Ecological Assessment of Selenium in the Aquatic Environment

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5 Bioaccumulation and Trophic Transfer of Selenium

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CONTENTS

5.1   INTRODUCTION

In this chapter we identify the state-of-the-science regarding selenium (Se) bioaccumulation and trophic transfer. We discuss Se bioaccumulation and how its unique attributes tie bioaccumulation to toxicity. We identify biodynamic modeling as a promising approach that can provide a unified view of the processes contributing to bioaccumulation and illustrate how this kinetic modeling can be used and improved. We also discuss the most important uncertainties that need to be addressed if we are to better understand and model Se bioaccumulation.

5.1.1   AREAS OF GENERAL SCIENTIFIC AGREEMENT

Concerns about environmental contaminants stem from their potential negative impacts on populations or even whole ecosystems. Potential impacts begin when individual organisms accumulate the contaminant, because organisms respond only to chemicals that are somehow associated with them (i.e., bound to membrane components or transported into cells). Contaminants that remain in abiotic environmental compartments (e.g., sediments, water) will not have direct effects. This fact is as true for biologically essential elements as for nonessential elements: Only the accumulated element can provide nutritional support for the organism. Thus, it is critical to understand the accumulation of these substances in order to evaluate their biological effects (nutritive or toxic). Selenium, which is both essential at low concentrations and toxic at elevated concentrations, is not unlike other essential but potentially toxic elements (e.g., Cu, Zn) where the organism must accumulate it from the environment in order to perform normal physiological functions but must regulate or otherwise refrain from accumulating too much to avoid toxicity.

Understanding bioaccumulation and trophic transfer is central to managing ecological risks from Se. Selenium bioaccumulation is relatively well studied, but there remain many research areas where advances in understanding could aid better management of ecological risks. Managing ecological risks from this element has been controversial in part due to the fact that at least some of the relatively well-established principles contradict the conventional preconceptions
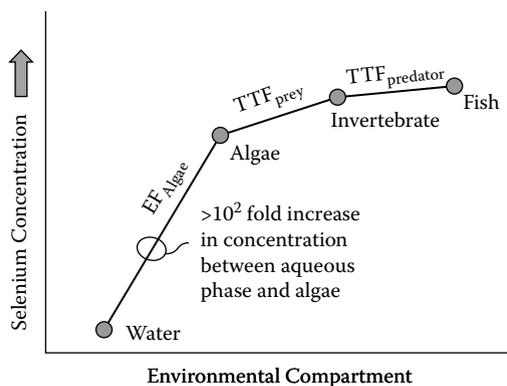
FIGURE 5.1 Selenium enrichment and trophic transfer in aquatic food webs. Enrichment function represents the increase in Se concentration between water and the base of the aquatic food web, which often is algae (EF_{algae}; range 10^2 to 10^6). Trophic transfer function represents the increase in Se concentration between algae and invertebrates (TTF_{prey}; range 0.6 to 23) and invertebrates and fish ($TTF_{predator}$; range 1 to 3).

and traditional approaches that are often used to manage metal contaminants. But the greatest challenge with managing risks is that neither Se bioaccumulation nor toxicity can be predicted from environment to environment based solely upon Se concentrations in water. This inability to predict is likely the basic reason for international incoherence and differences between freshwater and marine waters in water quality guidelines.

Ecological risks from Se are affected by uptake at the base of the food web, dietary exposure, dietary toxicity, and transfer through the food web. The direct toxicity of waterborne Se alone (the basis of most traditional risk assessment and risk management activities) tells us little if anything about ecological risks of exposure to Se. There is strong evidentiary support for the fundamental concept that the concentration of Se taken up into primary producers and microbes at the base of the food web is preserved and/or further concentrated as it is passed on to consumer organisms and their predators (Presser and Luoma in press; Luoma and Presser 2009) (Figure 5.1).

Ultimately, the poor linkage between dissolved Se and either bioaccumulated Se in the food web or Se toxicity is the reason that new risk assessment and risk management strategies are necessary for this element. That poor linkage at least partly reflects variability at each of the intervening steps in the conceptual model linking dissolved Se to its effects (Chapters 3 and 4). Uptake at the base of the food web is species- and environment-specific. Differences among species and environments also occur in the efficiency with which Se is assimilated and retained by consumer organisms at the second trophic level. Differences occur in the types of prey eaten by predators. Finally, risk assessments need to consider the toxic effects of the dose of Se achieved by each species (cf. Chapters 6 and 7).

5.1.2   ECOSYSTEM-SCALE AND BIODYNAMIC MODELS

Ecological risks from Se are distinguished by a complex interplay between bio-geochemical, biological, and ecological considerations. Biodynamic models can be useful in explaining the interactions among the biology- and environment-specific functions that ultimately define bioaccumulation and therefore ecological risks from Se, especially if the model is used as part of the process of defining linkages in the ecosystem-scale conceptual model for Se risks (Chapter 3). Biodynamic modeling can help risk managers understand their ecosystem and forecast the outcomes of risk management decisions. But use of those models requires application of biological and ecological principles heretofore underutilized in ecotoxicology, risk assessment, and risk management.

Selenium partitioning to biological material in the first step of the food web is difficult to predict and sometimes to measure. Selenium partitioning from water to tissues is not adequately described by useful constructs (e.g., fugacity) for understanding organic contaminant behavior, nor are geochemical or thermody-namic equilibrium approaches even remotely predictive. Rather, Se partitioning is primarily a biologically mediated process. For this reason, water–organism bio-accumulation factors (BAFs) have limited predictive value because critical inter-vening steps in the food web between water and higher organisms that vary from environment to environment cannot be considered in this simple ratio. However, a slightly more complex model can consider those factors. For example, the concen-tration of Se in plants or microbes at the base of the food web is a crucial input to such a model, although isolation of algae and microorganisms from whole seston or sediment samples from the field can be difficult. If it is not possible or practical to isolate biotic and abiotic components of particulate phases, an environment-specific EF may be operationally based on the relationship between Se concentra-tion in water and whole seston or sediment. But better strategies for quantifying uptake at this first step of the food web are an important research need.

The combined influence of environmental Se concentrations and physiologi-cal processes on bioaccumulation can be integrated in a biodynamic or biokinetic model (Luoma et al. 1992; Wang et al. 1996a; Luoma and Fisher 1997; Wang and Fisher 1999; Luoma and Rainbow 2005; Wang and Rainbow 2008). These models provide a broad framework for addressing controls of contaminant bioaccumula-tion and can be used for evaluating contaminant bioavailability and determining the relative importance of different routes of contaminant accumulation (Wang et al. 1996a; Wang and Fisher 1999). They are flexible enough to incorporate environmental variability in contaminant sources, contaminant concentrations, food availability, and organism growth rates in their predictions of the concen-trations of Se accumulated by an organism. One widely used version of these models treats contaminant accumulation as a first-order function of contaminant concentrations in particles and water and is expressed as

$$\frac{dC}{dt} = (k_u \times C_w) + (\text{AE} \times \text{IR} \times C_f) - (k_e + k_g) \times C \tag{1}$$

where C is the contaminant concentration in the animals (mg/kg), t is the time of exposure (d), k_u is the uptake rate constant from the dissolved phase (L/g/d), C_w is the contaminant concentration in the dissolved phase (µg/L), AE is the assimilation efficiency from ingested particles (%), IR is the ingestion rate of particles (mg/g/d), C_f is the contaminant concentration in ingested particles (µg/mg), k_e is the efflux rate constant (/d), and g is the growth rate constant (/d). At steady state, this equation simplifies to

$$C_{ss} = \frac{(k_u \times C_w) + (AE \times IR \times C_f)}{(k_e + k_g)} \tag{2}$$

where C_{ss} is the steady-state concentration of contaminant in the organism (mg/kg). The efflux parameter, k_e, can be further split into solute (k_{ew}) and food (k_{ef}) components if the loss rates from these exposure regimes differ, where

$$C_{ss} = \frac{k_u \times C_w}{k_{ew} + k_g} + \frac{(AE \times IR \times C_f)}{k_{ef} + k_g} \tag{3}$$

If it is assumed that food is the dominant source of uptake of Se, a particularly useful format from the model is derivation of a trophic transfer function (TTF), where

$$TTF = \frac{(AE \times IR)}{(k_{ef} + k_g)} \tag{4}$$

The TTF is species-specific, may vary with dietary Se concentration, and is affected by factors that affect AE and IR. It will be affected by factors that affect AE and IR. Indeed, a number of environmental and biological factors can influence each of the parameters used in the equations (AE, k_e, k_u, etc.) and that caution should be used in applying just a single value. In Section 5.3 we consider the elements of the biodynamic model in detail and discuss ways to improve application of this concept (see also Text Box 1). We also evaluate sensitivities to uncertainties in model parameters and conduct some simple forecasts to demonstrate uses of the model.

