AQUATIC FOOD WEB MODULE: BACKGROUND AND IMPLEMENTATION FOR THE MULTIMEDIA, MULTIPATHWAY, AND MULTIRECEPTOR RISK ASSESSMENT (3MRA) FOR HWIR99

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Steve Beaulieu, Keith Little, and Randy Williams of Research Triangle Institute developed the aquatic food web module. Amy Cole of Research Triangle Institute, tested and implemented the current version of the model.

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1.0 Module Overview and Summary of Functionality

1.1 Overview

The Aquatic Food Web (AqFW) module calculates chemical concentrations in aquatic organisms that are consumed by human and ecological receptors (e.g., fish filet; aquatic macrophytes). These concentrations are used as input to the human and ecological exposure modules to determine the applied dose to receptors of interest. The module is designed to predict concentrations in aquatic organisms for coldwater and warmwater aquatic habitats. Because the behavior of chemical constituents is largely a function of chemical properties, the AqFW module includes a series of chemical-specific switches that turn on appropriate subroutines depending on whether the chemical is organic (with affinity for lipid defined by K_{ow}), readily metabolizable, a metal, or mercury. For hydrophobic organic chemicals, the module is based on theory developed by F.A.P.C. Gobas et al. (1993), R.V. 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; Zaranko et al., 1997). For hydrophilic[1] organic chemicals, the regression equations developed by Bertelsen et al. (1998) were applied to express the relationship between log K_{ow} and tissue concentration (as a function of tissue lipid content). The theory presented 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. For readily metabolizable organics (e.g., polycyclic aromatic hydrocarbons or PAHs), metals and other inorganics, the AqFW module requires empirical data on uptake and accumulation of chemicals into the tissues of aquatic organisms. These data are discussed in detail in the data collection documentation - Section 12, Data Requirements for the Aquatic Food Web Module.

The underlying framework for the AqFW module is the development of representative freshwater habitats for warmwater and coldwater systems. Four basic types of freshwater systems were included for the two temperature categories: streams/rivers, permanently flooded wetlands ponds, and lakes. As described in Section 3.1, simple food webs were constructed for each of the eight freshwater habitats (four coldwater and four warmwater) that specify: (1) the predator-prey interactions, (2) the physical and biological characteristics of the species that are assigned to each habitat (e.g., size, lipid content), and (3) the dietary preferences for fish in trophic levels 3 (TL3) and 4 (TL4). Extensive literature research was used to support the development of a database on prey preferences based on optimal foraging theory (OFT). The

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[1] Hydrophobicity is, of course, a relative term and includes a full range of descriptors from hydrophilic (log $K_{ow} \leq 1$), to weakly hydrophobic (log K_{ow} 2-3), and superhydrophobic (log $K_{ow} > 6$). For the AqFW module, hydrophobicity is defined in terms of the model construct used to predict tissue concentrations. Organic chemicals with log $K_{ow} < 4.0$ are referred to as hydrophilic; organic chemicals with log $K_{ow} \geq 4.0$ are considered hydrophobic.

OFT (Gerking, 1994) asserts that fish will typically prefer prey items that offer a higher return per investment of energy. For example, OFT would suggest that a piscivorous TL4 fish will often prefer to consume larger trophic level 3 fish, all things being equal. For each freshwater habitat, the feeding guilds for various types and sizes of fish (e.g., medium benthivore) were used to construct a simple food web and to map dietary preferences for organisms in each habitat.[2] The habitat types are less important for some constituents (e.g., metals) since empirical data are used to relate the water concentration to tissue concentration. However, the food web structure and species assignments are critical in determining concentrations of hydrophobic constituents in aquatic organisms.

The AqFW methodology introduces several new approaches to modeling representative aquatic systems. First, the AqFW module uses a probabilistic algorithm that cycles through the database on prey preferences to select dietary fractions for TL3 and TL4 fish. This algorithm served as the basis for the approach developed for the Ecological Exposure module to construct the diet for ecological receptors. However, the AqFW module applies this algorithm to represent the feeding preferences of fish in predicting tissue concentrations rather than in predicting exposures to ecological receptors. Second, the AqFW module implements an efficient, flexible matrix which allows for the simultaneous solution of all compartments (e.g., benthos, zooplankton, fish) in the system. For example, the AqFW module simultaneously calculates the concentration of a hydrophobic contaminant in plankton, aquatic macrophytos, benthic organisms, zooplankton, several species of TL3 fish, and a TL4 apex predator fish in a warmwater lake. This functionality allows the module to perform calculations efficiently and provides the flexibility for further enhancements such as adding additional compartments and/or interactions to the food web structure.

The only concentration inputs required by the AqFW module are provided by the Surface Water module (SW). These inputs are described in Appendix A and include:

Average, reach-specific total concentration in sediment
Average, reach-specific total concentration in surface water
Average, reach-specific dissolved concentration in surface water

1.2 Summary of Functionality

The major computational functions performed by the Aquatic Food Web module may be summarized as follows:

Time series management. The AqFW module determines the overall duration of the time period to be simulated (including concentration data from discontinuous time periods), and identifies the individual years within the overall duration that will be simulated.

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[2] Data on fish characteristics (e.g., lipid fraction, size, feeding preferences) were assembled in a hierarchical fashion from disparate sources of information, and are aggregated by habitat type at the national level and by major hydrologic regions in the conterminous U.S. The development of these data are discussed in the data collection documentation.

- *Module loops over the time series, through aquatic habitats, and reaches.* The AqFW module has three basic loops: (1) over the time series, (2) over each aquatic habitat delineated at the site, and (3) over the "fishable" reaches within each aquatic habitat. The module considers all reach order 3 streams, ponds, lakes, and certain types of permanently flooded wetlands as fishable by human and ecological receptors.

- *Calculation of time series tissue concentrations for fish and other aquatic organisms.* The AqFW module predicts concentrations for each year of the simulation for aquatic organisms assigned to each habitat. These concentrations are defined spatially for each reach even though a stream habitat or wetland may contain multiple reaches.[3] Similarly, the module predicts concentrations in ponds and lakes as though the system is fully-mixed and at steady state.

The major steps performed by the Aquatic Food Web module that are required to predict concentrations in aquatic organisms may be summarized as follows:

- Select fishable reach of interest (i.e., stream or wetland reach, pond, or lake).

- Determine temperature and set aquatic habitat type (e.g., coldwater stream).

- Construct dietary matrix for fish in aquatic habitat.

- Calculate whole-body tissue concentrations (for ecological receptors)

    - Identify chemical type (e.g., hydrophobic organic, metal, mercury).

    - If chemical type is not readily metabolizable (i.e., special), check K_{ow} value.

    - If chemical is hydrophobic ($\log K_{ow} \geq 4.0$ is true), run matrix solution to estimate whole-body tissue concentrations.

    - If chemical is hydrophilic ($\log K_{ow} < 4.0$ is true), run regression models to estimate whole-body tissue concentrations.

    - If chemical is metal, readily metabolizable, or mercury, get empirical bioaccumulation data and calculate whole-body tissue concentrations.

- Calculate filet concentrations (for human receptors).

The calculation of time series exposures is described in detail in Section 3.0.

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[3] Reaches are defined in the site layout file and modeled by the Surface Water module as homogeneous segments (i.e., there is no concentration gradient throughout the reach).

2.0 Assumptions and Limitations

The methodology used in the Aquatic Food Web module reflects a number of assumptions and/or limitations, which are listed below. It should be noted that, because the AqFW module relies on the Surface Water module to provide concentrations in surface water and sediment, the assumptions and limitations identified for the SW module are relevant to the AqFW module. For example, the SW module provides annualized average concentrations for stream reaches and other waterbodies. Consequently, the methods developed to estimate tissue concentrations in aquatic organisms were developed to be use the annual average surface water concentrations predicted with the Surface Water model. The assumptions and limitations implicit in the SW module are not discussed in detail in this section.

2.1 Assumptions

Study area is bounded at 2 km. EPA assumed that significant exposures to source-related contaminants do not occur for ecological receptors that are beyond 2 km of the source. Consequently, concentrations were not calculated in aquatic organisms in waterbodies outside of the study area, measured from the corner of the source to a point 2 km away.

All waterbodies that define aquatic habitats are fishable. The module assumes that all third order stream reaches (and above), ponds, lakes, and certain permanently flooded wetlands support a multi-compartment aquatic food web. The simple food webs developed for each of these aquatic habitats provide a useful framework for predicting tissue concentrations in aquatic organisms for a national assessment. Nevertheless, it is a certainty that not all of the waterbodies designated as fishable in this analysis will be of sufficient quality to sustain a multi-compartment food web.

Variability in aquatic systems is reasonably represented. The underlying framework developed for the AqFW module (as applied in a national analysis) is the eight representative aquatic habitats. It is implicitly assumed that these eight habitats provide adequate resolution of the major types of freshwater systems within the constraints of available data and modeling tools.

Hydrophobic organics may be defined as organic chemicals with log $K_{ow} \geq 4.0$. Although a strict definition for hydrophobic organics has not appeared in the literature, the AqFW module assumes that a reasonable cutoff is a log K_{ow} value of 4.0. Comparisons of predicted bioaccumulation factors (BAFs) derived with mechanistic models versus BAFs derived using regression equations suggests

that, below log $K_{ow} = 4.0$, the difference in BAF estimates is below the level of resolution that these models are capable of.

The model construct is applicable to waterbodies other than coldwater lakes. A number of journal articles (e.g., Morrison et al., 1997) and reference texts (e.g., Rand, 1995) were reviewed in evaluating appropriate mechanistic models to simulate the uptake and accumulation of hydrophobic organics in aquatic organisms. From that review, it was determined that the underlying theory for these models is remarkably similar and that there is no inherent advantage in selecting one model over another. Although the Gobas (1993) model was calibrated for coldwater lakes (i.e., Lake Ontario), it was determined that this model construct was appropriate for use on other aquatic systems under the general assumption of steady-state conditions.

2.2 Limitations

Steady-state conditions are generally assumed. Because annual average concentrations are provided by the SW module,[4] the AqFW module assumes steady-state conditions. As a result, the module can not 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. For example, a storm event may contaminate a given reach for relatively short periods of time, probably well below the duration required for organisms to reach steady-state for most chemicals.

The module relies heavily on empirical data for many chemicals. For chemicals that have not been shown to be readily metabolizable (e.g., other than PAHs, selected phthalates), mechanistic models are not used to predict tissue concentrations. Hence, the AqFW module estimates tissue concentrations by multiplying empirical factors (primarily bioconcentration factors, or BCFs) by water concentrations. As discussed in the data collection documentation on the AqFW parameters, these BCFs are measured under conditions that may not be relevant to all possible conditions (and species) included in the HWIR99 analysis.

The module does not allow for separate treatment of essential metals. Bioconcentration of essential metals is not linear and modeling approaches are available to account for nonlinearity (see Bergman and Dorward-King, 1997). Bioconcentration of essential metals tends to be much greater at low concentrations than at higher concentrations since organisms actively seek to sequester necessary nutrients. Because many metals are regulated in biological

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[4] The SW module uses annual average loadings to the waterbody to predict annual average surface water concentrations using a dynamic solution. Therefore, it is conceivable that an aquatic food web module could be developed to take advantage of this functionality. However, developing a dynamically-linked solution to estimate concentrations in aquatic organisms was regarded as infeasible given the current modeling system and available data.

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 AqFW module was developed, primarily, to utilize dissolved and total contaminant concentrations to predict tissue concentrations. Although sediment concentrations are used in predicting uptake and accumulation into benthic dwellers, the AqFW module lacks the necessary algorithms to use these data directly to predict concentrations in plants or fish. For certain constituents (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.* Much of the modeling theory on which the AqFW module is based is widely accepted and has been used in numerous analyses. In particular, the methods used to predict concentrations of hydrophobic organics have been validated in coldwater lakes. However, the module has not been validated for other freshwater aquatic habitats, nor has it been validated *in toto* for application in a national-scale analysis.

