described by the peer reviewers, “many of the model parameters are highly uncertain and several of the assumptions have a tenuous scientific basis” (USEPA, 1999). Although the approach was consistent with current scientific

thinking, the peer reviewers recommended using site-specific data as much as feasible to develop AWQC at a local level. In addition, the peer reviewers felt that the proposed FCMs were not broadly applicable and should only be used after more detailed field verification. Other concerns voiced by the peer review panel included the calculation of a default lipid value and the equation to estimate the freely dissolved fraction. In both cases, the reviewers agreed that additional data and analysis were necessary before the methods could be used on a national scale. Finally, the peer reviewers conclude, "that most of the uncertainties in the new methodology would result in an overestimate of BAFs and a lowering of AWQC values" (USEPA, 1999). A complete report of the peer review is available on the internet at www.epa.gov/ost/humanhealth/peer.html.

4.2 State Initiatives

State initiatives regarding bioaccumulation are most often related to determination of water quality standards. Similar to the process described for the GLI, BAF is a critical factor in the calculation of numerical criteria for the protection of human health and wildlife. Once in place, these standards are then used by states to set limits for either general or individual permits.

Under the Clean Water Act, USEPA develops criteria for water quality. These criteria are calculated using dose-response data on health and environmental effects, and do not take into account economic considerations or technological feasibility. In addition, USEPA considers bioaccumulation of chemicals by aquatic organisms in order to protect both human and wildlife consumers (USEPA, 1985c). The criteria developed by USEPA are to be used by states to calculate water quality standards that provide the basis for controlling the discharge of chemicals into surface water bodies. 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 (63 FR 68355). USEPA strongly encourages states to update their water quality standards within five years of USEPA's publication of new or revised criteria.

Consistent with the federal requirements described above, states develop water quality standards that: (1) define the water quality goals of a water body by designating the use or uses to be maintained; (2) set criteria to protect these uses; and (3) protect water quality through antidegradation policies (63 FR 36745). As a result, water quality standards include provisions for restoring and maintaining the chemical, physical, and biological integrity of water bodies, as well as providing water quality for the protection and propagation of fish, shellfish, and wildlife, and recreation. To achieve these goals, states usually define both numerical (chemical-specific) and narrative water quality criteria.

Numerical standards may be set consistent with criteria derived by USEPA. However, because USEPA criteria are designed to be protective of the majority of water bodies nationwide, standards are calculated using species that are sensitive to many chemicals, and based on tests conducted in soft water that is low in particulate and organic matter (USEPA, 1985c). As a result, some states choose to set their own standards using species and water conditions more applicable to the state. Narrative criteria are general goals to be attained by all waters. Examples of narrative standards include standards for taste and odor in drinking water, changes in color, oil and grease contamination, and floating debris. The specific narrative and numerical standards to be met may depend on the use designation for the water body. Once standards are set, they are used to develop water quality based effluent limits to be included in NPDES permits.

Sections 4.2.1 through 4.2.5 describe the water quality programs in specific states of interest to the petroleum industry as of spring 1999: Louisiana, Texas, Indiana, New York, and Washington. In most cases, the states have implemented the basic provisions of the water quality standards as promulgated by USEPA. However, where specific changes are made to USEPA's program, they are clearly noted. Readers are urged to check the web sites and references listed for each state to obtain the most current information.

4.2.1 Louisiana

The state of Louisiana sets narrative and numerical water quality standards to promote restoration, maintenance, and protection of state

waters. The criterion established for a substance represents the permissible level that allows the continued support of a designated use. Narrative and numeric criteria are sometimes developed to take into account site-specific conditions within the state; however, in most instances, Louisiana has adopted aquatic and human health criteria promulgated by USEPA in the following documents: (1) Water Quality Criteria, 1972 (USEPA, 1973; commonly referred to as the Blue Book); (2) Quality Criteria for Water, 1976 (USEPA, 1976; commonly referred to as the Red Book); (3) Ambient Water Quality Criteria, 1980 (USEPA, 1980); (4) Ambient Water Quality Criteria, 1984 (USEPA, 1984a); and (5) Quality Criteria for Water, 1986 (USEPA, 1986b) - with updates (commonly referred to as the Gold Book).

In those instances where an aquatic life criterion is not derived in the USEPA documents listed above, Louisiana may develop a criterion by applying an appropriate application factor for acute and chronic effects to the lowest LC50 value for a representative Louisiana species. The exact application or uncertainty factor applied will depend on the chemical and the quality of the studies available.

Most Louisiana water quality standards for the protection of human health are based on a lifetime cancer risk of 1×10^{-6} , with the exception of 2,3,7,8-TCDD and lindane (gamma-BHC) which are based on a lifetime cancer risk of 1×10^{-5} . In the GLI, USEPA calculates water quality criteria assuming a cancer risk of 1×10^{-5} . For those criteria that are calculated by the state, a fish consumption rate of 20 grams/day is assumed. In comparison, USEPA uses a fish consumption rate of 6.5 grams/day in the national criteria and 15 grams/day in the GLI. As a result, standards calculated in Louisiana will be more stringent than those calculated using national guidance or the GLI.

Additional information on Louisiana water quality standards can be found at: www.deq.state.la.us/planning/regs/title33/33v09.pdf. Part IX, Chapter 11 of the Water Quality Regulations contains information on surface water quality standards, as well as the application of these standards (Section 1115) related to waste water discharges.

4.2.2 Texas

Similar to Louisiana, the state of Texas has both narrative and numerical criteria. The narrative criteria are applicable to all waters of the state and define general goals to be attained (i.e., free of floating debris, no changes in turbidity or color). Numeric criteria are established for those chemicals determined to have adequate toxicity information and have potential adverse effects in humans. In 1987, Texas adopted 30 criteria to protect aquatic life. An additional five criteria were added in 1991 and an additional four in 1995 for a total of 39 chemical criteria to protect aquatic life. Human consumption of fish and drinking water is protected by numerical criteria for 65 chemicals.

