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Methodology for Deriving Ambient Water Quality Criteria for the Protection of Human Health (2000)

Technical Support Document
Volume 2: Development of National Bioaccumulation Factors

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Technical Support Document Volume 2: Development of National Bioaccumulation Factors

Final

Office of Science and Technology
Office of Water
U.S. Environmental Protection Agency
Washington, DC 20460

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NOTICE

The policies and procedures set forth in this document are intended solely to describe EPA methods and guidance for developing or revising ambient water quality criteria to protect human health, pursuant to Section 304(a) of the Clean Water Act, and to serve as guidance to States and authorized Tribes for developing their own water quality criteria. This guidance does not substitute for the Clean Water Act or EPA's regulations, nor is it a regulation itself. Thus, it does not impose legally binding requirements on EPA, States, Tribes, or the regulated community, and may not apply to a particular situation depending on the circumstances.

This document has been reviewed in accordance with U.S. EPA policy and approved for publication. Mention of trade names or commercial products does not constitute an endorsement or recommendation for use.

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FOREWORD

In 2000, the U.S. Environmental Protection Agency (EPA) published the *Methodology for Deriving Ambient Water Quality Criteria for the Protection of Human Health (2000)* ("2000 Human Health Methodology"), updating and revising the existing 1980 Guidelines and Methodology. The 2000 Human Health Methodology includes guidance on chemical risk assessment, exposure, and bioaccumulation. The process EPA followed in developing the 2000 Human Health Methodology included gathering information from multiple stakeholders, convening a national issues workshop, securing EPA Science Advisory Board review and public review and comment period on the *draft* Human Health Methodology. A more detailed chronology can be found in the *Federal Register* (65FR66444).

As part of the 2000 Human Health Methodology, EPA developed detailed procedures and guidelines for estimating bioaccumulation factor (BAF) values for use in deriving or revising ambient water quality criteria. This *Technical Support Document Volume 2: Development of National Bioaccumulation Factors* discusses the technical basis for developing national BAFs, the underlying assumptions and uncertainties inherent to the approach, and applying the bioaccumulation component of the 2000 Human Health Methodology. The scientific approaches, assumptions and science policy decisions included in this document have been peer-reviewed as part of the comprehensive review of the 2000 Human Health Methodology. Detailed information about this peer review process can be found on EPA's website (www.epa.gov/waterscience).

EPA will use this technical support document to develop new ambient water quality criteria and to revise existing recommended water quality criteria. This technical support document will not be used alone to derive bioaccumulation factors, but rather in conjunction with the earlier *Methodology for Deriving Ambient Water Quality Criteria for the Protection of Human Health (2000)*.

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The following professionals were part of the External Peer Review Workgroup–Bioaccumulation Workgroup, that provided technical and scientific review regarding the content and technical approach in the July 1998 *Draft Ambient Water Quality Criteria Derivation Methodology: Human Health*. Their comments were reviewed and incorporated where appropriate to develop this final document.

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Potential areas for conflict of interest were investigated via direct inquiry with the peer reviewers and review of their current affiliations. No conflicts of interest were identified.

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1. INTRODUCTION

In 2000, the U.S. Environmental Protection Agency (EPA) published the Methodology for Deriving Ambient Water Quality Criteria for the Protection of Human Health (USEPA, 2000a). That document (referred to here as the 2000 Human Health Methodology) presents technical guidance and the steps that EPA will follow for deriving new and revised national recommended ambient water quality criteria (AWQCs) for the protection of human health under Section 304(a) of the Clean Water Act. The 2000 Human Health Methodology includes guidance on chemical risk assessment, exposure, and bioaccumulation. To supplement the 2000 Human Health Methodology, EPA is developing series of Technical Support Documents (TSD) on Risk Assessment, Exposure Assessment, and Bioaccumulation. The first volume, (Volume 1: Risk Assessment; EPA-822-B-00-005), was published with the 2000 Methodology in October 2000. This volume (Volume 2) of the Technical Support Document (TSD) focuses on the technical components of the 2000 Human Health Methodology that pertain to the assessment of chemical bioaccumulation.

The 2000 Human Health Methodology incorporates a number of scientific advancements made over the past two decades. One of these advancements is in the assessment of chemical exposure to humans through the aquatic food web pathway. For certain chemicals, exposure via the aquatic food web is more important than exposure from ingestion of water. Such chemicals tend to be highly hydrophobic, to partition in aquatic environments to surficial sediments, and to accumulate in high concentrations in fish and shellfish through the process of bioaccumulation. One method for incorporating chemical exposure to humans through the aquatic food web involves estimating the amount of a chemical expected to bioaccumulate in fish and shellfish that are commonly consumed by populations in the United States. Previously, EPA primarily used bioconcentration factors (BCFs) to estimate chemical accumulation of waterborne chemicals by aquatic organisms. The BCF reflects contaminant exposure and accumulation by fish and shellfish only through the water column. Over the past two decades, however, science has shown that all the routes (e.g., food, sediment, and water) by which fish and shellfish are exposed to highly bioaccumulative chemicals may be important in determining the chemical accumulation in the organism's body, and that these chemicals can be transferred to humans when they consume contaminated fish and shellfish. The EPA's approach to estimating uptake into fish and shellfish now emphasizes the use of a bioaccumulation factors (BAFs), which account for chemical accumulation from all potential exposure routes.

The generalized ambient water quality criterion (AWQC) formula for noncancer effects is shown below (Equation 1-1) as an example of how the BAFs are used in the calculation of a recommended national AWQC for the protection of human health (USEPA, 2000a). In Equation 1-1, trophic-level specific BAFs are used in the denominator, along with information on the amount of fish consumed on a daily basis (FI) for each trophic level (i), to estimate human exposure to contaminants through the aquatic food web.

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$$AWQC = RfD \cdot RSC \cdot \left(\frac{BW}{DI + \sum_{i=2}^{4} (FI_i \cdot BAF_i)} \right)$$

(Equation 1-1)

where:

RfD = reference dose for noncancer effects (mg/kg/day)
RSC = relative source contribution to account for nonwater sources of exposure
BW = human body weight (kg)
DI = drinking water intake (L/day)
FI = fish intake (kg/day) at trophic level i (i = 2, 3, 4)
BAF_i = bioaccumulation factor (L/kg) at trophic level i (i = 2, 3, 4)

1.1 PURPOSE

This TSD volume:

- Presents the technical basis for the EPA's approach to developing national BAFs for the different trophic levels of fish and shellfish commonly consumed by humans,
- Discusses the underlying assumptions and uncertainties inherent in the approach, and
- Provides further detail on applying the BAF component of the 2000 Human Health Methodology.

As indicated in Equation 1-1 of Section 1, the national, trophic level–specific BAFs for a given contaminant are used by the EPA in the derivation of AWQC for the protection of human health. A subsequent volume (Volume 3: Development of Site-Specific Bioaccumulation Factors) provides guidance to States and authorized Tribes for developing site-specific BAFs for the various trophic levels when BAFs that are more representative of local conditions are preferred. Neither of the bioaccumulation TSDs should be used alone to derive BAFs, but rather in conjunction with the 2000 Human Health Methodology. The intended audience for both of these documents includes the EPA scientists who are responsible for deriving water quality criteria, State and Tribal risk assessors and stakeholders interested in the technical basis of EPA's national BAF methodology, and other users interested in bioaccumulation issues for other applications.

1.2 SCOPE

The goal of EPA's approach for developing national BAFs is to represent the long-term average bioaccumulation potential of a pollutant in aquatic organisms that are commonly consumed by humans throughout the United States. National BAFs are not intended to reflect

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fluctuations in bioaccumulation over short periods (e.g., a few days) because human health AWQCs are generally designed to protect humans from long-term exposures (over a lifetime) to waterborne chemicals.

National BAFs are also intended to account for some major chemical, biological, and ecological attributes that can affect bioaccumulation in bodies of water across the United States. For this reason, EPA's approach includes separate procedures for deriving national BAFs according to the type of chemical (e.g., nonionic organic, ionic organic, inorganic, and organometallic). For the purposes of the 2000 Human Health Methodology, nonionic organic chemicals are defined as organic compounds that do not ionize substantially in natural bodies of water. These chemicals are also referred to as "neutral" or "nonpolar" organics in the scientific literature. Ionic organic chemicals are considered to include those chemicals that contain functional groups with exchangeable protons, such as hydroxyl, carboxylic, and sulfonic and nitrogen (pyridine) groups. Ionic organic chemicals undergo ionization in water, the extent of which depends on the pH and the pKa of the water. Ionic chemicals are considered separately when deriving national BAFs because the behavior of the anionic or cationic species of these chemicals in aquatic systems is much different from those of their neutral (un-ionized) counterparts. Inorganic and organometallic chemicals include inorganic minerals, other inorganic compounds and elements, metals, metalloids, and organometallic compounds. This TSD document focuses primarily on the procedures for determining BAFs for nonionic organic chemicals that bioaccumulate. The procedures for estimating bioaccumulation of nonionic organic chemicals are generally better developed than those for ionic chemicals. Therefore, both the conditions under which these procedures can be applied and the limitations associated with their application warrant further explanation.

In addition, EPA's national BAFs are derived separately for each trophic level to account for potential biomagnification of some chemicals in aquatic food webs and broad physiological differences among organisms that may influence bioaccumulation. As discussed in Chapter 3, lipid contents of aquatic organisms and the amounts of organic carbon in ambient waters affect bioaccumulation of nonionic organic chemicals in aquatic food webs. National trophic-level specific BAFs incorporate adjustments for the lipid content of commonly consumed fish and shellfish and for the freely dissolved fraction of the chemical in ambient water by using nationwide averages for these two parameters. Further discussion of these parameters is provided in Section 4.

1.3 IMPORTANT BIOACCUMULATION AND BIOCONCENTRATION CONCEPTS

Several attributes of the bioaccumulation process are important to understanding the approach used to develop national BAFs used in setting national recommended AWQCs for the protection of human health. First, the term *bioaccumulation* refers to the uptake and retention of a chemical by an aquatic organism from all surrounding media (e.g., water, food, sediment). The term *bioconcentration* refers to the uptake and retention of a chemical by an aquatic organism from water only. For some chemicals (particularly those that are highly persistent and hydrophobic), the magnitude of bioaccumulation by aquatic organisms can be substantially greater than the magnitude of bioconcentration. For such chemicals, an assessment of

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bioconcentration alone will underestimate the extent of accumulation in aquatic biota. Accordingly, EPA's 2000 Human Health Methodology emphasizes the consideration of chemical bioaccumulation by aquatic organisms, whereas EPA's 1980 Methodology emphasized the measurement of bioconcentration.

Another important aspect of the bioaccumulation process is the steady-state condition. Specifically, bioaccumulation can be viewed simply as the result of competing rates of chemical uptake and depuration (chemical loss) by an aquatic organism. The rates of chemical uptake and depuration can be affected by various factors, including the properties of the chemical, the physiology of the organism in question, water quality and other environmental conditions, the ecological characteristics of the water body (e.g., food web structure), and the concentration and loadings history of the chemical. When the rates of chemical uptake and depuration are equal, tissue concentrations remain constant over time and the distribution of the chemical between the organism and its source(s) is said to be at steady state. For constant chemical exposures and other conditions, the steady-state concentration in the organism represents the highest accumulation potential of the chemical in that organism under those conditions. The time needed for a chemical to achieve steady state in the organism has been shown to vary according to the properties of the chemical, the variability of environmental conditions, and other factors. For example, some highly hydrophobic chemicals can require long periods (e.g., many months) to reach steady state between environmental compartments, whereas highly hydrophilic chemicals usually reach steady state relatively quickly (e.g., hours to days).

National recommended AWQCs for the protection of human health are typically designed to protect humans from harmful lifetime or long-term exposures to waterborne contaminants. Given this goal, assessing bioaccumulation that equals or approximates steady-state accumulation is one of the principles underlying the derivation of national BAFs. For chemicals that require relatively long periods to reach steady state in aquatic organisms, changes in the concentration of the chemical in the water column may occur much more rapidly than corresponding changes in concentrations in tissue. Thus, if the system departs substantially from steady-state conditions and water concentrations are not averaged over a sufficient time period, the ratio of the chemical concentration in tissue of organisms to that in water (i.e., the BAF) may have little resemblance to the steady-state ratio and have little predictive value for long-term bioaccumulation potential. Therefore, BAF measurements should be based on chemical concentrations in the water column, averaged over a sufficient period for the chemical of interest. In addition, the BAFs used in deriving national recommended AWQCs for the protection of human health should be based on adequate spatial averaging of chemical concentrations in both tissue of consumed organisms and the water column.

The concept of proper temporal averaging for the determination of BAFs is illustrated in Figure 1-1 (taken from Burkhard, 2003). Figure 1-1A shows the daily concentrations of a hypothetical nonionic organic chemical, using a simple dilution model and daily flow data for the Mississippi River at St. Paul, Minnesota. These daily chemical concentrations in the river can be transformed into daily chemical concentrations in fish by using the kinetic models of Gobas (1993). Figure 1-1B shows the results of these transformations in piscivorous fish for chemicals

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with log *n*-octanol-water partition coefficients (K_{ow}s) ranging from 2 to 9 for a simple hypothetical food web. Together, Figures 1-1A and 1-1B show that concentrations of nonionic organic chemicals in fish change over time, relative to the concentration of the chemical in the ambient water, at speeds dependent upon the hydrophobicity of the chemical, i.e., the chemical's K_{ow}. The response is graded in magnitude, and the rate of change decreases with increasing K_{ow}. For chemicals with low K_{ow}s (e.g., log K_{ow}s of 2 and 3), the speed of change is very fast, such that concentrations of the chemical in fish mimic the trends of the chemical concentration in ambient

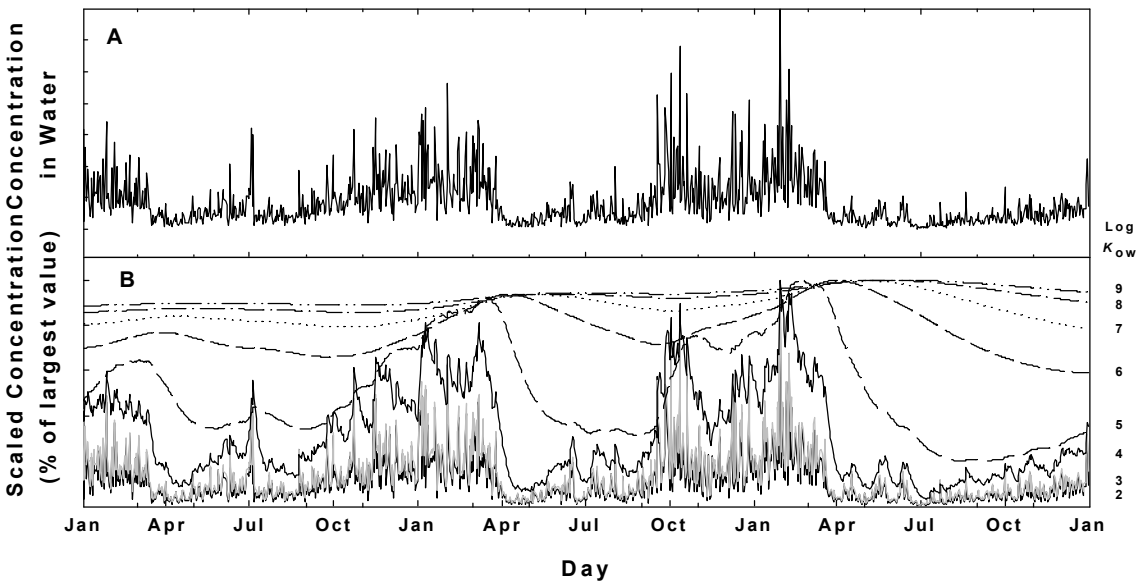

Figure 1-1 (A). Daily concentrations of a hypothetical nonionic organic chemical over time in the water column, predicted using a simple dilution model and daily flow data for the Mississippi River at St. Paul, Minnesota.
(B) Daily chemical concentrations in piscivorous fish found using the kinetic food web models of Gobas (1993) with the daily chemical concentrations in the water column for nonionic organic chemicals with log *n*-octanol-water

water. For chemicals with large K_{ow}s (e.g., log K_{ow}s of 6 and 7), concentrations of the chemical in fish change slowly relative to those in the water, and in general, the concentrations in fish follow the long-term trends for the chemical concentration in the water.

Clearly, BAFs based on inappropriate temporal averaging of chemical concentrations in the water will have little predictive power; thus, BAFs should be based on concentrations in the water column that are averaged over a sufficient period of time that is appropriate for the chemical of interest. For this reason, a BAF was defined in the 2000 Human Health Methodology as representing the ratio (in liters per kilogram) of the concentration of a chemical in the tissue of an aquatic organism to its concentration in the ambient water in situations where the organism and its food are exposed and *the ratio does not change substantially over time* (i.e., the ratio reflects bioaccumulation at or near steady state). Similarly, a BCF was defined as the ratio (in liters per kilogram) of the concentration of a chemical in the tissue of an aquatic organism to the chemical's concentration in the ambient water, in situations where the organism is exposed through the water only and *the ratio does not change substantially over time*.

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From the perspective of sampling for determining BAFs, chemicals with large K_{ow}s will generally require that numerous water samples be averaged over time to establish the long-term chemical concentrations in the water. In contrast, for chemicals with low K_{ow}s, because the concentrations in the fish mimic those in water, the time scale for establishing the chemical concentrations in the water shrinks to concurrent sampling of both fish and water; current chemical concentrations in the water provide a good predictor of the chemical concentration in the fish. Burkhard (2003) provides additional details on BAF sampling design and EPA will provide additional information on field sampling designs for determination of BAFs in TSD Volume 3: Development of Site-Specific Bioaccumulation Factors.

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2. DEFINITIONS

The following terms and their definitions are used throughout this document.

2.1 BIOACCUMULATION

Bioaccumulation. The net accumulation of a chemical by an aquatic organism as a result of uptake from all environmental sources.

Bioaccumulation factor (BAF). The ratio (in liters per kilogram of tissue) of the concentration of a chemical in the tissue of an aquatic organism to its concentration in water, in situations where both the organism and its food are exposed and the ratio does not change substantially over time. The BAF is calculated as:

$$\mathbf{BAF} = \frac{C_t}{C_w} \qquad \text{(Equation 2-1)}$$

where:

C_t = concentration of chemical in tissue
C_w = concentration of chemical in water

Because chemical concentrations in tissue and water can be defined in terms of chemical partitioning to different biological or chemical phases (e.g., total concentrations in tissue or water, concentration in lipid, concentration that is freely dissolved in water), the general equation for BAF (Equation 2-1) is further refined below to delineate among these different phases.

Total bioaccumulation factor ($\mathbf{BAF_T^t}$). A BAF based on the *total* concentration of chemical in the organism and the water. The total concentration of the chemical in tissue includes that in either a specific tissue or a whole organism and is based on wet tissue. The total concentration of the chemical in water includes chemical associated with particulate organic carbon, chemical associated with dissolved organic carbon, and chemical freely dissolved in the water. A BAF_T^t is often referred to as a "field-measured" BAF because it is derived from analysis of tissue and water samples collected from the field. The BAF_T^t is expressed in liters per kilogram of lipid. The BAF_T^t is calculated as:

$$\mathbf{BAF_T^t} = \frac{C_t}{C_w} \qquad \text{(Equation 2-2)}$$

where:

C_t = *total* concentration of chemical in tissue
C_w = *total* concentration of chemical in water

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Baseline bioaccumulation factor (Baseline BAF or BAF_L^{fd}). For nonionic organic chemicals (and certain ionic organic chemicals to which similar lipid and organic carbon partitioning behavior applies[1]), a BAF that is based on the concentration of chemical freely dissolved in water and the concentration of the chemical in the lipid fraction of tissue. The baseline BAF is expressed in liters per kilogram of lipid. The baseline BAF is determined using the equation:

$$\text{Baseline BAF} = BAF_L^{fd} = \left[\frac{BAF_T^t}{f_{fd}} - 1\right] \cdot \frac{1}{f_L} \qquad \text{(Equation 2-3)}$$

where:

BAF_T^t	=	Total BAF
f_{fd}	=	fraction of the total concentration of chemical in water that is freely dissolved
f_L	=	fraction of tissue that is lipid

Baseline BAF can also be defined as:

$$\text{Baseline BAF} = BAF_L^{fd} - \frac{1}{f_L} \qquad \text{(Equation 2-4)}$$

where:

BAF_L^{fd}	=	lipid-normalized and freely dissolved-based bioaccumulation factor (see definition below)
f_L	=	fraction of tissue that is lipid

Note: Appendix A presents the derivation of the baseline BAF and refers to it as "BAF_L^{fd}." The subscript "L" signifies concentration of the chemical specifically in lipid, in contrast to "R," which refers to lipid normalization in which the concentration of the chemical in total tissue is divided by the fraction of the tissue that is lipid (f_L). The superscript "fd" signifies the chemical that is freely dissolved in water rather than total chemical in water. Based on an equilibrium partitioning assumption for the chemical's distribution in both the organism and the water, concentrations based on the "L" and "fd" chemical expressions can be calculated using measured or predicted values of the fraction of tissue that is lipid and fraction of total chemical that is freely dissolved in water, respectively (see

[1]As described in Section 3.2.2 and illustrated by Figure 3-1, baseline BAFs for certain ionic organic chemicals can be derived using methods developed for nonionic organic chemicals, which rely on lipid and organic carbon partitioning theory. In these cases, similar lipid and organic carbon partitioning behavior should be known or inferred (i.e., based on negligible ionization) for the ionic chemical in question.

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Appendix A). This avoids practical limitations associated with the direct analytical measurement of concentrations of total chemical in lipid and freely dissolved chemical in water.

Lipid-normalized and freely dissolved-based bioaccumulation factor (BAF_R^{fd}). The ratio (in liters per kilogram of lipid) of the lipid-normalized concentration of a chemical in tissue of an organism to the concentration of the chemical freely dissolved in water, in situations where both the organism and its food are exposed and the ratio does not change substantially over time. The BAF_R^{fd} is calculated as:

$$BAF_R^{fd} = \frac{C_R}{C_w^{fd}} \qquad \text{(Equation 2-5)}$$

where:

C_R = lipid-normalized concentration of chemical in tissues
C_w^{fd} = concentration of chemical that is freely dissolved in water

National trophic-level specific bioaccumulation factor (National $BAF_{TL\ n}$). A BAF based on nationwide average lipid content for trophic level "n" and nationwide average organic carbon in ambient waters. The national $BAF_{(TL\ n)}$ is expressed in liters per kilogram wet tissue. The national $BAF_{(TL\ n)}$ is calculated using the equation:

$$\text{National } BAF_{TL\ n} = [(\text{Final Baseline } BAF)_{TL\ n} \cdot (f_R)_{TL\ n} + 1] \cdot f_{fd} \qquad \text{(Equation 2-6)}$$

where:

Final Baseline $BAF_{TL\ n}$ = mean baseline BAF for trophic level "n"
$f_{R(TL\ n)}$ = fraction of tissue that is lipid in aquatic organisms at trophic level "n"
f_{fd} = fraction of the total concentration of chemical in water that is freely dissolved

2.2 BIOCONCENTRATION

Bioconcentration. The net accumulation of a chemical by an aquatic organism as a result of uptake directly from the ambient water, through gill membranes or other external body surfaces.

Bioconcentration factor (BCF). The ratio (in liters per kilogram of tissue) of the concentration of a chemical in the tissue of an aquatic organism to its concentration in water, in situations where the organism is exposed through the water only and the ratio does not change substantially over time. The BCF is calculated as:

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$$BCF = \frac{C_t}{C_w} \qquad \text{(Equation 2-7)}$$

where:

C_t = concentration of chemical in tissue
C_w = concentration of chemical in water

Because chemical concentrations in tissue and water can be defined in terms of chemical partitioning to different biological or chemical phases (e.g., total concentrations in tissue or water, concentration in lipid, concentration that is freely dissolved in water), the general equation for BCF (Equation 2-7) is further refined below to delineate among these different phases.

Total bioconcentration factor (BCF_T^t). A BCF based on the *total* concentration of chemical in the organism and the water. The total concentration of the chemical in tissue includes that in either a specific tissue or a whole organism and is based on wet tissue. The total concentration of the chemical in water includes chemical associated with particulate organic carbon, chemical associated with dissolved organic carbon, and chemical freely dissolved chemical in the water. A BCF is often referred to as a "laboratory-measured BCF" because it can be measured only in the laboratory. The BCF_T^t is expressed in liters per kilogram of lipid. The BCF_T^t is calculated as:

$$BCF_T^t = \frac{C_t}{C_w} \qquad \text{(Equation 2-8)}$$

where:

C_t = *total* concentration of chemical in tissue
C_w = *total* concentration of chemical in water

Baseline bioconcentration factor (Baseline BCF or BCF_L^{fd}). For nonionic organic chemicals (and certain ionic organic chemicals to which similar lipid and organic carbon partitioning behavior applies[2]), a BCF that is based on the concentration of chemical freely dissolved in water and the concentration of the chemical in the lipid fraction of tissue. The baseline BCF is expressed in liters per kilogram of lipid. The baseline BCF is determined using the equation:

[2]As described in Section 3.2.2 and illustrated by Figure 3-1, baseline BCFs for certain ionic organic chemicals can be derived using methods developed for nonionic organic chemicals, which rely on lipid and organic carbon partitioning theory. In these cases, similar lipid and organic carbon partitioning behavior should be known or inferred (i.e., based on negligible ionization) for the ionic chemical in question.

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$$\text{Baseline BCF} = BCF_L^{fd} = \left[\frac{BCF_T^t}{f_{fd}} - 1 \right] \cdot \frac{1}{f_R} \qquad \text{(Equation 2-9)}$$

where:

BCF_T^t	=	Total BCF
f_{fd}	=	fraction of the total concentration of chemical in water that is freely dissolved
f_R	=	fraction of tissue that is lipid

Baseline BCF can also be defined as:

$$\text{Baseline BCF} = BCF_R^{fd} - \frac{1}{f_R} \qquad \text{(Equation 2-10)}$$

where:

BCF_R^{fd}	=	lipid-normalized and freely dissolved-based bioconcentration factor (see definition below)
f_R	=	fraction of tissue that is lipid

Note: Appendix A presents the derivation of the baseline BCF and refers to it as "BCF_L^{fd}." The subscript "L" signifies concentration of the chemical specifically in lipid, in contrast to "R," which refers to lipid normalization in which the concentration of the chemical in total tissue is divided by the fraction of the tissue that is lipid (f_R). The superscript "fd" signifies the chemical that is freely dissolved in water rather than total chemical in water. Based on an equilibrium partitioning assumption for the chemical's distribution in both the organism and the water, concentrations based on the "L" and "fd" chemical expressions can be calculated using measured or predicted values of the fraction of tissue that is lipid and fraction of total chemical that is freely dissolved in water, respectively (see Appendix A). This avoids practical limitations associated with the direct analytical measurement of concentrations of total chemical in lipid and freely dissolved chemical in water.

Lipid-normalized and freely dissolved-based bioconcentration factor (BCF_R^{fd}). The ratio (in liters per kilogram of lipid) of the lipid-normalized concentration of a chemical in tissue of an organism to the concentration of the chemical freely dissolved in water, in situations where both the organism is exposed through water only and the ratio does not change substantially over time. The BCF_R^{fd} is calculated as:

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$$BCF_{\ell}^{fd} = \frac{C_{\ell}}{C_w^{fd}} \qquad \text{(Equation 2-11)}$$

where:

C_R	=	lipid-normalized concentration of chemical in tissues
C_w^{fd}	=	concentration of chemical that is freely dissolved in water

2.3 ADDITIONAL TERMS

Biomagnification. The increase in concentration of a chemical in the tissue of organisms along a series of predator-prey associations, primarily through the mechanism of dietary accumulation.

Biomagnification factor (BMF). The ratio (unitless) of the concentration of a chemical in a predator organism at a particular trophic level to the concentration of the chemical in the tissue of its prey organism at the next lowest trophic level for a given water body and chemical exposure.

For nonionic organic chemicals (and certain ionic organic chemicals to which similar lipid and organic carbon partitioning behavior applies), a BMF can be calculated using lipid-normalized concentrations of chemical in the tissue of organisms at two successive trophic levels as:

$$BMF_{(TL,\ n)} = \frac{C_{\ell\ (TL,\ n)}}{C_{\ell\ (TL,\ n-1)}} \qquad \text{(Equation 2-12)}$$

where:

$BMF_{(TL,\ n)}$	=	biomagnification factor for trophic level “n” (TL “n”)
$C_{R\ (TL,\ n)}$	=	lipid-normalized concentration of chemical in tissue of predator organism at a given trophic level (TL “n”)
$C_{R\ (TL,\ n-1)}$	=	lipid-normalized concentration of chemical in tissue of prey organism at the next lower trophic level from the predator (TL “n–1")

For those inorganic, organometallic, and ionic organic chemicals for which lipid and organic carbon partitioning does not apply (see Section 5.6), a BMF can be calculated using chemical concentrations in the tissue of organisms at two successive trophic levels as:

$$BMF_{(TL,\ n)} = \frac{C_{t\ (TL,\ n)}}{C_{t\ (TL,\ n-1)}} \qquad \text{(Equation 2-13)}$$

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where:

$BMF_{(TL, n)}$	=	biomagnification factor for trophic level “n” (TL “n”)
$C_{t\ (TL, n)}$	=	concentration of chemical in tissue of predator organism at a given trophic level (TL “n”)
$C_{t\ (TL, n-1)}$	=	concentration of chemical in tissue of prey organism at the next lower trophic level from the predator (TL “n-1")

Biota-sediment accumulation factor (BSAF). For nonionic organic chemicals (and certain ionic organic chemicals to which similar lipid and organic carbon partitioning behavior applies), the BSAF is the ratio (in kilograms of sediment organic carbon per kilogram of lipid) of the lipid-normalized concentration of a chemical in tissue of an aquatic organism to its organic carbon-normalized concentration in surface sediment, in situations where the ratio does not change substantially over time, both the organism and its food are exposed, and the surface sediment is representative of average surface sediment in the vicinity of the organism. The BSAF is calculated as:

$$\mathbf{BSAF} = \frac{C_R}{C_{SOC}} \qquad \text{(Equation 2-14)}$$

where:

C_R	=	lipid-normalized concentration of chemical in tissue
C_{soc}	=	concentration of chemical in dry sediment, normalized to sediment organic carbon

Depuration. Loss of a chemical from an organism as a result of any active or passive process.

Equilibrium. A thermodynamic condition under which a chemical’s activity, or fugacity, is equal among all phases composing the system of interest. In systems at equilibrium, chemical concentrations in all phases will remain unchanged over time.

Food-chain multiplier (FCM). For nonionic organic chemicals (and certain ionic organic chemicals to which similar lipid and organic carbon partitioning behavior applies), the ratio of a baseline BAF for an organism of a particular trophic level to the baseline BCF (usually determined for organisms in trophic level one). For inorganic, organometallic, and certain ionic organic chemicals to which lipid and organic carbon partitioning does not apply, a FCM can be derived based on total (wet or dry weight) concentrations of the chemical in tissue as described in Sections 4.4.1 and 4.4.2.

Freely dissolved concentration (C_w^{fd}). For nonionic organic chemicals, the concentration of the chemical that is dissolved in ambient water, excluding the portion sorbed onto particulate or dissolved organic carbon (POC or DOC). The freely dissolved chemical concentration is considered to represent the most bioavailable form of an organic chemical in water and therefore

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is the form that best predicts bioaccumulation. The freely dissolved concentration can be determined as:

$$C_w^{fd} = C_w^t \cdot f_{fd} \qquad \text{(Equation 2-15)}$$

where:

C_w^t	=	total concentration of chemical in water
f_{fd}	=	fraction of the total concentration of chemical in water that is freely dissolved

Hydrophilic. Having affinity for water; the extent to which a chemical is attracted to partitioning into the water phase. Hydrophilic organic chemicals have a greater tendency to partition into polar phases (e.g., water) than do hydrophobic chemicals.

Hydrophobic. Lacking affinity for water; the extent to which a chemical avoids partitioning into the water phase. Highly hydrophobic organic chemicals have a greater tendency to partition into nonpolar phases (e.g., lipid, organic carbon) than do hydrophilic chemicals.

Lipid-normalized concentration (C_l). The total concentration of a chemical in a tissue or whole organism divided by the fraction of that tissue or whole organism that is lipid. The lipid-normalized concentration can be calculated as:

$$C_l = \frac{C_t}{f_l} \qquad \text{(Equation 2-16)}$$

where:

C_t	=	concentration of chemical in tissue
f_l	=	fraction of tissue that is lipid

***n*-Octanol-water partition coefficient (K_{ow}).** The ratio of the concentration of a chemical in the *n*-octanol phase to its concentration in the aqueous phase in an equilibrated two-phase *n*-octanol-water system. For log K_{ow}, the log of the *n*-octanol-water partition coefficient is a base 10 logarithm.

Sediment organic carbon-normalized concentration (C_{soc}). For sediments, the total concentration of a contaminant in sediment divided by the fraction of organic carbon in sediment. The sediment organic carbon-normalized concentration can be calculated as:

$$C_{soc} = \frac{C_s}{f_{soc}} \qquad \text{(Equation 2-17)}$$

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where:

C_s	=	concentration of chemical in dry sediment
f_{soc}	=	fraction of dry sediment that is organic carbon

Sediment-water column concentration quotient (Π_{socw}). The ratio (in liters per kilogram of organic carbon) of the concentration of chemical in the sediment, on an organic carbon basis, to that in the water column, on a freely dissolved basis. Π_{socw} when divided by the K_{ow} of the chemical provides a measure, for a given ecosystem, of the chemical's thermodynamic gradient between the sediment and the water column. The sediment-water column concentration quotient is calculated as:

$$\Pi_{socw} = \frac{C_{soc}}{C_w^{fd}} \qquad \text{(Equation 2-18)}$$

where:

C_{soc}	=	concentration of chemical in dry sediment, normalized to sediment organic carbon
C_w^{fd}	=	concentration of chemical that is freely dissolved in water

Steady state. A condition reached by a system when rates of chemical movement between phases and reactions within phases are constant so that concentrations of the chemical in the phases of the system are unchanged over time. A system at steady state is not necessarily at equilibrium; steady-state conditions often exist when some or all of the phases of the system have different activities or fugacities for the chemical.

Uptake. Movement of chemical from the environment into an organism as the result of any active or passive process.

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3. OVERVIEW OF THE NATIONAL BAF METHODOLOGY

This section provides an overview of the methodology EPA will use for deriving national BAFs for setting AWQCs for the protection of human health. As mentioned in Section 1, national BAFs are intended to account for some major chemical, biological, and ecological attributes that can affect bioaccumulation in bodies of water across the United States. Therefore, EPA will use separate procedures for deriving national BAFs depending on the type of chemical (i.e., nonionic organic, ionic organic, inorganic, and organometallic). In addition, to account for other factors, such as biomagnification and broad physiological differences between trophic levels, EPA's national BAFs are derived separately for each trophic level. The methodology results in three national trophic level–specific BAFs for each chemical, one specific for each of trophic levels 2, 3, and 4 (BAF_2, BAF_3, and BAF_4).

BAFs can be measured or estimated with a variety of methods, ranging from empirically driven approaches that rely on measurements of chemical concentrations in aquatic organisms and their surrounding environmental media (water and sediment) to mechanistically driven approaches that rely on food web models in combination with information about the properties of chemicals and ecosystems to estimate bioaccumulation. The four methods that EPA will use for deriving national BAFs are described in the following sections. For a given chemical, the choice of which method to use for deriving a national BAF depends on several factors. These factors include the properties of the chemical of interest, the relative strengths and limitations of the BAF method, and the level of uncertainty associated with the bioaccumulation or bioconcentration measurements. Because multiple evaluation steps are involved in selecting the most appropriate BAF method(s) for a given chemical and data set, EPA has developed a decision framework for deriving national BAFs (Figure 3-1). This framework illustrates the major steps and decisions that will ultimately lead to calculating a national BAF. Use of this framework leads to selection of one of six possible procedures (shown at the bottom of Figure 3-1) for deriving national BAFs. Each procedure includes those BAF derivation methods that are suitable for the class and properties of chemicals to which the procedure applies. The following subsections are a prelude to the detailed discussion of the national BAF methodology provided in Sections 4 through 7. Section 3.1 introduces each of the four methods available for deriving national BAFs, including a discussion of their relative strengths and limitations. Section 3.2 provides additional discussion and explanation of the BAF derivation framework that applies to all chemical types.

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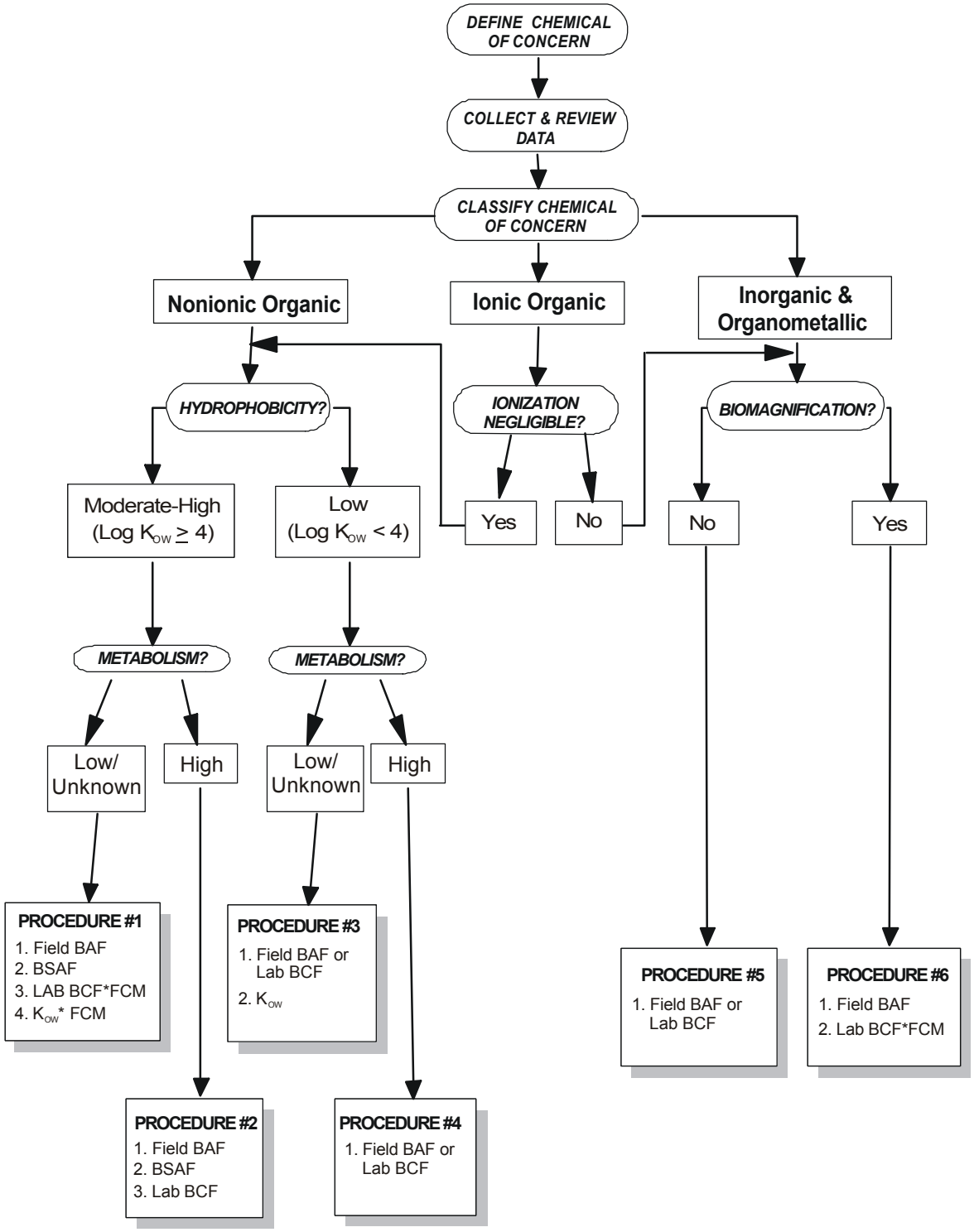

Figure 3-1. Framework for selection of methods for deriving national BAFs.

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3.1 SUMMARY OF FOUR BIOACCUMULATION METHODS

Bioaccumulation factors used to derive national trophic level–specific BAFs can be measured or predicted using one or more of the following four methods, depending on the type of chemical and its properties:

1. Measured BAFs derived from data obtained from a field study (i.e., field-measured BAFs)

2. BAFs predicted from biota-sediment accumulation factors (BSAFs) obtained from a field study (i.e., field-measured BSAFs)

3. BAFs predicted from laboratory-measured BCFs, with or without adjustment by a food-chain multiplier

4. BAFs predicted from a chemical's *n*-octanol-water partition coefficient (K_{ow}), with or without adjustment by a food-chain multiplier

Each of the four methods is summarized below. Details of each of the four methods are described in Section 5.

3.1.1 Field-Measured BAFs

A BAF derived from data obtained from field-collected samples of tissue and water—referred to here as a "field-measured BAF"—is the most direct measure of bioaccumulation. A field-measured BAF is determined from measured chemical concentrations in an aquatic organism and the ambient water collected from the same field location. Because the data are collected from a natural aquatic ecosystem, a field-measured BAF reflects an organism's exposure to a chemical through all relevant exposure routes (e.g., water, sediment, diet). A field-measured BAF also reflects factors that influence the bioavailability and metabolism of a chemical that might occur in the aquatic organism or its food web. Therefore, field-measured BAFs are appropriate for all chemicals, regardless of the extent of chemical metabolism in biota.

3.1.2 BAFs Predicted from a Field-Measured BSAF

For nonionic organic chemicals (and certain ionic organic chemicals to which similar lipid and organic carbon partitioning behavior applies), BAFs can also be predicted from BSAFs. A BSAF is similar to a field-measured BAF in that the concentration of a chemical in biota is measured from field-collected samples and it reflects an organism's exposure to all relevant exposure routes. A BSAF also accounts for bioavailability and chemical metabolism that might occur in the aquatic organism or its food web. A BSAF references the concentration of the chemical in an organism to the concentration of chemical in sediment, but it may be converted to a BAF when the chemical's distribution between sediments and water can be estimated. The BSAF procedure is used only to predict a BAF for moderate to highly hydrophobic organic chemicals.

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3.1.3 BAFs Predicted from Laboratory-Measured BCFs

A laboratory-measured BCF can be used to estimate a BAF for organic and inorganic chemicals either with or without adjustment with a food-chain multiplier, depending on the importance of nonaqueous exposure routes. However, unlike a field-measured BAF or one predicted from a field-measured BSAF, a laboratory-measured BCF typically reflects only the accumulation of chemical through the water exposure route. A laboratory-measured BCF may therefore underpredict BAFs for chemicals for which accumulation from sediment or dietary sources is important. In these cases, laboratory-measured BCF can be adjusted by a factor known as a food-chain multiplier (FCM) to better reflect accumulation through the food web from dietary exposures. Because a laboratory-measured BCF is determined by using the measured concentration of a chemical in an aquatic organism and its surrounding water, a laboratory-measured BCF often reflects metabolism of the chemical that occurs in the organism during the BCF measurement, but not in the food web.

3.1.4 BAFs Predicted from K_{ow}

A chemical's K_{ow} (measured or predicted) can also be used to predict a BAF for nonionic organic chemicals. This procedure is appropriate for nonionic organic chemicals but can also be applied to certain ionic chemicals that have lipid and organic carbon partitioning behavior similar to that of nonionic organics. The K_{ow} is strongly correlated with the BCF for nonionic organic chemicals, in particular those chemicals that are poorly metabolized by aquatic organisms. For nonionic organic chemicals where food web exposure is important, use of the K_{ow} alone, as an estimate of BCF, will underpredict the BAF because the BCF accounts only for chemical exposure from water. In such cases, the K_{ow} is adjusted with an FCM as described for the BAF method in Section 3.1.3.

3.1.5 Advantages and Limitations of BAF Methods

Each BAF derivation method summarized above has strengths and limitations associated with it that will be considered and balanced when deriving national BAFs. These strengths and limitations, as summarized in Table 3-1, form the basis for the Framework for selecting methods for deriving national BAFs (Figure 3-1) that is described in Section 3.2. For example, use of the field-measured BAF method is advantageous in that it applies to all chemical types, and accounts for site-specific factors that affect bioavailability, biomagnification, and metabolism. However, the current database of acceptable field-measured BAFs is relatively limited, in terms of both number of sites and chemicals for which they have been derived. Furthermore, field-measured BAFs cannot be readily determined for chemicals that are very difficult to accurately measure in the water column (e.g., 2,3,7,8-TCDD). BAFs derived from field-measured BSAFs offer a number of the same strengths as field-measured BAFs (e.g., they account for biomagnification, metabolism, and site-specific factors affecting bioavailability). In addition, the BSAF method is the only field-based method that can be used for chemicals such as 2,3,7,8-TCDD that are difficult to measure in ambient water. In EPA's framework, however, application of the BSAF method is currently limited to nonionic organic chemicals of moderate to high hydrophobicity. BAFs predicted from laboratory-measured BCF can be applied to all chemical types, and data are

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generally more plentiful than with field-measured BAFs. However, laboratory-based BCFs by themselves do not address chemical biomagnification in food webs unless they are adjusted with a field- or model-derived FCM. In addition, acceptable BCFs for highly hydrophobic chemicals (i.e., those with a log K_{ow} > 6) appear to be very limited, often because of lack of ancillary data that affect bioavailability (e.g., dissolved organic carbon). Finally, the model-derived BAF derivation method (using K_{ow} and FCMs where appropriate) offers a distinct advantage in that no laboratory data (besides a K_{ow}) or field data are needed to derive a BAF. However, this method is limited to nonionic organic chemicals and is currently constrained by the lack of in vivo data on chemical metabolism.

Table 3-1. Strengths and Limitations of the Four BAF Methods for Deriving National BAFs

BAF derivation method	Strengths	Limitations
1. Field-measured BAF	• Applicable to all chemical types • Incorporates chemical biomagnification and metabolism • Reflects site-specific attributes that affect bioavailability and dietary exposure	• High-quality data currently limited to few sites and chemicals • Representative chemical concentration in water may be difficult to quantify
2. BAF predicted from field-measured BSAF	• Incorporates chemical biomagnification and metabolism • Reflects site-specific attributes that affect bioavailability and dietary exposure • Useful for chemicals that are difficult to analyze in water • Use of chemical concentrations in sediment reduces temporal variability	• Limited to nonionic organic chemicals with log K_{ow} $ 4 • High-quality data currently limited to few chemicals and sites • Accuracy depends on representativeness and quality of estimate of chemical distribution between sediment and water
3. BAF predicted from lab-measured BCF × FCM	• Applicable to all chemical types • BCF may account for chemical metabolism in test organisms • Large BCF database available • Standardized test methods	• Chemical metabolism, when present in food web, generally not accounted for • High-quality data currently limited for highly hydrophobic chemicals, in part because of lack of ancillary data that affect bioavailability
4. BAF predicted from a K_{ow} × FCM	• Readily applied with minimal input data	• Limited to nonionic organic chemicals • Chemical metabolism, when present, not accounted for • Accuracy depends on accuracy of K_{ow}

3.2 FRAMEWORK FOR DERIVING NATIONAL BAFs

The EPA's framework for deriving national BAFs is depicted in Figure 3-1. The goal of this framework and the BAF guidance presented in the 2000 Human Health Methodology is to facilitate the full use of available data and methods for deriving national BAFs while prioritizing and restricting the use of certain BAF methods based on their inherent strengths and limitations, as summarized in Section 3.1. Use of this decision framework results in selection, based on the class and properties of the chemical, of one of six "Procedures," each of which can be used to

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derive national BAFs for a chemical having the specified class and properties. Each procedure includes one or more of the methods described in Section 3.1. Within a procedure, the number next to each BAF method indicates its general order of preference in the hierarchy for calculating national BAFs. For example, a field-measured BAF is generally given the highest preference for deriving a national BAF using Procedure 1, followed by a BAF predicted from a BSAF, a BAF predicted from a BCF x FCM, and, finally, a BAF predicted from a K_{ow} × FCM However, the hierarchy of methods within each procedure is not intended to be inflexible, as explained in Section 6.1 and in the 2000 Human Health Methodology. Some situations may indicate that greater uncertainty is likely to occur when applying a BAF derived from a "more highly preferred" method (e.g., a field-measured BAF within Procedure 1) than with a "less preferred" method (e.g., BAF predicted from BCF × FCM within Procedure 1), for example, when data from the more preferred method are limited in terms of their representativeness, quantity, or quality relative to the lower-tier method. In these situations, data from the lesser preferred, but least uncertain, method should be used to derive the national BAFs.

The first step in the national BAF derivation framework involves precisely defining the chemical of concern. The purpose of this step is to ensure consistency between the form(s) of chemical used to derive national BAFs and the form(s) used as the basis of the health assessment (e.g., the reference dose or point of departure/uncertainty factor). Although this step is usually unambiguous for single chemicals that are stable in the environment, complications can arise when assessing chemicals that occur as mixtures or undergo complex transformations in the environment.

The second step of the framework consists of collecting and reviewing data on bioaccumulation and bioconcentration. The third step involves classifying the chemical into one of three broadly defined categories: nonionic organic, ionic organic, and inorganic/organometallic. This step is important because some of the four BAF methods summarized in Section 3.1 are specific to certain chemical groups (e.g., the BSAF method for nonionic organic chemicals). For the purposes of the 2000 Human Health Methodology, nonionic organic chemicals are defined as organic compounds that do not ionize substantially in natural bodies of water. These chemicals are also referred to as "neutral" or "nonpolar" organics in the scientific literature. Ionic organic chemicals are considered to include those chemicals that contain functional groups with exchangeable protons, such as hydroxyl, carboxylic, sulfonic, and nitrogen (pyridine) groups. Ionic organic chemicals undergo ionization in water, the extent of which depends on the pH and the pKa of the chemical. Ionic chemicals are considered separately when deriving national BAFs because the behavior of the anionic or cationic species of these chemicals is much different from those of their neutral (un-ionized) counterparts. Inorganic and organometallic chemicals include inorganic minerals, other inorganic compounds and elements, metals, metalloids, and organometallic compounds. Additional guidance on the first three steps of the framework is found in Section 5.3 of the 2000 Human Health Methodology.

Once the chemical is classified into one of the three chemical categories, additional evaluation steps are necessary to determine which of the BAF procedures should be used to derive a national BAF. These steps are summarized below for each of the three chemical categories.

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3.2.1 BAF Derivation Procedures for Inorganic and Organometallic Chemicals

For inorganic and organometallic chemicals, the primary factor to be evaluated is the likelihood that the chemical will undergo biomagnification in the food web. At present, evaluating the biomagnification potential for this group of chemicals is almost exclusively limited to analyzing empirical data on the importance of food web (dietary) exposure and biomagnification in determining chemical concentrations in aquatic species. For example, available data indicate that methylmercury biomagnifies in aquatic food webs, whereas other chemicals in this category do not routinely biomagnify (e.g., copper, zinc, lead). If biomagnification is considered to be likely, then field-measured BAFs are the preferred BAF method, followed by laboratory-measured BCF adjusted with an FCM. If biomagnification is determined to be unlikely, field-measured BAFs and laboratory-measured BCF are considered to be of equal utility for deriving national BAFs, all other factors being equal. Additional guidance on determining national BAFs for inorganic and organometallic chemicals is provided in Section 5.6 of the 2000 Human Health Methodology. It should be noted that metal bioaccumulation can vary substantially across organisms due to a number of factors, including physiological differences and variation in mechanisms by which organisms take up, distribute, detoxify, store, and eliminate metals from their tissues. As a result of the complexity of assessing the fate and effects of metals in the environment, EPA has embarked on an initiative to provide additional guidance on conducting metal assessments, including metals bioaccumulation by aquatic organisms (USEPA, 2002).

3.2.2 BAF Derivation Procedures for Ionic Organic Chemicals

For chemicals classified as ionic organic chemicals, the primary evaluation step involves estimating the relative extent of ionization and evaluating their partitioning behavior with lipids and organic carbon. If the relative extent of ionization that is likely to occur at pH ranges that are typical of U.S. surface waters is negligible (see the 2000 Human Health Methodology for guidelines on this determination), and if the un-ionized form of the ionic chemical behaves like a nonionic organic chemical, in which lipid and organic carbon partitioning controls the behavior of the chemical, then the chemical can be treated essentially as a nonionic chemical for the purposes of deriving national default BAFs. If ionization is considered potentially important, or if non-lipid and non-organic carbon mechanisms control the behavior of the chemical, then the ionic chemical is treated in the same way as inorganic and organometallic chemicals for deriving national BAFs. Additional guidance for deriving national BAFs for ionic organic chemicals is provided in Section 5.5 of the 2000 Human Health Methodology.

Perfluorinated alkyl acids are an example of ionic organic chemicals. Some of these chemicals bioconcentrate and biomagnify in food webs via non-lipid mediated mechanisms; i.e., lipid and organic carbon partitioning behavior observed for nonionic organic chemicals does not apply. For the perfluorinated alkyl acids, Procedure 6 (Figure 3-1) would be used to derive national default BAFs.

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3.2.3 BAF Derivation Procedures for Nonionic Organic Chemicals

Deriving national BAFs for nonionic organic chemicals is somewhat more complex than for the other two chemical classes. First, four national BAF derivation procedures are applicable to nonionic organic chemicals. Second, selecting the most appropriate derivation procedure depends greatly on chemical properties, which are evaluated in two decision steps (see Figure 3-1). Finally, once the derivation procedure is selected, additional adjustments are made to the BAFs in order to account for differences in factors that affect bioaccumulation of this group of chemicals in aquatic organisms (e.g., lipid content in test organisms and organic carbon content in water).

Figure 3-2 shows the national BAF derivation process for nonionic organic chemicals. This process is divided into four steps:

Step 1. Selecting the BAF derivation procedure
Step 2. Calculating individual baseline BAFs
Step 3. Selecting final baseline BAFs
Step 4. Calculating national BAFs from the final baseline BAFs

A summary of each step follows.

Step 1: Selecting a BAF Derivation Procedure

Step 1 of the approach determines which of the four BAF procedures described in Section 3-1 will be appropriate for deriving the national BAF for a given nonionic organic chemical. As shown in Figure 3-1, there are two decision points. The first decision point requires knowledge of the chemical's hydrophobicity (i.e., the K_{ow} of the chemical). The K_{ow} provides an initial basis for assessing whether nonaqueous (e.g., food web, sediment) exposure and biomagnification may be a concern for nonionic organic chemicals. Knowledge of the likely importance of nonaqueous routes of exposure determines whether or not some methods (e.g., lab-measured BCF, K_{ow}-derived BAF) require additional adjustments to account for this exposure. Guidance for selecting the K_{ow} for a chemical is provided in Appendix B of this TSD. For the purposes of the 2000 Human Health Methodology, nonionic organic chemicals with log K_{ow} values equal to or greater than 4.0 are classified as "moderately to highly hydrophobic." For moderately to highly hydrophobic nonionic organic chemicals, available data indicate that exposure through the diet and other nonaqueous routes can become important in determining chemical residues in aquatic organisms (e.g., Russell et al., 1999; Fisk et al., 1998; Oliver and Niimi, 1983, 1988; Niimi, 1985; Swackhammer and Hites, 1988). Below a log K_{ow} of 4, available information indicates that nonaqueous exposure to these chemicals is not likely to be important.

The second decision point involves assessing the importance that chemical metabolism might have in determining chemical concentrations in aquatic organisms. Assessing metabolism is important because it affects the degree to which a chemical bioaccumulates (and biomagnifies) in aquatic food webs. For example, some polynuclear aromatic hydrocarbons have K_{ow} values that would warrant initial concern for biomagnification (i.e., log $K_{ow} > 4$), but chemical

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metabolism by higher organisms (primarily fish) often results in reduced concentrations in fish (Endicott and Cook, 1994; Burkhard, 2000). Guidance for assessing whether a high or low rate of metabolism is likely for a given chemical is provided in Section 5.4.2.3 of the 2000 Human Health Methodology.

Together, the hydrophobicity and metabolism decision points lead to the selection of one of four BAF procedures. Procedure 1 applies to chemicals with moderate to high K_{ow}s, where (1) the influence of chemical metabolism is suspected to be minor (e.g., polychlorinated biphenyls [PCBs], dichlorodiphenyltrichloroethane [DDT], dieldrin, etc.) or (2) there are insufficient data on chemical metabolism to make a determination (this reflects a policy decision to err on the side of public health protection in the absence of data). Procedure 2 applies to moderate-to-high K_{ow} chemicals for which the influence of chemical metabolism on bioaccumulation is considered to be important (e.g., selected polynuclear aromatic hydrocarbons). Within this procedure, the use of K_{ow}-based estimates (with or without FCMs) of BAFs is restricted because the K_{ow} may substantially overpredict bioaccumulation for chemicals that are metabolized. Procedure 3 applies to low-K_{ow} chemicals for which chemical metabolism is not considered significant. For such chemicals, no preference is given to field-measured BAFs over laboratory-measured BCF (i.e., both methods are appropriate), since biomagnification is not considered important for low-K_{ow} chemicals. Procedure 4 applies to low-K_{ow} chemicals for which metabolism is considered to be important. In this procedure as in Procedure 2, use of K_{ow}-predicted BAFs is not recommended because the K_{ow} may substantially overpredict bioaccumulation.

Step 2: Calculating Individual Baseline BAFs

Step 2 involves calculating individual, species-specific baseline BAFs using all of the methods available within the selected BAF derivation procedure. Calculating an individual baseline BAF involves normalizing the field-measured BAF_T^t (or laboratory-measured BCF_T^t), which are typically based on *total* concentrations in tissue and water by the lipid content of the study organism and the fraction of total chemical that is freely dissolved in the ambient water. Both the lipid content in the organism and the freely dissolved chemical concentration (as influenced by organic carbon in water) have been shown to be important factors that influence the bioaccumulation of nonionic organic chemicals (e.g., Mackay, 1982; Connolly and Pederson, 1988; Thomann, 1989; Suffet et al., 1994). Therefore, baseline BAFs, which are expressed on the basis of the chemical concentration in the lipid fraction of tissue and freely dissolved in water, are considered more amenable to being applied across different species and bodies of water than are BAFs or BCF expressed on the basis of the total concentrations in the tissue and water. Because bioaccumulation can be strongly influenced by the trophic position of aquatic organisms (through either biomagnification or physiological differences), extrapolation of baseline BAFs should not be performed between species of different trophic levels. An example of how a baseline BAF is calculated from a field-measured BAF_T^t is shown by Equation 3-1. Equations for calculating baseline BAFs differ according to the BAF derivation method. Examples of baseline BAF equations for other BAF derivation methods are provided in Sections 5.1 through 5.4 of this TSD and in Sections 5.4.3 through 5.4.6 of the 2000 Human Health Methodology.