Lastly, in some situations it may not be practical or even possible to derive a food web model based on kinetic data. For example, kinetic data for Se bioaccumulation in freshwater invertebrates are largely lacking (Section 5.2.6.2). Also, some biota consume such a wide variety of prey species that generating kinetic data for each food web linkage could be time consuming and costly. In such cases, it may be more appropriate to generate a TTF based on a ratio of the field-measured Se concentration in a consumer to that found in known or inferred dietary organisms. Such values could be used in addition to, or as an alternative to, laboratory-derived kinetic data for construction of a site-specific food web model.

TEXT BOX 5.1: NEW TERMINOLOGY

Traditionally the term "K_d" has been used to describe the relationship between contaminant concentration in water and accumulation by particles, including living cells. In addition, the term "uptake rate constant" (K_u) has been used to describe the relationship between contaminant concentration in water and uptake rate by single-celled organisms, invertebrates, and fish. The relationship between prey and predatory contaminant concentration is traditionally referred to as the "trophic transfer factor." In this book we refer to enrichment of Se by particles, including single-celled organisms, such as algae, as "enrichment function" (EF); uptake from the dissolved phase is referred to as "uptake rate function"; and trophic transfer is referred to as "trophic transfer function" (TTF). These new terms recognize that entry into the food web from the dissolved phase, and likely also transfer from prey to predator, are dependent on concentration in a non-linear manner.

For Se and many other elements, uptake by microorganisms and multicellular organisms is governed by specific transport pathways that facilitate the movement of the element in question from the environment and across cell membranes or epithelia into the organism. These transport pathways, which consist of trans-membrane proteins, may differ with respect to specificity but typically display high affinity for the element and a limited maximal capacity for uptake (Section 5.2.2). An important consequence of such high-affinity, limited-capacity uptake pathways is that elemental uptake from low ambient concentrations, is highly efficient but becomes less efficient at higher concentrations due to saturation of the uptake pathway. This non-linear relationship between ambient concentration and uptake rates is better described by a Michaelis-Menten relationship (Section 5.3.1.1) than by a single constant or factor. Recognizing that non-linear relationships exist between uptake and ambient concentrations, we recommend the use of "enrichment function" and "uptake rate function" as terms to describe uptake from water by microorganisms and multicellular organisms, respectively.

Elemental uptake from dietary sources is also conducted via more or less specific uptake pathways (Section 5.2.2), resulting in relatively high uptake efficiency (or assimilation efficiency [AE]) from low dietary elemental concentrations and less efficient uptake at higher concentrations. This non-linear relationship between dietary exposure concentration and AE (Section 5.3.1.2) has implications for trophic transfer. These implications are particularly relevant for Se for which dietary sources in general dominate its accumulation by animals; the concentration dependence of AE leads to predictions of a nonlinear relationship between dietary exposure and trophic transfer. For this reason, we suggest "trophic transfer function" rather than "trophic transfer factor" to describe how biomagnification may depend on elemental (in this case, Se) concentrations in prey organisms.

5.2 PROCESSES THAT CONTROL Se CONCENTRATIONS IN FOOD WEBS

5.2.1 Physiological Requirements for Se

A total of 30 seleno-protein families are known, and seleno-proteins are found in all lineages of life illustrating the essentiality of Se (Kryukov et al. 2003; Kryukov and Gladyshev 2004; Castellano et al. 2005; Zhang et al. 2005). Specifically, proteins containing the 21st natural amino acid selenocysteine (Sec) are found in all 3 major forms of life (bacteria, Archaea, and eukaryotes) (Hatfield et al. 1999). Fish possess the most prolific selenoproteomes, with as many as 30 individual selenoproteins, but in general selenoproteomes are small (Vanda Papp et al. 2007). Although the function of many selenoproteins remains to be described, some, such as glutathione peroxidases, thioredoxin reductases, iodothyronine deiodinases, and selenophosphate synthetases, have been ascribed physiological functions. Studies with mice have illustrated the essentiality of at least some thioredoxin reductases and glutathione peroxidases (Vanda Papp et al. 2007). All the above proteins have oxidoreductase functions; a process as fundamental as DNA synthesis, for example, depends on Se in the catalytic site of thioredoxin reductases (Vanda Papp et al. 2007).

A minimum Se intake (or uptake) is required for normal physiological function. The recommended daily Se intake in humans is ~0.6 µg Se/kg/d as organic Se, a dose that is hypothesized to have primarily antioxidant and immune-strengthening effects, while doses as much as 10-fold higher have been reported to have specific cancer-preventive properties (Rayman 2002; Bügel et al. 2008). In comparison, channel catfish have been reported to require 0.1 to 0.5 mg Se/kg diet (ww) as inorganic Se, which, with an assumed feeding ration of 5% body weight per day, translates to 5 to 25 µg/kg/d (Gatlin and Wilson 1984), and rainbow trout requires a minimum of 3.5 µg/kg/d as inorganic Se (Hilton et al. 1980). In agreement with these studies are more recent studies of juvenile grouper fed a diet containing selenomethionine indicating a requirement of 0.7 mg Se/kg or, at 5% body weight daily ration, 35 µg/kg/d for optimal growth (Lin and Shiau 2005). Aquatic birds show deficiencies below dietary concentrations of 0.3 to 1.1 mg Se/kg (Puls 1988; Ohlendorf 2002), suggesting similar Se demands in most vertebrates examined to date. Limited information is available about Se requirements for aquatic invertebrates, which clearly marks a subject in need of study. However, a single study demonstrates that 20 mg/kg Se as inorganic Se appears optimal for shrimp (Tian and Lui 1993), a value that falls well above the range reported for optimal vertebrate physiology. Selenium requirements have been documented for the unicellular freshwater green alga *Chlamydomonas reinhardtii* in which 3.9 µg/L enhanced growth compared to "Se" conditions (Novoselov et al. 2002). *Dunaliella viridis*, a green alga typically found in saline systems, showed increased growth with increasing Se concentrations up to 18 µg/L (Martin Grosell, University of Miami, personal communication). In comparable experiments, diatoms in general appear to accumulate substantially more Se than green algae (Table 5.1), but interestingly seemed to have a lower Se requirement of 0.7 µg Se/L for 50% maximal growth (Price et al. 1987; Harrison et al. 1988). For the freshwater cladoceran *Daphnia magna*, Keating and Dagbusan (1984) suggested that 1 µg Se/L was sufficient to satisfy minimal needs.

TABLE 5.1

Degrees of Enrichment (× 10^4) of Se in Algal Cells Relative to Ambient Seawater (Dissolved) Following Exposure to Either 0.15 nM (0.012 μg/L) or 4.5 nM (0.36 μg/L) Selenite for 4 Days. Values are Calculated as Moles Se/μm^3 Cell Volume Divided by Moles Se/μm^3 in Water. nd: Not Determined. Data from Baines and Fisher (2001)

Algal Species	Selenite Concentration (nM)	
	0.15	4.5
Diatoms		
Chaetoceros gracilis	2.8	0.21
Thalassiosira pseudonana	45	2.5
Skeletonema costatum	0.004	0.01
Chlorophytes		
Chlorella autotrophica	0.4	0.003
Dunaliella tertiolecta	1.0	0.04
Nannochloris atomus	0.5	0.002
Cryptophytes		
Chroomonas sp.	nd	0.02
Cryptomonas sp.	41	1.1
Rhodomonas salina	nd	0.007
Dinoflagellate		
Prorocentrum minimum	26	1.3
Prasinophytes		
Pycnococcus provasolii	nd	15
Tetraselmis levis	nd	1.0
Prymnesiophytes		
Emiliania huxleyi	280	8.2
Isochrysis galbana	nd	6.8