3.0 Methodology

The methodology and equations used in the Aquatic Food Web module consist of two components: (1) an underlying framework of eight representative aquatic habitats and (2) chemical-specific subroutines that are used to calculate tissue concentrations in fish and other aquatic organisms. A critical first step in developing the AqFW module was to create a framework that could capture the variability in aquatic habitats and fish species found in various hydrological regions across the United States. To represent this variability, simple freshwater food webs were constructed to depict the major functional and structural components of a "healthy" aquatic ecosystem (see Figure 3-1 for lake example). Taxa of plants, prey, and predatory fish were selected to represent components of the aquatic food webs according to major categories of aquatic biota in freshwater systems: aquatic macrophytes, phytoplankton, periphyton, zooplankton, benthic detritivores, benthic filter feeders, and fish in trophic levels 3 and 4. Four functional classes of TL3 fish were selected based on feeding guilds[5] and habitat niche, and included zooplanktivores, benthivores, omnivores, and piscivores. The TL3 fish classes were further grouped according to size (small, medium, and large) to ensure that feeding habits were reasonable (i.e., small fish do not eat large fish). These habitat-specific food webs simulate pathways of chemical movement and biological uptake in the system, and are used to estimate exposure concentrations in aquatic food items consumed by predators that inhabit the margins of the waterbody (e.g., stream corridor; lake margins). The development of freshwater food webs for representative aquatic habitats is described in Section 3.1.

The methodology developed to estimate tissue concentrations is largely based on the physical and chemical properties of the constituents of concern. Mechanistic models, regression equations, and empirical data (derived using a weight-of-evidence approach) are all used to predict the tissue concentrations in aquatic biota. The AqFW module recognizes five chemical types (designated by the variable ChemType) and, based on the chemical properties, calls the appropriate subroutines and data.[6] The chemical types include: dioxin-like chemicals (D), organic chemicals (O), special chemicals (S), metals (M), and mercury (Hg). The conceptual

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[5] In this application of guild theory, fish classes were determined based upon available data on feeding preferences as well as the niche to which various species were assigned in a given aquatic habitat. However, it is widely recognized that many (if not all) species of fish tend to be opportunistic feeders with dietary preferences changing with prey availability as well as from juvenile to adult stages.

[6] Ionizable organics include a number of organic constituents that are sensitive to pH. For example, the Ambient Water Quality Criterion for pentachlorophenol is calculated using an empirical equation that accounts for this effect. For this analysis, pH-dependent log K_{ow} values have been generated by ORD and, therefore, it is possible to utilize either the bioaccumulation model (for hydrophobics) or the regression equation (for hydrophilics), as appropriate, to predict tissue concentrations in fish. However, ionizable organics behave differently in living tissues and, as a result, additional uncertainty is associated with this approach.

approach for each chemical type is summarized below and the calculations are described in detail in Section 3.2.

Dioxin-like chemicals (D) - Dioxin-like chemicals and other relatively insoluble organic chemicals (designated as O) are considered hydrophobic organics by the AqFW module. As noted above, the cutoff for hydrophobic organics is log $K_{ow} \geq 4.0$ and, therefore, all "D" constituents and any "O" constituent with a log K_{ow} in that range are modeled using a steady-state bioaccumulation model based on the work of Dr. F.A.P.C Gobas et al. (1993). In addition to the log K_{ow} for the chemical of interest, the module requires inputs on the species assigned to the aquatic food web (e.g., lipid fraction; body weight; dietary preferences) as well as selected variables on the water body such as the fraction organic carbon in bed sediment. The module does not require information on water quality parameters such as dissolved and particulate organic carbon (DOC and POC, respectively); the Surface Water module performs the partitioning and provides contaminant concentrations in surface water (dissolved and total) and in sediment (dissolved in pore water and total). The AqFW module contains a subroutine that calculates whole-body tissue concentrations (adjusted for lipid content) for aquatic macrophytes, benthic organisms, and TL3 and TL4 fish, and outputs these values for use by the Ecological Exposure module. The AqFW module also calculates the filet concentrations for TL4 fish and for species of TL3 fish presumed to be edible for humans, and outputs these values for use by the Human Exposure module.

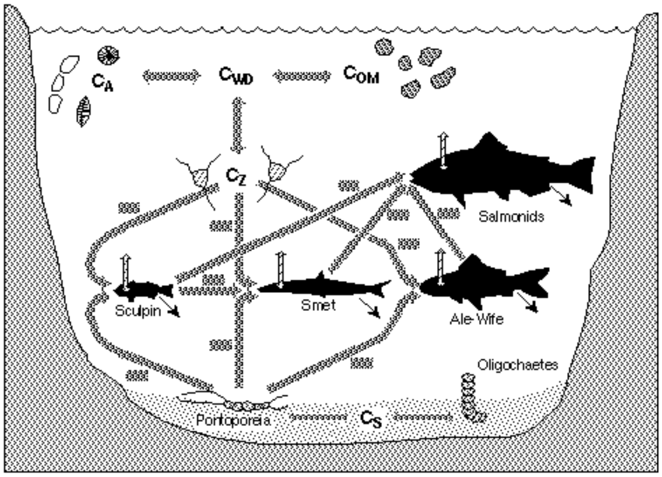

Figure 3-1. Example of simplified food web for lake habitat (Gobas et al., 1993).

Organic chemicals (O) - As noted above, the AqFW module recognizes hydrophobic organics as those constituents for which ChemType = "D" or ChemType = "O" *and* the log K_{ow} value is greater than, or equal to, 4.0. Other organic chemicals are considered as hydrophilic and the dominant exposure route is presumed to be via gill uptake (i.e., gill uptake is much greater than food/particle ingestion). This is a particularly important assumption since it is the concentration gradient in the fish gut that is believed to be the mechanism by which the tissue concentration in fish increases up the food chain for certain contaminants (i.e., biomagnification). If the uptake via gill exposure is the dominant pathway, a more simplistic approach is appropriate, namely, the use of empirically derived regression equations. Following a review of numerous regressions used to predict the bioconcentration factors (BCFs) in fish, the methodology developed by Bertelsen et al., 1998, was chosen as the most appropriate approach. In addition, the Bertelsen methodology provides an algorithm to directly calculate the BCF for muscle tissue (i.e., filet) in fish. The tissue concentrations in aquatic organisms other than fish (e.g., benthos) are predicted using a partitioning approach as described in Gobas et al. (1993).

Special chemicals (S) - This chemical type includes, primarily, constituents for which "special" subroutines or data are required for the module to execute. For the AqFW module, this chemical type is generally used to indicate an organic constituent is significantly metabolized by fish. For example, it is widely accepted that aquatic organisms (particularly fish) readily metabolize polycyclic aromatic hydrocarbons (PAHs) and that BAFs predicted for PAHs with log K_{ow} values greater than ~ 5.0 overestimate the bioaccumulation potential. Consequently, empirical data on either bioaccumulation or metabolism are needed to predict tissue concentrations for PAHs. For the proposed HWIR95, BAFs were identified from the open literature and from an EPA report developed to support the Great Lakes Water Quality Initiative (*Derivation of Proposed Human Health and Wildlife Bioaccumulation Factors for the Great Lakes Initiative*, Stephan, 1993). Subsequent to HWIR95, the EPA Office of Solid Waste (OSW) performed additional analyses to investigate other data sources for PAH bioaccumulation factors as well as alternative methods for their derivation. After a comprehensive literature survey and review, it was determined that the empirical database on PAH bioaccumulation was insufficient to support defensible BAFs for most PAHs. Thus, two alternatives have been proposed to estimate tissue concentrations for PAHs. The first alternative involves the use of interval analysis (or fuzzy arithmetic) to derive a BAF from empirical data as described by Spencer and Beaulieu, 1997. In brief, the interval analysis predicts a range of bioaccumulation factors associated with a given likelihood. The second alternative requires metabolic rates for use in the bioaccumulation model. The model developed by Gobas et al. (1993) is designed to predict appropriate BAFs at steady-state conditions for hydrophobic organic chemicals, provided that the metabolic rates are available. These alternatives, of course, are not mutually exclusive and research is ongoing to determine the most appropriate approach for PAHs.

Metals (M) - Bioaccumulation factors for metals are estimated exclusively from empirical data. Few 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, OSW has devoted considerable effort toward identifying studies and developing criteria for selecting appropriate bioaccumulation factors for metals. The relatively complex environmental behavior of metals in surface water with respect to bioaccumulation and water quality criteria has been a topic of discussion in peer reviewed journals and texts, notably:

- *Evaluation of Bioaccumulation Factors in Regulating Metals* (Chapman et al., 1996)
- *Rethinking Water Quality Standards for Metals Toxicity* (Renner, 1997)
- *The Importance of Trace Metal Speciation to Water Quality Criteria* (Allen and Hansen, 1996)
- *Reassessment of Metals Criteria for Aquatic Life Protection* (Bergman and Dorward-King, 1997)

Although uptake and accumulation is 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 may be used to predict bioavailability (e.g., the Windermere Humic Aqueous Model - WHAM), and water effects ratios (WER) provide empirical ratios that may 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 3-2, the effects and accumulation of essential metals change with concentration (i.e., bioconcentration is nonlinear); thus, a single BCF ratio may be inappropriate.

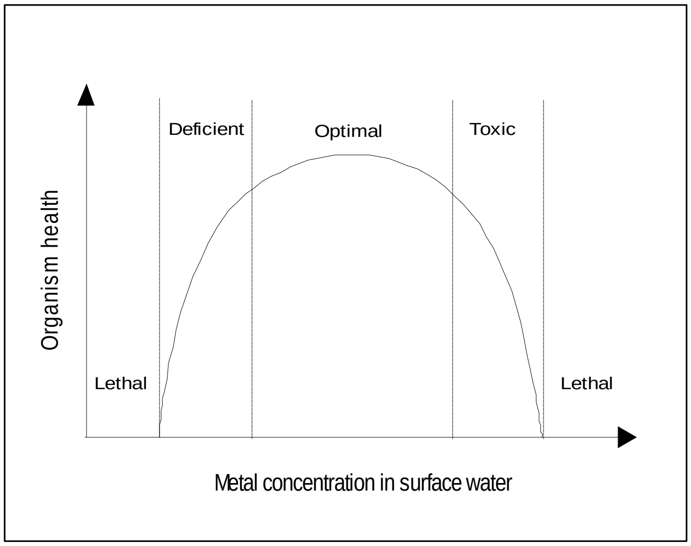

Figure 3-2. Relationship between essential metal concentration and organism health (adapted from Chapman et al., 1996).

Based on current information on accumulation of metals in aquatic organisms, essential metals (e.g., Cu, Zn) were distinguished from nonessential metals (e.g., Cd, Pb) in evaluating data on uptake and accumulation. In addition, information on speciation was considered in deriving appropriate BCFs or BAFs since the environmental form of the metal may be very different than the metal salt studied in the laboratory. As discussed in the data collection documentation, a weight-of-evidence approach has been used to derive BAFs for metals that recognizes the importance of considering the essentiality of metals and the potential effects of water quality parameters.[7]

Mercury (Hg) - Tissue concentrations of mercury were estimated using empirical data from the *Mercury Report to Congress* (U.S. EPA, 1997). The development of the Surface Water module and the AqFW module were closely coordinated so that mercury modeling is conducted in a consistent manner by both modules. Specifically, the AqFW module calls for the concentration of methyl mercury in surface waters provided by the SW module and applies bioaccumulation factors for methyl mercury for TL3 and TL4 fish, as appropriate, to calculate the tissue concentration. Although OSW recognizes that the surface water (and sediment) characteristics exert a significant influence on the uptake and accumulation of mercury in the tissues of aquatic organisms, the modeling system was not designed to accommodate the level of complexity in site-specific models such as the Mercury Cycling Model (MCM - Hudson et al., 1994). To reduce the uncertainty in fish tissue concentrations of mercury, future research could be conducted on distributions of BAFs for methyl mercury relative to the water quality characteristics of the aquatic habitat. (Alternatively, the modeling system could be modified to incorporate a mercury-specific module into the system that would bypass both the SW module and the AqFW module. The ChemType variable could be used to initiate a “sub-module” in the system and provide a more mechanistic option for mercury modeling in aquatic systems.) As implemented in the current AqFW module, point estimates for methyl mercury BAFs will be used to predict tissue concentrations in aquatic organisms.

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[7] Despite these efforts, it was not possible to account for regional variability in water quality and species characteristics in deriving the majority of bioaccumulation factors for metals.