Numerical criteria to protect aquatic life are developed using the USEPA guidance document, *Guidelines for Deriving Numerical Site-Specific Water Quality Criteria* (USEPA, 1984b). In those instances where insufficient information is available to implement USEPA guidelines, the following provisions are applied:

- Acute criteria are calculated as the product of 0.3 and the LC50 of the most sensitive aquatic organism;
- Criteria for non-persistent toxic materials are either lower than chronically toxic concentrations or calculated as the product of 0.1 and the LC50 of the most sensitive aquatic organism;
- Criteria for persistent toxic materials that do not bioaccumulate are either lower than chronically toxic concentrations or calculated as the product of 0.05 and the LC50 of the most sensitive aquatic organism; and
- Criteria for toxic materials that bioaccumulate are either lower than chronically toxic concentrations or calculated as the product of 0.01 and the LC50 of the most sensitive aquatic organism.

To protect human health, Texas has established standards for three categories of waters: (1) waters that support drinking water and freshwater fish consumption; (2) waters that only support freshwater fish consumption; and (3) waters that only support saltwater fish consumption.

To develop these standards, Texas uses an acceptable risk level of 1×10^{-5} and the following exposure assumptions: (a) fish consumption rate of ten grams/day freshwater and 15 grams/day marine; (b) water consumption rate of two liters/day; and (c) bioconcentration factor in fish tissue estimated based on $\log K_{ow}$ and comparisons to molecular structure (using the USEPA Quantitative Structure Activity Relationships Database), and correcting to a fish tissue lipid concentration of three percent.

Additional standards are also set for waters that do not have a sustainable fishery, but do have aquatic life use. For these water bodies, criteria are calculated assuming: (1) fish consumption of 1.0 gram/day for inland waters and 1.5 grams/day for coastal waters and (2) an acceptable cancer risk of 1×10^{-5} . Numerical criteria for bioaccumulative pollutants are calculated consistent with USEPA (1994b), *Assessment and Control of Bioconcentratable Contaminants in Surface Waters*.

Once stream-specific use designations are set (i.e., streams are classified based on the appropriate level of protection), the state determines acceptable pollutant loads that allow specified criteria to be maintained. More detail on implementation of water quality standards can be found in, *Implementation of the Texas Natural Resource Conservation Commission Standards via Permitting*. This document is available at www.tnrcc.state.tx.us/admin/topdoc/wqual.html.

Texas surface water quality rules are available at: www.tnrcc.state.tx.us/oprd/rules/indxpdf.html. Chapter 307 of the Texas Administrative Code contains information on surface water quality criteria and implementation of these criteria through NPDES permits. General information on water quality standards and the Texas Pollutant Discharge Elimination System (TPDES) may be found at: www.tnrcc.state.tx.us/water/quality/index.html.

4.2.3 Indiana

As a Great Lakes state, Indiana has adopted the GLI into its state regulations. Therefore, aquatic, wildlife, and human health water quality criteria are calculated using the methodology and equations specified in

the GLI. Bioaccumulation is considered when calculating human health and wildlife water quality criteria. The Permitting Branch of the Indiana Department of Natural Resources issues NPDES permits to ensure that discharges comply with Clean Water Act standards and provisions.

Information on the Indiana water quality program may be found at www.ai.org/idem/owm/planbr/wqs/criteria.htm. Details on the wastewater permit program can be found at www.state.in.us/idem/owm/; www.state.in.us/idem/owm/dwb/guide/index.html, and www.state.in.us/idem/owm/npdes/municipal/background.html.

4.2.4 New York

Similar to Indiana, New York has also adopted the GLI into its state regulations. Aquatic, wildlife, and human health water quality criteria are calculated using the methodology and equations specified in the GLI with a few specific changes. First, New York assumes that individuals consume 33 grams/day of fish. In comparison, the GLI assumes that individuals consume 15 grams/day of fish. As a result, the same calculation in New York will result in more stringent criteria. Second, New York has determined human health water quality standards for carcinogenic compounds based on a risk level of 1×10^{-6} , while the GLI calculates standards based on a carcinogenic risk level of 1×10^{-5} . Again, this will result in more stringent criteria in comparison to the GLI.

Bioaccumulation is considered when calculating human health and wildlife water quality criteria. New York uses the same criteria as the GLI when selecting BAFs for organic and inorganic chemicals in its calculations. As result, BAFs must meet the data requirements discussed in Appendix C.

Additional information on New York water quality standards and State Permit Discharge Elimination System (SPDES) permits may be found at: www.dec.state.ny.us/website/dow/togs/tog_cont.htm. This web site contains several Technical and Operational Guidance (TOGs) on: (1) procedures to derive standards for the protection of aquatic life and wildlife; (2) procedures for deriving bioaccumulation factors; and (3) SPDES program priorities and definitions. Additional information on the

SPDES program may be found at:
www.dec.state.ny.us/website/dcs/EP_Qpermits/spdes_01.html.

4.2.5 Washington

Water quality criteria used in Washington are developed using USEPA (1985c) guidance, *Guidelines for Deriving Numerical National Water Quality Criteria for the Protection of Aquatic Organisms and Their Uses* (PB58-227049) and *USEPA Quality Criteria for Water* (USEPA, 1986b) (PB87-226759). Based on this guidance, the state calculates water quality standards that protect public health, fish populations, and wildlife. Most recently, the state has calculated specific marine criteria for copper and cyanide. These criteria are based on a risk of 1×10^{-6} . In most instances, however, the state simply adopts USEPA's criteria.