5.2.2 CELLULAR SE UPTAKE PATHWAYS

The essentiality of Se means that specific cellular uptake pathways have evolved to facilitate high-affinity Se uptake. Unicellular algae possess Se uptake pathways, allowing for accumulation during exposure to low ambient concentrations (see Section 5.2.3), and can absorb inorganic as well as organic Se. Freshwater green algae display uptake of selenite, selenate, and selenomethionine, with the uptake rates for selenomethionine exceeding those for inorganic Se. Uptake of both selenate and selenomethionine shows saturation kinetics illustrating the involvement of specific transmembrane transport proteins (i.e., carriers) (Fournier et al. 2006). In contrast, uptake of selenite in freshwater green algae was found to be a linear function of ambient concentration, showing no evidence for carrier-mediated uptake (Fournier et al. 2006). Such Se uptake patterns are not unique to green algae and have been reported also for cyanobacteria and diatoms, along with strong evidence for non-passive, carrier-mediated uptake of selenate, selenomethionine, and also

selenite (Riedel et al. 1991). To our knowledge, the molecular identity of carriers involved in uptake of inorganic Se in algae remains to be revealed, but it is clear there is a competitive interaction between sulfate (or phosphate) and selenate. Such competitive interactions are not unique to algae and have been documented by either sulfate-induced differences in Se toxicity or Se uptake or accumulation for higher plants (Hurd-Karrer 1938), yeast (Fels and Cheldelin 1949), bacteria (Brown and Shrift 1980, 1982), and a range of invertebrates from freshwater and saline environments (Hansen et al. 1993; Maier et al. 1993; Forsythe and Klaine 1994; Ogle and Knight 1996; Brix et al. 2001). At least in humans, it appears that the interaction between cellular sulfate and Se uptake pivots around a NaS_2 transporter capable of cellular uptake of oxyanions of Se and chromium (Miyauchi et al. 2006) and is thus dependent on the electrochemical gradient for Na^+.

While the pathway of seleno-amino acid absorption by algae displays high affinity, its molecular identity is unknown. However, recent studies on Se uptake by human intestinal and renal cells reveal the nature of carrier-mediated Se uptake by vertebrate intestinal epithelia and the nature of renal seleno-amino acid re-absorption (Nickel et al. 2009). The major route for cellular selenomethionine uptake by intestinal cells and kidney cells appears to be a b^0 family of amino acid transporters, which show high substrate affinity. In kidney cells the b^0 transporter, which is an electrogenic Na^+:amino-acid co-transporter, transporting uncharged amino acids, confers high affinity selenomethionine uptake. In intestinal cells, the b^0 amino-acid transporter, $b^{0,+}$ rBAT which is a Na^+-independent, high-affinity transport system for neutral and dibasic acids, is responsible for selenomethionine uptake. The $b^{0,+}$ rBAT, transporter functions as an exchanger and is found both in the kidney and intestine (Nickel et al. 2009). Both intestinal and kidney b^0 seleno-amino acid transporters display affinity constants in the sub-mM range, which makes them likely candidates for Se uptake from diets containing Se concentrations in the low mg/kg range. Notably, only seleno-aminoacids, and not seleno-derivates like selenobetaine and selenocystamine, are transported by the b^0 amino acid transporters.

The generality of b^0 transporters being involved in dietary Se uptake in lower vertebrates and in invertebrates remains to be examined. However, studies of Se assimilation efficiency by *Artemia fransiscana* fed Se-enriched green algae demonstrates that part of the intestinal Se absorption in this invertebrate is by transport systems with an affinity for Se in the low mg/kg range (Martin Grosell, University of Miami, personal communication). The similarity between intestinal affinity for dietary Se uptake in *Artemia*, dietary Se requirements in the low mg/kg range for fish and birds (Section 5.2.1), and the affinity constant for the mammalian seleno-amino acid transport systems in the b^0 family suggests a widespread distribution of seleno-amino acid transport systems. It thus appears that cellular selenoproteomes, as well as membrane-associated Se uptake pathways, are evolutionarily conserved to support homeostasis of the essential element Se.

5.2.3 IMPLICATIONS OF CELLULAR UPTAKE PATHWAYS FOR SE ACCUMULATION IN FOOD WEBS

As a consequence of high-affinity Se uptake pathways, aquatic organisms display an ability to accumulate Se concentrations sufficient for normal physiological function even in the presence of low ambient and dietary Se concentrations. The implications

of saturable, high-affinity uptake systems for Se accumulation in aquatic organisms might then include expectations of apparent bioconcentration, bioaccumulation, and TTFs to be highest at the lowest ambient and dietary Se concentration and decline as Se exposure concentrations increase. A relationship of decreasing bioconcentration factors (BCFs) or BAF with increasing aqueous exposures has been documented for a number of metals and Se on the basis of field observations (McGeer et al. 2003; DeForest et al. 2007). However, no such relationship has been documented for TTFs for metals relative to dietary exposures. Indeed, laboratory experiments to test these mechanisms are difficult to conduct because at the highest concentrations, factors other than physiology, such as behavior (e.g., feeding inhibition), become more important in regulating uptake by organisms (Croteau and Luoma 2008). In the field, determining such relationships becomes even more difficult due to shifting biological species found across the spectrum of dietary exposures being tested and the paucity of organisms found at the highest concentrations. Finally, multiple transport systems are known for other constituents wherein a higher-capacity, lower-affinity transport process takes over once the high-affinity, low-capacity system is saturated (i.e., at higher concentrations in the gut or, for algae, in the water). One result is the perception of linear uptake over a wide range of concentrations, albeit at a lower slope than in the low concentration system. Much remains to be learned about Se transport and its implications for bioaccumulation across wide concentration ranges.

5.2.4 FOOD WEB BASE

5.2.4.1 Accumulation of Inorganic Se by Algae

Understanding the extent to which Se builds up in aquatic food webs necessarily starts at the base of each food web because diet comprises the largest, and often nearly the entire, source of Se for most aquatic animals, and because by far the largest bioconcentration step of Se from the aqueous phase into organisms is its bioconcentration by the microorganisms (algae and bacteria) that serve as the food web base. Considerably more studies have been conducted to assess the factors that govern the bioaccumulation of Se into algae than have addressed the bioaccumulation of Se into bacteria or other microorganisms (e.g., protozoa, fungi).

Like many other inorganic and organic contaminants, the microorganisms at the base of the food web bioconcentrate Se up to 10^6-fold from ambient water (Baines and Fisher 2001), but there are several key factors that distinguish the accumulation of Se from that of most other contaminants. First, Se is an essential element for algae (Doucette et al. 1987; Price et al. 1987) and its uptake is a non-passive, carrier-mediated process (Section 5.2.2). That is, cells need to expend energy to take up dissolved Se, and dead cells display negligible uptake of Se (Fisher and Wente 1993). Further, the various dominant species of aqueous Se — selenite, selenate, and organic selenides — can be accumulated at significantly different rates, and can be greatly influenced by water chemistry. This is particularly true for selenate because this form of Se is taken into algal cells through the sulfate uptake pathway (Shrift 1954; Fisher and Wente 1993). Indeed, when excess concentrations of Se are taken into a cell, Se can behave as an S analog in algae and other plants; the proteins and enzymes that have Se substituting for S may not function properly and this may account for

Se's toxicity. Because sulfate concentrations in seawater are 7 orders of magnitude greater than selenate concentrations, the uptake rate of selenate by marine algae is particularly low and often unmeasurable, unlike in fresh waters where sulfate levels are far lower. Selenite, by contrast, is rapidly accumulated by these same cells and is generally the preferred form over selenate taken up by diverse algal cells (Riedel et al. 1991; Hu et al. 1997).

Selenium exists primarily in anionic form and does not appreciably sorb to suspended particles (which carry a negative surface charge), so mixtures of living phytoplankton and non-living material that commonly compose seston (especially in coastal waters) would be expected to display lower degrees of Se enrichment than in pure phytoplankton assemblages, which is consistent with field observations (Cutter 1989; Doblin et al. 2006). Because the uptake of Se is carrier mediated and follows typical Michaelis-Menten kinetics, Se concentrations in algae do not linearly reflect ambient concentrations, particularly as ambient concentrations approach those that saturate carrier systems (approximately 10 nM [0.79 µg/L] for selenite for diatoms) (Baines and Fisher 2001). Consequently, increases in dissolved selenite concentrations in the 0.1 to 10 nM (0.0079 to 0.79 µg/L) range result in a 3.5-fold increase in marine algal Se levels.

Because Se uptake requires energy, equilibrium partitioning between dissolved and particulate phases does not apply for Se. Further, once cells take up Se, it is rapidly converted to organic selenides, so the concept of equilibrium partitioning between organic selenides and ambient inorganic Se is inappropriate. Thus, the term "distribution coefficient" (K_d) as a descriptor of the enrichment of Se in particulate matter relative to ambient water, is misleading. Still, it is recognized that microorganisms such as bacteria and algae can become greatly enriched relative to ambient water for selenite. Degrees of enrichment can exceed 10^6 in axenic cultures, with most algal species exceeding 10^4 (Baines and Fisher 2001). This initial bioconcentration step (from the dissolved phase into living cells) is clearly the greatest of any of the accumulation steps in an aquatic food chain. Therefore, the extent to which algal or bacterial cells are enriched with Se is a major determinant of Se contamination throughout a food web.