3.1 Constructing Food Webs for the Representative Aquatic Habitats

Eight representative habitats were selected to capture the variability in aquatic systems associated with water temperature,[8] flow (i.e., flowing waters versus "static" systems such as ponds), water quality characteristics based on hydrological regions, the food web structure for pelagic versus littoral zones,[9] and the differences in fish species in different habitats. The eight habitats include warmwater streams, wetlands, ponds, and lakes; and coldwater streams, wetlands, ponds, and lakes. The fish species assigned to each of the eight representative habitats were characterized according to the functional niche that the species belong to (e.g., feeding guild; trophic level). For example, because the plankton density in streams tends to be low, a fish species that is 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 plantivorous species of fish as an integral part of the food web. Thus, the concept of functional niche is particularly important in the construction of food webs since 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).

In reviewing literature sources on aquatic habitats and food webs, it was apparent that the variability in food web structures and aquatic species created a substantial overlap across different types of aquatic habitats. There are common elements to virtually all aquatic communities and, depending upon the nature of the study data and the characteristics of the habitat, food webs could have been developed such that the habitats were almost indistinguishable from one another. Clearly, the development of complicated food webs that illustrate the possible (rather than the probable) would have been contrary to the goals of a national scale, site-based analysis. Consequently, food webs were constructed for the representative habitats so that the major functional elements were represented as simply as possible. Certain tenets emerged from the literature review and were adopted as guidelines in developing the aquatic food webs:

- # Periphyton, benthic detrivores, and aquatic macrophytes are common elements in all healthy freshwater aquatic systems.

- # 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.

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[8] For example, the food web structure of a warmwater stream is typically more complex than an analogous coldwater stream. Hence, there are frequently more functional niches in a warmwater stream than might be found in a coldwater stream.

[9] In general, pelagic and littoral zones are highly coupled, dynamic systems. The characteristics of the fish communities themselves will affect the magnitude of littoral-pelagic interactions (Schindler et al., 1996). However, these interactions are just beginning to be understood and a simpler approach was adopted for the AqFW module to be consistent with the goals of a national-scale assessment.

- Size distinctions within feeding guilds of fish should consider: (1) the potential biomass of the most preferred prey item and (2) 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 have low plankton density and, as a result, zooplankton are not an important food web component.

- Flowing systems, in general, tend to be less complex than standing systems such as lakes and ponds.

- Warmwater systems tend to support a more diverse aquatic community than coldwater systems and, as a consequence, they tend to have more functional niches and are more complex.

It is certainly conceivable that different tenets could have been adopted and that the food webs could have been drawn in many different ways. Nonetheless, the aquatic food webs provide a useful framework for the AqFW module, offer a reasonable representation of energy flows typical of different habitats, and capture variability in a manner that is appropriate for a national scale assessment.

The sources used to construct the aquatic 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. Examples of these sources include:

- Monitoring studies (e.g., National Ambient Water Quality Assessments, USGS)

- Regional habitat surveys (e.g., Prairie Pothole Region in ND, SD, MN, USGS)

- State habitat and biodiversity assessments (e.g., Washington Department of Fish and Wildlife, Warmwater Fish of Washington)

- Freshwater fishing references (e.g., Sternberg, 1996)

- Bioaccumulation field studies (e.g., Zaranko et al., 1997; Morrison et al., 1997; Traas et al., 1996)

- Government agency databases (e.g., Fish and Wildlife Service; National Biological Survey);

- Academic societies (e.g., American Fisheries Society)

- # Freshwater habitat reference texts (e.g., *Wetlands*, Mitsch and Gosselink, 1993)
- # Freshwater fish reference texts (e.g., Lee et al., 1980)

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 coldwater or warmwater. For the AqFW, the threshold for categorizing waters as warm or cold is based on a maximum temperature of 25 degrees Celsius - the water temperature above which stenothermic fish (i.e., coldwater species) can not survive. Species that are found in both warmwater and coldwater habitats were sometimes assigned to both categories; however, species that clearly preferred one temperature category were assigned only to that category (e.g., salmon were only assigned to coldwater habitats).

3.1.1 Major Elements in Aquatic Food Webs

The aquatic food webs constructed for the AqFW module contain between eight and twelve of biota types possible in freshwater systems. Table 3-1 presents the complete list of biota types possible in aquatic habitats in the AqFW module and indicates how many food webs each biota type has been assigned to. It should be noted that 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 other biota (e.g., periphyton, benthos, detritus) and, therefore, planktivores were not included in the wetland food webs. Hence, the inclusion of various biota types reflects the desire to account for significant predator-prey interactions without imposing artificial constraints on the food web structure. Table 3-2 summarizes the food webs constructed for the AqFW module. This matrix shows which biota types are assigned to each of the eight representative habitats.

Below, Sections 3.1.2 through 3.1.5 discusses the rationale behind the food web structure for the representative aquatic habitats: warmwater and coldwater streams, wetlands, ponds, and lakes. Distinctions between warmwater and coldwater systems are drawn, as appropriate. As expected, there was a great deal more information available on the structure of freshwater communities found in lakes and streams than on ponds and wetlands. For convenience, the discussion is structured around four major taxa into which all of the biota types may be classified: (1) algae/phytoplankton/plants, (2) zooplankon, (3) benthos, and (4) fish. These taxa are summarized below:

1. *Algae/phytoplankton/plants* - The occurrence and density of algae, phytoplankton, and aquatic plants in freshwater systems is a critical component of the representative habitats. The presence or absence of periphyton, macrophytes, and phytoplankton determines the food base for the system.

Table 3-1. Prevalence of Biota Types in Freshwater Food Webs

Biota Type	Description	Number of Food Webs
periphyton	algal species typical of freshwater systems, adhere to rocks, detrital material	8
phytoplankton	primary producers in pelagic systems	6
aquatic macrophytes	vascular aquatic plants (e.g., submerged, emergent)	8
zooplankton	various invertebrates that graze on phytoplankton	6
benthic detrivores	benthic dwellers that break down detritus in sediment (e.g., amphipods)	8
benthic filter feeders	benthic organisms that feed through filtration mechanism	4
TL3benth_sm	small TL3 fish whose primary feeding preference is benthic organisms	3
TL3benth_med	medium size TL3 fish whose primary feeding preference is benthic organisms	7
TL3benth_lg	large size TL3 fish whose primary feeding preference is benthic organisms	1
TL3zoop_sm	small TL3 fish whose primary feeding preference is zooplankton	1
TL3zoop_med	medium size TL3 fish whose primary feeding preference is zooplankton	2
TL3zoop_lg	large size TL3 fish whose primary feeding preference is zooplankton	1
TL3omni_sm	small TL3 fish whose primary classified as omnivores (i.e., no clear feeding preferences)	5
TL3omni_med	small TL3 fish whose primary classified as omnivores (i.e., no clear feeding preferences)	6
TL3omni_lg	small TL3 fish whose primary classified as omnivores (i.e., no clear feeding preferences)	3
TL4pisc	piscivorous fish that serves as the apex predator for the community	7

Table 3-2. Matrix of Biota Types in Food Webs of Representative Aquatic Habitats

Biota type	Coldwater habitats				Warmwater habitats			
	Stream	Wetland	Pond	Lake	Stream	Wetland	Pond	Lake
periphyton	√	√	√	√	√	√	√	√
phytoplankton		√	√	√		√	√	√
aquatic macrophytes	√	√	√	√	√	√	√	√
zooplankton		√	√	√		√	√	√
benthic detrivores	√	√	√	√	√	√	√	√
benthic filter feeders	√			√	√			√
TL3benth_sm	√				√			√
TL3benth_med	√	√	√	√	√	√	√	
TL3benth_lg								√
TL3zoop_sm			√					
TL3zoop_med				√			√	
TL3zoop_lg								√
TL3omni_sm		√	√	√		√	√	
TL3omni_med	√	√	√		√	√		√
TL3omni_lg				√			√	√
TL4pisc	√	√	√	√	√	√		√

2. *Zooplankton* - Zooplankton are the primary predators of phytoplankton, and are an important prey base for secondary consumers. In aquatic ecosystems where zooplankton are abundant, this predator and prey item acts as a critical trophic link between primary producers and fish.

3. *Benthos* - The categories of benthos include both benthic detritivores (e.g., aquatic insects and amphipods) and benthic filter feeders (e.g., freshwater mussels). Benthos act as the prey base for benthivorous fish species, and the composition of these communities varies depending factors such as flow rate and substrate type.

4. *Fish* - Fish are crucial elements in freshwater food webs and, in the HWIR99 analysis, of critical importance in predicting exposure. Information on various fish species was evaluated to discern which species could be considered "typical" of the representative aquatic habitats. The TL3 species were then assigned to biota types according to feeding guild and size and attributed to those freshwater food webs based on how well they "fit" a given niche (e.g., benthivore in trophic level 3). In addition, an apex predator TL4 fish was assigned to all but one of the food webs.

3.1.2 Food Web Structure for Stream Habitat

Stream habitats for the AqFW module include primarily 3rd through 5th order classifications. Streams tend to be more heterogeneous than standing waters because of the microhabitats that typically form along a stream reach. Pools, riffles, rapids, and riparian areas create different habitat niches for the freshwater community and, therefore, it is not uncommon to encounter vastly different communities within the same stream reach. The inherent complexity associated with microhabitats was not represented in the stream food web.

Algae/phytoplankton/plants - The stream food web includes periphyton and aquatic macrophytes, typically the primary producers. With adequate light and stream clarity, periphyton are an essential food base in stream systems (Mulholland and Lenat, 1992), serving as a critical food source for benthivorous and omnivorous fish (Lowe and Laliberte, 1996). Macrophytes, on the other hand, are more sensitive to reduced light caused by the vegetative canopy and have not adapted as successfully as periphyton to high stream velocity. Thus, macrophytes are more likely to thrive in riparian wetlands and in slow flowing stream beds (5th order streams) rather than higher velocity streams (3rd and 4th order streams) (Felley, 1992). Given their functional importance to fish species that depend on aquatic vegetation for protection and reproduction (i.e., eggs adhering to stems and leaves), they were included (Mitsch and Gosselink, 1993; Smith, 1994). Phytoplankton are not usually observed in high enough abundance to be a large contributor to the prey biomass.

Zooplankton - Zooplankton do not constitute an important trophic element in stream ecology and were not included as a food web component. Zooplankton commonly found in streams, such as rotifers, copepods, and cladocerans, can occur in pools surrounding wood debris and temporary ponds of headwater streams. However, the abundance of these species is usually localized and minimal in most streams (Palmer and Strayer, 1996; Smock and Gilinsky, 1992; Garman and Nielsen, 1992).

Benthos- Benthic macroinvertebrates occur in virtually all stream habitats. Their adaption to flowing systems creates large, diverse benthos in many streams, and both benthic detritivores and filter feeders were included in the stream food web. Benthic detritivore populations are typically composed of amphipods, isopods, odonates, oligochaetes and chironomids, although the relative numbers vary depending on the type of substrate (e.g., cobbles, sand, silt). Benthic filter feeders (i.e., clams, mussels, and some species of aquatic insects) are also important food web components in clear (i.e., low suspended solids) productive streams (Wallace et al., 1992). Although filter feeders are generally less abundant than benthic detritivores, they occupy a unique niche and are important prey items to fish and other mammalian and avian receptors (Hauer and Resh, 1996).

Fish - Fish species found in stream habitats include, primarily, three feeding guilds: omnivores, benthivores, and piscivores. Because plankton density is low in streams, it is unlikely that obligate planktivores are present in most streams. In coldwater streams, small and medium species of benthivores are typical (e.g., darters, sculpins, and shiners). Larger TL3 and TL4 species of omnivores and piscivores are commonly reported (e.g., bullheads, chubs, sunfish, and bass). Although warmwater streams tend to be characterized by somewhat more complex food webs, the variation observed in the literature suggested that it was reasonable to use the same food web for warmwater streams as that proposed for coldwater streams. However, different species of fish were assigned to the various biota types in warmwater streams. Examples include dace as small benthivores, minnows as medium benthivores, madtoms as medium omnivores, and bowfins as TL4 piscivores. As constructed, the stream food web includes benthivores and omnivores foraging on the benthic detritivores, benthic filter feeders, and periphyton. Omnivores and piscivores have an adequate prey base of forage fish as a significant portion of the diet (Goldstein and Simon, 1998; Li and Li, 1996; Gelwick and Matthews, 1996).

