12.0 Aquatic Food Web Module

12.1 Purpose and Scope

The Aquatic Food Web Module calculates steady-state contaminant concentrations in aquatic organisms (e.g., fish, benthic invertebrates, aquatic plants) consumed by human and ecological receptors. These concentrations are used as input to the Human Exposure and Ecological Exposure Modules to calculate applied dose to receptors of interest. Figure 12-1 shows the relationship and information flow between the Aquatic Food Web Module and the 3MRA modeling system.
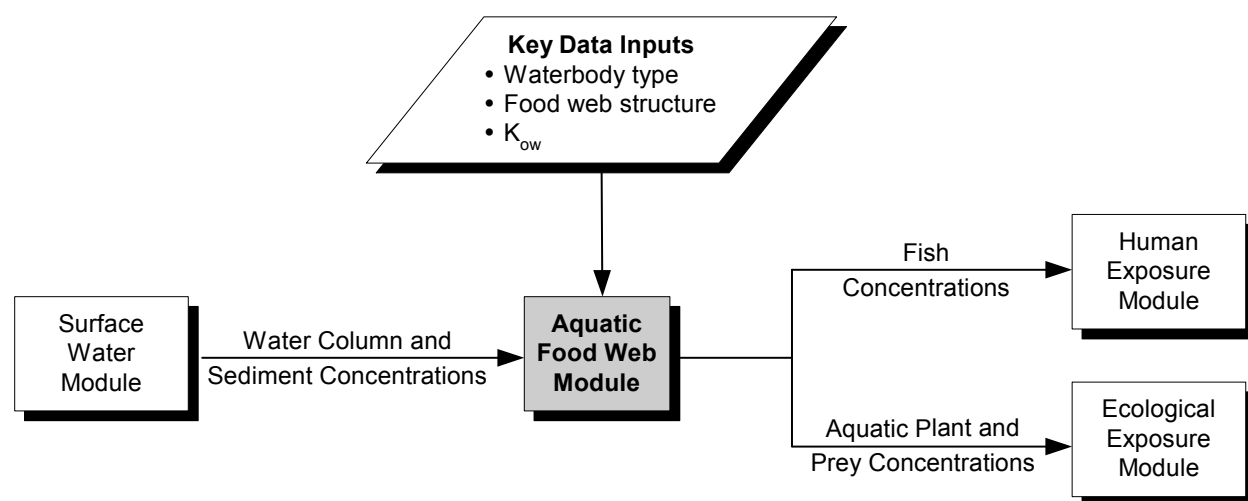
Key Data Inputs
- Waterbody type
- Food web structure
- K_{ow}

Figure 12-1. Information flow for the Aquatic Food Web Module in the 3MRA modeling system.

For each year in the simulation, the Aquatic Food Web Module predicts annual average contaminant concentrations in aquatic biota in freshwater waterbodies in the area of interest (AOI) considered capable of supporting fish (referred to as "fishable" waterbodies). The model is flexible enough to be applied to different types of waterbodies, including stream reaches, rivers, lakes, ponds, and permanently flooded wetlands. Simple freshwater food webs were constructed for each type of waterbody to depict the major functional and structural components of "healthy" freshwater ecosystems. The components of each food web represent major categories of aquatic biota in freshwater systems: aquatic macrophytes, phytoplankton, periphyton, zooplankton, benthic detritivores, benthic filter feeders, and various feeding guilds of fish. Some of these concentrations are used internally to calculate concentrations in fish, while other concentrations are reported as a time series for use in calculating exposures to wildlife and humans, as well as to calculate ecological hazard (e.g., hazard to sediment

dwellers). Thus, the Aquatic Food Web Module determines which data are appropriate for use in a given waterbody and calculates concentrations in the aquatic biota assigned to that waterbody. Specifically, the Aquatic Food Web Module performs the following functions:

1. **Selects food web appropriate for each waterbody.** The Aquatic Food Web Module matches an appropriate food web with each waterbody identified as fishable within the AOI. Eight freshwater food webs were developed to capture the variability in freshwater systems. They represent warmwater streams/rivers, wetlands, ponds, and lakes; and coldwater streams/rivers, wetlands, ponds, and lakes.

2. **Constructs dietary matrix for food web.** The Aquatic Food Web Module uses a constrained, random prey preference sampling approach that selects preference fractions at random between the minimum and maximum, assuming a uniform distribution. This approach allows for the dietary composition to reflect the full range of variability inherent in the diets of freshwater fish.

3. **Calculates contaminant concentrations in food web.** The Aquatic Food Web Module calculates concentrations for the biota assigned to each freshwater food web. The biota categories include

   - Phytoplankton,
   - Periphyton,
   - Zooplankton,
   - Aquatic plants (macrophytes),
   - Benthic filter feeders,
   - Benthic detritivores,
   - Fish in various feeding guilds, and
   - Apex predator fish.

   The model will only calculate concentrations for biota that are assigned to a particular food web and waterbody. The calculations involve mechanistic models or the use of empirical data on bioaccumulation.