Another significant difference between Se bioconcentration in algae and that of most cationic metals is the large inter-specific variations among algal taxa (Wrench and Measures 1982; Harrison et al. 1988; Vandermeulen and Foda 1988; Riedel et al. 1991; Fisher and Wente 1993; Baines and Fisher 2001; Wang and Dei 2001), not unlike the variability in terrestrial plant Se requirements (Brown and Shrift 1982). In fact, degrees of Se enrichment relative to ambient water among different marine algae vary up to 5 orders of magnitude, from about 30 to well over 10^6 under the same environmental conditions (Baines and Fisher 2001). Such differences probably result from inter-specific differences in Se cellular requirements but possibly also from different capabilities of cells to regulate Se uptake. In contrast, inter-specific differences in uptake for metals that require no energy expenditure typically display less than 1 order of magnitude variation in cell volume-normalized concentration factors (Fisher and Reinfelder 1995). Much of the inter-specific variability for cationic metal concentration factors can be attributed to cell size, with highest concentration factors associated with the smallest cells and thus the

highest surface-to-volume ratios (Fisher and Reinfelder 1995). This pattern is not seen for Se.

Because of the high inter-specific variability in Se bioconcentration, it follows that the degree to which organisms at the base of the food web can be enriched sources of Se could vary tremendously with algal species composition (Table 5.1). Spatial and temporal variability in algal community structure could therefore have a pronounced effect on the bioavailable Se in algal cells. Typically, among marine forms, the chlorophytes show the lowest degree of enrichment (Wang and Fisher 1996a; Baines and Fisher 2001; Wang and Dei 2001), possibly reflecting lower cellular requirements or, alternatively, greater regulation of Se uptake. While there is some regulation of Se uptake in algal cells, there also appears to be "luxury" uptake, in excess of requirements, of this nutrient in at least some algal species (Harrison et al. 1988; Baines and Fisher 2001), as has been noted for many other nutrients.

In any case, bodies of water that are dominated by chlorophytes could be expected to have lower algal Se available for herbivores than waters dominated by other algae (e.g., diatoms, prasinophytes, dinoflagellates, prymnesiophytes). Even within the same taxonomic group, Se uptake can also vary greatly. For example, the diatom *Skeletonema costatum* accumulates much less Se than other diatom species such as *Thalassiosira pseudonana* (Table 5.1). The species composition of algal communities varies with nutrient concentrations and ratios (Chisholm 1992), vertical stratification and mixing (Margalef 1978), selective grazing pressure (Smetacek et al. 2004), and salinity variations (Cloern and Dufford 2005). Thus, a body of water could have seasonally variable Se concentrations in herbivores that reflect these changes in algal communities. As will be evident later in this chapter, such differences in algal composition could result not just in differences in herbivore Se levels but in differences in Se tissue concentrations in organisms higher in the food web.

5.2.4.2   Accumulation of Se by Bacteria

Marine and freshwater bacteria have also been shown to bioconcentrate selenite from water (Foda et al. 1983; Riedel and Sanders 1996; Baines et al. 2004). For example, in California's San Francisco Bay Delta waters, Se uptake in the 0.2 to 1.0 µm size fraction accounted for 34% to 67% of the Se uptake in the dark, and bacterial Se:C ratios were up to 13 times those of phytoplankton (Baines et al. 2004). Consequently, bacterial cells may serve as especially enriched sources of organic selenides for bacterivores. This is an understudied aspect of the biogeochemical cycling of Se in aquatic food webs that deserves further study.

5.2.4.3   Organic Selenide Uptake and Cycling

Once selenite is taken into a cell, it is readily converted to organo-selenium compounds such as selenomethionine and selenocysteine, as well as to polypeptides (Shrift 1954; Wrench 1978; Wrench and Campbell 1981; Bottino et al. 1984; Fisher and Reinfelder 1991; Besser et al. 1994; Riedel et al. 1996), such as glutathione peroxidase (Price and Harrison 1988). Thus, animals that ingest algae are exposed primarily to organic forms of Se rather than inorganic forms. The assimilation of ingested selenides by herbivores grazing on phytoplankton is considered in Section 5.2.5. For some algal

species, such as the common centric diatom *Skeletonema costatum*, the degree of enrichment of Se varies with the physiological state of the cell, where rapidly growing cells are far less enriched than cells entering senescence; many other species, including other diatoms, do not display this pattern (Baines and Fisher 2001). Thus, biological variability in Se demand, perhaps in response to oxidative stress, is likely to account for some of the pronounced differences in algal Se concentrations.

Plants, phytoplankton, and epilithic organisms release their organic selenides into ambient water through excretion, through cell lysis, or when grazed upon by herbivores. Once cells die and decompose, Se is released rapidly into ambient water, at rates comparable to that of organic carbon (Lee and Fisher 1992a, 1993; Fisher and Wente 1993). Similarly, for dead zooplankton, Se is lost from copepod carcasses and fecal pellets at rates similar to that of carbon with half-lives of only about 1 day in copepod carcasses (Lee and Fisher 1992b). In general, bacterial decomposition enhances Se loss from decomposing phyto- and zooplankton. Viral lysis of algal cells has also been shown to enhance Se release rates into seawater, and this released Se is as highly bioavailable as selenite to other algal cells (Gobler et al. 1997). This finding is consistent with observations that organic selenides (i.e., lysates of diatoms) are accumulated by marine phytoplankton at rates and to extents comparable to those for selenite (Baines et al. 2001). As with selenite, the chlorophytes display significantly lower accumulation of organic selenides than other algal forms (Baines et al. 2001). Similarly, Riedel et al. (1991) showed that selenomethionine can be readily accumulated by freshwater phytoplankton. Thus, models that consider the bioaccumulation of Se in aquatic food webs must take into consideration the high bioavailability of organic selenides, especially at the base of the food web. Given that organic selenide concentrations can approach those of inorganic Se forms and can account for 80% of the dissolved Se in open ocean surface waters (Wrench 1983; Cutter 1989; Cutter and Cutter 1995), bioaccumulation of organic selenides by algae and bacteria is arguably important and has largely been under-studied. Although much of the organic selenide pool in ocean surface waters is surely more refractory than the labile forms released by algal cell lysis (Cutter and Bruland 1984; Cutter and Cutter 1998), the cycling of dissolved organic carbon (DOC) and dissolved organic Se (DOSe) in the oceans suggest that DOC has a much longer residence time and is probably more resistant to biological degradation and uptake than organic selenides (Baines et al. 2001). The release of organic selenides and their subsequent bioaccumulation by plankton (i.e., biological recycling) helps explain the nutrient-type vertical profile seen for Se in oceanic water columns (Measures and Burton 1980; Cutter and Bruland 1984) and its relatively long residence times in ocean surface waters (Broecker and Peng 1982). Enhanced recycling of organoselenium released by decomposing biological material likely also contributes to elevated Se in biota inhabiting lentic compared to lotic freshwater environments (Orr et al. 2006).

5.2.5 IMPORTANCE OF DIETARY INTAKE OF SE

If only contaminants that are associated with an organism can elicit toxic effects, then understanding the extent to which Se can be accumulated by different aquatic organisms under different environmental conditions is of toxicological relevance.

In addition, toxicity is dependent on the exposure route (aqueous vs. dietary; Hook and Fisher 2001), so delineating the sources of Se accumulation is important for the toxicological interpretation of contamination to aquatic organisms. Water quality criteria or guidelines for Se recognize that chronic toxicity tests in which organisms were exposed to Se only through water require unrealistically high aqueous concentrations to reach body burdens and elicit chronic responses seen in nature (USEPA 2004). Dietary exposures (and trophic transfer) are important pathways for Se accumulation in aquatic invertebrates and fish (Lemly and Dimmick 1982; Luoma et al. 1992; Besser et al. 1993).