Consistent with USEPA guidelines, criteria are calculated to protect aquatic organisms, to protect wildlife, and to protect recreationally or commercially important fish populations from exceeding FDA action levels. Both the wildlife and human health criteria are calculated as the ratio of the maximum permissible tissue concentrations and the specified BAF or BCF. Because USEPA guidance is over ten years old, it currently recommends using BCFs rather than BAFs. As described in Section 4.1.2, it is expected that future USEPA guidance will emphasize the BAF approach adopted as part of the GLI.

More information on the Washington water quality standards program can be found at: www.wa.gov/ecology/wq/standards.

5. References

- Adams, W.J., K.V. Brix, A. Fairbrother, and R. Cardwell. 1997. Understanding Selenium in the Aquatic Environment. *SETAC News*.
- API. 1997. *Bioaccumulation: How Chemicals Move from the Water into Fish and Other Aquatic Organisms*. American Petroleum Institute. Health and Environmental Sciences Department. Washington, D.C. Publication No. 4656. May.
- API. 1998. Arsenic: Chemistry, Fate, Toxicity, and Wastewater Treatment Options. American Petroleum Institute. Health and Environmental Sciences Department. Washington, D.C. Publication No. 4676. October.
- ATSDR. 1996. Toxicological Profile for Selenium. Agency for Toxic Substances and Disease Registry Atlanta, GA, U.S. Department of Health and Human Services, Public Health Service. Report No. 205-93-0606.
- ATSDR. 1998. Toxicological Profile for Chlorinated Dibenzo-*p*-Dioxins. Draft for Public Comment (update). Agency for Toxic Substances and Disease Registry Atlanta, GA, U.S. Department of Health and Human Services, Public Health Service. Report No. 205-93-0606.
- Babukutty, Y. and J. Chacko. 1995. Chemical partitioning and bioavailability of lead and nickel in an estuarine system. *Environ. Toxicol. Chem.* 14(3): 427-434.
- Beckvar, N., J. Field, S. Salazar, and R. Hoff. 1996. Contaminants in Aquatic Habitats at Hazardous Waste Sites: Mercury. NOAA Technical Memorandum NOS ORCA 100. National Oceanic and Atmospheric Administration, Seattle, WA.
- Berends, A.G., E.J. Boelhouwers, J.L.G. Thus, J. de Gerlache and C.G. de Rooij. 1997. Bioaccumulation and lack of toxicity of octachlorodibenzofuran (OCDF) and octachlorodibenzo-*p*-dioxin

(OCDD) to early-life stages of zebra fish (*brachydanio rerio*).
Chemosphere 35(4):853-865.

Bloom, N.S. 1992. On the chemical form of mercury in edible fish and marine invertebrate tissue. *Can J. Fish. Aquat. Sci.* 49:1010-1017.

Canton, S. and W. Van Derveer. 1997. Selenium toxicity to aquatic life: An argument for sediment-based water quality criteria. *Environ. Toxicol. and Chem.* 16(6): 1255-1259.

Connell, D.W. 1989. Bioaccumulation of Xenobiotic Compounds. CRC Press, Inc. Boca Raton, Florida.

Cook, P. M., D. W. Kuehl, M.K. Walker, and R.E. Peterson. 1991. Bioaccumulation and toxicity of TCDD and related compounds in aquatic ecosystems. In: Banbury Report 35: Biological Basis for Risk Assessment of Dioxins and Related Compounds. Cold Spring Harbor Laboratory Press pp. 143-167.

Cullen, W. and K. Reimer. 1989. Arsenic speciation in the environment. *Chemical Reviews* 89(4): 713-764.

Eisler, R. 1986. Dioxin hazards to fish, wildlife, and invertebrates: A synoptic review. Biological Report 85(1.8). Contaminant Hazard Reviews Report No. 8. May.

Eisler, R. 1987. Polycyclic Aromatic Hydrocarbon Hazards to Fish, Wildlife, and Invertebrates: A Synoptic Review. Biological Report 85(1.11) Contaminant Hazard Reviews Report No. 11. May 1987.

Eisler, R. 1988. Arsenic Hazards to Fish, Wildlife and Invertebrates: A Synoptic Review. US Fish and Wildlife Service. Biological Report 85(1.12) Contaminant Hazard Reviews Report No. 12. January 1988.

Fox, G.A., D.V. Weseloh, T.J. Kubiak and T.C. Erdman. 1991. Reproductive outcomes in colonial fish-eating birds: A biomarker for developmental toxicants in Great Lakes food chains. *J. Great Lakes Res.* 17(2):153-157.

- Giesy, J.P., J.P. Ludwig and D.E. Tillitt. 1994. Deformities in birds of the Great Lakes Region assigning causality. *Environ. Sci. Technol.* 28(3):128-135.
- Gilmour, C.C. and E.A. Henry. 1991. Mercury methylation in aquatic systems affected by acid deposition. *Environ. Pollut.* 71:131-169.
- Goodyear, K.L. and S. McNeill. 1999. Bioaccumulation of heavy metals by aquatic macro-invertebrates of different feeding guilds: a review. *Sci. Total Environ.* 229:1-19.
- Jonnalagadda, S. B. and P. V. V. P. Rao. 1993. Toxicity, Bioavailability and Metal Speciation. *Comp. Biochem. Physiol.* 106(3): 585-595.
- Karickhoff, S.W. and J.M. Long. 1995. *Internal Report on Summary of Measured, Calculated and Recommended Log K_{OW} Values.* Prepared for U.S. Environmental Protection Agency, Risk Assessment and Management Branch, Standards and Applied Science Division, Office of Water, Washington, DC.
- Lemly, A.D. 1998. A position paper on selenium in ecotoxicology: A procedure for deriving site-specific water quality criteria. *Ecotoxicol and Environ. Saf.* 39: 1-9.
- Loonen, H., C. van de Guchte, R.J. Parsons, P. de Voogt, and H.A.J. Govers. 1996. Ecological hazard assessment of dioxins: Hazards to organisms at different levels of aquatic food webs (Fish-eating birds and mammals, fish and invertebrates). *Science of the Total Environment* 182(1-3): 93-103.
- Lyman, W.J., W.G. Reehl and D.H. Rosenblatt. 1990. *Handbook of Chemical Property Estimation Methods: Environmental Behavior of Organic Compounds.* American Chemical Society, Washington, DC.
- McKim, J., P. Schmieder, G. Veith. 1985. Absorption dynamics of organic chemical transport across trout gills as related to octanol-water partition coefficient. *Toxicol. App. Pharmacol.* 77: 1-10.