4. **Reports contaminant concentrations for fish consumed by wildlife and humans.** Food webs for freshwater aquatic systems typically have a single apex predator species (trophic level 4 [TL4]) and a number of other fish species that occupy different feeding guilds, such as benthic feeders (e.g., catfish). These other species are, for the purposes of exposure assessment, often grouped into the category of trophic level 3 (TL3), indicating that they are both predator and prey in the food web. To predict exposures for wildlife and humans that eat TL3 fish, the model calculates an average contaminant concentration—both wholebody and filet—for fish that fall into the category of TL3. In addition, the Aquatic Food Web Module reports the tissue concentration for the apex predator fish in each waterbody. The wholebody fish concentrations are used by the Ecological Exposure Module, and the filet concentrations are used by the Human Exposure Module.

12.2   Conceptual Approach

12.2.1 Select Food Web Appropriate for Each Waterbody

The 3MRA modeling system was designed to use site-based data to support a national-level assessment strategy. Consequently, an important goal for the Aquatic Food Web Module was to capture the variability in freshwater systems across the contiguous United States, particularly with respect to species composition and dietary preferences. The first step in accomplishing this was to develop a set of representative food webs. The second was to assign each waterbody in the AOI to one of these representative food webs.

Develop Representative Freshwater Food Webs. Upon reviewing literature sources on freshwater systems and food webs, it was apparent that the food web structure and, in many instances, the fish species, are similar across many different freshwater habitats (Schindler et al., 1996). There are common elements to virtually all aquatic communities (e.g., periphyton, benthic detrivores, aquatic plants). Many options to represent variability were considered, ranging from a basic food web consisting of three compartments, to a complex food web that could represent virtually any type of freshwater system. However, the development of a single food web—whether basic or complex—was not consistent with the 3MRA framework goal to use site-based information to support national-scale assessments. Moreover, considerable data were identified to vary the complexity of the food web and represent many different species of fish. To take advantage of these data, freshwater food webs were constructed such that the major functional elements were represented as simply as possible. Several useful tenets from the literature were adopted as guidelines in developing the aquatic food webs. They are summarized in the text box.

> **Basic tenets in constructing aquatic food webs**
>
> - Predator-prey interactions should follow common sense (i.e., larger fish eat smaller fish) and the system should be balanced in the sense that all prey items are connected in the food web.
> - Size distinctions within feeding guilds of fish should consider the potential biomass of the most preferred prey item and the interactions with other components of the food web.
> - Larger waterbodies tend to support more functional elements, and therefore, are typically more complex than smaller waterbodies (e.g., lakes are more complex than ponds).
> - Flowing waters tend to be less complex than still waters and have low plankton density; as a result, zooplankton are not an important food web component.
> - Warmwater systems tend to support a more diverse aquatic community than coldwater systems; as a result, they tend to have more functional niches and are more complex.

The resulting freshwater food webs provide a useful framework to model contaminant transport and fate in freshwater waterbodies, offer a reasonable representation of energy flows typical of different habitats, and capture variability in a manner that is appropriate for the application of the 3MRA modeling system. Figure 12-2 shows an example of a freshwater lake food web.

The sources used to construct the freshwater food webs reflect a broad perspective, ranging from biodiversity assessments to game fishing enthusiasts. These data sources were not only used in constructing the food webs, but also in characterizing the fish species and in

deciding which species of fish are eaten by human receptors. These sources offered a wide range of detail on food webs: from site-specific assessments to more general constructs developed for regional analyses. Many sources included qualitative descriptions of aquatic habitats, as well as indications of fish species that are considered "typical" for these habitats; in particular, the fishing references provided very useful information on the characteristics of fish that inhabit various freshwater systems. Many of these texts also indicated whether the preferred water temperature for a given species of fish was cold water or warm water.
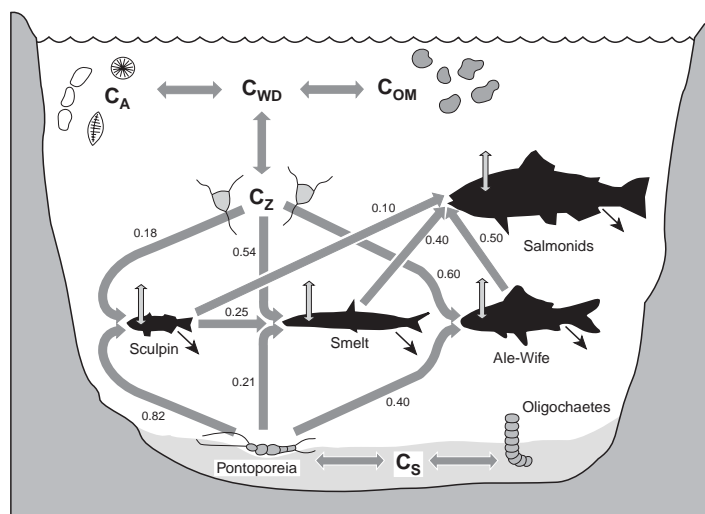

Figure 12-2. Example of simplified food web for freshwater lake (Gobas et al., 1993).

The food web for each type of freshwater system reflects a number of characteristics of the waterbody, such as water temperature, flow (i.e., flowing versus static systems), dominant zones (e.g., pelagic versus littoral zones), and preferences of fish species for certain aquatic systems. The fish species assigned to the eight representative food webs represent a specific functional niche to which the species belong (e.g., feeding guilds; trophic level; size). For example, because the zooplankton density in streams tends to be low, a fish species that primarily feeds on zooplankton is unlikely to be assigned to stream habitats. In contrast, piscivore-dominated lakes are characterized by large-bodied zooplankton with high grazing rates (Schindler et al., 1996). In these lake systems, we would expect to find planktivorous species of fish as an integral part of the food web. Thus, the concept of functional niche is particularly important in the selection of food webs because these niches were used to inform the selection of appropriate fish species and associated data for each habitat (e.g., lipid fraction, body weight, dietary preferences).