Figure 5.2 shows the relative contribution of dietary trace element uptake in various aquatic invertebrates, which can be inferred based on Equation 5:

$$\% \text{ Dietary uptake} = \frac{(\text{AE} \times \text{IR} \times C_f)/(k_{ef} + g)}{C_{ss}} \times 100 \tag{5}$$

It is clear from this figure that Se, more than any other trace element considered, is accumulated overwhelmingly from dietary exposure. The relative importance of dietary exposure for other trace elements varies among metals and with such factors as aqueous metal concentration, metal content in food, and food quantity. For Se, the contribution of dietary intake in a variety of aquatic organisms (i.e., marine worms, bivalves, crustaceans) that consume very different diets was consistently high, with more than 90% of Se body burdens derived from dietary exposure. This difference in the relative importance of metal uptake pathways is likely due to relatively high assimilation efficiencies for Se and low uptake rates from solution.
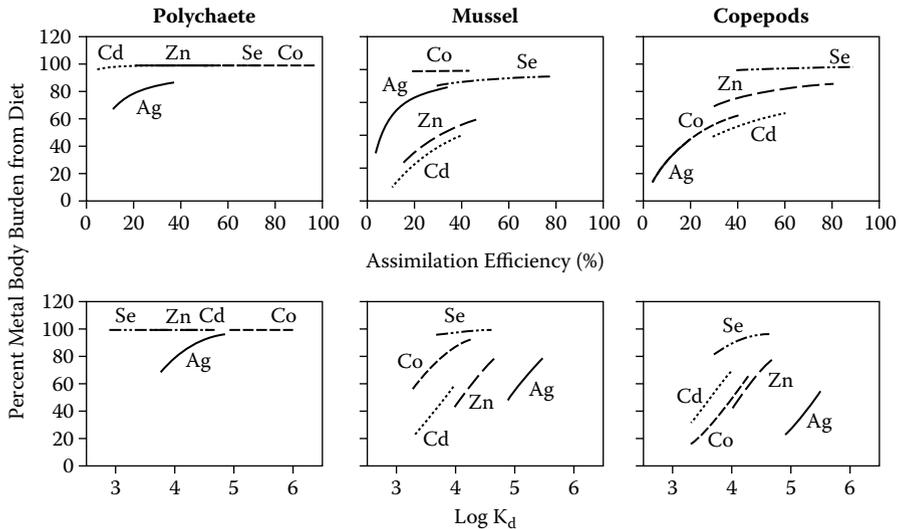

FIGURE 5.2 Percent of uptake from diet of different metal species by marine invertebrates as a function of assimilation efficiency and K_d. Reprinted from Wang and Fisher 1999, with permission from Elsevier.

For organisms higher in the food web (e.g., fish, birds) more kinetic data are needed, but nevertheless, there is evidence from both laboratory and field studies that dietary exposure is a major route for Se accumulation (Besser et al. 1993). In the mangrove snapper, *Lutjanus argentimaculatus*, nearly all Se in the fish was due to dietary uptake primarily because of the extremely low aqueous uptake rate (lowest k_u = 0.0008 L/g/d; Xu and Wang 2002a). Presser and Luoma (in press) examined the relationship between predicted (from food alone) and measured Se body burdens in fish collected in the field (both freshwater and marine). They observed a striking 1:1 relationship between model predictions and measured Se body burdens in fish, suggesting that Se body burdens in fish can be accurately predicted solely on the basis of dietary intake. Indeed, field studies have shown that dietary pathways (rather than aqueous Se concentrations) can explain differences in Se body burdens between predator fish (Stewart et al. 2004).

Presser and Luoma (in press) further examined the relationship between modeled and observed Se body burdens in aquatic invertebrates, neglecting aqueous intake of Se. Predicted Se concentrations in invertebrates were lower than observed by about 15% (slope = 0.86). This prediction suggests that while dietary intake is still the most important exposure route for Se accumulation in invertebrates, aqueous uptake may not be negligible for certain species. For example, *Dreissena polymorpha* (zebra mussel), *Artemia fransiscana*, and *Daphnia magna* show very high uptake from water (k_u = 0.05 to 0.43). In addition to the high uptake rates of dissolved Se, the zebra mussel exhibits low dietary Se assimilation efficiency (<46%) leading to an estimated 24% to 61% contribution from dissolved Se to the Se burden in this bivalve (Roditi and Fisher 1999; Roditi et al. 2000a, 2000b). Tsui and Wang (2007) predicted that about 20% to 40% of Se body burden in the freshwater cladoceran *D. magna* was due to uptake from the aqueous phase; this percentage was noted to be higher than predicted for a variety of marine animals. A higher contribution of aqueous Se was mainly due to moderate dietary assimilation efficiency (20% to 60%), as well as relatively high aqueous uptake of Se in daphnids (Yu and Wang 2002). In contrast, relatively high dietary Se assimilation efficiencies (>80%) in *A. fransiscana* still amount to a relatively modest dietary Se uptake when feeding on green algae, because the green algae contain relatively low Se concentrations compared to diatoms (Section 5.2.4.1) (Martin Grosell, University of Miami, personal communication). Thus, the relatively low dietary Se uptake in *Artemia* combined with a high K_u results in a contribution from dissolved Se of >50% (Martin Grosell, University of Miami, personal communication).

A partial explanation for the relatively high contribution of dissolved Se uptake in the 3 species discussed in the previous paragraph could be that green algae, in general, accumulate less Se than other unicellular algae (Sections 5.2.2 and 5.2.5) and that dietary uptake, even with a high assimilation efficiency, is limited due to low dietary Se concentrations. Under conditions of modest dietary Se availability, uptake from the dissolved phase across respiratory surfaces (uptake rate function) may be elevated to meet requirements for essential Se. However, low Se accumulation in green algae cannot be the only universal explanation for the above 3 examples of relatively high contributions from the dissolved phase. Zebra mussels, for example, show low assimilation efficiency of Se regardless of whether they are feeding on

green algae, diatoms, cyanobacteria, or bacteria (Roditi and Fisher 1999). Thus, it appears that, in addition to the limited Se availability in diets consisting of green algae, overall low assimilation efficiency in the zebra mussel may be part of the explanation for the relatively high contribution from dissolved Se. The form of Se may also play a role in the importance of dissolved uptake. Where bioaccumulation studies have distinguished between inorganic and organic Se uptake, it has been found that organic forms of Se are more readily accumulated from aqueous exposure (Besser et al. 1993; Baines et al. 2001), so in water bodies where organic Se concentrations are elevated, aqueous Se uptake may not be negligible.

5.2.6 INVERTEBRATES

Invertebrates form a critical link in ecosystems between primary producers and higher-level consumers and can play an important role in the trophic transfer of many contaminants. In the case of Se, where dietary exposure pathways tend to dominate, the ways in which invertebrates differ in their accumulation are central to the discussion of Se behavior and effects in ecosystems. While we cannot ignore that there are cases where accumulation of Se from water can be important in invertebrates, most of this discussion will focus on dietary exposure pathways. With this in mind, there are 2 major ways in which invertebrates can differ in their Se accumulation from the environment: 1) diet choice (different species ingest food items that are differentially loaded with Se) and 2) physiological processing (differential assimilation and retention of dietary Se in tissues). Given the tremendous biodiversity of aquatic invertebrates, these life history (diet choices) and physiological processes (Se assimilation, retention) can and do vary widely.

Differences in Se concentrations in invertebrate tissues among sympatric species can be profound. Until biodynamic modeling approaches provided a mechanistic understanding of why and how inter-specific differences in Se body burdens occur, we were limited to simply describing them from site to site with limited predictive power. Biodynamic modeling now provides a mechanistic basis for understanding and predicting Se bioaccumulation differences among species.

5.2.6.1   Biodynamic Controls on Se Accumulation

Typically, marine invertebrate assimilation of Se from primary producers is an efficient process (usually 70% to 90%) (Table 5.2). One major driver of Se bioaccumulation differences among species is elimination (K_e). For example, in San Francisco Bay, Se concentrations in benthic clams ranged from 5 to 20 mg/kg dw, while crustacean zooplankton ranged from 1 to 4 mg/kg dw over the same exposure period and location (Stewart et al. 2004). This difference was largely explained by the fact that clams tend to eliminate Se at a rate that is 8 to 10 times slower than crustaceans. Variations within taxonomic groups exist, but to a lesser degree (~2-fold differences). The reasons for these differences in loss are not well understood but appear to be related to the efficiency with which organisms recycle proteins that contain Se (Wright and Manahan 1989; Manahan 1990; Wright 1995).