- Neff, J.M. 1985. Polycyclic aromatic hydrocarbons. In: *Fundamentals of Aquatic Toxicology*. Eds. G. M. Rand and S. R. Petrocelli. pp. 416-454. Washington, Hemisphere Publishing Corporation.
- Neff, J.M. 1997. Ecotoxicology of arsenic in the marine environment. *Environ. Toxicol. Chem* 16(5):917-927.
- National Research Council (NRC). 1985. *Oil in the Sea: Inputs, Fates, and Effects*. National Academy Press, Washington, DC.
- Opperhuizen, A, E.W. Velde, F.A. Gobas, D.A. Liem, J.M. Steen. 1985. Relationship between bioconcentration in fish and steric factors of hydrophobic chemicals. *Chemosphere* 14(11/12):1871-1896.
- Peterson, J.A. and A.V. Nebeker. 1992. Estimation of waterborne selenium concentrations that are toxicity thresholds for wildlife. *Arch. Environ. Contam. Toxicol.* 23:154-162.
- Phillips, D. J. H. 1990. Arsenic in aquatic organisms: A review, emphasizing chemical speciation. *Aquat. Tox.* 16: 151-186.
- Shuttleworth, K.L. and C.E. Cerniglia. 1995. Environmental aspects of PAH biodegradation. *Applied Biochemistry and Biotechnology* 54: 291-302.
- Spacie, A and J.L. Hamelink. 1982. Alternative models for describing the bioconcentration of organics in fish. *Environ. Toxicol. Chem.* 1:309-320.
- Spacie, A. and J.L. Hamelink. 1985. Bioaccumulation. In G.M. Rand, and S.R. Petrocelli, eds. *Fundamentals of Aquatic Toxicology*. Hemisphere Publishing Corporation, Washington, D.C. pp. 495-525.
- Tracey, G.A. and D.J. Hansen. 1996. Use of biota-sediment accumulation factors to assess similarity of nonionic organic chemical exposure to benthically-coupled organisms of differing trophic mode. *Arch. Environ. Contam. Toxicol.* 30:467-475.

- USEPA. 1973. *Water Quality Criteria 1972 (The Blue Book)*. United States Environmental Protection Agency, Washington, DC. EPA-R3-73-033.
- USEPA. 1976. *Water Quality Criteria 1976 (The Red Book)*. United States Environmental Protection Agency, Washington, DC. EPA-440/9-76-023. July.
- USEPA. 1980. *Ambient Water Quality Criteria 1980*. United States Environmental Protection Agency, Washington, DC. EPA 440/5-80.
- USEPA. 1984a. *Ambient Water Quality Criteria 1984*. United States Environmental Protection Agency, Washington, DC. EPA 440/5-84-85.
- USEPA. 1984b. *Guidelines for Deriving Numerical Site-Specific Water Quality Criteria*. . United States Environmental Protection Agency, Office of Research and Development, Environmental Research Lab, Duluth, MN. EPA 600/3-84-099.
- USEPA. 1985a. *Ambient Water Quality Criteria for Arsenic - 1984*. United States Environmental Protection Agency, Office of Water. Washington, D.C. EPA 440/5-84-033. January.
- USEPA. 1985b. *Ambient Water Quality Criteria for Mercury*. United States Environmental Protection Agency, Office of Water. Washington D.C. EPA 440/5-84-026.
- USEPA. 1985c. *Guidelines for Deriving Numerical National Water Quality Criteria for the Protection of Aquatic Organisms and their Uses*. United States Environmental Protection Agency, Office of Science and Technology. Washington, D.C. EPA 822/R-85-100.
- USEPA. 1986a. *Ambient Water Quality Criteria for Nickel - 1986*. United States Environmental Protection Agency, Office of Water. Washington, D.C. EPA 440/5-86-004. September.

- USEPA. 1986b. *Quality Criteria for Water (The Gold Book)*. 1986. United States Environmental Protection Agency, Office of Water Regulations and Standards. Washington, D.C. EPA 440/5-86-001. May.
- USEPA. 1987. *Ambient Water Quality Criteria for Selenium*. 1987. United States Environmental Protection Agency, Office of Water. Washington D.C. EPA 440/5-87-006.
- USEPA. 1993. *Interim Report on Data and Methods for Assessment of 2,3,7,8-Tetrachlorodibenzo-p-dioxin Risks to Aquatic Life and Associated Wildlife*. United States Environmental Protection Agency, Office of Research and Development. Washington, D.C. EPA/600/R-93/055. March.
- USEPA. 1994a. *Waste Minimization National Plan*. United States Environmental Protection Agency. Washington, D.C. EPA530-R-94-045.
- USEPA. 1994b. *Assessment and Control of Bioconcentratable Contaminants in Surface Waters*. United States Environmental Protection Agency, Office of Water. Washington, D.C. (56 FR 13150).
- USEPA. 1995. *Great Lakes Water Quality Initiative Technical Support Document for the Procedure to Determine Bioaccumulation Factors*. United States Environmental Protection Agency, Office of Water. Washington, D.C. EPA-820-B-95-005. March.
- USEPA. 1997a. *Update: Listing of Fish and Wildlife Advisories*. United States Environmental Protection Agency, Office of Water. Washington, D.C. EPA-823-F-97-007. June.
- USEPA. 1997b. *Mercury Study Report to Congress, Volume III: Fate and Transport of Mercury in the Environment*. United States Environmental Protection Agency, Office of Air Quality Planning & Standards and Office of Research and Development. Washington, D.C. EPA-452/R-97-005. December.