3.1.3 Food Web Structure for the Wetland Habitat

For the HWIR99 analysis, only *permanently flooded wetlands* were presumed to support a relatively static aquatic food web.[10] Temporarily flooded wetlands usually have dramatic shifts in community structure from initial flood conditions to more swampy conditions that occur after the water has evaporated or percolated into the groundwater. Nevertheless, it is important to recognize that there is substantial variability in the food webs in permanently flooded wetlands as well due, in large part, to the variety of mechanisms associated with wetland formation,such as watershed run off, groundwater flow, river channel changes (oxbow wetlands), and riparian

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[10] Freshwater wetlands include a diverse group of habitats ranging from the southern deepwater swamps to inland freshwater marshes, to northern peatlands, with many variations in between (e.g., riparian forested wetlands). The intent of including wetlands among the representative aquatic habitats was to include a habitat of substantial ecological significance. Similarly, constructing a single food web to represent this variability is intended to represent major elements common to many types of wetlands.

areas. The process of creating a wetland food web was simplified by assuming that wetlands are typically characterized by low dissolved oxygen and high productivity.

Algae/phytoplankton/plants - Periphyton, phytoplankton, and aquatic macrophytes are key structural and functional attributes of wetlands (Mitsch and Gosslink, 1993) and were included in both the warmwater and coldwater wetland food webs. Many species of fish indigenous to wetlands rely on this group during at least one stage of the life cycle. Periphyton occurs in areas where light can penetrate to sediments usually in the littoral zones of wetlands. Phytoplankton are more abundant in wetlands with open waters, whereas in highly vegetated wetlands, they are not likely to be abundant (Menzel and Cooper, 1992). Aquatic macrophytes are important in nutrient cycling wetlands and as a food base and protective habitat for fish (e.g., Smith, 1994; Killgore and Hoover; 1992).

Zooplankton - Zooplankton populations are potentially important to certain types of wetland communities, particular those with open waters. They serve as both predator and prey and are a key link in the food web of developmental juvenile fish (i.e., phytoplankton ---> zooplankton---> juvenile fish) (Smith, 1994). Zooplankton abundance fluctuates over time depending the abundance of prey and predators. Although not a major food source throughout the life cycle of most fish found in wetlands, zooplankton are likely to be present in sufficient numbers to constitute an important food source for critical life stages of certain fish species (Mitsch and Gosslink, 1993).

Benthos - The organic sediments and high productivity (assumed in this food web) are favorable conditions for benthic detritivores, and they are present in most types wetlands. However, their diversity can be limited by depleted oxygen in the water column. Coldwater wetlands may have greater diversity in benthic detritivores because of the higher dissolved oxygen in surface waters. Typical benthos of wetlands include species of worms, midges, snails, and amphipods. In areas of low nutrients, midges dominate but species of crayfish, isopods, and Diptera are also found (Mitsch and Gosslink, 1993). Wetlands with relatively clear waters may contain species of benthic filter feeders, but their populations are probably not significant; therefore, they were not included in the wetland food webs for either warmwater or coldwater wetland food web.

Fish - Fish abundance and diversity in wetlands is high. Wetlands provide shelter from predation, needed structures for reproduction, and a rich source of prey for many fish species. Both warmwater and coldwater food webs were constructed using the same fish community. In general, wetland fish communities are usually composed of species capable of tolerating conditions of low dissolved oxygen. Medium benthivores (e.g., swampfish) and small and medium omnivores (e.g., mudminnow, killifish, pumpkinseed), and piscivores (e.g., bass, pike, carp) are common elements to many wetland food webs. These categories of fish are consistent with the abundant prey base available in wetlands. Fish communities may vary considerably for wetlands that are have transient connections to other waterbodies, such as when piscivorous fish migrate from a lake to take advantage of the potentially high prey density in a wetland (Killgore and Hoover, 1992).

3.1.4 Food Web Structure for Pond Habitat

The pond habitat in the HWIR99 anlaysis refers to relatively small standing waters (< 10 hectares) typical of farm ponds. These types of ponds are often man-made and are managed and stocked with fish species for recreational fishing. In constructing this food web, the aim was to characterize both the "natural" food webs (i.e., no human intervention) as well as managed ponds that are stocked with various game fish. Based on the GIS information regarding waterbodies in the study area of many sites, there appears to be a substantial number of farm ponds as well as "natural" ponds (ponds that do not appear to be associated with cropland).

Algae/phytoplankton/plants - The composition of aquatic vegetation populations fluctuates over space and time during growing seasons, and at any given time, it is likely that one of the three vegetation functional types may dominate (Menzel and Cooper, 1992; Smith, 1994). Nevertheless, periphyton, phytoplankton, and macrophytes are all common to pond habitats and each plays a significant role in the oxygenation and primary production in "healthy" ponds. The structure of the pond is similar to lakes in that there are littoral areas that provide habitat for periphyton and macrophytes while open waters in ponds provide needed light and standing water that are optimal for populations of phytoplankton.

Zooplankton - Zooplankton are often an essential link in the pond food web. Cladocera and copepoda contribute significantly to the biomass and energy flow in farm pond ecosystems Their role in ponds as predators is seen in their consumption of bacteria, algae, and other smaller aquatic invertebrates. As prey, they provide a food source for pond vertebrates. Even though zooplankton make up a small fraction of the overall biomass present in a pond, they are a relatively abundant species and have a high rate of reproduction which, at certain times, can contribute significantly to the energy transfer in the pond aquatic food web. Hence, they were included in the pond food web (Menzel and Cooper, 1992).

Benthos - Review of the literature indicated that detritivores are the predominant benthic taxa present in ponds. For example, benthic taxa noted in southeastern ponds are represented by detritus feeding organisms such as odonate and chironomid larvae. Although benthic filter feeders occur in some ponds, their biomass is not likely to contribute significantly to the prey base, and they do not appear to fill a critical niche in the pond ecosystem (in general). High siltation tends to limit the abundance of filter feeders in ponds and, lacking data to the contrary, they were excluded from the pond food web (Menzel and Cooper, 1992).

Fish - Since pond classification was limited to those waterbodies smaller than 10 hectares, the fish community was constrained by the waterbody size and biomass that the pond could support. For managed ponds, sources indicated that a "balanced" pond community should be composed of approximately three to six times more forage fish than piscivorous fish, and the selection of fish biota types recognized that guideline even though this ratio varies widely for "natural" ponds. In coldwater ponds, the literature indicated that medium benthivores (e.g., suckers), small zooplanktivores (e.g., minnow), small and medium omnivores (e.g., sunfish, killifish, shiner), and piscivores (e.g., bullheads) are common. In warmwater ponds, medium benthivores (e.g., mudminnow, shad), medium zooplanktivores (e.g., banded sunfish) small omnivores (e.g., mosquitofish), and large omnivores (e.g., catfish, white crappie) are represented (Smith, 1994; Soballe et al., 1992). Few examples of strictly piscivorous species were identified in warmwater ponds; therefore, piscivores were not included in the food web. Often, the pond food web is dominated by a large omnivore that contributes the highest percentage of the total pond biomass; the remaining fish consist of small forage fish populations.

3.1.5 Food Web Structure for Lake Habitat

Variables that influence the lake community include the number and chemical composition of freshwater inflows, the depth and morphology of the basin, frequency of thermal stratification, and the types of microhabitats present. The structure of lake food webs varies according to characteristics typical of waterbodies ranging the deep glacial lakes in the Pacific Northwest to the shallow productive lakes in the Southeast. Within this range, human intervention (e.g., reservoirs, electric power) may create significant changes in comunity structure directly through habitat alteration or indirectly through adaptation of fish and benthic invertebrates to habitat changes. Recognizing the wide variability in lake systems, the food web was constructed to represent a reasonably diverse ecosystem.

Algae/phytoplankton/plants - Aquatic macrophytes, phytoplankton, and periphyton occur in most lakes. Aquatic macrophytes and periphyton are abundant in littoral areas near the shoreline, whereas phytoplankton are typical of deep, oxygenated waters of the pelagic zone. These algal and aquatic plant communities not only contribute significantly to the energy processing in the lake system, but also act to meet the habitat needs of fish species. Aquatic macrophytes play an important role in nutrient cycling in lakes. The phytoplankton community is generally composed of a diverse assemblage of major taxonomic groups with significant fluctuations in population sizes over time and space (Wetzel, 1983). Algae and aquatic plants, although likely to be patchy in distribution across lakes, constitute a critical food base in the lake food web.

Zooplankton - Zooplankton constitute a critical link in the aquatic food web of lakes and include two major taxa: rotifers and crustacea. Zooplankton act as prey and predator in the pelagic and littoral zones of lakes providing a prey base for fish and acting as predators of bacteria, algae, phytoplankton, and other smaller aquatic invertebrates. The abundance of zooplankton in lakes contributes significantly to energy transfer in the lake food web (Wetzel, 1983; Soballe et al., 1992).

Benthos - Benthic detritivores and benthic filter feeders were both included in the lake food web. Distributions of benthic biota are heterogeneous, and their abundance and diversity are a function of habitat requirements for feeding, development and reproduction. Typical species of benthic detritivores found in lake sediments include flatworms, nematodes, isopods, amphipods, gastropods, and aquatic insects. Benthic filter feeders in lakes include ostracods, mysids, mussels, and clams. Both functional taxa play key roles in the lake food web and contribute significantly to the biomass and prey base found in the food web (Wetzel, 1983; Soballe et al., 1992).

Fish - Fish are a significant component of the lake food web even though their contribution to carbon and energy fluxes is minor. Although examples of all fish biota types were identified in the literature reviewed (U.S. EPA, 1998a; Smith, 1994), a preponderance of data suggested that: (1) larger fish are the most common (perhaps because many fish reach full maturation in lakes), (2) lakes are one of the few aquatic habitats capable of supporting species of large zooplanktivores (U.S. EPA, 1998a; Smith, 1994; Wetzel, 1983), and (3) substantial populations of forage fish are required to support large omnivores and piscivores (e.g., small benthivores and omnivores). The fish biota types selected for the warmwater lake food web included: small and large benthivores (e.g., carpsuckers, sunfish, silversides, minnows, daces), large zooplanktivores (e.g., hitch), medium and large omnivores (e.g., perch, sucker, shad, crappie), and piscivores (e.g., carp, catfish, and eels). The fish assigned to the coldwater lake food web included medium benthivores (e.g., whitefish), medium zooplanktivores (e.g., lake chub), small and large omnivores (e.g., smelt, brook trout), and piscivores (e.g., gar, walleye).

3.1.6 Dietary Preferences in the Aquatic Food Webs

Static point estimates for prey preferences are frequently used in modeling aquatic food webs; however, in most cases, these fractions are derived for site-specific analyses in which predator-prey interactions are relatively well characterized. For an assessment at the national scale, these dietary preferences are not known with certainty and, in fact, there is tremendous variability in the dietary preferences of fish associated with life stage, region, prey density, and a host of other conditions. While the practice of using point estimates is appropriate for food webs that are characterized on a site-specific basis, it does not address the wide variability in the diets of fish across various freshwater systems. Therefore, data gleaned from literature sources were evaluated to create a database[11] of prey preference ranges (min/max) for biota types considered in the AqFW module (e.g., benthic detrivores, zooplankton, aquatic macrophytes, small fish). The module uses the database to: (1) construct the habitat-specific dietary composition (what does it eat), (2) rank prey items from most preferred to least preferred (defined by the maxima), and (3) estimate the prey preferences for each biota type (how much of each item is in the total diet). 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 subroutine that performs this task is described in Text Box 3-1.

3.2 Calculation of Tissue Concentrations in Biota Types Assigned to Representative Aquatic Food Webs

The AqFW module calculates concentrations in periphyton, benthic detrivores, and aquatic macrophytes for all representative aquatic habitats. The module also calculates tissue concentrations for a subset fish and other aquatic organisms, depending upon the structure of the food web and the properties of the chemical:

- Phytoplankton (only dioxin-like chemicals and other hydrophobic organics)
- Zooplankton (only dioxin-like chemicals and other hydrophobic organics)

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[11] Development of the database on minimum and maximum prey preferences was guided by optimal foraging theory (OFT) which suggests that fish tend to prefer larger prey because the energy return per energy invested is greater. Although fish tend to be highly opportunistic feeders, the OFT provides a unifying theme with which to establish a reasonable hierarchy for prey preferences.