The freshwater food webs contain between eight and 12 of the biota types possible in freshwater systems. The following biota are found in freshwater food webs:

- ■ **Periphyton:** algal species typical of freshwater systems that adhere to rocks and detrital material; also includes small crustaceans, which are not modeled in the Aquatic Food Web Module;

- ■ **Phytoplankton:** primary producers in pelagic systems;

- ■ **Aquatic macrophytes:** vascular aquatic plants (e.g., submerged, emergent);

- ■ **Zooplankton:** various invertebrates that graze on phytoplankton;

- ■ **Benthic detrivores:** benthic dwellers that break down detritus in sediment (e.g., amphipods);

- ■ **Benthic filter feeders:** benthic organisms that feed through a filtration mechanism;

- ■ **TL3 benthivore:** TL3 fish whose primary feeding preference is benthic organisms (divided into small, medium, and large);

- ■ **TL3 planktivore:** TL3 fish whose primary feeding preference is zooplankton;

- ■ **TL3 omnivore:** TL3 fish who have no clear feeding preferences (divided into small, medium, and large); and

- ■ **TL4 piscivore:** TL4 piscivorous fish that serve as the apex predator for the community.

Table 12-1 summarizes the food webs constructed for use in modeling contaminant movement in the freshwater food webs. This matrix indicates which food web components are assigned to each aquatic habitat. The presence of a prey item such as zooplankton may not require that an obligate planktivore be assigned to the food web. In wetlands, for example, omnivorous fish tend to feed on zooplankton, as well as on other biota (e.g., periphyton, benthos, detritus); therefore, the biota assignments reflect the goal of accounting for significant predator-prey interactions without imposing artificial constraints on the food web structure. Additional details on the development of habitat-specific food webs (e.g., warmwater wetland) are found in the 1999 background documents (U.S. EPA, 1999).

Assign Each Waterbody in the AOI to a Representative Food Web. The structure of aquatic food web and the fish species used to parameterize the Aquatic Food Web Module were based largely on the type of waterbody. The waterbody characteristics were developed using information from geographical information system (GIS) data sources (e.g., National Wetlands Inventory, or NWI), landscape data on the size of standing waterbodies, and certain conventions used in fish ecology to identify coldwater, stenothermic fish (i.e., coldwater species with narrow tolerance for temperature changes). For example, the threshold adopted for categorizing waters as warm or cold is based on a maximum temperature of 25°C—the water temperature above which coldwater, stenothermic fish cannot survive. The food web structure for warmwater streams is typically more complex than an analogous coldwater stream; as a result, there are frequently more functional niches in a warmwater stream than might be found in a coldwater stream. Stenothermic fish with clear temperature preferences were generally assigned either to warmwater or coldwater systems, but not to both. Other species that are found in both warmwater and coldwater habitats were assigned to both categories.

Table 12-1. Matrix of Biota in Food Webs for Freshwater Systems in 3MRA

Biota	Coldwater habitats				Warmwater habitats			
	Stream	Wetland	Pond	Lake	Stream	Wetland	Pond	Lake
Periphyton	✔	✔	✔	✔	✔	✔	✔	✔
Phytoplankton		✔	✔	✔		✔	✔	✔
Aquatic macrophytes	✔	✔	✔	✔	✔	✔	✔	✔
Zooplankton		✔	✔	✔		✔	✔	✔
Benthic detrivores	✔	✔	✔	✔	✔	✔	✔	✔
Benthic filter feeders	✔			✔	✔			✔
TL3 benthivore (small)	✔			✔	✔			✔
TL3 benthivore (medium)	✔	✔	✔	✔	✔	✔	✔	
TL3 benthivore (large)								✔
TL3 planktivore (small)			✔					
TL3 planktivore (medium)				✔			✔	
TL3 planktivore (large)								✔
TL3 omnivore (small)		✔	✔	✔		✔	✔	
TL3 omnivore (medium)	✔	✔	✔		✔	✔		✔
TL3 omnivore (large)				✔			✔	✔
TL4 piscivore	✔	✔	✔	✔	✔	✔		✔

12.2.2 Construct Dietary Matrix for Food Web

The aquatic food webs provide the framework for the Aquatic Food Web Module simulations; the food webs identify fish and other biota presumed to be present for each waterbody and indicate the predator-prey interactions. However, most fish are opportunistic feeders, leading to significant variability in the dietary composition, even within feeding guilds. There is also tremendous variability in the dietary preferences of fish associated with life stage, region, prey density, and a host of other conditions. For many contaminants, the primary route of exposure is through gill exchange, and therefore, the dietary preferences are not important contributors to bioaccumulation of contaminants. However, for contaminants shown to biomagnify with trophic level, the dietary composition may have a significant influence on fish contaminant concentrations.