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$$\text{Baseline BAF} = BAF_L^{fd} = \left[\frac{BAF_T^t}{f_{fd}} - 1 \right] \cdot \frac{1}{f_l} \qquad \text{(Equation 3-1)}$$

where:

BAF_T^t	=	Total BAF
f_{fd}	=	fraction of the total concentration of chemical in water that is freely dissolved
f_R	=	fraction of the tissue that is lipid

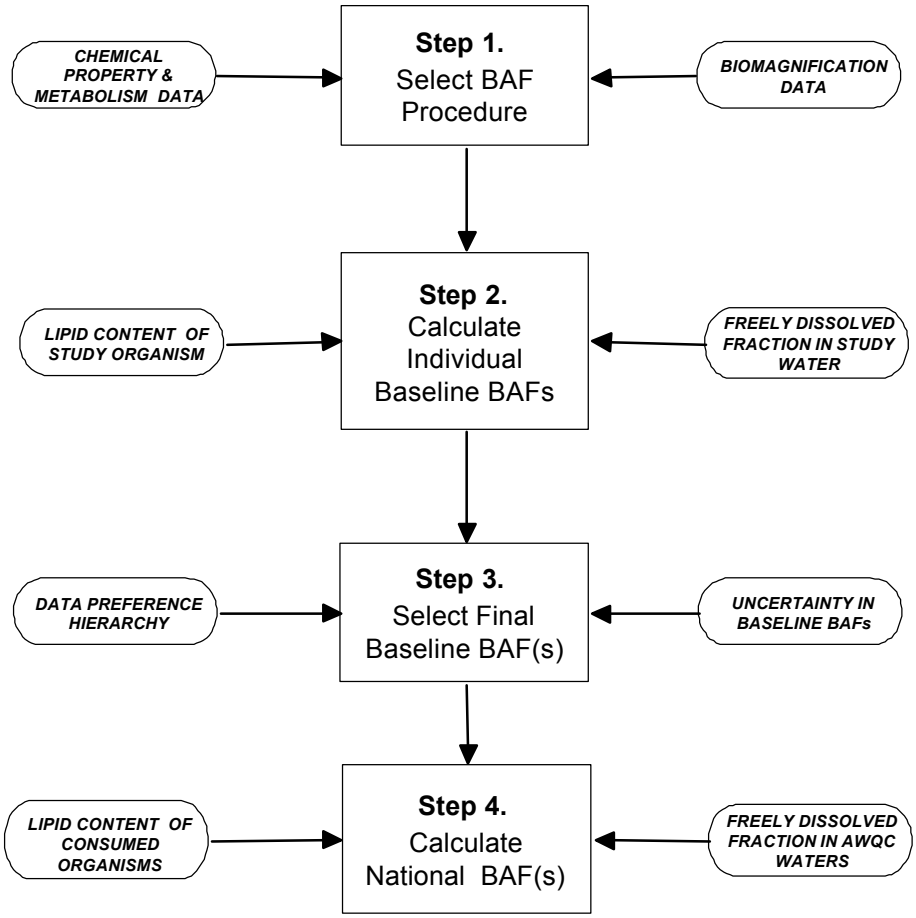

Figure 3-2. BAF derivation for nonionic organic chemicals.

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Step 3: Selecting Final Baseline BAFs

Step 3 of the methodology consists of selecting the final baseline BAFs from the individual baseline BAFs by using a weight-of-evidence approach that takes into account the uncertainty in the individual BAFs and the data preference hierarchy (i.e., field-measured BAFs are preferred over BAFs derived using the other methods). The individual baseline BAFs should be calculated using as many of the methods as possible under the appropriate BAF derivation procedure. As described earlier, the data preference hierarchy discussed in Section 5.4.2 of the 2000 Human Health Methodology is not inflexible. Rather, it is intended to be a guide for selecting the most appropriate final BAF when the uncertainty is similar between two individual baseline BAFs calculated using different methods. Section 6.1 of this TSD and Section 5.4.3.2 of the 2000 Human Health Methodology provide more detailed discussions of this step.

Step 4: Calculating National BAFs

The fourth and final step in calculating national BAFs for nonionic organic chemicals involves calculating three trophic-level specific BAFs that will be used in the equation to calculate national recommended AWQC for the protection of human health. This step involves adjusting final baseline BAFs to reflect the average lipid content of commonly consumed fish and shellfish and bioavailability of the chemical in waters to which the national recommended AWQC will apply. Converting baseline BAFs to national BAFs requires information on (1) the percent lipid of the aquatic organisms commonly consumed in the United States and (2) the fraction of chemical that is freely dissolved that is expected to be present in the ambient waters of interest. Baseline BAFs are not used directly in the derivation of the national AWQC because they do not reflect the conditions that affect chemical bioavailability in U.S. waters or chemical accumulation due to lipid content of the fish and shellfish residing in U.S. waters. The equation for calculating a national BAF for each trophic level is:

$$\text{National BAF}_{TL\ n} = [(\text{Final Baseline BAF})_{TL\ n} \cdot (f_l)_{TL\ n} + 1] \cdot f_{fd} \quad \text{(Equation 3-2)}$$

where:

Final Baseline $BAF_{TL\ n}$	=	mean baseline BAF for trophic level “n”
$f_{l(TL\ n)}$	=	fraction of tissue that is lipid in aquatic organisms at trophic level “n”
f_{fd}	=	fraction of the total concentration of chemical in water that is freely dissolved

The technical basis of Equation 3-2 is provided in Section 4. Procedures EPA will use for determining each component of Equation 3-2 are provided in Sections 6.4 and 6.5.

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4. BACKGROUND INFORMATION ON LIPID NORMALIZATION, BIOAVAILABILITY, AND BIOMAGNIFICATION

National trophic-level specific BAFs are intended to represent the long-term, average bioaccumulation potential of a pollutant in aquatic organisms of a particular trophic level (i.e., 2, 3, or 4) that are commonly consumed by humans throughout the United States. For certain chemicals (e.g., nonionic organics), chemical bioavailability, biota lipid content, and trophic transfer can affect bioaccumulation potential and ultimately the magnitude of BAFs. Because chemical bioavailability, biota lipid content, and trophic transfer can vary across locations and species, these factors should be accounted for in the derivation of national BAFs. Figure 3-2 in Section 3.2.3 presents EPA's stepwise process for developing national BAFs for nonionic organics, of which a key step is derivation of baseline BAFs.

The scientific basis for the lipid and freely dissolved fraction normalizations for nonionic organic chemicals are presented in Sections 4.1 through 4.3. Section 4.4 presents a discussion on how biomagnification is incorporated into the baseline BAFs in certain BAF methods.

4.1 LIPID NORMALIZATION

4.1.1 Background and Theory

The importance of lipid content in influencing the bioaccumulation of nonionic organic chemicals in aquatic organisms is well documented. Early work by Reinert (1969) and Reinert et al. (1972) demonstrated that nonionic organic chemicals concentrate in the lipids of organisms, and that differences in DDT concentrations between species and size groups are reduced when the concentrations of chemicals are normalized by lipid content. Numerous other studies have confirmed the role of lipid content in the bioconcentration and bioaccumulation of organic chemicals by aquatic organisms (e.g., Baron, 1990; van den Heuvel, et al., 1991; Leblanc, 1995; Stow et al., 1997). The lipid compartment is fundamental to equilibrium partitioning theory and to most bioaccumulation models of organic chemicals, wherein bioconcentration is described as a chemical partitioning process between the lipid and water compartments (e.g., Mackay, 1982; Barber et al., 1991; Gobas, 1993; Thomann, 1989; Di Toro et al., 1991). Although other compartments are assumed to exist in aquatic organisms (e.g., interstitial water, nonlipid biological material), partitioning to lipids becomes increasingly important as chemical hydrophobicity increases.

Recognition of the importance of lipids when assessing and predicting bioaccumulation of nonionic organic chemicals has led to the practice of normalizing chemical concentrations in tissue by lipid content. Lipid normalization, which is the process of dividing the total concentration of a chemical in tissue by the fraction of the tissue that is lipid (f_R), is usually performed to account for variation in bioaccumulation between species (or individuals within a species) that results from differences in lipid content alone. Although quantifying chemical concentrations in lipids would be a direct measure of chemical partitioning to lipids, it is technically difficult to do this because of the diffuse nature of lipids in tissues of aquatic organisms. Lipid normalization has been conducted since at least the 1980s for deriving AWQC

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for the protection of human health (USEPA, 1980), and more recently in developing Equilibrium Partitioning Sediment Benchmarks (USEPA, 2000b).

In the 2000 Human Health Methodology, EPA continues to recommend that BAFs be adjusted by the fraction of tissue that is lipid in order to account for differences in bioaccumulation that result from variation in lipid content among aquatic species (USEPA, 2000a). As depicted by Figure 3-2, BAFs are adjusted by lipid fraction (f_{ℓ}) in two separate steps. In the first step, data on the fraction of tissue that is lipid (f_{ℓ}) and data on the freely dissolved chemical concentration in water (C_w^{fd}) are used to calculate a baseline BAF from a field-measured BAF_T^t or a lab-measured BCF_T^t. This step is illustrated by Equation 3-1 for field-measured BAF_T^ts. Here, lipid normalization is conducted to enable more precise estimates of BAFs across multiple sites and species within a trophic level by accounting for the confounding influence of lipid variability on BAF_T^ts. In the second step, the final baseline BAF calculated in step 1 is converted to a national BAF that reflects the lipid fraction of commonly consumed aquatic organisms (and the fraction of chemical that is freely dissolved calculated for U.S. surface waters). This step is illustrated by Equation 3-2 in Section 3.2.3.

4.1.2 Assumptions and Limitations

Although theory and empirical evidence support the concept of adjusting BAFs and BCFs by lipid content to facilitate their extrapolation between species and sites, this practice nevertheless involves making a series of assumptions that deserve to be explicitly stated and evaluated. These assumptions can be stated as:

1. *For a given species and exposure condition*, the total concentration of a nonionic organic chemical in the tissue of an organism at or near steady state varies in direct proportion to the lipid content in the tissue of interest.

2. The degree of proportionality of chemical concentration with lipid content does not depend on the amount or composition of lipids present in tissue.

As described in Section 4.1.1, the first assumption is generally supported by the empirical evidence and underlying theory that supports many widely used bioaccumulation models. This assumption is also supported by the findings that for organic chemicals that are not metabolized, BCF is strongly correlated with $K_{ow.}$ (e.g., Veith et al., 1979b; Isnard and Lambert, 1988; de Wolf et al., 1992). In determining K_{ow}s, *n*-octanol is considered to be a surrogate for lipid. Chiou (1985) used triolein (glyceryl trioleate) as a surrogate for lipid and also found good agreement between BCFs and triolein/water partition coefficients. Evidence of the utility of lipid normalization is presented in Section 5.1.3, Figure 5-2, where it is shown that normalization by the fraction of tissue that is lipid (f_{ℓ}) and the fraction of chemical in water that is freely dissolved (f_{fd}) substantially reduces variation in BAF_T^ts.

Although the general utility of lipid normalization has been well established, this adjustment does not account for all of the variation in BAFs that may occur. Bioaccumulation can be affected by other factors that differ between species, such as composition of diet, growth

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rate, chemical metabolism, and trophic position. Ecosystem factors, such as chemical loading history, food web structure, and bioavailability also contribute to variation in BAFs (EPA's calculation of baseline and national BAFs address some differences in trophic position and bioavailability). Therefore, the effectiveness of lipid normalization in reducing variability in BAFs and BCFs is likely to be greatest when conducted between species (or individuals within a species) that are substantially different in lipid content but have experienced similar chemical exposure conditions. In situations where the difference in lipid content between species is minimal, or when the aforementioned factors (e.g., loadings history, food web structure) differ substantially between sites, the efficacy of lipid normalization may be substantially reduced or masked. Such situations may have contributed to reports of little or questionable benefit derived from lipid normalization in some field studies (e.g., Amrhein et al., 1999; Bergen et al., 2001). Other procedures, such as analysis of covariance, have been proposed to improve the statistical basis of lipid normalization (Hebert and Keenleyside, 1995). When sufficient data exist, analysis of covariance may improve in the statistical basis for lipid-normalizing BAFs. However, the limited data associated with typical BAF/BCF studies often restrict application of this approach for deriving national BAFs.

The second assumption pertains to the utility of the total lipid content as a normalizing factor for species and tissues with widely varying lipid fractions and lipid compositions. The process of normalizing BAFs and BCFs on the basis of the total fraction of tissue that is lipid assumes that lipids are a single, uniform compartment. In reality, total lipid content in fish includes different lipid classes, including relatively polar phospholipids, which are common in cell membranes, and generally nonpolar triacylglycerols, which are common in storage lipids (Henderson and Tocher, 1987). The variation in lipid-partitioning behavior of nonionic organic chemicals is thought to be a function of differences in polarity of lipid classes, as fewer chemicals become associated with the more polar "membrane-bound" lipids than storage lipids (Ewald and Larsson, 1994; van Wezel and Opperhuizen, 1995; Randall et al., 1998).

In practical terms, the potential impact that differences in lipid composition might have on chemical partitioning and lipid normalization seems to be most relevant for very lean tissues (e.g., those less than 1%–2% total lipids). This suggestion is based on observations that lean tissues of some fish species contain a much greater proportion of polar phospholipids (24%–65%) than do "fatty" tissues (1.5%–8.7%; Ewald and Larsson, 1994). Similar observations have been made with populations of ribbed mussels, for which Bergen et al. (2001) reported significantly higher fractions of polar lipids in leaner populations compared with fatter populations. Because of their greater polarity with respect to lipid content, very lean tissues are likely to exhibit different chemical/lipid-partitioning behavior than fatty tissues. Bergen et al. (2001) reported stronger correlations between chemical concentrations and mussels with higher total (and nonpolar) lipid content, which led to their suggestion that lipid normalization may work best above some threshold of lipid content. However, the narrow range of lipid content evaluated in their study (about a factor of two) and the reliance on total PCB measurements (as opposed to individual congeners) might have limited their ability to identify meaningful trends between chemical concentrations and lipid content.

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Differences in lipid composition in tissues of aquatic organisms also relate to a complication associated with methods used to determine lipid content. Specifically, different solvents have been used to extract lipids, which leads to different quantities (and types) of lipid being extracted from the same tissue of aquatic organisms. In a study by Randall et al. (1991), lipid fraction varied by nearly fourfold among four extraction methods but varied twofold or less among two of the more common extraction methods (chloroform-methanol and acetone-hexane). Following up on their previous work, Randall et al. (1998) report that if different solvents are used to extract lipids and PCB congeners, differences among lipid-normalized concentrations can vary more than fivefold, depending on the solvent combination. The relative difference among lipid extraction methods depends not only on the polarity of the solvent but also the lipid content of the tissue. Because lean tissues contain proportionally more polar lipids than fatty tissues, differences in the lipid extraction efficiency for different solvents tend to be greatest for lean tissues (de Boer, 1988; Ewald et al., 1998). This finding led these authors to caution the use of lipid data from lean tissues that have been extracted using strictly nonpolar solvent systems. Notably, other attributes (e.g., high temperature, pH, lipid decomposition due to exposure to light and oxygen) can also affect lipid extractions, but these have been less studied than has extraction solvent.

Although a variety of solvent systems that extract various lipid classes have been proposed for use in normalizing tissue chemical concentrations by lipid content, a clear consensus has not emerged on which method is most appropriate for all tissues, species, and nonionic organic chemicals. Although it is desirable to have one standardized lipid extraction method for normalizing concentrations of nonionic organic chemicals, it seems possible that no single method would be equally appropriate for all chemical and tissue types, because different tissues have different lipid compositions that, in turn, may alter the chemical/lipid partitioning process. From a toxicological perspective, the science is not presently clear on which classes of lipids (e.g., phospholipids, free fatty acids, mono-, di-, and triglycerides) are most relevant with respect to different organic chemicals. For example, DDT has been reported to bind to relatively polar membrane–bound lipids, which suggests membrane lipids might be relevant to DDT toxicity (Chefurka and Gnidec, 1987). Randall et al. (1998) reported that 27% of extractable PCBs were associated with the more polar, membrane–bound lipid pool (i.e., extractable with chloroform/methanol), whereas 73% were associated with the neutral lipid pool (i.e., extractable with hexane). Similarly, de Boer (1988) reported that chlorobiphenyls were associated with both bound (membrane) and unbound (storage) lipid pools in fish. These findings further suggest that membrane-bound lipids should not be ignored when selecting lipid extraction methods.

To promote consistency in measuring BAFs and BSAFs in field studies, EPA recommends the continued use of the Bligh and Dyer (1959) chloroform/methanol extraction method (or the less toxic solvent system of Hara and Radin (1978), in which hexane/isopropanol) in combination with gravimetric measurement of lipid. The Bligh-Dyer method is recommended because it is widely used for lipid measurements and has been well characterized in terms of the types of lipids extracted. The Bligh-Dyer method also extracts both polar and nonpolar lipids. Based on these and other considerations, Randall et al. (1998) also recommend the Bligh-Dyer method as a standard technique for total lipid extraction pending more research to identify the complex neutral chemical/lipid relationships and subsequent development of a definitive standard

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method. Randall et al. (1998) also recommend that if other lipid extraction methods are used, results should be compared to results obtained using the Bligh-Dyer method to allow conversion of the results to Bligh-Dyer equivalents. When using exiting data on lipid fraction, EPA may consider it appropriate to exclude certain data when differences in baseline BAFs or BCFs are substantial and are believed to be caused largely by differences in lipid extraction methods.

4.2 TECHNICAL BASIS OF FREELY DISSOLVED NORMALIZATION OF CHEMICAL CONCENTRATION IN WATER

The 2000 Human Health Methodology for deriving trophic-level specific national BAFs for nonionic organic chemicals uses baseline BAFs in an intermediate step. The baseline BAFs are based on the concentration of chemical that is freely dissolved in water (C_w^{fd}) and the fraction of the organism that is lipid (f_ℓ). EPA uses these adjustments because they express the BAF on a thermodynamic or fugacity basis and allow better extrapolation of BAFs from one ecosystem to another.

By basing the baseline BAFs on C_w^{fd}, EPA does **not** ignore the chemical-associated dissolved organic carbon (DOC) and particulate organic carbon (POC) in the water column. As discussed in the following sections, a chemical associated with DOC and POC in the water column is assumed to be in equilibrium with the chemical freely dissolved in the water column (an assumption made by EPA; see Section 4.2.3). Therefore, any additions or removal of chemical from any of the three phases (i.e., freely dissolved chemical, chemical associated with DOC, and chemical associated with POC) will cause a re-equilibration of the chemical among the three phases. Due to the equilibrium conditions among these three phases, the chemical concentration in the water column expressed using any of the three phases, individually or in combination, is indicative of the chemical concentrations in the other water column phases for a given set of ecosystem conditions. Therefore, a BAF could be based on any combination of the three phases and include the influences of the other water column phases.

The relationship among the freely dissolved chemical and the chemical associated with DOC and POC, presented below, assumes equilibrium among these phases. For a given ecosystem, DOC and POC define the partitioning of the chemical among the three phases. National BAFs, calculated from the baseline BAFs, require both the average lipid content of fish and shellfish consumed by the U.S. population as well as average DOC and POC values for the nation's waters. These required parameters result in expression of national BAFs on the basis of the weight of fish/shellfish tissue and total chemical concentration in the water column, i.e., (micrograms of chemical per kilogram of wet tissue) / (micrograms of chemical per liter of water).

4.2.1 Background Theory and Basic Equation

Experimental evidence shows that hydrophobic organic chemicals exist in water in three phases: (1) the freely dissolved phase, (2) sorbed to suspended solids (particulate organic carbon), and (3) sorbed to dissolved organic matter (Hassett and Anderson, 1979; Carter and Suffet, 1982; Landrum et al., 1984; Gschwend and Wu, 1985; McCarthy and Jimenez, 1985a;

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Eadie et al., 1990, 1992). The total concentration of the chemical in water is the sum of the concentrations of the freely dissolved chemical and the sorbed chemical (Gschwend and Wu, 1985; USEPA, 1993):

$$C_w^t = C_w^{fd} + POC \cdot C_{poc} + DOC \cdot C_{doc}$$

(Equation 4-1)

where:

C_w^t	=	total concentration of chemical in water
C_w^{fd}	=	concentration of chemical that is freely dissolved in water
C_{poc}	=	concentration of the chemical partitioned to the particulate organic carbon in the ambient water
C_{doc}	=	concentration of the chemical sorbed to the dissolved organic carbon in the water
POC	=	concentration of particulate organic carbon in water (kilograms of particulate organic carbon per liter of water)
DOC	=	concentration of dissolved organic carbon in water (kilograms of dissolved organic carbon per liter of water)

The above equation can also be expressed using partitioning relationships as:

$$C_w^t = C_w^{fd} \cdot (1 + POC \cdot K_{poc} + DOC \cdot K_{doc})$$

(Equation 4-2)

where:

K_{poc}	=	C_{poc} / C_w^{fd}
K_{doc}	=	C_{doc} / C_w^{fd}
K_{poc}	=	equilibrium partition coefficient of the chemical between POC phase and the freely dissolved phase of water (liters of water per kilogram of particulate organic carbon)
K_{doc}	=	equilibrium partition coefficient of the chemical between DOC phase and the freely dissolved phase of water (liters of water per kilogram of dissolved organic carbon)

From Equation 4-2, the fraction of the chemical that is freely dissolved in the water can be calculated using the following equation:

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$$f_{fd} = \frac{C_w^{fd}}{C_w^{t}} = \frac{1}{1 + POC \cdot K_{poc} + DOC \cdot K_{doc}}$$

(Equation 4-3)

Experimental investigations by Eadie et al. (1990, 1992), Landrum et al. (1984), Yin and Hassett (1986, 1989), Chin and Gschwend (1992), and Herbert et al. (1993) have shown that K_{doc} is directly proportional to the K_{ow} of the chemical and is less than the K_{ow}. When measured values of K_{doc} are not available, it can be estimated using the following equation:

$$K_{doc} \approx K_{ow} * 0.08$$

(Equation 4-4)

Experimental investigations by Eadie at al. (1990, 1992) and Dean et al. (1993) have shown that K_{poc} is approximately equal to the K_{ow} of the chemical. When measured K_{poc} values are not available, it can be estimated using the following equation:

$$K_{poc} \approx K_{ow}$$

(Equation 4-5)

By substituting Equations 4-5 and 4-6 into Equation 4-4, the following equation is obtained:

$$f_{fd} = \frac{1}{1 + POC \cdot K_{ow} + DOC \cdot 0.08 \cdot K_{ow}}$$

(Equation 4-6)

Burkhard et al. (1997) evaluated the utility of using Equation 4-6 to derive baseline BAFs that are applicable to multiple sites. In their study, Burkhard et al. (1997) measured BAFs for various chlorinated butadienes, chlorinated benzenes, and hexachloroethane for three species of forage fish and blue crab in Bayou d'Inde of the Calcasieu River system in Louisiana. Using Equation 4-6, field-measured BAFs were converted to baseline BAFs and compared to baseline BAFs determined for other trophic level three species in two other field studies (Pereira et al.,

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1988; Oliver and Niimi, 1988). One of these field studies, by Pereira et al. (1988), was conducted in different sites within the Calcasieu River system; the other study, by Oliver and Niimi (1988), was carried out in Lake Ontario. Burkhard et al. (1997) found no significant difference between baseline BAFs determined in their own study and those determined by Pereira et al. (1988) (Tukey's, " = 0.05). However, for one chemical (hexachlorobutadiene), a difference between the two studies of about 1 order of magnitude was observed in the baseline BAFs. Burkhard et al. (1997) further noted that their own baseline BAFs were not substantially different from those derived for similar trophic level fish in Lake Ontario, suggesting broader applicability of properly derived baseline BAFs.

The EPA's BAF methodology incorporates four decisions/assumptions associated with the three-phase partitioning model for estimating the concentrations of nonionic organic chemicals that are freely dissolved in ambient waters. These four decisions/assumptions are:

1. Sorption of the chemical to DOC and POC reduces chemical bioavailability to aquatic organisms.

2. Chemicals in the freely dissolved phase of the water are in equilibrium with chemical associated with the DOC and POC (including plankton) phases of the water column.

3. $K_{poc} = K_{ow}$

4. $K_{doc} = 0.08 \text{ C } K_{ow}$

These assumptions are based on experimental evidence referenced above. Detailed discussions of the evidence and other information supporting these assumptions are presented in the following subsections: assumption 1 in Section 4.2.2, assumption 2 in Section 4.2.3, and assumptions 3 and 4 in Sections 4.2.4 and 4.2.5.

4.2.2 Effects of Chemical Sorption to DOC and POC on Chemical Bioavailability

Numerous reports demonstrate the partitioning of hydrophobic nonionic organic chemicals to POC and DOC (see Section 4.2.4). Concurrent with the research on partitioning of hydrophobic nonionic organic chemicals to POC and DOC, research efforts have focused on bioavailability of hydrophobic nonionic organic chemicals to fish and other aquatic organisms in the presence of DOC and POC. The results of this research show that the concentration of chemical that is freely dissolved in sediment porewaters and ambient surface waters is the best measure currently available of the fraction of nonionic organic chemicals available for uptake by aquatic organisms (Suffet et al., 1994; DiToro et al., 1991).

Reduced chemical uptake by aquatic organisms in the presence of DOC has been extensively reported for both ambient waters and waters containing added DOC (Leversee et al., 1983; Landrum et al., 1985; McCarthy and Jimenez, 1985b; McCarthy et al., 1985; Carlberg et al., 1986; Black and McCarthy., 1988; Servos and Muir, 1989; Kukkonen et al., 1989). For example, it

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has been reported that the percentage reduction in gill uptake efficiency of benzo[a]pyrene and 2,2',5,5'-tetrachlorobiphenyl in rainbow trout is equal to the percentage reduction in freely dissolved chemical concentration in the presence of DOC (Black and McCarthy, 1988). The authors of this study concluded that only the chemical that was freely dissolved in the water was available for uptake by the fish. Similarly, Landrum et al. (1985), McCarthy et al. (1985), and Servos and Muir (1989) reported that chemical uptake rates were reduced when DOC was present and that the concentration of chemical that is freely dissolved in the water column decreases in proportion to the amount of DOC present in the water. These studies clearly support EPA's assumption that chemical bioavailability of nonionic organic chemicals to aquatic organisms is reduced in the presence of DOC and POC. Excellent reviews on the science of bioavailability are provided by Hamelink et al. (1994) and Kukkonen (1995).

There are a few reports in the scientific literature of increases in the bioavailability of nonionic organic chemicals to aquatic organisms in the presence of low concentrations of DOC (see Haitzer et al., 1998). In their review, Haitzer et al. (1998) compared BCFs determined using laboratory waters with those determined using lake waters and laboratory waters with added DOC as the exposure media. When BCFs derived from laboratory water experiments were smaller than those derived from the other waters, the authors concluded that increased bioavailability had occurred. The EPA believes that some of these findings are artifacts of the experimental design. For example, Haitzer et al. (1998) reported that bioavailability of hepta- and octa-chlorodibenzo-p-dioxins to rainbow trout was enhanced when DOC was low. Careful examination of the original report by Servos et al. (1989), however, reveals that the solubility limits for the hepta- and octa-chlorodibenzo-p-dioxins were exceeded in the experiment, and therefore any conclusions about increased bioavailability are clearly suspect. The EPA also believes that other factors could explain reports of apparent increases in bioavailability. Verhaar et al. (1999) and others have pointed out that in performing any experiment from which BCFs will be derived, the organisms will introduce DOC—for example, from mucous layers, feces, and urine—into the aqueous phase. Because the measurements made to determine BCF do not typically measure 'bioavailable' chemical (i.e., the concentration of chemical that is freely dissolved) but rather the total concentration of chemical that is in the exposure water, addition of DOC by the organisms during the experiment most certainly confounds the assumption that DOC concentrations were actually low. It is entirely possible that the concentration of chemical that was freely dissolved in experiments using laboratory waters was substantially different from that in experiments using lake waters and laboratory waters with added DOC. A recent report by the authors of the 1998 review (i.e., Haitzer et al.) supports EPA's belief that the increased bioavailability in the presence of low concentrations of DOC for BCF measurements is caused by experimental artifacts. After very careful study of BCF measurements performed with low DOC concentrations, Haitzer et al. (2001) concluded that "... BCF enhancements that have been reported in the literature are more likely the result of random, experimental variations than the result of systematic enhancement of bioconcentration."

On the basis of the information presented above, EPA has assumed that the bioavailability of nonionic organic chemicals to aquatic organisms is reduced in the presence of DOC and POC. EPA acknowledges that there are a few reports of increased bioavailability in the

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scientific literature and believes that the causes of the increased bioavailability are, in all likelihood, experimental artifacts of the BCF measurements.

4.2.3 Sorptive Behavior of Nonionic Organic Chemicals with DOC and POC (Including Plankton) in the Water Column

In using the three-phase partitioning model to determine the concentration of chemical that is freely dissolved in the water column, EPA has assumed that the chemical freely dissolved in the water column is in equilibrium with the chemical associated with DOC and POC. The basis for this assumption is presented below.

In the development of the fluorescence quenching technique for measuring partitioning between the freely dissolved chemical and DOC, investigators have studied the time required for PAHs to equilibrate with DOC. Gauther et al. (1986), McCarthy and Jimenez (1985a), and Schlautman and Morgan (1993) have reported times ranging from less than 1 minute to approximately 10 minutes for PAHs to equilibrate with DOC. These very short equilibration times suggest that equilibrium conditions should exist between nonionic organic chemicals and DOC in the environment.

K_{poc} data are quite limited, however, and EPA is unaware of any research efforts studying the kinetics of partitioning of nonionic organic chemicals between the POC and the freely dissolved phases of water. Insights into the behavior and kinetics of partitioning with POC can be gained by examining the experimental evidence on partitioning of nonionic organic chemicals in sediments/soils. Karickhoff et al. (1979) and Gschwend and Wu (1985) have shown that sorption and desorption of nonionic organic chemicals to sediment and soil organic carbon are reversible. In the 1980s, most investigators believed that time periods on the order of hours to a few days were required for chemical to equilibrate between the freely dissolved and organic carbon phases (Tomson and Pignatello, 1999). More recently, it had been found that attainment of steady-state/equilibrium conditions in these systems takes substantially longer periods of time (e.g., upwards of 100 days), and the time period is dependent on the concentration of suspended solids in the system (Jepsen et al., 1995).

Numerous investigations have studied the kinetics of sorption and desorption of nonionic organic chemicals to sediment and soil organic carbon, and these studies suggest the existence of fast and slow sorption and desorption phases (Pignatello and Xing, 1996). The desorption process can be characterized as having a fast initial release of chemical followed by a slow, prolonged release of the chemical. Numerous models have been developed to explain this behavior (Chen et al., 1999). Many investigators have modeled the sorption process at the surface of the organic carbon as a quick equilibrium process between the organic carbon surface and the chemical freely dissolved in the water column (Schwarzenbach et al., 1993). Examples include the retarded diffusion model of Lick and Rapaka (1996) and the radial diffusion model of Wu and Gschwend (1986).

There is no clear consensus on a kinetic model for describing the partitioning of nonionic organic chemicals between POC (or sediment/soil particles) and the freely dissolved phases (see

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Chen et al. [1999] for a listing of models). Such a model would have to account for both fast and slow sorption/desorption processes. Given the limited amounts of K_{poc} data, as well as kinetic data for sorption/desorption processes with POC, the selection of an appropriate kinetic model is clearly problematic. From an uncertainty standpoint, modeling nonequilibrium conditions using equilibrium condition assumptions would cause the freely dissolved concentration of the chemical to be too small, because the K_{poc} for kinetic conditions would be less than that for equilibrium conditions.

In some situations, the concentration of chemical that is determined to be freely dissolved using the three-phase model might be too large. As discussed by Gustafsson et al. (1997), PAHs partition more strongly to soot (i.e., organic carbon derived from incomplete combustion) than to organic carbon in sediments, whereas other chemical classes, such as PCBs, do not appear to be influenced by the soot phase. Unfortunately, the soot contents of natural waters are largely unknown. In situations where significant amounts of soot exist, the three-phase model could be modified to include a fourth phase consisting of soot. Gustafsson et al. (1997) describe a methodology for estimating the partition coefficients for soot.

By definition, POC is material retained by filtering or by centrifugation. Therefore, POC includes plankton. Because EPA assumes that the chemical associated with POC is in equilibrium with the chemical freely dissolved in water, chemical in plankton retained by the filter must be in equilibrium with the chemical freely dissolved in water. Under certain conditions—for example, algal blooms—the plankton is probably not in equilibrium with the chemical freely dissolved in water. However, because EPA's basis for deriving AWQC involves long-term average, steady-state, or near steady-state conditions, EPA believes that it is reasonable to assume that chemicals associated with plankton (in the POC) is on average in equilibrium with the chemicals freely dissolved in water. It should be noted that larger plankton is not included in POC samples because a prefiltering step is generally used to remove larger particulates before filtering or centrifuging to separate POC; see, for example, Broman et al. (1991), who used a 100-µm prefilter to define the upper size cutoff for POC.

The EPA, in using the three-phase model for determining the concentration of chemical that is freely dissolved, assumes equilibrium exists between the chemical associated with the POC and the chemical that is freely dissolved. This assumption is based on the consideration that POC in the environment is constantly exposed to the chemical of interest, and the sorption and desorption processes for the chemical to and from the POC are dominated by fast-phase kinetics specifically, the quick equilibrium process occurring at the surface of the organic carbon (Schwarzenbach et al., 1993). Because of fast-phase kinetics, short-term fluctuations in ambient concentrations are quickly accounted for in natural waters. Furthermore, AWQCs are developed with the assumption that conditions in ambient waters are representative of long-term averages, which are best captured using steady-state or near steady-state conditions. EPA believes that the three-phase partitioning model provides a reasonable approximation of these types of conditions.

Errors associated with calculation of the freely dissolved concentration are somewhat offset by using the three-phase partitioning model twice in EPA's methodology for developing national BAFs. First, a baseline BAF is calculated from a measured BAF_T^t wherein the measured

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BAF_T^t is lipid- normalized and corrected for bioavailability considerations using the fraction of chemical that is freely dissolved. Second, a national BAF_T^t is calculated using the average lipid content for species consumed in the United States and the fraction of chemical that is freely dissolved in U.S. waters. EPA believes that use of the freely dissolved concentration for converting both to and from the intermediate baseline BAF value, that is, from measured BAF-to-baseline BAF and again from baseline BAF-to-national BAF offsets the error associated with calculating the freely dissolved concentration.

Given the above considerations, EPA has decided to use the three-phase partitioning model with the assumption of equilibrium conditions for the calculation of the freely dissolved concentrations for nonionic organic chemicals for the following reasons:

1. Available data indicate complete, rapid partitioning to DOC;

2. Initial partitioning to POC is also rapid and near complete and although some kinetic limitations on chemical partitioning with POC occur, these are not likely to be important on the time scale applicable to human health water quality criteria;

3. No consensus exists on available kinetic models specific to POC; and

4. Use of the freely dissolved fraction twice in derivation of national BAFs offsets model error.

4.2.4 Values for the Particulate and Dissolved Organic Carbon Partition Coefficients K_{poc} and K_{doc}

In using the three-phase partitioning model for calculating the fraction of a chemical's concentration that is freely dissolved in water (f_{fd}), EPA will define K_{poc} and K_{doc} as follows:

$K_{poc} = K_{ow}$ with 95% conference limits of a factor of 8 in either direction.

$K_{doc} = 0.08 \cdot K_{ow}$ with 95% confidence limits of a factor of 20 in either direction.

The basis for these relationships is presented below.

The separation of POC from DOC in water samples is operationally defined by filtering or centrifugation. With both techniques, the operational cutoffs between POC and DOC fractions can differ depending upon membrane selection and hardware; for example, a membrane with a 0.45-µm cutoff may be used in one study, whereas centrifugation that retains all particles with a size of 1.0 µm or greater may be used in another study. Typically, the size cutoff between POC and DOC fractions is 0.1-1 µm. DOC is principally composed of carbohydrates, carboxylic acids, amino acids, hydrocarbons, hydrophilic acids, and humic and fulvic acids. POC is principally composed of some larger humic acids, microbes, small plankton, plant litter, and ligneous matter (Suffet et al., 1994; Thurman, 1985). The material retained by filtration or centrifugation is the POC fraction. Organic carbon and chemical-specific analyses are performed on the POC fraction

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to determine POC and C_{poc}, respectively. The DOC fraction is defined as the ambient water remaining after filtration or centrifugation is performed. The DOC fraction contains both the chemicals that are freely dissolved and the chemicals associated with the DOC. To determine the concentration of chemical that is freely dissolved in the DOC fraction, a variety of analytical techniques are available, for example, fluorescence quenching, purging or sparging techniques, solid phase microextraction (SPME), equilibrium dialysis, solubility enhancement, ultrafiltration, reverse-phase separation, size exclusion chromatography, and liquid-liquid extraction. Some of these techniques directly measure the concentration of chemical that is freely dissolved, whereas others physically separate the DOC-bound chemical fraction from the freely dissolved chemical fraction.

All of the methods for measuring freely dissolved chemical in water have limitations that can lead to uncertainties in the K_{poc} and K_{oc}. However, limitations associated with some methods can lead to larger uncertainties than others. The methods that appear to have smaller biases are sparging, fluorescence quenching, SPME, and possibly equilibrium dialysis. An excellent discussion on the individual techniques (except SPME) and their limitations is presented by Suffet et al. (1994). The reader can refer to Poerschmann et al. (1997) or Ramos et al. (1998) for further information on the SPME method.

A review of the scientific literature reveals that K_{poc} measurements are not as prevalent as K_{doc} and K_{oc} measurements. K_{oc} is defined as the partition coefficient of the chemical concentration on soils or sediments (on an organic carbon basis) to the chemical concentration in water after the removal of the solid phase. K_{oc} is expressed as liters of water per kilogram of organic carbon. K_{poc} is defined as the partition coefficient of the chemical concentration on the water column particles (on an organic carbon basis) to the chemical concentration freely dissolved in the water. K_{poc} is expressed as liters of water per kilogram of organic carbon. Measured K_{oc} values should not be assumed to be equal to K_{poc}, because (1) the types of organic carbon in the soils and sediments can be very different from those in the water column, and (2) their denominators are different. Sediments and soils tend to be more weathered than water column particulates, because the latter include organic matter derived from sources such as recently deceased as well as live plankton and algae and fecal matter from aquatic organisms. However, in some cases, the organic matter composing the K_{oc} and K_{poc} might be very similar, because sediment resuspension and erosional inputs could be responsible for a majority of the particulates in the water column. In all cases, the chemical concentrations in water used in measuring K_{oc} and K_{poc} are different. The determination of K_{poc} is based on the concentration of chemical freely dissolved in the water (see Section 4.2.1 for derivation), whereas K_{oc} is determined by using an operational definition of “dissolved” in water. This operational definition includes both freely dissolved chemical and chemical sorbed to DOC in the aqueous phase.

Data for K_{poc} are limited for a number of reasons. First, the measurement of K_{poc} in field situations is often very difficult because of the extremely low concentrations of hydrophobic pollutants in natural waters, often 1 ppt or less on a total basis. With low concentrations, large volumes of water must be processed in order to obtain enough of the chemical to measure. For example, Broman et al. (1991) processed approximately 2,000 L of Baltic Sea water to obtain measurable amounts of polychlorinated dioxins and furans on the particulates retained by

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filtering and in the water passing through the filter. Second, the techniques developed for measuring freely dissolved concentrations of chemical in natural waters are not amenable to field sampling situations in which large volumes of water need to be processed. Third, in laboratory studies, many investigators use sediment particles as a surrogate for naturally occurring water column particulates, and it is somewhat tenuous to assume that sediment particles are equivalent to water column particulates. Fourth, because of operational and analytical factors, K_{oc}s and K_ds (K_{oc}s expressed on the basis of dry weight rather than organic carbon on the solids, i.e., $K_{oc} = K_d/f_{oc}$) are more often reported than K_{poc} values, because K_{oc}s and K_ds are much easier to determine.

K_{poc} measurements found in a search of the scientific literature are reported in Table 4-1 and plotted in Figure 4-1. These values were determined by using the reverse-phase, sparging, and ultrafiltration method with samples primarily from Great Lakes ecosystems. An equation of the form $\log K_{poc} = a + b \cdot \log K_{ow}$ was computed by using the geometric mean regression technique (Ricker, 1973); this equation is:

$$\log K_{poc} = + 1.19\ (\pm 2.18) + 0.81\ (\pm 0.11) \cdot \log K_{ow} \qquad df = 14,\ r = 0.84,\ s_{xy} = 0.40$$

The geometric mean regression technique was used because the X variable ($\log K_{ow}$) was measured with error. The equation and its 95% confidence limits for any single predicted $\log K_{poc}$ are plotted in Figure 4-1. The slope of this regression line is not significantly different from 1.0 (" = 0.05). Assuming a slope of 1.0 results in an equation of the form $\log K_{poc} = \log K_{ow} + B$. This equation, by rearrangement, results in $B = \log K_{poc} - \log K_{ow} = \log (K_{poc}/K_{ow})$, and "B" can be found by averaging the differences of the $\log K_{poc}$ and $\log K_{ow}$ for the individual chemicals or by averaging the logarithms of the ratio of the K_{poc} to K_{ow} for the individual chemicals. For this data set, an average difference (standard deviation, number of data points) of 0.023 (0.426, 16) was obtained. Transforming the average difference to an antilog scale results in predictive relationship of $K_{poc} = 1.05 \cdot K_{ow}$ with 95% confidence limits of a factor of 8 [$10^{(\text{standard deviation} \cdot t(" = 5\%,\ df = 15))} = 10^{(0.426 \cdot 2.131)}$] in either direction from the mean predicted K_{poc}.

Based on the data presented above, EPA will use the following relationship for determining K_{poc} values for use in the three-phase partitioning model:

$K_{poc} = 1.0 \cdot K_{ow}$ with 95% confidence limits for a predicted K_{poc} of a factor of 8 in either direction from the mean predicted K_{poc}.

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Table 4-1. K_{poc} Data

Compound	Ecosystem	Log K_{ow}	Log K_{poc}	sd	n	Measurement Method	Reference
Mirex	Lake Ontario	6.89	6.81			Sparging	Yin & Hassett, 1989
Mirex	Lake Ontario	6.89	6.54			Sparging	Yin & Hassett, 1989
Mirex	Oswego River	6.89	6.72			Sparging	Yin & Hassett, 1989
Mirex	Oswego River	6.89	6.38			Sparging	Yin & Hassett, 1989
4-Chlorobiphenyl	Lake Michigan	4.69	4.71	0.50	73	Reverse phase	Eadie et al., 1990
Pyrene	Lake Michigan	5.11	5.65	0.46	73	Reverse phase	Eadie et al., 1990
2,2',5,5'-Tetrachlorobiphenyl	Lake Michigan	5.84	5.83	0.40	73	Reverse phase	Eadie et al., 1990
Benzo[a]pyrene	Lake Michigan	6.13	6.66	0.40	73	Reverse phase	Eadie et al., 1990
p,p'-DDT	Lake Michigan	6.91	6.36	0.31	73	Reverse phase	Eadie et al., 1990
2,2',4,4',5,5'-Hexachlorobiphenyl	Lake Michigan	6.92	6.76	0.30	73	Reverse phase	Eadie et al., 1990
4-Dichlorobiphenyl	Green Bay	4.69	4.70	0.29	23	Reverse phase	Eadie et al., 1992
Pyrene	Green Bay	5.11	5.79	0.19	23	Reverse phase	Eadie et al., 1992
2,2',5,5'-Tetrachlorobiphenyl	Green Bay	5.84	5.74	0.19	23	Reverse phase	Eadie et al., 1992
Benzo[a]pyrene	Green Bay	6.13	6.38	0.15	23	Reverse phase	Eadie et al., 1992
p,p'-DDT	Green Bay	6.91	6.24	0.12	23	Reverse phase	Eadie et al., 1992
	Lake Michigan	5.85	6.78	0.11	2	Ultrafiltration	Dean et al., 1993
2-Chlorobiphenyl	Hudson River	4.46	5.65			Calculated	Butcher et al., 1998
2,4'-Dichlorobiphenyl	Hudson River	5.07	5.67			Calculated	Butcher et al., 1998
2,2',5-Trichlorobiphenyl	Hudson River	5.24	5.40			Calculated	Butcher et al., 1998
2,4,4'-Trichlorobiphenyl	Hudson River	5.67	5.84			Calculated	Butcher et al., 1998
2,4',5-Trichlorobiphenyl	Hudson River	5.67	5.80			Calculated	Butcher et al., 1998
2,2',3,3'-Tetrachlorobiphenyl	Hudson River	5.75	5.85			Calculated	Butcher et al., 1998
2,2',5,6'-Tetrachlorobiphenyl	Hudson River	5.62	5.82			Calculated	Butcher et al., 1998
2,3',4,4'-Tetrachlorobiphenyl	Hudson River	6.20	6.27			Calculated	Butcher et al., 1998
2,3',4',5-Tetrachlorobiphenyl	Hudson River	6.20	6.15			Calculated	Butcher et al., 1998
2,2',4,5,5'-Pentachlorobiphenyl	Hudson River	6.38	6.18			Calculated	Butcher et al., 1998
2,3',4,4',5-Pentachlorobiphenyl	Hudson River	6.74	6.41			Calculated	Butcher et al., 1998
2,2',3,4,4',5-Hexachlorobiphenyl	Hudson River	6.83	6.43			Calculated	Butcher et al., 1998
2,2',3,5,5',6-Hexachlorobiphenyl	Hudson River	6.64	6.55			Calculated	Butcher et al., 1998
2,2',4,4',5,5'-Hexachlorobiphenyl	Hudson River	6.92	6.38			Calculated	Butcher et al., 1998

The data used to derive the above relationship were primarily from the Great Lakes ecosystem. K_{poc} data from Butcher et al. (1998) for the Hudson River, which are not used in deriving the predictive relationship, are also plotted in Figure 4-1 (circles) and are in good agreement with the K_{poc} data from the Great Lakes. The comparability of the Hudson River data to those obtained from the Great Lakes ecosystem indicates that the above relationship for determining K_{poc} has broader applicability than just the Great Lakes ecosystem.

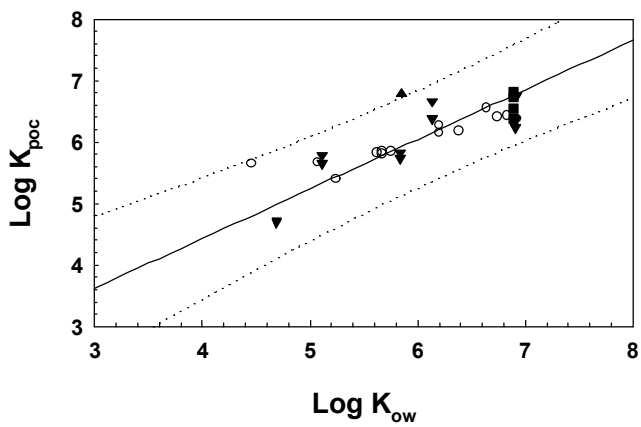

Figure 4-1. K_{poc}s determined using the reverse phase (downwards triangle), sparging (square), ultrafiltration (upwards triangle), and model-derived (open circles) techniques. The geometric mean regression and their 95% prediction confidence limits are plotted.

In comparison to K_{poc} data, numerous K_{doc} measurements are reported in the scientific literature. Sorption of hydrophobic organic chemicals to DOC has been studied by using DOC from a variety of sources. Sources of DOC include ambient waters; sediment and soil pore waters; and humic and fulvic acids isolated from ambient waters, sediments, and soils. In general, humic substances are the major component of the natural organic carbon in water and soil systems, e.g., 50–80% (Perminova et al., 1999; Thurman, 1985). For this reason, much research has focused on determining the sorption and binding affinity of hydrophobic organic chemicals to humic substances, specifically as related to composition and structure of the humic substances, e.g., the aromaticity, hydrogen-to-carbon (H/C)and oxygen-to-carbon (O/C) atomic ratios, ultraviolet absorptivity, pH, and molecular weight.

To develop a predictive relationship for K_{doc}, a literature search for K_{doc} data for nonionic organic chemicals was performed and K_{doc}s from more than 70 references collected (Burkhard, 2000). A predictive relationship, $K_{doc} = 0.08\ K_{ow}$ with 95% confidence limits of a factor of 20 in either direction, was developed using K_{doc} data based on naturally occurring dissolved organic carbon. The following text provides a brief summary of the literature search and the development of the predictive equation. Further details and a complete listing of the K_{doc} data can be found in Burkhard, 2000.

In Figure 4-2, log K_{doc}s are plotted as a function of chemical log K_{ow} for five DOC sources: (1) Aldrich humic acid, (2) humic and fulvic acids isolated from sediments, natural waters, and soils, (3) sediment porewaters, (4) soil porewaters and groundwaters, and (5) surface waters. For DOCs consisting of Aldrich humic acid and sediment porewaters, the relationships between log K_{doc} and log K_{ow} were linear, with slopes of approximately 1 for both and correlation coefficients of 0.77 and 0.64, respectively (Table 4-2). In contrast, for humic and fulvic acids without Aldrich humic acids (i.e., Aldrich humic acid data excluded), soil porewaters and groundwaters, and surface water, the log K_{doc}s are only somewhat dependent on log K_{ow}; that is, the correlation

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coefficients for the relationship are rather small, .0.3, although the slopes are similar to 1. The small dependence of K_{doc} on K_{ow} for DOC from natural waters is consistent with the findings of Kukkonen and Oikari (1991) and Evans (1988), which suggest that factors other than the hydrophobicity are important in the sorption or association of nonionic organic chemicals with surface water DOC.

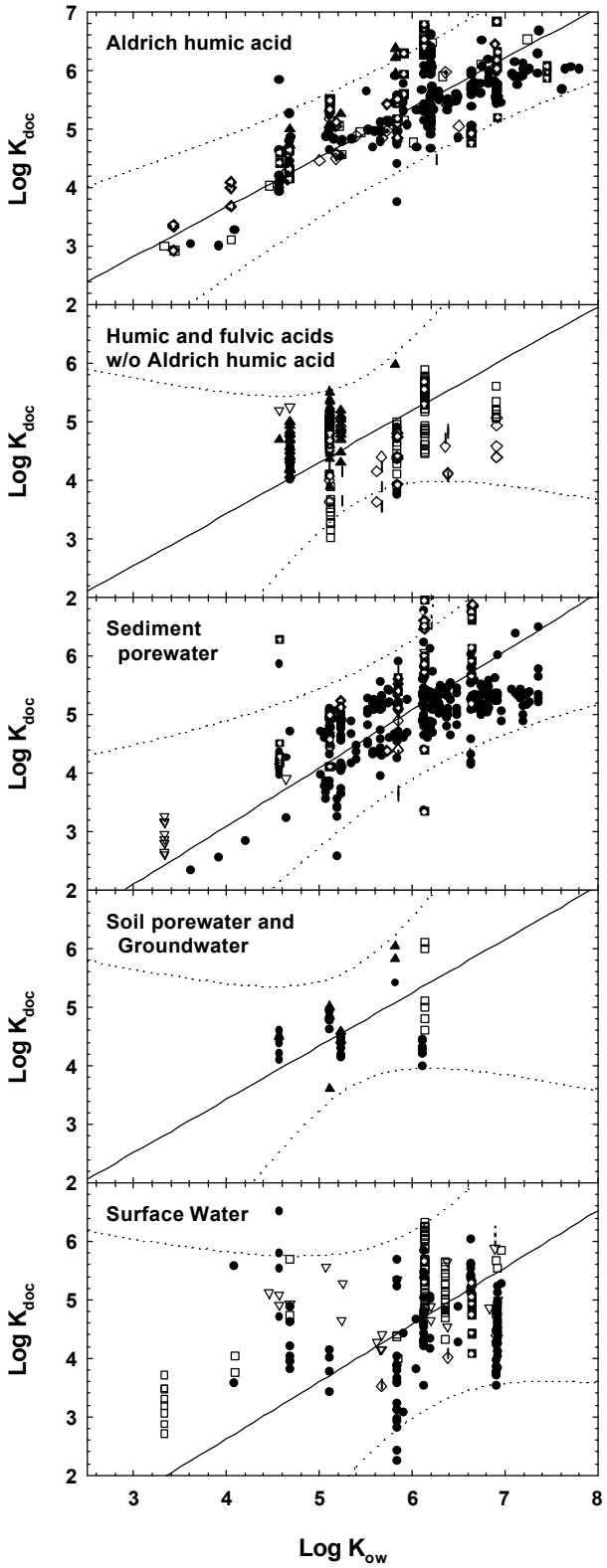

Figure 4-2. K_{doc}s determined using the reverse phase (circle), equilibrium dialysis (open square), sparging (plus diamond), calculated/model-derived (downwards triangle), fluorescence quenching (upwards triangle), solubility enhancement (open diamond), biological (plus square), and solid phase microextraction (open plus diamond) techniques for DOCs from different sources. The geometric mean regression and their 95% prediction confidence limits are plotted.

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The K_{doc} data from surface water DOC appear to have more variability than that observed for the other DOC sources (Figure 4-2). On a diagenesis basis, DOC from the water column might be expected to be more variable than that from sediments and humic and fulvic acids, because surface water DOC contains detritus from recently deceased plankton and algae, macrophytes, and so forth. Some of the variability in all five graphs in Figure 4-2 is caused by differences among the measurement techniques. Comparisons of the reverse-phase and dialysis techniques by Landrum et al. (1984) and Kukkonen and Pellinen (1994) suggest that differences of an order of magnitude or more can occur between these two methods, but that typically the dialysis technique provided values that were a factor of 2-5 higher. Biphenyl with a log K_{ow} of 4.09 provides an example of the differences that are possible between these two techniques. Landrum et al. (1984) performed side-by-side K_{doc} measurements with biphenyl, using water samples from Lake Erie and Huron River. The K_{doc} data derived from the two techniques differed by a factor of 3 for the Lake Erie samples and by a factor of 34 for the Huron River samples. The variability in the K_{doc} data from these surface water DOC might also be related to the time period in which the measurements were made. Most of the measurements occurred in the 1980s, when methods for measuring K_{doc} were new and/or evolving.

Table 4-2. Regression Equations for Dependence of K_{doc} (Geometric Means) on K_{ow}

DOC Source	Geometric Mean Regression Equation	n	r	s_{xy}
Aldrich humic acid	log K_{doc}= 0.85 (±0.03)[a] ¢ log K_{ow}+ 0.27 (±0.20)	269	0.77	0.52
Humic and fulvic acids without Aldrich humic acid	log K_{doc}= 0.88 (±0.06) ¢ log K_{ow}- 0.11 (±0.31)	230	0.29	0.65
Sediment porewaters	log K_{doc}= 0.99 (±0.04) ¢ log K_{ow}- 0.88 (±0.23)	396	0.64	0.66
Soil porewaters and groundwaters	log K_{doc}= 0.91 (±0.13) ¢ log K_{ow}- 0.22 (±0.68)	47	0.31	0.61
Surface waters	log K_{doc}= 0.97 (±0.06) ¢ log K_{ow}- 1.27 (±0.40)	210	0.32	0.99
All DOC including Aldrich humic acid	log K_{doc}= 0.85 (±0.04) ¢ log K_{ow}- 0.11 (±0.21)	223	0.78	0.52
Naturally occurring DOC (no Aldrich humic acid)	log K_{doc}= 0.85 (±0.06) ¢ log K_{ow}- 0.25 (±0.34)	127	0.67	0.60

n = number of data points, r = correlation coefficient, s_{xy} = standard error of estimate, [a] (±standard deviation).

To compare the K_{doc}s for all DOC sources, K_{doc} values for each chemical were averaged across analytical methods within each DOC source and replotted (Figure 4-3). Average K_{doc} values were used in part because of the unevenness in the numbers of measurements per chemical. For example, biphenyl and benzo[a]pyrene had 4 and 49 K_{doc} measurements, respectively, for DOC from surface waters. The plot of log K_{doc} versus log K_{ow} shows considerable consistency, and a strong dependence of K_{doc} upon K_{ow} is apparent (Figure 4-3). The average K_{doc}s for the Aldrich humic acids are on average higher than those derived from natural sources (Figure 4-3). These results are consistent with the differences in affinities for Aldrich humic acid and naturally occurring organic carbon reported in the literature for nonpolar organic chemicals (Suffet et al., 1994).

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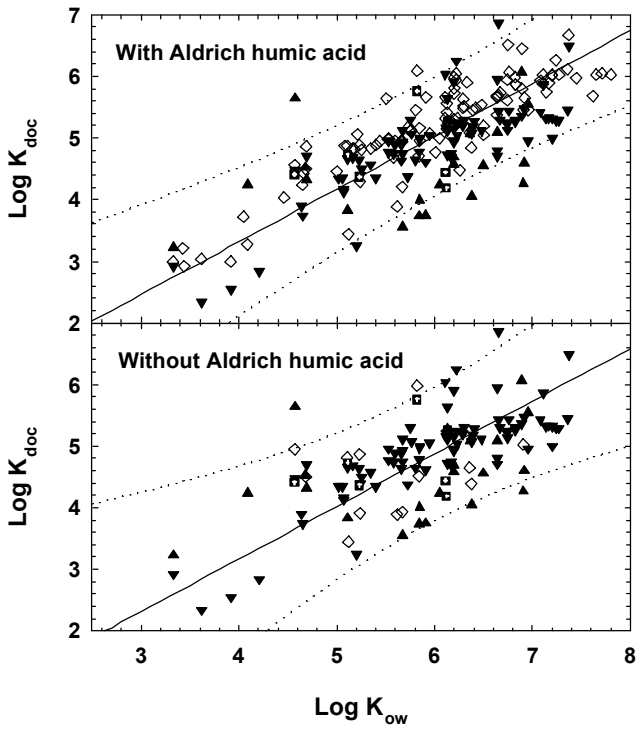

Figure 4-3. Average K_{doc}s for individual chemicals for different DOC sources: humic and fulvic acids (open diamond), sediment porewaters (downwards triangle), soil porewaters and groundwaters (plus square), and surface waters (upwards triangle). The geometric mean regression and their 95% prediction confidence limits are plotted.