Text Box 3-1. Sampling Algorithm Used to Select Prey Preferences in Aquatic Food Webs

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:

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

where

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

$$P_{ij} = LB_{ij} + RND(UB_{ij} - LB_{ij})$$

with the variables defined as follows:

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

where

LB is the lower bound of the range
UB is the upper bound of the range
RND is the uniform random deviate (0-1)
RP is the remaining probability (or resource)

- Benthic filter feeders (all chemicals)
- All biota types for TL3 fishes (all chemicals)
- Top piscivorous TL4 fish (all chemicals)

The tissue calculations for fish require two basic steps. First, fish tissue concentrations are estimated for each TL3 biota type and for the TL4 top predator. For organic chemicals, the distinction across various functional niches (e.g., medium TL3 benthivore) is important because the tissue concentration is largely a function of dietary preferences and lipid content. For other chemical types, the functional niches are less important because the model algorithms rely on empirical data from studies that generally do not consider the specific dietary preferences or other characteristics of the study species. Second, average tissue concentrations for whole-body and filet are estimated for TL3 fish on a reach-specific basis. The average whole-body concentrations include all TL3 biota types assigned to the reach; these concentrations are reported to the output file (af.grf) and read by the Ecological Exposure module in calculating applied dose. The filet concentrations reflect only those TL3 biota types that include species typically eaten by humans; the filet concentrations are also reported to the af.grf and read by the Human Exposure module in calculating the applied dose to fishers. Sections 3.2.1 through 3.2.5 describe the methods used to calculate whole-body tissue concentrations in fish and other aquatic organisms for each of the five major chemical types, respectively. Section 3.2.6 summarizes the calculations of filet concentrations for these chemical types.

3.2.1 Dioxin-like Chemicals and Other Hydrophobic Organics

The AqFW module recognizes this group of chemicals using two switches: (1) ChemType = "D" is true, and (2) ChemType = "O" is true *and* Kow $\geq$ 10,000. If either of these conditions is satisfied, the module calls the subroutine for hydrophobic organic chemicals that is based, primarily, on the model developed by Gobas et al. (1993).[12] For aquatic biota assigned to a given food web, the tissue concentrations are predicted simultaneously using the matrix solution described in Text Box 3-2. In the matrix solution, the concentrations in fish are predicted using Equation 3-1 and the concentrations in biota other than fish are predicted using simple partitioning theory as shown in Equations 3-6 through 3-11.

$$C_{fish^{i}_{BiotaType}} = \frac{(k_1 \cdot C_w^{fd} + k_D \sum Frac^{i}_{BiotaType} \cdot C^{i}_{BiotaType})}{(k_2 + k_E + k_M + k_G)} \tag{3-1}$$

where

$C_{fish}{}^{i}{}_{BiotaType}$ = whole-body concentration in fish of biota type i (mg/kg wet weight)

C_w^{fd} = freely dissolved concentration in surface water (mg/L)

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[12] The subroutine in the AqFW module used to predict tissue concentrations of hydrophobic organics does not include equations from Gobas et al. (1993) and Burkhard (1998) to account for sorption to dissolved organic carbon (DOC) and particulate organic carbon (POC) in estimating the freely dissolved chemical concentration (C_{fd}). The C_{fd} is estimated by the Surface Water module and called by the AqFW module from the SW output file (sw.ssf).

Text Box 3-2. Solution Algorithm for Food Web Concentrations

Collectively, the equations describing the relationships between chemical concentrations in food web prey and resultant concentrations in food web predators constitute a system of linear, algebraic equations. An efficient and flexible matrix solution technique was developed to solve this system of equations using principles of linear algebra. It should be noted that the form of the specific equations used in the AqFW module does not require a system-based solution; the equations, while coupled, can be solved sequentially one-at-a-time. (The coefficient matrix is triangular.) However, to accommodate the future use of more complex predator/prey relationships, which may involve true, *feedforward* and *feedback* simultaneity, a more generic, system solution was believed desirable and was developed. The system solution was coded as a subroutine so that it is called repeatedly to solve the different systems of equations comprising the predator-prey combinations in the eight representative aquatic food webs for each time step (year).

A matrix representation of a system of "N" simultaneous, linear, algebraic equations is:

$$\mathbf{A}\underline{\mathbf{x}} = \underline{\mathbf{b}}$$

where

$\underline{\mathbf{x}}$ is an Nx1 vector ("state" variables) that will, upon solution, contain the concentrations in the N predator/prey species comprising the food web;

A is an NxN matrix that contains the coefficients of the elements of the $\underline{\mathbf{x}}$ vector, (i.e., the food web parameters); and

$\underline{\mathbf{b}}$ is an Nx1 vector ("forcing function") that contains those remaining terms in the equations that are not functions of the state variables (i.e. not contained in the **A** coefficient matrix).

Given numerical values for all elements of matrix **A** and vector $\underline{\mathbf{b}}$, the solution (the values of the elements of vector $\underline{\mathbf{x}}$) can be determined by a variety of numerical methods, many of which take advantage of certain structures (e.g., tri-diagonal) of the **A** matrix, if present. The method selected for AqFW module does not assume any particular structure, rather, it can accommodate any arbitrary structure and is nonetheless reasonably computationally efficient. The method, called "LU decomposition" is described in numerous numerical methods references (e.g., Hoffman, 1992).

$C^{i}_{BiotaType}$ = concentration in biota type i in diet (mg/kg wet weight)
$Frac^{i}_{BiotaType}$ = fraction of biota type i included in diet

and

k_1 = rate constant for chemical uptake from water (1/kg-day)
k_2 = rate constant for chemical elimination to water (1/day)
k_D = rate constant for chemical uptake from food (1/day)
k_E = rate constant for elimination by faecal egestion (1/day)
k_M = rate constant for metabolic transformation of chemical (1/day)
k_G = rate constant for growth dilution (1/day)

with the rate constants defined as follows:

$$k_1 = \frac{88.3 \; BWfish^{i}_{BiotaType}{}^{0.6}}{BWfish^{i}_{BiotaType} \; (1 + \frac{100}{K_{ow}})} \tag{3-2}$$

the chemical elimination (k_2) is defined in terms of the uptake rate (k_1):[13]

$$k_2 = \frac{k_1}{LipFrac^{i}_{BiotaType} \; K_{ow}} \tag{3-3}$$

$$k_D = \frac{\frac{1}{(5.3E{-}08 \; K_{ow} + 2.3)} \; (0.022 \; (BWfish^{i}_{BiotaType})^{0.85} \quad e^{\,0.06T^{j}_{water}})}{BWfish^{i}_{BiotaType}} \tag{3-4}$$

$$k_E = 0.25 \; k_D \tag{3-5}$$

and the rate constants for growth dilution are sensitive to water temperature. For warm waters (defined by average annual temperatures $\geq$ 17 C):

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[13] The equations for some of the rate constants such as k_2 do not appear to produce the correct units. The reason for this discrepancy is that the rate constants are based, in part, on empirical equations to estimate some of the variables. The empirical equations (Gobas et al., 1993) include the necessary conversion to produce the correct units.

$$k_G \;=\; 0.00251\;\left(BWfish^{\,i}_{BiotaType}\right)^{-0.2} \tag{3-6}$$

and for cold waters (defined by average annual temperatures < 17 C):

$$k_G \;=\; 0.000502\;\left(BWfish^{\,i}_{BiotaType}\right)^{-0.2} \tag{3-7}$$

where

$Bwfish^{i}_{BiotaType}$ = body weight of fish in biota type i (kg)
$LipFrac^{i}_{BiotaType}$ = lipid fraction in biota type i (kg lipid / kg tissue)
T^{j}_{water} = annual average temperature in reach j (degree Celsius)
K_{ow} = octanol-water partition coefficient

The rate constant for metabolism (k_M) in fish is a chemical-specific property and is called from the cp.ssf file. Metabolic rate constants are frequently not available for most constituents. Given the general paucity of data on metabolic rate constants in fish, the k_M was set to a default zero until data can be developed for a larger universe of hydrophobic organic chemicals. The intent of setting a default of zero for k_M is not to provide conservative estimates *per se*, rather it is intended to avoid introducing a data bias into the module calculations of fish tissue concentrations. As data are developed on a wider range of chemicals and species, these values can be incorporated into the databases that support the AqFW. As discussed in Section 3.2.5, tissue concentrations for hydrophobic organic chemicals known to be readily metabolizable (e.g., PAHs) are derived using empirical data.

For fish in TL3, the average concentration across all biota types assigned to a given reach must be calculated since the dietary preferences in the Ecological Exposure module do not distinguish among the different biota types. The whole-body tissue concentrations for TL3 fish derived using Equation 3-1 are summed and the average concentration is calculated:[14]

$$C^{j}_{TL3fish} \;=\; \frac{\sum C_{TL3fish^{\,i}_{BiotaType}}}{TL3Num^{j}_{fish}} \tag{3-8}$$

where

$C^{j}_{TL3fish}$ = average concentration in TL3 fish in reach j (mg/kg wet weight)
$C_{TL3fish^{\,i}_{BiotaType}}$ = concentration in TL3 fish of biota type i (mg/kg wet weight)
$TL3Num^{j}_{fish}$ = number of TL3 fish in reach j

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[14] Since only one TL4 fish is assigned to each aquatic food web, it is not necessary to calculate an average (i.e., there is only one biota type for the TL4 fish).

Assuming steady-state conditions, the tissue concentrations in phytoplankton, periphyton, aquatic macrophytes, and zooplankton are estimated using the model from Gobas et al. (1993).[15] This approach assumes that the bioconcentration factor (BCF) is satisfactorily approximated by K_{ow} and is shown in Equation 3-9:

$$C^{i}_{BiotaType} = LipFrac^{i}_{BiotaType} \times K_{ow} \times C^{fd}_{w} \qquad (3\text{-}9)$$

where

$C^{i}_{BiotaType}$ = concentration in biota type i (mg/kg wet weight)
C_{w}^{fd} = freely dissolved concentration in surface water (mg/L)
$LipFrac^{i}_{BiotaType}$ = lipid fraction in biota type i (kg lipid / kg tissue)
K_{ow} = octanol-water partition coefficient (assume L/kg lipid)

The tissue concentrations in benthic detrivores and benthic filter feeders are also derived assuming steady-state conditions. As described in Gobas et al. (1993), equilibrium partitioning theory may be used to predict concentrations in benthic organisms as indicated in Equation 3-10:

$$C^{i}_{benthos} = \frac{C_{sediment} \times \left(\dfrac{\rho_{OC}}{foc_{sediment}}\right)}{\left(\dfrac{\rho_{lip}}{LipFrac^{i}_{benthos}}\right)} \qquad (3\text{-}10)$$

where

$C^{i}_{benthos}$ = concentration in benthos i (mg/kg wet weight)
$C_{sediment}$ = total concentration in sediment (mg/kg)
ρ_{oc} = density of organic carbon in sediment (kg/L)
ρ_{lip} = density of lipids in benthos (kg/L)
$foc_{sediment}$ = fraction of organic carbon in sediment
$LipFrac^{i}_{benthos}$ = fraction of lipid in benthos i (kg lipid / kg tissue)

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

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[15] A more detailed description of the development of this model may be found in Gobas et al. (1993), Geyer et al. (1984), Gobas et al. (1991), and Clayton et al. (1977).

3.2.2 Hydrophilic Organics

The AqFW module recognizes organic chemicals that are classified as hydrophilic using one switch: ChemType = O is true *and* $K_{ow} < 10,000$. For chemicals that satisfy this condition, the module: (1) uses partitioning Equations 3-8 and 3-9 to predict concentrations in aquatic macrophytes and benthic filter feeders, respectively, (2) calls a regression equation to predict the bioconcentration factor (BCF) specific to fish of each biota type, (3) uses this BCF to calculate the tissue concentration in fish, and (4) calculates the whole-body concentration in the TL4 fish and an average whole-body concentration for TL3 fish for each fishable reach. Note that for these organic constituents, gill exchange is considered to be the dominant mechanism by which the chemical is taken up. Uptake through the food web is assumed to be negligible and, therefore, it is not necessary to calculate the concentration in all of the prey items in the aquatic food web. See Gobas et al. (1993) for an excellent discussion on the mechanism by which the concentration of organic chemicals increases with trophic level (i.e., biomagnification).