To address these variabilities in dietary composition, a random sampling algorithm was developed to select prey preference fractions for each type of fish assigned to a food web. The model constructs this dietary matrix for each simulation (defined as the combination of a site, waste management unit [WMU], and contaminant) so that the predicted concentrations in fish reflect the substantial variability in the diet. Data obtained from literature sources were evaluated to create a database of prey preference ranges for biota in various food webs. The Aquatic Food Web Module uses the database to (1) construct the food web-specific dietary composition, (2) rank prey items from most preferred to least preferred, and (3) estimate the prey

preferences for each biota type (how much of each item is in the total diet). In this context, the dietary composition refers to both the dietary items consumed (e.g., zooplankton, small benthivorous fish) and the fraction of each dietary item consumed by various fish components in the food web.

The approach to construct the dietary matrix and select prey preferences in the food web was based on two objectives: (1) to observe the bounds as defined by the empirical data on prey preferences, and (2) to allow variability within the bounds to be exercised. Estimating prey preferences is accomplished using a constrained, random prey preference sampling algorithm that selects preference fractions at random between the minimum and maximum, assuming a uniform distribution. The algorithm maintains overall dietary preferences and allows for the dietary composition to reflect the full range of variability inherent in the diets of freshwater fish. The algorithm developed to solve this problem treats each dietary fraction as a "resource" to be allocated among the prey items for a particular fish. Before any dietary fractions are assigned for a given fish, the value of the resource remaining to be allocated is 1 (i.e., complete diet). After all dietary fractions have been assigned (zero fractions are allowed), the value of the resource remaining to be allocated is zero. Thus, for a given fish and prey item, the assignment prey preference fraction must consider the minimum and maximum preference values for that prey item, as well as the amount of resource remaining (dietary fraction yet to be assigned). The algorithm used to perform the random sampling is described in the text box on the next page.

12.2.3 Calculate Contaminant Concentrations in Food Web

The Aquatic Food Web Module was developed to be flexible to use empirical data, mechanistic models, or simple regression equations that use physical-chemical properties to calculate contaminant concentrations in food web biota. The choice of method is determined by the type of contaminant modeled, as well as by the availability of suitable empirical data on bioaccumulation. The Aquatic Food Web Module can model the following three groups of contaminants:[1]

- ■ **Hydrophobic, non-ionizable organics.** This group includes dioxin, dioxin-like chemicals and high-molecular-weight, highly halogenated organics that tend to bioaccumulate in aquatic systems. Biota concentrations for these contaminants are estimated using either a mechanistic model or empirical data on bioaccumulation from the surface water column or the sediment. Currently, the Aquatic Food Web Module uses a mechanistic model based on the work of Gobas (e.g., Gobas, 1993) to predict tissue concentrations in aquatic biota. The module uses data on metabolism when available.

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[1]The predictive models in the Aquatic Food Web Module can also be applied to ionizable organics. Chemical property values such as the octanol-water partition coefficient (K_{ow}) generated by the chemical properties processor reflect environmental conditions (e.g., pH) that affect ionization in sediment and surface water.

Random Sampling Algorithm Used to Determine Aquatic Prey Preferences

The issue for the aquatic food web is to select prey preferences throughout the food web matrix such that the observed bounds are honored (i.e., the empirical data on prey preferences), yet the allowable variability within the bounds is exercised in a Monte Carlo sense and the diet is complete. Expressed mathematically, the problem is:

$$Select \quad P_{ij} \quad i = 1,...,N \quad j = 1,...,M \quad Such \ that$$
$$Min_{ij} \leq P_{ij} \leq Max_{ij} \quad i = 1,...,N \quad j = 1,...,M$$
$$\sum_{j=1}^{M} P_{ij} = 1.0 \quad i = 1,...,N$$

where

N	=	number of biota types that are fish
M	=	number of prey items
P_{ij}	=	dietary fraction of the prey item for fish i for prey item j
Min_{ij}	=	minimum observed dietary fraction of fish i for prey item j
Max_{ij}	=	maximum observed dietary fraction of fish i for prey item j.

The algorithm that was developed to solve this problem treats P_{ij} as a "resource" to be allocated among the M prey items for a given biota type of fish. Before any dietary fractions are assigned for a given fish i, the value of the resource remaining to be allocated is 1.0 (i.e., complete diet). After all dietary fractions have been assigned (zero fractions are allowed), the value of the resource remaining to be allocated is 0. For a given fish i and prey item j, the assignment (P_{ij}) must consider both the Min_{ij} and the Max_{ij}, as well as the amount of resource remaining (dietary fraction yet to be assigned). The assignment equation for biota type i, assuming a uniform distribution for P_{ij}, is:
with the variables defined as follows:

$$LB_{ij} = Maximum[Min_{ij}, \ RR_{ij} - \sum_{k=j+1}^{N} Max_{ik}]$$
$$RR_{ij} = 1.0 - \sum_{k=1}^{j-1} P_{ik}$$
$$UB_{ij} = Minimum[Max_{ij}, \ RR_{ij} - \sum_{k=j+1}^{N} Min_{ik}]$$

where

LB	=	lower bound of the range
UB	=	upper bound of the range
RND	=	uniform random deviate (0-1).