On a theoretical basis, the equation log K_{doc}, K_{poc}, or K_{oc}= A ℂ log K_{ow}+ B has a slope of 1 when the ratio of the activity coefficients of the chemical in *n*-octanol to that in the organic carbon phase is constant for chemicals with different K_{ow}s (Seth et al., 1999). The relationships of log K_{oc} = A ℂ log K_{ow}+ B derived by Seth et al. (1999), DiToro et al. (1991), and Karickhoff (1984) had slopes of 1 and are clearly consistent with the hypothesis that the ratio of activity coefficients is constant. Given the above theoretical basis and experimental data, a slope of 1 is assumed for the relationship in this investigation, that is, log K_{doc} = log K_{ow}+ B. This equation, by rearrangement, results in B = log K_{doc} ! log K_{ow} = log (K_{doc}/K_{ow}), and B can be found by averaging the differences of the log K_{doc} and log K_{ow} for the individual chemicals or by averaging the logarithms of the ratio of the K_{doc} to K_{ow} for the individual chemicals. For the data set consisting of naturally occurring DOC (no Aldrich humic acid), an average difference (standard deviation, number of data points) of -1.11 (0.659, 127) was obtained. Transforming the average difference to an antilog scale results in a predictive relationship of K_{doc} = 0.08 K_{ow}, with the 95% confidence limits of a factor of 20 in either direction from the predicted mean K_{doc}. When Aldrich humic acids are included, an average difference of -0.966 (standard deviation, 0.578; number of data points, 223) was obtained, resulting in a predictive relationship of K_{doc} = 0.11 K_{ow}, with 95% confidence limits of a factor of 14 in either direction.

On the basis of the above data, EPA will use the following relationship for determining K_{doc} values for use in the three-phase partitioning model:

K_{doc} = 0.08 ℂ K_{ow}

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The 95% confidence limits for a predicted log K_{doc} are:

$$\pm \text{ standard deviation } \times t_{(\alpha = 5\%,\ df = 127)} = \pm 0.659 \times 1.979 = \pm 1.30$$

and transforming the 95% confidence limits to an antilog basis results in a factor of 20 in either direction from the mean predicted K_{doc} value.

In Figure 4-4, the residuals, that is, measured log K_{doc}s minus log K_{doc}s predicted by using the relationship $K_{doc} = 0.08 \times K_{ow}$, along with the 95% confidence limits are plotted. The distribution of the residuals is normally distributed (α = 10%) with 64 negative and 63 positive residuals. The residuals for the log K_{doc}s predicted for naturally occurring DOC have a slight dependence on the K_{ow} (Figure 4-4).

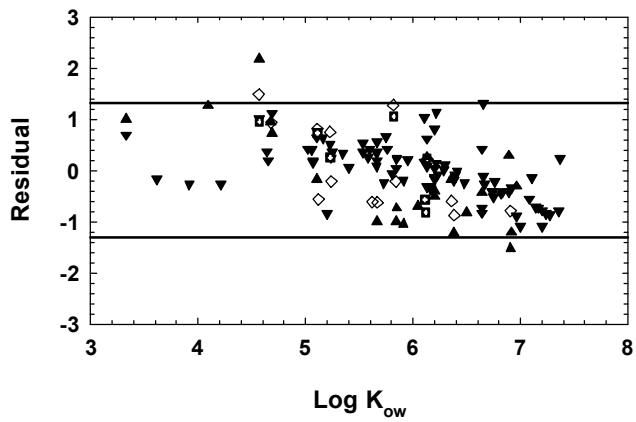

Figure 4-4. The residuals between measured log K_{doc}s and log K_{doc}s predicted using relationship of K_{doc} = 0.08 K_{ow}. DOC sources: humic and fulvic acids without Aldrich humic acid (open diamond), sediment porewaters (downwards triangle), soil porewaters and groundwaters (plus square), and surface waters (upwards triangle). The 95% confidence limits are plotted.

In a recent evaluation of the K_{oc} data by Seth et al. (1999), K_{oc} was found to be equal to $0.35 \times K_{ow}$ with 95% confidence boundaries of a factor of 2.5 in either direction. The variability of the above predictive relationship for K_{doc}s is much larger than the factor of 2.5 reported by Seth et al. (1999) and is larger than the variability observed with only the Aldrich humic acid (Figure 4-2), by approximately a factor of 14 in either direction or ($s_{xy} \times t_{(\alpha = 5\%,\ df = 190)} = 0.59 \times 1.972$). This larger variability is, however, consistent with Kukkonen and Oikari (1991) and others, who have found that hydrophobicity of the chemical is not the only factor affecting the association of the nonionic organic chemicals to DOC.

4.2.5 Selection of Appropriate K_{ow}s for Partitioning (Bioavailability) Predictions

The basis of partitioning theory and its relationship to log K_{ow}s are discussed in Sections 3 and 4.2 and Appendix A. The K_{ow} is used in several components of the BAF methodology, for example, to estimate BAFs, hydrophobicity, and partitioning in water, as well as other procedures (including the BSAF method and use of the food web model). Thus, it is important to select the most appropriate $K_{ow}$for a given chemical. A variety of methods are available to estimate or predict K_{ow} values. The reliability of these methods varies according to the K_{ow} of the chemical.

In the 1998 draft TSD (USEPA, 1998a) EPA proposed and solicited comments on two options for selecting reliable K_{ow} values. The first option was EPA's guidance published in the Great Lakes Water Quality Initiative (USEPA, 1995a). The second option was a more detailed

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approach to selecting K_{ow} values, which EPA developed and had peer reviewed more recently. Based on EPA's own scientific rationales and the comments received from the peer reviewers, EPA will select K_{ow} values based on the guidance contained in the more recently developed protocol. EPA's methodology for selecting K_{ow} values divides the range of K_{ow}s into three groups to reflect the differences in chemical properties and behaviors with differing hydrophobicities. Specific details of the K_{ow} guidance are presented in Appendix B.

4.3 IMPORTANCE OF SEDIMENT-WATER CONCENTRATION QUOTIENT (J_{socw})

The distribution of a chemical between surface sediments and the water column in an ecosystem is most effectively described as the sediment-water concentration quotient (J_{socw}), which is further defined below. BAFs for nonionic organic chemicals are sensitive, in proportion to hydrophobicity, to differences in the chemical's J_{socw} in an ecosystem. J_{socw} is either implicitly (field-measured BAFs) or explicitly (modeled BAFs) involved in each of the four BAF methods described in Section 5. The national BAF procedure for nonionic organic chemicals involves setting BAFs to the extent possible on the basis of current national average values for several key parameters, including J_{socw}. In the case of BAF methods 1 and 2, this is done by averaging measured BAFs from different ecosystems. For methods 3 and 4, a national value for J_{socw} that was selected by EPA on the basis of high-quality measurements from three different ecosystems (Section 4.5.1) was used with the Gobas food chain model (Gobas, 1993) to determine food chain multipliers (FCMs).

Bioaccumulation of hydrophobic nonionic organic chemicals in aquatic organisms is dependent on a number of ecosystem conditions including food chain length (Rasmussen et al., 1990), food web composition (Vander Zanden and Rasmussen, 1996; Burkhard, 1998), and the chemical distribution between sediments and water (Thomann, 1992; Endicott and Cook, 1994). The impacts of food web composition and chemical distribution between sediments and water are interrelated because sediments and water are the primary exposure media for the benthic and pelagic components, respectively, of the food web (Burkhard, 1998). For a benthic food web, chemical concentrations in benthic invertebrates at the base of the benthic food web are directly controlled by the concentrations of chemicals in the sediments. Chemical concentrations at the base of the pelagic food web, for example, in phytoplankton and diatoms, are directly controlled by the concentration of chemicals in the water. Therefore, differences in distribution of chemical between sediment and water, as well as differences in benthic versus pelagic food web composition, will affect the bioaccumulation of nonionic organic chemicals in forage and piscivorous fish.

The distribution of chemical between the sediment and overlying water in a water body or a zone of reference within a water body is described by the sediment-water (column) concentration quotient (J_{socw}), which is defined as:

$$\Pi_{socw} = \frac{C_{soc}}{C_w^{fd}} \qquad \text{(Equation 4-7)}$$

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where:

C_{soc}	=	concentration of chemical in dry sediment, normalized to sediment organic carbon
C_w^{fd}	=	concentration of chemical that is freely dissolved in water

By expressing the concentration of chemical in sediment on an organic carbon normalized basis and the concentration of chemical in water on a freely dissolved basis, this quotient is a measure of the degree to which the chemical's distribution between the surface sediment and the water column approaches or deviates from a condition of thermodynamic equilibrium for the water body. The degree of disequilibrium (departure from equilibrium) is proportional to the degree to which J_{socw}/K_{ow} for the chemical diverges from a value of 1.0 ($J_{socw} = K_{ow}$).

In the aquatic environment, three factors are primarily responsible for causing J_{socw} to differ among ecosystems. First, concentrations of nonionic organic chemicals in the water column and sediment are the result of well-known fate and transport processes, such as particle sedimentation and resuspension, chemical sorption to and desorption from suspended particles and the sediments, and ecosystem hydrodynamic properties. These processes vary among ecosystems. Second, the chemical loading history to the ecosystem plays an important role in its J_{socw}. For example, increasing the loading of a chemical to the water column causes an immediate rise in the concentration of the chemical in the water, and over time, the concentration of the chemical in the sediment will gradually increase through sedimentation processes. If the loading of a chemical to the water column is decreased, the concentration of the chemical in the water column drops quickly, whereas the concentration of the chemical in the sediments decreases slowly through burial of older and more contaminated sediments by newer and less contaminated sediments. Third, differences in organic carbon content in water column particulates (or suspended solids) and surface sediment vary among ecosystems. The ratio of organic carbon contents (water column to surface sediment) approximates the steady-state value of J_{socw}/K_{ow} for the ecosystem due to diagenesis processes on the newly deposited surface sediments.

The importance of chemical loading on J_{socw} is illustrated in Figure 4-5 for three different loading scenarios: (a) constant loading of a chemical to the ecosystem over time, (b) constant loading of chemical to the ecosystem with a doubling of loading at year 50, and (c) constant loading of chemical to the ecosystem with an 80% reduction in loading at year 50. These figures were created by using a two-compartment mass balance model consisting of a sediment surficial layer and the water column for a nonmetabolizable chemical with a log K_{ow} of 6, using conditions and parameters for a large lake ecosystem. In all three loading scenarios, the concentration of the chemical in the water column responds quickly to the change in loading, in contrast to the relatively slow response of the concentration of chemical in sediment. In these scenarios, sediment and water column particulates had organic carbon contents of 3% and 15%, respectively. In all three scenarios, J_{socw}/K_{ow} reaches a plateau of a value of 4.91, nearly equal to the ratio between the percentage of organic carbon in suspended particulates and surface

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sediments. Many chemicals that have been available as sediment contaminants for many years, such as PCBs and DDTs, which are now no longer manufactured or used, are often found to be present in sediments in concentrations that exceed thermodynamic equilibrium with the water column.

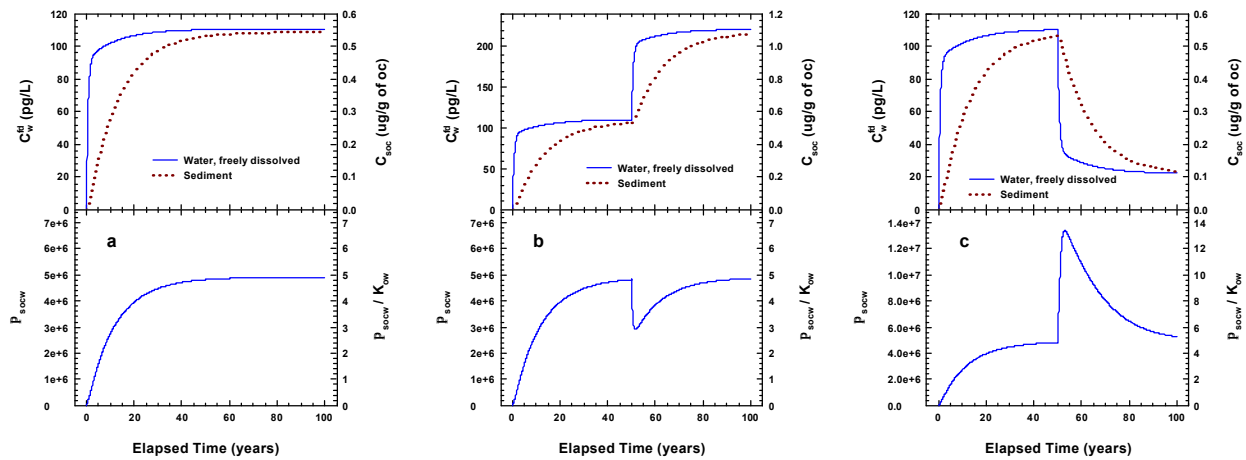

Figure 4-5. The sediment-water chemical concentration quotient (J_{socw}) for three different chemical loading scenarios: (a) constant loading of a chemical to the ecosystem overtime, (b) a constant loading of chemical to the ecosystem with a doubling of loading at year 50, and (c) a constant loading of chemical to the ecosystem with an 80% reduction in loading at year 50. Simulations performed for a chemical with a log K_{ow} of 6 using Lake Ontario conditions and parameters.

The latter portion of scenario (c) described above (constant loading of chemical to the ecosystem with and 80% reduction in loading at year 50) illustrates how J_{socw} changes over time. Differences in ecosystem parameters and conditions, such as hydraulic retention rates, sedimentation and resuspension rates, water column and surficial sediment layer volumes, and chemical loading rates between ecosystems, affect the specific time scales and slopes of the changes in C_w^{fd}, C_{soc}, and J_{socw} associated with changes in chemical loading over time.

Ecosystems at thermodynamic equilibrium, a condition that rarely exists in nature, should theoretically have J_{socw}s equal to the chemical's K_{ow}. Consequently, ecosystem models typically characterize J_{socw} by using its ratio to K_{ow} as a measure of the degree to which the ecosystem is in disequilibrium (Thomann et al., 1992), or, alternatively, as a measure of the fugacity ratio (Campfens and Mackay, 1997). A J_{socw}/K_{ow} ratio of 1 is equivalent to equilibrium conditions between the sediments and the water column. A ratio of 25, which has been typical of Lake Ontario conditions for PCBs and DDTs since the 1970s, is a disequilibrium condition in which the chemical is enriched in the sediments relative to the water column because of greater loadings of the chemical to the ecosystem in the past. For ratios less than 1, the chemical is enriched in the water column relative to the sediments; in this situation, the aquatic ecosystem is being loaded with the chemical, but sediments have not reached steady state with the water (J_{socw} constant). With continued loading, sediment contamination increases until a steady-state condition is reached (J_{socw} constant) and the J_{socw}/K_{ow} ratio is in the 2–10 range. The lower bound of 2 arises

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from minimum expected differences in the organic carbon content of particulate matter in the water column and sediments. The upper bound of 10 allows for the effects of chemical gradients and greater relative organic carbon amounts in the water column. Green Bay, a fairly shallow and vertically well-mixed ecosystem receiving a continuous load of PCBs from the contaminated Fox River in Wisconsin, has a J_{socw}/K_{ow} ratio of approximately 5. This ratio indicates that the system is close to steady state and that most or all of the disequilibrium is attributable to differences in organic carbon in the water and sediments.

Guidelines for sampling and measurement of J_{socw} are identical to those for sampling and measurement of C_w^{fd} under BAF method 1, as described in Sections 1.2 and 5.1, and C_{soc} under BAF method 2, as described in Section 5.2. Because concentrations of bioaccumulative chemicals in surficial sediments are relatively constant on an annual basis in most carbonaceous, fine-sediment depositional areas, determination of an appropriate average C_w^{fd} in systems with temporal fluctuations is the greatest challenge in measurement or estimation of J_{socw}. On the basis of monitoring reports and historical loading data, EPA expects that most persistent nonionic organic chemicals will have J_{socw}/K_{ow} ratios in the range of 2-40. This expectation does not apply when such chemicals have not been present in an ecosystem long enough to approach expected steady-state concentrations in surficial sediments. In this case, J_{socw}/K_{ow} will be substantially lower than 2, indicating low exposure potential through the benthic food web. Because the national BAF methodology assumes that BAFs are determined for approximate long-term average conditions, J_{socw}/K_{ow} values of less than 2 are unlikely to be relevant for persistent, hydrophobic chemicals.

4.4 DERIVATION AND USE OF FOOD CHAIN MULTIPLIERS

FCMs are used in Procedure 1 (Figure 3-1) to estimate the dietary transfer of a chemical up the food web for chemicals where metabolism is believed or assumed to be negligible. In Procedure 1, FCMs are used with two of the four methods for deriving national BAFs. FCMs are determined using a food web model and/or field data, and FCMs represent a measure of the chemical's tendency to biomagnify in aquatic food webs. By definition, an FCM is:

$$\text{FCM} = \frac{\text{Baseline BAF}}{K_{ow}} \approx \frac{\text{Baseline BAF}}{\text{Baseline BCF}} \qquad \text{(Equation 4-8)}$$

This equation assumes that a BCF that is corrected for growth dilution, lipid normalized, and corrected for bioavailability considerations—that is, a baseline BCF—is equal to K_{ow}. The scientific basis for this assumption is presented in Section 5.4.2. Because a baseline BCF is determined by using a water-only exposure to the chemical, it represents a trophic level 1 exposure for the organisms. When organisms occupy higher trophic levels in food webs, concentrations of certain chemicals in their tissues can exceed those that are due to water exposure only because of dietary uptake of the chemical. The baseline BCF, when multiplied by the FCM for the organism's trophic level, accounts for the influences of dietary uptake by the

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organism. Dietary uptake of the chemical generally becomes important when the chemical's hydrophobicity exceeds a log K_{ow} of 4 and the rate of chemical metabolism by the organism is small. Thus, for nonionic organic chemicals, the third and fourth methods of Procedure 1 are applicable only to chemicals with log K_{ow}s of 4 or greater.

4.4.1 Derivation of FCMs Using a Food Web Model

To derive FCMs using a food web model, a model and its input parameters must be selected. The following subsections discuss how EPA selected a food web model for use in the 2000 Human Health Methodology. Also described are the parameters used with the model—the food web structure, J_{socw} (or, equivalently, C_w^{fd} and C_{soc}), and the chemical metabolism rate in the food web. Because all food web models require the above input parameters, these input parameters are not unique to the food web model selected by EPA.

Selection of a Food Web Model

For a food web model to provide useful predictions, it must have the following general characteristics and qualities. First, the model must include all biotic components of the food web, that is, plankton, benthic invertebrates, forage fish, and piscivorous fish. Second, the model must account for chemical uptake and loss from both food and water for all organisms. Third, the model must include chemical concentrations in sediment and the water column, because these environmental compartments are the primary exposure media for benthic invertebrates and phytoplankton, respectively, and these organisms reside at the base of the benthic and pelagic food web. Fourth, because AWQCs for the protection of human health are designed for long-term average conditions in ambient waters, steady-state solutions for predicting bioaccumulation in the food chain model are preferred over time-variant dynamic solutions for the food chain model (see Section 1.2). Other desirable qualities include (1) the model is easy to run by the average user, (2) the model does not mix fate and transport models with the food chain model, (3) the model code does not require substantial validation each time it is used, and (4) the model is easy to parameterize.

Food chain models with the characteristics and desirable qualities summarized above include the models of Gobas (1993) and Thomann et al. (1992). Other models are available, for example, Levels I, II, and III fugacity models (Mackay, 1991); RIVER/FISH (Abbott et al., 1995); AQUATOX (USEPA, 2000c,d); Iannuzzi et al. (1996); Ecofate (Gobas et al., 1998); and BASS/FGETS (Barber, 2000). The AQUATOX (USEPA, 2000c,d), Iannuzzi et al. (1996), and Ecofate (Gobas et al., 1998) models incorporate the submodels of Gobas (1993) and Thomann et al. (1992) for modeling chemical uptake and loss. The RIVER/FISH (Abbott et al., 1995), AQUATOX (USEPA, 2000c,d), Ecofate (Gobas et al., 1998), and BASS/FGETS (Barber, 2000) models have extensive input data requirements and are principally designed for time and spatially variant dynamic solutions for the food web. The time and spatially variant models include fate and transport submodels along with the bioaccumulation submodel, and thus model predictions include the uncertainties associated with both of the submodels. The fugacity models (Mackay, 1991) are designed for assessing the general behavior of chemical in model environments. On the basis of the above characteristics and desirable qualities, EPA selected the models of Gobas

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(1993) and Thomann et al. (1992) for further consideration and evaluation for calculation of FCMs. These two models are widely accepted in the scientific community and are being used in a number of scientific and regulatory applications.

Burkhard (1998) performed a thorough evaluation of the Gobas (1993) and Thomann et al. (1992) steady-state food web models for predicting chemical concentrations in aquatic food webs. Burkhard (1998) assessed (1) the accuracy and precision of the models, (2) the sensitivity of the predicted concentrations to changes in input parameters, and (3) the uncertainty associated with the concentrations predicted by the models. These evaluations were performed with field data from the Lake Ontario and its food web structure. A brief summary of this evaluation is provided in this TSD. For further details, the reader can refer to Burkhard (1998).

Model Scope and Theoretical Basis. The Gobas and Thomann models are quite similar in many ways. Both models include benthic and pelagic food web components, thereby incorporating exposure of organisms to chemicals from both the sediments and the water column. Both models contain rate equations for the estimation of steady-state conditions but also treat some chemical distributions as equilibrium partitioning. Both models require specification of the food web structure and the lipid contents and weights of the organisms. Both models also incorporate the organic carbon contents of the sediment and the water column. However, the two models also have distinct differences. The major difference pertains to the methods used to predict chemical concentrations in benthic invertebrates and zooplankton. With the Gobas (1993) model, concentrations are predicted by using equilibrium partitioning, whereas with the Thomann (1992) model, concentrations are predicted by using uptake and loss rates based on respiration, dietary consumption, and growth of the organism.

The Gobas and Thomann models do not include solubility limits or controls for the concentration of the chemical in any compartment. Thus, for a given ratio of the chemical concentration in sediment to that in the water column, the models will predict the same BAF and BSAF regardless of the numerical values used for the chemical concentrations, provided the ratio is maintained. If these models are used to predict chemical concentrations in aquatic organisms, the actual chemical concentrations in the sediment and water column will be required.

Model Accuracy. Burkhard's (1998) evaluation using field data from Lake Ontario (Oliver and Niimi, 1988) demonstrated that the Gobas and Thomann models have similar predictive ability for all species for chemicals with log K_{ow}s ranging from 3 to 8 (Figure 4-6). The baseline BAFs predicted with the Gobas model were in slightly better agreement with measured baseline BAFs (using Lake Ontario field data) than those predicted with the Thomann model. For chemicals with log K_{ow}s of 8 or greater, the models provided significantly different predictions. For the Gobas model, average ratios of the predicted to the measured baseline BAFs were 1.6 for sculpin, 1.0 for alewife, 1.4 for small smelt, 1.2 for large smelt, and 1.2 for piscivorous fish. For the Thomann model, average ratios of the predicted to the measured baseline BAFs were 4.0 for sculpin, 2.2 for alewife, 3.1 for small smelt, 3.0 for large smelt, and 2.5 for piscivorous fish. On average, the Thomann model predicted slightly higher baseline BAFs than the Gobas model. For piscivorous fish, the 10th and 90th percentile ratios (predicted/measured) were 0.4 and 5.6 for the Thomann model and 0.3 and 2.1 for the Gobas model, respectively. Assuming a predicted

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concentration of 5 ppb in piscivorous fish, these ranges in baseline BAFs translate into concentrations in fish of 2–28 ppb for the Thomann model and 1.5-10.5 ppb for the Gobas models. These ranges are relatively narrow, varying by a factor of about 10.

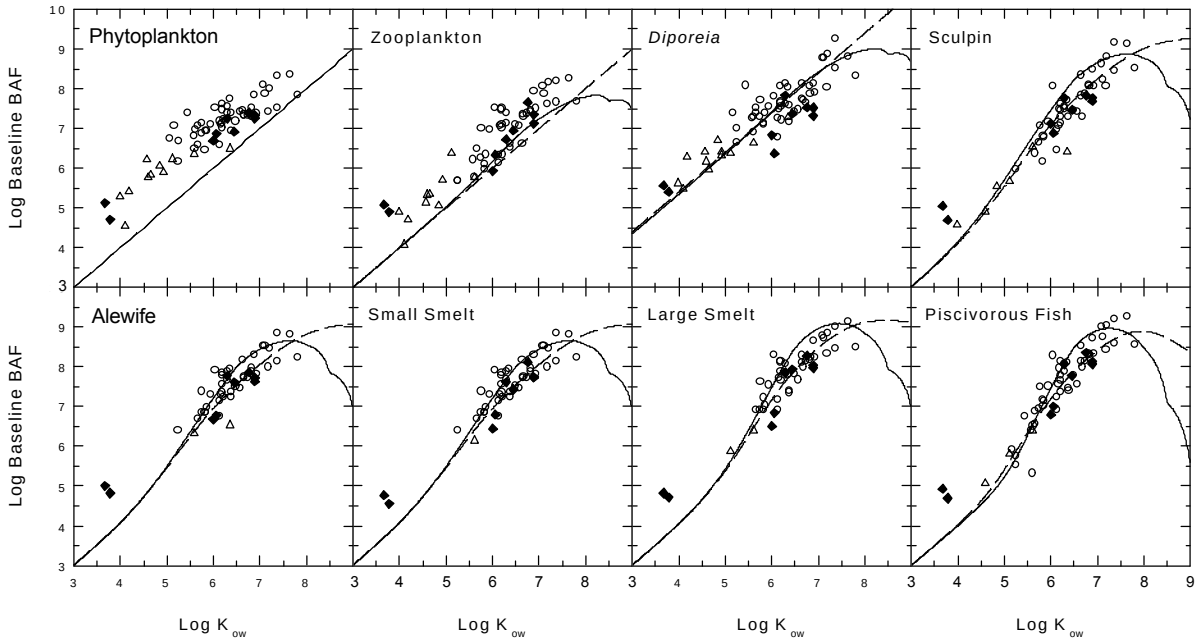

Figure 4-6. Measured baseline BAFs for PCBs (•), chlorinated pesticides (,), and chlorinated benzenes, chlorinated toluenes, and hexachlorobutadiene (ª) from the data of Oliver and Niimi (1988) and BAF_R^{fd}s predicted using the Gobas (– –) and Thomann (—) models plotted against K_{ow} for all organisms (Burkhard 1998). For phytoplankton, the predicted baseline BAFs were the same for both models and thus both lines coincide in the phytoplankton plot.

Model Sensitivity. A sensitivity analysis was performed to evaluate which input parameters most affected the model. The sensitivity analysis of the input parameters used by the Thomann and Gobas models revealed that J_{socw}, K_{ow}, lipid contents of the organisms, feeding preferences of forage fish upon benthic invertebrates, and feeding preferences of the benthic invertebrates (Thomann model only) were the most sensitive input parameters for the models.

Sensitivity analyses were performed using a variety of deviations to the input parameters (i.e., ±10%, ±25%, ±50%, and ±75%). For both models, the magnitude of effect of a given change in J_{socw}, organism weight, and organism feeding preferences on the overall model outcome was directly proportional to the change in each of the input parameters. Input parameters with moderate nonproportionalities were lipid content (Thomann model) and temperature (Gobas model). Input parameters with large nonproportionalities were lipid content (Gobas model) and K_{ow} for both models. For both models, J_{socw}, lipid content, and feeding preferences upon forage fish showed little or no sensitivity for chemicals with log K_{ow}s of less than 4, a steep increase (or decrease) in sensitivity for chemicals with log K_{ow}s between 4 and 6, and sensitivities of approximately 1 (or –1) for chemicals with log K_{ow}s exceeding 6. A sensitivity of 1 means that a

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10% change in an input parameter results in a 10% change in the predicted baseline BAF. The greater sensitivity of the models to the K_{ow} input parameter is logical, because all submodels use the hydrophobicity of the chemical to define rates of chemical uptake and loss. In general, a +10% change in the K_{ow} parameter results in a +10% to +20% change in the chemical concentration in fish for log K_{ow}s up to .7. The Thomann model was also extremely sensitive to the feeding preference of the benthic invertebrates upon phytoplankton. For log K_{ow}s exceeding 4, the sensitivities became very large and approached values of –20 (in response to a +10% change in the input parameter) for chemicals with log K_{ow}s of 6 or greater. The large sensitivity for this input parameter occurs because the sediments are the predominant source of the chemical to the benthic invertebrates but are only a minor part of the diet for the organism. Sensitivities for other input parameters, such as organism weight, temperature (Gobas model), and other feeding preferences, were relatively small.

Model Uncertainty. Uncertainty analyses performed with Monte Carlo simulations and the Lake Ontario food web demonstrated that the input parameters K_{ow} and J_{socw} were the dominant sources of uncertainties for the predicted baseline BAFs in piscivorous fish for both models (Burkhard, 1998). These analyses were performed by using distributions and variances for each input variable based on field data, and each simulation was performed with 100,000 iterations. To assess the importance of individual as well as groups of individual parameters, simulations were performed by setting the variances for individual or groups of individual input parameters to zero and comparing the ranges of the predicted baseline BAFs for the predictions with the nonzeroed and zeroed variances.

For piscivorous fish, overall uncertainties in the predicted baseline BAFs ranged from a factor of 3.3 to 5.5 in the Gobas model and from a factor of 3.3 to 8.7 in the Thomann model for chemicals with log K_{ow}s of less than 7.6 (based on the ratio of the 10th to 90th percentile predictions in the distribution of possible values). To provide a perspective of the differences in predictions between the models and their uncertainties, one can assume that for piscivorous fish the Gobas model predicts concentrations of 4 ppb (with 1.8 and 9.4 ppb for the 10th and 90th percentile predictions) for a chemical with a log K_{ow} of 5.0 and a concentration of 4 ppb (2.1 and 7.6 ppb) for a chemical with a log K_{ow} of 6.6. The Thomann model would predict a concentration of 2.6 ppb (1.2 and 4.6 ppb) for a chemical with a log K_{ow} of 5.0 and a concentration of 16.1 ppb (8.5 and 30.1 ppb) for a chemical with a log K_{ow} of 6.6. In general, these differences are not large, and from the perspective of quantifying these concentrations analytically, these differences are almost indistinguishable.

Burkhard's (1998) evaluation of the Gobas and Thomann food web models reveals that the models provide quite similar predictions for all organisms in the food web and that the predictions are not significantly different for piscivorous fish. The comparison of predicted and measured baseline BAFs based on field data from Lake Ontario suggests that the Gobas model provides slightly more accurate predictions than the Thomann model. The sensitivities of the input parameters are similar for both models, with the exception of benthic invertebrate feeding preferences. The Thomann model was extremely sensitive to small changes in this input parameter, and the Gobas model, because of its assumption of equilibrium partitioning for benthic invertebrates, does not use this input parameter. Uncertainty analyses performed with

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both models indicate that K_{ow} and J_{socw} are the dominant sources of uncertainty in the predicted baseline BAFs. These analyses suggested that the uncertainties associated with predictions by the Gobas model are slightly smaller than those with the Thomann model.

Based on the evaluation of the Gobas and Thomann food web models described above, EPA will use the Gobas model for calculating food chain multipliers (FCMs) due to the considerations listed below:

1. The Gobas model includes both benthic and pelagic food webs, thereby incorporating exposure of organisms to chemicals from both the sediments and the water column.

2. The input data needed to run the model can be readily defined.

3. The baseline BAFs predicted using the model are in good agreement with field-measured baseline BAFs for chemicals, even those with very high log K_{ow}s.

4. The Gobas model had smaller uncertainties associated with the baseline BAFs for fish compared to the Thomann model.

5. The Gobas model is readily available via the Internet in a Windows-based format at http://www.rem.sfu.ca/toxicology/models.htm.

6. The model predicts chemical concentrations in benthic organisms using equilibrium partitioning theory, which is consistent with EPA's draft equilibrium partitioning sediment benchmarks (ESBs) (USEPA, 2000b).

Because models are continually being refined, in the future EPA may consider the use of other appropriately validated food web models for the derivation of FCMs. Any model considered would need to have the characteristics and qualities outlined in Section 4.4. and would have to be subjected to a validation process to address the issues of (1) accuracy and precision of the model predictions, (2) input parameter sensitivities, and (3) uncertainties associated with the model predictions.

Selection of the Sediment-Water Concentration Quotient (J_{socw})

Calculations of FCMs with the Gobas food web model requires the ratio of the chemical concentrations in the sediments (expressed on an organic carbon basis) to those in the water column (expressed on a freely dissolved basis). Unfortunately, measured J_{socw}s are rather limited in ecosystem type, chemical classes, and quality because of a number of factors. These include (1) the difficulties in measuring the concentrations of hydrophobic organic chemicals in natural waters because they occur at very low concentrations, that is, less than 1 ng/L; (2) the collection of sediment and water samples that are not temporally and/or spatially connected; (3) collection of bulk sediment samples rather than the uppermost 1 or 2 cm of the sediments; (4) the fact that measurements of POC and DOC were not performed on the water samples analyzed for the

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hydrophobic organic chemicals; (5) the lack of determination of the sediment organic carbon content; and (6) the fact that studies designed specifically for determining J_{socw} are not usually performed. In addition, combining sediment measurements from one study with water measurements from another study can result in large biases in J_{socw}s due to differences in analytical methodologies (e.g., different surrogates for recovery corrections, different standards).

Review of a number of different data sets, as described in Burkhard (1998), revealed three data sets of suitable quality for which J_{socw}s could be determined. These data sets were from Lake Ontario (Oliver and Niimi, 1988), Hudson River (USEPA, 1997; USEPA, 1998b), and Green Bay in the Lake Michigan ecosystem (www.epa.gov/grtlakes/gbdata/). The Green Bay and Hudson River data sets contained data for PCBs only, and the Lake Ontario data set contained data for chlorinated pesticides, PCBs, and a few chlorinated benzenes, toluenes, and butadiene. The data for the chlorinated benzenes, toluenes, and butadiene in the Lake Ontario data set were not used in this analysis because these chemicals volatilize to the atmosphere relatively easily in comparison with the higher molecular weight PCBs and chlorinated pesticides.

Figure 4-7 shows the J_{socw}s for selected PCB congeners in five different zones of Green Bay. For the individual PCB congeners, the geometric mean regressions were performed on data for the five different zones in the Green Bay system because both variables were measured with error (Ricker, 1973). The slopes of the log J_{socw}-log K_{ow} regressions from the different zones were not significantly different among the five zones (comparison of slope test, " = 5%). Therefore, average J_{socw}s were determined for each PCB congener with data from all zones (Figure 4-8). The geometric mean regression statistics are reported in Table 4-3 for each zone and for the average of all zones. Examination of Figures 4-7 and 4-8 and Table 4-3 reveals that for PCBs, J_{socw} is strongly dependent on the K_{ow} and slopes of slightly less than 1 were obtained. Examination of J_{socw}s for Lake Ontario and Hudson River reveals trends similar to those in Green Bay; a strong dependence of J_{socw} on K_{ow} for the PCBs and chlorinated pesticides (Figures 4-8 and 4-9 and Table 4-3) and slopes of 1 and slightly less than 1 were obtained.

Table 4-3. Geometric Mean Regression Equations (log J_{socw} = A C log K_{ow}+ B) for Polychlorinated Biphenyls (PCBs) and Chlorinated Pesticides

Ecosystem	Slope (±sd)	Intercept (±sd)	n	r	s_{xy}
Green Bay (PCBs)					
Zone 1	0.95 (±0.04)	1.21 (±0.22)	46	0.97	0.17
Zone 2a	0.92 (±0.09)	1.13 (±0.61)	31	0.82	0.34
Zone 3a	0.87 (±0.06)	1.61 (±0.36)	63	0.86	0.37
Zone 3b	0.83 (±0.06)[a]	1.88 (±0.36)	60	0.85	0.33
Zone 4	0.86 (±0.08)	1.31 (±0.53)	46	0.76	0.46
All zones, congener averages	0.92 (±0.06)	1.20 (±0.38)	77	0.82	0.43
Hudson River (PCBs)					
RM 189	0.87 (±0.08)	1.81 (±0.45)	32	0.86	0.13
RM 194	0.72 (±0.08)[a]	3.16 (±0.42)	27	0.84	0.16
Lake Ontario (PCBs and chlorinated pesticides)	1.05 (±0.08)	0.83 (±0.49)	55	0.84	0.46

n = number of data points, r = correlation coefficient, sd = standard deviation, s_{xy} = standard error of estimate, [a] slope significantly different from 1.0, " = 1%.

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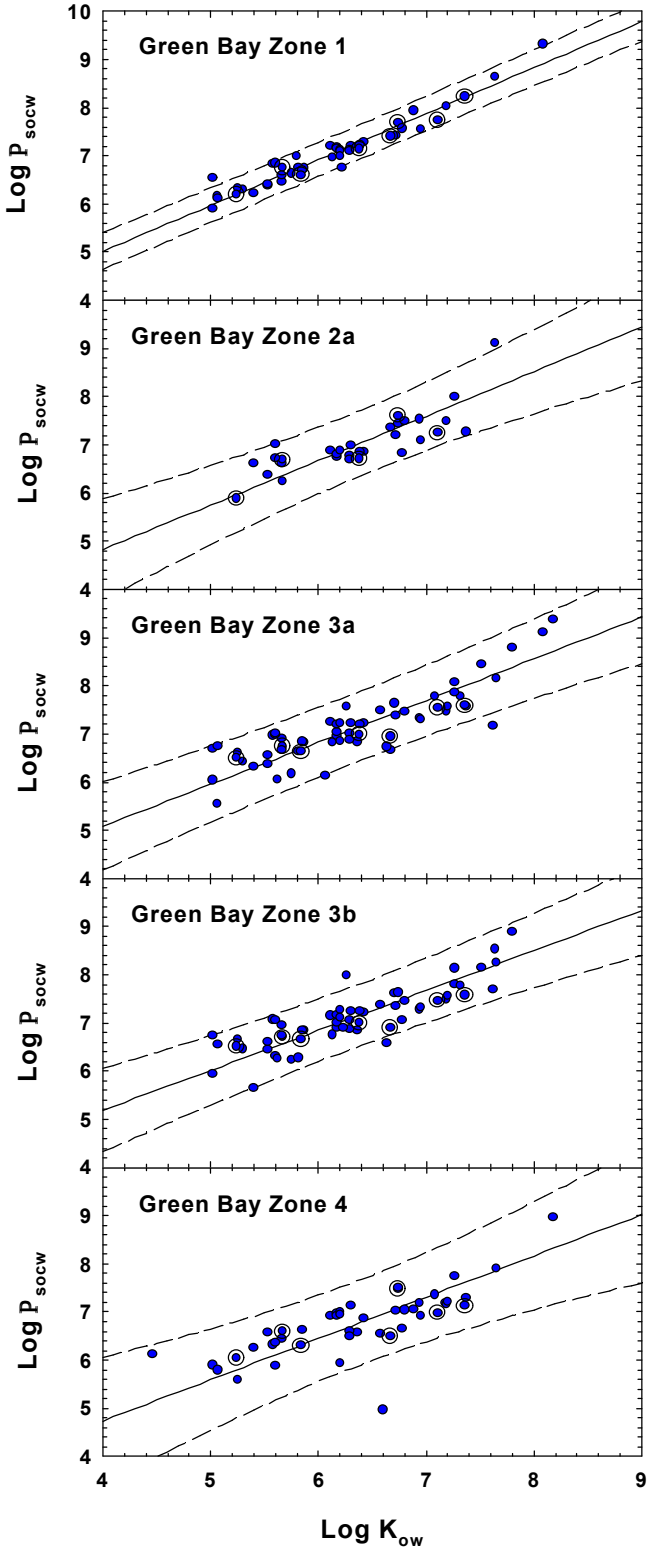

Figure 4-7. Sediment-water column concentration quotient (J_{socw}) for PCBs in five different geographical zones in Green Bay, Lake Michigan. The circled data points are the PCB congeners numbers (log K_{ow}) 18 (5.24), 28 + 31 (5.67), 52 (5.84), 101 (6.38), 118 (6.74), 149 (6.67), 174 (7.11), and 180 (7.36). The geometric mean regression and their 95% confidence limits are plotted.

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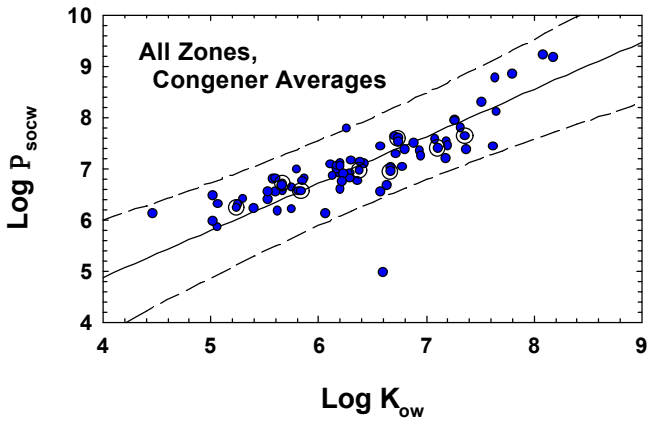

Figure 4-8. Average sediment-water column concentration quotients (J_{socw}) for individual PCB congeners across the five different geographical zones in Green Bay, Lake Michigan. The circled data points are the PCB congeners numbers (log K_{ow}) 18 (5.24), 28 + 31 (5.67), 52 (5.84), 101 (6.38), 118 (6.74), 149 (6.67), 174 (7.11), and 180 (7.36). The geometric mean regression and their 95% confidence limits are plotted.

In the Green Bay ecosystem, chemical concentrations in both sediments and the water column decrease with increasing zone number. Zone 1 is at the mouth of the Fox River, the source of PCBs to the bay, and zone 4 connects the bay to Lake Michigan. Zone 1, the region of highest chemical concentrations, has much less variability in the measured J_{socw}s and the largest slope for the log J_{socw}–log K_{ow} relationship among all sampling zones in Green Bay. Comparison of the variability existing in zones 1 through 4, as illustrated by the 95% confidence intervals in Figure 4-7, suggests that variability increases with increasing distance from the source of the PCBs (Table 4-4), and this trend parallels the concentration gradient in Green Bay. The tightness, consistency, and slope of the J_{socw}s–K_{ow} relationship observed in zone 1 data might be more illustrative of the underlying J_{socw}s–K_{ow} relationship than those of the other zones because of lower uncertainties associated with the analytical measurements.

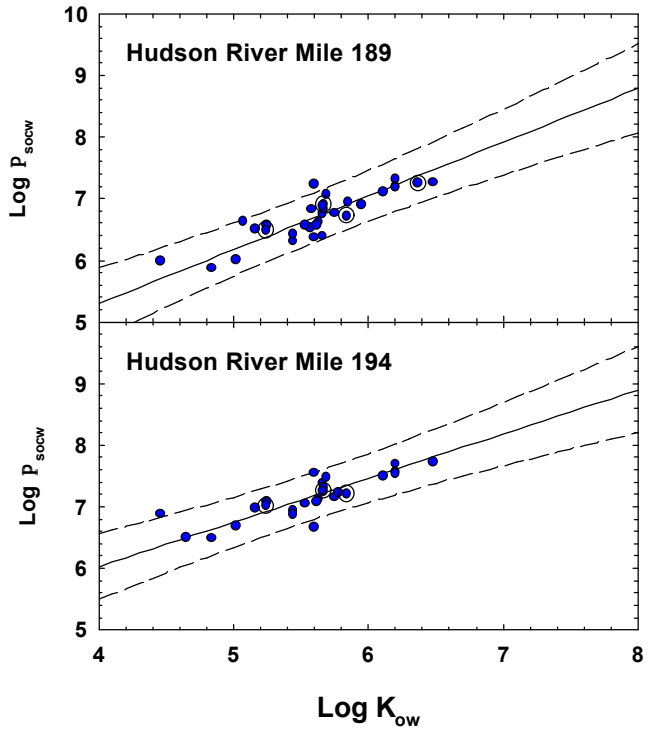

Figure 4-9. Sediment-water column concentration quotient (J_{socw}) for PCBs at river miles 189 and 194. The circled data points are the PCB congeners numbers (log K_{ow}) 18 (5.24), 28 + 31 (5.67), 52 (5.84), 101 (6.38), 118 (6.74), 149 (6.67), 174 (7.11), and 180 (7.36). The geometric mean regression and their 95% confidence limits are plotted.

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Table 4-4. Average J_{socw}/K_{ow} Ratios for Three Different Ecosystems

Ecosystem	Average Ratio (±sd)	Percentile 5%	10%	90%	95%
Green Bay (PCBs)					
Zone 1	9.15 (±4.97)	4.34	5.55	13.8	17.3
Zone 2a	6.35 (±6.73)	1.24	1.37	13.1	21.0
Zone 3a	10.3 (±13.3)	1.27	1.88	21.7	25.6
Zone 3b	9.48 (±10.6)	1.68	2.00	20.1	29.9
Zone 4	4.49 (±6.68)	0.60	0.75	6.95	8.10
All zones, congener averages	7.21 (±6.68)	1.01	1.76	13.3	16.5
Hudson River (PCBs)					
RM 189	14.3 (±8.98)	6.03	7.36	23.4	34.7
RM 194	48.4 (±47.6)	18.9	22.6	69.5	83.6
Lake Ontario (PCBs and chlorinated pesticides)	23.4 (±25.1)	2.96	3.57	52.6	82.4
Overall average J_{socw}/K_{ow}=	23.3 (±18.0)				

sd = standard deviation

From a theoretical standpoint, log J_{socw}–log K_{ow} relationships will have a slope of 1 if the ecosystem is at equilibrium. In addition, EPA believes that ecosystems at steady state or with conditions that approximate the longer term average conditions will also have slopes nearly equal to 1. A number of factors could cause the slope to be less than 1; these include volatilization losses (volatilization rates decrease with increasing molecular weight), sorption/desorption hysteresis (desorption rates decrease with increasing molecular weight), inaccuracies in the calculation of the concentration of chemical that is freely dissolved in the water column (the denominator in the J_{socw} term), and measurement error in determining the concentrations of chemical in the sediments and/or water column. The log J_{socw}–log K_{ow} relationships for the Hudson River, Lake Ontario, and Green Bay ecosystems have slopes that are 1 or slightly less than 1 for PCBs and chlorinated pesticides (Table 4-3). The smallest slopes were observed with the Hudson River ecosystem data. The Hudson River ecosystem is much more dynamic and possibly further from steady-state conditions than are the Lake Ontario and Green Bay ecosystems, because of changing flows over time and recent changes in PCB loadings. Given the similarity in slopes among all three ecosystems, the conditions in the Hudson River do not appear to be greatly different from those in the other two ecosystems.

Given that the slopes for the log J_{socw}–log K_{ow} relationships in Green Bay, the Hudson River, and Lake Ontario are close to 1, and the fact that ecosystems tend to move toward the theoretical slope of 1 over time, EPA assumes a slope one for this relationship. This causes the log J_{socw} = A ℂ log K_{ow} + B relationship to become log J_{socw} = log K_{ow} + B. Rearrangement of this equation gives B = log K_{doc} - log K_{ow}= log (K_{doc}/K_{ow}), and B can be found by averaging the differences of the log K_{doc} and log K_{ow} for the individual chemicals or by averaging the logarithms of the ratios of the K_{doc} to the K_{ow} for the individual chemicals. This averaging was performed for the three ecosystems (Table 4-4), yielding average J_{socw}/K_{ow} ratios of 7.21 for Green Bay, 14.3 and 48.4 for Hudson River, and 23.4 for Lake Ontario. The large differences in average J_{socw}/K_{ow} ratios between the two Hudson River sampling stations suggest distinctly different behaviors in the two sampling stations, and, therefore, an overall ratio was not computed for the Hudson

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River. An average J_{socw}/K_{ow} ratio was computed for the three ecosystems by using the average values for Green Bay and Lake Ontario with the two ratios from the Hudson River. An average J_{socw}/K_{ow}ratio for the three ecosystems of 23.3 with a standard deviation of 18.0 was obtained (Table 4-4).

The EPA believes that the differences in average J_{socw}/K_{ow} ratios among the three ecosystems evaluated here illustrate the range of variability that occurs among ecosystems across the nation. Because J_{socw}s are a function of both current and past chemical loadings to the ecosystems, J_{socw}/K_{ow} ratios both larger and smaller than those observed exist in the nation. For highly contaminated sites, for example, Superfund sites with large concentrations of chemicals in the sediments, J_{socw}/K_{ow} ratios could become very large. For new chemicals that are just being introduced or discharged into the environment, J_{socw}/K_{ow} ratios will be small because very little of the chemicals is present in the sediment. Degradation processes such as hydrolysis, photolysis, and metabolism can also strongly influence the J_{socw}/K_{ow} ratio, depending on where these processes occur (i.e., the sediment and/or the water column).

Because the degradation rates for the PCBs and chlorinated pesticides in the environment are extremely slow, the average J_{socw}/K_{ow} ratio of 23.3 for the three ecosystems is representative of chemicals that are very slowly degraded (or have long half-lives in the environment). Chemicals with higher degradation rates will, in all likelihood, have J_{socw}/K_{ow} ratios that are different from those for the PCBs and chlorinated pesticides, and EPA believes that the J_{socw}/K_{ow} ratios will be smaller for such chemicals, on average, than those for the PCBs and chlorinated pesticides.

On the basis of the data and information presented above, EPA will use the average value of 23 for the J_{socw}/K_{ow} ratio for deriving FCMs with the Gobas model.

Selection of a Food Web Structure

To determine FCMs with the Gobas model, a food web structure is needed. The information necessary to construct a food web includes the diet of the individual organisms composing the food web and their weights and lipid contents. The sensitivity analysis performed with the Gobas model indicated that the model predictions were relatively insensitive to organism weights (largest sensitivity, < 0.1) and feeding preferences of piscivorous fish (largest sensitivity, < –0.3) for all K_{ow}s. The predictions were more sensitive for J_{socw}, feeding preferences of forage fish upon benthic invertebrates, and lipid contents for chemicals with higher log K_{ow}s (Burkhard, 1998). The more sensitive input parameters attain sensitivities of approximately 1 or –1 at log K_{ow}s of 6 (J_{socw}), 5 (feeding preferences of forage fish upon benthic invertebrates), and 7 (lipid content). The most sensitive input parameter was the feeding preferences of forage fish, that is, the percentage of zooplankton (pelagic component) and benthic invertebrates (benthic component) in their diet. The benthic/pelagic composition of the food web is, EPA believes, the most important characteristic for defining the structure of the food web for piscivorous fish because transfer of chemicals from the sediment to piscivorous fish occurs almost exclusively via their diet.

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The uncertainty analysis performed with the Gobas model revealed that the J_{socw} and K_{ow} input parameters were the dominant sources of uncertainty associated with the model prediction. The higher sensitivities associated with the J_{socw} and feeding preferences of forage fish are related to higher sources of uncertainty associated with the J_{socw} input parameter. As concluded in the previous section, due to past chemical loadings and ecosystem interactions, many sediments across the United States are currently enriched relative to the water column (i.e., J_{socw}/K_{ow}= 23). This thermodynamic difference results in substantially different concentrations of the chemical in benthic organisms and pelagic organisms (zooplankton). In the Gobas model, the difference in lipid-normalized chemical concentrations between benthic and pelagic organisms is a factor of 23, precisely the disequilibrium between the concentrations of chemical in sediment and the water column. Consequently, small changes in the benthic portion of the diet of forage fish will result in very different amounts of the chemical in the diets of both forage fish and their predators. This large concentration difference is responsible for the overwhelming importance of the benthic/pelagic composition in defining the food web. However, in ecosystems where the disequilibrium (J_{socw}/K_{ow}) is small (or approaches equilibrium conditions), the differences in lipid-normalized chemical concentrations between the benthic and pelagic organisms will be much smaller. At equilibrium conditions (J_{socw}/K_{ow} = 1), the lipid-normalized chemical concentrations in the benthic and pelagic organisms are equal and differ by the ratio of the fraction lipid of the organisms (f_R), on a wet-weight basis. Therefore, for ecosystems at or near equilibrium conditions, the benthic/pelagic composition of the food web is much less important, because there are small differences between the chemical concentrations in the benthic and pelagic organisms.

Food webs differ widely in their benthic/pelagic compositions among ecosystems, among individual species, and among different age classes of species within an ecosystem. Of all the ecosystem types, the purely pelagic food webs might be the least common for piscivorous fish. However, purely pelagic food webs have been found in remote Ontario lakes for lake trout (Rasmussen et al., 1990) and in Adirondack lakes for brook trout and yellow perch (Havens, 1992). Purely benthic food webs are more common than purely pelagic food webs, but are still rather limited in nature. Some examples of purely benthic food webs can be found in tidal and estuarine ecosystems, such as the food webs for flounder in New Bedford harbor (Connolly, 1991) and striped bass in the tidal Passaic River (Iannuzzi et al., 1996). Mixed food webs are common in all ecosystems and, EPA believes, far outnumber the purely pelagic and benthic food webs. There are numerous examples of mixed benthic/pelagic food webs, such as the food webs for lake trout in the Great Lakes (Flint, 1986; Morrison et al., 1997), lobster in the New Bedford harbor (Connolly, 1991), whitefish and rainbow trout in the Fraser River (Gobas et al., 1998), white perch in the Chesapeake Bay (Baird and Ulanowicz, 1989), and perch, bass, and crappie in Little Rock Lake (Martinez, 1991). Purely pelagic and/or benthic species can exist in ecosystems containing species with a mixed benthic/pelagic food web, for example, flounder and lobster in New Bedford harbor (Connolly, 1991).

Attributes of a common aquatic food web might include multiple trophic levels, the presence of forage and piscivorous fishes, a mixed benthic-pelagic structure, and benthic invertebrates as important components. From the perspective of the fish and shellfish consumed on average by the U.S. population, EPA believes that the common food web just described

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provides a reasonable representation of the potential exposures of humans to various segments of the food web, for example, benthic filter feeders/detritivores such as shrimp and clams and top predators such as trout and salmon. For birds and wildlife, such a food web might not be reasonable because their diets, in all likelihood, are different from those of the U.S. human population.

In selecting a food web structure for determining FCMs used in the third method of Procedure 1 of the BAF methodology, EPA considered a number of approaches for deriving or selecting a food web. These approaches included (1) developing a hypothetical food web structure consistent with the desirable characteristics described above; (2) developing food web structures for different ecosystem types and then averaging data to derive the typical food web for the nation; (3) using fish consumption survey data, developing food web structures for different species consumed by the U.S. population, and then averaging to derive the typical food web for the nation; and (4) simply selecting an existing food web with the desirable characteristics described above. In selecting an average or typical food web structure for the nation, all of these approaches are somewhat problematic because of the large differences in food webs across the country. For this reason, EPA strongly encourages States and Tribes to make site-specific modifications to EPA's national BAFs (USEPA, 2000a).

The use of a purely benthic food web structure for the national BAF methodology with the J_{socw}/K_{ow} value of 23 will result in the largest FCMs for fish. In contrast, the use of a purely pelagic food web structure for the national BAF methodology with the J_{socw}/K_{ow} value of 23 will result in the smallest FCMs for fish when the Gobas model is used. Because the goal of EPA's national BAF methodology is to represent the long-term, average bioaccumulation potential of pollutants in aquatic organisms that are commonly consumed by humans throughout the United States, neither the purely benthic nor the purely pelagic food web structure represents average conditions. Rather, the purely benthic and the purely pelagic food web structures are the extremes in food web structure resulting in the largest and smallest FCMs, respectively.

On the basis of the above information and discussion, EPA will use the mixed food web structure from the Lake Ontario ecosystem as the representative food web for determining FCMs for the national methodology (Table 4-5) (Flint, 1986; Gobas, 1993). This selection is based on the following considerations:

1. The Lake Ontario food web possesses the characteristics of the average or typical food web described above, that is, four trophic levels and a benthic/pelagic composition ration of 55:45 for the piscivorous fish (Table 4-5).

2. The Lake Ontario food web structure is not overly complex but does include multiple forage fish with differing diets that are consumed by piscivorous fish (Table 4-5).

3. Comparisons of measured baseline BAFs and baseline BAFs predicted by using FCMs based on the Lake Ontario data demonstrated good agreement for other ecosystems, such as Green Bay, Hudson River, and Bayou d'Inde.

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4. None of the other approaches considered by EPA for deriving an average or typical food web for the nation would have substantially lower uncertainties than those associated with using the Lake Ontario food web.

5. A detailed investigation of the sensitivities and uncertainties for this specific food web structure with the Gobas model can be performed (Burkhard, 1998), whereas use of the other possible approaches described above for selecting food web structure is not amenable to such analysis.

6. This selected food web does not represent either extreme in benthic/pelagic composition and thus is consistent with EPA's goal for the national methodology of representing the long-term average bioaccumulation potential of pollutants in aquatic food webs.

Table 4-5. Food Web Structure for National BAF Methodology (Flint, 1986; Gobas, 1993)

Species	Trophic Level	Lipid Content	Weight	Diet
Phytoplankton	1	0.5%		
Zooplankton (mysids [*Mysis relicta]*)	2	5.0%	100 mg	
Benthic Invertebrates (*Diporeia)*	2	3.0%	12 mg	
Sculpin (*Cottus cognatus)*	3	8.0%	5.4 g	18% zooplankton, 82% *Diporeia*
Alewife (*Alosa pseudoharengus)*	3	7.0%	32 g	60% zooplankton, 40% *Diporeia*
Smelt (*Osmerus mordax*)	3-4	4.0%	16 g	54% zooplankton, 21% *Diporeia*, 25% sculpin
Salmonids (*Salvelinus namaycush, Oncorhynchus mykiss, Oncorhynchus velinus namaycush*	4	11%	2,410 g	10% sculpin, 50% alewife, 40% smelt

Calculation of Food Chain Multipliers

One additional input parameter is necessary before FCMs can be determined with the Gobas food web model. This parameter, the rate of metabolism in forage and piscivorous fish, is difficult to define because of the general lack of data on metabolism rate constants for individual compounds. Procedure 1 of EPA's BAF methodology (see Section 3.1, Figure 3-1) assumes that the rates of metabolism for the chemicals of interest are low. Consequently, EPA assumes no metabolism; that is, metabolism rates are set equal to zero in the model when FCMs are calculated for methods 3 and 4 in Procedure 1.