For fish in both trophic levels (TL) 3 and 4, whole-body BCF values are calculated for each biota type as shown in Equation 3-11 taken from Bertelsen et al. (1998):

$$\log(BCF^{i}_{BiotaType\,TL} - WaterFrac_{fish}) = a_{fish} \cdot \log\ K_{ow} + b_{fish} \cdot \log\ LipFrac^{i}_{BiotaType} + c_{fish} \qquad (3\text{-}11)$$

where

$BCF^{i}_{BiotaType\ TL}$ = BCF for fish in biota type i for each trophic level (L/kg tissue)
$WaterFrac_{fish}$ = fraction of whole-body fish that is water (wet weight)
a_{fish} = primary slope term
b_{fish} = secondary slope term
c_{fish} = empirical error term
$LipFrac^{i}_{BiotaType}$ = lipid fraction in biota type i (kg lipid / kg tissue)
K_{ow} = octanol-water partition coefficient (assume L/kg lipid)

Equation 3-12 provides the solution for the BCF:

$$BCF^{i}_{BiotaType\,TL} = 10^{(a_{fish} \cdot \log\ K_{ow} + b_{fish} \cdot \log LipFrac^{i}_{BiotaType} + c_{fish})} + WaterFrac_{fish} \qquad (3\text{-}12)$$

For fish in TL3, the average concentration across all biota types assigned to a given reach is calculated in two steps. First, the tissue concentration in each TL3 biota type is calculated as shown in Equation 3-13. This equation is also used to calculate the tissue concentration in the single TL4 fish assigned to the aquatic food web.

$$C^{i}_{BiotaType_{TL3}} = BCF^{i}_{BiotaType_{TL3}} \cdot C_w^{fd} \tag{3-13}$$

where

$C^{i}_{BiotaType\ TL3}$ = concentration in TL3 fish of biota type i (mg/kg wet weight)
$BCF^{i}_{BiotaType\ TL3}$ = BCF for fish in biota type i for each trophic level (L/kg tissue)
C_w^{fd} = freely dissolved concentration in surface water (mg/L)

The second step is to calculate the average concentration in TL3 fish for the stream reach of interest:

$$C^{j}_{TL3fish} = \frac{\sum C^{i}_{BiotaType_{TL3}}}{TL3Num^{j}_{fish}} \tag{3-14}$$

where

$C^{j}_{TL3fish}$ = average concentration in TL3 fish in reach j (mg/kg wet weight)
$C^{i}_{BiotaType\ TL3}$ = concentration in TL3 fish of biota type i (mg/kg wet weight)
$TL3Num^{j}_{fish}$ = number of TL3 fish in reach j

3.2.3 Special Chemicals

Constituents known to be significantly metabolized by fish or that otherwise require specific methods and/or data were categorized as special chemicals. Currently, the special chemicals include hydrophobic PAHs and phthalates because the use of K_{ow} as a surrogate for bioaccumulation has been shown to greatly overestimate the tissue concentrations for these chemicals. The subroutine for “S” chemicals may be modified to accommodate other constituents such as DDT that are the subject of other EPA studies; in essence, the ChemType variable can be used to override modeling subroutines and call for empirical data from the chemical properties file (cp.ssf). The AqFW module recognizes the special chemicals using the ChemType variable and reads a value for the BAF from the chemical properties database. For readily metabolizable organic chemicals, the empirically-derived bioaccumulation factors[16] are used in Equation 3-15 to estimate the whole-body tissue concentrations in various biota in the aquatic food web:

$$C^{i}_{BiotaType} = BAF^{i}_{BiotaType} \cdot C_w^{fd} \tag{3-15}$$

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[16] In this discussion, the bioaccumulation factor (or BAF) simply reflects the ratio between the tissue concentration in fish and the freely dissolved surface water concentration reported in the study (i.e., C_{fish}/C_w). In this context, the terms BAF and BCF may be used interchangeably and refer to ratio derived from empirical data.

where

$C^{i}_{BiotaType}$ = concentration of biota type i (mg/kg wet weight)
$BAF^{i}_{BiotaType}$ = bioaccumulation factor for biota type i (L/kg tissue)
C_w^{fd} = freely dissolved concentration in surface water (mg/L)

In general, the BAF data for PAHs are not sufficient to distinguish between the feeding guilds of fish (e.g., benthivores, planktivores), nor are they specific to trophic level. The result is that this subroutine actually estimates a single, whole-body concentration for fish in a given reach

In addition to fish tissue concentration, the module estimates concentrations for aquatic macrophytes and benthic filter feeders. The concentration in aquatic macrophytes is estimated using Equation 3-15. For benthic filter feeders, the tissue concentration is calculated based on the total concentration in sediment, as shown in Equation 3-16:

$$C_{Benthic_{ff}} = BSAF_{Benthic_{ff}} \cdot C_{sediment} \tag{3-16}$$

where

$C_{Benthic\_ff}$ = concentration in benthic filter feeders (mg/kg wet weight)
$BSAF_{Bentic\_ff}$ = biota-sediment accumulation factor (kg sediment/kg tissue)
$C_{sediment}$ = freely dissolved concentration in surface water (mg/L)

3.2.4 Metals

Metal constituents are recognized as "M" using the ChemType variable. Concentrations in aquatic biota are estimated using empirical bioaccumulation factors based on the ratio between the tissue concentration and the total concentration in surface water (rather than freely dissolved). The empirical BAFs selected for inclusion in the chemical properties database are discussed in the data collection section for the aquatic food web. In brief, these data were generally of insufficient quality to adequately address issues relevant to essentiality and bioavailability. The tissue concentration of metals in benthic filter feeders is calculated using Equation 3-16. Equation 3-17 presents the calculation of tissue concentrations in other biota.

$$C^{i}_{BiotaType} = BAF^{i}_{BiotaType} \cdot C^{t}_{w} \tag{3-17}$$

where

$C^{i}_{BiotaType}$ = concentration of biota type i (mg/kg wet weight)
$BAF^{i}_{BiotaType}$ = bioaccumulation factor for biota type i based on total C_w (L/kg tissue)
C_w^{t} = total concentration in surface water (mg/L)

3.2.5 Mercury

Rather than include mercury in the category of special chemicals, a unique ChemType (Hg) was defined for mercury to retain flexibility in the model for future revisions. EPA has devoted substantial effort in developing empirical BAFs for trophic level 3 and 4 fish that reflect the complex speciation dynamics in aquatic systems. Although it was recognized that water quality characteristics exert a significant influence on mercury uptake and accumulation, incorporating a mercury-specific module into the HWIR modeling system was determined to be infeasible at this time. Consequently, empirical BAFs developed for methyl mercury bioaccumulation in fish were used to estimate tissue concentrations in TL3 and TL4 fish, respectively. The form of this equation is identical to that of Equation 3-18 for estimating concentrations in aquatic macrophytes, TL3 fish, and TL4 fish; for convenience, it is repeated below:

$$C^{i}_{BiotaType} = BAF^{i}_{BiotaType} \cdot C^{fd}_{MeHg} \tag{3-18}$$

where

$C^{i}_{BiotaType}$ = concentration of biota type i (mg/kg wet weight)
$BAF^{i}_{BiotaType}$ = bioaccumulation factor for biota type i based on dissolved C_w (L/kg tissue)
C^{fd}_{MeHg} = freely dissolved concentration of methyl mercury in surface water (mg/L)

For benthic filter feeders, Equation 3-16 is used to predict the tissue concentration based on the total concentration of mercury in sediment.

3.2.6 Estimating Concentrations in Fish Filet for Human Exposure

The AqFW module implements additional subroutines to calculate the chemical concentration in the filet of fish. As with the whole-body tissue concentrations, the filet calculations are different for each of the different chemicals types. However, the filet subroutines calculate concentrations only for fish that are presumed to be eaten by humans; not all biota types assigned to trophic level 3 are assumed to be edible. Table 3-3 presents the biota types in the representative aquatic food webs that are considered edible for humans. In essence, the filet subroutines calculate filet concentrations by either: (1) adjusting the whole-body tissue concentrations for the filet fraction or (2) making minor modifications to the “whole-body” equations. Consequently, the discussion on filet concentrations is brief and refers to equations 3-1 through 3-18, as appropriate.

Dioxin-like Chemicals and Other Hydrophobic Organics - The concentrations of hydrophobic organic chemicals in filet are calculated by adjusting the whole-body tissue concentration by the relative lipid content of filet (or muscle) versus the whole-body of the fish. The theory supporting the bioaccumulation of hydrophobic organic chemicals suggests that

Table 3-3. Biota Types of Fish Presumed to be Eaten by Humans

Aquatic Food Web	TL3 Edible Biota Types	TL4 Edible Biota Type
coldwater stream	TL3 omnivore - medium	TL4 piscivore
coldwater wetland	TL3 omnivore - medium	TL4 piscivore
coldwater pond	TL3 omnivore - large	TL4 piscivore
coldwater lake	TL3 omnivore - medium	TL4 piscivore
warmwater stream	TL3 omnivore - medium	TL4 piscivore
warmwater wetland	TL3 omnivore - large	TL4 piscivore
warmwater pond	TL3 planktivore - medium TL3 omnivore - medium	none assigned
warmwater lake	TL3 benthivore - large TL3 omnivore - medium TL3 omnivore - large	TL4 piscivore

virtually all of the chemical accumulates in the lipid tissue. Thus, by adjusting for the differences in lipid content between the filet and whole-body, the concentration in filet can be estimated from the whole-body tissue concentration. This term is referred to as filet fraction (FiletFrac) and is calculated by dividing the lipid fraction in filet by the lipid fraction in the whole-body. For example, if the lipid fraction in filet is 3 percent and the lipid fraction in whole-body is 10 percent, the FiletFrac is 0.3 (and the fraction for whole-body would be 0.7). Equation 3-19 presents the calculation of filet concentration:

$$C_{filet^{\,i}_{BiotaType}} = C_{fish^{\,i}_{BiotaType}} \cdot FiletFrac \qquad (3\text{-}19)$$

where FiletFrac is defined above and

$C_{filet\ BiotaType}^{\ \ i}$ = concentration in fish filet of biota type i (mg/kg wet weight)
$C_{fish\ BiotaType}^{\ \ i}$ = concentration in fish of biota type i (mg/kg wet weight)

For two warmwater habitats - pond and lake - there are more than one TL3 biota type considered to be edible for humans. Therefore, the average concentration in TL3 fish filets is calculated for each reach using the same approach as Equation 3-8:

$$C^{\,j}_{TL3filet} = \frac{\sum C_{TL3fish^{\,i}_{BiotaType}}}{TL3NumEdible^{\,j}_{fish}} \qquad (3\text{-}20)$$

Hydrophilic Organics - In addition to the equation for whole-body concentrations, Bertelsen et al. (1998) also developed a regression specific to muscle tissue (or filet) in fish:

$$BCF^{i}_{filet_{BiotaType_{TL}}} = 10^{\left(a_{filet} \cdot \log K_{ow} + b_{filet} \cdot logLipFrac^{i}_{filet_{BiotaType}} + c_{filet}\right)} + WaterFrac_{filet} \tag{3-21}$$

where

$BCF^{i}_{filet\ BiotaType\ TL}$ = BCF for filet (muscle) in biota type i (L/kg filet wet weight)
$WaterFrac_{filet}$ = fraction of whole-body fish that is water (wet weight)
a_{filet} = primary slope term
b_{filet} = secondary slope term
c_{filet} = empirical error term
$LipFrac^{i}_{filet\ BiotaType}$ = lipid fraction in biota type i (kg lipid / kg filet)
K_{ow} = octanol-water partition coefficient (assume L/kg lipid)

As with the hydrophobic organics, the average concentration in edible TL3 fish is calculated for two warmwater habitats (pond and lake) using Equation 3-20.