Table 5.2 summarizes the studies that have been conducted on assimilation of Se from algal diets in diverse invertebrates. Presently, marine and estuarine invertebrates

TABLE 5.2

Reported Assimilation Efficiencies (AEs), Efflux Rates Following Dietary Uptake (k_{ef}), Uptake Rate Constants from the Aqueous Phase (k_u), and Elimination Rates Following Uptake from the Aqueous Phase (k_{ew}) for Animals Feeding on Phytoplankton. All Data Are for Marine Animals Except _D. polymorpha_, Which Is a Freshwater Species. When More Than 1 Algal Species Was Used as a Diet, a Range of Values Is Given. When Only 1 Algal Species Was Used, Mean Values + 1 SD Are Given, Where Available. *Denotes Study with _M. edulis_ of Different Sizes (1.5 to 5 cm)

Species		AE (%)	k_{ef} (/d)	k_u (L/g/d)	k_{ew} (/d)	Reference
Mytilus edulis	Mussel	74–86; 15–72; 8–86; 72–81*	0.02–0.05; 0.02; 0.055–0.065; 0.048–0.075*	0.035; 0.032–0.039; 0.033–0.082*	0.019 + 0.005; 0.018–0.022*	Wang et al. 1995; Wang and Fisher 1996a, 1996b, 1997; Reinfelder et al. 1997
Dreissena polymorpha	Mussel	18–46	0.022–0.026	0.05–0.10	0.035 + 0.001	Roditi and Fisher 1999
Macoma balthica	Clam	74–78; 86	0.03–0.03; 0.01			Luoma et al. 1992; Reinfelder et al. 1997
Mercenaria mercenaria	Clam	92 + 2	0.01 + 0.004			Reinfelder et al. 1997
Mercenaria mercenaria	Clam larvae	100 + 2				Reinfelder and Fisher 1994a
Crassostrea virginica	Oyster	70 + 6	0.07 + 0			Reinfelder et al. 1997
Crassostrea virginica	Oyster larvae	105 + 6				Reinfelder and Fisher 1994a
Artemia salina	Brine shrimp nauplii	60 + 6	0.60			Mathews and Fisher 2008
Acartia tonsa and Temora longicornis	Copepods	97 + 2; 71–94; 58–59	0.42–1.14; 0.26–0.34; 0.25–0.29	0.024	0.155	Fisher and Reinfelder 1991; Reinfelder and Fisher 1991; Wang et al. 1996b; Wang and Fisher 1998
Sesarma reticulatum	Crab larvae	63				Anastasia et al. 1998
Dyspanopeus sayi	Crab larvae	78				Anastasia et al. 1998
Uca pugnax	Crab larvae	61				Anastasia et al. 1998
Balanus amphitrite	Barnacle	62–79	0.0141			Wang et al. 1999
Elminius	Barnacle	34–66				Rainbow and Wang 2001
Semibalanus balanoides	Barnacle larvae	93				Anastasia et al. 1998

comprise the vast majority of invertebrate taxa for which biodynamic models have been developed.

More work has considered bivalves, in part because these animals (especially the blue mussel *Mytilus edulis*) are used worldwide as bioindicator organisms of coastal contamination (Phillips and Rainbow 1993).

It is noteworthy that assimilation efficiencies of ingested Se tend to be high (often >60%) for most herbivore and algal species combinations, although exceptions are noted. The exceptions are most commonly found for animals consuming chlorophytes, which themselves tend to have lower degrees of Se enrichment (Table 5.1). These assimilation efficiencies tend to be higher than for all metals except methylmercury, for which they are approximately comparable. In contrast to methylmercury, however, the efflux rates of Se from invertebrates tend to be relatively fast, with rate constants of loss of about 2% to 6%/d for bivalves and values exceeding 25%/d for crustacean zooplankton (Table 5.2).

Uptake of selenite from the aqueous phase tends be slow, which helps explain the predominance of the dietary pathway as a Se source for the marine invertebrates (Wang and Fisher 1999). In contrast, uptake rates from the aqueous phase for freshwater zebra mussels are considerably higher, which can help explain the higher fraction of Se taken into zebra mussels from the aqueous phase than is commonly observed for marine mussels (Wang et al. 1996a; Roditi et al. 2000b). The kinetic parameters given in Table 5.2 have been used in biodynamic models to predict steady-state Se concentrations in mussels and copepods in Long Island Sound, San Francisco Bay, diverse freshwater systems in New York State, and in the western Mediterranean; in every case predicted values closely matched field measurements of Se concentrations in these animals (Wang et al. 1996a; Fisher et al. 2000; Roditi et al. 2000a). The close match of model-predicted concentrations and independent field measurements suggests that we can account for the major processes governing Se concentrations in these animals, and that laboratory-derived kinetic parameters are applicable to field conditions.

Biodynamic parameters can be used to estimate TTFs for Se in invertebrates and provide clarity in understanding and predicting Se movement through food webs (Table 5.3).

TABLE 5.3
Trophic Transfer Functions Derived from Laboratory Studies with Marine and Estuarine Invertebrates.
Data from Presser and Luoma (in press)

Taxon	Group	TTF (Range)	Nr of Studies
Bivalves	Clams	3.6–23.0	7
	Oysters	1.6–2.5	2
	Mussels	3.8–8.8	2
Crustaceans	Copepods	1.3–3.1	4
	Mysids	1.1– 1.3	1
	Amphipods	0.6	1
	Barnacles	9.9–22.6	2

For example, Se efflux rates for marine bivalves are typically lower than for zooplankton, so bivalve Se concentrations are generally higher than zooplankton in the same body of water (despite AEs that are less than or equal to those in zooplankton). Thus, marine bivalves should be a more enriched source of Se for their predators than for predators of zooplankton. Indeed, TTFs calculated from laboratory studies showed clams having TTFs up to 7-fold higher than those for copepods (Table 5.3).

The importance of differential Se bioaccumulation in invertebrates and their trophic transfer is clearly demonstrated in San Francisco Bay, where Se concentrations of the clam *Corbula amurensis* are 6- to 8-fold higher than in amphipods (Stewart et al. 2004). These differences are propagated up food webs, resulting in differential Se concentrations in apex predators. We can similarly use experimentally derived TTF values to predict that predators consuming barnacles, for example, are much more likely to have higher Se concentrations in their tissues than those consuming amphipods.

5.2.6.2   Freshwater Environments

Relative to our mechanistic understanding of Se bioaccumulation in marine invertebrates, our understanding of freshwater invertebrates is limited. Very few laboratory studies exist that have quantified biodynamic parameters (e.g., freshwater cladocerans, zebra mussels), so most of our inferences must be drawn from field data. Relying on field studies alone is limiting in 3 major ways. First, accurate assessment of food concentrations at the base of food webs is difficult. The separation of algae and/or bacteria from other particulate material or sediments is extremely challenging and rarely done. Thus, estimates of Se in invertebrate diets are generally crude. Second, in many field studies of Se bioaccumulation, invertebrates are often pooled and measured as composite benthic samples, or grossly separated to extremely coarse taxonomic levels (orders or higher). This type of composite sampling obscures species-specific patterns of Se bioaccumulation and trophic transfer; however, this may not matter in the case of non-selective consumers (e.g., some benthivorous fish) for which samples of pooled taxa may suffice to describe dietary concentrations. Finally, the dietary preferences of many invertebrates are not well known.

Presser and Luoma (in press) generated estimates of freshwater invertebrate TTFs from an analysis of existing field data (Table 5.4). Note that these estimates cannot be interpreted identically to laboratory-derived TTFs for some of the reasons described above, and do not provide the mechanistic understanding of how and why species vary in their Se content (AE, k_e, etc). Until a more mechanistic understanding of Se bioaccumulation in freshwater invertebrates is established, these values should be viewed as coarse guides.

One important observation to make from field data is that, relative to other taxa, freshwater clams are not necessarily strongly accumulative as is the case with their marine counterparts. In some systems such as the Mud Reservoir (WV, USA), clams tend to be high in Se relative to crayfish and dragonflies, for example (Presser and Luoma in press). In other systems such as the San Diego Creek Watershed (CA, USA), clams are comparable in Se content with zooplankton and are lower than dragonflies (Presser and Luoma in press). These differences could be a result of taxonomic variation or site-specific factors that are not well understood. Also noteworthy is the high TTF measured

TABLE 5.4
Trophic Transfer Function Estimates from Field Data. Data are from Presser and Luoma (in press) and Andrahennadi et al. (2007)

Taxon	TTF
Presser and Luoma (in press)	
Amphipod	0.9
Zooplankton	1.5
Crayfish	1.6
Daphnia sp.	1.9
Aquatic Insects – bulk	2.1– 3.2
Clam (*C. fluminea*)	1.4–4.0
Zebra mussel	4.5–7.0
Andrahennadi et al. 2007	
Aquatic insects – species	
Rhithrogena sp.	1.6–2.7
Drunella sp.	1.5–1.6
Epeorus sp.	1.2–1.5

in the zebra mussel. These organisms filter water at a substantial rate, and thus, uptake of dissolved Se can be an important route of exposure in this organism (Section 5.2.6). Similar to other invasive marine bivalves, this invasive freshwater species could be particularly problematic in Se-rich ecosystems to species that consume it.