Inputs to the Gobas model (MS-DOS version) include concentrations of chemicals in the sediment (expressed on a wet-weight basis) and in the water column (expressed on a total basis). Because the Gobas model does not have solubility limits or controls for the concentration of chemical in any compartment (i.e., sediment, water, and biota), the chemical concentration in the water used with the model is arbitrary for determining the BAFs. In other words, the BAF obtained by using a concentration of chemical of 1 ng/L will be equal to that obtained using a

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concentration of chemical of 150 µg/L for a specified K_{ow}. Thus, in deriving the FCMs, 1 ng/L (concentration of chemical freely dissolved in the water column, C_w^{fd}) is used and the corresponding chemical concentration in the sediment is calculated by using $J_{socw}/K_{ow} = 23$ relationship, or $C_s = 23 \cdot K_{ow} \cdot (1\ ng/L) \cdot f_{oc}$.

In applying the Gobas model, EPA does not use Gobas's method of accounting for bioavailability. Gobas's method for determining the freely dissolved (bioavailable) concentration of the chemical in water makes no distinction between POC and DOC phases but rather treats these two phases as one. In Section 4.2 of this document, the procedure used in the 2000 Human Health Methodology for determining the concentration of chemical that is freely dissolved in the ambient water, C_w^{fd}, is presented. To avoid using Gobas's method of accounting for bioavailability, EPA set the concentration of the DOC in the model to an extremely small number, 1.0×10^{-30} kilograms per liter. The Gobas model takes the total concentration of the chemical in the water that is input to the model and, before doing any predictions, performs a bioavailability correction by calculating the C_w^{fd}. The C_w^{fd} is then used *in all subsequent calculations by the model*. By setting the concentration of the DOC to 1.0×10^{-30} kilograms per liter, the total concentration of the chemical put into the model becomes essentially equal to the C_w^{fd}, because the bioavailability correction with the method of Gobas is extremely small.

For each value of K_{ow} input to the Gobas model, predicted baseline BAFs are reported by the model for each organism in the food web. FCMs are calculated from the predicted BAFs using the following equation:

$$FCM = \frac{\text{Baseline BAF}}{K_{ow}} \qquad \text{(Equation 4-9)}$$

where:

Baseline BAF	=	BAF that is based on the concentration of chemical freely dissolved in water (C_w^{fd}) and the concentration of chemical in the lipid fraction of tissue
K_{ow}	=	*n*-octanol-water partition coefficient

Using Equation 4-10, FCMs were calculated for each organism in the Lake Ontario food web with the reported BAFs (Oliver and Niimi, 1988). Table 4-6 lists the FCMs for trophic level 2 (zooplankton), trophic level 3 (forage fish), and trophic level 4 (piscivorous fish). The FCMs for the forage fish, trophic level 3, were determined by taking the geometric mean of the FCMs for sculpin and alewife. The FCMs for the smelt were not used in determining the mean FCMs for the forage fish because the diet of this organism includes small sculpin. This diet causes smelt to be at a trophic level slightly higher than 3 but less than trophic level 4. In contrast, the diets of the sculpin and alewife were solely trophic level 2 organisms (i.e., zooplankton and *Diporeia sp*.)

FCMs were determined with the Gobas model, the food web structure in Table 4-5, $J_{socw}/K_{ow} = 23$, and the environmental parameters and conditions listed in Table 4-7. The resulting FCMs, used for the national BAF methodology, are shown in Table 4-6.

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Table 4-6. Food-Chain Multipliers for Trophic Levels 2, 3, and 4 (Mixed Pelagic and Benthic Food Web Structure and J_{socw}/K_{ow}= 23)

Log K_{ow}	Trophic Level 2	Trophic Level 3[a]	Trophic Level 4	Log K_{ow}	Trophic Level 2	Trophic Level 3[a]	Trophic Level 4
4.0	1.00	1.23	1.07	6.6	1.00	12.9	23.8
4.1	1.00	1.29	1.09	6.7	1.00	13.2	24.4
4.2	1.00	1.36	1.13	6.8	1.00	13.3	24.7
4.3	1.00	1.45	1.17	6.9	1.00	13.3	24.7
4.4	1.00	1.56	1.23	7.0	1.00	13.2	24.3
4.5	1.00	1.70	1.32	7.1	1.00	13.1	23.6
4.6	1.00	1.87	1.44	7.2	1.00	12.8	22.5
4.7	1.00	2.08	1.60	7.3	1.00	12.5	21.2
4.8	1.00	2.33	1.82	7.4	1.00	12.0	19.5
4.9	1.00	2.64	2.12	7.5	1.00	11.5	17.6
5.0	1.00	3.00	2.51	7.6	1.00	10.8	15.5
5.1	1.00	3.43	3.02	7.7	1.00	10.1	13.3
5.2	1.00	3.93	3.68	7.8	1.00	9.31	11.2
5.3	1.00	4.50	4.49	7.9	1.00	8.46	9.11
5.4	1.00	5.14	5.48	8.0	1.00	7.60	7.23
5.5	1.00	5.85	6.65	8.1	1.00	6.73	5.58
5.6	1.00	6.60	8.01	8.2	1.00	5.88	4.19
5.7	1.00	7.40	9.54	8.3	1.00	5.07	3.07
5.8	1.00	8.21	11.2	8.4	1.00	4.33	2.20
5.9	1.00	9.01	13.0	8.5	1.00	3.65	1.54
6.0	1.00	9.79	14.9	8.6	1.00	3.05	1.06
6.1	1.00	10.5	16.7	8.7	1.00	2.52	0.721
6.2	1.00	11.2	18.5	8.8	1.00	2.08	0.483
6.3	1.00	11.7	20.1	8.9	1.00	1.70	0.320
6.4	1.00	12.2	21.6	9.0	1.00	1.38	0.210
6.5	1.00	12.6	22.8				

[a] The FCMs for trophic level 3 are the geometric mean of the FCMs for sculpin and alewife.

Table 4-7. Environmental Parameters and Conditions Used for Determining FCMs for the National BAF Methodology

Mean water temperature: 8°C
Organic carbon content of the sediment: 2.7%
Dissolved organic carbon content of the water column: 1.0E-30 mg/L
Density of lipids: 0.9 kg/L
Density of organic carbon: 0.9 kg/L
Metabolic transformation rate constants (all organisms): 0.0 d^{-1}
$J_{socw} = 23 \cdot K_{ow}$

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4.4.2 Derivation of Food Chain Multipliers Using Field Data

In addition to model-derived estimates of FCMs, field data can also be used to derive FCMs for nonionic organic chemicals. Compared with the model-based FCMs described previously, field-derived FCMs account for any metabolism of the pollutant of concern by the aquatic organisms used to calculate the FCM.

Field-derived FCMs should be calculated with lipid-normalized concentrations of the nonionic organic chemical in appropriate predator and prey species, using the following equations:

$$FCM_{TL2} = BMF_{TL2} \quad \text{(Equation 4-10)}$$
$$FCM_{TL3} = (BMF_{TL3}) \times (BMF_{TL2}) \quad \text{(Equation 4-11)}$$
$$FCM_{TL4} = (BMF_{TL4}) \times (BMF_{TL3}) \times (BMF_{TL2}) \quad \text{(Equation 4-12)}$$

where:

FCM = food chain multiplier for designated trophic level (TL2, TL3, or TL4).

The basic difference between FCMs and BMFs is that FCMs relate back to trophic level 1 (or trophic level 2, as assumed by the Gobas model [1993]), whereas BMFs always relate back to the next lowest trophic level. For nonionic organic chemicals, BMFs can be calculated from lipid-normalized concentrations of chemical in tissues of biota at a site according to the following equations:

$$BMF_{TL2} = (C_{R,TL2}) / (C_{R,TL1}) \quad \text{(Equation 4-13)}$$
$$BMF_{TL3} = (C_{R,TL3}) / (C_{R,TL2}) \quad \text{(Equation 4-14)}$$
$$BMF_{TL4} = (C_{R,TL4}) / (C_{R,TL3}) \quad \text{(Equation 4-15)}$$

where:

C_R = lipid-normalized concentration of chemical in tissue or whole organism at a specified trophic level (TL2, TL3, or TL4).

In addition to the acceptability guidelines pertaining to field-measured BAFs, the following procedural and quality assurance guidelines apply to field-measured FCMs.

1. Information should be available to identify the appropriate trophic levels for the aquatic organisms and appropriate predator-prey relationships for the site from which FCMs are being determined. Information about trophic status is most accurate when obtained from the site(s) of interest, because predator-prey relationships for some species can vary widely over space and time. When a predator species consumes multiple prey species at a particular trophic level, chemical concentrations in prey species should be appropriately weighted (if the data are available) when used to calculate field-based FCMs. General information

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on determining trophic levels of aquatic organisms can be found in USEPA (2000 e-g).

2. The aquatic organisms sampled from each trophic level should reflect the most important exposure pathways leading to human exposure via consumption of aquatic organisms. For higher trophic levels (e.g., 3 and 4), aquatic species used to calculate FCMs should be those that are commonly consumed by humans. The species sampled should also reflect size and age ranges that are typical of human consumption patterns.

3. The study from which the FCMs are derived should contain enough supporting information to determine that tissue samples were collected and analyzed according to appropriate, sensitive, accurate, and precise methods.

4. The percent of tissue that is lipid should be either measured or reliably estimated for the tissue(s) used to determine the FCM.

5. The chemical concentrations in the tissues/organisms used to calculate FCMs should reflect long-term average exposures of the target species to the chemical of interest; longer averaging periods are generally necessary for chemicals with greater hydrophobicity.

4.4.3 Food Chain Multiplier Uncertainties

Uncertainties associated with predictions from the Gobas model have been assessed by Burkhard (1998) as described in Section 4.4.1. Monte Carlo analyses were conducted by varying all input parameters except K_{ow} and J_{socw}. The results of these analyses are shown in Figure 4-10. Because the FCMs were calculated from baseline BAFs predicted with the Gobas model, the uncertainties shown in Figure 4-10 are directly applicable to the FCMs. These results suggest that the FCMs have fairly low uncertainties, because, in their calculation, J_{socw} was fixed and the K_{ow}s were assumed to have no error. For example, for a log K_{ow} of 6.5, the ratio from the Monte Carlo analysis was 1.74 for the 90th to 10th percentile predicted baseline BAFs (Figure 4-10). For trophic level 4 fish, the FCM is 22.8 and the 10th and 90th percentile FCMs would be 17.3 and 30.1, respectively.

Application of the FCMs, calculated with the assumed food web (Table 4-5) and disequilibrium (J_{socw}/K_{ow}) of 23, to ecosystems and/or organisms with vastly different food webs and/or disequilibriums can cause substantial biases in the baseline BAFs predicted for use in methods 3 and 4 of Procedure 1. Although the degree and magnitude of error will vary among sites, some general statements can be made about the direction and relative uncertainty associated with these biases. Food webs that are more pelagic-based will tend to have smaller FCMs, whereas food webs that are more benthic-based will tend to have larger FCMs. In Figure 4-11, FCMs for purely pelagic and purely benthic food webs, created by modifying the assumed Lake Ontario food web and rerunning the Gobas model, are shown along with the FCMs from

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4-11, FCMs for purely pelagic and purely benthic food webs, created by modifying the assumed Lake Ontario food web and rerunning the Gobas model, are shown along with the FCMs from Table 4-5. These two modified food webs represent the extremes in benthic/pelagic composition. Decreasing the disequilibrium (J_{socw}/K_{ow}) will cause the FCMs to become smaller, whereas increasing the disequilibrium (J_{socw}/K_{ow}) will cause the FCMs to become larger (Figure 4-12). The FCMs for the 2000 Human Health Methodology were derived assuming no metabolism of the chemical in the food web. If metabolism does exist within the food web, the FCMs will be smaller than those calculated without metabolism.

FCMs derived from field measurements (see Section 4.4.2) do not have the above biases because the measurements incorporate the conditions existing at the field site where the measurements were performed. This includes the existing disequilibrium, chemical metabolism, and influences due to the structure of the food web (i.e., predator-prey relationships and benthic-pelagic components).

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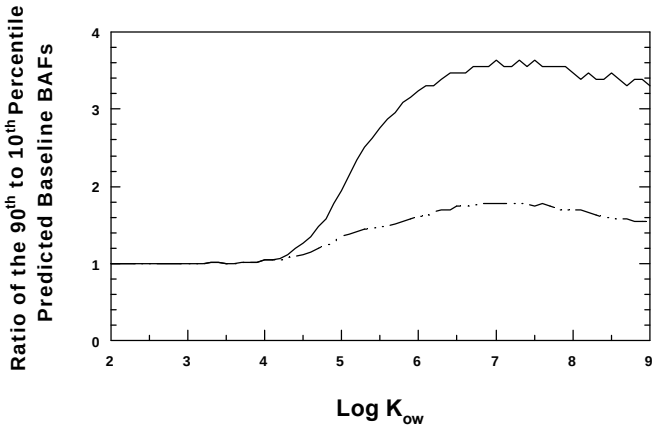

Figure 4-10. The ratio of the 90th to 10th percentile baseline BAF predictions for piscivorous fish from 100,000 Monte Carlo simulations using the Gobas model as a function of *n*-octanol-water partition coefficient (K_{ow}) (Burkhard 1998). The ratio when all parameters except K_{ow} ( )))) and except J_{socw} and K_{ow} ( ) ••)) are varied.

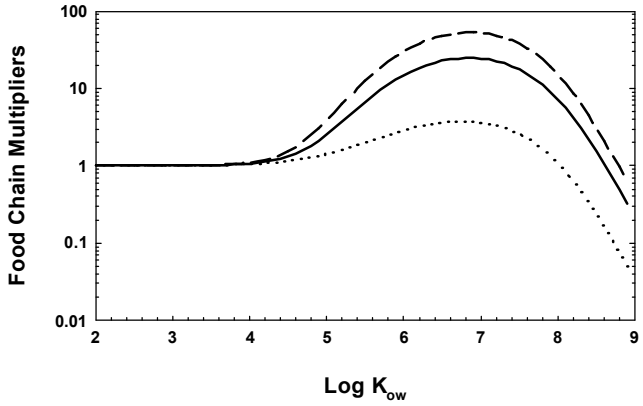

Figure 4-11. FCMs for purely pelagic (CCCC) and purely benthic (! ! !) food webs derived by modifying the Lake Ontario food web ( )))).

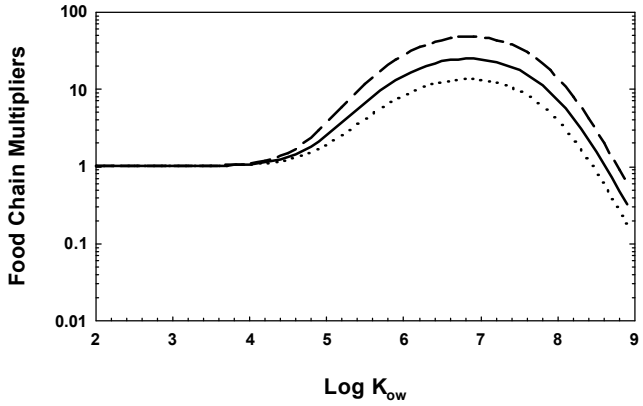

Figure 4-12. FCMs predicted using the Lake Ontario food web with disequilibriums of 11.5 (CCCC), 23 ( )))), and 46 (! ! !).

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5. CALCULATING BASELINE BAFS FOR NONIONIC ORGANIC CHEMICALS USING THE FOUR METHODS

This section presents each of the four BAF methods as they are applied to nonionic organic chemicals under Procedure 1. Application of the four BAF methods under Procedure 1 is generally more complex than for Procedures 2-4, and thus, more detailed discussions are warranted on how to appropriately apply them. Nonetheless, the same general data quality considerations, assumptions, strengths, and limitations that apply to the BAF methods under Procedure 1 are generally relevant to Procedures 2-4, even though each method is not applied in the same manner (or may not be used at all) under these other three procedures. The equations for each BAF method under Procedure 1 are shown in this section, and the ability of each method to predict BAFs is discussed, as are assumptions and limitations inherent to each method.

5.1 METHOD 1: DERIVING BASELINE BAFs FROM TOTAL BAFs (BAF_T^ts)

As has been noted, BAFs derived from data from samples collected in the field BAF_T^t are the first preference in EPA's BAF hierarchy for deriving individual baseline BAFs. In Section 2, the term "total BAF," denoted BAF_T^t , was introduced to refer to "field-measured" BAFs. The BAF_T^t is defined as:

$$BAF_T^t = \frac{C_t}{C_w} \qquad \text{(Equation 5-1)}$$

where:

C_t = *total* concentration of the chemical in tissue
C_w = *total* concentration of chemical in water

The BAF_T^t shown in Equation 5-1 is calculated on the basis of the total concentration of chemical in the appropriate wet tissue of the aquatic organism sampled and the total concentration of the chemical in the ambient water at the sampling site.

A baseline BAF is calculated from a BAF_T^t as shown in Equation 5-2 by using information on the lipid fraction (f_ℓ) of the tissue of concern for the study organism and the fraction of the total chemical that is freely dissolved in the study water (f_{fd}). Appendix A provides more detailed information on derivation of the baseline BAF equation.

$$\text{Baseline BAF} = \left[\frac{BAF_T^t}{f_{fd}} - 1\right] \cdot \frac{1}{f_\ell} \qquad \text{(Equation 5-2)}$$

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where:

BAF	=	Total BAF ($BAF_T^t = C_t/C_w$)
f_{fd}	=	fraction of the total concentration of chemical in water that is freely dissolved
f_R	=	fraction of tissue that is lipid

In calculating BAFs using method 1, EPA will use appropriate BAF_T^t data obtained from the open literature (e.g., peer-reviewed journals, government reports, professional society proceedings) when sufficient information is provided to indicate the quality and usability of data. In general, the bioaccumulation data used should make it possible to calculate reliable BAF_T^ts and to make some assessment of the overall uncertainty in the BAF_T^t value.

5.1.1 Sampling and Data Quality Considerations

The data used to calculate a BAF_T^t should be thoroughly reviewed to assess the quality of the data and the overall uncertainty in the BAF value. The following general criteria apply in determining the acceptability of BAF_T^ts. Because no guidance can address all of the variation in experimental designs and data found in the literature, best professional judgment will be necessary to supplement these data quality guidelines in selecting the best available information and using it appropriately.

1. Aquatic organisms used to calculate a field-measured BAF_T^t should generally be representative of those aquatic organisms commonly consumed by the general population in the United States. An aquatic organism that is not commonly consumed by the general U.S. population can be used to calculate a field-measured BAF_T^t provided that the organism is considered to be a reasonable surrogate for a commonly consumed organism. Information on the ecology, physiology, and biology of the organism should be reviewed when assessing whether an organism is a reasonable surrogate for a commonly consumed organism.

2. The trophic level of the study organism should be determined by taking into account its life stage, diet, and the food web structure at the study location. Information from the study site (or similar sites) is preferred when evaluating trophic status of an organism. If such information is lacking, general information for assessing trophic status of aquatic organisms can be found in USEPA (2000e-g).

3. In some cases, assessments of size, age, and reproductive status of the organisms might be useful in assigning appropriate trophic levels for the study organisms. Additionally, accumulation of chemical can vary as a result of other factors such as different growth rates and pre-spawning versus post-spawning organisms. Thus, the above ancillary information might be useful in deciding whether the study organisms are appropriate representatives for field sites.

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4. The percent lipid of the tissue used to determine the BAF_T^t needs to be known, either as measured in the field study or reliably estimated. This parameter is necessary to permit lipid normalization of the concentration of chemical in tissue when deriving baseline BAFs.

5. The study from which the BAF_T^t is derived should contain sufficient supporting information from which to confirm that tissue and water samples were collected and analyzed according to appropriate, sensitive, accurate, and precise analytical methods.

6. The site of the field study should not be so unusual that the BAF_T^t cannot be reasonably extrapolated to other locations where the national BAF and resulting AWQC will apply.

7. The water concentration(s) used to derive the BAF_T^t should reflect the average exposure experienced by the study organism(s). The extent of spatial and temporal averaging that is necessary for the water samples is a function of the variability in chemical concentration in the ecosystem. In general, greater temporal and spatial averaging of chemical concentrations in water will be necessary with increasing K_{ow}. More water samples over time and space (i.e., more averaging) will be necessary for chemicals with higher K_{ow}s and higher variability in chemical concentrations than in ecosystems with lower variabilities in chemical concentrations. For chemicals with higher K_{ow}s, BAF_T^ts determined with composite water samples over time will generally be more accurate than those measured by individual "grab samples." For chemicals with lower K_{ow}s, BAF_T^t s determined with composite water samples over time will, in general, be more accurate than those measured with individual "grab samples."

8. The home range of the organisms that are collected for determining BAF_T^t s should be determined or assessed such that the appropriateness of the spatial sampling design can be evaluated within the context of the organism's mobility. For more mobile organisms, greater spatial averaging will generally be necessary.

9. The concentrations of POC and DOC in the study water should be measured or reliably estimated so that baseline BAFs can be derived.

10. The field study should not be conducted in an ecosystem that has recently experienced a major change or disruption in chemical loadings or flows (for example, a 100-year flood or the removal of a major chemical source) because it takes time for the ecosystem to return to long-term average or steady-state conditions. The response times depend on a number of factors, including the nature of the disruption; the chemical's loading to and from the ecosystem; the hydrodynamics and solids transport of the ecosystem; fish-specific parameters, such as growth rates, chemical uptake, and depuration rates; and the K_{ow} of the chemical. For chemicals with higher K_{ow}s, response times might range from

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months to years, whereas for those with lower K_{ow}s, the response times would be shorter, possibly less than a year.

The EPA is presently developing guidance for designing and conducting field studies for determining field-measured BAF_T^ts and for determining minimum data quality and quantity requirements. This guidance will provide detailed information on how to design field sampling studies that will yield BAF_T^ts that are representative of the long-term average conditions in an ecosystem and have low bias and good accuracy.

5.1.2 Assumptions and Limitations

Several assumptions and limitations are inherent in the use of BAF_T^ts for deriving national BAFs for nonionic organic chemicals. First, it is assumed that properly derived BAF_T^ts can provide a reasonable estimate of the bioaccumulation that would occur under the long-term conditions that exist in the ecosystem. This assumption is important because human health AWQCs are generally intended to protect humans from long-term (chronic) exposure to chemical concentrations in water and fish. To address this assumption, concentrations of chemicalin water and tissue must be averaged over appropriate temporal and spacial scales so that a steady-state or long-term BAF can be reasonably approximated. Complications can arise in situations where variability in chemical concentrations in water is high relative to concentrations of chemical in tissue (as is usually the case with highly hydrophobic chemicals), when rapid changes occur in chemical loadings to the ecosystem, and when organisms move between areas in which they experience greatly differing chemical exposures. As discussed in Section 5.1.1, achieving the most appropriate temporal and spatial averaging for determining BAF_T^ts can be specific to the chemical, species, and study site. In this regard, adherence to the aforementioned sampling and data quality guidelines with respect to temporal and spatial averaging is the best way to ensure that BAF_T^ts reflect the bioaccumulation that would be expected at or near steady state.

The second major assumption associated with the use of BAF_T^ts for nonionic chemicals is that by adjusting the BAF_T^t for the organism's lipid content (f_ℓ) and the chemical concentration that is freely dissolved (f_{fd}), it is possible to make reasonable predictions of bioaccumulation across different species (within a trophic level) and sites. In reality, other factors influence bioaccumulation. These factors include differences in chemical loadings histories (i.e., sediment-water disequilibrium); food web structure; organism health and physiology; water quality factors such as temperature; and food quality—all of which may vary across ecosystems.

Burkhard et al. (2003a) have evaluated the effectiveness of adjusting BAF_T^ts by lipid content and freely dissolved chemical concentration for increasing the reliability of extrapolating BAFs across ecosystems and species. The results of these comparisons, which are discussed further in Section 5.1.3, suggest that adjusting by f_ℓ and f_{fd} reduces much of the variability in BAF_T^ts. Furthermore, this analysis suggests that BAFs can be extrapolated among species within a trophic level and across ecosystems with reasonable accuracy. Nevertheless, some variation in BAF_T^ts occurs from "other factors," such as those mentioned above.

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A third assumption involved in the use of BAF_T^ts for deriving national BAFs is that, within reasonable limits, BAF_T^ts are independent of exposure concentration (i.e., BAF_T^ts do not vary as a function of exposure concentrations). This assumption is made when applying BAF_T^ts derived from one set of chemical exposure concentrations to another set of concentrations (e.g., from higher to lower chemical concentrations or vice versa). For nonionic chemicals, this assumption is consistent with the mechanism of chemical uptake (i.e., passive diffusion across cell membranes) and is widely supported by reports in the literature. However, it is theoretically possible for BAF_T^ts to become dependent on exposure concentrations if these concentrations are so high that they affect an organism's health and, subsequently, its rate of chemical uptake, elimination, or metabolism. Although this is an issue typically associated with BCF studies in which exposure concentration is controlled by the investigator, this issue will be considered during data review in order to avoid using BAF_T^ts from organisms that show overt signs of toxicity. Although deviation from the concentration-independency assumption may be possible under some circumstances, EPA is not aware of data that demonstrate the extent to which this assumption might be violated under environmentally realistic exposure conditions. Furthermore, it would probably be difficult to measure the extent of deviation from the concentration-independency assumption, given the presence of other contributors, particularly differences in bioaccumulation over space and time, to the overall variability on BAF_T^ts.

Currently, the greatest limitation in using BAF_T^ts to derive national BAFs is the paucity of high-quality field data. The primary deficiencies that limit the use of available BAF_T^t data include the lack of proper spatial and temporal averaging, insufficient ancillary data (e.g., DOC, POC, lipid content of organisms), and the lack of samples co-located in space and time. These deficiencies often reflect limitations on available resources, but they also reflect study designs that are inconsistent with the goals of a BAF study. These data gaps are expected to be filled as additional field-measured data are generated to meet demands for site-specific BAFs and as future guidance is developed for properly designing field BAF studies.

5.1.3 Validation of Method 1

As has been mentioned, use of baseline BAFs for nonionic organic chemicals allows BAF_T^ts to be extrapolated among species and across locations and improves the accuracy of this extrapolation. To validate this approach, Burkhard et al. (2003a) EPA made two different evaluations. In the first evaluation, BAF_T^ts for PCBs and several aquatic species from Green Bay, Lake Michigan, were compared among different geographical areas of the Bay (zones) and across the entire Bay. In the second evaluation, BAF_T^ts and baseline BAFs for six PCB congeners were compared among species and across ecosystems.

In the Green Bay evaluation, BAF_T^ts and baseline BAFs for the PCB congeners 18, 52, 149, and 180 in adult alewife, age 4 walleye, and age 10 carp were compared. These species were selected because they were those species most frequently sampled across the different zones. The PCB congeners used in the evaluation are major components of the PCB mixture present in Green Bay, and uncertainties associated with their measurement are low. In addition, these congeners had hydrophobicities that spanned a wide range: log K_{ow}s are 5.24 for PCB 18, 5.84 for PCB 52, 6.67 for PCB 149 and 7.36 for PCB 180. BAF_T^ts and baseline BAFs were calculated for

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six different zones. Comparing across the zones, the baseline BAFs varied less than the BAF_T^ts; that is, the baseline BAFs were more constant across zones than were the BAF_T^ts (Figure 5-1; Burkhard et al., 2003a). The BAF_T^ts increased from zone 1 to 4 (Figure 5-1; Burkhard et al., 2003a), and the differences are more pronounced for the more hydrophobic PCBs 149 and 180, which is consistent with equilibrium partitioning theory. The observed trend of increasing BAF_T^ts across zones is due to increasing bioavailability of dissolved PCBs, which is caused by decreasing POC and DOC across zones. This trend appeared to disappear with the adjustment of the BAF_T^ts to baseline BAFs (Figure 5-1; Burkhard et al., 2003a) because, as presented in Section 4, the baseline BAF adjustment of chemical concentration to that which is freely dissolved accounts for differences in POC and DOC.

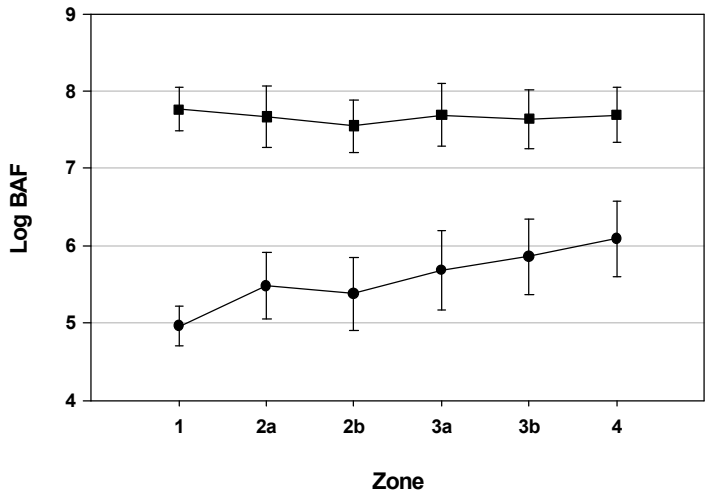

Figure 5-1. BAF_T^ts (●) and Baseline BAFs (■) for PCB congener 149 (2,2N,3,4N,5N,6-hexachlorobiphenyl) (±1 sd) for adult alewife for different Green Bay zones.

To further evaluate the relative variances associated with BAF_T^ts and baseline BAFs, bay-wide BAFs were compared. Bay-wide BAF_T^ts and baseline BAFs were calculated using a sample-size weighted average of the BAFs for each of the geographical zones. The variances of the bay-wide BAF_T^ts and baseline BAFs were calculated as described in detail in Burkhard et al., 2003a. The results of these calculations are summarized, by species, using the ratio of 90th to 10th and 95th to 5th percentile exceedance limits in Table 5-1 and Burkhard et al., 2003a. Overall, the baseline BAFs had smaller ratios than the BAF_T^ts and the adjustment/conversion of BAF_T^ts to baseline BAFs resulted in an approximately twofold decrease in variability (Burkhard et al., 2003a).

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Table 5-1. BAF_T^ts and Baseline BAFs Exceedance Limit Ratios for Green Bay (All Zones Combined)

PCB Congener	90th to 10th Percentile Exceedance Limit Ratio		95th to 5th Percentile Exceedance Limit Ratio	
	BAF_T^ts	Baseline BAFs	BAF_T^ts	Baseline BAFs
Adult alewife				
18	4.98	3.11	7.86	4.30
52	5.48	2.85	8.90	3.84
149	3.33	1.88	4.70	2.26
180	4.08	2.20	6.10	2.76
Age 4 walleye				
18	3.57	3.50	5.14	5.00
52	4.04	2.74	6.01	3.65
149	3.11	2.12	4.30	2.62
180	3.96	2.12	5.87	2.63
Age 10 carp				
18	4.87	4.23	7.65	6.39
52	6.75	3.49	11.6	4.99
149	5.96	1.87	9.91	2.24
180	7.09	2.17	12.4	2.71

To assess across-ecosystem variability, Burkhard et al. (2000a) assembled BAF_T^ts and baseline BAFs for six PCB congeners—PCBs 22, 52, 85, 118, 146, and 149—from the Green Bay, Lake Ontario, and Hudson River ecosystems for 13 fish species (Figure 5-2). When possible, age class BAF_T^ts were assembled, and trophic levels for the different species were assigned with nominal/rounded trophic levels. These assignments caused species with slightly lower trophic level positions (e.g., adult gizzard shad, with an average trophic level of 2.5) to be lumped with species with slightly higher trophic levels (e.g., adult alewife, with an average trophic level of 3.5) within the nominal trophic levels shown in Figure 5-2. As shown in Figure 5-2, the baseline BAFs had substantially lower variability than the BAF_T^ts for trophic level 3 and 4 fish. The coefficients of variation (in arithmetic space) for the trophic level 3 baseline BAFs were 85% for PCB 22, 73% for PCB 52, 70% for PCB 85, 61% for PCB 118, 92% for PCB 146, and 59% for PCB 149. For the BAF_T^ts, these values were 116% for PCB 22, 97% for PCB 52, 104% for PCB 85, 104% for PCB 118, 615% for PCB 146, and 68% for PCB 149 (Burkhard et al., 2003a). Similar differences in the coefficients of variation were found for trophic level 4 fish (Burkhard et al., 2003a). On average, the $75^{th}/25^{th}$ and $90^{th}/10^{th}$ percentile ranges in baseline BAFs were .2x and .5x smaller than the ranges for BAF_T^ts. These results suggest that the corrections for tissue or organism lipid content (f_R) and the fraction of chemical concentrations that is freely dissolved in water (f_{fd}) reduce variability when BAFs are extrapolated among species of similar trophic levels and across ecosystems. The variability (that is, the remaining spread or range in the baseline BAFs for each trophic level) that was not due to differences in lipid content and freely dissolved concentration of chemical is shown in Figure 5-2. Sources of the underlying variability could include differences in nominal versus actual trophic level assignments for the individual species, differences in disequilibrium of the ecosystem, and differences in age, size, growth rate, and/or reproductive status of the individual organisms.

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5.2 METHOD 2: DERIVING BASELINE BAFS FROM BSAFs

When acceptable BAF_T^ts are not available for a nonionic organic chemical with a log K_{ow} of $4, EPA recommends the use of BSAFs to predict the baseline BAF as the second method in the BAF data preference hierarchy under Procedure 1 or 2. Although BSAFs may be used for measuring and predicting bioaccumulation directly from concentrations of chemicals in surface sediment, they also can be used to estimate baseline BAFs (USEPA, 1995b; Cook and Burkhard, 1998). Because BSAFs based on field data incorporate the effects of metabolism, biomagnification, growth, and other factors, baseline BAFs estimated from BSAFs will also account for all these factors. The BSAF approach is particularly beneficial for developing AWQCs for chemicals that are detectable in fish and shellfish tissues but are difficult to detect and measure in ambient water. The BSAF method is also beneficial for measuring the degree to which bioaccumulation is reduced for chemicals, such as polychlorinated dibenzo-p-dioxins, dibenzofurans, certain biphenyl congeners, and polycyclic aromatic hydrocarbons, through metabolism in food webs or the species of concern.

Prediction of a baseline BAF from a BSAF requires data for one or more reference chemicals for which concentrations in ambient water, as well as sediment, can be measured, preferably from a common sediment-water-biota data set. This method, in effect, translates relative differences between measured BSAFs for two chemicals into relative differences in baseline BAFs for the chemicals when the baseline BAF for one chemical cannot be measured. Relative differences in bioaccumulation can be accurately measured when each chemical's concentrations are analyzed from the same or equivalent environmental samples collected from a site suitable for this purpose. BSAFs must be measured for the chemical of interest in order to provide the basic measure of the chemical's bioaccumulation potential. Specifically, this method uses measured sediment-water concentration quotients (J_{socw}s) for reference chemicals to estimate values of C_w^{fd} that cannot be measured for the chemical of interest. Each chemical's K_{ow} must also be acquired, because the ratio of J_{socw} to K_{ow} provides the basis for relating reference chemicals to the chemicals of interest. The following sections describe more completely the determination of BSAF values; the relationship of baseline BAFs to BSAFs; the derivation of the BSAF method equation; sampling and data quality considerations; assumptions and limitations associated with the method; and the validation of this method for estimating baseline BAFs with data from Lake Ontario and other ecosystems.

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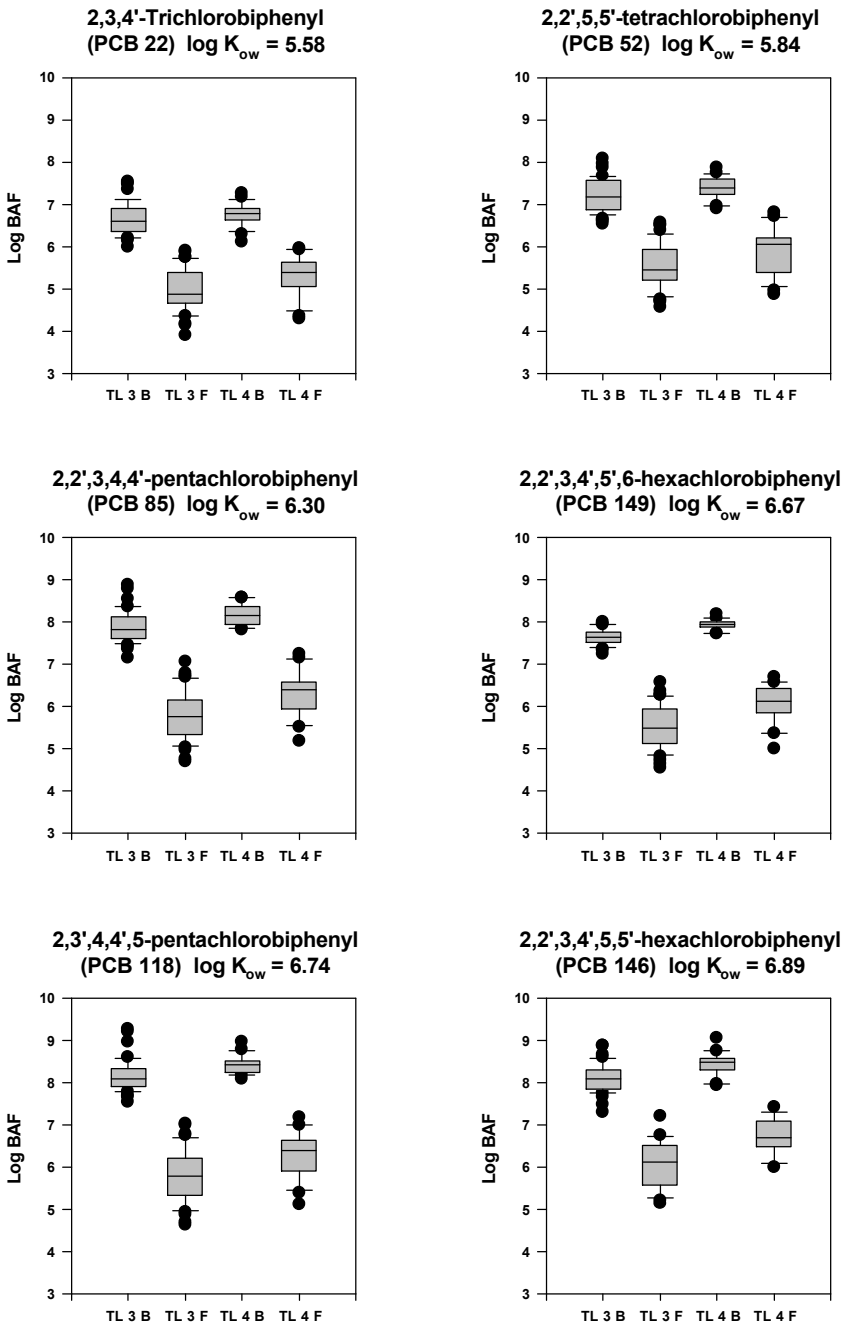

Figure 5-2. Box plots comparing baseline (TL 3 or 4 B) and field-measured (TL 3 or 4 F) BAFs for six PCB congeners obtained from Green Bay, Lake Ontario, and Hudson River ecosystems for 13 fish species with samples segregated according to year classes and sampling location, e.g., 4-year-old walleye from zone 4 in Green Bay and adult perch from RM 194 in the Hudson River. For box plots, the median is the line inside the box, the 25th and 75th percentiles are the ends of the box, the 10th and 90th percentiles are the T-lines, and outliers, points beyond the 10th and 90th percentiles, are the dots (●).

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5.2.1 Determination of BSAF Values

As shown in Equation 5-3, the BSAF is determined by relating the lipid-normalized concentration of a chemical in a tissue or organism to the organic carbon-normalized concentration of the chemical in surface sediment. A BSAF is expressed in grams of organic carbon in sediment per gram lipid in tissue.

$$\mathbf{BSAF} = \frac{C_l}{C_{soc}} \qquad \text{(Equation 5-3)}$$

where:

C_R = lipid-normalized concentration of chemical in tissues
C_{soc} = concentration of chemical in dry sediment, normalized to sediment organic carbon

The lipid-normalized concentration of a chemical in an organism (C_R) is determined by:

$$C_l = \frac{C_t}{f_l} \qquad \text{(Equation 5-4)}$$

where:

C_t = concentration of chemical in tissue
f_R = fraction of the tissue that is lipid

The sediment organic carbon-normalized concentration (C_{soc}) is determined by:

$$C_{soc} = \frac{C_s}{f_{soc}} \qquad \text{(Equation 5-5)}$$

where:

C_s = concentration of chemical in dry sediment
f_{soc} = fraction of dry sediment that is organic carbon

The appropriate use of BSAFs for calculation of baseline BAFs does not require the existence of steady state between the chemical mass loading and concentrations in sediments. However, BSAFs are most useful when measured under conditions in which chemical concentrations in water are linked to slowly changing concentrations in sediment. BSAFs

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measured when concentrations in water are rapidly changing, either through onset of contamination or the abrupt cessation of loading to the water, are likely to be unreliable without additional modeling to extrapolate the values to longer term or steady-state conditions.

BSAFs are rarely measured for ecosystems at thermodynamic equilibrium, so a BSAF inherently includes a measure of the "disequilibrium" associated with the distribution of a chemical in the ecosystem. The deviation of a BSAF from the expected equilibrium value of approximately 1-2 is determined by the net effect of all factors that contribute to the disequilibrium between sediment and aquatic organisms. A value greater than 1-2 can occur through biomagnification or when surface sediment has not reached steady state with water. A value of less than 1-2 can occur from diagenesis of organic carbon in sediments, kinetic limitations for chemical transfer from sediment to water or water to the food web, and biological processes (such as growth or metabolism/biotransformation of the chemical in biota or its food web).

5.2.2 Relationship of Baseline BAFs to BSAFs

Both BSAFs and baseline BAFs can provide good measures of the relative bioaccumulation potential of hydrophobic organic chemicals if based on accurate measurements of concentrations in appropriate samples of biota, sediment, and water. When calculated from a common organism-sediment-water sample set, chemical-specific differences in BSAFs or baseline BAFs reflect the net effect of biomagnification, metabolism, bioenergetics, and bioavailability factors on each chemical's bioaccumulation. The purpose of method 2 is to convert the bioaccumulation information contained in a measured BSAF to the corresponding baseline BAF value for a chemical. The relationship between a measured BSAF for a chemical and its baseline BAF depends strictly on the value of the chemical's sediment-water concentration quotient, (J_{socw}). Method 2 uses measurements of J_{socw} for reference chemicals (r), $(J_{socw})_r$s, to determine the value of (J_{socw}) for a chemical of interest, i, which is unmeasurable. $(J_{socw})_r$s are determined by:

$$(J_{socw})_r = \frac{(C_{soc})_r}{(C_w^{fd})_r} \qquad \text{(Equation 5-6)}$$

where:

$(C_{soc})_r$ = concentration of a reference chemical in dry sediment, normalized to sediment organic carbon

$(C_w^{fd})_r$ = concentration of the reference chemical that is freely dissolved in water

From the definitions of BAF_R^{fd} (Equation 2-5), BSAF (Equation 2-14), and J_{socw}, the sediment-water column concentration quotient (Equation 2-18), the relationship between J_{socw}, BAF_R^{fd} and BSAF may be derived for chemical i:

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$$(\Pi_{socw})_i = \frac{(C_{soc})_i}{(C_w^{fd})_i} = \frac{(BSAF_R^{fd})_i}{(BSAF)_i} \qquad \text{(Equation 5-7)}$$

Equation 5-7 can be rearranged to give $(BAF_R^{fd})_i = (BSAF)_i \cdot (\Pi_{socw})_i$. Then $(BSAF)_i \cdot (\Pi_{socw})_i$ can be substituted for $(BAF_R^{fd})_i$ in equation 2-4 to express the baseline BAF for chemical i as:

$$(\text{Baseline BAF})_i = (BSAF)_i \, (\Pi_{socw})_i - \frac{1}{f_t} \qquad \text{(Equation 5-8)}$$

Equation 5-8 reveals that a baseline BAF could be directly estimated from a BSAF if a reasonably certain estimate of Π_{socw} is available for the chemical. Since ecosystems are often not under steady-state chemical loading conditions, uncertainty is expected to be less when $(\Pi_{socw})_i$ is based on measurements for chemicals with similar K_{ow}s.

5.2.3 Derivation of the Baseline BAF Equation for Method 2

In many cases, the fugacity ratios between sediments and water (Π_{socw}/K_{ow}) for both reference chemicals and the chemical of interest are arguably similar. In fact, this similarity provides a useful criterion for the selection of reference chemicals. In cases where evidence exists for a significant difference, the explicit difference may be represented by $D_{i/r}$:

$$D_{i/r} = \frac{(\Pi_{socw})_i / (K_{ow})_i}{(\Pi_{socw})_r / (K_{ow})_r} \qquad \text{(Equation 5-9)}$$

Thus,

$$(\Pi_{socw})_i = \frac{(D_{i/r}) \, (\Pi_{socw})_r \, (K_{ow})_i}{(K_{ow})_r} \qquad \text{(Equation 5-10)}$$

By substituting Equation 5-10 into Equation 5-8, the method 2 equation (5-11) is obtained. For each aquatic species for which a field-measured BSAF for a chemical of interest, i,

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is available, a baseline BAF may be calculated using the following equation with an appropriate value of $(J_{socw}/K_{ow})_r$:

$$(\text{Baseline BAF})_i = (\text{BSAF})_i \frac{(D_{i/r})\,(J_{socw})_r\,(K_{ow})_i}{(K_{ow})_r} - \frac{1}{f_i} \qquad \text{(Equation 5-11)}$$

where:

$(BSAF)_i$	=	biota-sediment accumulation factor for chemical of interest "i"
$(J_{socw})_r$	=	sediment-water column concentration quotient of reference chemical "r"
$(K_{ow})_i$	=	*n*-octanol-water partition coefficient for chemical of interest "i"
$(K_{ow})_r$	=	*n*-octanol-water partition coefficient for reference chemical "r"
$D_{i/r}$	=	ratio between J_{socw}/K_{ow} for chemicals "i" and "r" (normally chosen so that $D_{i/r} = 1$)

5.2.4 Sampling and Data Quality Considerations

Reference chemicals with J_{socw}/K_{ow} similar to that of the chemical of interest are preferred for method 2 and often are available. Theoretically, the difference between sediment-to-water fugacity ratios for two chemicals, "i" and "r" ($D_{i/r}$), can be used when reliable reference chemicals that meet the fugacity equivalence condition are not available. Nonionic organic chemicals with concentrations in water at approximate steady state with respect to concentrations in surface sediments should have similar, if not equal, values of J_{socw}/K_{ow} that are related to the fraction of organic carbon in suspended solids when compared with the fraction of organic carbon in the surface sediments. When steady-state conditions are not present, as is often the case, J_{socw}/K_{ow} values for related chemicals may be similar. Similarity of J_{socw}/K_{ow} for two chemicals can be indicated on the basis of similarities in molecular structure, which lead to similar physical chemical behavior in water (persistence, volatilization), similar mass loading histories, and similar concentration profiles in sediment cores. In many cases, PCBs serve as effective reference chemicals.

The following sampling and data quality considerations should be met when field-measured BSAFs are used to predict BAFs:

1. The reference chemicals and the chemical of interest should have similar physicochemical properties, as well as persistence in water and sediment.

2. When possible, $(J_{socw})_r$ data for several reference chemicals with similar K_{ow}s should be obtained from the same water and sediment samples to ensure that predictions are more robust than those that would be obtained with only one reference chemical.

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3. Data for several reference chemicals and the chemical of interest should come from a common organism-water-sediment data set for a particular site. $(C_{soc})_r$ and $(C_{soc})_i$ should be measured from the same sediment samples, because this eliminates uncertainty attributable to spatial heterogeneity of C_{soc}.

4. The K_{ow} value for the target and reference chemicals should be selected as described in Section 4.5 of this TSD.

5. Whenever possible, the loadings history of the reference chemicals and the chemical of interest should be similar, such that their sediment-water disequilibrium ratios (J_{socw}/K_{ow}) would not be expected to be substantially different ($D_{i/r}$ ~ 1).

6. Samples of surface sediments (0-1 cm is ideal) should be collected from locations in which carbonaceous sediment, containing the reference chemicals and the chemical of interest, is regularly deposited and is representative of average surface sediment in the vicinity of the organism.

7. All sampling and data quality considerations described in Section 5.1.1 for determining BAF_T^ts should also be met.

5.2.5 Assumptions and Limitations

Although EPA is currently restricting the application of this method for baseline BAF derivation to nonionic organic chemicals with a log K_{ow} of $4, this restriction primarily reflects lack of validation of this method as applied to chemicals with a log K_{ow} of < 4. In addition, the need for this method is greater for chemicals with higher log K_{ow}s because of the difficulties associated with detecting and measuring such chemicals in ambient water. Future development and evaluation of this method may lead to its application to a broader range of chemicals.

The primary assumptions and limitations discussed in Section 5.1.1 for method 1 also apply to method 2. The primary limitation associated with method 2 for calculating and applying the baseline BAF—namely, variability of C_w^{fd}—is common to all methods and models for predicting and measuring BAFs. In deriving Equation 5-10, the assumption is made that J_{socw} values are chosen from a common sediment data set (i.e., both BSAF and J_{socw} are based on the same value for C_{soc}). In the event that this cannot be done, the relative percent error in the baseline BAF associated with the C_{soc} inequality will equal 100 times the difference in C_{soc}s used for the BSAF and J_{socw}, divided by the C_{soc} used for the BSAF measurement.

Although EPA recommends that C_{soc} values represent spatially averaged surface sediment contamination levels in the region affecting the organism's exposure, method 2 should be accurate even when the C_{soc} value used for the BSAF and J_{socw} does not well represent spatially averaged conditions. This is because the C_{soc} need only reflect the relative level of contamination of sediments over time. The magnitude of errors associated with fluctuations in C_w^{fd} will be the

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same for method 2 as for method 1. Temporal changes in C_w^{fd} are responsible for most deviations from steady state between biota, water, and sediments.

Inaccuracies associated with the use of J_{socw}/K_{ow} from reference chemicals to estimate C_w^{fd}s for chemicals of interest under method 2 have a linear impact on the accuracy of baseline BAFs. For example, if J_{socw}/K_{ow} is 10 but the estimate used is 20, the calculated baseline BAF will be greater than the true value by a factor of 2. The measurements of J_{socw}/K_{ow} to date indicate an expected range of 5–40 for most contamination scenarios. If the data quality considerations for choosing J_{socw}/K_{ow} for the chemical of interest are followed, the magnitude of the errors associated with the choice of J_{socw}/K_{ow} should be no greater than twofold.

The strength of method 2 is that it utilizes measurements of relative (not absolute) differences in bioaccumulation between chemicals with structural similarity. When properly sampled, sediments provide time-stable measures of concentrations of persistent bioaccumulative chemicals in aquatic systems. Method 2 is currently the only viable method for estimating baseline BAFs for nonionic organic chemicals with (1) a log K_{ow} of $4, (2) concentrations in water that are often undetectable, and (3) significant rates of chemical metabolism by organisms. Important examples of chemicals with these characteristics are polychlorinated dibenzo-*p*-dioxins, polychlorinated dibenzofurans, and non-orthochlorinated biphenyls.

5.2.6 Validation of Method 2

For method 2, validation efforts were conducted with data collected from three aquatic ecosystems in the United States: Lake Ontario; Green Bay/Fox River, Wisconsin; and the Hudson River, New York. EPA previously published information on validation of the method 2 approach by using data on PCBs, chlorinated benzenes, pesticides, and 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD) collected from Lake Ontario and the mid-bay region of Green Bay (USEPA, 1995c). Baseline BAFs for PCBs, chlorinated benzenes, and some pesticides were predicted from BSAFs for Lake Ontario salmonids and compared with measured baseline BAFs from the same system. The baseline BAFs predicted from BSAFs were within a factor of 4 of the measured baseline BAFs. Furthermore, when predicted baseline BAFs for TCDD and PCBs from Green Bay salmonids and Lake Ontario brown trout were compared, the baseline BAFs predicted from BSAFs were generally within a factor of 2 of the measured baseline BAFs. Although there were a few outliers in the observed trends, the results of this validation effort showed method 2 generally works well, not only for predicting baseline BAFs with data from the same ecosystem (Lake Ontario), but also for predicting baseline BAFs between systems (Green Bay vs. Lake Ontario).

For this TSD, Burkhard et al. (2003a) extended the previous validations for method 2 by comparing results of field-measured baseline BAFs with baseline BAFs predicted from BSAFs using additional PCB data collected from Green Bay/Fox River and the Hudson River. The data sets for this latest validation effort were selected from the 1989–1990 Green Bay Mass Balance Study (http://www.epa.gov/grtlakes/gbdata) and the Hudson River PCBs Reassessment Remedial Investigation/Feasibility Study (USEPA, 1998). The former study included data from the lower Fox River and the inner, middle, and outer zones of Green Bay. The Hudson River data were

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collected over several years by a number of Federal and State agencies and private groups and were assembled into a single database (USEPA, 1998) from which data were selected for this analysis. The reference PCB congeners used in this validation effort included those used in the previous validations (PCB 52, 105, 118) (USEPA, 1995b) as well as PCBs 18, 28, 149, 174, and 180. This validation was performed using the geometric mean of the baseline BAFs predicted by using as many as possible of the eight reference PCB congeners listed above. As noted previously (see Section 5.4.2), EPA recommends that several reference chemicals be used with method 2 and that K_{ow}s be matched as closely as possible because slightly smaller predictive errors were observed in the validation study when the chemicals of interest and the reference chemicals had more closely matched K_{ow}s (Burkhard et al., 2003a). The recent validation effort by Burkhard et al. (2003a) also included baseline BAFs for several fish species in addition to salmonids (e.g., carp, walleye, shad, alewife, yellow perch, white perch, pumpkinseed, red-breasted sunfish, and largemouth bass), some of which spanned several age classes.

A summary of the validation exercise is presented here and a detailed discussion is provided by Burkhard et al. (2003a). Baseline BAFs predicted with method 2 were plotted against field-measured baseline BAFs. The geometric mean baseline BAF predicted from BSAFs are plotted; these differ from the individual reference chemical predictions only in terms of vertical displacement due to the differences in congener-specific J_{socw}. The ratio of predicted-to-measured congener-specific baseline BAFs ($BAF_{predicted}/BAF_{measured}$) was used to evaluate the agreement between method 2-derived baseline BAFs and field-measured baseline BAFs. Table 5-2 presents zone (Green Bay data) and location-specific (Hudson River data) statistics for the $BAF_{predicted}/BAF_{measured}$ ratio. Table 5-2 also presents the percentage of $BAF_{predicted}/BAF_{measured}$ ratios that fall within specified ranges of the distribution. In general, the agreement between method 2-predicted baseline BAF and field-measured baseline BAF values is very good, with a majority of predicted BAF values falling within a factor of 2 of the field-measured BAF values. In addition, >90% of method 2-predicted BAFs (95% from Green Bay and 91% from Hudson River) are within a factor of 5 of the field-measured baseline BAFs. Table 5-3 presents exceedance levels (i.e., certain points within the data distribution) for the ratio of predicted to measured congener-specific baseline BAFs ($BAF_{predicted}/BAF_{measured}$) for each fish species and ecosystem zone/location. For most zones in Green Bay, the 95% exceedance levels (i.e., 95% of the $BAF_{predicted}/BAF_{measured}$ values) fall within the range of 0.2 (one-fifth of the predicted baseline BAF) to 5.0 (five times the predicted baseline BAF). Results for the Hudson River indicated generally similar agreement between method 2-predicted baseline BAFs and field-measured baseline BAFs, although exceedance levels are noticeably wider at river mile (RM) 169. Method 2 also appears to overpredict BAFs at RM 122 and 114, the only locations where bias in this method was found. Overall, these analyses support the use of method 2 to estimate baseline BAFs from field-measured BSAFs.

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Table 5-2. Validation Statistics for Method 2: Ratio of Baseline $BAF_{predicted}$/Baseline $BAF_{measured}$[a]

Location	Method 2: Exceedance Levels and Comparison Statistics					
	95%	Mean	Median	5%	% within 2x	% within 5x
Green Bay						
Zone 1	0.39	0.88	0.88	1.66	87.6	100
Zone 2a	0.25	1.27	0.89	3.47	69.8	92.8
Zone 3a	0.21	1.25	0.73	3.78	51.5	94.1
Zone 3b	0.16	1.08	0.69	2.71	53	91.4
Zone 4	0.31	3.33	1.07	3.79	31.9	97.4
All zones	0.22	1.53	0.81	3.29	55.7	94.5
Hudson River						
RM 194	0.46	1.12	0.99	2.12	81.9	95.2
RM 189	0.33	1.00	1.03	1.55	87.5	100
RM 169	0.11	2.01	0.59	9.91	19.0	68.3
RM 144	0.67	1.19	0.97	2.14	92.3	100
RM 122	0.70	2.43	2.16	4.81	45.8	95.8
RM 114	1.20	3.86	3.78	6.91	16.7	83.3
All stations	0.13	1.50	1.10	4.42	64.9	90.7

[a]Includes number of species and range in "n" across sites
RM = river mile.