Special Chemicals - As with the whole-body tissue concentration, the filet concentration for special chemicals is calculated using empirical bioaccumulation data only (see Equation 3-15). Given the large uncertainty inherent in these values, it was considered inappropriate to apply a FiletFrac variable to account for differences in the lipid content between the muscle and the entire fish. Although it is likely that organic residues from constituents that are readily metabolized tend to concentrate in the lipid tissue in fish, the paucity of empirical data on either whole-body or filet uptake and accumulation does not warrant the use of an adjustment factor.

Metals - Filet concentrations of metals were calculated as shown in Equation 3-17 using empirical data on bioaccumulation in muscle tissue. Because metals do not bioaccumulate preferentially in lipid tissue, whole-body BAFs were used as a surrogate value for muscle BAFs when the latter were unavailable. The filet concentration in biota types for fish in TL3 was calculated using the same BAF and, therefore, only a single TL3 fish concentration is calculated.

Mercury - Concentrations of methyl mercury in fish filets were calculated as recommended in the *Mercury Study Report to Congress* (MSRTC - U.S. EPA, 1997). The MSRTC uses the whole-body BAFs for methylmercury in TL3 and TL4 fish, respectively, to calculate filet concentrations. Consequently, that methodology has been adopted for the AqFW module.

4.0 Implementation

The flowchart shown in Figure 4-1 illustrates the generalized structure of the Aquatic Food Web module.

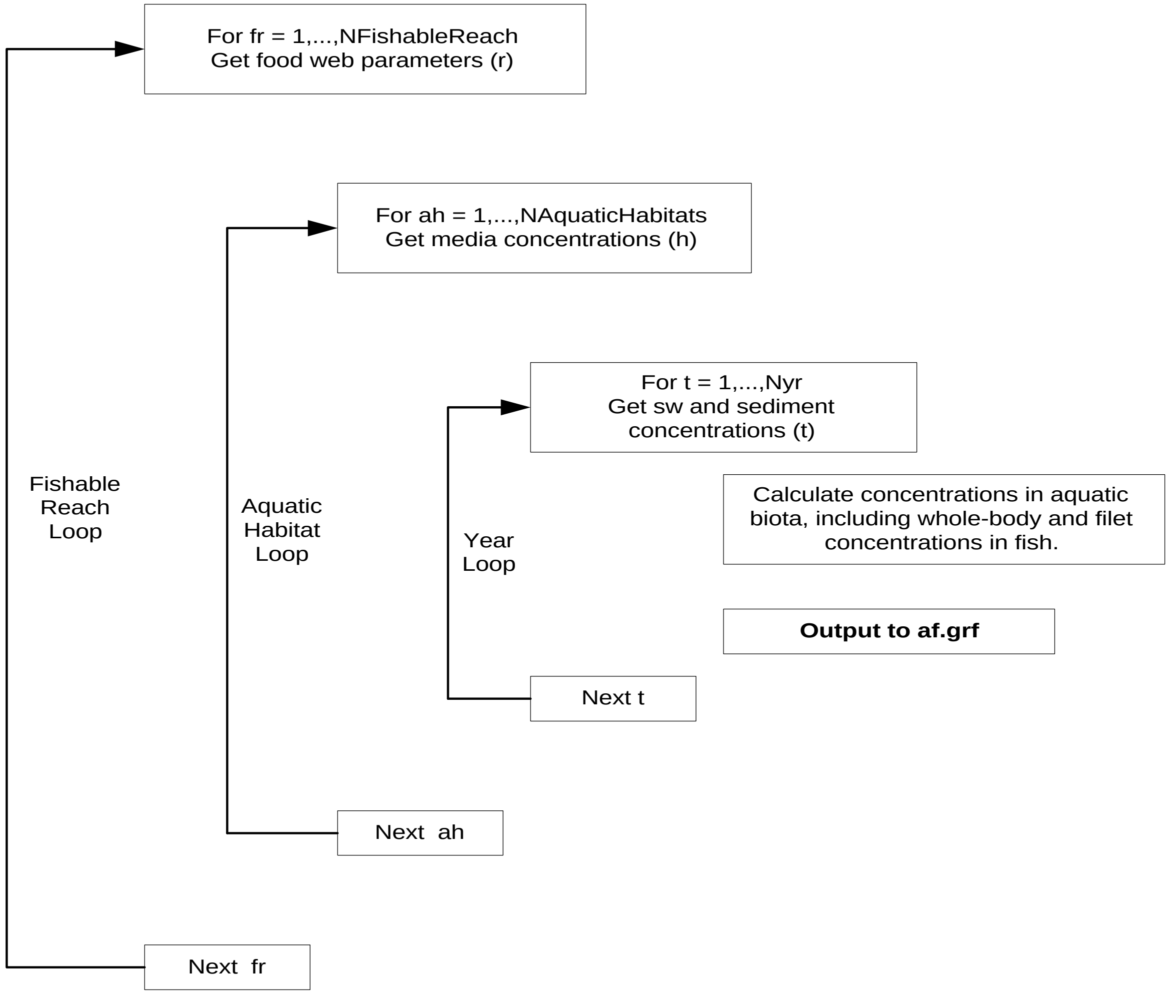

Figure 4-1. Conceptual flow diagram of major functionality of Aquatic Food Web module.

5.0 References

Abbott, Joan D., Steven W. Hinton, and Dennis L. Borton. 1995. Pilot scale validation of the river/fish bioaccumulation modeling program for nonpolar hydrophobic organic compounds using the model compounds 2,3,7,8-TCDD and 2,3,7,8-TDCF. *Environmental Toxicology and Chemistry*, 14(11):1999-2012.

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 Ressessment of Metals Criteria for Aquatic Life Protection 10-14 February 1996.

Bertelsen, Sharon L., Alex D. Hoffman, Carol A. Gallinat, Colleen M. Elonen, and John W. Nichols. 1998. Evaluation of log KOW and tissue lipid content as predictors of chemical partitioning to fish tissues. *Environmental Toxicology and Chemistry*, 17(8):1447-1455.

Burkhard, Lawrence P. 1998. Comparison of two models for predicting bioaccumulation of hydrophobic organic chemicals in a Great Lakes food web. *Environmental Toxicology and Chemistry*, 17(3):383-393.

Campfens, Jan, and Donald Mackay. 1997. Fugacity-based model of PCB bioaccumulation in complex aquatic food webs. *Environmental Science & Technology*, 31(2):577-583.

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.

Clayton, John R., Jr., Spyros P. Pavlou, and Norman F. Breitner. 1977. Polychlorinated biphenyls in coastal marine zooplankton: bioaccumulation by equilibrium partitioning. *Environmental Science & Technology*, 11(7):676-682. July.

Felley, J. D. 1992. Chapter 6: Medium--Low-Gradient Streams of the Gulf Coastal Plain. In: *Biodiversity of the Southeastern United States - Aquatic Communities*, C. T. Hackney, S. M. Adams, and W. H. Martin (eds.). John Wiley & Sons, Inc., New York, NY. pp. 233-269.

Garman, G. C., and L. A. Nielsen. 1992. Chapter 8: Medium-sized Rivers of the Atlantic Coastal Plain. In: *Biodiversity of the Southeastern United States - Aquatic Communities,* C. T. Hackney, S. M. Adams, and W. H. Martin (eds.). John Wiley & Sons, Inc., New York, NY. pp. 315-349.

Gelwick, F. P., and W. J. Matthews. 1996. Chapter 22: Trophic Relations of Stream Fishes. In: *Methods in Stream Ecology,* F. R. Hauer and G. A. Lamberti (eds.). Academic Press, San Diego, CA. pp. 475-492.

Gerking, Shelby D. 1994. *Feeding Ecology of Fish.* Academic Press, Inc., San Diego, CA.

Geyer, H., G. Politzki, and D. and Freitag. 1984. Prediction of ecotoxicological behaviour of chemicals: relationship between n-octanol/water partition coefficient and bioaccumulation of organic chemicals by alga Chlorella. *Chemosphere,* 13(2):269-284.

Gobas, Frank A. P. C., Kathryn E. Clark, Wan Ying Shiu, and Donald Mackay. 1989. Bioconcentration of polybrominated benzenes and biphenyls and related superhydrophobic chemicals in fish: role of bioavailability and elimination into the feces. *Environmental Toxicology and Chemistry,* 8:231-245.

Gobas, Frank A. P. C., Edmund J. McNeil, Lesley Lovett-Doust, and G. Douglas Haffner. 1991. Bioconcentration of chlorinated aromatic hydrocarbons in aquatic macrophytes. *Environmental Science and Technology,* 25(5):924-929.

Gobas, Frank A. P. C. 1993. A model for predicting the bioaccumulation of hydrophobic organic chemicals in aquatic food-webs: application to Lake Ontario. *Ecological Modelling,* 69:1-17.

Gobas, Frank A. P. C., Jim R. McCorquodale, and G. D. Haffner. 1993. Intestinal absorption and biomagnification of organochlorines. *Environmental Toxicology and Chemistry,* 12:567-576.

Goldstein, Robert M., and Thomas P. Simon. 1998. Chapter 7: Toward a united definition of guild structure for feeding ecology of North American freshwater fishes. In: *Assessing the Sustainability and Biological Integrity of Water Resources Using Fish Communities,* Thomas P. Simon (ed.). CRC Press, Boca Raton, FL. pp. 123-138.

Hauer, F. Richard and Gary A. Lamberti (eds.). 1996. *Methods in Stream Ecology.* Academic Press, San Diego, CA.

Hauer, F. R., and V. H. Resh. 1996. Chapter 16: Benthic Macroinvertebrates. In: *Methods in Stream Ecology,* F. R. Hauer and G. A. Lamberti (eds.). Academic Press, San Diego, CA. pp. 339-369.

Hoffman, Joe D. 1992. *Numerical Methods for Engineers and Scientists.* McGraw-Hill, Inc., New York, NY.

Hudson, Robert J. M., Steven A. Gherini, Carl J. Watras, and Donald B. Porcella. 1994. Chapter V.1: Modeling the biogeochemical cycle of mercury in lakes: the mercury cycling model (MCM) and its application to the MTL study lakes. In: *Mercury Pollution: Integration and Synthesis,* Carl J. Watras and John W. Huckabee (eds.). Lewis Publishers, Boca Raton, FL. pp. 473-523.

Isnard, P., and S. Lambert. 1988. Estimating bioconcentration factors from octanol-water partition coefficient and aqueous solubility. *Chemosphere,* 17(1):21-34.

Killgore, Jack and Jan Jeffrey Hoover 1992. *A Guide for Monitoring and Evaluating Fish Communities in Bottomland Hardwood Wetlands.* WRP Technical Note FW-EV-2.2. U.S. Army Engineers, Waterway Experimental Station, Vicksburg, MS. January.

Landrum, Peter F., Henry Lee, II, and Michael J. Lydy. 1992. Toxicokinetics in aquatic systems: model comparisons and use in hazard assessment. *Environmental Toxicology and Chemistry,* 11:1709-1725.

Lee, David S., Carter R. Gilbert, Charles H. Hocutt, Robert E. Jenkins, Don E. McAllister, and Jay R. Stauffer, Jr. 1980. *Atlas of North American Freshwater Fishes, 1980- Et Seq.* North Carolina State Museum of Natural History, Raleigh, NC.

Li, H. W., and J. L. Li. 1996. Chapter 18: Fish Community Composition. In: *Methods in Stream Ecology,* F. R. Hauer and G. A. Lamberti (eds.). Academic Press, San Diego, CA. pp. 391-406.

Lowe, R. L., and G. D. Laliberte. 1996. Chapter 13: Benthic Stream Algae: Distribution and Structure. In: *Methods in Stream Ecology,* F. R. Hauer and G. A. Lamberti (eds.). Academic Press, San Diego, CA. pp. 269-293.

Mackay, D. 1982. Correlation of bioconcentration factors. *Environmental Science and Technology,* 16(5):274-278.

Menzel, R. G., and C. M. Cooper. 1992. Chapter 10: Small Impoundments and Ponds. In: *Biodiversity of the Southeastern United States - Aquatic Communities,* C. T. Hackney, S. M. Adams, and W. H. Martin (eds.). John Wiley & Sons, Inc., Ney York, NY. pp. 389-420.