■   **Hydrophilic, non-ionizable organics.** This group includes straight-chain aliphatics, as well as low-molecular-weight organics such as benzene, that do not tend to bioaccumulate in aquatic systems. Biota concentrations for these contaminants can be estimated using a regression model, a mechanistic model, or empirical data on bioaccumulation. Currently, the Aquatic Food Web Module uses a regression model to predict bioaccumulation factors (BAFs), unless the contaminant is considered to be easily metabolized. For metabolizable organic chemicals, the Aquatic Food Web Module uses empirical BAFs to predict tissue concentrations. Tissue concentrations in aquatic plants and benthic filter feeders are calculated based on sediment concentrations and biota sediment accumulation factors (BSAFs).

■   **Metals and mercury.** This group includes metals in various valence states as well as mercury as methyl mercury. Biota concentrations are predicted using empirical data on bioaccumulation. For metals, the Aquatic Food Web Module uses median values of BAFs based on a data set that meets specific data quality objectives (see Volume II). For mercury, tissue concentrations of mercury are estimated using empirical BAFs based on dissolved methyl mercury concentrations from the *Mercury Report to Congress* (U.S. EPA, 1997). The *Mercury Report to Congress* provides methyl mercury BAFs for fish in TL3 and TL4. For both metals and mercury, tissue concentrations in aquatic plants and benthic filter feeders are calculated based on sediment concentrations and BSAFs.

Depending on the contaminant of concern, the Aquatic Food Web Module requires inputs on the characteristics of the fish species assigned to each food web (e.g., lipid fraction, body weight, dietary preferences), as well as characteristics of the waterbody (e.g., the fraction organic carbon in bed sediment). The Surface Water Module generates contaminant concentrations in surface water (dissolved and total) and in sediment (dissolved in pore water and total); therefore, the Aquatic Food Web Module is not required to predict contaminant concentrations in the different phases in the environmental media (i.e., sorbed versus freely dissolved phases) but gets these from the Surface Water Module. For all contaminants, the Aquatic Food Web Module calculates tissue concentrations for benthic filter feeders, aquatic plants, and TL3 and TL4 fish. Intermediate concentrations in food items such as zooplankton and benthic detritivores are calculated only for hydrophobic organic chemicals and are used by the mechanistic model as dietary inputs.

The technical approach implemented by the Aquatic Food Web Module to predict contaminant concentrations in biota is summarized below for the three groups of contaminants. More detailed discussions on the algorithms and data sources used by the Aquatic Food Web Module can be found in the 1999 background documents (U.S. EPA, 1999) and in Volume II of this report, respectively.

Hydrophobic, Non-Ionizable Organic Contaminants. For hydrophobic, non-ionizable organic chemicals, the Aquatic Food Web Module is based on the modeling constructs developed by Gobas et al. (1993), Thomann (e.g., Thomann et al., 1992), and a number of other researchers (e.g., Abbott et al., 1995; Campfens and Mackay, 1997; Morrison et al., 1997; and Zaranko et al., 1997). These models were chosen because they were developed specifically for

organic chemicals with significant potential to bioaccumulate in the food web, they do not have prohibitive data requirements, they are flexible in their application to different waterbodies and food webs, they have been peer reviewed and validated with field data, and the series of linear equations can be solved using a flexible matrix solution technique. The form of model does not require a system-based solution; the equations, while coupled, can be solved sequentially. However, to accommodate the future use of more complex predator-prey relationships, which may involve true simultaneity, a more generic, system solution was believed desirable and was developed for the Aquatic Food Web Module. In the matrix solution, the contaminant concentrations in fish are predicted as follows:

$$C_{fish}{}^{i} = \frac{[k_1 \times C_{fd} + k_D \sum (Frac_j \times C_j)]}{(k_2 + k_E + k_M + k_G)} \tag{12-1}$$

where

$C_{fish}{}^{i}$	=	annual average whole-body concentration in fish i (mg/kg wet weight [WW])
k_1	=	rate constant for contaminant uptake from water (L/kg-d)
$C_w{}^{fd}$	=	annual average freely dissolved concentration in surface water (mg/L)
k_D	=	rate constant for contaminant uptake from food (L/d)
$Frac_j$	=	fraction of prey item j included in diet (unitless)
C_j	=	annual average concentration in prey item j in diet (mg/kg WW)
k_2	=	rate constant for contaminant elimination to water (L/d)
k_E	=	rate constant for elimination by fecal egestion (L/d)
k_M	=	rate constant for metabolic transformation of contaminant (L/d)
k_G	=	rate constant for growth dilution (L/d).

Under steady-state conditions, the contaminant concentrations in periphyton, phytoplankton, zooplankton, and aquatic macrophytes are predicted as follows, assuming that the BCF is satisfactorily approximated by K_{ow}:

$$C_j = C_w{}^{fd} ((LipFrac_j \, K_{ow}) + (NonLipFrac_j \, 0.033 \, K_{ow}) + WaterFrac_j) \tag{12-2}$$

where

C_j	=	annual average concentration in prey item j (mg/kg WW)
$LipFrac_j$	=	lipid fraction in prey item j (unitless)
K_{ow}	=	octanol-water partition coefficient (L/kg lipid)
$C_w{}^{fd}$	=	annual average freely dissolved concentration in surface water (mg/L)
$NonLipFrac_j$	=	nonlipid organic carbon fraction in prey item j (unitless)
$WaterFrac_j$	=	water fraction in prey item j (unitless).