Table 5-3. Exceedance Levels for Ratio of Method 2-Predicted Baseline BAFs (Geometric Mean) to BAF_T^ts from Green Bay and Hudson River

Location	Percentile			
	5%	10%	90%	95%
Green Bay Zone 1				
Adult alewife	0.34	0.45	1.27	1.39
Age 1 carp	0.4	0.48	1.21	1.4
Age 1 walleye	0.4	0.5	1.26	1.61
Age 3 walleye	0.4	0.49	1.26	1.63
Age 4 walleye	0.4	0.49	1.2	1.4
Green Bay Zone 2a				
YOY alewife	0.27	0.37	2.88	3.22
Adult alewife	0.29	0.42	2.89	3.28
Age 2 carp	0.33	1.42	2.89	3.31
Age 8 carp	0.27	0.37	2.88	3.22
YOY shad	0.2	0.3	2.88	3.19
YOY smelt	0.27	0.36	2.89	3.25
Adult smelt	0.27	0.37	2.88	3.22
Age 3 walleye	0.27	0.37	2.88	3.22
Age 4 walleye	0.27	0.37	2.88	3.22
Green Bay Zone 3a				
YOY alewife	0.22	0.3	2.62	3.87
Adult alewife	0.22	0.31	2.45	3.25
Age 1 carp	0.24	0.28	2.44	2.94

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Location	Percentile			
	5%	10%	90%	95%
YOY smelt	0.2	0.27	2.74	3.93
Adult smelt	0.2	0.26	2.53	3.82
Age 2 brown trout	0.2	0.26	2.45	3.21
Age 3 brown trout	0.2	0.26	2.59	3.85
Age 4 walleye	0.2	0.26	2.44	3.17
Green Bay Zone 3b				
Adult alewife	0.15	0.26	2.27	2.66
Age 8 carp	0.15	0.23	2.18	2.67
Age 10 carp	0.17	0.27	2.25	2.65
YOY smelt	0.15	0.23	2.25	2.65
Adult smelt	0.15	0.23	2.25	2.65
Age 2 brown trout	0.15	0.23	2.25	2.65
Age 3 brown trout	0.15	0.23	2.25	2.65
Age 3 walleye	0.17	0.27	2.26	2.66
Age 4 walleye	0.15	0.23	2.24	2.65
Green Bay Zone 4				
Adult alewife	0.31	0.33	2.92	3.79
Age 10 carp	0.33	0.34	2.91	3.37
YOY smelt	0.31	0.33	2.92	3.44
Adult smelt	0.29	0.33	3	3.81
Age 2 brown trout	0.31	0.33	2.91	3.29
Age 3 brown trout	0.32	0.34	2.96	3.8
Age 4 walleye	0.32	0.34	2.91	3.34
Age 5 walleye	0.32	0.34	2.91	3.32
Hudson River RM 194				
Carp	0.46	0.53	1.78	2.02
Yellow perch	0.51	0.66	1.85	2.06
Red-breasted sunfish	0.46	0.54	1.77	2.01
Largemouth bass	0.46	0.54	1.77	2.01
Hudson River RM 189				
Yellow perch	0.32	0.46	1.53	1.78
Pumpkinseed	0.33	0.48	1.52	1.75
Red-breasted sunfish	0.33	0.5	1.52	1.73
Largemouth bass	0.33	0.5	1.52	1.73
Hudson River RM 169				
Yellow perch	0.11	0.12	4.79	6.85
Pumpkinseed	0.11	0.12	4.97	7.09
Red-breasted sunfish	0.11	0.12	4.79	6.85
Largemouth bass	0.11	0.12	4.79	6.85
Hudson River RM 144				
Yellow perch	0.67	0.7	1.82	2.14
Hudson River RM 122				
Yellow perch	0.86	1.05	4.41	5.37
White perch	0.64	0.77	3.29	4.01
Hudson River RM 114				
White perch	1.2	1.43	4.99	6.91

RM = river mile; YOY = young of year.

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5.3 METHOD 3: DERIVING BASELINE BAFs FROM LABORATORY-MEASURED BCFs (BCF_T^ts) AND FCMs

Method 3 in Procedure 1 is appropriate for nonionic organic chemicals that have moderate-to-high hydrophobicity (log K_{ow} $4) and low potential for being metabolized. For method 3, a laboratory-measured BCF (BCF_T^t) and FCM are used to predict a baseline BAF. The BCF_T^t must be used in conjunction with an FCM because nonaqueous routes of exposure and subsequent biomagnification are of concern for the types of chemicals to which Procedure 1 applies. Although a BCF_T^t accounts for chemical metabolism that occurs in the organism used to calculate the BCF_T^t, it does not account for metabolism that may occur in other organisms of the aquatic food web. Method 3 uses the following baseline BAF and BCF equations:

$$\text{Baseline BAF} = \text{FCM} \cdot \left[\frac{BCF_T^t}{f_{fd}} - 1 \right] \cdot \frac{1}{f_l} \qquad \text{(Equation 5-12)}$$

where:

BCF_T^t	=	Total BCF ($BCF_T^t = C_t/C_w$)
f_{fd}	=	fraction of the total concentration of chemical in water that is freely dissolved
f_l	=	fraction of the tissue that is lipid
FCM	=	the food-chain multiplier for the appropriate trophic level, obtained by linear interpolation (Table 4-6) or from appropriate field data

The technical basis for Equation 5-12 is provided in Appendix A. Presented below are detailed discussions and information on selecting appropriate BCF_T^ts and FCMs and the derivation of FCMs using food web models and field data.

5.3.1 Sampling and Data Quality Considerations

The BCF_T^t should be calculated by using information on the total concentration of the chemical in the tissue of the organism and the total concentration of the chemical in the laboratory test water. The data used to calculate a BCF_T^t should be thoroughly reviewed to assess the quality of the data and the overall uncertainty in the BCF value. The following general criteria apply in determining the acceptability of BCF_T^t. Because no guidance can address all of the variation in experimental designs and data found in the literature, best professional judgment will be necessary to supplement these data quality guidelines in selecting the best available information and using it appropriately.

1. Aquatic organisms used to calculate a BCF_T^t should be representative of those aquatic organisms commonly consumed in the United States. An aquatic organism that is not commonly consumed in the United States can be used to calculate an acceptable BCF_T^t provided that the organism is considered to be a reasonable surrogate for a commonly consumed organism. Information on the

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ecology, physiology, and biology of the organism should be reviewed when assessing whether an organism is a reasonable surrogate.

2. The test organism should not be diseased, unhealthy, or adversely affected by the concentration of the chemical, because these conditions may alter accumulation of chemicals.

3. The test organisms should be exposed to the chemical under flow-through or renewal conditions.

4. The concentrations of the chemical in the laboratory test water must not exceed the solubility of the chemical in water. Micelles, which indicate the chemical is not dissolved, should not be present in the exposure water. Older BCF_T^t measurements for highly hydrophobic chemicals, such as those with a log K_{ow} of > .6 are often unreliable because solubility limits were exceeded or the chemical was present in the exposure water in the form of micelles.

5. The total concentration of the chemical in the water should be measured and should be relatively constant during the exposure period.

6. The concentrations of POC and DOC in the study water should be measured or reliably estimated.

7. The percent of the tissue or organism that is lipid (i.e., fraction lipid, f_R) must be measured or reliably estimated to permit lipid normalization.

8. The calculation of the BCF_T^t should appropriately address growth dilution, which can be particularly important for poorly depurated chemicals.

9. Other aspects of the methodology used should be similar to those described by the American Society of Testing and Materials (ASTM, 1990) and U.S. EPA Ecological Effects Test Guidelines (USEPA, 1996).

10. If BCF_T^t consistently increases or decreases as the concentration of the chemical increases in the test solutions (and this variation is not due to changes in lipid fraction of organisms, freely dissolved fraction of chemical in water, or changes in health of the organisms), the BCF determined at the concentration of chemical that is closest to the expected AWQC concentration should be used in deriving the AWQC.

11. BCF_T^t may be based on measurement of radioactivity only when the BCF_T^t is intended to include metabolites, when there is confidence that there is no interference due to metabolites of the parent chemical, or when studies are conducted to determine the extent of metabolism, thus allowing for a proper correction.

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12. All considerations described in Section 4.4.2 for determining FCMs should also be met.

5.3.2 Assumptions and Limitations

In using method 3, EPA will assume that (1) a high-quality BCF_T^t is a better measure of the bioconcentration potential of a chemical than simply assuming that the baseline BCF is equal to K_{ow}, an assumption used with method 4, (2) the measured BCF_T^t and the baseline BAF predicted with method 3 are independent of chemical concentration in the water, and (3) FCMs account for biomagnification processes caused by the consumption of contaminated food in aquatic food webs. Assumptions, limitations, and uncertainties associated with FCMs and concentration independence of BCF_T^t and BAF_T^t are discussed in Sections 4.4.1 and 5.1.4, respectively.

BCF_T^t for chemicals that are metabolized by the test organisms incorporate the effects of the metabolism on the concentration of chemical that is accumulated in the organism. However, if induction of metabolic systems is required or co-occurring contaminants (i.e., that exist in the environment) are required for the metabolism to take place, then the effect of metabolism may not be captured in the BCF_T^t measurement. Therefore, the range of effects of metabolism on BCF_T^t will be chemical specific. Nevertheless, EPA believes that high-quality BCF_T^ts provide a better measure of bioconcentration potential for chemicals than simply assuming the baseline BCF is equal to the chemical's K_{ow} because of the potential of the BCF_T^t to include the effects of metabolic processes. Furthermore, BCF_T^ts can be obtained for specific species of interest. This specificity may reduce uncertainties associated with extrapolating bioaccumulation factors among species with known or suspected differences in metabolic pathways or capacity.

For method 3, baseline BAFs are calculated with the FCM and the BCF_T^t. As discussed in Section 4.4, FCMs that will be used by EPA in deriving national BAFs are derived using the Gobas food web model with a number of assumptions and input parameters, namely, no metabolism, an assumed food web structure, and $J_{socw}/K_{ow} = 23$. Limitations and uncertainties associated with the FCMs have been discussed previously (see Section 4.4.1), and these limitations and uncertainties are incorporated into the baseline BAFs derived using method 3.

The baseline BAFs derived with method 3 for chemicals that are metabolized will not include the effects of all metabolism processes because of the assumption of no metabolism used in deriving the FCMs. However, the method will incorporate those metabolism processes or effects that are captured in the BCF measurement. Baseline BAFs predicted from measured BCF for chemicals that are metabolized will be smaller than those predicted from measured BCFs for chemicals of equal hydrophobicity but which are not metabolized.

A major limitation associated with method 3 is the current lack of high-quality measured BCF data for highly hydrophobic chemicals in any organism class. This lack of data is due principally to the difficulties associated with performing BCF measurements for highly insoluble (hydrophobic) chemicals. Conditions appropriate for performing these measurements are described in Section 5.3.1. When evaluating literature BCF data, one often finds measurements

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performed with (1) conditions that do not meet current standards, for example, a solvent carrier such as acetone is used to introduce the chemical into the aqueous phase or chemical solubilities in water are exceeded, and (2) poor and/or incomplete reporting of measurement conditions and parameters, for example, no lipid data, no POC and DOC data, and/or an inability to determine whether steady-state conditions were obtained in the experiment. In addition, some BCFs were measured with chemical mixtures, such as Aroclors, and resolving the effects of co-occurring chemicals on micelle formation is often intractable. As BCF data become available for highly hydrophobic chemicals in the future, the impact of this limitation will lessen.

5.3.3 Validation of Method 3

To date, EPA has performed only a limited number of evaluations of method 3 because of a lack of BCF data of the appropriate quality, as described in Section 5.1.2. and in Section 5.3.2. For example, EPA invested considerable effort in examining the scientific literature for measured BCFs for PCB congeners and was not able to find BCFs of appropriate quality.

Burkhard et al. (1997) evaluated method 3 by using field data for chlorinated benzenes, butadienes, and hexachloroethane from Bayou d'Inde, Lake Charles, Louisiana. The results of this evaluation showed that field-measured baseline BAFs were within a factor of 3 for 88% and a factor of 5 for 94% of the baseline BAFs predicted using method 3 (n = 32) (Figure 5-3). The median of the ratios of the field-measured baseline BAFs to predicted baseline BAFs was 1.03, and approximately one-half of the predicted baseline BAFs were less than the measured baseline BAFs (53%, n = 32). The chemicals whose field-measured baseline BAFs were in least agreement with the predicted baseline BAFs were hexachloroethane, Z-pentachlorobutadiene, and hexachlorobutadiene for *Callinectes sapidus* (blue crab). Metabolism of these chemicals by *C. sapidus* is suggested as the cause of the poor agreement between the field-measured BAFs and the baseline BAFs predicted using method 3 (Burkhard et al., 1997).

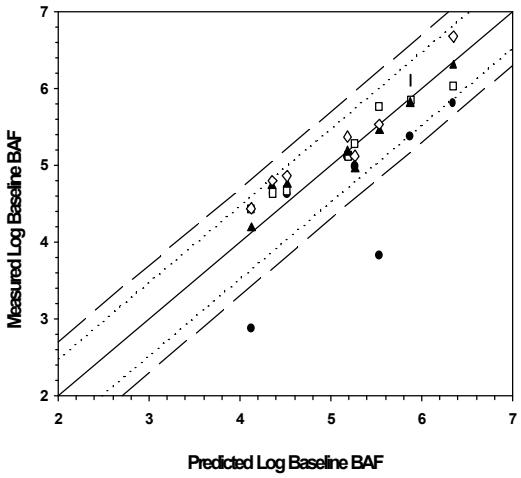

Figure 5-3. Relationship between measured and predicted baseline BAFs for method 3. The dotted and dashed lines represent a factor of 3 and 5 difference between the measured and predicted baseline BAFs, respectively. Baseline BAFs measured using *Callinectes sapidus* (Ž), *Micropoganias undulatus* (•), *Fundulus heteroclitus* (~), and *Brevoortia patronus* (•).

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5.4 METHOD 4: BASELINE BAF DERIVED FROM K_{ow} × FCM

Method 4 in the tiered hierarchy of Procedure 1 consists of using K_{ow} and an appropriate FCM for estimating the baseline BAF. In Procedure 1, this method is used only for nonionic, moderate to highly hydrophobic chemicals whose metabolism is considered negligible or is unknown. In this method, the K_{ow} is assumed to be equal to the baseline BCF, and thus the organic carbon and lipid normalization procedures are not needed. To account for biomagnification in method 4, the K_{ow} value is multiplied by an appropriate FCM. Method 4 uses the following baseline BAF equation:

$$\text{Baseline BAF} = K_{ow} \times \text{FCM} \qquad \text{(Equation 5-13)}$$

where:

FCM = food-chain multiplier for the appropriate trophic level, obtained by linear interpolation (Table 4-7) or from appropriate field data

K_{ow} = *n*-octanol-water partition coefficient

Detailed information on selection of appropriate FCMs and K_{ow} values can be found in Section 4.4 and Appendix B, respectively.

5.4.1 Assumptions and Limitations

A number of assumptions are associated with baseline BAFs predicted with method 4. First, it is assumed that the K_{ow} is equal to the chemical's baseline BCF for a non-metabolized chemical. Second, it is assumed that there is no metabolism of the chemical in the food web. Third, the assumptions incorporated into the FCMs—namely, $J_{socw}/K_{ow} = 23$, mixed benthic and pelagic food web, and adequacy of the Gobas model—are directly incorporated into the predictions made with method 4. Discussion of these assumptions and limitations is presented below.

Method 4 assumes that the K_{ow} is equal to the chemical's baseline BCF. Use of the K_{ow} in place of the baseline BCF is supported by equilibrium partitioning theory. This theory assumes that (1) the bioconcentration process can be viewed as a partitioning of a chemical between the lipid of aquatic organisms and water and the K_{ow} is a useful surrogate for this partitioning process, and (2) a linear relationship exists between the K_{ow} and the BCF. Mackay (1982) demonstrated the usefulness of K_{ow} as a surrogate for this partitioning process by presenting a thermodynamic basis for the partitioning process for bioconcentration. In theory, it follows that the baseline BCF (i.e., BCF based on the concentration of chemical in lipid of organisms and freely dissolved in water) should be similar, if not equal, to the K_{ow} for organic chemicals. Numerous investigations have provided empirical data to support this theory. As summarized by Isnard and Lambert (1988), numerous studies have demonstrated a linear relationship between the log K_{ow} for organic chemicals and the log BCF measured for fish and other aquatic organisms exposed to those chemicals. In addition, when the regression equations are constructed with BCFs reported on a lipid-normalized basis, the slopes and intercepts are not significantly different from 1 and 0,

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respectively. For example, de Wolf et al. (1992) adjusted a relationship reported by Mackay (1982) to a 100% lipid basis (lipid-normalized basis) and obtained the following relationship:

$$\log BCF = 1.00 \log K_{ow} + 0.08 \qquad \text{(Equation 5-14)}$$

For chemicals with large log K_{ow}s (>6.0), reported BCFs are often not equal to the K_{ow} even for nonmetabolized chemicals, because the measurements were not performed and/or reported with appropriate experimental conditions. BCFs for nonmetabolized chemicals are equal to the K_{ow} when the BCFs are reported on a lipid-normalized basis; determined using the concentration of the chemical that is freely dissolved in the exposure water; corrected for growth dilution; determined under steady-state conditions or from accurate measurements of the chemical's uptake (k_1) and elimination (k_2) rate constants; and determined with no solvent carriers in the exposure. If, when reviewing the literature for BCFs, EPA cannot verify that measured BCFs are measured under the appropriate conditions, as described in Section 5.3.1, EPA will use the K_{ow} as an approximation of the baseline BCF.

As discussed in Section 3.1.4, method 4 is used only for nonionic organic chemicals with log K_{ow}s greater than or equal to 4 and low rates of metabolism (Figure 3-1). The restriction of the use of method 4 to only non-metabolized chemicals is based on the fact that the assumption that K_{ow} equals BCF is valid only for non-metabolizable chemicals. When a chemical is metabolized by an organism during the measurement of BCF, the measured BCF will be smaller than the K_{ow}. In addition, as discussed in Section 4.4, FCMs are also calculated using the assumption that no metabolism of the chemical takes place in the food web. If method 4 is used when metabolism of the chemical occurs in the food web, predicted BAFs will be larger than field-measured BAFs. For detailed information on the assumptions incorporated into the FCMs, refer to Section 4.4.

5.4.2 Validation of Method 4

As noted in Section 5.2.6, Burkhard et al. (2003a) have performed exercises to validate the predictive power of methods 2 and 4. The validation exercises were performed by using data collected from Lake Ontario, Green Bay/Fox River, the Hudson River, and Bayou d'Inde, Louisiana. With these data sets, baseline BAFs predicted using method 4 were plotted against field-measured baseline BAF values. The agreement between baseline BAFs predicted using method 4 and field-measured baseline BAF values is generally good for Green Bay, although not as good as was seen for method 2 (see Section 5.2.5 and Burkhard et al., 2003a). In Green Bay, 59% of the baseline BAFs predicted using method 4 are within a factor of 2 and 93% are within a factor of 5 of the measured baseline BAFs (Table 5-4). The validation exercises using the Green Bay/Fox River and Hudson River data are described in detail in Burkhard et al. (2003a).

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Table 5-4. Validation Statistics for Method 4: Ratio of Baseline $BAF_{predicted}$/Baseline $BAF_{measured}$

Location	Method 4: Exceedance Levels and Comparison Statistics					
	95%	Mean	Median	5%	% within 2x	% within 5x
Green Bay						
Zone 1	0.32	1.17	0.89	2.75	69.8	98.1
Zone 2a	0.17	1.17	0.74	3.40	54.6	91
Zone 2b	0.23	1.18	0.83	3.01	61.0	94.9
Zone 3a	0.33	1.58	1.05	4.71	64.0	94.7
Zone 3b	0.23	1.35	0.90	4.15	60.5	94
Zone 4	0.15	1.43	0.61	5.28	40.5	82.2
All zones	0.21	1.30	0.84	3.90	58.6	92.7
Hudson River						
RM 194	0.06	0.16	0.11	0.38	3.6	25.3
RM 189	0.12	0.26	0.20	0.55	9.0	55
RM 169	0.10	0.95	0.41	1.89	35.3	76.5
RM 144	0.42	0.72	0.67	1.14	76.5	100
RM 122	0.40	0.70	0.67	1.27	80.0	100
RM 114	0.40	0.78	0.73	1.29	76.9	100
All stations	0.08	0.5	0.24	1.07	26.3	60.7

RM = river mile.

The accuracy of baseline BAFs predicted with method 4 in the Hudson River varied among sites. Generally, the predicted baseline BAFs are biased low; this is evident in Table 5-4, where the mean and median predicted/measured ratios are less than 1 for all locations. At three of the six stations in the Hudson River (river miles 114, 122, and 144), there was good agreement between predicted and measured baseline BAFs (>75% within a factor of 2 and 100% within a factor of 5; Table 5-4). However, for river mile 169, agreement was not as good (35% within a factor of 2; 76% within a factor of 5). Finally, at two sites (river miles 189 and 194), there was substantial underprediction of measured baseline BAFs with method 4. On the other hand, for the Hudson River data set, the variability associated with baseline BAFs predicted using method 4 was generally smaller than that associated with method 2 (see Section 5.2.5 and Burkhard et al., 2003a).

Factors that might be involved with the underprediction of the baseline BAFs for river miles 169, 189, and 194 using method 4 include (1) the use of FCMs (Table 4-7) derived using conditions and parameters for the nation instead of for the Hudson River, (2) the use of field samples that were not temporally and/or spatially coordinated and/or representative of the ecosystem, and (3) the sampling of an ecosystem with rapidly changing conditions in recent

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Table 5-5. Summary Statistics: Differences Between Log Baseline BAFs Predicted with Method 4 and Log Baseline BAFs Measured from Lake Ontario (Oliver and Niimi, 1988) for Chemicals with Log K_{ow}s Exceeding 4

Statistic	Organism				
	Sculpin	Alewife	Small smelt	Large smelt	Piscivorous fish
Average	!0.01	!0.04	0.09	!0.28	!0.08
Standard deviation	0.35	0.36	0.37	0.35	0.36
Count	51	49	46	47	57
Median	!0.02	!0.06	0.14	!0.30	!0.08
Within 2x	63%	59%	61%	47%	58%
Within 5x	94%	94%	94%	92%	96%
Negative residual	53%	53%	59%	72%	56%
Positive residual	47%	47%	41%	28%	44%

history due to the collapse of the Allen Mill gate in 1991. Burkhard et al. (2003a) evaluated the influences of site-specific J_{socw}/K_{ow} values, the most important site-specific parameter in calculating FCMs (Burkhard, 1998), by deriving site-specific FCMs for river miles 169, 189, and 194 using J_{socw}/K_{ow} values of 40, 13, and 40, respectively, in comparison to the national value of 23 (see Section 4.4.1). The predictions using method 4 with the site-specific FCMs were still too small. Increasing the J_{socw}/K_{ow} values for river miles189 and 194 to 80 or 120 resulted in agreement between predicted and measured baseline BAFs comparable to that observed in Green Bay for method 4 (Table 5-4). The better agreement with much larger J_{socw} values is consistent with the possibility that the samples were not representative of the ecosystem. However, the collapse of the Allen Mill gate (see below) 2 years prior to the collection of the field samples in 1993 introduces substantial and unresolvable uncertainty into the existing conditions in the river.

The gate collapse introduced elevated and variable PCB concentrations (by orders of magnitude) into the river for approximately 15 months (QEA, 1999), and average concentrations in water declined substantially from 1992 to 1993 for all congeners. Since the Allen Mill gate is upstream of all the river mile locations used in this study, the most dramatic effects of this episodic loading would be observed at the upstream locations, with a lessening of its effect with increasing distance downstream. Better agreement with increasing distance downstream was observed and is consistent with the expected lessening of the effect with increasing distance downstream. Coincident with the gate failure, the lipid content of large mouth bass (and other fishes as well) declined to extremely low levels of 0.25% in 1991 and then recovered in 1992 and 1993, to 1.0% and 1.5%, respectively. Although the causative factors are unclear for the rapid decline in lipid contents, it appears that the food web was significantly disrupted. The overall importance of the gate collapse and rapidly declining chemical concentrations between 1992 and 1993 and unusual lipid contents in fish for river miles 189 and 194 upon the bias observed with method 4 at river miles 189 and 194 cannot be fully assessed with available data. At best, one can conclude that river miles 189 and 194 were strongly influenced by the gate collapse and that conditions in the river were not stable (e.g., sediment–water column chemical relationships, chemical concentrations in the water, and fish lipid contents were rapidly changing). In the derivation of FCMs for method 4, steady-state conditions in the food web are used, and chemical concentrations in the sediment and water are constant over time. The conditions present in the

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river at river miles 189 and 194 clearly violate the latter assumption of relatively stable chemical concentrations in sediment and water over time. Some or all of the above factors including sample representativeness might be responsible for the observed constant biases at river miles 169, 189, and 194. These biases have also been observed using a complex, time-dependent food web bioaccumulation model, calibrated to site-specific data for food web dynamics, species-specific bioenergetics, and chemical uptake and elimination data in the same time period at the same Hudson River locations as method 4 (QEA, 1999). These results further suggest unusual conditions in the river.

Burkhard et al. (1997) evaluated the predictiveness of method 4 against field-measured baseline BAFs for trophic level 3 fish sampled from the Bayou d'Inde for selected chlorinated benzenes, chlorinated butadienes, and hexachloroethane. Bayou d'Inde is a lowland channel that meanders through a brackish-freshwater marsh that is influenced by tide. This ecosystem is very different from either the Great Lakes or the Hudson River and provides a useful demonstration of the applicability of method 4 across different ecosystems. Because this evaluation of method 4 was conducted before the development of the final National BAF Methodology, it was performed with FCMs and default values for POC and DOC that are marginally different from those that are used in the National BAF Methodology (USEPA, 2000a). Burkhard et al. (1997) found good agreement between the predicted and measured baseline BAFs for both the fish and invertebrates sampled. Overall, approximately 90% of the predicted baseline BAFs were within a factor of 5 of the measured baseline BAFs, and the median ratio of the predicted baseline BAFs to the measured baseline BAFs was 1.64. As was observed in evaluating method 2, the baseline BAFs predicted with method 4 for hexachloroethane, Z-1,1,2,3,4-pentachlorobuta-1,3-diene, and hexachlorobuta-1,3-diene for blue crabs (*C. sapidus*) were smaller than the measured baseline BAFs. Higher Phase II metabolism activities in this species for this class of chlorinated chemicals is suggested to contribute to the difference between the predicted and measured BAFs.

The EPA also compared the baseline BAFs predicted with method 4 to measured BAFs for the Lake Ontario ecosystem (Table 5-5). The average differences between measured and predicted baseline BAFs were small for both forage and piscivorous fish, and more than 90% of the baseline BAFs predicted with method 4 were within a factor of 5 of the measured BAFs. The residuals (predicted minus measured) were evenly distributed, except for the large smelt. The trophic level for the large smelt is estimated to be .3.5, owing to its consumption of smaller forage fish, and consequently, it was anticipated that the predicted baseline BAFs with trophic level 3 FCMs would be slightly lower than the measured BAFs for this species.

As summarized above, the predictive accuracy of method 4 has been evaluated with field data from four different ecosystems. For the Lake Ontario, Green Bay/Fox River, and Bayou d'Inde ecosystems, baseline BAFs predicted with method 4 were in excellent agreement with the measured BAFs: More than 90% of the predicted baseline BAFs were within a factor of 5 of the measured baseline BAFs. In the Hudson River, for three of the sampling stations, baseline BAFs predicted with method 4 were in excellent agreement with measured BAFs: 100% of the predictions were within a factor of 5 of the measured baseline BAFs. For the other three sampling stations in the Hudson River, baseline BAFs predicted with method 4 were much smaller than the

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measured BAFs, but the predictions were consistent with those based on the complex site-specific time-dependent food web bioaccumulation model.

Overall, EPA believes that method 4 provides excellent predictions for ecosystems that have not recently experienced a major change or disruption in chemical loadings or flows. Of all the ecosystems examined, the extreme temporal dynamics observed for several important factors (e.g., fish lipid content, food web structure, exposure concentrations) in the Hudson River makes this site a severe test of all the BAF methodologies. In fact, the Hudson River data set may arguably fail to meet the sampling and data quality considerations specified in Section 5.1.2 for deriving baseline BAFs from field data. Nonetheless, EPA believes that the application of the BAF methods to this location was a useful exercise and illustrates that useful predictions are possible using method 4 in ecosystems with extreme temporal dynamics.

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6. DERIVATION OF NATIONAL BAFS FOR NONIONIC ORGANIC CHEMICALS

This section describes the process and technical documentation for determining national BAFs for nonionic organic chemicals once all appropriate individual baseline BAFs have been determined by using the methods described in Section 5. The distinction between national and baseline BAFs is important and is illustrated by Figure 3-2 in Section 3. Specifically, baseline BAFs are BAFs that have been adjusted to account for the lipid content of the tissues and the amount of freely dissolved chemical in water. As explained in Section 4, these two factors are important in affecting the bioaccumulation of nonionic organic chemicals. However, baseline BAFs are not directly used to determine national human health AWQC, because they do not reflect the lipid content of target aquatic organisms and the fraction of chemical that is freely dissolved in water for the sites to which the AWQC applies. In effect, baseline BAFs are "normalized" by lipid fraction and are based on the freely dissolved chemical (i.e., expressed on a 100% lipid and 100% freely dissolved basis). Furthermore, baseline BAFs need to be converted to BAFs, expressed as total concentrations in tissue and water, to be compatible with national human health AWQCs, which are based on the total concentration of a chemical in water.

To calculate national BAFs from baseline BAFs, two additional steps must be taken. First, a final baseline BAF must be determined for each trophic level from all appropriate individual baseline BAFs calculated by the methods described in Section 5. Guidance for determining a final baseline BAF is provided in Section 6.1. After a final baseline BAF has been selected for each trophic level, national BAFs are calculated for each trophic level using information on lipid fraction of consumed aquatic organisms and the fraction of chemical that is freely dissolved in water at the sites to which the AWQC applies. The calculation of a national BAF from a final baseline BAF is shown in Equation 6-1.

$$\text{National BAF}_{(TL\ n)} = [(\text{Final Baseline BAF})_{TL\ n} \cdot (f_l)_{TL\ n} + 1] \cdot (f_{fd}) \qquad \text{(Equation 6-1)}$$

where:

Final Baseline BAF	=	mean baseline BAF for trophic level "n"
$f_{l(TL\ n)}$	=	fraction of tissue that is lipid in aquatic organisms at trophic level "n"
f_{fd}	=	fraction of the total concentration of chemical in water that is freely dissolved

For deriving national BAFs, EPA uses national default values of lipid fraction (f_l) that are specific to each trophic level. The national default values of lipid fraction are:

Trophic Level 2: 0.019
Trophic Level 3: 0.026
Trophic Level 4: 0.030

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These national default values reflect consumption-weighted mean values of the lipid fraction of aquatic organisms that are commonly consumed throughout the United States. The technical basis of EPA's national default values for lipid fraction is presented in Section 6.2.

The same equation used to estimate the fraction of a chemical that is freely dissolved (f_{fd}) for deriving baseline BAFs (Equation 4-6) is used here to estimate the chemical's freely dissolved fraction for deriving national BAFs. For deriving national BAFs, EPA uses national default values DOC and POC for estimating a representative fraction of chemical that is freely dissolved in U.S. surface waters. The national default values of DOC and POC are:

DOC: 2.9 mg/L
POC: 0.5 mg/L

These national default values reflect central tendency estimates of DOC and POC for bodies of water distributed throughout the United States. The technical basis of EPA's national default values for POC and DOC is presented in Section 6.3.

Once the national BAFs are determined for each trophic level, they are used in Equation 1-1, 1-2, or 1-3 in the 2000 Human Health Methodology to derive national human health AWQCs. As discussed earlier in this document, both the fraction of tissue that is lipid (f_{ℓ}) and the fraction of chemical that is freely dissolved (f_{fd}) are two parameters that may be adjusted by States and Tribes to reflect local or regional conditions. Details on adjusting national BAFs to reflect local or region-specific values for lipid fraction of consumed aquatic organisms and the fraction of chemical that is freely dissolved at the site(s) of interest are provided in a subsequent volume of this TSD (Volume 3: Development of Site-Specific Bioaccumulation Factors).

6.1 SELECTING FINAL BASELINE BAFs

Once individual baseline BAFs have been determined by using the appropriate BAF methods within the applicable BAF derivation procedure, the next step in deriving national BAFs for nonionic organic chemicals consists of selecting the final baseline BAF for each trophic level (Section 3, Figure 3-2). As shown by Equation 6-1, final baseline BAFs are used to derive national BAFs by adjusting for the organic carbon content expected in representative U.S. surface waters and the lipid content of commonly consumed aquatic organisms. Determination of the final baseline BAF for each trophic level from individual baseline BAFs essentially involves a series of data aggregation steps. First, for each BAF method and trophic level, the mean of the corresponding individual baseline BAFs is calculated for each species to produce a set of "species-mean baseline BAFs." Next, for each BAF method and trophic level, the mean of the corresponding species-mean baseline BAFs is calculated to produce a set of "trophic level-mean baseline BAFs." Finally, a single "final baseline BAF" is selected or derived for each trophic level from the available set of trophic level-mean baseline BAFs. Although simple in concept, the process for calculating final baseline BAFs involves the use of best professional judgment in combination with other considerations, including the data preference hierarchy, the relative uncertainty among BAF estimates, and the weight of evidence among BAF methods. A summary of the steps involved in determining final baseline BAFs is provided in Section 5.4 of the 2000

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Human Health Methodology. Additional guidance for determining final baseline BAFs is described below.

6.1.1 Calculating Species-Mean Baseline BAFs for Each BAF Method

For each trophic level and BAF method combination, species-mean baseline BAFs are calculated as the geometric mean of acceptable baseline BAFs. An illustration of this step is provided in Figure 6-1 for the four BAF methods of Procedure 1. Procedure 1 is the derivation procedure that applies to nonionic organic chemicals with moderate-to-high hydrophobicity and negligible or unknown metabolism rates. All four BAF methods can be used in Procedure 1. Each unique species–trophic level–BAF method combination "sub-cube" in Figure 6-1 may consist of multiple baseline BAFs (illustrated on the right face of the entire cube in Figure 6-1 for BAF methods 1, 2, and 3 under trophic level 4). Species delineations are lacking for method 4 (K_{ow} × FCM) because this method produces a single baseline BAF for each trophic level. This is illustrated by the single "baseline BAF column" for each trophic level of method 4 rather than a sub-cube for each species. For illustration purposes, Figure 6-1 implies that, for each of the applicable BAF methods, one or more baseline BAFs are available for each sub-cube in trophic level 4. In practice, acceptable baseline BAFs may not be available for a BAF method or may be available for only one or two trophic levels for a BAF method.

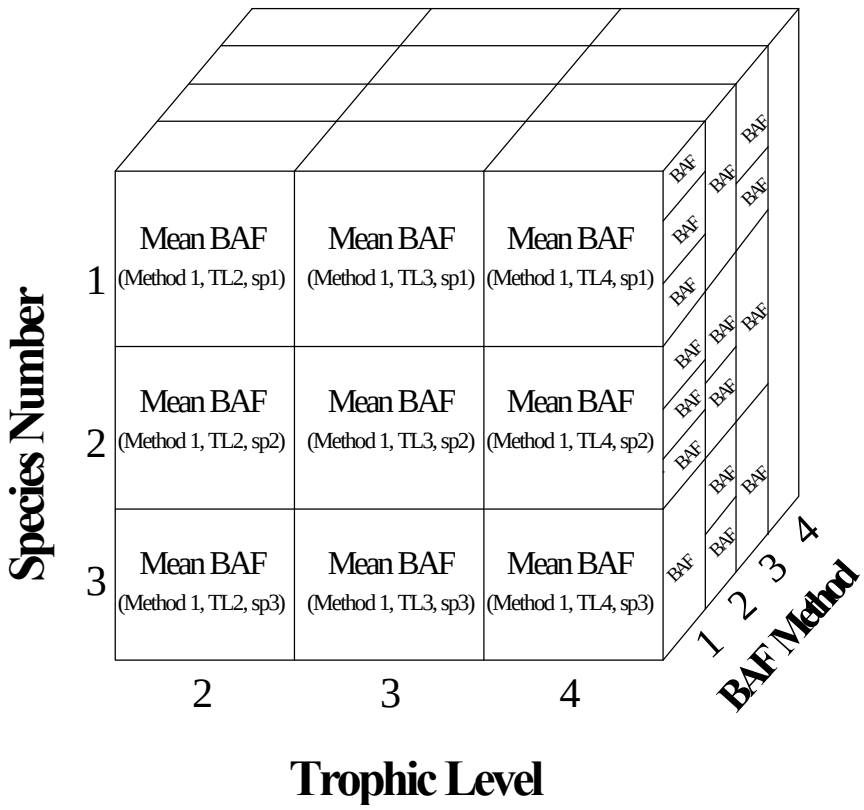

Figure 6-1. A schematic illustrating the aggregation of baseline BAF data by species, trophic level, and BAF method type for nonionic organic chemicals under Procedure 1.

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When species-mean baseline BAFs are being calculated, individual baseline BAFs should be reviewed carefully to assess their quality, variability, and overall uncertainty. This evaluation will support decisions about whether to exclude certain baseline BAFs from the calculation of national BAFs. This evaluation will usually be qualitative, because the availability of bioaccumulation data is currently limited for many chemicals. Highly uncertain baseline BAFs should not be used. Large differences in individual baseline BAFs for a given species (e.g., greater than a factor of 10) should be investigated further. Some or all of the baseline BAFs for a given species might not be used. Although all of the procedural and quality assurance guidelines described in Section 5 apply for evaluating the quality, variability, and uncertainty of baseline BAFs, several issues of special concern are discussed below. These issues include:

1. Temporal and spatial averaging of chemical concentrations
2. Spatial and temporal connectivity of samples
3. Chemical loadings history and steady state
4. Differences in food web structure
5. Reliability of lipid and organic carbon measurements

Temporal and Spatial Averaging of Chemical Concentrations

The extent of temporal and spatial averaging of chemical concentrations that are used to calculate each baseline BAF should be explicitly evaluated as part of determining its overall reliability (or uncertainty). Sufficient temporal and spatial averaging of chemical concentrations is critical for accurately determining baseline BAFs from BAF_T^ts and BSAFs (i.e., methods 1 and 2 of Procedure 1). As discussed previously, the extent of averaging that is considered ideal varies according to the chemical properties (e.g., hydrophobicity) and the variability of chemical concentrations in compartments of the ecosystem (e.g., water, sediment, tissue). Greater spatial and temporal averaging will be needed for highly hydrophobic chemicals in ecosystems showing high variability in chemical concentrations than for chemicals of lower hydrophobicity or those from ecosystems with low variability in chemical concentrations (see Section 1.2). Spatial sampling of chemical concentrations should in all likelihood span the immediate/local home range of the aquatic species. As illustrated by Figure 1-1, variability of chemical concentrations in water does not necessarily equate to variability of chemical concentrations in sediment and biota, particularly for highly hydrophobic chemicals where variability of chemical concentrations in sediments and biota tends to be dampened compared to that in water. Therefore, the extent of temporal averaging of chemical concentrations required to achieve accurate estimates of baseline BAFs that reflect steady-state conditions may vary depending on the environmental compartment. For baseline BAFs derived from BAF methods 1 and 2, which incorporate measurements of chemical concentrations in ambient water, variability in chemical concentrations in water may be especially important.

In situations where variability in chemical concentrations is not well characterized, some inference may be made from the overall hydrodynamics and chemical loading patterns in an ecosystem. For example, estuaries and rivers generally display greater hydrologic fluctuations than do large lake systems and, all else being equal, would generally be expected to have greater variability in chemical concentrations in water and sediments, and thus potentially in biota.

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Chemical loadings that are highly variable over time and/or are spatially complex (e.g., multiple point sources at different locations) will also contribute to greater variability in chemical concentrations in an ecosystem compared with more constant and uniform loading situations (e.g., continuous releases of similar magnitude over wide geographic areas, such as PCB releases from sediments in Lake Ontario). For moderately to highly hydrophobic chemicals with low rates of metabolism, less confidence (greater uncertainty) should usually be assigned to baseline BAFs derived from studies with minimal or no spatial or temporal averaging than with those from studies with greater averaging, unless overall variability in concentrations is very small. Moderately to highly hydrophobic chemicals that lack persistence in the environment may require less spatial or temporal averaging to the extent that their distributions are known to be limited with respect to more persistent chemicals of similar hydrophobicity. Concentrations in water and tissue of chemicals of low hydrophobicity (i.e., log K_{ow} #3) tend to parallel one another temporally because of rapid uptake and elimination kinetics. Thus, less temporal and spatial averaging of contemporaneous concentrations in water and tissue is required to produce reliable BAFs for chemicals of low hydrophobicity.

Temporal and Spatial Connectivity of Samples

The connectivity of samples in space and time should be evaluated for assessing the reliability of baseline BAFs for accurately representing steady-state bioaccumulation. Depending on chemical and ecosystem properties, BAF_T^ts that are derived from tissue samples that are widely separated in space or time from water samples can be highly uncertain. Special attention should be paid to situations in which geographic gradients in concentrations are known or suspected, because geographic asynchrony in tissue and water samples can lead to erroneous or biased estimates of a BAF_T^t under these circumstances. For example, if water samples are collected from an area of high concentrations in an exposure gradient (e.g., near a discharge) and fish are collected from a “down gradient” area (i.e., where exposure concentrations in water are expected to be substantially lower), BAF_T^ts can be underestimated because of overestimated chemical concentrations in water relative to those in tissue. Even when water, sediment, and biological samples are co-located in space, the mobility of organisms such as fish can be problematic when strong gradients in chemical concentrations exist. For highly hydrophobic chemicals whose metabolism is not important, modeling results suggest that fish tissue should be sampled toward the end of the water sampling period in order to account for the time lag associated with the slow accumulation kinetics of these compounds. For chemicals of low hydrophobicity, rapid uptake and elimination kinetics indicates that tissue and water samples should be closely connected temporally and spatially to produce reliable estimates of the BAF_T^t (e.g., sampling fish and water at the same time and location).

Chemical Loadings History and Steady State

As discussed in Section 4.3, the history of chemical loadings to an ecosystem has a direct bearing on the extent of the disequilibrium between chemical concentrations in water and sediment (J_{socw}/K_{ow}). This in turn can affect the magnitude of the BAF_T^t for nonionic organic chemicals (Burkhard et al., 2003b). Furthermore, rapid changes in chemical loadings to an ecosystem can lead to biased estimates of long-term BAF_T^ts when sufficient time is not allowed

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for tissue, water, and sediment concentrations to approach steady state, or when concentrations are not averaged properly over space and time. A longer time is generally necessary for highly hydrophobic chemicals in fish to reach steady state with respect to water than for chemicals with low hydrophobicity. For BCF_T^t measurements, evaluation of steady state is particularly important when the steady-state method is used, because highly hydrophobic chemicals may require substantially longer than the 28-day test duration typical of many bioconcentration tests to reach or approach steady state. Therefore, when variability and uncertainty in baseline BAFs are being evaluated for a given species, special attention should be paid to differences in chemical loadings history and the likelihood that BAF_T^ts (or BCF_T^ts) reflect steady-state conditions as possible explanatory factors. For highly hydrophobic chemicals (e.g., log K_{ow} of approximately 5 or greater), baseline BAFs may be highly biased when derived from field measurements in ecosystems where there has been a recent and substantial change in chemical loadings or chemical concentrations. Values of BAF_T^t that are known or suspected of being substantially biased with respect to representing steady-state bioaccumulation conditions should not be used in calculating species-mean baseline BAFs.

Food Web Structure

Another factor to evaluate when comparing baseline BAFs derived from BAF_T^ts or BSAFs is the difference in food web structure that may exist across sites (or even season) for the same species. Although there is no one "right" food web structure from which to judge the acceptability of a baseline BAF, differences in food web structure may help to explain some of the variation observed in baseline BAFs for a given species across sites. Model predictions and field observations indicate that food web structure can affect the magnitude of bioaccumulation, particularly for highly hydrophobic organic chemicals. While the trophic position of a given organism (and, by extension, the magnitude of its dietary exposure) can vary as a function of its age, size, and reproductive status, variations in the availability of and competition for prey items can directly influence dietary exposures. In some cases, individual organisms of the same species that differ in size or age are classified into separate trophic levels because of size or age-related differences in feeding preference and diet. Finally, for highly hydrophobic chemicals, for which significant disequilibrium exists between water and sediment concentrations, models indicate that a species with a benthic-driven diet tends to accumulate higher concentrations than does the same species with a pelagic-driven diet (see Section 4.4 and Burkhard et al., 2003b).

Organic Carbon and Lipid Measurements

The reliability of organic carbon (DOC, POC) and lipid measurements is also important to review when evaluating uncertainty in baseline BAFs. Both are used directly in deriving baseline BAFs from field or laboratory data. Concentrations of DOC and POC in a body of water are expected to vary over time as a function of precipitation events, season, hydrodynamics, and numerous other attributes of a watershed. Thus, sufficient sampling of DOC and POC concentrations over space and time is needed to achieve representative estimates of baseline BAFs, the extent of which will vary according to the variability in the particular ecosystem and the hydrophobicity of the chemical in question. Samples for the analysis of DOC and POC should be collected simultaneous with water samples collected for the analysis of the chemical of

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interest. For highly hydrophobic chemicals where greater temporal and spatial averaging of chemical concentrations is needed to determine a BAF_T^t that is representative of long-term conditions, DOC and POC concentrations will need to be similarly averaged when used to calculate the corresponding baseline BAF for the study site. This is especially important for highly hydrophobic chemicals because the impact of DOC and POC on calculation of the baseline BAFs is greatest with these chemicals (see Section 6.3).

In estimating lipid fraction for use in deriving a baseline BAF, care should be taken to review the differences in the extraction method used to measure the lipid content of a given species across studies. As discussed in Section 4.1, differences in the polarity of solvents used to extract lipids from tissue can result in the extraction of different amounts of lipid. This can lead to variation in lipid-normalized concentrations and, consequently, in baseline BAFs because of the solvent system used. Of particular concern are differences in the solvent extraction efficiencies of lipid and chemicals in extremely lean tissues (e.g., <1%-2% lipid). In such tissues, more polar (or mixed polar/nonpolar) solvent systems tend to extract more lipids than do nonpolar solvent systems. This phenomenon is believed to result from the proportionately greater fraction of polar lipids in lean tissues as compared with fatty tissues. Variation in solvent extraction efficiencies can be exacerbated when solvents of different polarities are used to quantify lipid content and the target analyte (Randall et al., 1998). Thus, some of the variation in baseline BAFs might be due to differences in the solvent systems used to extract lipids. It may be appropriate to exclude certain data for which differences in baseline BAFs are believed to be largely due to differences in extraction methods.

6.1.2 Calculating the Trophic Level–Mean Baseline BAF for Each BAF Method

After species-mean baseline BAFs have been calculated as described previously, the next step in determining a final baseline BAF involves calculating a trophic level–mean baseline for each BAF method, where this is possible. A trophic level–mean baseline BAF is calculated as the geometric mean of acceptable species-mean baseline BAFs in that trophic level. With Figure 6-1 as an illustration, the result of this calculation is a single mean baseline BAF for each vertical "column" of Figure 6-1. Trophic level–mean baseline BAFs should be calculated for trophic levels 2, 3, and 4, because available data on U.S. consumers of fish and shellfish indicate significant consumption of organisms in these trophic levels. Special attention should be focused on trophic level assignments, because they can be somewhat ambiguous for a number of aquatic organisms, particularly because trophic position is actually a continuous function of an organism's diet over time, rather than a discrete category.

6.1.3 Selecting the Final Trophic Level–Mean Baseline BAFs

Final baseline BAFs are selected among the trophic level–mean baseline BAFs for each trophic level using best professional judgment and considerations of:

1. The data preference hierarchy that is applicable to chemical of interest
2. The uncertainty associated with the baseline BAFs

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3. The weight of evidence suggested by BAFs determined by different BAF derivation methods.

The data preference hierarchy for each BAF derivation procedure is summarized in Figure 3-1 and further detailed in Table 6-1. It is based on the relative strengths and limitations of each BAF method and reflects the general preference of field-measured data over laboratory- or model-based estimates of bioaccumulation. Importantly, this hierarchy is intended for use as a guide for selecting the final baseline BAF rather than as a steadfast rule. Departures from this data preference hierarchy are entirely appropriate when considerations of uncertainty and weight of evidence indicate that a lower tier method would be preferred over a higher tier method.

In general, when trophic level–mean baseline BAFs are available for more than one BAF method within a given trophic level, the final trophic level–mean baseline BAF should be selected from the most preferred BAF method, as defined by the data preference hierarchy for the applicable derivation procedure (Figure 3-1; Table 6-1). If uncertainty in a trophic level–mean baseline BAF based on a higher tier (more preferred) method is judged to be substantially greater than one from a lower tier method, and the weight of evidence from the various methods suggests that a BAF value from a lower tier method is likely to be more accurate, then the final baseline BAF for that trophic level should be selected from the lower tier method.

Table 6-1. Data Preference Hierarchy for Selecting Final Baseline BAFs for Nonionic Organic Chemicals

BAF Derivation Procedure	Applicability	Data Preference Hierarchy
1	K_{ow} $4, metabolism negligible or unknown	1. Baseline BAF from an acceptable BAF_T^t (method 1) 2. Baseline BAF predicted from an acceptable BSAF (method 2) 3. Baseline BAF predicted from an acceptable BCF_T^t and FCM (method 3) 4. Baseline BAF predicted from an acceptable K_{ow} and FCM (method 4)
2	K_{ow} $4, metabolism significant	1. Baseline BAF from an acceptable BAF_T^t (method 1) 2. Baseline BAF from an acceptable BSAF (method 2) 3. Baseline BAF from an acceptable BCF_T^t (method 3)
3	K_{ow} <4, metabolism negligible or unknown	1. Baseline BAF from an acceptable BAF_T^t (method 1) or BCF_T^t (method 3) 2. Baseline BAF predicted from an acceptable K_{ow} value (method 4).
4	K_{ow} <4, metabolism significant	1. Baseline BAF from an acceptable BAF_T^t (method 1) or BCF_T^t (method 3)

When the weight of evidence among the various BAF methods is being considered, greater confidence in a final baseline BAF is generally assumed when baseline BAFs are in agreement across a greater number of methods within a given trophic level. However, lack of agreement among baseline BAFs derived from different methods does not necessarily indicate less confidence, if such disagreements can be adequately explained. For example, if the chemical of concern is metabolized by aquatic organisms represented by a baseline BAF value, one would

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expect disagreement between a baseline BAF derived from a BAF_T^t (the highest priority data) and a baseline BAF predicted from a K_{ow} and model-derived FCM. In addition, consideration should also be given to the quantity and diversity of bioaccumulation measurements that underlie the calculation of a trophic level–mean baseline BAF. This is particularly relevant because national BAFs are intended to reflect central tendency estimates of bioaccumulation expected across U.S. surface waters. In some cases, the uncertainty associated with very limited BAF data from a "more preferred" method may be offset by the greater quantity and diversity of data that are available from an otherwise "less preferred" method for a given data preference hierarchy.

6.2 BASIS FOR THE NATIONAL DEFAULT LIPID FRACTION (f_R) OF COMMONLY CONSUMED FISH AND SHELLFISH

This section provides the technical basis of EPA's recommended national default values of lipid fraction (f_R) that are used to derive national BAFs for nonionic organic chemicals (0.019 for trophic level 2 organisms, 0.026 for trophic level 3 organisms, and 0.030 for trophic level 4 organisms). As indicated by Equation 6-1 and Figure 2-2, the lipid fraction of commonly consumed aquatic species is needed to adjust a baseline BAF (which reflects partitioning to 100% lipids) to a BAF that reflects the lipid fraction of aquatic organisms commonly eaten by U.S. consumers. Information on lipid content is used to adjust BAFs for nonionic chemicals because it has been shown to influence the magnitude of bioaccumulation in aquatic organisms (Mackay, 1982; Connolly and Pederson, 1988; Thomann, 1989). Therefore, lipid content in consumed aquatic organisms is considered to be an important factor for characterizing potential human exposure to nonionic organic chemicals.

Although EPA uses national default values of lipid fraction to derive national human health AWQC, EPA encourages States and authorized Tribes to use local or regional data on the lipid content and consumption rates of consumed aquatic species when adopting criteria into their own water quality standards. The use of such locally or regionally derived data is encouraged over national-scale data because local or regional consumption patterns of fish and shellfish (and thus the amount of lipid consumed from aquatic organisms) can differ from national consumption patterns. Additional guidance on developing local or region-specific values of lipid fraction, including a database of lipid fraction for many commonly consumed aquatic organisms, is found in a subsequent volume of this TSD (Volume 3: Development of Site-Specific Bioaccumulation Factors). Nevertheless, EPA recognizes that there will be situations when such local or regional data are not available or are inadequate for deriving representative values of lipid fraction for setting State or Tribal water quality standards. In these cases, EPA recommends the use of its national default values of lipid fraction for deriving BAFs and resulting water quality criteria.

6.2.1 Variability in Lipid Content

One issue associated with setting national default values of lipid fraction in consumed aquatic organisms is how to address intraspecies and interspecies variability in lipid content. For example, the mean percent lipid in fillets of lake trout, *Salvelinus namaycush*, a notoriously "fatty" species, is estimated to be about 12%. This value is about 18 times the mean percent lipid

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found in fillets of northern pike, *Esox lucius* (0.7%). Wide variation in lipid content can also occur within a species. Based on data presented later in this section, the coefficient of variation of percent lipid can approach or, in some cases, exceed 100% within a species, even when data are limited to specific tissue types.

A number of factors can lead to variability in lipid content of aquatic organisms. Many of these factors are fundamentally related to differences in physiology, metabolism, organism health or condition, and feeding ecology among and within species. These factors and, consequently, the lipid content in a particular tissue can vary as a function of season, temperature, reproductive status, migratory patterns, sampling location (both within and across water bodies), age, size, life stage, the availability of prey, and other factors. In addition, the distribution of lipids in a particular aquatic organism is not uniform across all tissue types, thus resulting in differences in lipid fraction depending on the tissue sampled (e.g., fillet, whole body, muscle). Finally, differences among analytical methods used to extract and measure lipids and associated analytical error can contribute to variability in reported values of lipid fraction (see Section 6.2.2).

For the purposes of deriving national default values of lipid fraction, EPA has addressed the issue of variability in lipid content in several ways. First, only data for the most commonly consumed aquatic species in the United States were considered. The identity of these species was determined by the U.S. Department of Agriculture's *Continuing Survey of Food Intake by Individuals* (CSFII) (USDA, 1998) for 1994 through 1996 (the most recent data at the time of this analysis). Second, data were limited to the tissues that are most commonly consumed within a species. Third, when size information was available, data were further limited to sizes of aquatic species that are typically eaten by U.S. consumers. Finally, national default values of lipid fraction were determined by weighting individual mean values of lipid fraction for each species (or group of species) by the appropriate consumption rates determined for the U.S. population. In this manner, EPA's national default values of lipid fraction better reflect national consumption patterns of aquatic organisms in comparison to simply weighting the lipid fraction for each species equally.

The following sections present the data sources, analysis, assumptions, and uncertainty associated with the derivation of national default lipid values.

6.2.2 Data Sources

The national default values of lipid fraction (f_R) were derived by using three types of nationally aggregated data:

1. National per capita consumption rates of aquatic organisms
2. Lipid fraction in consumed aquatic organisms
3. Trophic status of consumed aquatic organisms

A summary and description of this information are provided below.

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National Mean Per Capita Fish Consumption Rates

Information on the types and quantity of aquatic organisms consumed in the United States was obtained from the CSFII (USDA, 1998). This national survey provides daily mean per capita estimates of fish consumption for the U.S. population for categories of estuarine, freshwater, and marine fish and shellfish (among other dietary categories). Although other regional or local surveys were available, the CSFII was selected because it provided consumption information on a national basis and contained the most recent data available. Furthermore, information from the same USDA survey was used to derive national default values of fish consumption rates for calculating national human health AWQCs. Reliance on the same fish consumption survey ensures consistency between the derivation of national default values for lipid fraction and national default values of fish consumption rates.

Table 6-2 shows the habitat classification, CSFII consumption categories, estimated mean per capita consumption rates, and fraction of total estuarine and freshwater consumption represented by each category in the CSFII. Mean per capita consumption rates were estimated for individuals aged 18 years and older for categories of freshwater and estuarine aquatic organisms. This same category of consumers was used to calculate the national default value of fish consumption for the general adult population and sport anglers (i.e., a 90th percentile total intake rate of 17.5 g per person per day, as described in the 2000 Human Health Methodology). However, sufficient data were not available in the CSFII survey to adequately describe the pattern of fish consumption (as opposed to the total fish and shellfish intake rate) for individuals constituting the 90th percentile. Therefore, the consumption pattern represented by the mean per capita consumption rates was chosen for this analysis. In calculating the estimated mean consumption rates, two CSFII consumption categories were classified as being unknown by the survey (i.e., “unknown fish” and “unknown seafood”). By using the same approach adopted for deriving the national default value for fish consumption, 39% of these two “unknown” fish consumption categories were apportioned to the freshwater and estuarine consumption categories on a consumption rate-weighted basis. Further details of the mean per capita consumption rates from the CSFII survey data and assignment of habitat designations for fish and shellfish can be found in the Exposure Assessment volume of this Technical Support Document.

It is apparent from Table 6-2 that estimated mean per capita consumption rates vary widely across categories and that consumption in a relatively few categories dominates the overall consumption pattern of freshwater and estuarine organisms. For example, the consumption rate in the “shrimp category” constitutes about 35% of the total estimated mean per capita consumption rate of freshwater and estuarine organisms. Similarly, the consumption rates corresponding to the flounder, catfish (fresh and estuarine), and flatfish categories constitute approximately 30% of the total consumption rate of freshwater and estuarine organisms. To account for the disproportional nature of the national per capita consumption rates revealed by the CSFII survey, the derivation of national default values of lipid fraction were determined on a consumption-weighted basis, as described later in this section.

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Table 6-2. Categories and Mean Per Capita Consumption Rates from the USDA CSFII

Habitat	USDA CSFII Consumption Category	Estimated Mean Consumption Rate (g/person/day)	Proportion of Total Freshwater and Estuarine Consumption Rate (%)
Estuarine	Shrimp	2.65492	35.4
	Flounder	0.73482	9.8
	Catfish (estuarine)	0.60335	8.0
	Flatfish (estuarine)	0.45173	6.0
	Crab (estuarine)	0.42111	5.6
	Perch (estuarine)	0.22331	3.0
	Croaker	0.17792	2.4
	Oyster	0.17485	2.3
	Herring	0.16428	2.2
	Trout, mixed spp. (estuarine)	0.15305	2.0
	Salmon (estuarine)	0.05915	0.8
	Anchovy	0.05815	0.8
	Rockfish	0.05428	0.7
	Mullet	0.04512	0.6
	Clam (estuarine)	0.01732	0.2
	Smelts (estuarine)	0.00880	0.1
	Eel	0.00466	0.06
	Scallop (estuarine)	0.00140	0.02
	Smelts, rainbow (estuarine)	0.00076	0.01
	Sturgeon (estuarine)	0.00018	0.002
Freshwater	Catfish (freshwater)	0.60335	8.0
	Trout (rainbow)	0.25361	3.4
	Perch (freshwater)	0.22331	3.0
	Carp	0.19071	2.5
	Trout, mixed spp. (freshwater)	0.15305	2.0
	Pike	0.04021	0.5
	Whitefish (freshwater)	0.01309	0.2
	Crayfish	0.01028	0.1
	Snails (freshwater)	0.00207	0.03
	Cisco	0.00179	0.02
	Salmon (freshwater)	0.00118	0.02
	Smelts, rainbow (freshwater)	0.00076	0.01
	Sturgeon (freshwater)	0.00018	0.002
Total		7.50273	100.0

Source: USDA combined 1994–1996 Continuing Survey of Food Intakes by Individuals (CSFII) (USDA, 1998).