Mitsch, William J., and James G. Gosselink. 1993. *Wetlands.* 2nd Edition. Van Nostrand Reinhold, New York, NY.

Morrison, Heather A., Frank A. P. C. Gobas, Rodica Lazar, D. Michael Whittle, and G. Douglas Haffner. 1997. Development and verification of a benthic/pelagic food web bioaccumulation model for PCB congeners in western Lake Erie. *Environmental Science & Technology,* 31(11):3267-3273.

Mulholland, P. J., and D. R. Lenat. 1992. Chapter 5: Streams of the Southeastern Piedmont, Atlantic Drainage. In: *Biodiversity of the Southeastern United States - Aquatic Communities*, C. T. Hackney, S. M. Adams, and W. H. Martin (eds.). John Wiley & Sons, Inc., New York, NY. pp. 193-231.

Palmer, M. A., and D. L. Strayer. 1996. Chapter 15: Meiofauna. In: *Methods in Stream Ecology*, F. R. Hauer and G. A. Lamberti (eds.). Academic Press, San Diego, CA. pp. 315-337.

Rand, Gary M. (ed.). 1995. *Fundamentals of Aquatic Toxicology: Effects, Environmental Fate, and Risk Assessment.* 2nd Edition. Taylor & Francis, Washington, DC.

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

Schindler, Daniel E., Stephen R. Carpenter, Kathryn L. Cottingham, Xi He, James R. Hodgson, James F. Kitchell, and Patricia A. Soranno. 1996. Chapter 8: Food web structure in the littoral zone coupling to pelagic trophic cascades. In: *Food Webs: Integration of Patterns & Dynamics*, Gary A. Polis and Kirk O. Winemiller (eds.). Chapman and Hall, New York, NY. pp. 96-105.

Smith, C. Lavett. 1994. *Fish Watching: An Outdoor Guide to Freshwater Fishes.* Cornell University Press, Ithaca, NY.

Smock, L. A., and E. Gilinsky. 1992. Chapter 7: Coastal Plain Blackwater Streams. In: *Biodiversity of the Southeastern United States - Aquatic Communities*, C. T. Hackney, S. M. Adams, and W. H. Martin (eds.). John Wiley & Sons, Inc., New York, NY. pp. 271-313.

Soballe, D. M., B. L. Kimmel, R. H. Kennedy, and R. F. Gaugush. 1992. Chapter 11: Reservoirs. In: *Biodiversity of Southeastern United States - Aquatic Communities*, C. T. Hackney, S. M. Adams, and W. H. Martin (eds.). John Wiley & Sons, Inc., New York, NY. pp. 421-474.

Spencer, Matthew, and Steve Beaulieu. 1997. Bioaccumulation Factors for Polycyclic Aromatic Hydrocarbons in Fish: Methods for Dealing With Uncertainty (Unpublished).

Stephan, C. E. 1993. *Derivation of Proposed Human Health and Wildlife Bioaccumulation Factors for the Great Lakes Initiative*. Environmental Research Laboratory, Office of Research and Development, U.S. Environmental Protection Agency, Duluth, MN. March.

Sternberg, Dick. 1996. *Freshwater Gamefish of North America.* Cowles Creative Publishing, Inc., Minnetonka, Minnesota.

Thomann, Robert V., John P. Connolly, and Thomas F. Parkerton. 1992. An equilibrium model of organic chemical accumulation in aquatic food webs with sediment interaction. *Environmental Toxicology and Chemistry*, 11:615-629.

Traas, Theo P., Joan A. Stäb, P. Roel Kramer, Wim P. Cofino, and Tom Aldenberg. 1996. Modeling and risk assessment of tributyltin accumulation in the food web of a shallow freshwater lake. *Environmental Science & Technology,* 30(4):1227-1237.

U.S. EPA (Environmental Protection Agency). 1997. *Mercury Study Report to Congress. Volumes I - VIII.* EPA 452/R-97/003. U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards and Office of Research and Development, Washington, DC. Website at http://www.epa.gov/ttn/uatw/112nmerc/mercury.html. December.

U.S. EPA (Environmental Protection Agency). 1998a. *Lake and Reservoir Bioassessment and Biocriteria. Technical Guidance Document.* EPA 841-B-98-007. U.S. Environmental Protection Agency, Office of Wetlands, Oceans, and Watersheds, Office of Water, Office of Science and Technology, Washington, DC. August.

U.S. EPA (Environmental Protection Agency). 1998b. *Guidelines for Ecological Risk Assessment.* (Final). EPA/630/R-95/002F. U.S. Environmental Protection Agency, Risk Assessment Forum, Washington, DC. April.

U.S. EPA (Environmental Protection Agency). 1998c. *Ambient Water Quality Criteria Derivation Methodology Human Health. Technical Support Document.* (Final Draft). EPA/822/B-98/005. U.S. Environmental Protection Agency, Office of Science and Technology, Washington, DC. July.

Veith, G. D., K. J. Macek, S. R. Petrocelli, and J. Carroll. 1980. An evaluation of using partition coefficients and water solubility to estimate bioconcentration factors for organic chemicals in fish. In: *Aquatic Toxicology, ASTM STP 707,* J. G. Eaton, P. R. Parrish, and A. C. Hendricks (eds.). American Society for Testing and Materials, pp. 116-129.

Wallace, J. B., J. R. Webster, and R. L. Lowe. 1992. Chapter 4: High-Gradient Streams of the Appalachians. In: *Biodiversity of the Southeastern United States - Aquatic Communities,* C. T. Hackney, S. M. Adams, and W. H. Martin (eds.). John Wiley & Sons, Inc., New York, NY. pp. 133-191.

Wetzel, Robert G. 1983. *Limnology.* 2nd Edition. Saunders College Publishing, Fort Worth, TX.

Zaranko, Danuta T., Ronald W. Griffiths, and Narinder K. Kaushik. 1997. Biomagnification of polychlorinated biphenyls through a riverine food web. *Environmental Toxicology and Chemistry,* 16(7):1463-1471.

Appendix A

Inputs and Outputs

Appendix A
Inputs and Outputs

The Aquatic Food Web module receives inputs from its module-specific input file, af.ssf, the generic site layout file (sl.ssf), the chemical properties file (cp.ssf), and modeled inputs from the Surface Water module (sw.grf). The Aquatic Food Web module outputs are written to the af.grf file. (All AqFW module outputs are 3-dimensional arrays indexed on time, waterbody network, and reach.)

All input and output variables are listed and described in Tables A-1 through A-5.

Table AF-1. Af.ssf Parameter Inputs (Module-Specific Inputs)

Input Parameters	Units	Description
a_fish	unitless	Slope of BCF regression equation across all tissues in fish.
a_mus	unitless	Slope of BCF regression equation for muscle tissue in fish.
b_fish	unitless	Slope (2) of BCF regression equation across all tissues in fish.
b_mus	unitless	Slope (2) of BCF regression equation for muscle tissue in fish.
BiotaTypeIndex	unitless	Numerical index of each biota type.
BwFish	unitless	Fish body weight.
c_fish	unitless	Error term in BCF regression equation across all tissues in fish.
c_mus	unitless	Error term in BCF regression equation for muscle tissues in fish.
FiletFrac	unitless	Fraction of fish that is a filet based on lipid content.
FishWaterFrac	unitless	Water fraction across all tissues of fish.
LipFrac	unitless	Lipid fraction.
LipFracMus	unitless	Lipid fraction in fish muscle.
MaxPreyPref	unitless	Maximum dietary preference for item in the aquatic food web.
MinPreyPref	unitless	Minimum dietary preference for item in the aquatic food web.
MusWaterFrac	unitless	Water fraction in muscle of fish.
NumBiotaTypes	unitless	Number of biota types in the aquatic food web.
rho_lip	kg/L	Density of organic carbon.
rho_oc	kg/L	Density of lipids.
T3EdibleFish	unitless	Edible trophic level 3 fish for human consumption.
T3NumEdibleFish	unitless	Number of edible trophic level 3 fish in the aquatic food web.
T3NumFish	unitless	Number of trophic level 3 fish in the aquatic food web.

Table AF-2. Sl.ssf Input Parameters (Module-Specific Site Layout Inputs)

Input Parameters	Units	Description
NumWBN	unitless	Number of waterbody networks.
WBNFishableRchIndex	unitless	Index of reaches that are fishable.
WBNNumFishableRch	unitless	Number of fishable reaches.
WBNRchArea	m^2	Reach surface area.
WBNRchOrder	unitless	Reach order of stream.
WBNRchBodyType	unitless	Type of waterbody (e.g., pond, stream).
WBNTemp	degrees Celsius	Median temperature of waterbody network.
WBNTempMax	degrees Celsius	Maximum temperature of reaches in the waterbody network.

Table AF-3. Cp.ssf Input Parameters (Module-Specific Chemical Inputs)

Input Parameters	Units	Description
ChemT3musBAFm	L/kg ww	Empirical bioaccumulation factor in filet of TL3 fish.
ChemT3fishBAFm	L/kg ww	Empirical bioaccumulation factor in whole-body of TL3 fish.
ChemT4musBAFm	L/kg ww	Empirical bioaccumulation factor in filet of TL4 fish.
ChemT4fishBAFm	L/kg ww	Empirical bioaccumulation factor in whole-body of TL4 fish.
ChemaqmpBCFm	L/kg ww	Empirical bioconcentration factor for aquatic macrophytes.
ChembenthffBAFm	L/kg ww	Empirical bioaccumulation factor in benthic filter feeders.
ChemKm	1/day	Metabolic rate constant for fish.
ChemKow	unitless	Octanol/water partition coefficient.
ChemType	NA	Chemical Type.

Table AF-4. Sw.grf Input Parameters (Surface Water Input Parameters)

Input Parameters	Units	Description
WBNConcBenthTot	μg/g	Concentration of contaminant in benthic solids.
WBNConcBenthTotNY	unitless	Number of years in the time series corresponding to this variable.
WBNConcBenthTotYR	year	Time series of years corresponding to this variable.
WBNConcWaterTot	mg/L	Total contaminant concentration in surface water.
WBNConcWaterTotNY	unitless	Number of years in the time series corresponding to this variable.
WBNConcWaterTotYR	year	Time series of years corresponding to this variable.
WBNConcWaterDiss	mg/L	Freely dissolved contaminant concentration in surface water.
WBNConcWaterDissNY	unitless	Number of years in the time series corresponding to this variable.
WBNConcWaterDissYR	year	Time series of years corresponding to this variable.
WBNfocBenth	fraction	Benthivore fraction of organic carbon.
WBNfocBenthNY	unitless	Number of years in the time series corresponding to this variable.
WBNfocBenthYR	year	Time series of years corresponding to this variable.

Table AF-5. Af.grf Output Parameters (Aquatic Food Web Outputs)

Output Parameters	Units	Description
Caqmp	mg/kg ww	Concentration of contaminant in aquatic plants.
CaqmpNY	unitless	Number of years in the time series corresponding to this variable.
CaqmpYR	year	Time series of years corresponding to this variable.
Cbenthff	mg/kg ww	Concentration of contaminant in benthic filter feeders.
CbenthffNY	unitless	Number of years in the time series corresponding to this variable.
CbenthffYR	year	Time series of years corresponding to this variable.
CT3Filet	mg/kg ww	Concentration in filet of contaminant in TL3 fish.
CT3FiletNY	unitless	Number of years in the time series corresponding to this variable.
CT3FiletYR	year	Time series of years corresponding to this variable.
CT3Fish	mg/kg ww	Whole-body concentration of contaminant in TL3 fish.
CT3FishNY	unitless	Number of years in the time series corresponding to this variable.
CT3FishYR	year	Time series of years corresponding to this variable.
CT4Filet	mg/kg ww	Concentration in filet of contaminant in TL4 fish.
CT4FiletNY	unitless	Number of years in the time series corresponding to this variable.
CT4FiletYR	year	Time series of years corresponding to this variable.
CT4Fish	mg/kg ww	Whole-body concentration of contaminant in TL4 fish.
CT4FishNY	unitless	Number of years in the time series corresponding to this variable.
CT4FishYR	year	Time series of years corresponding to this variable.