USEPA. 1997c. *Guidance for Assessing Chemical Contaminant Data for Use in Fish Advisories. Volume 2. Risk Assessment and Fish Consumption Limits Second Edition*. United States Environmental Protection Agency, Office of Water. Washington, D.C. EPA 823-B-97-009. July.

USEPA. 1998a. *Report on the Peer Consultation Workshop on Selenium Aquatic Toxicity and Bioaccumulation*. United States Environmental Protection Agency, Office of Water. Washington, D.C. EPA-8322-R-98-007. September.

USEPA. 1998b. Fact Sheet. *Draft Revisions to the Methodology for Deriving Ambient Water Quality Criteria for the Protection of Human Health*. United States Environmental Protection Agency, Office of Water. Washington, D.C. EPA-822-F-98-004. July.

USEPA. 1999. *Revisions to the Methodology for Deriving Ambient Water Quality Criteria for the Protection of Human Health: Summary Report*. United States Environmental Protection Agency, Office of Water. Washington, DC. EPA-822-R-99-015. September.

Van den Berg, M., L. Birnbaum, A.T.C. Bosveld, B. Brunstrom, P. Cook, M. Feeley, J.P. Giesy, A. Hanberg, R. Hasegawa, S. Kenndey, T. Kubiak, J.C. Larsen, F.X. Rolaf van Leeuwen, A.K. Djien Liem, C. Nolt, R.E. Peterson, L. Poellinger, S. Safe, D. Schrenk, D. Tillitt, M. Tysklind, M. Younes, F. Waern, T. Zacharewski. 1998. Toxic equivalency factors (TEFs) for PCBs, PCDDs, PCDFs for humans and wildlife. *Environ. Health Perspec.* 106(12):775-792.

Van der Oost, R., H. Heida, A. Opperhuizen, and N.P.E. Vermeulen. 1991. Interrelationships between bioaccumulation of organic trace pollutants (PCBs, organochlorine pesticides and PAHs), and MFO-induction in fish. *Comp. Biochem. Physiol. C* 100 (1/2): 43-47.

Weseloh, D.V., S.M. Teeple and M. Gilbertson. 1983. Double-crested cormorants of the Great Lakes: egg-laying parameters, reproductive failure, and contaminant residues in eggs, Lake Huron 1972-1973. *Can. J. Zool.* Vol. 61.

- Westcott, K. and J. Kalff. 1996. Environmental factors affecting methyl mercury accumulation in zooplankton. *Canadian Journal of Fisheries and Aquatic Sciences* 53(10): 2221-2228.
- Zabik, M.E., M.J. Zabik, A.M. Booren, S. Daubenmire, M.A. Pascall, R. Welch, and H. Humprey. 1995. Pesticides and total polychlorinated biphenyl residues in raw and cooked walleye and white bass harvested from the Great Lakes. *Bull. Environ. Contam. Toxicol.* 54:396-402.
- Zabik, M.E., A.M. Booren, M.J. Zabik, R. Welch, and H. Humprey. 1996. Pesticide residues, PCBs and PAHs in baked, charbroiled, salt broiled, and smoked Great Lakes lake trout. *Fd. Chem.* 55(3):231-239.

Appendix A. Fish Consumption Advisory Calculations

EPA calculates allowable daily consumption limits for individual fish species using the following equations for carcinogenic and noncarcinogenic chemicals.

Carcinogenic

$$CR_{lim} = \frac{ARL \times BW}{CSF \times C_m}$$

Noncarcinogenic¹

$$CR_{lim} = \frac{RfD \times BW}{C_m}$$

where,

CR_{lim} = Maximum allowable fish consumption rate (kg/d);

ARL = Maximum acceptable individual risk level (unitless) (i.e., 1×10^{-5} , 1×10^{-6});

BW = Fish consumer body weight (kg);

CSF = Cancer slope factor (mg/kg-d)⁻¹;

RfD = Reference dose (mg/kg-d); and

C_m = Chemical concentration measured in fish (mg/kg).

CR_{lim} for both carcinogenic and noncarcinogenic chemicals may be converted to a meal consumption limit:

$$CR_{mm} = \frac{CR_{lim} \times T_{ap}}{MS}$$

¹ Because the risk level for noncarcinogenic chemicals is always set at one, a risk level is not included in the allowable fish consumption equation.

where,

CR_{mm} = Maximum allowable fish consumption rate (meals/month);

T_{ap} = Averaging period (365.25 days/12 months); and

MS = Meal size (kg fish/meal).

These equations may be modified to calculate overall daily consumption limits based on exposure to single chemicals in a multiple species diet or to use site-specific body weights or meal sizes (USEPA, 1997).

Appendix B. Data Requirements for Bioaccumulation Factors in the GLI

The GLI describes the data sources and data requirements for obtaining BAFs and BCFs for use in water quality criteria calculations (60 FR 15401). Consistent with the GLI, measured BAFs, BSAFs and BCFs may be assembled from the following sources:

- EPA Ambient Water Quality Criteria documents issued after January 1, 1980.
- Published scientific literature.
- Reports issued by EPA or other reliable sources.
- Unpublished data. One useful source of references is the Aquatic Toxicity Information Retrieval (AQUIRE) database.