Notes: (1) Estimates were based on 2-day averages and are projected from a sample of 9,596 individuals 18 years of age and older in the U.S. population of 190,931,846 individuals 18 years of age or older, using 3-year combined survey weights. Weights are for uncooked fish and shellfish. (2) The fish component of foods containing fish was calculated by using data from the recipe file of USDA's Nutrient Database for individual food intake surveys. (3) Values reflect apportionment of 39% of the consumption rate of "unknown fish" and "unknown seafood" categories to freshwater and estuarine categories. (4) The number of digits does not imply their statistical significance. See Section 6.2.2 and the Exposure Assessment volume of this Technical Support Document for additional information about the CSFII and habitat classification.

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Lipid Content of Consumed Aquatic Species

In reviewing the available literature, EPA was unable to find a single comprehensive database containing information on the lipid content of consumed aquatic organisms (fresh and estuarine). As a result, information on the lipid fraction of aquatic organisms was obtained from a variety of primary and secondary sources. The following major sources of lipid data were used in the derivation of national default values of lipid fraction:

- EPA's National Sediment Quality Survey database (USEPA, 2001a)
- EPA's National Study of Chemical Residues in Fish (USEPA, 1992a)
- EPA's Green Bay Mass Balance Study (USEPA, 1992b, 1995c),
- U.S. Department of Agriculture's (USDA) Nutrient Data Bank (Exler, 1987)
- A review from National Marine Fisheries Service of the National Oceanic and Atmospheric Administration (NOAA) (Sidwell, 1981)
- Two California databases (California Toxic Substances Monitoring Program and Bay Protection and Toxic Cleanup Program)

When insufficient data were available from the above sources for certain species, targeted literature searches were conducted and data from primary literature were used. Importantly, care was taken to avoid duplication of data among the various data sources. For example, examination of the National Sediment Quality Survey lipid data and data from various studies conducted on the Hudson River revealed significant overlap and apparent duplication. Similarly, multiple literature reviews (e.g., USDA and NOAA reports) were not used for a given species unless it was clear that the primary literature upon which each was based was unique. Each of these data sources is discussed in more detail below.

National Sediment Quality Survey. Data on lipid content were extracted from a prerelease version of EPA's National Sediment Quality Survey (NSQS) database from 1980 through 1998, the last year for which data were made available in this version of the database. A description of the NSQS database can be found in USEPA (2001a). The primary source of data contained in the NSQS was EPA's STORET (Storage and Retrieval of U.S. Waterways Parametric Data) database, recently renamed the Legacy Data Center database. STORET is a waterway-related monitoring database that contains data from many Federal and State government agencies. Geographically, the lipid data extracted from the NSQS database were mostly limited to organisms in freshwater habitats. More than 47,000 records of lipid content were extracted, representing more than 200 species and taxonomic groupings. Despite a large number of species represented in the database, the quantity of lipid data was not evenly distributed among species. For example, 10 species (mostly catfish, bass, perch, and salmonids) represented 60% of the total number of records. Data on lipid content (e.g., percent lipid, tissue type), organism attributes (e.g., common name, scientific name, and, where available, age, weight, length, and sex), and sampling station (e.g., latitude, longitude, sampling date, investigator names) were extracted and combined in an MS ACCESS® database. Information on the method of lipid analysis was not reported in the NSQS database.

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National Study of Chemical Residues in Fish (NSCRF). Data on the lipid content of aquatic organisms were extracted from EPA's National Study of Chemical Residues in Fish (USEPA). This study represents a one-time screening investigation to determine the prevalence of selected bioaccumulative pollutants in fish. Samples were collected from 388 locations in the United States that included targeted sites near point and non-point pollution sources, background sites with minimal expected pollution sources, and a few sites corresponding to the U.S. Geological Survey's National Stream Quality Accounting Network (NASQAN) to obtain nationwide coverage. Species represented in the study generally included a bottom-feeder and a game-fish species. Carp was the most common species sampled, followed by largemouth bass, white sucker, channel catfish, and smallmouth bass. Three to five fish collected from one location were used for each composite sample. For each composite sample, two measurements of the lipid content were obtained, one from the test for dioxins/furans and one from the test for other xenobiotics. The average of the two lipid values was used to represent each sample data point in the lipid database. Location and sampling date information was available, as were the common name of the species collected and the tissue type sampled (whole body, fillet). Lipids were measured gravimetrically after extraction with hexane and methylene chloride (1:1).

U.S. Department of Agriculture (USDA). Information on the composition of finfish and shellfish products (including lipid content) was summarized by Exler (1987), using data from USDA's Nutrient Data Bank. These data were particularly useful because they included estuarine species that were poorly represented by the other databases. Sources of the data summarized by Exler (1987) included journal articles, technical reports, and other scientific and technical literature (published and unpublished). Raw data on lipid content were not reported by Exler; only summary statistics (mean, standard error, and number of samples) were reported. Because it was not possible to combine the summary data from Exler (1987) with individual records from other sources and still maintain statistical reliability, the Exler (1987) data were used on an exclusive basis for a given species. Tissue types were restricted to the "edible portion" of species. Although data were available on various lipid fractions (e.g., saturated, monosaturated, and polyunsaturated fatty acids; cholesterol), only total lipid data were used in raw (unprocessed) samples. Information on the method of lipid analysis used was not reported.

National Marine Fisheries Service. Data on the lipid content of estuarine species from the National Marine Fisheries Service of NOAA were available from a review by Sidwell (1981). This review consists of compilations of data from primary literature sources. Information on the specific location and number of individuals per value was not available in these reviews. Data were restricted to species collected in North America, when information was available to make this distinction. Information was available on species' common and Latin names, tissue type, and method of preparation (e.g., raw, cooked). Only samples that were indicated as being fresh or raw (or for which no preparation information was available) were used in the analysis of lipid data. Other information, such as the number of individuals in a sample and their age, weight, and sex, was not available. Importantly, the Sidwell (1981) data were not used in combination with the USDA data for a given species, because both represent reviews of the primary literature and may contain redundant data. A later review was also available from the National Marine Fisheries Service (Kryznowek and Murphy, 1987); however, this was not used because its data were presented in an aggregated format.

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California Toxic Substances Monitoring Program. Lipid data were obtained from the Toxic Substances Monitoring Program (TSMP) database sponsored by the California Environmental Protection Agency, California State Water Resources Control Board, via downloading from their Internet site (www.swrcb.ca.gov). The TSMP was initiated in 1976 to provide a uniform statewide approach to monitor for toxic substances in freshwater and, to a limited extent, in estuarine and marine waters, through the analysis of fish tissue and other aquatic life. Samples are collected annually and composite samples of six fish are collected when possible. The database provides information on age, sample collection date, location, number of organisms per sample, weight, and length. Most samples for the species of interest are fillet samples, although some whole-organism samples are also present. Lipids were measured gravimetrically with petroleum ether solvent. A complete description of the TSMP database is found in Rasmussen (1998).

Bay Protection and Toxic Cleanup Program. Relevant information on lipid content was extracted from two small databases available from the Bay Protection and Toxic Cleanup Program (BPTCP) (also at www.swrcb.ca.gov). One database contained samples from San Francisco Bay, and the second included samples from San Francisco Bay and other California locations. Lipids were measured gravimetrically with methylene chloride as the extraction solvent.

Green Bay Mass Balance Study. The 1989–1990 Green Bay Mass Balance Study (GBMB) was conducted to generate a comprehensive data set for modeling the fate, transport, and bioaccumulation of several toxic chemicals, including polychlorinated biphenyls, in Green Bay, Lake Michigan. Six species were represented in the database for lipid content (walleye, brown trout, carp, alewife, rainbow smelt, and gizzard shad). All data are from composite samples of whole-body tissue. Included in the database is information on collection date, zone of bay in which the sample was collected, age, and number of fish in the composite. Data were retrieved from the Green Bay Relational Database, which is maintained by EPA's Office of Research and Development. Lipids were measured gravimetrically after extraction with hexane/methylene chloride (1:1).

6.2.3 Data Analysis

The following steps were taken in the calculation of national default values of lipid fraction:

- Removing suspect data (e.g., duplicate records, extreme values)
- Classifying species into CSFII consumption categories
- Excluding data for tissue types and size ranges not typically consumed
- Calculating mean lipid fraction for CSFII species
- Assigning trophic levels to species and CSFII consumption categories
- Calculating consumption-weighted values of lipid fraction within each trophic level

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Each of these steps is further described below.

Removing Suspect Data

Data from the NSQS database were screened to ensure that all records in the database included, at a minimum, fields for common name, scientific name, species code, lipid content, tissue type, sample data, and sample location. Most NSQS records contained additional information beyond this subset. Records for common name, scientific name, and species code were cross-checked for consistency, and erroneous entries were corrected or removed if they were ambiguous. Furthermore, data were removed from all database sources that were collected before 1980. Extreme values of lipid content (e.g., zero values and those above 35% for finfish other than lake trout) were removed to minimize the impact of suspected outliers on the analysis. For lake trout, values of up to 45% were tolerated because fillets of this species are notoriously high in fat content, which on rare occasions can approach this value. The trimming of the high extreme values resulted in the removal of very few records (i.e., fewer than 30 of more than 47,000). Finally, records from multiple sources were compared to identify and remove duplicate records.

Classifying Species into CSFII Consumption Categories

The next step in calculating the national default values of lipid fraction involved assigning species to the CSFII consumption categories shown in Table 6-2. This step was conducted to maintain consistency in the data used to determine national default consumption rates of fish and shellfish and lipid fraction. In most cases, information was not available from the CSFII to identify exactly which species were represented by the consumption rates listed in Table 6-2. Therefore, assignment of a species to a CSFII category was based on several factors, including (1) its taxonomic and publicly perceived linkage to a CSFII category, (2) its likelihood of being caught (either recreationally or commercially) and consumed in the United States, and (3) its likelihood of inhabiting either fresh or estuarine waters for at least some portion of its life cycle. Information from numerous published sources was used to help determine whether a species met these criteria. Because several of the CSFII species categories were broad in terms of the types of species that could be included, some species were assigned to multiple CSFII categories. For example, flounder species fit into both estuarine flatfish and flounder categories. In such cases, appropriate records were included in both CSFII categories. Data for species that could not be unambiguously assigned to a CSFII consumption category were omitted from the analysis. Notably, this resulted in the exclusion of lipid data for some species that are commonly consumed in the United States but were not associated with a CSFII category (e.g., largemouth bass and walleye).

Screening by Tissue Type and Size Ranges

As discussed previously, lipid content can vary widely by the type of tissue in which it is measured. To derive national default values of lipid fraction and national BAFs that are representative of human exposure potential, lipid data were screened according to the types of tissues most commonly consumed by the U.S. population. Because lipid data originated from a

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variety of sources that differed in nomenclature used to classify the type of tissue, a variety of commonly consumed tissues were accepted, depending on the species and the availability of data. The following types of tissues reported by various data sources were included in the derivation of the national default values of lipid fraction:

- Finfish (except anchovy and smelt): standard fillet, fillet (with skin, without skin, skin unspecified), edible portion
- Anchovy, smelt: whole body
- Clam: whole/raw, adductor muscle
- Crab: edible portion, muscle, standard fillet, muscle and hepatopancreas
- Crayfish, oyster, scallop, shrimp: edible portion
- Snails: whole/raw

Lipid Content of Species in CSFII Categories

On the basis of lipid data from the aforementioned sources, the average percent lipid was calculated for each of the species in the CSFII consumption categories (Table 6-3). Next, the average percent lipid of all species in each CSFII category was determined as the average of the corresponding individual species-mean lipid values. Average values of lipid content were determined because national BAFs are designed to reflect central-tendency estimates. Ideally, if sufficient national consumption data were available at the species level, the overall average lipid value for each CSFII category would be determined on a consumption-weighted basis. However, sufficient consumption data were not available below the CSFII category level at a national scale. Therefore, equal weights were assigned to each species' mean lipid value. For example, lipid data were available for several species of trout (e.g., rainbow trout, brown trout, and others), whereas consumption rates were available from the CSFII only for trout as a group. Thus, mean percent lipid values for all trout species were averaged and combined with the consumption rate for trout from the CSFII.

Trophic Level Assignments to Species and CSFII Consumption Categories

National fish and shellfish consumption data from the CSFII (see Table 6-2) indicate that, on average, individuals consume aquatic organisms from a variety of trophic levels (e.g., oysters and clams in trophic level 2, whitefish and herring in trophic level 3, perch and trout in trophic level 4). Because trophic position (in particular, dietary composition) can affect the extent of bioaccumulation in aquatic organisms, national BAFs are derived separately for each trophic level. Similarly, because lipid content can vary by species, national default values of lipid fraction are derived separately for each trophic level. To estimate trophic level–specific values of lipid fraction, a trophic level designation must be assigned to each of the CSFII consumption rate categories shown in Table 6-2. This same trophic level assignment is used to discern the fraction of the national default fish consumption rate (17.5 g/d) that occurs at each trophic level (see the 2000 Human Health Methodology).

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Table 6-3. Lipid Content of Aquatic Organisms Used to Derive National Default Values of Lipid Fraction (f_l)

CSFII Consumption Category (Habitat)[a]	Common Name	Scientific Name	Species Mean Lipid Content (%)	CV[b]	No. Obs.	Data Source[c]	CSFII Mean Lipid (%)
Anchovy (estuarine)	Striped anchovy	*Anchoa hepsetus*	2.8	NR	23	1	6.1
	European anchovy	*Engraulis encrasicholus*	4.8	0.34	26	2	
	Northern anchovy	*Engraulis mordax*	10.7	NR	16	1	
Carp (freshwater)	Common carp	*Cyprinus carpio*	5.4	0.86	2,792	3	5.4
Catfish (freshwater)	White catfish	*Ameiurus catus*	4.3	0.58	204	3, 4, 5	2.9
	Black bullhead	*Ameiurus melas*	1.1	0.70	113	3, 4, 5	
	Yellow bullhead	*Ameiurus natalis*	1.4	0.99	95	3, 5	
	Brown bullhead	*Ameiurus nebulosus*	2.6	0.72	988	3, 4, 5	
	Channel catfish	*Ictalurus punctatus*	5.3	0.71	1,427	3, 4, 5	
Catfish (estuarine)	White catfish	*Ameiurus catus*	4.3	0.58	204	3, 4, 5	4.0
	Brown bullhead	*Ameiurus nebulosus*	2.6	0.72	988	3, 4, 5	
	Channel catfish	*Ictalurus punctatus*	5.3	0.71	1,427	3, 4, 5	
Cisco (freshwater)	Cisco	*Coregonus Artedii*	1.9	0.65	69	2	1.9
Clam (estuarine)	Hard shell clam	*Mercenaria mercenaria*	0.7	NR	47	1, 6	1.3
	Soft shell clam	*Mya arenaria*	1.2	NR	3	1	
	Venus clam (Littleneck Japanese)	*Tapes (venerupis) decussatus*	1.2	NR	15	1	
	Venus clam (Shortneck)	*Tapes japonica*	1.8	NR	3	1	
	Venus clam (Asari)	*Tapes philippinarum*	2.6		3	1	
	Venus clam	*Venus gallina*	0.9	NR	29	1	
	Venus clam (hard)	*Venus lusoria*	0.6	NR	5	1	
Crab (estuarine)	Blue crab	*Callinectes sapidus*	1.3	1.19	101	3	1.1
	Dungeness crab	*Cancer magister*	1.0	0.26	24	2	
	Queen crab	*Chionoectes opilio*	1.2	0.30	6	2	
Crayfish (freshwater)	Crayfish (mixed sp.)	*Astacus and Orconectes*	1.1	NR	5	2	1.1
Croaker (estuarine)	White croaker	*Genyonemus lineatus*	4.2	0.88	37	4, 5, 6, 7	3.0
	Atlantic croaker	*Micropogonias undulatus*	3.2	0.47	8	2	
	Yellowfin croaker	*Umbrina roncador*	1.8	0.70	3	5	
Eel (estuarine)	Eel, mixed species	*Anguilla spp.*	11.7	0.28	14	2	11.7
Flatfish (estuarine)	Sole and flounder	*Bothidae and Pleuronectidae*	1.2	0.80	596	2	1.2
Flounder (estuarine)	Sole and flounder	*Bothidae and Pleuronectidae*	1.2	0.80	596	2	1.2
Herring (estuarine)	Blueback herring	*Alosa aestivalis*	7.2	0.45	92	3	10.0
	Atlantic herring	*Clupea harengus*	9.0	0.51	2,524	2	
	Pacific herring	*Clupea pallasi*	13.9	0.39	128	2	
Mullet (freshwater)	Striped mullet	*Mugil cephalus*	3.8	0.62	43	2	3.8
Oyster (estuarine)	Pacific oyster	*Crassostrea gigas*	2.3	0.33	13	2	2.4

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CSFII Consumption Category (Habitat)[a]	Common Name	Scientific Name	Species Mean Lipid Content (%)	CV[b]	No. Obs.	Data Source[c]	CSFII Mean Lipid (%)
	Eastern oyster	*Crassostrea virginica*	2.5	0.56	193	2	
Perch (estuarine and freshwater)	White perch	*Morone americana*	3.5	0.72	682	3, 4	2.3
	Yellow perch	*Perca flavescens*	1.0	0.79	841	3, 5	
Pike (freshwater)	Northern pike	*Esox lucius*	0.6	1.01	904	3, 4	0.7
	Muskellunge	*Esox Masquinongy*	1.1	0.87	35	3	
	Chain pickerel	*Esox niger*	0.4	0.74	72	3, 4	
Rockfish (estuarine)	Striped bass	*Morone saxatilis*	5.3	0.59	7,657	3, 4, 5, 7	3.5
	Rockfish	*Sebastes spp.*	1.6	NR	81	2	
Salmon (estuarine & freshwater)	Pink salmon	*Oncorhynchus gorbuscha*	3.5	0.49	144	2	4.7
	Chum salmon	*Oncorhynchus keta*	3.8	0.62	13	2	
	Coho salmon	*Oncorhynchus kistuch*	2.9	0.75	617	3	
	Sockeye salmon	*Oncorhynchus nerka*	8.6	0.32	48	2	
	Chinook salmon	*Oncorhynchus tshawytscha*	3.4	0.93	873	3	
	Atlantic salmon	*Salmo salar*	6.3	0.74	7	2	
Scallop (estuarine)	Scallop, mixed species	*Pectinidae*	0.8	0.35	114	2	0.8
Shrimp (estuarine)	Shrimp, mixed species	*Panaeidae and Pandalidae*	1.7	0.39	100	2	1.7
Smelt, rainbow (estuarine & freshwater)	Rainbow smelt	*Osmerus mordax mordax*	4.1	0.46	130	3, 8	4.1
Snails (freshwater)	Snails, mixed species	*Vivaparadidae, Helixidae*[d]	1.4	0.75	11	1	1.4
Sturgeon (estuarine & freshwater)	Lake sturgeon	*Acipenser fulvescens*	9.4	0.63	51	3	5.4
	White sturgeon	*Acipenser transmontanus*	1.3	0.67	7	4, 5, 7	
Trout, mixed spp. (freshwater)	Rainbow trout	*Oncorhynchus mykiss*	5.1	0.67	556	3, 4, 5	6.0
	Cutthroat trout	*Salmo clarki clarki*	1.2	0.79	15	3	
	Brown trout	*Salmo trutta*	7.4	0.73	615	3, 4, 5	
	Brook trout	*Salvelinus fontinalis*	4.0	0.56	96	3, 4, 5	
	Lake trout	*Salvelinus namaycush*	12.3	0.62	910	3, 4, 5	
Trout, mixed spp. (estuarine)	Rainbow trout	*Oncorhynchus mykiss*	5.1	0.67	556	3, 4, 5	3.2
	Cutthroat trout	*Salmo clarki clarki*	1.2	0.79	15	3	
Trout, (freshwater)[e]	Rainbow trout	*Oncorhynchus mykiss*	5.1	0.67	556	3, 4, 5	5.1
Whitefish	Whitefish, mixed spp.	*Coregonus spp.*	5.9	0.64	68	2	5.9

[a] Habitat designation (freshwater, estuarine) assigned to the CSFII consumption categories. See the Exposure Assessment volume of this Technical Support Document for details.
[b] Coefficient of variation.
[c] Data sources: 1 = Sidwell (1981), 2 = Exler (1987), 3 = NSI (USEPA, 2001a), 4 = USEPA (1992a), 5 = CATSMP, 6 = primary literature, 7 = BPTCP, 8 = GBMB. See Section 6.2.2 for a description of data sources.
[d] In addition to these two families, specific genera represented include *Ampullaria, Vivaparus, Achatina, Murex, Thais, Nassa,* and *Aporrhais.*
[e] Information from the CSFII survey indicates that rainbow trout is appropriate for the "trout, freshwater" category.

The EPA recognizes that the dietary composition of an aquatic species (and, henceforth, its trophic position) can vary as a function of size, age, life history, season, and food web structure of the water body. As in the discussion presented at the beginning of Section 6.2 for deriving values of lipid fraction in general, States and Tribes are encouraged to use local or regional information to estimate the trophic position of consumed aquatic organisms for setting local or regional criteria. The use of such local or regional information is encouraged because factors that can affect trophic position often vary on a local or regional basis.

In the case of deriving national AWQC, and in situations where sufficient local or regional data are not available, an assessment of the trophic position of consumed aquatic organisms is necessary. Estimating the trophic level position of aquatic species requires information on the identity, size, age, and diets of the individual aquatic species consumed. As previously discussed, very limited data were available to further delineate the identity and size of species consumed within each of the CSFII categories in Table 6-2. For most of the CSFII categories, this lack of information was not viewed as problematic, because rather unambiguous assignments of trophic position could be made to these categories (e.g., all oysters are considered to be trophic level 2). However, for other CSFII categories, assignment of trophic position required some assumptions to be made, which introduces greater uncertainty. To assist in estimating the trophic position of species represented by the CSFII consumption survey, EPA relied on information summarized in a report entitled *Trophic Level and Exposure Analysis for Selected Piscivorous Birds and Mammals* (USEPA, 2000e-g). Although focused on piscivorous birds and mammals, this report contains information on dietary composition and trophic status for numerous species in the aquatic food web by virtue of the fact that the aquatic food web serves as the dietary basis for piscivorous wildlife. The following procedures were used in assigning trophic position to the CSFII consumption categories.

1. **Species Trophic Level Assignments.** Species trophic level assignments were performed as follows:

    a. For game fish that correspond to the CSFII categories, data were used for edible size ranges (about 20 cm [8 inches] or larger).
    b. For species where multiple size ranges were available, preference was given to the larger specimens in determining the species trophic level.
    c. Trophic level 2 was assigned to a species if appropriate trophic level data ranged between 1.6 and 2.4; trophic level 3 if trophic level data ranged from 2.5 to 3.4; and trophic level 4 if trophic level data were 3.5 or higher. This is consistent with the approach taken in the Great Lakes Water Quality Initiative guidance (USEPA, 1995b).

2. **CSFII Consumption Category Trophic Level Assignments.** Once trophic levels were assigned to each species that could reasonably correspond to a CSFII consumption category, this information was used to assign a trophic level to each CSFII consumption category, as follows:

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a. In situations where a CSFII category was represented by the vast majority of species within a single trophic level, that trophic level was assigned to the CSFII category (e.g., trout, pike, smelt).

b. For some CSFII consumption categories, the trophic status of representative species spanned two trophic levels. In this case, consumption rate for that category was evenly divided between the two trophic levels (e.g., for flounder, 50% to trophic level 3 and 50% to trophic level 4). This situation occurred for opportunistic species such as flounder and flatfish, catfish, croaker (all evenly divided between trophic levels 3 and 4), and shrimp (divided between trophic levels 2 and 3).

3. The results of the trophic level assignments are shown in Table 6-4.

Calculation of Consumption-Weighted Lipid Content, by Trophic Level. The national consumption-weighted mean lipid fraction for each trophic level (i.e., the national default values of lipid fraction) was calculated according to the following equation.

$$f_R = \Sigma\left[\frac{CR_i}{CR_{tot}} \bullet f_{R,i}\right]$$

(Equation 6-2)

where:

f_R = national consumption-weighted mean lipid fraction of consumed aquatic organisms at a given trophic level

CR_i = mean per capita consumption rate of species in CSFII consumption category "i" at the same trophic level

CR_{tot} = mean per capita consumption rate of species in all CSFII consumption categories at the same trophic level

$f_{R,i}$ = average lipid fraction of species in CSFII consumption category "i"

Using Equation 6-2, EPA's national default values of lipid fraction were calculated for trophic levels 2, 3, and 4 in Table 6-5.

These values were calculated with consumption rate data (CR_i and CR_{tot}) that originated from the USDA CSFII in Table 6-2, average values of lipid fraction for aquatic species described in Table 6-3, and trophic level designations of each CSFII consumption category described in Table 6-4. The calculation of the national default values of lipid fraction is illustrated in Table 6-6.

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Table 6-4. Trophic Level Assignment of Aquatic Species Corresponding to CSFII Consumption Categories

CSFII Consumption Category	Common Name	Scientific Name	Size	Trophic Level [a] (Mean)	Trophic Level [a] (Range)	Notes [a]	Species Assigned Trophic Level [b]	CSFII Assigned Trophic Level [c]
Anchovy	Bay anchovy	*Anchoa mitchilli*	Adult	2.8	—	9% Microinvertebrates, 58% zooplankton, 33% organic detritus.	3	2(50%) 3(50%)
	Northern anchovy	*Engraulis mordax*	—	2.3	2.1–2.5	Feeds primarily on phytoplankton and some zooplankton.	2	
Carp	Common carp	*Cyprinus carpio*	—	—	2.2–3.1	Young feed on zooplankton, small carp feed on benthic invertebrates and detritus, larger carp become more herbivorous.	3	3
			10-23 cm	3	2.8–3.1	Up to 23 cm, feed primarily on benthic invertebrates.		
			> 23 cm	2.4	2.2–2.6	Larger carp (approx >23 cm) feed primarily on plants and detritus (60%–70%), benthic invertebrates (15–35%), and some zooplankton (<15%).		
Catfish	Black bullhead	*Ameiurus melas*	—	3	2.9–3.2	Seem to consume zooplankton and benthic invertebrates throughout life. Individuals >15 cm may consume some small fish, but also plant materials.	3	3 (50%) 4 (50%)
	Blue catfish	*Ictalurus furcatus*	—	3	—	Assumption.	3	
	Brown bullhead	*Ameiurus nebulosus*	—	—	2.7–3.3	Diet changes with size.	3	
			>10 cm	3.0	2.7–3.2	Those >10 cm feed on 20%–30% plants and 70%–100% benthic invertebrates (burrowing mayfly, scud, chironomid types). Some consume small fish as well.		
	Channel catfish	*Ictalurus punctatus*	36–54 cm	—	2.8–4	Changes with age; can grow up to $50 cm. Three studies indicate it consumes plants; one other did not.	4	
			5–30 cm	3.1	—	5–30 cm; consumes largely benthic invertebrates (60%–80%), detritus (10%–15%), and zooplankton (10%–25%).		
			30–35 cm	3.3	3–3.5	30–35 cm; consumes fish (32%), benthic invertebrates (40%), zooplankton (12%), and detritus (15%). Some populations consume up to 25% algae.		

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Table 6-4. Trophic Level Assignment of Aquatic Species Corresponding to CSFII Consumption Categories (continued)

CSFII Consumption Category	Common Name	Scientific Name	Size	Trophic Level [a] (Mean)	Trophic Level [a] (Range)	Notes [a]	Species Assigned Trophic Level [b]	CSFII Assigned Trophic Level [c]
Catfish	Channel catfish	*Ictalurus punctatus*	35-45 cm	3.8	3.5–3.9	35–45 cm; consumes fish (67%), benthic invertebrates (25%), and detritus (8%). Some populations consume up to 25% algae.		
			> 45 cm	4	4.0–4.2	>45 cm; consumes fish (100%).		
	Flat bullhead	*Ictalurus platycephalus*	—	3.2	3–4	Can grow to large sizes; feeds on mollusks (primarily clams), bryozoans, and worms.	4	
	Flathead catfish	*Pylodictis olivaris*	—	3.8	—	Diet consists primarily of fish with some crayfish, and mollusks.	4	
	Yellow bullhead	*Ictalurus natalis*	30–46 cm	2.6	—	Scavenger; often consumes minnows, crayfish, insect larvae, worms, and algae.	3	
Cisco	Cisco	*Coregonus artedii*	20–30 cm	3.0	3.0–3.1	Primarily a plankton feeder. Occasionally eats eggs, small fish.	3	3
Clam	Clam (general)	—	—	2.2	2.1–2.4	Filter feeder on plankton, detritus; includes zooplankton.	2	2
	Hardshell clam	*Mercenaria spp.*	—	2.2	2.1–2.3	Selective filter feeder, consumes primarily planktonic microalgae.	2	
	Softshell clam	*Mya arenaria*	—	2.2	2.1–2.3	Nonselective filter feeder.	2	
	Manila clam	*Venerupis japonica*	—	2.2	2.1–2.3	Nonselective filter feeder.	2	
	Geoduck	*Panopea abrupta*	—	2.2	2.1–2.3	Filter feeder.	2	
	Amethyst gemclam	—	—	2.2	2.1–2.3	Filter feeder.	2	
	Atlantic rangia	*Rangia cuneata*	—	2.2	2.1–2.3	Filter feeder.	2	
	Baltic macoma	*Macoma balthica*	—	2.2	2.1–2.3	Filter feeder.	2	
	Dwarf surf clam	*Mulina lateralis*	—	2.2	2.1–2.3	Filter feeder.	2	
Crab	Blue crab	*Callinectes sapidus*	—	3.2	3.0–3.4	Feeds primarily on bivalves, organic debris fish, crustaceans, plants, and worms.	3	3
	Rock crab	*Cancer spp.*	—	3.3	3.1–3.5	Feeds on herbivorous snails, amphipods, shrimp, polychaetes, and sea urchins.	3	
	Dungeness crab	*Cancer magister*	—	3.5–3.7	3.3–4.1	Carnivorous; shrimp are preferred prey.	4	
	Stone crab	*Menippe spp.*	—	3.4	3.2–3.7	Carnivorous, feeding primarily on mollusks.	3	

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Table 6-4. Trophic Level Assignment of Aquatic Species Corresponding to CSFII Consumption Categories (continued)

CSFII Consumption Category	Common Name	Scientific Name	Size	Trophic Level [a] (Mean)	Trophic Level [a] (Range)	Notes [a]	Species Assigned Trophic Level [b]	CSFII Assigned Trophic Level [c]
Crayfish	Crayfish	*Astacidae*	—	2.4	2.0–2.7	Primarily herbivorous, omnivorous; animal food minor part of diet if vegetation is available.	2	2
Croaker	White (Pacific) croaker	*Genyonemus lineatus*	—	3.4	3.2–3.7	Opportunistic bottom feeder on small fish, squid, shrimp, polychaetes, crabs, and clams.	3	3 (50%) 4 (50%)
	Atlantic croaker	*Micropogonias undulatus*	—	3.7-4.0	3.3–4.7	Opportunistic bottom feeder; feeds mostly on polychaetes, copepods, mysids, and small clams.	4	
Eel	American eel	*Anguilla rostrata*	—	3.9	3.7–4.3	Feeds on small fish, young alewives, salmon and trout fry, shrimp, and crabs.	4	4
Flatfish and flounder	Gulf flounder	*Paralichthys albigutta*	—	3.5–3.9	3.3–4.1	*Paralichthys* genus are primarily piscivorous as adults but also eat polychaetes, crustacea, echinoderms, and mollusks.	4	3 (50%) 4 (50%)
	California halibut	*Paralichthys californicus*	>56 cm	3.5	3.3–4.0	Feeds on anchovies and other small fish.		
	Summer flounder	*Paralichthys dentatus*	—	3.5–3.9	3.3–4.1	See Gulf flounder.	4	
	Southern flounder	*Paralichthys lethostigma*	—	3.5–3.9	3.3–4.1	See Gulf flounder.	4	
	Starry flounder	*Platichthys stellatus*	—	3.2–3.6	2.7–3.8	Feeds primarily on small crustacea, polychaetes, bivalves, and echinoderms. Few fish.	3	
	Winter flounder	*Pseudopleuronectes americanus*	—	3.0–3.6	2.7–3.8	Feeds primarily on benthic polychaetes, amphipods, coelenterates, shrimp, plant material, and detritus.	3	
Herring	Atlantic herring	*Clupea harengus*	—	3.2	3.1–3.3	Feeds primarily on copepods and krill.	3	3
	Pacific herring	*Clupea pallasi*	—	3.2	3.1–3.3	Feeds primarily on copepods and krill.	3	
Mullet	Mullet	*Mugil spp.*	—	2.1	2.0–2.3	Bottom feeding herbivore/detritivore; consumes some benthic animals.	2	2
Oyster	American oyster	*Crassostrea virginica*	—	2.2	2.1–2.3	Filter feeder on phytoplankton, detritus, and bacteria.	2	2
	Pacific oyster	*Crassostrea gigas*	—	2.2	2.1–2.3	Filter feeder on phytoplankton, detritus, and bacteria.	2	

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Table 6-4. Trophic Level Assignment of Aquatic Species Corresponding to CSFII Consumption Categories (continued)

CSFII Consumption Category	Common Name	Scientific Name	Size	Trophic Level [a] (Mean)	Trophic Level [a] (Range)	Notes [a]	Species Assigned Trophic Level [b]	CSFII Assigned Trophic Level [c]
Perch	Silver perch	*Bairdiella chrysoura*	> 8 cm	3.6	3.3–4.2	Feeds on polychaetes, shrimp, and mollusks; becomes more piscivorous with age.	4	4
	White perch	*Morone americana*	adult	3.6	3.3–4.2	Benthic predator, becoming increasingly piscivorous with age.	4	
	Yellow perch	*Perca flavescens*	20-30 cm	3.4	3.1–3.8	20–30 cm; consumes 10% zooplankton, 50% benthic invertebrates, 34% fish (some populations); nearly 100% fish in other populations.	3	
Pike	Northern pike	*Esox lucius*	>10 cm	4	—	> 10 cm; diet primarily all fish.	4	4
	Pickerel (redfin & grass)	*Esox americanus*	larger specimens	4	—	Larger specimens consume small fish.	4	
Rockfish	Striped bass	*Morone saxatilis*	>10 cm	3.9	—	> 10 cm consumes 85%–97% fish.	4	4
Salmon	Pink salmon	*Oncorhynchus gorbuscha*	—	3.8	—	Feeds at sea; consumes krill, amphipods, squid, and copepods.	4	4
	Coho salmon	*Oncorhynchus kistuch*	45–60 cm	4	4.0–4.5	Adults feed primarily on alewife and smelt. In Lake Michigan, this could result in a higher trophic level where alewife feed on *Mysis*.	4	
	Sockeye salmon	*Oncorhynchus nerka*	—	4	—	Assume trophic level 4 for large specimens.	4	
	Chinook salmon	*Oncorhynchus tshawytscha*	young	3	—	Young in fresh water feed on terrestrial insects taken at water surface.	3	
			adult	4	—	Marine adults consume primarily fish, some amphipods, and other inverts.	4	
Scallop	Bay scallop	*Argopecten irradians*	—	2.2	2.1–2.3	Smaller feeder than ocean scallop.	2	2
	Sea scallop	*Placopecten magellanicus*	—	2.2	2.1–2.4	Filter feeder, consuming primarily algae but also zooplankton, bacteria, and detritus.	2	
Shrimp	Northern shrimp	*Pandalus borealis*	—	2.7	2.3–2.9	Large; feeds on polychaetes, copepods, benthic and planktonic microorganisms, and algae.	3	2 (50%) 3 (50%)
	Brown shrimp	*Pandalus aztecus*	—	2.7	2.3–3.0	Omnivore/predator, consuming polychaetes, amphipods, detritus, and algae.	3	

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Table 6-4. Trophic Level Assignment of Aquatic Species Corresponding to CSFII Consumption Categories (continued)

CSFII Consumption Category	Common Name	Scientific Name	Size	Trophic Level [a] (Mean)	Trophic Level [a] (Range)	Notes [a]	Species Assigned Trophic Level [b]	CSFII Assigned Trophic Level [c]
Shrimp	Pink shrimp	*Panaeus duorarum*	—	2.4	2.1–2.9	Benthic omnivore, consuming polychaetes, other crustaceans, mollusks, algae, and vascular plant detritus.	2	
	White shrimp	*Penaeus setiferus*	—	2.3	2.1–2.7	Omnivore, but consuming more plant material than do other shrimp.	2	
Smelt	Jacksmelt	*Atherinopsis californiensis*	adult	2.5	2.2–2.8	Omnivorous; feeds on algae, diatoms, detritus, and small crustaceans.	3	3
	Surf smelt	*Hypomesus pretiosus*	—	3.1	3.0–3.2	Consumes primarily amphipods, euphausiids, copepods, other zooplankton.	3	
	Rainbow smelt	*Osmerus mordax*	—	3.4	3.2–3.8	Feeds on krill, amphipods, polychaetes, plant debris, small fish, including herring cunner, anchovy, and silversides.	3	
Smelt	Eulachon	*Thaleichthys pacificus*	adult	3.1	3.0–3.2	Feeds primarily on zooplankton, including krill and copepods.	3	
Snail	Snail	—	—	2	—	Most species are strictly herbivorous, grazing on periphyton or other plant materials.	2	2
Sturgeon	Green sturgeon	*Acipenser medirostris*	> 1 m	3.7	3.5–4.0	Benthic carnivore, feeding on invertebrates and small fish.	4	4
	White sturgeon	*Acipenser transmontanus*	> 1.2 m	3.7	3.5–4.0	Adults are benthic carnivores, feeding on invertebrates, including shrimp and bivalves. Larger juveniles and adults feed on fish, including eulachon, anchovies, minnows, and suckers.	4	
	Lake sturgeon	*Acipenser rubicundus*	—	—	3–4	Can grow up to 100 pounds, averages about 40–50 pounds for adults; primarily a bottom feeder, reportedly feeding on small gastropods, crustaceans, insect larvae, and small fishes.	4	
Trout	Brook trout	*Salvelinus fontinalis*	10–40 cm	3.2	—	10–40 cm; at most, 7%–8% fish in diet; remainder primarily benthic invertebrates but also some zooplankton in some populations.	3	4
	Cutthroat trout	*Salmo clarki*	< 40 cm	3	—	< 40 cm; consumes invertebrates.	4	

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Table 6-4. Trophic Level Assignment of Aquatic Species Corresponding to CSFII Consumption Categories (continued)

CSFII Consumption Category	Common Name	Scientific Name	Size	Trophic Level [a] (Mean)	Trophic Level [a] (Range)	Notes [a]	Species Assigned Trophic Level [b]	CSFII Assigned Trophic Level [c]
			> 40 cm	3.2	—	> 40 cm; becomes piscivorous.		
			old adults	4	—	Assumption for oldest specimens.		
	Dolly Varden trout	*Salvelinus malma*	—	—	3–4	Trophic level changes with age.	4	
			10–30 cm	3	—	10–30 cm; diet 100% benthic invertebrates.		
	Dolly Varden trout	*Salvelinus malma*	30–40 cm	3.75	—	30–40 cm; diet 75% fish, 17% benthic invertebrates.		
			> 40 cm	4	—	> 40 cm; diet consists of 100% fish.		
	Lake trout	*Salvelinus namaycush*	20–30 cm	3.7	3.5-4.0	20–30 cm; feeds primarily on small fish (70%) and benthic invertebrates (30%).	4	
			30–40 cm	3.9	3.7-4.1	30–40 cm; feeds primarily on fish (90%) and some benthic invertebrates (10%).		
			>40 cm	4.2	4.0-4.5	> 40 cm; feeds entirely on fish; in Lake Michigan, feed on alewives, which feed on *Mysis*, which feed on zooplankton.		
Trout	Rainbow trout	*Oncorhynchus mykiss*	< 30 cm	3	—	< 30 cm; diet completely of benthic invertebrates or both invertebrates and zooplankton.	4	
			30–50 cm	3.6	—	30–50 cm; diet 35–90% fish, 25–75% benthic invertebrates, zooplankton, terrestrial insects.		
			> 50 cm	4	—	> 50 cm; diet of 100% fish.		
Whitefish	Round whitefish	*Prosopium cylindraceum*	20–30 cm	3	—	Young probably feed on zooplankton; adults feed primarily on benthic invertebrates.	3	3
	Mountain whitefish	*Prosopium williamsoni*	> 30 cm	3.5	—	Greater than 30 cm; consumes large invertebrates and small fish.	4	

[a] Unless otherwise specified, information on trophic status was obtained from USEPA (2000e-g). Game fish data were limited to specimens considered to be representative of the edible size range (i.e., 20 cm or larger).

[b] In determining species trophic level assignments, preference was given to data on larger specimens. Trophic level 4 was assigned to a species with data indicating trophic level 3.5 or higher; trophic level 3 was assigned to a species with data indicating trophic level 2.5–3.4; trophic level 2 was assigned for trophic level 1.5–2.4.

[c] In determining CSFII category trophic level assignments, best professional judgment was used. For example, the CSFII category for catfish includes four species that are assigned to trophic level 3 and three species assigned to trophic level 4. Thus, it is assumed that half (50%) of consumption in the catfish CSFII category is from TL3 and half from TL4. Except for shrimp, all other CSFII categories included species that either were exclusively or predominately one trophic level (e.g., trout, estuarine flatfish, smelt).

Table 6-5. National Default Values of Lipid Fraction

Trophic Level	National Default Value (percentage)
2	1.9%
3	2.6%
4	3.0%

6.2.4 Uncertainty and Sensitivity Analysis

This section discusses the uncertainty and sensitivity associated with the calculation of national default values of lipid fraction described in the previous section. The objective here is to identify the major sources of uncertainty in the present analysis and, where possible, provide some insight into their potential magnitude and direction of impact on the national default values of lipid fraction. In this way, the overall confidence in the default lipid values can be assessed (at least qualitatively) and steps to reduce this uncertainty can be identified. Although ideally one would attempt to address each source of uncertainty quantitatively, available data and resources did not permit complete quantitative analysis of uncertainty. A quantitative analysis of selected sources of uncertainty is provided at the end of this section.

Qualitative Analysis

Applicability of Fish Consumption Rate Data. An integral part of EPA's calculation of national default values of lipid fraction involved the estimation of the type and quantity of fish and shellfish consumed by the U.S. population. As described previously, data on fish and shellfish consumption were obtained from USDA's CSFII for the years 1994–1996 (USDA, 1998). A number of uncertainties are associated with the use of the CSFII consumption data, some of which are described in more detail in the Exposure Assessment volume of this Technical Support Document. First and foremost, the mean per capita rates of fish and shellfish consumption derived from the CSFII are national in scope. As a result, the national pattern of fish and shellfish consumption developed from the CSFII may differ from the consumption patterns represented by various human subpopulations, particularly on local or regional scales. Although the magnitude of this uncertainty has not been quantified here, its impact on the national default values of lipid fraction is believed to be bidirectional (i.e., resulting in an overestimation or underestimation of lipid fraction applicable to local or regional scenarios). Because the CSFII consumption rates are weighted toward leaner aquatic organisms (e.g., shrimp, flounder, flatfish), it is conceivable that they may lead to a greater tendency in the national default values of lipid fraction to underestimate lipid fraction associated with some local and regional consumption patterns compared with overestimating lipid fraction. The magnitude of uncertainty in applying the CSFII consumption rates to local or regional situations will depend on the extent to which local consumption patterns differ from the pattern represented by the CSFII.

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Table 6-6. Calculation of National Default Values of Consumption-Weighted Mean Lipid Fraction

Habitat	CSFII Consumption Category	Assigned Trophic Level	Trophic Level Weighting Factor	Mean Percent Lipid	Mean Consumption Rate (g/person/d)	Trophic Level Weighted Consumption Rate (g/person/day)	CSFII Category Weights	Consumption Weighted Percent Lipid Values
Estuarine	Anchovy	2	0.5	6.1	0.05815	0.02907	0.01809	0.11057
Estuarine	Clam	2	1	1.3	0.01732	0.01732	0.01077	0.01380
Freshwater	Crayfish	2	1	1.1	0.01028	0.01028	0.00640	0.00678
Estuarine	Mullet	2	1	3.8	0.04512	0.04512	0.02807	0.10638
Estuarine	Oyster	2	1	2.4	0.17485	0.17485	0.10877	0.25941
Estuarine	Scallop	2	1	0.8	0.00140	0.00140	0.00087	0.00066
Estuarine	Shrimp	2	0.5	1.7	2.65492	1.32746	0.82575	1.42855
Freshwater	Snails	2	1	1.4	0.00207	0.00207	0.00129	0.00181
Estuarine	Anchovy	3	0.5	6.1	0.05815	0.02907	0.00844	0.05162
Freshwater	Carp	3	1	5.4	0.19071	0.19071	0.05538	0.29671
Estuarine	Catfish	3	0.5	4.0	0.60335	0.30168	0.08761	0.35292
Freshwater	Catfish	3	0.5	2.9	0.60335	0.30168	0.08761	0.25541
Freshwater	Cisco	3	1	1.9	0.00179	0.00179	0.00052	0.00099
Estuarine	Crab	3	1	1.1	0.42111	0.42111	0.12229	0.13928
Estuarine	Croaker	3	0.5	3.0	0.17792	0.08896	0.02584	0.07865
Estuarine	Flatfish	3	0.5	1.2	0.45173	0.22586	0.06559	0.07806
Estuarine	Flounder	3	0.5	1.2	0.73482	0.36741	0.10670	0.12697
Estuarine	Herring	3	1	10.0	0.16428	0.16428	0.04771	0.47898
Estuarine	Shrimp	3	0.5	1.7	2.65492	1.32746	0.38551	0.66693
Estuarine	Smelts	3	1	4.1	0.00880	0.00880	0.00256	0.01048
Estuarine	Smelts, rainbow	3	1	4.1	0.00076	0.00076	0.00022	0.00090
Freshwater	Smelts, rainbow	3	1	4.1	0.00076	0.00076	0.00022	0.00090
Freshwater	Whitefish	3	1	5.9	0.01309	0.01309	0.00380	0.02228
Estuarine	Catfish	4	0.5	4.0	0.60335	0.30168	0.12305	0.49566
Freshwater	Catfish	4	0.5	2.9	0.60335	0.30168	0.12305	0.35871
Estuarine	Croaker	4	0.5	3.0	0.17792	0.08896	0.03629	0.11046
Estuarine	Eel	4	1	11.7	0.00466	0.00466	0.00190	0.02218
Estuarine	Flatfish	4	0.5	1.2	0.45173	0.22586	0.09212	0.10963
Estuarine	Flounder	4	0.5	1.2	0.73482	0.36741	0.14986	0.17833
Estuarine	Perch	4	1	2.3	0.22331	0.22331	0.09108	0.20599
Freshwater	Perch	4	1	2.3	0.22331	0.22331	0.09108	0.20599
Freshwater	Pike	4	1	0.7	0.04021	0.04021	0.01640	0.01190
Estuarine	Rockfish	4	1	3.5	0.05428	0.05428	0.02214	0.07638

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Table 6-6. Calculation of National Default Values of Consumption-Weighted Mean Lipid Fraction (continued)

Habitat	CSFII Consumption Category	Assigned Trophic Level	Trophic Level Weighting Factor	Mean Percent Lipid	Mean Consumption Rate (g/person/d)	Trophic Level Weighted Consumption Rate (g/person/day)	CSFII Category Weights	Consumption Weighted Percent Lipid Values
Estuarine	Salmon	4	1	4.7	0.05915	0.05915	0.02412	0.11420
Freshwater	Salmon	4	1	4.7	0.00118	0.00118	0.00048	0.00227
Estuarine	Sturgeon	4	1	5.3	0.00018	0.00018	0.00007	0.00039
Freshwater	Sturgeon	4	1	5.3	0.00018	0.00018	0.00007	0.00039
Freshwater	Trout (rainbow)	4	1	5.1	0.25361	0.25361	0.10344	0.53028
Estuarine	Trout, mixed sp.	4	1	3.2	0.15305	0.15305	0.06242	0.19788
Freshwater	Trout, mixed sp.	4	1	6.0	0.15305	0.15305	0.06242	0.37425

Trophic Level	Consumption Rate (g/person/day)	Sum of Weights	Consumption-Weighted Mean Percent Lipid
2	1.60757	1.00000	**1.9**
3	3.44341	1.00000	**2.6**
4	2.45175	1.00000	**3.0**
Total	7.50273	—	—

Of particular importance will be the extent to which the lipid contents of locally consumed aquatic organisms differ from those corresponding to species that drive EPA's calculation of the national default lipid values (e.g., shrimp, flounder, flatfish, catfish). Interestingly, an analogous derivation of consumption-weighted values of lipid fraction specific for the Great Lakes region resulted in estimates that were similar to the national default values (i.e., 1.8% for trophic level 3, 3.0% for trophic level 4), despite considerable differences in consumption patterns (USEPA, 1995b). To address uncertainty associated with potential differences in consumption patterns and associated lipid fraction, EPA recommends that States and Tribes use local or regional information on fish and shellfish consumption to calculate values for lipid fraction whenever possible.

Specificity of Fish Consumption Rate Data. Another attribute associated with the CSFII-derived consumption rates that leads to uncertainty in the national default values of lipid fraction is the lack of specificity in the consumption rate categories (trout, flatfish, catfish). Specifically, consumption rate information was not available at the species level (e.g., lake trout, brook trout). Therefore, within a CSFII consumption category, equal weighting of lipid fraction among species was assumed. Obviously, to the extent that this assumption is violated, uncertainty will be introduced into the default values of lipid fraction.

To provide some insight into the effect of violating EPA's assumption of equal weighting among species lipid values on the national default values of lipid fraction, the default values of lipid fraction were recalculated assuming 100% weighting to the species with the *highest* mean lipid value within a CSFII consumption category, and again assuming 100% weighting to the species with the *lowest* mean lipid value. Values of lipid fraction calculated with the species with the lowest and highest mean lipid values are provided in Table 6-7, along with EPA's national default values of lipid fraction (calculated with the average of species mean lipid values).

It is apparent from this exercise that substantially different assumptions about the weighting of species mean lipid values within a CSFII consumption category have relatively little impact on the national default values of lipid fraction (i.e., <50% increase or decrease). However, this analysis was constrained by the limited availability of lipid data for multiple species within a CSFII consumption category. Specifically, of the consumption categories

Table 6-7. Sensitivity of National Default Values of Lipid Fraction to Different Weighting Assumptions Among Species

Trophic Level	Calculated Using Lowest Species Mean Lipid Values	Calculated Using Average of Species Mean Lipid Values[a]	Calculated Using Highest Species Mean Lipid Values
2	1.9	1.9	2.0
3	2.1	2.6	3.1
4	1.8	3.0	4.4

[a] Weighting assumption used for calculating the national default values of lipid fraction.

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constituting the bulk of the total consumption rate (shrimp, catfish, flounder, flatfish), only the catfish category was represented by multiple species. Therefore, the impact of different assumptions about the weighting of species mean lipid values is likely to be underestimated by the present analysis.

Model Uncertainty, Measurement Error, and Variability in CSFII-Derived Fish Consumption Rates. Other sources of uncertainty in EPA's national default values of lipid fraction include model uncertainty, measurement error, and variability associated with the estimates of mean fish consumption rates from the CSFII study. Even though data and resource limitations prevented EPA from assessing the magnitude and direction of these sources of uncertainty, it is still considered instructive to discuss their overall characteristics. The term *model uncertainty* is used here to represent uncertainty originating from the design of the CSFII study and its application to AWQC derivation. Specifically, the fish consumption rates from the CSFII study were based on a 2-day dietary recall from a stratified random sample of the U.S. population. In many situations, AWQCs are derived to protect against adverse effects from long-term (chronic) exposures to chemicals from sources including fish consumption. Under these AWQC applications, so-called model uncertainty is introduced in the estimated fish consumption rates to the extent that daily mean per capita consumption rates estimated over a 2-day period deviate from the "true" daily consumption rates over the long term.

The term *measurement error* refers to the error associated with recalling from memory the type and quantity of fish and shellfish actually consumed. Interestingly, although the previous discussion of model uncertainty might lead one to favor survey designs with longer recall periods (e.g., weekly, monthly), measurement error can increase substantially for longer survey recall periods.

Finally, one can expect the variability associated with the estimated mean per capita consumption rates to affect the derivation of national default values of lipid fraction. This variability would reflect variation in the amount and types of fish and shellfish actually consumed across individuals, in addition to differences in the ability of individuals to recall what they ate in the past (measurement error). To assess the effect of this source of variability on the default consumption rates, one would need some estimate of the variance of mean per capita consumption rates for each CSFII category. However, limitations in the CSFII study prevent accurate estimates of this variance at the CSFII category level.

For a more detailed discussion of uncertainty associated with the use of data from the CSFII study, see the Exposure Assessment volume of the Technical Support Document.

Uncertainty in Trophic Level Classification. As illustrated by Table 6-4, variation exists in the trophic position of commonly consumed aquatic organisms. Sources of this variability can be attributed to numerous factors, including the size and life stage of the organism, the season, the organism's life history (e.g., migratory behavior), and spatial heterogeneity in the food web structure. To calculate national default values of lipid fraction, EPA relied on a synthesis of data on the trophic position of aquatic organisms (USEPA, 2000e-g). Data from these syntheses of trophic positions were ultimately rounded to nominal values (e.g., 1, 2, 3, 4), when in reality a

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continuum exists for an organism's trophic position (e.g., 1.3, 2.6, 3.7). To the extent that the trophic position of consumed aquatic organisms at various locations differs from EPA's assessment of trophic position, uncertainty will be introduced in derivation of the national default lipid values. For some organisms (e.g., clams, oysters, scallops), the variability in trophic position appears small (Table 6-3) and the likely impact on the default values of lipid fraction is expected to be minimal. For other groups of organisms, (e.g., anchovy, catfish, croaker, flatfish, flounder, shrimp), wider variation exists in trophic position within and across species, in part because of their opportunistic feeding style. For these CSFII categories, EPA weighted the consumption rates equally between multiple trophic levels (Table 6-6). By chance, these more "opportunistic" species make up a large fraction of the total rate of consumption of freshwater and estuarine species. To assess the sensitivity of EPA's national default values of lipid fraction to the assumption of equal weighting of consumption rates across trophic levels for selected species (anchovy, catfish, croaker, flatfish, flounder, and shrimp categories), national default values of lipid fraction were recalculated by assuming that 100% of the consumption occurred in the lower trophic level, and again assuming that 100% of the consumption occurred in the higher trophic level. For example, calculations were performed assuming that all of the consumption of catfish species occurred at trophic level 3 and again at trophic level 4. Results from this sensitivity analysis are shown in Table 6-8.

It is apparent from Table 6-8 that the national default values of lipid fraction are relatively insensitive to assumptions made about the trophic position of those species for which the trophic position is particularly variable (anchovy, catfish, croaker, flatfish, flounder, and shrimp).

Table 6-8. Sensitivity of National Default Values of Lipid Fraction to Different Weighting Assumptions Among Trophic Levels[a]

Trophic Level	Calculated Assuming 100% Consumption at the Lower Trophic Level	Calculated Assuming 50% Consumption at Lower and Higher Trophic Level[b]	Calculated Assuming 100% Consumption at the Higher Trophic Level
2	2.5	1.9	1.9
3	2.3	2.6	2.8
4	2.8	3.0	3.7

[a] Different weighting assumptions were made for anchovy, catfish, croaker, flatfish, flounder, and shrimp CSFII consumption categories.
[b] Weighting assumption chosen for calculating the national default values of lipid fraction.

Limitations in the Lipid Data. A number of limitations in the lipid data contribute to uncertainty in the national default values of lipid fraction. First, the lipid data used to calculate the national default values of lipid fraction were originally generated for a variety of purposes and by a variety of methods. These data almost certainly do not represent a random sampling of aquatic organisms that is properly stratified over potentially important variables such as age, tissue type, and season. As a result, the data set may contain hidden biases that are difficult to assess without a comparison with a truly random, stratified sample. For example, some species data sets may be overrepresented by one or more tissue types, where multiple tissue types are being consumed

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(e.g., fillet with and without skin). Other species data sets might contain biases that result from overrepresentation of certain lipid measurement methods. Second, the sample size is small for a number of species (i.e., <10 for certain species of clam, crayfish, croaker, sturgeon, and salmon). In general, the lower sample sizes for these species result in lower confidence in the species mean values of lipid fraction. Some commonly consumed species may not be represented at all in a given CSFII consumption category because lipid data were simply unavailable. Third, the number of species represented in certain CSFII consumption categories is small or unknown. The latter situation occurred for shrimp, flounder, flatfish, crayfish, eel, and whitefish categories, where lipid data were available only in an aggregated form (e.g., at the family level for shrimp). Finally, the quality of some of the lipid data (in particular, the STORET-based NSQS data) was not documented and could not be verified directly.

Quantitative Analysis

Variability in Lipid Data. As shown in Table 6-3, estimates of variation around the species mean value of lipid content are available for most species. Multiple sources of variation are believed to contribute to the observed variation in species lipid content. Within a species, these sources include measurement error; differences in lipid extraction and quantification methods; inclusion of data from different tissue types, ages, and sizes of organisms; and different dietary habits among individuals within a species, to name a few.

To assess how these and other sources of variability in lipid content affect the uncertainty in EPA's calculation of national default values of lipid fraction, a probabilistic-based uncertainty analysis was conducted, using the estimated variance and mean values shown in Table 6-2. This analysis relied on several assumptions:

1. Mean and coefficient of variations in species lipid content were defined from the data summarized in Table 6-3.

2. The values of lipid content for each species were assumed to be log-normally distributed. This assumption was consistent with the positive skewness (and non-negative nature) of percentage data and was supported by visual inspection of frequency distributions from selected lipid data sets.