Another key observation is the relatively high TTFs estimated for aquatic insects. This is important both in terms of the trophic transfer of Se from insects to fish and birds, as well as potential risks to the insects themselves. Insects are fundamentally important components of freshwater food webs, particularly in lotic systems, because they process organic materials and are key to nutrient dynamics. Because insects are the primary food source of many socially important fish species (e.g., salmonids) and birds, understanding of Se dynamics in insects in a comparative context is critical. In a rare study of streams in Alberta, Canada, TTFs were estimated for periphyton-grazing mayflies (Andrahennadi et al. 2007). Within a given genus, TTFs varied slightly among sites, which the authors suggest may be a function of periphyton community structure. A recent laboratory study examined selenite bioaccumulation in natural biofilms and subsequent transfer to the grazing mayfly *Centroptilum triangulifer* (Conley et al. 2009). In that study TTFs in adult mayflies (post–egg release) ranged from 1.9 to 2.4. Importantly, these mayflies transferred significant proportions of their body burdens to eggs. It is not yet clear how the inclusion of egg Se would modify these TTF estimates because reliable measures of egg weights could not be obtained in this study. However, Se loads of gravid adults were 36% to 51% higher than Se loads in those same animals post–egg release.

It is important to reiterate that we lack the mechanistic understanding of inter-specific Se bioaccumulation in freshwater invertebrates, and thus, to the extent possible, the lowest achievable taxonomic units should be used in reports of field data. For example, there are >1,500 species of Trichoptera described to date in the Americas north of Mexico, and we should expect to see variation among families and genera. Differences in Se bioaccumulation patterns among species are not idio-syncratic. Rather, they are mediated by evolutionarily derived life history (ecologi-cal) and physiological processes, which may ultimately prove to be predictable using comparative phylogenetic approaches (Buchwalter et al. 2008). Because of the ten-dency for closely related species to resemble one another, we might expect to find major phylogenetic differences among taxa in terms of propensity to bioaccumulate Se in tissues. Such phylogenetically based patterns could be extremely helpful in determining which species to sample in an assessment or monitoring context.

5.2.6.3   Intra-specific Differences: Size Influences Se Enrichment in Bivalves

There is evidence that size can play a role in the uptake of Se by bivalves. Selenium concentrations in the estuarine clam *C. amurensis* exposed to dissolved sources of Se(IV) in the laboratory were found to decrease by 50% as mean shell length of the clams increased by ~30% (Lee et al. 2006). Smaller clams had higher Se concen-trations than larger clams. In the marine black mussel *Septifer virgatus*, Se uptake decreased with increasing body size (quantified as tissue dry weight), with a power coefficient of –0.317 (Wang and Dei 1999a). A similar response was observed in replicate composites of field-collected *C. amurensis* exposed to aqueous sources of Se (Stewart et al. 2004). The cause of the size-specific difference may be specific to bivalves and size-specific filtration rates. Wang and Dei (1999b) found that the power coefficient of the Se uptake as a function of tissue dry weight (–0.317) in the black mussels was directly comparable to the power coefficient of the mussel filtration rate as the function of tissue dry weight (–0.32), which strongly suggested that the allometric change of Se uptake in the mussels was controlled by the same process as the filtration activity, such as the gill surface to volume ratios. Consequences of size-specific differences in Se uptake in bivalves are not trivial. Minor differences in clam size can modify apparent Se concentrations by up to 50%, creating problems in interpretation of monitoring data collected spatially and temporally. Further, shifts in size distributions of the bivalve community due to food availability and predation may alter Se exposures to higher trophic levels and their risks of Se toxicity.

5.2.6.4   Subcellular Distribution in Controlling Se Trophic Transfer

There has been substantial interest in understanding the various processes control-ling dietary Se AE in a variety of marine herbivores and carnivores. Reinfelder and Fisher (1991) found that the Se AE in marine copepods was nearly comparable to the Se distribution in diatom (prey) cytoplasm, implying that the assimilation was controlled by the Se cytosolic fraction. Marine copepods (*Acartia spincauda*) were able to assimilate the Se-associated diatom detritus (either freshly prepared from the cellular debris of diatoms or the decomposed products) at an efficiency of 44% to 57%, which indicated that the Se associated with the diatom cell walls

might also be available to copepods (Xu and Wang 2002b). The assimilation processes of marine predators may be even more complicated than those of herbivores. For Se, Dubois and Hare (2009) quantified the subcellular Se distributions in the oligochaete *Tubifex tubifex* and in the insect *Chironomus riparius* and how they affected Se trophic transfer to a predatory insect (the alderfly *Sialis velata*). In their study, the predator assimilated about 66% of the Se from the prey, which was similar to the Se distribution of 62% in the protein and organelle fractions. In the marine fish grunt, *Terapon jarbua*, the Se AEs varied by prey (copepods, barnacles, clams, mussels, and fish viscera) over a range of 13% to 36% (Zhang and Wang 2006). Such variation was significantly related to the heat-stable protein fraction of Se in prey. Again, subcellular forms of Se in the fish prey similarly affected Se assimilation by the predator. Further experiments using purified subcellular fractions of copepods and mussels as fish diets suggested that Se bound with the insoluble fraction (including metal-rich granules [MRG], cellular debris, and organelles) had a much lower AE (29% to 33%) than Se bound with the protein fractions (41% to 54%) (Zhang and Wang 2006). However, feeding processes also affected the Se assimilation in fish. Selenium AE was significantly dependent on the ingestion rate of fish and gut passage time of Se.

5.2.7 FISH

Elevated Se concentrations in fish found in contaminated areas have raised environmental as well as public health concerns (Lawrence and Chapman 2007) because the consumption of fish may represent a significant source of Se to humans (Thompson et al. 1975; Schubert et al. 1987). Predicting Se accumulation from the aqueous Se concentration in a given system is not straightforward because Se body burdens in fish and other aquatic animals may vary widely among species within the same water body (Stewart et al. 2004). Fish are often considered to be the most sensitive group of organisms to chronic Se exposure (Hamilton et al. 1990; Hermanutz 1992; Hermanutz et al. 1992; Coyle et al. 1993). A quantitative understanding of the variables affecting Se accumulation in fish is therefore needed to properly evaluate the biological and ecosystem-level effects of Se contamination, and to set appropriate environmental quality criteria or guidelines.

As with invertebrates, toxicity to fish can occur when Se is present at levels above the concentrations that are required for metabolic functions. Differences in choice of diet (prey selectivity), seasonal movements or migration, habitat utilization, and tissue allocations that occur both within and among species are sources of variability that are important to consider in interpreting Se levels in fish tissues. Ecological impacts to fish are usually associated with effects on early life stages as a result of maternal transfer of Se to eggs (Lemly 1993; Holm 2002). Therefore, fish are particularly vulnerable during the period when eggs are being formed, although the precise timing and duration of this vulnerability varies based on differences in reproductive characteristics among species (Section 5.2.7.4).

5.2.7.1 Trophic Transfer Patterns

Relative to other trace elements, Se is efficiently assimilated into fish from diet (Reinfelder and Fisher 1994b; Baines et al. 2002; Xu and Wang 2002a), and where

TABLE 5.5

Trophic Transfer Functions (TTFs) for Fish from Laboratory Studies

Species		Type of Prey	TTF	Reference
Juvenile striped bass	*Morone saxatilis*	Crustacean zooplankton	0.94–2.8	Baines et al. 2002
Juvenile sea bream	*Sparus auratus*	Crustacean zooplankton	0.46–0.69	Mathews and Fisher 2008
Juvenile black sea bream	*Acanthopagrus schlegeli*	Crustacean zooplankton	0.5–1.5	Zhang and Wang 2007
Mangrove snapper	*Lutjanus argentimaculatus*	Crustacean zooplankton and bivalve	1.07–2.09	Xu and Wang 2002a
Intertidal mudskipper	*Periophthalmus cantonensis*	Polychaetes	1.13–1.68	Ni et al. 2005
Juvenile sea bass	*Dicentrarchus labrax*	Juvenile fish	0.5–1.3	Mathews and Fisher 2008

loss rates are slow, Se has the potential to biomagnify in aquatic food chains (TTF > 1) (Wang 2002; Zhang and Wang 2007). Both laboratory and field studies used to determine TTFs for fish report remarkably similar results, despite the fact that they are derived through different methods. Trophic transfer functions are sometimes derived from field studies by dividing the Se concentrations in consumers by that measured in known or presumed prey (Presser and Luoma in press). Laboratory studies are usually based on food chains that are short and linear to generate the kinetic data used to calculate TTF values (Table 5.5). Laboratory-derived TTFs for Se have been reported for marine fish that were fed crustacean, bivalve, and fish diets (Xu and Wang 2002a; Zhang and Wang 2007; Mathews and Fisher 2008). The TTF values varied with AE and IR, resulting in a range of TTF values rather than a single best estimate. Although TTF values were lower for predatory fish fed a crustacean diet than for fish fed either bivalve or fish diets, the spread of TTF values was relatively narrow regardless of the prey consumed, ranging from 0.5 to 1.5 for the intermediate ingestion rates considered.