Once a measured BAF, BSAF, or BCF is identified, it must also meet certain procedural and quality assurance requirements. These requirements ensure that the BAFs, BSAFs, and BCFs used are of consistent quality and, therefore, do not unjustly bias the criteria calculations. The specific data requirements described at 60 FR 15401 are presented below.

Field-Measured BAFs

- The field studies used shall be limited to those conducted in the Great Lakes system with fish at or near the top of the aquatic food chain (i.e., in trophic levels 3 and/or 4);
- The trophic level of the fish species shall be determined;
- The site of the field study should not be so unique that the BAF cannot be extrapolated to other locations where the criteria and values will apply;
- For organic chemicals, the percent lipid shall be either measured or reliably estimated for the tissue used in the determination of the BAF;
- The concentration of the chemical in the water shall be measured in a way that can be related to particulate organic carbon (POC) and/or dissolved organic carbon (DOC) and should be relatively constant during the steady-state time period;

- For organic chemicals with $\log K_{ow}$ greater than four, the concentrations of POC and DOC in the ambient water shall be either measured or reliably estimated; and
- For inorganic and organic chemicals, BAFs shall be used only if they are expressed on a wet weight basis; BAFs reported on a dry weight basis cannot be converted to wet weight unless a conversion factor is measured or reliably estimated for the tissue used in the determination of the BAF.

Field-Measured BSAFs

- The field studies used shall be limited to those conducted in the Great Lakes system with fish at or near the top of the aquatic food chain (i.e., in trophic levels 3 and/or 4);
- Samples of surface sediments (0-1 cm is ideal) shall be from locations in which there is net deposition of fine sediment which are representative of average surface sediment in the vicinity of the organism;
- The K_{ows} used shall be of acceptable quality;
- The site of the field study should not be so unique that the resulting BAF cannot be extrapolated to other locations where the criteria and values will apply;
- The trophic level of the fish species shall be determined; and
- The percent lipid shall be either measured or reliably estimated for the tissue used in the determination of the BAF.

Laboratory-Measured BCFs

- The test organism shall not be diseased, unhealthy, or adversely affected by the concentration of the chemical;
- The total concentration of the chemical in the water shall be measured and should be relatively constant during the steady-state time period;
- The organisms shall be exposed to the chemical using a flow-through or renewal procedure;
- For organic chemicals, the percent lipid shall be either measured or reliably estimated for the tissue used in the determination of the BCF;

- For organic chemicals with $\log K_{ow}$ greater than four, the concentrations of POC and DOC in the test solution shall be either measured or reliably estimated;
- Laboratory-measured BCFs should be determined using fish species, but BCFs determined with mollusks and other invertebrates may be used with caution. For example, because invertebrates metabolize some chemicals less efficiently than vertebrates, a baseline BCF determined for such a chemical using invertebrates is expected to be higher than a comparable baseline BCF determined using fish;
- If laboratory-measured BCFs increase or decrease as the concentration of the chemical increases in the test solutions in a bioconcentration test, the BCF measured at the lowest test concentration that is above concentrations existing in the control water shall be used. The concentrations of an inorganic chemical in a bioconcentration test should be greater than normal background levels and greater than levels required for normal nutrition of the test species if the chemical is a micronutrient, but below levels that adversely affect the species. Bioaccumulation of an inorganic chemical might be overestimated if concentrations are at or below normal background levels due to, for example, nutritional requirements of the test organisms;
- For inorganic and organic chemicals, BCFs shall be used only if they are expressed on a wet weight basis. BCFs reported on a dry weight basis cannot be converted to wet weight unless a conversion factor is measured or reliably estimated for the tissue used in the determination of the BAF;
- BCFs for organic chemicals may be based on measurement of radioactivity only when the BCF is intended to include metabolites or when there is confidence that there is no interference due to metabolites;
- The calculation of the BCF must appropriately address growth dilution;
- Other aspects of the methodology used should be similar to those described by ASTM (1990).

Predicted BCFs

- The K_{ow} used shall be of acceptable quality; and
- The predicted baseline BCF shall be calculated using the equation:

$$\text{predicted baseline BCF} = K_{ow}$$

where,

K_{ow} = octanol - water partition coefficient.

Appendix C. Calculation of Human Health and Wildlife BAFs

C-1 Human Health and Wildlife BAFs for Trophic Levels 3 and 4

To calculate a human health BAF for an organic chemical at trophic levels 3 and 4, USEPA recommends using Equations 1 and 2.

For trophic level 3:

$$\text{Equation (1)} \quad \text{Human Health } BAF_{TL3}^{HH} = [(baseline \text{ BAF})(0.0182) + 1](f_{fd})$$

For trophic level 4:

$$\text{Equation (2)} \quad \text{Human Health } BAF_{TL4}^{HH} = [(baseline \text{ BAF})(0.0310) + 1](f_{fd})$$

where:

f_{fd} = Fraction of the total chemical in the ambient water that is freely dissolved, and

0.0182 and 0.0310 are the standardized fraction lipid values for trophic levels 3 and 4, respectively, that are used to derive human health criteria and values for the GLI (60 FR 15404). Baseline BAFs are calculated using the methodology described below in Section C-2.

The wildlife BAFs for an organic chemical shall be calculated using Equations 3 and 4:

For trophic level 3:

$$\text{Equation (3)} \quad \text{Wildlife } BAF_{TL3}^{WL} = [(baseline \text{ BAF})(0.0646) + 1](f_{fd})$$

For trophic level 4:

$$\text{Equation (4)} \quad \text{Wildlife } BAF_{TL4}^{WL} = [(baseline \text{ BAF})(0.1031) + 1](f_{fd})$$

where:

0.646 and 0.1031 are the standardized fraction lipid values for trophic levels 3 and 4, respectively, that are used to derive wildlife criteria for the GLI (60 FR 15404). Baseline BAFs are calculated using the methodology described below in Section C-2.