3. In a few situations (e.g., striped anchovy, northern anchovy, rockfish [*Sebastes* spp.]), estimates of variance around the mean value were not available. In these cases, the coefficient of variation was assumed to be equal to that calculated from another species in the same CSFII consumption category.

4. For two CSFII consumption categories (clam, crayfish), no information on variance was available from any species. As a result, no variance was assumed around the mean values.

5. Trophic level designations and mean per capita consumption were held constant.

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6. All input distributions were assumed to be independent (i.e., no correlation among distributions).

With the aforementioned information and supporting assumptions, a probabilistic uncertainty analysis was run, using a Monte Carlo simulation technique for calculating the national default values of lipid fraction. The Monte Carlo simulation used Crystal Ball® version 4.0 software (Decisioneering, Inc., Denver, Colorado) in combination with a Microsoft Excel® 97 spreadsheet application. For each iteration of the simulation, a consumption-weighted average value of lipid fraction (i.e., a default value of lipid fraction) was calculated for each trophic level, using a randomly selected value of lipid fraction from each of the species input distributions. The simulation was run for 10,000 iterations, thus producing a distribution of default values of lipid fraction for each trophic level. Repeated simulations indicated that 10,000 iterations produced highly stable estimates of the mean and extreme percentiles of the default lipid values.

Figures 6-2 and 6-3 show the results of the Monte Carlo simulations. The x-axis of Figure 6-2 refers to the default value of lipid fraction (expressed as a percentage), and the y-axis displays the probability. It is apparent that the default values of lipid fraction comprise three distinct but somewhat overlapping distributions. For clarity, Figure 6-2 displays the same information in the form of a reverse cumulative frequency. The y-axis displays the frequency by which a given value of the default value of lipid fraction (x-axis) is exceeded in the data set. From Figure 6-3, one can estimate the likelihood that the default lipid fraction would exceed a particular value.

Relevant descriptive statistics from the output distributions of default values of lipid fraction are shown in Table 6-9. As expected, mean values produced from the Monte Carlo simulations were identical (to two significant digits) to the national default values (Table 6-4) calculated by using only the species mean values as inputs. Regarding variation surrounding the mean values, it is often useful to evaluate the range between the 5th and 95th percentiles of the distribution. From this measure, it is evident that the variability around the mean values of lipid fraction is relatively small (a factor of #2.5). The most sensitive input distributions to the calculated default values of lipid fraction are shrimp (for trophic level 2), shrimp and common carp (for trophic level 3), and rainbow trout (for trophic level 4). Each of these input distributions contributed approximately 25% or more to the variance in the calculated default lipid values.

Finally, EPA acknowledges that there is similarity among the national default value lipid fractions across trophic levels (i.e., 1.9, 2.6, 3.0) and that the uncertainty bounds somewhat overlap. This degree of similarity might support the notion of calculating a single national default value of lipid fraction rather than maintaining distinctions among trophic levels. Although EPA considered this option, it was ultimately rejected in favor of maintaining separate national default values of lipid fraction at each trophic level for various reasons. First, maintaining trophic level specificity in lipid fraction is consistent with EPA's derivation of national BAFs, which are calculated separately for trophic levels 2, 3, and 4. As explained in the 2000 Human Health Methodology (USEPA, 2000a), trophic level–specific BAFs are derived to account for factors that can affect bioaccumulation in aquatic organisms occupying different trophic positions in aquatic food webs (e.g., biomagnification and broad physiological differences such as clams versus fish). In addition to the improved technical accuracy associated with applying trophic level–specific

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values of lipid fraction, maintaining a separate distinction across trophic levels also provides flexibility to States and Tribes for adjusting EPA's national default lipid values. Specifically, adjustments can be made to the calculation of one trophic level–specific value of lipid fraction without affecting those determined for the other trophic levels. For example, a State or Tribe may wish to add or subtract lipid data for various top predator species (trophic level 4) without changing the values of lipid fraction for other trophic levels. Thus, EPA believes that its use of trophic level–specific values of lipid fraction not only achieves greater technical accuracy than does a single estimate, but also affords greater flexibility to States and Tribes in making desired adjustments to EPA's national default values of lipid fraction.

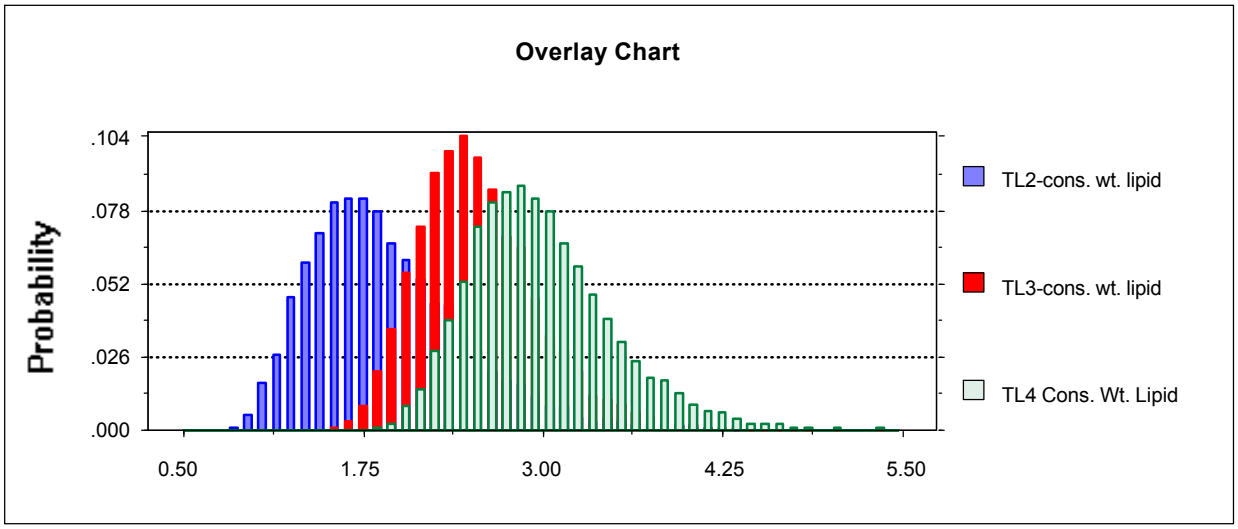

Figure 6-2. Frequency distribution of national default values of lipid fraction (10,000 iterations).

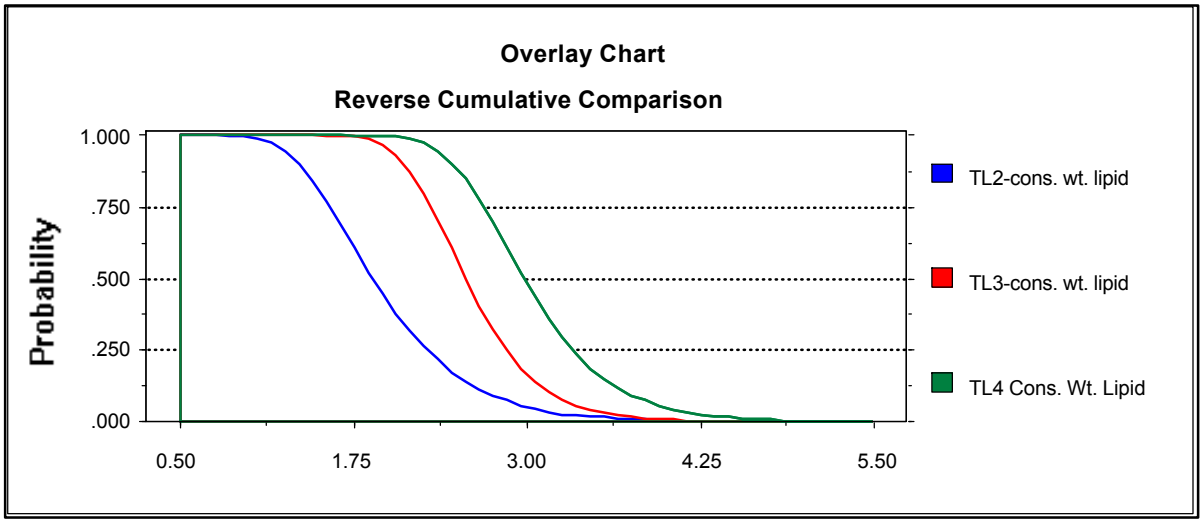

Figure 6-3. Reverse cumulative comparison of national default values of lipid fraction (10,000 iterations).

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Table 6-9. Descriptive Statistics of Monte Carlo Simulation of National Default Values of Lipid Fraction (10,000 Iterations)

Statistic/Percentile	Trophic Level 2	Trophic Level 3	Trophic Level 4
Mean	1.9	2.6	3.0
Median	1.8	2.5	2.9
CV	0.30	0.17	0.17
5th	1.2	2.0	2.3
95th	3.0	3.4	3.9
$95^{th}/5^{th}$	2.5	1.7	1.7
Minimum	0.7	1.4	1.6
Maximum	6.1	5.9	6.5

6.3 BASIS FOR THE NATIONAL DEFAULT VALUES OF DOC AND POC

This section provides the technical basis of EPA's calculation of national default values of DOC and POC concentrations in U.S. fresh and estuarine surface waters. As summarized in the National Human Health AWQC Methodology (USEPA, 2000a), EPA's national default values of DOC (2.9 mg/L) and POC (0.5 mg/L) are used in calculating national BAFs for nonionic organic chemicals. Information on DOC and POC is necessary to adjust a baseline BAF, which reflects the concentration in the lipid fraction of tissue and the freely dissolved concentration in water, to a national BAF expressed in terms of total chemical in water and tissue (Section 3, Figure 3-2). The national BAF incorporates values that are reflective of the lipid content of the fish and shellfish consumed by the U.S. population and the effects of chemical binding/associating with DOC and POC in representative U.S. surface waters. For deriving national human health AWQCs, EPA uses national default values of DOC and POC that are representative of U.S. surface waters for calculating the freely dissolved fraction of a nonionic organic chemical (see Equation 4-4).

Although EPA uses national default values of DOC and POC to derive national human health AWQC for nonionic organic chemicals, EPA encourages States and authorized Tribes to use local or regional data on the organic carbon content of applicable waters when adopting criteria into their own water quality standards. The EPA encourages the use of appropriately derived locally or regionally derived values of DOC or POC over nationally derived values because local or regional conditions that affect DOC and POC concentrations can differ substantially from those represented by nationally derived values. Additional guidance on developing local or region-specific values of DOC and POC is found in a subsequent volume of this TSD (Volume 3: Development of Site-Specific Bioaccumulation Factors). Nevertheless, EPA recognizes that there will be situations when such local or regional data are not available or are inadequate for deriving local or regional values of DOC and POC. In these cases, EPA

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recommends that States and Tribes use EPA's national default values of DOC and POC when deriving BAFs for use in establishing State or Tribal water quality criteria and standards.

The following sections present the data sources, analysis, and uncertainty associated with EPA's derivation of national default values of DOC and POC.

6.3.1 Data Sources

Data on the concentrations of DOC and POC in U.S. surface waters were obtained from two databases:

1. The U.S. Geological Survey's (USGS) WATSTORE database
2. EPA's historical STORET database (recently renamed the Legacy Data Center [LDC]database)

Although EPA's historical STORET database (henceforth called "LDC" for consistency with current EPA nomenclature) contains data from the USGS WATSTORE database, queries indicated that the USGS data contained in LDC were at least 2 years out of date. Therefore, non-USGS data were retrieved from the LDC database and USGS data were retrieved from the WATSTORE database in order to obtain a comprehensive data retrieval without duplicating records. Each database is described further below.

WATSTORE Database

The USGS developed the WATSTORE (National Water Data Storage and Retrieval System) for the storage and retrieval of water data collected through its activities. The WATSTORE database was established in 1972 to provide an effective and efficient means for processing and maintaining water data collected through USGS activities and to facilitate release of the data to the public. The system resides on the central computer facilities of the USGS at its National Center in Reston, Virginia, and consists of related files and databases. The Water Quality File was searched for retrieval of DOC and POC data. This file contains approximately 2 million analyses of water samples that describe the chemical, physical, biological, and radiological characteristics of both surface and groundwater. The method for analysis of POC followed *Standard Methods* #5310D—"Wet Oxidation Method for Total Organic Carbon" (APHA, 1995), with two modifications. First, silver filters were used instead of glass fiber filters. Second, a sonification step was added in 1997 to facilitate complete oxidation of organic carbon (USGS, 1997; Burkhardt et al., 1999). For analysis of DOC, the wet oxidation method (*Standard Methods* #5310D) was also used on filtered samples until approximately 1983. After 1983, the persulfate-ultraviolet oxidation method was used (*Standard Methods* #5310C*)* on filtered samples, which includes UV radiation with a reduced heating/digestion step (APHA, 1995; Kammer, 2000).

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LDC Database

EPA's LDC database is a waterway-related monitoring database that contains data collected by Federal, State, and local agencies; Indian Tribes; volunteer groups; academics; and others. All 50 States, territories, and jurisdictions of the United States, along with portions of Canada and Mexico, are represented in the database. The database used in this analysis was called the historical, or "old," STORET database but recently was renamed the Legacy Data Center (LDC). The LDC contains historical water quality data dating back to the early part of the 20th century and collected up to the end of 1998. The database contains raw biological, chemical, and physical data on surface water and groundwater. Each sampling result is accompanied by information on where the sample was taken (latitude, longitude, State, county, Hydrologic Unit Code, and a brief site identification), when the sample was gathered, the medium sampled (e.g., water, sediment, fish tissue), and the name of the organization that sponsored the monitoring. Information on the analytical methods used to quantify DOC and POC was not available in the LDC database. Although a newer version of STORET was initiated in 1999 that contained this and other QA/QC information, sufficient data were not available from this database at the time of this retrieval (i.e., the new STORET database contains data collected beginning in 1999, along with selected older data that have been properly documented and migrated from the LDC).

6.3.2 Data Retrieval and Screening

Data retrievals from the LDC and WATSTORE databases were conducted in January 2000 and combined into a single relational database. Originally, approximately 800,000 records containing data on POC, DOC, or total organic carbon (TOC) were retrieved for the period beginning in 1970 through the latest year data were available (1999 for WATSTORE; 1998 for LDC). This retrieval was limited to samples taken from ambient surface waters (i.e., samples from wells, springs, effluents, and other nonambient sources were excluded). Additionally, this initial retrieval included multiple types of POC and DOC measurements to ensure that the initial data retrieval would be sufficiently comprehensive.

Once these data were retrieved, the two data retrievals were combined into a single database. Numerous steps were then taken to process and screen the DOC and POC data so that only the most appropriate data would be retained for calculating the national default values. These processing and screening steps are outlined below.

1. *Organic Carbon Parameters*. The following parameter codes were retained in the database: 00680 (Carbon, Total Organic); 00681 (Carbon, Dissolved Organic); 00684 (Carbon, Dissolved Organic-Whatman GF/F); 00689 (Carbon, Suspended Organic); 80102 (Carbon, Organic Particulate). All units were expressed in milligrams per liter as C (Carbon).

2. *Uncertain Values*. Values that were coded in such a way as to suggest uncertainty in the measurement were deleted from the database. For example, values coded as "estimated value," "analyte detected in blank and sample," "sample held beyond

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normal holding time," "actual value is known to be greater reported value," and similar such indicators were deleted.

3. *Water Body and Station Types.* The database was further restricted to the following water body types: estuaries, lakes, reservoirs, and streams (including rivers). This step excluded other "ambient" surface water types, such as oceans, freshwater wetlands, and canals. Station types were restricted to those coded as "ambient" only. This step excluded so-called specialty stations (i.e., those stations designated for special purposes such as storm water runoff and biological and sediment monitoring).

4. *Sampling Period*. Although the initial retrieval contained data dating back to 1970, the time period for the final database was restricted to 1980 through 1999. Pre-1980 data were eliminated because of the greater uncertainty in using these data to represent present-day conditions that can affect organic carbon concentrations in surface waters (e.g., secondary treatment of effluents).

5. *Detection Levels.* Some values for POC and DOC were reported to be below analytical detection levels. In this situation, the value was assumed to be half of the reported detection level. Values with "high" detection levels (i.e., >1.0 mg/L for DOC and >0.2 mg/L for POC) were deleted from the database because of the greater uncertainty involved in estimating definitive values of DOC and POC in these situations.

6. *Calculated Values.* It was clear from reviewing the data that a substantial portion of samples contained values of DOC and TOC, but not POC. It is apparently not uncommon to determine the POC concentration by subtracting the DOC concentration from the TOC concentration determined from a given sample. In these situations, the parameter of interest (POC or DOC) was calculated by the difference from the other two measurements (i.e., POC = TOC – DOC; DOC = TOC – POC). This calculation was performed using data only from the same sample to avoid introducing error into calculated POC values. The end result was that about 40% of the total number of POC values in the database were determined by difference. The opposite condition (i.e., TOC and POC, but no DOC value) occurred rarely and resulted in only 0.4% of the total DOC samples being determined by difference.

7. *Extreme Values.* As a final quality control step, DOC and POC values at the extreme high end of the cumulative frequency distributions were reviewed for consistency with extreme values reported in natural surface waters of the United States. A small fraction of the DOC and POC concentrations in the LDC database exceeded concentrations considered to represent upper limits of DOC and POC concentrations reported in U.S. water bodies (i.e., 0.2% exceeded 60 mg/L for DOC and 0.6% exceeded 30 mg/L for POC). These extreme values were based on a review of organic carbon data by Thurman (1985), who reported extreme values

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of DOC concentrations of as high as 50 mg/L in distrophic lakes and 60 mg/L in tributaries draining wetland systems. Concentrations of POC between 1 and 30 mg/L encompass 99% of the world's river systems and are at the upper range of POC concentrations reported for U.S. rivers (as reviewed by Thurman, 1985).

The evaluation of extreme values revealed some "negative" values of POC (i.e., about 7% of the total number of POC values). These values occurred almost entirely as an artifact of calculating POC values by difference (see item 6 above) and the impact of measurement error on this process. For example, if both TOC and DOC were near analytical detection limits or were otherwise very similar in magnitude, it would not be surprising for reported values of DOC to be, on occasion, slightly higher than those for TOC as a result of measurement error. The vast majority of the negative values were relatively close to zero (i.e., between –1 mg/L and 0 mg/L).

To address concerns about the impact of extreme values on the calculation of national default values for DOC and POC, the extreme ends of the respective distributions were truncated. Specifically, values of DOC above 60 mg/L and of POC above 30 mg/L were omitted from the database. These values represent the 99.8th and 99.4th cumulative percentiles of the respective DOC and POC distributions. To avoid introducing bias into the median values of DOC and POC by truncating one side of the distribution, DOC and POC values below the lower 0.2% and 0.6%, respectively, were also omitted. This truncation of the lower tail of the POC distribution bounds had the impact of eliminating some, but not all, of the "negative" POC values.

6.3.3 Results

Using the screened databases described previously, national default values of DOC and POC were calculated to be 2.9 mg/L and 0.5 mg/L, respectively. These values represent median (50th percentile) values from approximately 110,000 measurements of DOC and 86,000 measurements of POC in U.S. fresh and estuarine surface waters. All 50 States are represented in the database. The EPA selected median values of DOC and POC for the national default values for consistency with the goal of national BAFs (i.e., as central-tendency estimates).

Table 6-10 shows descriptive statistics surrounding the median values for DOC and POC, in addition to values for specific water body types. It is evident from Table 6-10 that variation in DOC and POC concentrations is relatively large. For example, the coefficient of variations around the means are all above 100% and approach or equal 200% in some cases. Ratios of the 95th to the 5th percentiles range from a factor of 5 to 30, depending on water body type and parameter. This variation is not unexpected, given the high degree of temporal and spatial heterogeneity represented in the database. It is also apparent that the type of water body (lake, stream, estuary) has some impact on the DOC and POC distributions. For example, median values of DOC and POC from samples designated as "stream/river" are nearly twice those designated as "lakes." This difference is probably related to the differing hydrologic,

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biogeochemical, and watershed characteristics of streams and lakes. Given the relatively high degree of variation that is evident in DOC and POC concentrations in surface waters across the United States, EPA recommends that States and Tribes consider deriving appropriate values of DOC and POC by using local or regional data when sufficient data are available. However, for deriving national AWQC, and when States and Tribes lack sufficient local or regional data, EPA recommends the use of its national default values of DOC and POC.

Table 6-10. National Default Values for POC and DOC in U.S. Fresh and Estuarine Surface Waters

	DOC (mg/L)				POC (mg/L)			
Statistic	**All Types**	**Stream/ River**	**Lake/ Reservoir**	**Estuary**	**All Types**	**Stream/ River**	**Lake/ Reservoir**	**Estuary**
Median	2.9	3.8	2.1	2.7	0.5	0.6	0.3	0.9
Mean	4.6	5.6	2.9	3.4	1.0	1.3	0.5	1.2
Std.	5.1	5.9	3.0	2.6	2.0	2.5	1.0	1.8
CV	111%	105%	103%	76%	200%	192%	200%	150%
n	111,059	69,589	25,704	15,766	86,540	48,238	23,483	14,819
5th	0.8	0.7	1.0	1.7	0[a]	0[a]	0.08	0.1
10th	1.2	1.0	1.4	2.0	0	0[a]	0.1	0.3
25th	2.0	2.1	1.8	2.3	0.2	0.2	0.2	0.5
75th	5.4	6.9	2.6	3.2	1.1	1.4	0.5	1.4
90th	9.7	11.6	5.0	5.0	2.3	3.1	0.8	2.2
95th	14	16.5	7.8	9	3.9	5	1.3	3
95th/5th	17.5	23.6	7.8	5.3	—	—	16.3	30.0

[a] Values calculated to be less than zero because of measurement error; see Section 6.3.2 for explanation.
Source: U.S. EPA LDC and USGS WATSTORE databases. Data retrieval: January 2000; see Sections 6.3.1 and 6.3.2 for description.

6.3.4 Uncertainty/Limitations in National Default Values

This section describes sources of uncertainty associated with EPA's derivation of national default values of DOC and POC for establishing national human health AWQCs. This discussion of uncertainty is neither exhaustive nor entirely quantitative. Rather, it focuses on sources of uncertainty that are likely to have the greatest impact on the derivation and application of national default values of DOC and POC. Sources of uncertainty characterized below are grouped into the following categories: (1) sampling bias, (2) measurement error, and (3) natural variability in DOC and POC concentrations.

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Sampling Bias

The national default values of DOC and POC are intended to represent central tendency estimates of DOC and POC concentrations in U.S. surface waters. Ideally, the data used to generate these values should originate from a random sampling of U.S. surface waters and should be appropriately stratified and weighted by spatial and temporal factors that would be expected to influence organic carbon concentrations in aquatic ecosystems (e.g., water body type, hydrologic and watershed characteristics, ecoregion, season). However, this type of database was not available on a national scale. Therefore, EPA relied on data from USGS's WATSTORE and EPA's LDC databases to calculate its national default DOC and POC values. The strengths of these databases include their large number of records (e.g., >110,000 DOC values and >86,000 POC values), a representation of DOC and POC values for all 50 States, and the reasonably long period over which data were collected (1980–1999 for this analysis).

An important limitation of the WATSTORE and LDC databases is the fact that they do not reflect a random sampling of U.S. surface waters (i.e., they may contain biases because of sampling design). For example, about half of the DOC and POC values in the databases were sampled in Maryland, New York, Ohio, Florida, and Delaware. Thus, some States are disproportionally represented, even when one considers the relative area of surface water area likely to be contained within each State. In addition, organic carbon data from these databases were not weighted or aggregated in any way before national default (median) values were calculated. Given these potential biases in the underlying data, it is important to address the obvious question: How well do EPA's national default values of DOC and POC represent average conditions across the United States?

To address the question of sampling bias and its impact on the representativeness of EPA's national default DOC and POC values, two types of comparisons were made with the WATSTORE/LDC data. First, the national default values were compared with central-tendency estimates of DOC and POC obtained from independent reviews of the relevant scientific literature. This was done to provide a qualitative assessment of the comparability of national default values to "expected" values based on literature accounts. The second comparison was more quantitative in design and involved contrasting geographically distinct subsets of the WATSTORE/LDC databases with geographically similar subsets of data produced by EPA's Environmental Monitoring and Assessment Program (EMAP). Data contained in the EMAP databases are sampled by using a stratified, random sampling design that minimizes the effect of biases in sampling design on resulting statistical distributions of the data. Each of these comparisons is described below.

Comparisons with Literature Data. Thurman (1985) reviewed the literature on DOC and POC concentrations in surface waters throughout the world. The concentrations of DOC and POC were found to vary in surface waters as a function of water body type, trophic status (lakes), climate, watershed size and vegetation, and season of the year. Specifically, Thurman (1985) reported that mean values of DOC in some pristine streams range from 1 to 3 mg/L and those in rivers and lakes typically range from 2 to 10 mg/L. Ranges of DOC concentrations in estuaries are reported to be highest at the limit of tidal rise (i.e., essentially equivalent to DOC in rivers) and

lowest as dilution with seawater becomes complete (i.e., approximating 1 mg/L on average). For swamps, marshes, and bogs, DOC concentrations are reported to range from 10 to 30 mg/L. Concentrations of POC in lakes reportedly range from about 0.1 to 1.0 mg/L, whereas those in small streams range from 0.1 to 0.3 mg/L, or about 10% of the DOC. Finally, POC concentrations in rivers are reported to be about one-half the concentration of DOC (i.e., 1–5 mg/L), although POC may equal DOC in the largest rivers during times of high discharge. Although the ranges of DOC and POC concentrations reported by Thurman (1985) include surface waters found beyond the United States, they also appear to be representative of U.S. surface waters, based on data summarized by Thurman (1985) that were specific to the United States.

Despite the aforementioned limitations in EPA's DOC and POC databases with respect to potential sampling bias, EPA's national default values of DOC (2.9 mg/L) and POC (0.5 mg/L) compare favorably with the ranges of DOC and POC concentrations summarized by Thurman (1985). This comparison suggests that EPA's national default values of DOC and POC are not unreasonable in terms of representing typical organic carbon concentrations found in U.S. rivers, streams, lakes, and estuaries. With respect to wetland areas (marshes, swamps, bogs), it is likely that the national default values may significantly underestimate DOC and POC concentrations in these systems, owing to their poor representation in the DOC and POC databases. The impact of this underestimation on national BAFs will vary as a function of the K_{ow} of the chemical (see "Natural Variability in DOC and POC Concentrations," below). For some highly hydrophobic organic chemicals, this underestimation may result in a conservative estimate of the AWQC for these systems (i.e., a lower AWQC than what might be necessary) because of a likely overestimation of the bioavailable fraction and national BAF.

Comparisons with EMAP Data. Data generated by EPA's EMAP program are based on a stratified, random sampling strategy that is specifically designed to minimize the influence of sampling bias on the data and to enable statistically based extrapolations across geographic regions (Herlihy et al., 2000). Currently, however, the EMAP databases contain DOC measurements (but not POC measurements) and are limited to smaller geographic scales and specific water body types. Thus, DOC data from EMAP's 1997–1998 sampling of mid-Atlantic streams and rivers (http://www.epa.gov/emap/html/dataI/surfwatr/data) were compared with similar geographic subsets from the WATSTORE/LDC database. The mid-Atlantic EMAP database was chosen because sufficient data were available on DOC in rivers and streams to make meaningful comparisons at the State and ecoregion levels. Similarly, the mid-Atlantic region is also well represented in the WATSTORE/LDC database.

Figure 6-4 shows the cumulative frequency distributions of DOC contained in the EMAP mid-Atlantic database (top panel) and the WATSTORE/LDC database (bottom panel) for rivers and streams in Pennsylvania, Virginia, and West Virginia. Similar comparisons are made for four mid-Atlantic ecoregions (Piedmont, Ridge and Valley, Central Appalachians, Western Allegheny Plateau; Figure 6-5). Descriptive statistics are provided in Tables 6-11 and 6-12. From both sets of comparisons, it is apparent that the agreement between the WATSTORE/LDC and EMAP data is best at the middle to lower tails of the distributions and poorest at the higher end of the distributions. At the lower tails of the distributions (e.g., 10th, 25th percentiles), the WATSTORE/LDC DOC data are generally within 30% of the EMAP data (ecoregion 70 being

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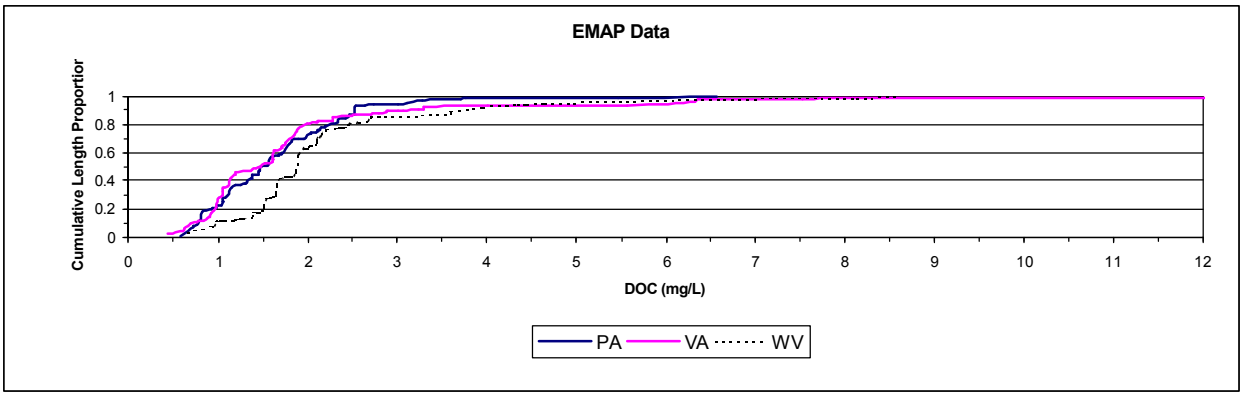
the only exception). The median DOC values of the WATSTORE/LDC data show a slightly higher bias compared with median values from the EMAP data but are usually within a factor of 1.5 (ecoregions 47 and 70 are about a factor of 2 greater). For a majority of comparisons made at the 75th and 90th percentiles (i.e., 11 of 14), the WATSTORE/LDC DOC values are approximately a factor of 2 greater than the corresponding percentiles from the EMAP data. This result is expected, given the greater focus of the WATSTORE/LDC sampling sites on larger river and stream systems and on areas receiving proportionately greater human influence compared with the EMAP sampling sites.



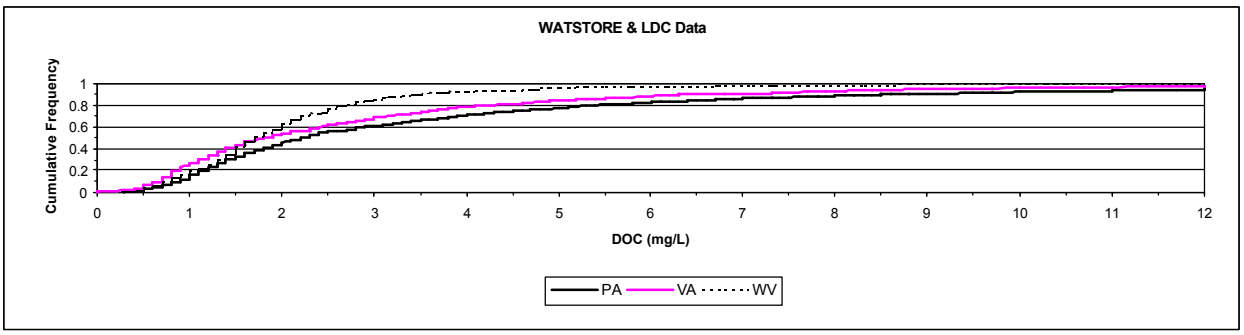


Figure 6-4. Ecoregion-level DOC distributions for rivers and streams from EPA's WATSTORE/LDC and EMAP databases.
Source: EMAP data were taken from EPA's Environmental Monitoring and Assessment Program, Mid-Atlantic Integrated Assessment, 1997–98 (http://www.epa.gov/emap/html/dataI/surfwatr/data).
USGS WATSTORE and EPA LDC retrievals are explained in Section 6.3.2.

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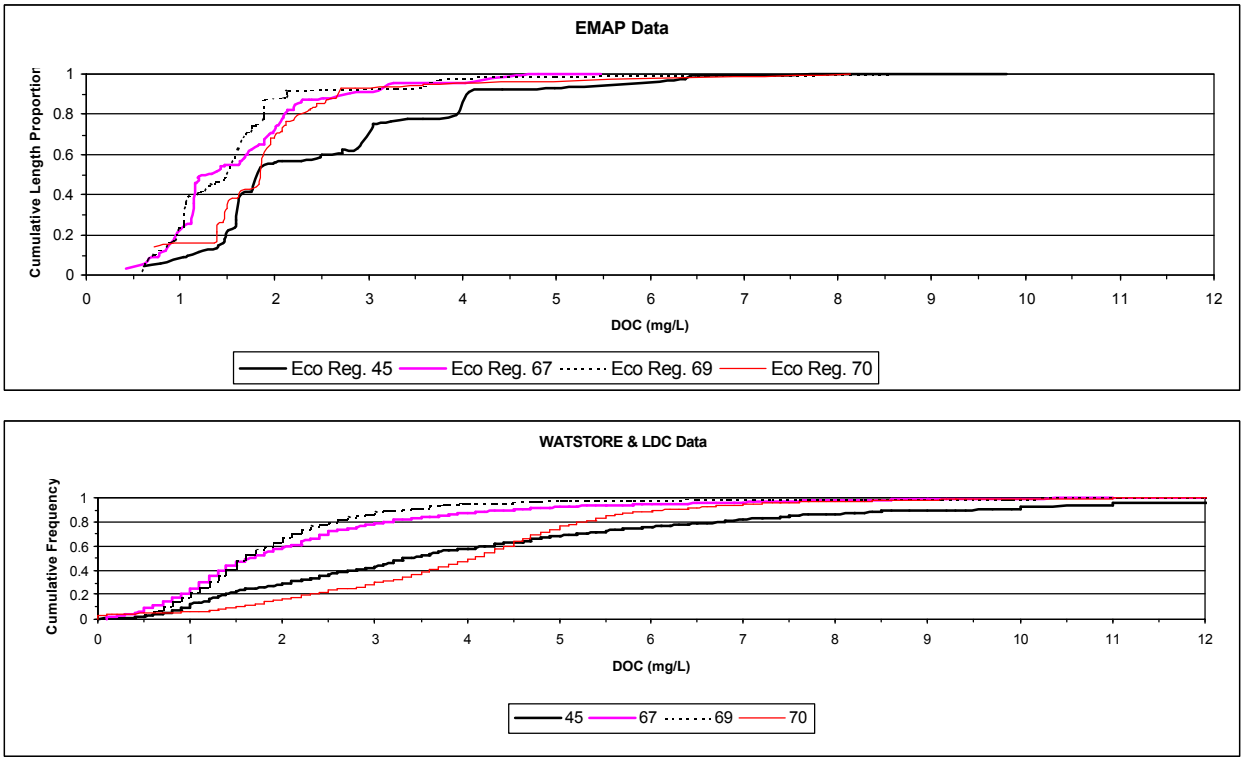

Figure 6-5. Ecoregion-level DOC distributions for rivers and streams from EPA's WATSTORE/LDC and EMAP databases.
Source: EMAP data were taken from EPA's Environmental Monitoring and Assessment Program, Mid-Atlantic Integrated Assessment, 1997–98 (http://www.epa.gov/emap/html/dataI/surfwatr/data). Ecoregion 45 = Piedmont; 67 = Ridge & Valley; 69 = Central Appalachians; 70 = Western Allegheny Plateau.
USGS WATSTORE and EPA LDC retrievals are explained in Section 6.3.2.

Table 6-11. Descriptive Statistics from the State-Level DOC Distributions

Statistic	EMAP (1997–1998)[a]			WATSTORE & LDC (1980–1999)		
	PA	VA	WV	PA	VA	WV
n	89	80	59	1,359	634	682
Mean	1.7	2.0	2.3	3.8	3.1	2.0
10th percentile	0.8	0.8	1.0	0.9	0.7	0.7
25th percentile	1.0	1.0	1.5	1.3	1.0	1.2
50th percentile	1.5	1.5	1.8	2.2	1.8	1.7
75th percentile	2.1	1.9	2.2	4.6	3.7	2.5
90th percentile	2.5	3.2	3.7	8.9	6.5	3.5

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Table 6-12. Descriptive Statistics from the Ecoregion-Level DOC Distributions

Statistic	EMAP MAIA (1997–1998)[a]				WATSTORE & LDC (1980–1999)			
	Ecoregion				Ecoregion			
	45	67	69	70	45	67	69	70
n	38	64	36	43	309	733	864	1,795
Mean	2.6	1.7	1.7	2.1	4.4	2.2	1.9	4.0
10th percentile	1.1	0.8	0.7	<0.7	1.0	0.6	0.7	1.6
25th percentile	1.6	1.1	1.0	1.4	1.7	1.0	1.1	2.7
50th percentile	1.8	1.3	1.5	1.8	3.4	1.7	1.6	4.1
75th percentile	3.1	2.0	1.8	2.1	5.9	2.8	2.3	5.0
90th percentile	4.0	2.7	2.1	2.7	9.3	4.5	3.3	6.1

[a] Length-weighted statistics for EMAP data. Ecoregion 45 = Piedmont; 67 = Ridge & Valley; 69 = Central Appalachians; 70 = Western Allegheny Plateau.
Source: EMAP data were taken from EPA's Environmental Monitoring and Assessment Program, Mid-Atlantic Integrated Assessment, 1997–98 (http://www.epa.gov/emap/html/dataI/surfwatr/data/).
USGS WATSTORE and EPA LDC retrievals are explained in Section 6.3.2.

The previous comparisons of DOC concentrations from the mid-Atlantic EMAP and WATSTORE/LDC databases are clearly limited with respect to evaluating the impact of possible sampling bias on EPA's national default values of DOC and POC (i.e., comparisons are restricted to the mid-Atlantic region and no comparisons could be made for POC). Despite these limitations, this analysis indicates that, at least for the three States that are well represented in the WATSTORE/LDC database, the degree of sampling bias at median values is not overly exaggerated. Best agreement between the two databases occurred at percentiles at or below the median values of the distributions. Assuming the EMAP data represent unbiased results, a noticeable and somewhat expected bias appears in the WATSTORE/LDC data, primarily at the higher percentiles. Results are mixed at the ecoregion level; two of the four DOC distributions compare favorably between the two databases (defined here as percentile values within a factor of 2). The greater discrepancy between DOC concentrations in ecoregions 45 and 70 appears to be related to the disproportionate influence of several stations from which large numbers of measurements were taken relative to the other stations.

Measurement Error. Other sources of uncertainty in EPA's national default values of DOC and POC concentrations include error associated with measuring DOC and POC concentrations. Measurement error refers to error associated with quantifying the particular variable of interest (e.g., DOC) and includes error associated with sample collection and handling and analytical techniques. Measurement error varies by analytical method, laboratory, and, to some extent, each batch of samples analyzed. For the LDC data, the analytical methods used to determine DOC and POC concentrations were not reported in the database. For analytical methods underlying the WATSTORE data, estimates of accuracy (percent recovery) and

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precision (relative standard deviation) are available for the analysis of TOC and POC. The mean percent recovery and relative standard deviation associated with TOC measurements with the wet oxidation method (*Standard Methods* #5310D) are reported as 103 ± 3.4% (APHA, 1995). Similarly, for TOC measurements using persulfate-ultraviolet oxidation (*Standard Methods* #5310C), the reported mean percent recovery and relative standard deviation of measurements in two matrices are 93 ± 7% and 106 ± 6% (APHA, 1995). Finally, the reported mean percent recovery and standard deviation for POC measurements with the wet oxidation method with silver filtration and sonification are 97 ± 11% (USGS, 1997; Burkhardt et al., 1999). Relative to other sources of uncertainty in national default DOC and POC values, error associated with analytical methods appears to be small, at least where it has been quantified.

Natural Variability in DOC and POC Concentrations. As one would expect, there is substantial variability in the median values of DOC and POC concentrations in U.S. surface waters (Table 6-10). Specifically, the range of 95th to 5th percentile estimates approximates or exceeds a factor of 20 in several types of surface waters. Although measurement error is reflected in this variability, the bulk of variability is believed to result from naturally occurring conditions and processes that contribute to spatial and temporal variability in the delivery and biogeochemical cycling of organic carbon in surface waters. Some of these factors include climatology (e.g., arid, arctic, alpine, and tropical zonal differences) and trophic status (e.g., oligotrophic, mesotrophic, and distrophic lakes), discharge volume and source (for streams and rivers), watershed size and landscape characteristics, season, and the extent of tidal influence (for estuaries). To address uncertainty in BAFs resulting from this natural variability in DOC and POC concentrations, EPA encourages States and authorized Tribes to use appropriate local or regional data on the organic carbon content of applicable waters when adopting criteria into their own water quality standards. Nevertheless, EPA recognizes that appropriate local or regional data will not always be available in sufficient quantity or quality. Therefore, it is appropriate to explore the degree to which variability in DOC and POC concentrations has an impact on national BAFs.

Figure 6-6 illustrates the effect of varying concentrations of DOC and POC on the freely dissolved fraction for nonionic organic chemicals with various K_{ow}s. The freely dissolved fraction was calculated according to Equation 5-12 of the 2000 Human Health Methodology (USEPA, 2000a) and has a 1:1 impact on the resulting national BAF (see Equation 5-28 of the 2000 Human Health Methodology).

From an examination of Figure 6-6, several observations can be made regarding how variability in organic carbon concentrations is predicted to affect the freely dissolved fraction (and subsequently the national BAF) for nonionic organic chemicals. First, the effect of DOC and POC concentrations on the freely dissolved fraction is highly dependent on K_{ow}. For nonionic organic chemicals with log K_{ow} values of about 4 or less, changes in DOC and POC concentrations within the 5th to 95th percentiles have very little impact on the freely dissolved fraction. Further analysis (not shown here) indicates that this insensitivity holds true for values of DOC and POC far exceeding the 5th and 95th percentiles. Thus, uncertainty in the DOC or POC concentrations has very little impact on the resulting national BAFs for low K_{ow} chemicals.

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A second observation is that, for nonionic organic chemicals with higher hydrophobicity (e.g., log K_{ow} >4), the impact of DOC and POC on the freely dissolved fraction increases as K_{ow} increases. Although the absolute range in the freely dissolved fraction corresponding to the 5th and 95th percentiles of DOC and POC peaks at a log K_{ow} of about 6 (i.e., from 0.89 at the 5th percentile to 0.17 at the 95th percentile), the relative difference in freely dissolved fraction (as measured by the ratio of freely dissolved fraction at various DOC and POC percentiles) increases with K_{ow}. Because the freely dissolved fraction is used in a multiplication step to calculate the national BAF, the relative differences in freely dissolved fraction are more meaningful for interpreting the impact of variability of organic carbon concentrations on the national BAF.

Table 6-13 illustrates the effect of organic carbon on the differences in freely dissolved fraction relative to that calculated with national default values of DOC and POC. Here, relative differences are expressed as ratios of the freely dissolved fraction calculated at various percentiles of DOC and POC (from Table 6-12) to that calculated at the national default values of DOC and POC. For chemicals with a log K_{ow} of 5.0, the relative impact of DOC and POC within these percentiles is still rather minor (i.e., a 10% increase at the 5th percentile DOC and POC values versus a 30% decrease at the 95th percentile). For chemicals with a log K_{ow} value of 6.0, the impact of organic carbon is more substantial, resulting in a 50% increase in the freely dissolved fraction at the 5th percentile DOC and POC values. The freely dissolved fraction associated with the 95th percentile DOC and POC values drops to 30% of the fraction calculated with the national default DOC and POC values. The effect of lower DOC and POC concentrations on the freely dissolved fraction is still somewhat muted compared with higher concentrations, in part because the freely dissolved fraction calculated with the national default values of DOC and POC is still relatively high (0.93 at K_{ow} 5.0 and 0.58 at K_{ow} 6.0), and it cannot increase beyond 1.0. The greatest impact of organic carbon on the freely dissolved fraction is seen at the highest K_{ow} (8.0), where the freely dissolved fractions calculated at the 5th and 95th percentiles are similar in magnitude to the changes in DOC and POC values (i.e., a fivefold increase in DOC concentration and an eightfold increase in POC concentration results in an approximately sevenfold decrease in the freely dissolved fraction).

A final observation is that for highly hydrophobic chemicals, the freely dissolved fraction is most sensitive to changes in POC relative to DOC. This fact is clear from examination of Equation 4-4 and relates to the higher partition coefficient for organic chemicals to POC (K_{poc} = 1.0 ⊂ K_{ow} L/kg) as compared with that for DOC (K_{doc} = 0.08 ⊂ K_{ow} L/kg). Therefore, in terms of reducing overall uncertainty associated with the application of national default values of DOC and POC, resources should be directed toward site- or region-specific organic carbon measurements for chemicals with higher hydrophobicity (e.g., about log K_{ow} of 5 and above). Although both DOC and POC measurements are needed, results indicate that particular attention should be paid to quantifying representative measurements of POC.

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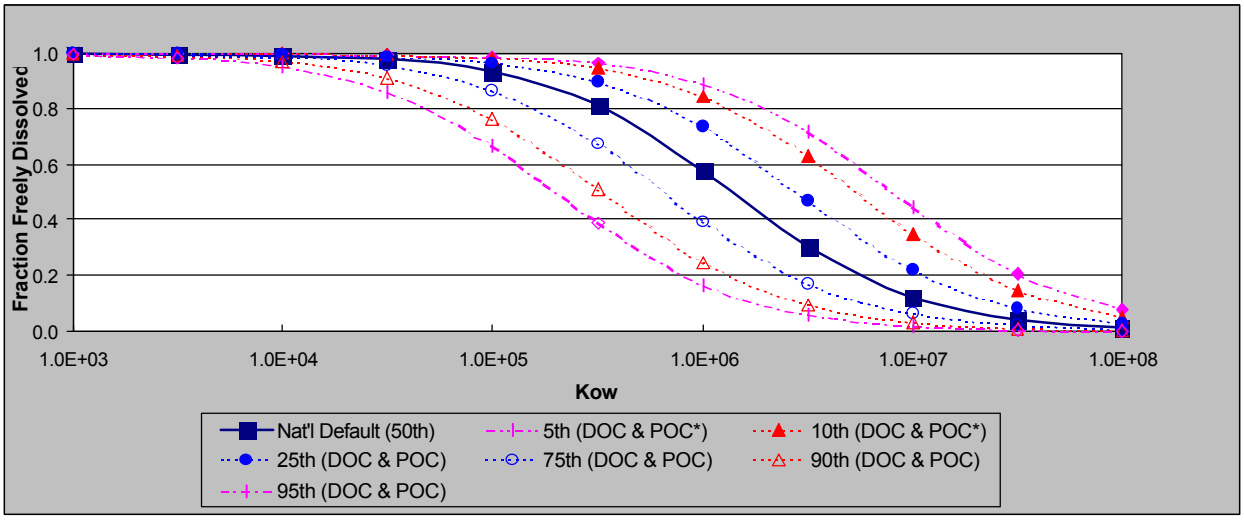

Figure 6-6. Effect of DOC, POC, and K_{ow} on the freely dissolved fraction (f_{fd}). The solid line (€) is the freely dissolved fraction that corresponds to EPA's national default values of DOC (2.9 mg/L) and POC (0.5 mg/L). The dashed lines reflect various percentiles from the distributions of DOC and POC concentrations used to derive the national default values (e.g., 5th, 10th, 25th, 75th, 90th, 95th percentiles from Table 6-9).

* Estimated value based on statistical parameters from the POC distribution (see Table 6-9), assuming data were log-normally distributed.

Table 6-13. Effect of DOC and POC Concentrations on the Freely Dissolved Fraction (f_{fd}) Relative to National Default Values of DOC and POC

Percentile	DOC (mg/L)	POC (mg/L)	Fraction Freely Dissolved (f_{fd}) and [Ratio to National Default]			
			Log K_{ow}			
			5.0	6.0	7.0	8.0
50th (National Default)	2.9	0.5	0.93	0.58	0.12	0.014
5th	0.8	0.06[a]	0.99 [1.1]	0.89 [1.5]	0.44 [3.7]	0.08 [5.5]
10th	1.2	0.09[a]	0.98 [1.1]	0.84 [1.5]	0.35 [2.9]	0.05 [3.8]
25th	2	0.2	0.97 [1.0]	0.74 [1.3]	0.22 [1.8]	0.03 [2.0]
75th	5.4	1.1	0.87 [0.9]	0.40 [0.7]	0.06 [0.5]	0.006 [0.5]
90th	9.7	2.3	0.77 [0.8]	0.25 [0.4]	0.03 [0.25]	0.003 [0.24]
95th	14	3.9	0.67 [0.7]	0.17 [0.3]	0.02 [0.16]	0.002 [0.15]

[a] Estimated value based on statistical parameters from the POC distribution (see text).

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7. EXAMPLES OF BAF CALCULATIONS

The examples presented in this section illustrate how national BAFs used in calculation of human health AWQC are developed for a chemical of interest (chemical i) with the four BAF methods under Procedure 1. The general process illustrated here is also applicable to chemicals under Procedures 2–4. The equations used in the examples given here are presented in Sections 4 and 5 and the terms used in the equations are defined in Section 2. For reference, the equation numbers provided here refer to the section where the equation was initially presented or derived.

7.1 EXAMPLE 1: CALCULATION OF A NATIONAL BAF FROM A FIELD-MEASURED BAF (BAF_T^t) (METHOD 1)

This example illustrates the development of a national trophic level 4 BAF using method 1 for a hydrophobic nonionic chemical (chemical i). Calculating national BAFs using method 1 requires the use of a BAF_T^t (also commonly referred to as a "field-measured" BAF). Determination of a BAF_T^t requires information on the *total* concentration of chemical i in fish tissue and the *total* concentration of chemical i in the ambient water.

7.1.1 Calculating a Total BAF (BAF_T^t)

In this example, data are available from Lake John Doe (a hypothetical lake) on the *total* concentration of chemical i in lake trout (100 µg/kg) and in the water column (1.6×10^8 µg/L). A review of the dietary preferences of the larger sizes of lake trout that are commonly consumed by the general U.S. population confirms that these organisms belong to trophic level 4 (USEPA, 2000e-g). Data obtained from field studies indicate that the mean concentration of the chemical in the water column reflects adequate temporal and spatial averaging, based on the K_{ow} of this chemical, and is representative of the average exposure of chemical i to the target fish. The BAF_T^t calculated for chemical i is 6.2×10^5 L/kg, as shown below.

$$BAF_T^t = \frac{100\mu g/kg}{1.6\times10^8\ \mu g/L} = 6.2\times10^5\ L/kg\ wet\ tissue$$

(See Equation 2-1)

7.1.2 Calculating a Baseline BAF

The BAF_T^t is converted to a baseline BAF for a specific trophic level by incorporating site-specific information on the fraction of the chemical that is freely dissolved in the ambient water (f_{fd}) and the fraction of tissue or aquatic organism sampled that is lipid (f_ℓ). The equation for calculating a baseline BAF from BAF_T^t is:

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$$\text{Baseline BAF} = \left[\frac{BAF_T^t}{f_{fd}} - 1 \right] \cdot \frac{1}{f_R}$$

(See Equation 5-2)

Determining the fraction of chemical i that is freely dissolved (f_{fd}) in the ambient water requires information on the POC and DOC in the ambient water where the samples were collected and the K_{ow} of chemical i. For this example, the median POC concentration from Lake John Doe is 0.6 mg/L (6.0×10^{-7} kg/L) and the median DOC concentration is 8.0 mg/L (8.0×10^{-6} kg/L). It is important that the POC and DOC concentrations used in calculating the freely dissolved fraction for baseline BAFs be determined from the water body used in the BAF study. It is not appropriate to use national default POC and DOC concentrations to derive baseline BAFs from BAF_T^ts. The K_{ow} for chemical i is 1.0×10^5, or a log K_{ow} of 5. Based on these data, the fraction of chemical i that is freely dissolved in water is 0.89, calculated as shown below:

$$f_{fd} = \frac{1}{[1 + (6.0\times10^{-7}\ \text{kg/L} \cdot 1\times10^5\ \text{L/kg}) + (8.0\times10^{-6}\ \text{kg/L} \cdot 0.08 \cdot 1\times10^5\ \text{L/kg})]} = 0.89$$

(See Equation 4-6)

The mean f_R of the fish species sampled in Lake John Doe is 0.08 (8%). Using this f_R and the BAF_T^t and f_{fd} calculated above, a baseline BAF for lake trout of 8.7×10^6 L/kg of lipid is calculated as follows:

$$\text{Baseline BAF} = \left[\frac{6.2\times10^5}{0.89} - 1 \right] \cdot \frac{1}{0.08} = 8.7\times10^6\ \text{L/kg of lipid}$$

(See Equation 5-2)

For the purposes of this example, it is assumed that only one acceptable BAF value is available for trophic level 4 organisms. Thus, the baseline BAF for trophic level 4 is the baseline BAF for lake trout. If acceptable BAF_T^ts are available for additional trophic level 4 organisms, baseline BAFs are calculated for each of the trophic level 4 species for which there is acceptable data and then the baseline BAF for trophic level 4 is calculated as the geometric mean of these baseline BAFs. Recall that in EPA's BAF methodology, BAFs are trophic-level specific. Hence, this calculation would be carried out similarly for each trophic level.

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7.1.3 Calculating a National BAF

After deriving all acceptable baseline BAFs for chemical i and selecting a final baseline BAF for trophic level 4, the next step is to calculate a national BAF for this trophic level that will be used to derive the AWQC. In this example, it is assumed that the baseline BAF calculated above represents the final baseline BAF for trophic level 4. For a given trophic level, calculating a national BAF involves adjusting the final baseline BAF to reflect conditions that are expected to affect the bioavailability of chemical i in ambient waters of the United States. This is accomplished through the use of national default values for f_R and f_{fd} that are based on national central tendency estimates. For each trophic level, the general equation for deriving a national BAF is:

$$\text{National BAF}_{TL\ n} = [(\text{Final Baseline BAF})_{TL\ n} \cdot (f_R)_{TL\ n} + 1] \cdot f_{fd}$$

(See Equation 3-2)

For the purposes of this example, a national BAF is calculated for aquatic organisms at only one trophic level (trophic level 4). In the 2000 Human Health Methodology, EPA divided the default fish intake rate into trophic-level 2-, 3-, and 4-specific rates. Hence, in the process of deriving national AWQC, EPA will derive national BAFs for trophic levels 2, 3, and 4.

For chemical i, the baseline BAF at trophic level 4 was calculated to be 8.7×10^6 L/kg of lipid. The freely dissolved fraction of chemical i that is estimated for all water bodies in the United States is calculated by using Equation 4-6 and the national default values of 5×10^{-7} kg/L for POC and 2.9×10^{-6} kg/L for DOC (Section 6.3), and the K_{ow} of chemical i which is 1.0×10^5 (log K_{ow} of 5). A value of 0.93 is calculated as shown below:

$$f_{fd} = \frac{1}{[1 + (5.0\times10^{-7}\ \text{kg/L} \cdot 1\times10^5\ \text{L/kg}) + (2.9\times10^{-6}\ \text{kg/L} \cdot 0.08 \cdot 1\times10^5\ \text{L/kg})]} = 0.93$$

(See Equation 4-6)

The national default f_R for trophic level 4 is 0.03 (3%; see Section 6.2). Using the f_{fd} calculated above and the national default f_R in the national BAF equation, the national BAF for trophic level 4 organisms is calculated to be 2.4×10^5 L/kg, as shown below:

National BAF for Trophic Level 4

= $[(8.7\times10^6$ L/kg of lipid) • (0.03 kg of lipid per kg of tissue) + 1] • 0.93

= 2.4×10^5 L/kg of wet tissue

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This national BAF relates the *total* concentration of chemical in water to the *total* concentration of chemical in tissue of trophic level 4 organisms.

7.2 EXAMPLE 2: CALCULATION OF A NATIONAL BAF FROM FIELD-MEASURED BSAFs (METHOD 2)

This example illustrates the development of a national trophic level 4 BAF using method 2 for PCB congener 126. Calculating national BAFs using method 2 requires the use of field-measured BSAFs for reference chemicals and the chemical of interest. In section 5.2.4, it is suggested that multiple reference chemicals be used to calculate a baseline BAF with method 2 because this results in a more accurate baseline BAF prediction (see Section 5.2.4).

In this example, data from Lake Ontario are used to derive baseline BAFs from BSAFs for chemicals like PCB 126, which cannot be readily detected in water (USEPA, 1995b; Cook and Burkhard, 1998). To simplify this example, a baseline BAF is derived for only one trophic level 4 organism, that is, age 5–7 lake trout. A review of the dietary preferences of the larger sizes of lake trout that are commonly consumed by the general U.S. population confirms that these organisms belong to trophic level 4. Previously, the PCB congeners 52, 105, and 118 have been used as the reference chemicals for calculating baseline BAFs for PCB 126 (USEPA, 1995b; Cook and Burkhard, 1998). These three congeners were selected because (1) they have similar physicochemical properties, (2) they are well quantified in sediment and biota, and (3) available data indicate they have loading histories similar to PCB 126 and thus their $(J_{socw})_r/(K_{ow})_r$ values should be similar. In this example, the detailed, step-by-step calculations for each component of the equation are shown only for reference PCB congener 118. In practice, the same steps are performed for all reference congeners, but for this example, only the final baseline BAFs are shown for PCBs 52 and 105.