The tissue concentrations in benthic detrivores and benthic filter feeders are also derived assuming steady-state conditions. As described in Gobas (1993), equilibrium partitioning theory may be used to predict concentrations in benthic organisms as follows:

$$C_j = \frac{C_{sediment} \times \left(\dfrac{\rho_{OC}}{foc_{sediment}}\right)}{\left(\dfrac{\rho_{lip}}{LipFrac_j}\right)} \tag{12-3}$$

where

C_j	=	annual average concentration in prey item j in benthos (mg/kg WW)
$C_{sediment}$	=	annual average total concentration in sediment (mg/kg)
ρ_{oc}	=	density of organic carbon in sediment (kg/L)
$foc_{sediment}$	=	fraction of organic carbon in sediment (unitless)
ρ_{lip}	=	density of lipids in benthos (kg/L)
$LipFrac_j$	=	fraction of lipid in prey item j in benthos (kg lipid/kg tissue).

Gobas points out that although more detailed models to estimate concentrations in benthos can be derived, this model has been shown to be in better agreement with field data (e.g., see Gobas et al., 1989; Landrum et al., 1992).

Hydrophilic, Non-Ionizable Organic Contaminants. For hydrophilic, non-ionizable organic chemicals (defined operationally as organic chemicals with an octanol-water partition coefficient value below 10,000), the Aquatic Food Web Module calculates concentrations in fish using the following equation:

$$C_{fish}{}^i = BAF_i \times C_w^{fd} \tag{12-4}$$

where

$C_{fish}{}^i$	=	annual average concentration in fish i (mg/kg WW)
BAF_i	=	bioaccumulation factor for fish i (L/kg tissue)
C_w^{fd}	=	annual average freely dissolved concentration in surface water (mg/L).

For these types of organic chemicals, bioaccumulation is primarily a function of gill exchange (rather than accumulation of contaminant through ingestion of contaminated food items). The BAF values are based on empirical data when available. Otherwise, the Aquatic Food Web Module calculates the BAF using the regression algorithm developed by Bertelsen et al. (1998):

$$BAF_i = 10^{(a_{fish} \cdot \log K_{ow} + b_{fish} \cdot \log LipFrac_i + c_{fish})} + WaterFrac_{fish}{}^i \tag{12-5}$$

where

BAF_i	=	bioaccumulation factor for fish i in trophic level p (L/kg tissue)
a_{fish}	=	primary slope term (unitless)
b_{fish}	=	secondary slope term (unitless)
c_{fish}	=	empirical error term (unitless)
$LipFrac_i$	=	lipid fraction in fish i (kg lipid/kg tissue)
K_{ow}	=	octanol-water partition coefficient (assume L/kg lipid)
$WaterFrac_{fish}^i$	=	fraction of wholebody fish i in trophic level p that is water (unitless).

The model developed by Bertelsen et al. extends previous work on the bioconcentration of hydrophilic organics in fish presented by Veith et al. (1980); Mackay (1982); Isnard and Lambert (1988); and others. Because gill exchange is considered to be the dominant mechanism by which hydrophilic organics are taken up, a simpler model could be used to predict tissue concentrations in fish. Uptake through the food web is assumed to be negligible; therefore, it is not necessary to calculate the concentration in all of the prey items in the aquatic food web.

Metals and Mercury. The contaminant concentration in fish tissue for metals and mercury is calculated as follows:

$$C_{fish}^i = BAF_{fish}^i \times C_w^{fd} \qquad (12\text{-}6)$$

where

C_{fish}^i	=	annual average concentration in fish i (mg/kg WW)
BAF_i	=	bioaccumulation factor (dissolved) for fish i (L/kg tissue)
C_w^{fd}	=	annual average freely dissolved concentration in surface water (mg/L).

BAFs based on dissolved concentrations are not always available for some contaminants; therefore, the total surface water concentration can also be used with a BAF based on total concentration. However, BAFs based on dissolved concentrations are preferred because they are applicable regardless of the characteristics of a particular waterbody. The tissue concentrations of mercury reflect the freely dissolved concentrations of methyl mercury in the water column, that is, the methyl mercury that is not sorbed to organic matter.

BAFs for metals are estimated exclusively from empirical data. Few mechanistic models are available that can be used in a national-scale analysis to estimate metals transport and accumulation in the food web from surface waters and sediments. Consequently, EPA has devoted considerable effort to identifying studies and developing criteria for selecting appropriate BAFs for metals. The relatively complex environmental behavior of metals in surface water with respect to bioaccumulation and water quality criteria has been a frequent and long-standing topic of discussion in peer-reviewed journals and texts, notably the following:

- ■ Allen, H. E., and D. J. Hansen. 1996. The importance of trace metal speciation to water quality criteria. *Water Environment Research,* 68(1):42-54. January.

■   Bergman, Harold L., and Elaine J. Dorward-King (eds.). 1997. *Reassessment of Metals Criteria for Aquatic Life Protection.* Society of Environmental Toxicology and Chemistry Press, Pensacola, FL. Proceedings of the Pellston Workshop on Reassessment of Metals Criteria for Aquatic Life Protection, February 10–14, 1996.

■   Chapman, Peter M., Herbert E. Allen, Kathy Godtfredsen, and Michael N. Z'Graggen. 1996. Evaluation of bioaccumulation factors in regulating metals. *Environmental Science & Technology,* 30(10):448A-452A.