For inorganic chemicals, the baseline BAFs for trophic levels 3 and 4 are both assumed to equal the BCF determined for the chemical with fish (i.e., the FCM is assumed to be one for both trophic levels 3 and 4). However, a FCM greater than one might be applicable to some metals, such as mercury, if, for example, an organometallic form of the metal biomagnifies (60 FR 15404).

C-2 Baseline BAFs for Trophic Levels 3 and 4

Baseline BAFs for use in human health and wildlife criteria calculations may be calculated from one of the following sources: (1) a field-measured BAF; (2) a predicted BAF derived from a BSAF; or (3) a laboratory-measured BCF. If a field-measured BAF or a predicted BAF derived from a BSAF is not available, USEPA recommends using a food chain multiplier (FCM) to derive a baseline BAF for trophic levels 3 and 4. For most organic chemicals the FCM is greater than one.

When a field-measured BAF is available, a baseline BAF should be calculated using Equation (5) (60 FR 15402).

$$\text{Equation (5)} \quad \text{Baseline BAF} = \left[\frac{\text{Measured } BAF_T^t}{f_{fd}} - 1 \right] \left[\frac{1}{f_l} \right]$$

where:

BAF_T^t = BAF based on total concentration in tissue and water;

f_l = Fraction of the tissue that is lipid; and

f_{fd} = Fraction of the total chemical that is freely dissolved in the ambient water.

Based on Equation 5, the baseline BAF is applicable to the trophic level of the organisms used in the determination of the field measured BAF (i.e., trophic level 3 or 4). If more than one measured BAF is available for a given species, a mean BAF should be calculated based on the available data (60 FR 15403).

When a field-measured BSAF is available, Equation 6 should be used to calculate a baseline BAF.

$$\text{Equation (6)} \quad (Baseline\ BAF)_i = (Baseline\ BAF)_r \cdot \frac{(BSAF)_i \cdot (K_{ow})_i}{(BSAF)_r \cdot (K_{ow})_r}$$

where:

$(BSAF)_i$ = BSAF for chemical “i”;

$(BSAF)_r$ = BSAF for the reference chemical “r”;

$(K_{ow})_i$ = Octanol-water partition coefficient for chemical “i”; and

$(K_{ow})_r$ = Octanol-water partition coefficient for the reference chemical “r”.

Predicting BAFs from BSAFs requires data from a steady-state (or near steady-state) condition between sediment and ambient water for both a reference chemical “r” with a field-measured BAF and the other chemical “i” for which BSAFs are to be determined (60 FR 15403). As stated above, the baseline BAF is applicable to the trophic level of the organisms used in the determination of the BSAF. If more than one BAF is predicted from a BSAF for a given species, a mean BAF should be calculated based on the available data (60 FR 15403).

Finally, Equation 7 should be used to convert a laboratory-measured BCF to a BAF:

$$\text{Equation (7)} \quad Baseline\ BAF = (FCM) \left[\frac{Measured\ BCF_T^t}{f_{fd}} - 1 \right] \left[\frac{1}{f_l} \right]$$

where:

BCF_T^t = BCF based on total concentration in tissue and water;

f_{fd} = Fraction of the total chemical in the test water that is freely dissolved; and

FCM = Food-chain multiplier.

As stated above, if more than one BAF is predicted from a laboratory-measured BCF for a given species, a mean BAF should be calculated based on the available data (60 FR 15403).

Appendix D. Calculation of Human Health and Wildlife Criteria

Human Health Criteria

The GLI specifies guidance for calculating Tier I and Tier II human health water quality criteria for both carcinogenic and noncarcinogenic chemicals. The major distinction between Tier I and Tier II criteria is the quantity and quality of data available. Although the fundamental components of the procedures are the same, Tier I values are to be derived for those chemicals that meet certain data requirements. Tier II values may be calculated when more limited data are available.

For development of a Tier I criterion, an organic chemical must meet certain minimum toxicity data requirements and have the following bioaccumulation data: (1) a field-measured BAF; (2) a BAF derived using the BSAF methodology; or (3) a chemical with a BAF less than 125 regardless of the BAF derivation. For inorganic chemicals, bioaccumulation data must be either: (1) a field-measured BAF or (2) a laboratory-measured BCF (60 FR 15408).

Tier I and Tier II human health water criteria for carcinogenic chemicals are calculated using Equation 1. Tier I criteria should generally be derived for known or probable human carcinogens (Class A or B). Possible human carcinogens may be evaluated for Tier I criteria on a case-by-case basis; but in general, should be reserved for Tier II. Specific exposure parameters are provided in the GLI, although the guidance does allow for consideration of higher levels of exposure where appropriate. The exposure parameters used in the GLI are also presented below.

$$\text{Equation (1)} \quad HCV = \frac{RAD \times BW}{WC + \left[(FC_{TL3} \times BAF_{TL3}^{HH}) + (FC_{TL4} \times BAF_{TL4}^{HH}) \right]}$$

where:

HCV = Human cancer value in milligrams per liter (mg/L);

RAD = Risk associated dose in milligrams toxicant per kilogram body weight per day (mg/kg/day) that is associated with a lifetime incremental cancer risk equal to one in 100,000;

BW = Weight of an average human (BW=70 kg);

WC = Per capita water consumption (both drinking and incidental exposure) for surface waters classified as public water supplies (two liters/day),

or

Per capita incidental daily water ingestion for surface waters not used as human drinking water sources (0.01 liters/day);

FC_{TL3} = Mean consumption of trophic level 3 of regionally caught freshwater fish (0.0036 kg/day);

FC_{TL4} = Mean consumption of trophic level 4 of regionally caught freshwater fish (0.0114 kg/day);

BAF_{TL3}^{HH} = Bioaccumulation factor for trophic level 3 fish, as derived using the BAF methodology in Appendix C; and

BAF_{TL4}^{HH} = Bioaccumulation factor for trophic level 4 fish, as derived using the BAF methodology in Appendix C.