7.2.1 Calculating a Field-Measured BSAF

The BSAF for PCB 126 is determined by relating lipid-normalized concentrations of the chemical in 5 to 7-year-old lake trout (C_R) to the average organic carbon-normalized concentration of the chemical in surface sediment (C_{soc}), using equation 5-2. On the basis of data collected from Lake Ontario, the C_R of PCB 126 in age 5–7 lake trout is 12.3 ng/g of lipid, and the C_{soc} of PCB 126 in the sediment is 3.83 ng/g of organic carbon (actual calculations for these normalized values are not shown here). Therefore:

$$BSAF_{126} = \frac{12.3 \text{ ng/g lipid}}{3.8 \text{ ng/g soc}} = 3.2$$

(See Equation 5-3)

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7.2.2 Determining a Sediment-Water Column Concentration Quotient $(\mathbf{J}_{socw})_r$

Sediment-water column concentration quotients for reference chemicals are determined by using equation 5-6. For this calculation, the concentration of reference chemical that is freely dissolved in water, $(C_w^{fd})_{PCB\ 118}$, is needed. To calculate the $(C_w^{fd})_{PCB\ 118}$, the fraction of reference chemical that is freely dissolved in water $(f_{fd})_r$ is needed. The $(f_{fd})_r$ is calculated by using equation 4-6. The measured DOC value is 2.0×10^{-6} kg/L; POC is set equal to zero (because all particulates were removed using a filter); and the K_{ow} for PCB 118 = 5.5×10^{6} (log K_{ow} of 6.7). Using Equation 4-6, the fraction of PCB 118 that is freely dissolved in water is calculated as follows:

$$(f_{fd})_{PCB\ 118} = \frac{1}{[1 + (0\ \text{kg/L} \cdot 5.5\times10^{6}\ \text{L/kg}) + (2.0\times10^{-6}\ \text{kg/L} \cdot 0.08 \cdot 5.5\times10^{6}\ \text{L/kg})]} = 0.53$$

(See Equation 4-6)

For this example, the measured concentration of reference congener PCB 118 in filtered Lake Ontario water is 34 pg/L. Thus, $(C_w^{fd})_{PCB\ 118}$ = 34 pg/L × 0.53 = 18 pg/L or 1.8×10^{-5} µg/L . The average $(C_{soc})_{PCB118}$ is 555 µg/kg of sediment organic carbon. By substituting these values into Equation 5-6, $\mathbf{J}_{socw}$ for the reference chemical, PCB 118, is calculated as:

$$(\Pi_{socw})_{118} = \frac{555\ \mu\text{g/kg soc}}{1.8\times10^{-5}\ \mu\text{g/L}} = 3.1\times10^{7}\ \text{L/kg soc}$$

(See Equation 5-6)

7.2.3 Calculating a Baseline BAF

For each species having an acceptable field-measured $(BSAF)_i$, a baseline BAF for the chemical of interest may be calculated with the following equation and an appropriate value of $(\mathbf{J}_{socw})_r/(K_{ow})_r$:

$$(\text{Baseline BAF})_i = (\text{BSAF})_i \cdot \frac{(D_{i/r}) \cdot (\Pi_{socw})_r \cdot (K_{ow})_i}{(K_{ow})_r} - \frac{1}{f_l}$$

(See Equation 5-11)

By using a commonly valid assumption—that $D_{i/r}$ ~ 1 for PCB congeners 118 and 126; substituting the BSAF for PCB 126 (3.2), $\mathbf{J}_{socw}$ for PCB 118 (3.1×10^{7}), the appropriate K_{ow} values for PCB 126 (7.8×10^{6} or log K_{ow} = 6.9) and PCB 118 (5.5×10^{6} or log K_{ow} = 6.7), and 0.20 (20%) fraction of lipid for lake trout into the baseline BAF equation (Equation 5-11), the baseline BAF for PCB 126 may be calculated as:

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$$\text{Baseline BAF}_{126} = 3.2 \cdot \frac{(1) \cdot (3.1\times10^{7}) \cdot (7.8\times10^{6})}{5.5\times10^{6}} - \frac{1}{.20} = 1.4\times10^{8}\ \text{L/kg}$$

(See Equation 5-11)

The baseline BAFs using reference PCB congeners 52 and 105 are derived in the same manner as for PCB 118. The predicted baseline BAFs that result are 3.7×10^{8} using congener 52 and 1.6×10^{8} using congener 105. Once all the baseline BAFs have been derived, the final baseline BAF is derived by calculating the geometric mean of the three baseline BAFs, which in this case is 2.0×10^{8} L/kg.

7.2.4 Calculating a National BAF

After deriving all acceptable baseline BAFs for chemical i and selecting a final baseline BAF for trophic level 4, the next step is to calculate a national BAF for this trophic level that will be used to derive the AWQC. In this example, it is assumed that the baseline BAF calculated above represents the final baseline BAF for trophic level 4. For a given trophic level, calculating a national BAF involves adjusting the final baseline BAF to reflect conditions that are expected to affect the bioavailability of chemical i in ambient waters of the United States. This is accomplished through the use of national default values for f_R and f_{fd} that are based on national central tendency estimates. For each trophic level, the general equation for deriving a national BAF is:

$$\text{National BAF}_{TL\ n} = [(\text{Final Baseline BAF})_{TL\ n} \cdot (f_R)_{TL\ n} + 1] \cdot f_{fd}$$

(See Equation 3-2)

For the purposes of this example, a national BAF is calculated only for aquatic organisms at one trophic level (trophic level 4). In the 2000 Human Health Methodology, EPA divided the default fish intake rate into trophic-level 2-, 3-, and 4-specific rates. Hence, in the process of deriving national AWQC, EPA will derive national BAFs for trophic levels 2, 3, and 4.

For PCB 126, the baseline BAF at trophic level 4 was calculated to be 2.0×10^{8} L/kg of lipid. The freely dissolved fraction of PCB 126 that is estimated to be applicable to all water bodies in the United States is calculated by using Equation 4-6 and the national default values of 5×10^{-7} kg/L for POC and 2.9×10^{-6} kg/L for DOC (Section 6.3), and the K_{ow} of PCB 126 which is 7.8×10^{6}, or a log K_{ow} = 6.9. A value of 0.15 is calculated as shown below:

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$$f_{fd} = \frac{1}{[1 + (5.0\times10^{-7}\ \text{kg/L} \cdot 7.8\times10^{6}\ \text{L/kg}) + (2.9\times10^{-6}\ \text{kg/L} \cdot 0.08 \cdot 7.8\times10^{6}\ \text{L/kg})]} = 0.15$$

(See Equation 4-6)

The national default f_R for trophic level 4 is 0.03 (3%; see Section 6.2). Using the f_{fd} calculated above and the national default f_R in the national BAF equation, the national BAF for trophic level 4 organisms is calculated to be 9.0×10^5 L/kg, as shown below:

National BAF for Trophic Level 4

= [(2.0×10^8 L/kg of lipid) • (0.03 kg of lipid per kg of tissue) +1] • (0.15)

= 9.0×10^5 L/kg of wet tissue

This example of a national BAF for PCB 126 relates the *total* concentration of chemical in water to the *total* concentration of chemical in tissue of trophic level 4 organisms.

7.3 EXAMPLE 3: CALCULATION OF A NATIONAL BAF FOR CHEMICAL i FROM BCF_T^t × FCM (METHOD 3)

This example illustrates the calculation of a national trophic level 4 BAF using method 3 for a hydrophobic nonionic chemical (chemical i). Calculating national BAFs using method 3 requires the use of a BCF_T^t (also commonly referred to as a "laboratory-measured BCF_T^t") and a FCM. Determination of a BCF_T^t requires information on the *total* concentration of chemical i in fish tissue and the *total* concentration of chemical i in the laboratory test water.

7.3.1 Calculating a Laboratory-Measured BCF_T^t

In this example, data are available from John Doe's laboratory (a hypothetical laboratory) on the *total* concentration of chemical i in fish tissue (10 µg/kg) and the laboratory test water (3.0×10^3 µg/L). The laboratory-measured BCF calculated for chemical i is 3.3×10^3 L/kg, as shown below:

$$BCF_T^t = \frac{10\mu g/kg}{3.0\times10^{-3}\ \mu g/L} = 3.3\times10^3\ \text{L/kg wet tissue}$$

(See Equation 2-8)

7.3.2 Calculating a Baseline BAF

The BCF_T^t is converted to a baseline BAF for a specific trophic level by incorporating site-specific information on the fraction of the chemical that is freely dissolved in the test water (f_{fd}), the fraction of tissue or aquatic organism tested that is lipid (f_R), and a food-chain multiplier (FCM) for the chemical. The equation for calculating a baseline BAF from BCF_T^t is:

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$$\text{Baseline BAF} = \text{FCM} \cdot \left[\frac{BCF_T^t}{f_{fd}} - 1 \right] \cdot \frac{1}{f_R}$$

(See Equation 5-12)

Determining the fraction of chemical i that is freely dissolved in the test water (f_{fd}) requires information on the POC and DOC in the test water and the K_{ow} of chemical i. For this example, the median POC concentration in the test water is 0.6 mg/L (6.0×10^{-7} kg/L) and the median DOC concentration is 8.0 mg/L (8.0×10^{-6} kg/L). It is important that the POC and DOC concentrations used in calculating the freely dissolved fraction for baseline BAFs be determined from the water used in the BCF study. It is not appropriate to use national default POC and DOC concentrations to derive baseline BAFs from BCF_T^ts. The K_{ow} for chemical i is 1×10^4, or a log K_{ow} of 4.0. Based on these data, the fraction of chemical i that is freely dissolved is 0.99, calculated as shown below:

$$f_{fd} = \frac{1}{[1 + (6.0\times10^{-7}\ \text{kg/L} \cdot 1\times10^4\ \text{L/kg}) + (8.0\times10^{-6}\ \text{kg/L} \cdot 0.08 \cdot 1\times10^4\ \text{L/kg})]} = 0.99$$

(See Equation 4-6)

The f_R of the fish species sampled in the laboratory in this example is 0.08 (8%). The FCM, based on a log K_{ow} of 4, is 1.07, as indicated in Table 4-6 (assuming a mixed benthic and pelagic food web structure and trophic level 4 for the tested species). Using this f_R and FCM with the BCF_T^t and f_{fd} calculated above, a baseline BAF of 4.5×10^4 L/kg of lipid is calculated as follows:

$$\text{Baseline BAF} = 1.07 \cdot \left[\frac{3.3\times10^3}{0.99} - 1 \right] \cdot \frac{1}{0.08} = 4.5\times10^4\ \text{L/kg of lipid}$$

(See Equation 5-12)

For the purposes of this example, it is assumed that only one acceptable BCF study is available for trophic level 4 organisms. Thus, the baseline BAF value for trophic level 4 is the baseline BAF for the tested organism. If acceptable BCF_T^ts are available for additional trophic level 4 organisms, baseline BAFs are calculated for each of the trophic level 4 species for which there are acceptable data and then the baseline BAF for trophic level 4 is calculated as the geometric mean of these baseline BAFs. Recall that in EPA's BAF methodology, BAFs are trophic-level specific. Hence, this calculation would be carried out similarly for each trophic level.

7.3.3 Calculating a National BAF

After deriving all acceptable baseline BAFs for chemical i and selecting a final baseline BAF for trophic level 4, the next step is to calculate a national BAF for this trophic level that will be used to derive the AWQC. In this example, it is assumed that the baseline BAF calculated above represents the final baseline BAF for trophic level 4. For a given trophic level, calculating a

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national BAF involves adjusting the final baseline BAF to reflect conditions that are expected to affect the bioavailability of chemical i in ambient waters of the United States. This is accomplished through the use of national default values for f_R and f_{fd} that are based on national central tendency estimates. For each trophic level, the general equation for deriving a national BAF is:

$$\text{National BAF}_{TL\ n} = [(\text{Final Baseline BAF})_{TL\ n} \cdot (f_R)_{TL\ n} + 1] \cdot f_{fd}$$

(See Equation 3-2)

For the purposes of this example, a national BAF is calculated for aquatic organisms at only one trophic level (trophic level 4). In the 2000 Human Health Methodology, EPA divided the default fish intake rate into trophic-level 2-, 3-, and 4-specific rates. Hence, in the process of deriving national AWQC, EPA will derive national BAFs for trophic levels 2, 3, and 4.

For chemical i, the baseline BAF at trophic level 4 was calculated to be 4.5×10^4 L/kg of lipid. The freely dissolved fraction of chemical i that is estimated for all water bodies in the United States is calculated by using Equation 4-6 and the national default values of 5×10^{-7} kg/L for POC and 2.9×10^{-6} kg/L for DOC (Section 6.3), and the K_{ow} of chemical i which is 1×10^4 (a log K_{ow} of 4.0). A value of 0.99 is calculated as shown below:

$$f_{fd} = \frac{1}{[\ 1 + (5.0\times10^{-7}\ \text{kg/L} \cdot 1\times10^4\ \text{L/kg}) + (2.9\times10^{-6}\ \text{kg/L} \cdot 0.08 \cdot 1\times10^4\ \text{L/kg})]} = 0.99$$

(See Equation 4-6)

The national default f_R for trophic level 4 is 0.03 (3%; see Section 6.2). Using the f_{fd} calculated above and the national default f_R in the national BAF equation, the national BAF for trophic level 4 organisms is calculated to be 1.3×10^3 L/kg, as shown below:

National BAF for Trophic Level 4

= $[(4.5\times10^4$ L/kg of lipid) • (0.03 kg of lipid per kg of tissue) + 1] • (0.99)

= 1.3×10^3 L/kg of wet tissue

This national BAF relates the total concentration of chemical in water to the total concentration of chemical in tissue of trophic level 4 organisms.

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7.4 EXAMPLE 4: CALCULATION OF A NATIONAL BAF FOR CHEMICAL i FROM K_{ow} × FCM (METHOD 4)

This example illustrates the development of a national trophic level 4 BAF using method 4 for a hydrophobic nonionic chemical (chemical i). Calculating national BAFs using method 4 does not require knowing the fraction of the chemical that is freely dissolved in the test water (f_{fd}) or the fraction of the species sampled that is lipid (f_R). This is because the K_{ow} is assumed to be equal to the baseline BCF, as discussed in Section 5.4 and Appendix A. Method 4 requires selection of an appropriate K_{ow} for the chemical and that the K_{ow} be multiplied by an appropriate FCM to account for biomagnification.

7.4.1 Selecting a K_{ow} and FCM

The procedures that EPA will follow in selecting chemical K_{ow}s are described in detail in Appendix B. For the purposes of this example, a K_{ow} value of 1×10^4 (log K_{ow}= 4.0) has been selected for chemical i. The FCM, based on a log K_{ow} of 4, is 1.07, as indicated in Table 4-6 (assuming a mixed benthic and pelagic food web structure and trophic level 4 for the tested species).

7.4.2 Calculating a Baseline BAF

Method 4 does not require adjusting a field- or laboratory-derived bioaccumulation factor with f_{fd} or f_R. The calculation of a baseline BAF, using the selected K_{ow} and FCM, is straightforward, as shown below:

$$\begin{aligned} \text{Baseline BAF} &= K_{ow} \times \text{FCM} \qquad \text{(See Equation 5-13)} \\ &= (1\times10^4) \times 1.07 \\ &= 1.1\times10^4 \text{ L/kg of lipid} \end{aligned}$$

For this example, only one K_{ow} is provided. As discussed in Appendix B, it is possible that several K_{ow} values may be located. The data quality considerations provided in Appendix B will be used for judging the quality of various K_{ow} values, and the procedures outlined in Appendix B will be used for selecting among or combining K_{ow} values of acceptable quality. Recall that in EPA's BAF methodology, BAFs are trophic-level specific. Hence, this calculation would be carried out similarly, with appropriate FCMs, for each trophic level.

7.4.3 Calculating a National BAF

After deriving all acceptable baseline BAFs for chemical i and selecting a final baseline BAF for trophic level 4, the next step is to calculate a national BAF for this trophic level that will be used to derive the AWQC. In this example, it is assumed that the baseline BAF calculated above represents the final baseline BAF for trophic level 4. For a given trophic level, calculating a national BAF involves adjusting the final baseline BAF to reflect conditions that are expected to affect the bioavailability of chemical i in ambient waters of the United States. This is accomplished through the use of national default values for f_R and f_{fd} that are based on national

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central tendency estimates. For each trophic level, the general equation for deriving a national BAF is:

$$\text{National BAF}_{TL\ n} = [(\text{Final Baseline BAF})_{TL\ n} \cdot (f_R)_{TL\ n} + 1] \cdot f_{fd}$$

(See Equation 3-2)

For the purposes of this example, a national BAF is calculated for aquatic organisms at only one trophic level (trophic level 4). In the 2000 Human Health Methodology, EPA divided the default fish intake rate into trophic-level 2-, 3-, and 4-specific rates. Hence, in the process of deriving national AWQC, EPA will derive national BAFs for trophic levels 2, 3, and 4.

For chemical i, the baseline BAF at trophic level 4 was calculated to be 1.1×10^4 L/kg of lipid. The freely dissolved fraction of chemical i that is estimated to be applicable to all water bodies in the United States is calculated by using Equation 4-6 and the national default values of 5×10^{-7} kg/L for POC and 2.9×10^{-6} kg/L for DOC (Section 6.3), and the K_{ow} of chemical i which is 1×10^4 (log K_{ow} = 4.0). A value of 0.99 is calculated as shown below:

$$f_{fd} = \frac{1}{[1 + (5.0\times10^{-7}\ \text{kg/L} \cdot 1\times10^4\ \text{L/kg}) + (2.9\times10^{-6}\ \text{kg/L} \cdot 0.08 \cdot 1\times10^4\ \text{L/kg})]} = 0.99$$

(See Equation 4-4)

The national default f_R for trophic level 4 is 0.03 (3%; see Section 6.2). Using the f_{fd} calculated above and the national default f_R in the national BAF equation, the national BAF for trophic level 4 organisms is calculated to be 1,344 L/kg, as shown below:

National BAF for Trophic Level 4

= [(1.1×10^4 L/kg of lipid) • (0.03 kg of lipid per kg of tissue) + 1] • (0.99)

= 3.3×10^4 L/kg of wet tissue

This national BAF relates the *total* concentration of chemical in water to the *total* concentration of chemical in tissue of trophic level 4 organisms.

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APPENDIX A

DERIVATION OF THE BASIC BIOCONCENTRATION AND BIOACCUMULATION EQUATIONS FOR ORGANIC CHEMICALS

1. DERIVATION OF THE BASIC BIOCONCENTRATION AND BIOACCUMULATION EQUATIONS FOR ORGANIC CHEMICALS

This appendix provides a detailed presentation of the derivation of the basic bioconcentration and bioaccumulation equations for organic chemicals that are the basis for the methods for deriving BCFs and BAFs in EPA's BAF methodology. The equations are based on widely accepted and peer-reviewed scientific principles and theories, as referenced in this appendix. This appendix was developed to provide additional background for the TSD. Therefore, some additional notations (e.g., subscripts and superscripts) have been added to the equation terms to provide clarity to the discussion of the equation derivations.

A.1.1 Bioconcentration

The basic BCF applicable to all classes of chemicals is defined as:

$$BCF_T^t = \frac{C_B^t}{C_w^t}$$

(Equation A-1)

where:

BCF_T^t = total bioconcentration factor (i.e., a BCF that is based on the total concentrations of the chemical in the water and in the aquatic biota)

C_B^t = total concentration of the chemical in the aquatic biota, based on the wet weight of the aquatic biota

C_w^t = total concentration of the chemical in the water around the aquatic biota

As more bioconcentration information was generated and reviewed by scientists, it was realized that extrapolation of BCFs for organic chemicals from one species to another would be more accurate if the BCFs were normalized on the basis of the amount of lipid in the aquatic biota exposed in the original bioconcentration test, because many nonpolar organic chemicals are hydrophobic, accumulating in direct proportion to the amount of lipid in a given aquatic organism (Mackay, 1982; Connolly and Pederson, 1988; Thomann, 1989). It was also realized that extrapolation of BCFs for organic chemicals from one water to another would be more accurate if the BCFs were calculated on the basis of the freely dissolved concentration of the organic chemical in the water around the aquatic biota. Thus, two additional BCFs were defined and used:

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$$BCF_l^t = \frac{C_l}{C_w^t}$$

(Equation A-2)

$$BCF_l^{fd} = \frac{C_l}{C_w^{fd}}$$

(Equation A-3)

where:

BCF	=	lipid-normalized total BCF (i.e., normalized to 100% lipid and based on the total concentration of the chemical in the water around the biota)
C_R	=	lipid-normalized concentration of the chemical in the aquatic biota
BCF_R^{fd}	=	lipid-normalized and freely dissolved-based BCF
C_w^{fd}	=	freely dissolved concentration of chemical in the water around the aquatic biota

The experimental definition of C_R is:

$$C_R = \frac{\text{the total amount of chemical in the aquatic biota}}{\text{the amount of lipid in the aquatic biota}}$$

$$= \frac{(B)(C_B^t)}{L} = \frac{(B)(C_B^t)}{(f_l)(B)} = \frac{C_B^t}{f_l}$$

(Equation A-4)

where:

B	=	wet weight of the aquatic biota
L	=	weight of the lipid in the aquatic biota
f_R	=	fraction of the aquatic biota that is lipid = L/B

Using Equation 4 to substitute for C_R in Equation 2 and then using Equation 1:

$$BCF_l^t = \frac{C_B^t}{(C_w^t)(f_l)} = \frac{BCF_T^t}{f_l}$$

(Equation A-5)

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If f_{fd} = the fraction of the chemical in the water around the aquatic biota that is freely dissolved, then:

$$f_{fd} = \frac{C_w^{fd}}{C_w^t}$$

(Equation A-6)

Using Equations 4 and 6 to substitute for C_R and C_w^{fd} in Equation 3 and then using Equation 1:

$$BCF_R^{fd} = \frac{C_B^t}{(f_l)(C_w^t)(f_{fd})} = \frac{BCF_T^t}{(f_l)(f_{fd})}$$

(Equation A-7)

Equations 1, 5, and 7 show the relationships among the three different BCFs.

Theoretical justification for use of both lipid normalization and the freely dissolved concentration of the organic chemical in the ambient water is based on the concept of equilibrium partitioning, whereas practical justification is provided by the general similarity of the value of BCF_R^{fd} for an organic chemical across both species and waters. This concept of equilibrium partitioning is discussed further in the following section. It will be demonstrated in Section A.2, however, that a more complete application of equilibrium partition theory shows that BCF_R^{fd} extrapolates well only for chemicals whose K_{ow}s are greater than 1,000, whereas a different BCF (BCF_L^{fd}) extrapolates well for organic chemicals whose K_{ow}s are greater than 1,000 as well as for chemicals whose K_{ow}s are less than 1,000.

A.2 PARTITION THEORY AND BIOCONCENTRATION

Equilibrium partition theory provides the understanding necessary to ensure proper use of K_{ow}s, BCFs, and BAFs in the derivation of water quality criteria for organic chemicals. For the purpose of applying partition theory, aquatic biota can be modeled as consisting of water, lipid, and nonlipid organic matter (Barber et al., 1991). In this model, an organic chemical in aquatic biota partitions into three phases:

1. The chemical that is freely dissolved in the water that is in the biota.

2. The chemical that is partitioned to the lipid that is in the biota.

3. The chemical that is partitioned to nonlipid organic matter in the biota.

The total concentration of chemical in the water inside the biota includes chemical that is partitioned to lipid and nonlipid organic matter in the water.

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According to this model:

$$C_B^t = (f_w)(C_{wB}^{fd}) + (f_L)(C_L) + (f_N)(C_N)$$

(Equation A-8)

where:

f_w = fraction of the aquatic biota that is water

C_{wB}^{fd} = freely dissolved concentration of the organic chemical in the water in the aquatic biota

f_L = fraction of the aquatic biota that is lipid

C_L = concentration of the organic chemical in the lipid

f_N = fraction of the aquatic biota that is nonlipid organic matter

C_N = concentration of the organic chemical in the nonlipid organic matter in the aquatic biota

The most important partitioning of the organic chemical within the aquatic biota is between the lipid and the water, which is described by the following equation:

where:

$$K_{LW} = \frac{C_L}{C_{wB}^{fd}}$$

(Equation A-9)

K_{LW} = the lipid-water partition coefficient

"K_{LW}" (Gobas, 1993) is used herein because it is more descriptive than "K_L" which is used by DiToro et al. (1991). This partition coefficient is central to the equilibrium partition approach that is used to derive sediment quality criteria (DiToro et al., 1991), the food chain multipliers based on the Gobas model, and the equations given here that are used to derive BCFs and BAFs for the national BAF methodology.

In order for Equations 8 and 9 to be correct, partition theory requires that the concentration of the organic chemical in the lipid, C_L, be defined as:

$$C_L = \frac{\text{the amount of chemical partitioned to lipid in aquatic biota}}{\text{the amount of lipid in the aquatic biota}}$$

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It is difficult to determine C_L experimentally because it is not easy to measure only the chemical that is partitioned to the lipid (i.e., it is not easy to separate the three different compartments within aquatic biota that the chemical partitions into according to the model). Because all of the organic chemical in the biota is measured when C_R is determined, C_R can be determined easily, and C_R is higher than C_L.

It is useful to define another BCF as:

$$BCF_L^{fd} = \frac{C_L}{C_w^{fd}}$$

(Equation A-10)

because C_L is lower than C_R, $BCF_L^{fd} < BCF_R^{fd}$.

The only difference between K_{LW} and BCF_L^{fd} is that the denominator in K_{LW} is C_{wB}^{fd}, whereas the denominator in BCF_L^{fd} is C_{wB}^{fd}. When partition theory applies, however, all phases are in equilibrium, and so:

$$C_w^{fd} = C_{wB}^{fd}$$

(Equation A-11)

Therefore, when the organic chemical is not metabolized by the aquatic biota and when growth dilution is negligible:

$$BCF_L^{fd} = K_{LW}$$

(Equation A-12)

In laboratory experiments it has been shown that the chemical octanol is a useful surrogate for lipid, thus a reasonable approximation is that:

$$K_{LW} = K_{ow}$$

(Equation A-13)

where:

K_{ow} = the *n*-octanol-water partition coefficient.

Thus:

$$\text{predicted } BCF_L^{fd} = K_{LW} = K_{ow}$$

(Equation A-14)

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By using Equations 9 and 11 to substitute for C_L and C_{wB}^{fd} in Equation 8:

$$C_B^t = (f_w)(C_w^{fd}) + (f_l)(BCF_L^{fd})(C_w^{fd}) + (f_N)(C_N)$$

(Equation A-15)

By using Equation 6 to substitute for C_w^{fd} in Equation 15:

$$C_B^t = (f_w)(f_{fd})(C_w^t) + (f_l)(BCF_L^{fd})(f_{fd})(C_w^t) + (f_N)(C_N)$$

(Equation A-16)

Dividing by C_w^t gives:

$$\frac{C_B^t}{C_w^t} = (f_w)(f_{fd}) + (f_l)(BCF_L^{fd})(f_{fd}) + \frac{(f_N)(C_N)}{C_w^t}$$

(Equation A-17)

Using Equation 1 and rearranging gives:

$$BCF_T^t = (f_{fd})[\ f_w + (f_l)(BCF_L^{fd}) + \frac{(f_N)(C_N)}{(f_{fd})(C_w^t)}\ ]$$

(Equation A-18)

Using Equation 6:

$$BCF_T^t = (f_{fd})[\ f_w + (f_l)(BCF_L^{fd}) + \frac{(f_N)(C_N)}{C_w^{fd}}\ ]$$

(Equation A-19)

Substituting $x = f_w + (f_N)(C_N/C_w^{fd})$ and rearranging gives:

$$BCF_T^t = (f_{fd})[\ x + (f_l)(BCF_L^{fd})\ ]$$

(Equation A-20)

The term "$(f_l)(BCF_L^{fd})$" accounts for the amount of organic chemical that is partitioned to the lipid in the biota, whereas in "x," the term "f_w" accounts for the amount of organic chemical that is freely dissolved in the water in the biota and the term "$(f_N)(C_N/C_W^{fd})$" accounts for the amount of organic chemical that is partitioned to nonlipid organic matter in the biota. The relative magnitudes of these three terms depend on the following:

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- Because of bones and other inorganic matter that make up the total mass of an organism, the sum of $f_w + f_R + f_N$ must be less than 1.

- f_w is usually about 0.7 to 0.9.

- f_R must be measured in the organism in question if the BAF or BCF is to be useful, or estimated from other similar biota; it is usually between 0.03 and 0.15.

- The term "(C_N/C_w^{fd})" is similar to BCF_L^{fd} (see Equation 10) and is therefore probably related to K_{ow} (see Equation 14), although the affinity of the chemical for nonlipid organic matter is probably much less than its affinity for lipid.

Although such considerations aid in understanding "x" in Equation 20, the magnitude of "x" is important only for chemicals whose log K_{ow}s are in the range of 1 to 3. For organic chemicals whose log K_{ow}s are about 1, f_{fd} is about 1. In addition, such chemicals distribute themselves so as to have similar concentrations in water and in the different organic phases in the aquatic biota, which means that BCF_T^t will be approximately 1 if both metabolism and growth dilution are negligible. An organic chemical whose log K_{ow} is less than 1 will also have a BCF_T^t on the order of 1 because water is the predominant component in aquatic biota. Setting "x" equal to 1 is about right in the range of log K_{ow}s in which it is not negligible (see also McCarty et al., 1992).

Substituting x = 1 into Equation 20:

$$BCF_T^t = (f_{fd})[\ 1 + (f_l)(BCF_L^{fd})\ ]$$

(Equation A-21)

Rearranging gives:

$$BCF_L^{fd} = \left(\frac{BCF_T^t}{f_{fd}} - 1 \right)\left(\frac{1}{f_l}\right)$$

(Equation A-22)

Because BCF_L^{fd} is normalized for both the aquatic biota lipid content and freely dissolved fraction of the chemical, it is called the "baseline BCF." The baseline BCF is the most useful BCF for extrapolating from one species to another and from one water to another for organic chemicals with both high and low K_{ow}s. The baseline BCF is intended to reference bioconcentration of organic chemicals to partitioning between lipid and water.

Equations 12, 13, and 22 demonstrate that both K_{ow} and

$$\left(\frac{BCF_T^t}{f_{fd}} - 1 \right)\left(\frac{1}{f_l}\right)$$

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are useful approximations of the baseline BCFs. It will probably be possible to improve both approximations within a few years, but such improvements might not affect the BCFs substantially and probably will not require changes in the rest of the equations or the terminology.

When BCF_T^t is greater than 1,000, the "-1" in Equation 22 is negligible, and so this equation becomes equivalent to Equation 7 (i.e., when BCF_T^t is large it generally indicates that the chemical readily partitions to and accumulates in the lipid portion of aquatic biota, and thus the BCF_R^{fd} is a useful approximation of the baseline BCF).

A.3 DERIVATION OF THE BASIC BAF AND BASELINE BAF EQUATIONS

As has been previously mentioned, bioaccumulation represents uptake and retention of a chemical from all routes of exposure, including water only (i.e., bioconcentration) and the food chain, therefore by analogy and substituting BAF for BCF in Equations 21 and 22:

$$BAF_T^t = (f_{fd})[\ 1 + (f_l)(BAF_L^{fd})\ ]$$

(Equation A-23)

$$BAF_L^{fd} = \left(\frac{BAF_T^t}{f_{fd}} - 1\right)\left(\frac{1}{f_l}\right)$$

(Equation A-24)

As with the BCF, the BAF_L^{fd} can be called the "baseline BAF" because it normalizes the factor to the lipid content of the aquatic biota and the freely dissolved fraction of the chemical in water. It too is the most useful BAF for extrapolating from one species to another and from one water to another for chemicals with both high and low K_{ow}s.

A.4 CALCULATION OF CRITERIA

Baseline BCFs and BAFs can be extrapolated between species and waters, but they cannot be used directly in the calculation of criteria that are based on the total concentration of the chemical in the water. The BCFs and BAFs that are needed to calculate such criteria can be calculated from measured and predicted baseline BCFs and BAFs using the following equations, which are derived from Equations 21 and 23:

$$BCF_T^t = (f_{fd})[\ 1 + (\text{Baseline BCF})(f_l)\ ]$$

(Equation A-25)

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$$BAF_T^t = (f_{fd})[\ 1 + (\text{Baseline BAF})(f_l)\ ]$$

(Equation A-26)

A.5 DERIVATION OF THE BASIC FCM AND BMF EQUATIONS

Food chain multipliers (FCM) are used in BAF methods 3 and 4 (see Sections 5.3 and 5.4) for estimating BAFs for chemicals that biomagnify up the food chain. The FCM can be defined as:

$$FCM = \frac{\text{Baseline BAF}}{\text{Baseline BCF}} = \frac{BAF_L^{fd}}{BCF_L^{fd}}$$

(Equation A-27)

Some of the consequences of Equation 27 are:

1. Substituting Equations 22 and 24 into Equation 27:

$$FCM = \frac{BAF_T^t - f_{fd}}{BCF_T^t - f_{fd}}$$

(Equation A-28)

Therefore, $BAF_T^t = (FCM)\ (BCF_T^t)$ only when f_{fd} is much less than BAF_T^t and BCF_T^t.

2. When FCM = 1 (as for trophic level 2 in the Gobas model):

$$\text{Baseline BAF} = \text{Baseline BCF}$$

(Equation A-29)

3. Predicted Baseline BAFs can be obtained using FCMs and the following rearrangement of Equation 27:

predicted Baseline BAF = (FCM)(Baseline BCF) (Equation A-30)

a. Using a laboratory-measured BCF in Equation 22:

predicted Baseline BAF = (FCM)(measured Baseline BCF) (Equation A-31)

$$= (FCM)\left(\frac{BCF_T^t}{f_{fd}} - 1\right)\left(\frac{1}{f_l}\right)$$ (Equation A-32)

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b. Using a predicted BCF in Equation 14:

$$\text{predicted Baseline BAF} = (\text{FCM})(\text{predicted } BCF_L^{fd}) \qquad \text{(Equation A-33)}$$

$$= (\text{FCM})(K_{ow}) \qquad \text{(Equation A-34)}$$

The FCMs used to calculate predicted baseline BAFs must be appropriate for the trophic level of the aquatic biota to which the predicted baseline BAF is intended to apply.

Although BAFs can be related to BCFs using FCMs, BAFs and BCFs can also be related using biomagnification factors (BMFs). The two systems are entirely compatible, but confusion can result if the terms are not used consistently and clearly. Because both FCMs and BMFs are used in the Guidance document and elsewhere, it is appropriate to explain the relation between the two here. The basic difference is that FCMs always relate back to trophic level one (TL1), whereas BMFs always relate back to the next trophic level. In the FCM system:

$$BAF_{TL1} = BCF$$

$$BAF_{TL2} = (FCM_{TL2})(BAF_{TL1})$$

$$BAF_{TL3} = (FCM_{TL3})(BAF_{TL1})$$

$$BAF_{TL4} = (FCM_{TL4})(BAF_{TL1})$$

In the BMF system:

$$BAF_{TL1} = BCF$$

$$BAF_{TL2} = (BMF_{TL2})(BAF_{TL1})$$

$$BAF_{TL3} = (BMF_{TL3})(BAF_{TL2})$$

$$BAF_{TL4} = (BMF_{TL4})(BAF_{TL3})$$

Therefore:

$$BMF_{TL2} = FCM_{TL2}$$

$$BMF_{TL3} = (FCM_{TL3})/(FCM_{TL2})$$

$$BMF_{TL4} = (FCM_{TL4})/(FCM_{TL3})$$

Both metabolism and growth dilution can cause BMFs to be less than 1.

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APPENDIX B

PROTOCOL FOR DETERMINING OCTANOL-WATER PARTITION COEFFICIENTS (K_{ow}) FOR COMPOUNDS WITH LOG K_{OW} VALUES > 5

PROTOCOL FOR DETERMINING OCTANOL-WATER PARTITION COEFFICIENTS (K_{ow}) FOR COMPOUNDS WITH LOG K_{OW} VALUES > 5

1. INTRODUCTION

The octanol-water partition coefficient (K_{ow}) is one of the most widely used chemical parameters. The K_{ow} of a chemical has been found to be representative of a chemical's propensity to partition into biotic and abiotic components of the environment as well as a chemical's propensity to accumulate in living organisms. Because of these associations, the K_{ow} is widely used to predict a chemical's behavior in the environment and to evaluate a chemical's impact on human health.

The octanol-water partition coefficient (K_{ow}) is a unitless measure and is defined as the ratio of the equilibrium concentrations, C, of a chemical in the two phases of a system consisting of *n* -octanol and water at standard temperature and pressure (STP, 25° C, 1 atm)

$$K_{ow} = C_{oct}/C_w$$

where C_{oct} represents the concentration in the *n* -octanol phase, and C_w represents the concentration in the water. The concentrations in the respective phases are expressed in the same volume-referenced units (i.e., mg/mL, mole/L, etc.), therefore, the K_{ow} is a unitless property. Since the value of the partition coefficient spans orders of magnitude, it is frequently expressed on a log scale (base ten) such that a given chemical has a log K_{ow} value which may range from 1 to >8. This parameter is also called the log P value.

Some specific applications of the K_{ow} within the U.S. EPA include: evaluation of a chemical's potential to bioaccumulate in aquatic life, wildlife and humans; modeling the fate, transport and distribution of a chemical in the environment; prediction of the distribution of a contaminant in a living organism; classification of persistent bioaccumulators for regulatory actions; derivation of soil screening levels; calculation of water quality benchmarks; and derivation of Sediment Quality Advisory Levels.

Although a seemingly simple experimental determination, K_{ow} measurement is beset with difficulties. The appropriateness and accuracy of laboratory methods to directly measure a K_{ow} are influenced by a number of factors which include the magnitude of the value itself. For chemicals with log K_{ow} values at or exceeding 5, common sources of error include: (1) failure to achieve equilibrium; (2) incomplete phase separation or interphase mixing during sampling; (3) emulsion effects derived from "excessive" mixing or induced by contaminants; (4) propensity of the chemical to self-associate, tautomerize or form hydrates; and (5) the presence of small quantities of contaminants with a lower K_{ow} value. These errors tend not to be random, but to give measured numbers lower than the true value, frequently by an order of magnitude or more. The likelihood and degree of error increases with increasing K_{ow} and also seems to be more prevalent for certain classes of chemicals (such as halogenated compounds or phthalate esters). As a result, in addition to direct experimental measurement methods, techniques to indirectly experimentally measure or estimate K_{ow} values have been developed.

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1.1 Experimental Measurement Techniques

- Direct experimental measurement techniques include the shake-flask approach, generator column, and slow-stir methods.
- The shake-flask method is the classical approach and fairly straight-forward for chemicals with log K_{ow} values below 5. For chemicals with higher log K_{ow} values, the shake-flask approach requires large volumes of water and formation of emulsions becomes a significant impediment to accurate measurements.
- The generator-column approach was developed to measure the partition coefficients of more hydrophobic chemicals (those with larger log K_{ow} values). This is a laborious method which results in more reliable data than the shake-flask approach for chemicals with higher log K_{ow} values, but some discontinuities in the data for higher-chlorinated PCB congeners have been observed.
- A third direct measurement technique is the slow-stir method. In this method, careful stirring and close temperature control can prevent or limit the formation of emulsions and reliable very high partition coefficients can be obtained relatively easily.

1.2 Indirect Experimental Measurement Techniques

An indirect experimental measurement technique is to incorporate a radioactive label into the chemical and use a radiotracer assay to evaluate the compound's distribution between the octanol and water phases. This approach can be used when you have small amounts of the compound. However, radiotracer assays do not directly measure the compound, and low K_{ow} values frequently result from the presence of impurities or instability of the compound.

1.3 Computer-based Estimation Techniques

Because of the difficulty of directly and accurately measuring K_{ow} values, various computer-based estimation methods exist. These can be divided into two types, those based upon fundamental chemical thermodynamics, and those requiring a training set of chemicals with measured K_{ow}s.

1.3.1 Technique based on fundamental thermodynamics

Computer methods based on fundamental chemical structure theory and are not limited by nor do they require a training set of chemicals with measured K_{ow}s. For example, the SPARC[3] model consists of a set of core models describing intra- and inter-molecular interactions. These

[3] SPARC (SPARC Performs Automated Reasoning in Chemistry) is a mechanistic model developed at the Ecosystems Research Division of the National Exposure Research Laboratory of the Office of Research and Development of the U.S. Environmental Protection Agency by Sam Karickhoff, Lionel Carreira, and co-workers. A prototype version was used for which no performance data for K_{OW} estimation is available. The model complements the aforementioned models because development, training, and testing were done away from K_{OW} data. (See Hilal, Carreira, and Karickhoff, 1994, for model description.)

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models are linked by appropriate thermodynamic relationships to provide estimates of reactivity parameters under desired conditions (e.g., temperature, pressure, solvent).

1.3.2 Techniques using a training set of chemicals

Methods requiring a training set of chemicals use Quantitative Property-Property Relationships (QPPRs) or Quantitative Structure Activity Relationships (QSARs) to derive K_{ow}s. In QPPRs, K_{ow} values are correlated with the values for other chemical parameters--either measured or calculated--using data available from a training set of chemicals. In QSARs, K_{ow} values are derived from fragment constants obtained from a training set of chemicals.

One application of QPPRs is estimating K_{ow}s indirectly from other experimental measurements. In this approach, the K_{ow} is correlated with another measured property. These techniques include the use of reversed-phase high performance liquid chromatography (HPLC) and reversed-phase thin-layer chromatography (TLC). In applying these approaches, K_{ow}s are estimated from linear equations relating retention times on the reversed-phase column to the K_{ow} values. The equations are developed based on a set of reference chemicals for which K_{ow} values are well established. These are relatively efficient methods because they do not require quantification of concentrations, but the linear equations can not be extrapolated beyond the K_{ow} range represented by the reference chemicals from which the equation was derived. In application, values for the reference chemicals are usually shake-flask values obtained from the literature, resulting in unreliable K_{ow} estimates for chemicals with higher log K_{ow} values.

In addition to direct and indirect measurement methods, QPPRs are also used to establish correlations between the K_{ow} and calculated properties. For example, Hawker and Connell (1988) developed a correlative relationship between log K_{ow} and molecular surface area using approximately two dozen PCBs. They then estimated log K_{ow}s for the remaining PCBs by inputting the molecular surface area of each PCB. This technique is limited to estimating K_{ow}s for chemicals which are similar to the chemicals used in developing the relationship.

In QSARs, hydrophobic fragment values are derived from a large database of measured K_{ow}s. These fragments constants are used to estimate K_{ow} in two ways: (1) One approach is to estimate the K_{ow} by adding up the values for all the fragments composing the chemical, either by atom or by functional group. (2) The other approach is to start with a measured K_{ow} value for a structurally similar compound and add or subtract the fragment constants for functional groups or atoms to estimate the K_{ow} for the specific compound. In both these cases, the calculated K_{ow} value must also be corrected for proximity effects between structurally close substituent groups, and the K_{ow} value derived is only as good as the data associated with the training set of chemicals. This method is also limited to predicting K_{ow}s for chemicals with structures similar to those within

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the training set. Computer-based models exist which apply QSAR approaches to estimate K_{ow}s. CLOGP[4] and LOGKOW[5] databases are both applications of this approach.

1.4 Recommendations

Given the numerous techniques available to determine the K_{ow} and its numerous and important applications across the Agency, the U.S. EPA has formed an Agency K_{ow} Work Group to determine recommended K_{ow} values for chemicals of concern to various EPA programs. In determining these recommended K_{ow} values, the preferable option would be to recommend actual measured values. For chemicals with log K_{ow} values below 5, the classical shake-flask approach is adequate to obtain these measurements. However, there is a serious shortage of reliable measured data for compounds with higher log K_{ow} values (Log $K_{ow} > 5$) and these chemicals frequently exhibit a propensity to accumulate in living tissues or bind to soils and sediments. For these reasons, this protocol has been restricted to chemicals with log K_{ow} values equal to or exceeding 5.

2. PROTOCOL FOR DETERMINING RECOMMENDED K_{OW} VALUES

Measured values are preferable to estimated values for determining recommended K_{ow} values. However, the absence or scarcity of reliable data necessitates the use of estimation methods in evaluating data and in assigning K_{ow}s. K_{ow} estimates used in this exercise include: calculation methods (e.g., CLOGP, LOGKOW, SPARC, and fragment additions or subtractions) and QPPRs (e.g., HPLC and TLC methods). All of these approaches except SPARC, an estimation method based on fundamental chemical structure theory, require measured K_{ow} values for a training set of chemicals.

Assigning a K_{ow} from these data will necessarily involve scientific judgement in evaluating not only the reliability of all data inputs but also the accretion/concretion of evidence in support of the recommended K_{ow} value. Supporting rationale will be provided for each recommended value.

2.1 Operational Guidelines

- "High quality" measured value are preferred over estimates. For chemicals with log $K_{ow} > 5$, it is highly unlikely to find multiple "high quality" measurements. (Note: "high quality" is data judged to be reliable based on the guidelines

[4] CLOGP is a molecular fragment-based model developed at Pomona College by Albert Leo, Corwin Hansch, and co-workers. This model has undergone extensive development and exhaustive testing; version 3.1 was used in this exercise. (See Hansch and Leo, 1995, for model description and performance data.)

[5] LOGKOW is essentially an expanded CLOGP with more recent training data and additional fragment constants. The developers were Philip Howard, William Meylan and co-workers at Syracuse Research Corporation; Version 1.51 was used in this exercise. (See Meylan and Howard, 1994, for model details and performance information.)

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presented in Appendix I). Due to the paucity of "high quality" data, assigning K_{ow}'s from estimation techniques may be necessary.

- K_{ow} measurements by slow stir are extendable to 10^8. Shake flask K_{ow} measurements are extendable to 10^6 with sufficient attention to micro emulsion effects; for classes of chemicals that are not highly sensitive to emulsion effects (i.e., polycyclic nuclear aromatic hydrocarbons) this range may extend to $10^{6.5}$.

- What is considered reasonable agreement in log K_{ow} data (measured or estimated) depends primarily on the magnitude of the log K_{ow} value. Therefore, the following ranges of acceptable variation have been established for this exercise: 0.5 for log $K_{ow} > 7$; 0.4 for 6 # log K_{ow} # 7 ; 0.3 for log $K_{ow} < 6$.

- Statistical methods should be applied to data as appropriate. However, it is recognized that application is limited by the paucity of data and the determinate/methodic nature of most measurement error(s).

2.2 Tiered Procedure for Selecting K_{OW} Values

I. Assemble/evaluate experimental and calculated data (e.g.,CLOGP, LOGKOW, SPARC).

II. If calculated log K_{ow}'s > 8:

A. Develop independent estimates
   1. Liquid Chromatography (LC) methods with "appropriate" standards. (See Appendix I for guidelines for LC application.)
   2. Structure Activity Relationship (SAR) estimates extrapolated from similar chemicals where "high quality" measurements are available.
   3. Property Reactivity Correlation (PRC) estimates based on other measured properties (solubility, etc.)

B. If calculated data are in reasonable agreement (as defined in section 2.1) and are supported by independent estimates described above, report the average calculated value.

C. If calculated/estimated data do not agree, use professional judgement to evaluate/blend/weight calculated and estimated data to assign the K_{ow} value.

D. Document rationale including relevant statistics.

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III. If calculated log K_{ow}'s in range 6 - 8:

A. Look for "high quality" measurements. These will generally be slow stir measurements, the exception being certain classes of compounds where micro emulsions tend to be less of a problem (i.e., polycyclic nuclear aromatic hydrocarbons; for these compounds, shake flask measurements are good to log K_{ow} of 6.5).

B. If measured data are available with reasonable agreement (both measurements and calculations), report average measured value.

C. If measured data are in reasonable agreement, but differ from calculated values, develop independent estimates and apply professional judgement to evaluate/blend/weight the measured, calculated and estimated data to assign the K_{ow} value.

D. If measured data are not in reasonable agreement (or if only one measurement is available), use II A, B, and C to produce a "best estimate"; use this value to evaluate/screen the measured K_{ow} data. Report the average value of the screened data. If no measurements agree with the "best estimate," apply professional judgement to evaluate/blend/weight the measured, calculated and estimated data to assign the K_{ow} value.

E. If measured data are unavailable, proceed through II A, B, C and report the "best estimate".

F. Document rationale including relevant statistics.

IV. If calculated log K_{ow}'s < 6:

A. Proceed as in III. Slow stir is the preferred method but shake flask data can be considered for all chemicals if sufficient attention has been given to emulsion problems in the measurement.

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ATTACHMENT I: GUIDELINES FOR EVALUATING MEASURED AND ESTIMATED K_{OW} VALUES

1. ASSESSMENT OF MEASURED K_{OW} VALUES

1.1 Molecular Speciation. In order to interpret measured data, it is necessary to understand the molecular species present in both the octanol and water phases including ionization, self-association, tautomerization, and hydrate formation. For these reasons, it is difficult to conduct or interpret such measurements for mixtures of unknown composition or for single molecules of unknown structure. Solutes composed of more than one molecular species may also show substantial temperature dependence of K_{ow} reflecting relative change in speciation in the octanol and water phases.

1.1.1 Ionization. This protocol is directed primarily towards assigning a log K_{ow} value for neutral (non-ionizable) organic compounds. In the case of weakly acidic or basic compounds a portion of the molecules may be ionized at environmental pH, and partitioning into biota or abiota will be correspondingly reduced. For weakly ionizable molecules, shake flask measurements are conducted in solutions of a stable, non-extractable buffer to suppress ionization. Measurements for weakly ionizable molecules can also be performed using a potentiometric titration method (Avdeef, 1992; 1993, Slater *et al.* 1994).

1.1.2 Self-Association - This protocol is directed primarily towards neutral (non-ionizable) organic compounds where self-association is generally not expected to be of concern. In some situations, self association can arise for very high log K_{OW} solutes because rather high concentrations of the solute in very small amounts of octanol will be required for the delivery of sufficient solute to the water phase for a successful measurement. For these types of molecules, it will be very difficult, if not impossible, to be sure that no self-association occurs in the octanol phase. Self association can also arise for molecules which have H-bonding donor and acceptor groups that could participate in such self-association at high concentration in the octanol phase. For the latter group of molecules, e.g., amines, carboxylic acids, and phenols, especially if cyclic dimers can form, measurements need to be conducted at a sufficiently low concentration so that K_{ow} reflects only the unassociated form of the molecule in both water and octanol phases. In either of the cases of self-association, it is recommended that measurements be performed using several solute concentrations in the octanol and water phases. No change in K_{ow} with differing solute concentrations provides an indication that measurements have been performed using the unassociated form of the molecule. If the K_{OW} decreases with decreasing solute concentration in octanol, extrapolation to infinite dilution is suggested.

1.1.3 Tautomerization - This protocol is directed primarily towards neutral (non-ionizable) organic compounds where tautomerization is generally not expected to be of concern. The most common tautomerism (keto-enol tautomerism) involves

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structures with a -OH attached to a doubly-bonded carbon (enol) which rapidly convert to the keto structure where the -OH becomes -C=O group and the hydrogen attaches to the other carbon of previously existing doubly-bonded carbon. If the molecule is likely to exist in more than one tautomeric forms, the ratio of tautomers is often quite different in the octanol and water phases. The measured value for a tautomeric chemical is meaningful. However, this value will in most cases lie somewhere among the values for the individual tautomeric forms; in essence, an average value for the ratio of tautomers is measured. The individual values for the tautomeric forms most often will have to be calculated because measurements can not be performed for the individual tautomeric forms since individual tautomeric forms rapidly requilibrate to the tautomeric mixture. Sometimes molecules exhibit both ionization and tautomerization, leading to further complications.

1.1.4 Hydrate Formation - Similar to the case of tautomerization, hydrates may exist to different degrees in the water and octanol phases thus confounding the interpretation of the measured value.

1.1.5 Photodegradation - If the compound is expected to be light-sensitive and subject to photodegradation, care should be taken to protect the substance from light during the experiment.

1.2 Shake Flask or Slow-Stirring Considerations. (1) Water and octanol phases should be free of impurities; (2) mixing should be of sufficient duration (e.g., 7 days for dioctyl phthalate) to reach steady state equilibrium, particularly for very hydrophobic chemicals; (3) when using volatile solutes, it is particularly important that both phases are analytically measured; (4) avoid formation of emulsions during mixing and centrifuge before measuring; (5) experimental protocol should be particularly scrutinized for K_{ow} measurements 4-6; (6) the ratio of octanol to water should be reduced for high K_{ow} chemicals; and (7) sorption to glass (e.g., for pyrethroids) during workup can be a problem.

1.3 General Considerations. Solute should be stable to hydrolysis during the course of the experiment. If stability can not be ensured, a calculated value may be used. Solutes should be of high purity as the presence of a less lipophilic impurity exerts a dominant effect in the measured K_{ow} value. Mixtures such as chlorinated paraffins (containing thousands of isomers, congeners, and degrees of chlorination) therefore cannot be determined except by chromatographic methods.

1.4 Indicators of Potential Concern. Inconsistency with other measured values, with estimated value, or inconsistency among estimated values. The importance of professional judgement and knowledge of chemistry cannot be overemphasized in making the best K_{ow} assignments. For example, inconsistency between measured and predicted may reflect only problems in the training set used based upon poor experimental values when better data have since become available.

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1.5 References. Listed below are references for the shake flask and slow stir methods for determining K_{ow} used by various governmental agencies and specified in EPA testing protocols. Selected references for measurement of ionizable compounds using potentiometric titration are also included.

OECD. 1994. OECD Guidelines for Testing of Chemicals, 2nd Ed. Method: 107. Partition Coefficient (n-octanol/water)(Flask-shaking Method (30 May 89).

US-Environmental Protection Agency. 1996. Product Properties Test Guidelines. OPPTS 830.7550. Partition Coefficient (n-Octanol/water), shake flask method. EPA 712-C-96-310 (1701). Public Draft.

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2. ASSESSMENT OF K_{OW} VALUES ESTIMATED FROM LIQUID CHROMATOGRAPHIC TECHNIQUES

An estimated K_{ow} value would be considered "appropriate" provided the following experimental conditions existed during its determination:

2.1 Kow''s used for the reference compounds consist of "high quality" slow stir measurements.

2.1.1 Better estimates for K_{ow}'s are obtained when reference and test chemicals are similar.

2.1.2 When solutes have hydrogen accepting and/or amphiprotic substituents, predictions of the log K_{ow}s from the log capacity factor (using relationships developed with non-hydrogen bonding solutes) will generally result in predicted log K_{ow}s which are too large and too small, respectively (Yamagami et al. 1994). The chromatographic behavior for solutes containing hydrogen accepting and/or amphiprotic substituents for the prediction of log K_{ow} has been extensively studied by Yamagami and coworkers. These studies concluded that "corrections for hydrogen-bond effects are required in most cases when polar functional groups are present" and that solvent composition in the chromatography system can greatly change the capacity factors for these chemicals relative to non-hydrogen bonding chemicals.

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2.2 A minimum of five chemicals are used in developing the log capacity factor (k')- log K_{ow} calibration relationship. The K_{ow}'s of the reference chemicals should be evenly distributed and should span 3 to 4 orders of magnitude.

2.3 The log k' - log K_{ow} calibration curve is linear and has a correlation coefficient greater than 0.95.

2.4 The K_{ow} estimated for the test chemical is within the range of K_{ow}s for the reference compounds or does not exceed the upper end of the range of K_{ow}s for the reference compounds beyond 0.5 log units without adequate justification.

2.5 Chemical speciation must be accounted for in performing the measurements. For example, with ionizable chemicals, measurements must be performed on the unionized form by using an appropriate buffer with a pH below the pK for an acid and above the pK for a base.

2.6 Reference and test chemicals are of known purity and structure. Independent confirmation of the identity and purity of the reference and test chemicals is required or highly desirable.

2.7 Chemical mixtures can be used as the source of test chemicals provided accurate identities can be assigned to individual chromatographic components.

2.8 References. These references for liquid chromatography techniques include methods recommended by various governmental agencies that would provide "appropriate" K_{ow}s when the reference compounds used in the determination are similar to the compound of interest.

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ATTACHMENT II: ESTIMATION OF K_{OW} FROM MOLECULAR FRAGMENTS

For computing thermodynamic properties it is often useful to consider a molecule as a collection of molecular fragments, each making a distinct contribution to the property of interest, which is relatively independent of the rest of the molecule. The rationale behind the method is that a large number of structures can be generated from a relatively small number of fragments, and thus a large number of estimates can be derived from a small number of experimentally determined fragment constants. The accuracy of the estimation, however, necessarily improves as the specificity of the fragment environment increases, which entails an increase in the number of fragments or corrective factors that must be considered. This approach is applied at different levels of sophistication. One user may employ a few fragment constants and generate 'first order' estimates whereas another may make numerous corrections or adjustments reflecting more fragment specificity for a given molecular environment. For a more complete discussion of group fragment methods one should consult Hansch and Leo, 1995. For this exercise, these methods will be used for molecule-to-molecule extrapolation (via addition or subtraction of fragments\substituents) rather than a priori estimation.

1. Addition of ring fragments

For condensed ring aromatics, the addition of rings is given by

$$f^{\alpha}_{(C_4H_2)} = \log K_{(OW)}(anthracene) - \log K_{(OW)}(naphthalene) \approx 1.20$$

$$f^{\beta}_{(C_3H)} = 0.5\,[\log K_{(OW)}(pyrene) - \log K_{(OW)}(naphthalene)] \approx 0.85$$

$$f^{\gamma}_{(C_2)} = \log K_{(OW)}(pyrene) - \log K_{(OW)}(phenanthrene) \approx 0.50$$

where $f^{\alpha}_{(C_4H_2)}$, $f^{\beta}_{(C_3H)}$, $f^{\gamma}_{(C_2)}$ are the fragment addition constants for ", $, and (condensation respectively.

2. Addition of substituents

The addition of a substituent, S (replacing a H atom) is a primary application of this method. In this case

$$\Pi_S = \log K_{(OW)}(R - S) - \log K_{(OW)}(R - H)$$

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where R is the base molecule and Π_S is a substituent constant, which is experimentally determined. Tables for common substituents are readily available or can be easily determined from measured data. One must distinguish (i.e., have different substituent constants for) attachment to aliphatic, ethylenic, acetylenic, and aromatic carbon atoms in 'R'. Also corrections must be made for multiple substitution if attachment is to the same or adjacent carbons. The following is an example of K_{ow} estimation. The fragment constant for Cl attached to aromatic carbon can be derived from:

$$\Pi_{Cl}^{arom} = \log K_{(OW)}(chlorobenzene) - \log K_{(OW)}(benzene) \approx 0.71$$

With this constant, one can derive

$$\log K_{(OW)}(1,3,5-trichlorobenzene) \approx \log K_{(OW)}(benzene) + 3(0.71) = 4.26$$

An exhaustive list of substituent constants is included in the aforementioned Hansch and Leo (1995) reference.

It should be noted that B-values are most often illustrated, as above, by replacing a hydrogen atom on a benzene ‘parent’ molecule. However, substituents that are strong electron donors or acceptors such as chlorine have different B-values when placed on other ‘parent’ aromatic molecules. For example, differences in log K_{OW}s of 0.71, 0.99, 0.71 and 0.85 are obtained between the 4-chloro-analogues and their parent molecules for benzene, aniline, nitrobenzene, and phenoxyacetic acid, respectively. The literature is replete with calculations making this type of error and the importance of using the correct B-values for the ‘parent’ molecule can not be under emphasized.

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