■   Renner, Rebecca. 1997. Rethinking water quality standards for metals toxicity. *Environmental Science & Technology,* 31(10):466A-468A.

Although uptake and accumulation are not of concern for all metals, the impact of surface water characteristics (particularly dissolved organic carbon) on bioavailability is significant. Several modeling approaches have been developed recently that can be used to predict bioavailability (e.g., the Windermere Humic Aqueous Model, or WHAM), and water effects ratios (WER) provide empirical ratios that can be used to adjust water quality criteria to account for the mitigating effects of natural waters (see Bergman and Dorward-King, 1997, for discussion). Moreover, as shown in Figure 12-3, the effects and accumulation of essential metals change with concentration (i.e., bioaccumulation is nonlinear); thus, a single BAF may be inappropriate.

The state of the science on metals transport and fate in aquatic systems strongly suggests that the uptake and accumulation of essential metals (e.g., copper, zinc) in fish and other aquatic organisms are fundamentally different than the uptake and accumulation of nonessential metals (e.g., cadmium, lead). Moreover, laboratory studies that report BCFs may have limited relevance to the behavior of metals in the field. The predominant metal species

Figure 12-3. Relationship between essential metal concentration and organism health (adapted from Chapman et al., 1996).

in a "natural" aquatic system may be very different than the metal salt studied in the laboratory, resulting in a very different accumulation profile. The characteristics of the aquatic system and the presence of other cationic metals significantly influence the uptake and accumulation of a single metal species. Although understanding of metals behavior has increased since the Aquatic
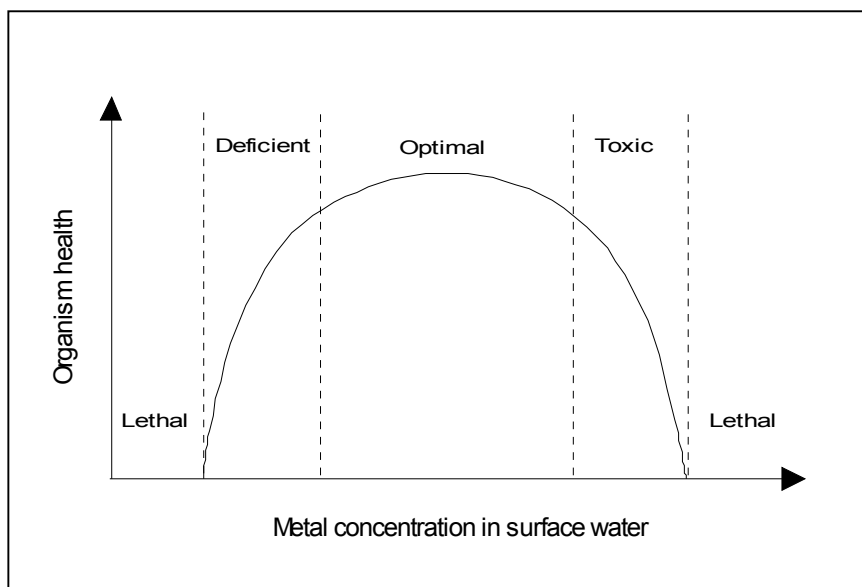
Food Web Module was developed, the module relies on empirical data and a simple model to predict metal concentrations in aquatic biota. EPA is currently reviewing recently published studies and data relevant to the development of alternative approaches to predict metal concentrations in aquatic biota (e.g., Bergman et al., 1992).

12.2.4 Report Contaminant Concentrations for Fish

The Human and Ecological Exposure Modules allow receptors to consume fish from any of the water bodies to which they have access. Both human and ecological receptors may consume fish assigned to TL3 and TL4; however, human receptors can only eat TL3 fish that are designated as edible by humans in the fish database. In addition, human receptors are assumed to eat only the filet portion of the fish, whereas ecological receptors are assumed to eat the entire fish. Therefore, the Aquatic Food Web Module performs two processing steps in generating concentrations of contaminants in fish for use by the exposure modules.

First, the Aquatic Food Web Module calculates the filet concentration by adjusting the wholebody concentrations of organic chemicals by the relative lipid content of filet (or muscle) versus the wholebody of the fish. The theory supporting the bioaccumulation of organic chemicals suggests that virtually all of the contaminant accumulates in the lipid tissue. The adjustment factor is calculated by dividing the lipid fraction in filet by the lipid fraction in the wholebody. For example, if the lipid fraction in filet is 3 percent and the lipid fraction in wholebody is 10 percent, the adjustment factor is 0.3 (and the fraction for wholebody would be 0.7). Thus, by adjusting for the differences in lipid content between filet and wholebody, the concentration in filet can be estimated from wholebody tissue concentration.

The calculation for hydrophobic organic chemicals is

$$C_{filet}^{\ i} \ = \ C_{fish}^{\ i} \ \times \ FiletFrac^{\ i} \tag{12-7}$$

where

$C_{filet}^{\ i}$	=	annual average concentration in filet for fish i (mg/kg WW)
$C_{fish}^{\ i}$	=	annual average concentration in fish i (mg/kg wet weight)
$FiletFrac^{i}$	=	the adjustment factor for filet (unitless).

For hydrophilic organic chemicals, the equation for calculating the BAF (Equation 12-5) is parameterized to calculate concentrations in filet directly as described in Bertelsen et al. (1998). For metals and mercury, the wholebody concentrations are presumed to provide a reasonable approximation of filet concentrations given other uncertainties.