Tier I and Tier II human health water criteria for noncarcinogenic chemicals are calculated using Equation 2. The minimum data set to derive a Tier I noncarcinogenic human health criterion is at least one well-conducted epidemiologic or animal study. An epidemiologic study of this caliber should quantify exposure levels and demonstrate a positive association between chemical exposure and adverse human health effects. An acceptable study in animals must demonstrate a dose-response relationship in animals that has a biologically relevant effect in humans (60 FR 15407). When these toxicological data requirements or the BAF requirements listed above cannot be met, a Tier II criterion value should be calculated. The exposure parameters used to calculate human health criteria for carcinogenic chemicals are also applicable to noncarcinogenic chemicals as detailed below.

$$\text{Equation (2)} \quad HNV = \frac{ADE \times BW \times RSC}{WC + \left[(FC_{TL3} \times BAF_{TL3}^{HH}) + (FC_{TL4} \times BAF_{TL4}^{HH}) \right]}$$

Where:

HNV = Human noncancer value in milligrams per liter (mg/L);

ADE = Acceptable daily exposure in milligrams toxicant per kilogram body weight per day (mg/kg/day); and

RSC = Relative source contribution factor of 0.8. An RSC derived from actual exposure data may be developed using the methodology outlined by the 1980 National Guidelines (see 45 FR 79354).

Wildlife Criteria

Tier I wildlife criteria are to be developed for the 22 BCCs identified in the GLI (see Table 4-1 in report). Tier I or Tier II criteria may be developed for any of the other chemicals listed in the GLI that are not considered to be bioaccumulative. In either case, the methodology specified in Appendix B and Appendix C must be used in the derivation of BAFs.

It is important to note that USEPA uses the term Tier I wildlife criterion interchangeably with the term Great Lakes Water Quality Wildlife Criterion (GLWC). In order to calculate a GLWC, a wildlife value (WV) must first be calculated for avian and mammalian wildlife (see Equation 3). The wildlife species selected for evaluation in the GLI are representative of avian and mammalian species resident in the Great Lakes Basin and are expected to have the highest exposures to bioaccumulative chemicals through the aquatic food web. These species include: bald eagle, herring gull, belted kingfisher, mink, and river otter. Exposure to these species is to be evaluated for most chemicals; however, on a case-by-case basis, other species may be used if the chemical is not expected to biomagnify to the same extent as the BCCs.

$$\text{Equation (3)} \quad WV = \frac{\frac{TD}{UF_A \times UF_S \times UF_L} \times Wt}{W + \sum (F_{TLi} \times BAF_{TLi}^{WL})}$$

where:

WV = Wildlife value in milligrams of substance per liter (mg/L);

TD = Test Dose (TD) in milligrams of substance per kilograms per day (mg/kg-d) for the test species. This shall be either a NOAEL or a LOAEL;

UF_A = Uncertainty factor (UF) for extrapolating toxicity data across species (unitless). A species-specific UF shall be selected and applied to each representative species, consistent with the equation. This value should be between one and ten;

UF_S = UF for extrapolating from subchronic to chronic exposures (unitless). This value should be between one and ten;

UF_L = UF for LOAEL to NOAEL extrapolations (unitless). Based on available toxicological data;

Wt = Average weight in kilograms (kg) for the representative species;

W = Average daily volume of water consumed in liters per day (L/d) by the representative species;

F_{TLi} = Average daily amount of food consumed from trophic level i in kilograms per day (kg/d) by the representative species; and

BAF_{TLi}^{WL} = Bioaccumulation factor (BAF) for wildlife food in trophic level i in liters per kilogram (L/kg), developed using the BAF methodology in Appendix C. For consumption of piscivorous birds by other birds (e.g., herring gull by eagles), the BAF is derived by multiplying the trophic level 3 BAF for fish by a biomagnification factor to account for the biomagnification from fish to the consumed birds.

The specific exposure parameters to be used in Equation 3 are presented in Table D-1. The avian WV should be calculated as the geometric mean of the WVs calculated for the three representative avian species. Similarly, the mammalian WV is the geometric mean of the WVs calculated for the two mammalian species. Using these data, the GLWC is calculated as the lower of the mammalian and avian WVs.

Table D-1. Exposure Parameters for the Five Representative Species Identified for Protection

Species	Adult Body Weight (kg)	Water Ingestion Rate (L/day)	Food Ingestion Rate of Prey in Each Trophic Level (kg/day)	Trophic Level of Prey (percent of diet)
Mink	0.80	0.081	TL3: 0.159; Other: 0.0177	TL3: 90; Other: 10
Otter	7.4	0.60	TL3: 0.977; TL4: 0.244	TL3: 80; TL4: 20
Kingfisher	0.15	0.017	TL3: 0.0672	TL3: 100
Herring gull	1.1	0.063	TL3: 0.192; TL4: 0.048 Other: 0.0267	Fish: 90--TL3: 80; TL4: 20 Other: 10
Bald eagle	4.6	0.16	TL3: 0.371; TL4: 0.0929 PB: 0.0283; Other: 0.0121	Fish: 92--TL3: 80; TL4: 20 Birds: 8--PB: 70; non-aquatic: 30

Note:

TL3 = Trophic level three fish

TL4 = Trophic level four fish

PB = Piscivorous birds

Other = Non-aquatic birds and mammals

Information about API Publications, Programs and Services is available on the World Wide Web at: <http://www.api.org>



Product No. I47010