Second, the Aquatic Food Web Module calculates a waterbody-specific annual average concentration for all TL3 fish filet presumed to be edible by humans, and all TL3 fish (wholebody) for ecological receptors. Because information on dietary preferences for TL3 fish is not available, this averaging implies that all TL3 fish have an equal probability of being eaten. This implies exposure to the average filet or wholebody concentration across TL3 fish in the waterbody for human and ecological consumption, respectively.

12.3   Module Discussion

12.3.1 Strengths and Advantages

The Aquatic Food Web Module was developed to predict contaminant concentrations in aquatic biota due to long-term chemical releases into surface water. The module offers a number of advantages relative to other approaches that were considered for the 3MRA modeling system. Some of the major strengths of the Aquatic Food Web Module include the following:

- ■   **Applicable to a wide variety of chemicals.** The Aquatic Food Web Module and supporting data can be applied to wide variety of chemical contaminants ranging from hydrophobic organics to metals. The module recognizes the type of contaminant and uses the appropriate data and algorithms to predict tissue concentrations. The module was designed in a modular fashion so that new science could be incorporated to address specific chemical types. For example, the simple approach used to predict mercury concentrations in biota could be upgraded to include a more complex speciation model to simulate mercury behavior in freshwater systems. The ability to handle such a broad range of chemicals in a single module, using either empirical data on bioaccumulation or mechanistic models, is a significant advantage to the 3MRA modeling system.

- ■   **Flexible enough to address any type of aquatic food web.** For bioaccumulative organic chemicals, the solution technique developed for this module is both computationally efficient and flexible. The module will accommodate simple food webs consisting of relatively few components or complex food webs with well-defined predator-prey interactions. As a result, the food webs that were defined for application to a national-scale analysis can be modified, and additional, site-specific food webs may be developed. This flexibility ensures that the Aquatic Food Web Module will be applicable to representative aquatic food webs for national-scale analyses as well as user-defined food webs for site-specific analyses.

- ■   **Based on peer-reviewed, validated models for organic chemicals.** The governing equations for the Aquatic Food Web Module are based on models that have been published in peer-reviewed journals and that have been validated using field and/or laboratory data. In particular, the algorithms used to predict the contaminant concentrations in aquatic biota reflect the state-of-the-science for hydrophobic organic chemicals. The module can use data on metabolic transformation and, because the chemical properties processor can predict properties based on environmental conditions, it may be applied to ionizable organics as well. The level of validation of these equations and their widespread application described in the open literature provides strong support for their use in the 3MRA modeling system.

- ■   **Random sampling algorithms represent dietary variability.** Dietary preferences—both in terms of preferred food items and fraction in the diet—are a potentially important source of variability in the chemical concentrations of

hydrophobic organics predicted by the Aquatic Food Web Module. Many species of fish tend to be opportunistic feeders, and the diet may shift significantly depending on the site conditions. To account for variability in the diet, the module includes a random sampling algorithm that selects dietary elements from the database, and constructs a dietary matrix of the preferences such that 100 percent of the diet is accounted for. The ability to represent this source of variability across different aquatic food webs is a substantial improvement over fixing the dietary composition and preferences.

12.3.2 Uncertainty and Limitations

The following uncertainties and limitations are inherent in the Aquatic Food Web Module:

- **The module is implemented assuming steady-state conditions.** The Aquatic Food Web Module cannot be used to evaluate the impacts from storm events, nor can it be used to distinguish the impacts on tissue concentrations from peak events and subsequent averaging from long-term, low-level exposures.

- **The module relies heavily on empirical data for many contaminants.** For contaminants other than dioxin-like compounds and organics, mechanistic models are not used to predict tissue concentrations. Hence, the Aquatic Food Web Module estimates tissue concentrations by multiplying empirical BAFs by water or sediment concentrations. As discussed in Volume II, these BAFs and BSAFs are measured under conditions that may introduce uncertainty for certain environmental settings and species.

- **The module does not allow for separate treatment of essential metals.** Bioconcentration of essential metals is not linear, and modeling approaches are now available to account for nonlinearity. Bioconcentration of essential metals tends to be much greater at low concentrations than at higher concentrations because organisms actively seek to sequester necessary nutrients. Because many metals are regulated in biological systems, the apparent bioconcentration of metals at low concentrations may simply result in metal accumulation at "healthy" levels.

- **The module currently lacks the capability to use sediment concentrations directly in predicting tissue concentrations.** The Aquatic Food Web Module was developed primarily to use dissolved and total contaminant concentrations to predict tissue concentrations. Although sediment concentrations are used in predicting uptake and accumulation into benthic dwellers, the Aquatic Food Web Module lacks the necessary algorithms to use these data directly to predict concentrations in plants or fish. For certain chemicals (e.g., dioxins), it may be useful to build this functionality into the module to provide greater flexibility in data use.

■ **The module has not been validated in field studies for all freshwater systems.**
Much of the modeling theory on which the Aquatic Food Web Module is based is
widely accepted and has been used in numerous analyses. In particular, the
methods used to predict concentrations of organics have been validated in
coldwater lakes. However, the module has not been validated for other
freshwater aquatic habitats, nor has it been validated for application in a national-
scale analysis.

12.4 References

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