Compared to the amount of data available on Se trophic transfer from invertebrate prey to fish, there are relatively few data in the laboratory or in the field that describe Se trophic transfer to piscivorous fish species. This is likely because of intrinsic difficulties in the measurement of whole-body Se levels in such large organisms. Mathews and Fisher (2008) report TTF values of 0.5 to 1.3 for sea bass fed on juvenile sea bream (for IR = 0.1 g/g/d). These laboratory-derived TTFs for piscivorous fish are comparable to the TTF values reported for fish feeding on invertebrates (Table 5.5).

In contrast to the simple, controlled food chains typical of laboratory-based studies, field-derived TTFs represent time-integrated Se accumulation and loss processes for fish consuming a varied diet, for which the specific composition of diet, food chain length, and food web pathway may be unknown or uncertain. Comparisons between field- and laboratory-derived TTFs are further complicated by the fact that, while

kinetic studies of Se accumulation in laboratory studies are based on whole-body analyses, field studies typically report as whole-body Se burdens for invertebrates while Se levels in field-collected fish are often reported with respect to specific tissues (muscle, liver, gonad). Despite this, the mean TTF for 15 freshwater and marine fish species feeding on invertebrate prey was estimated at 1.2, within a remarkably narrow range of 0.51 to 1.8 (Presser and Luoma in press) and showed close agreement with laboratory-derived values (Table 5.5). Muscatello et al. (2008) and Muscatello and Janz (2009) suggested that TTFs of up to 10 or more could occur in benthivorous fish (spottail shiner *Notropis hudsonius*, white sucker *Catostomus commersoni*, and stickleback *Pungitius pungitius*) through selective feeding on specific invertebrate guilds. However, actual fish diets were not determined. Lack of precise information about dietary habits of fish is a common limitation of field studies, for which it is difficult to track specific feeding habits over time. Assuming an average invertebrate concentration in the diet of fish based on data presented by the same authors, results in a TTF of ≤3, which is much more consistent with the data summarized by Presser and Luoma (in press) from other studies. Burbot (*Lota lota*), also classified as benthivorous by Muscatello and Janz (2009), had a TTF of ~7 based on an average of the Se concentrations in available invertebrate prey, but at 2 to 3 years of age the burbot diet may have included other fish (Scott and Crossman 1973). A piscivorous diet for the burbot in that study would yield TTF values up to 8.7 or higher, depending on choice of prey (e.g., 107 for stickleback). Analyses of gut contents in addition to stable isotopes of carbon, nitrogen, and/or sulfur can be useful in elucidating trophic relationships (Vander Zanden and Rasmussen 1999; Stewart et al. 2004; Orr et al. 2006) and, thus, provide for more precise TTF estimates. Nevertheless, the substantially higher TTF values for burbot are notable compared to other species. The higher values may be a consequence of the relatively larger contribution of liver tissue (known to concentrate and metabolize Se) compared to other tissues on a whole-body basis. Indeed, the hepatosomatic index (HSI, percent mass contribution of liver tissue to whole body) for burbot is up to 6% higher than for other freshwater species, including trout and salmon, and may lead to a higher TTF (Tom Johnston, Ontario Ministry of Natural Resources, personal communication).

Despite the confounding influences associated with field studies and differences between field- and laboratory-derived methods for determining trophic transfer of Se to fish, TTF values for fish appear to be relatively consistent and low relative to trophic transfer at lower food chain steps.

5.2.7.2   Other Factors That Influence Se Enrichment

5.2.7.2.1   *Lentic vs. Lotic Habitats*

Lentic systems, which are characterized by long hydraulic retention times, low oxygen content, and high carbon content, favor reducing conditions. In these environments, Se is often found as selenite, reflecting the recycling in which Se is progressively reduced to more bioavailable organic forms. In lotic systems that have higher flushing rates and lower productivity, Se is found in the more oxidized form of selenate, which does not easily migrate to sediments and thus is not as rapidly recycled. The reduced Se found in lentic sediments is readily accumulated at the base of the food web, passed on to benthic organisms, and transferred through the food chain to fish in

TABLE 5.6

Mean Se Concentrations Observed in Different Media Sampled from the Elk River Watershed, British Columbia, Spring 2006 (Minnow Environmental Inc. et al. 2007)

Habitat	Status	Location	Mean Water 2004–2006 (µg/L)	Sediment (mg/kg dw)	Composite Benthic Invertebrates (mg/kg dw)	Whole-Body Cutthroat Trout (mg/kg dw)	Trophic Transfer Function (Trout and Invertebrate)
Lotic	Reference	AL4	<1		3.9	4.4	1.1
		EL12	1.4		4.0	6.2	1.5
	Exposed	FO9	16.4		4.4	7.8	1.8
		LI8	22.7		7.8	9.3	1.2
		FO23	19.0		10.0		
		MI5	2.8	5.0	4.0	4.6	1.2
		MI3	1.4		6.2	5.7	0.9
		MI2	7.2		6.7	5.2	0.8
		EL1	5.9		7.1	4.8	0.7
Lentic	Reference	BA6	<1	3.9	3.3	7	2.1
		EL14	<1.5	2.5	4.4	4.5	1.0
	Exposed	FO10	23.2	25.1	17.5	45.9	2.6
		CL11	48.0	6.1	30.9	57.3	1.9
		HA7	25.0	7.9	22.4	21.1	0.9
						Mean	1.4

these systems. Selenium bioaccumulation in fish is significantly higher in lentic than in lotic systems (Orr et al. 2006); BAFs for fish in lentic systems have been reported to be greater than in lotic systems by a factor of 10 or more (Adams et al. 2000).

Trophic transfer functions were calculated for cutthroat trout collected in lotic and lentic habitats of the Elk River watershed (BC, Canada) by dividing whole-body fish Se levels by concentrations measured in benthic invertebrates collected in the same areas (Table 5.6). Trout TTF values ranged from 0.7 to 2.6, with a mean from all sites of 1.4. These values are comparable to the TTFs reported by Presser and Luoma (in press) for the same species (0.93 to 1.25; mean 1.0).

As noted in previous sections, differences in Se concentrations among fish in different locations can be largely ascribed to differences in uptake at the base of the food web and trophic transfer to invertebrates. This linkage between Se concentration in fish and their food web base is illustrated by differences in fish tissue concentrations between areas in Table 5.6, with higher concentrations in fish collected in lentic than in lotic areas, even when water concentrations are relatively similar (e.g., LI8 versus FO10). The higher concentrations in fish from lentic vs. lotic areas might be explained by the fact that organisms associated with lentic area sediments appear to accumulate more Se from water than epilithic organisms in lotic areas (Orr et al. 2006). The higher bioavailability of Se from the water to the base of the food web in

lentic environments may be due in part to longer hydraulic retention time in lentic environments allowing for more retention and recycling of organoselenium than in lotic environments (i.e., organoselenium is taken up more efficiently from water than selenate or selenite: Besser et al. 1993; Bowie et al. 1996).

5.2.7.2.2   Size and Age

Unlike other contaminants such as methylmercury, fish size and patterns of growth do not appear to significantly influence Se tissue body burdens, except in juvenile stages. For example, while tissue concentrations of mercury (Hg), cesium (Cs), and thallium (Tl) showed relationships with age, size, and trophic position in Arctic char (*Salvelinus alpinus*), indicating their potential to bioaccumulate and/or biomagnify, Se showed no such relationship (Gantner et al. 2009). Likewise, Se concentrations in adult or juvenile striped bass and white sturgeon collected in San Francisco Bay (CA, USA) showed no significant relationship with total length (Robin Stewart, U.S. Geological Survey, personal communication). In some species and locations, Se concentrations have been shown to vary significantly with length, but the changes are driven by ontenogenetic shifts in fish diets rather than size-specific effects. For example, inverse relationships with fish total length were observed in redear sunfish and Inland silversides in the San Francisco Bay and Delta (CA, USA). The relationships corresponded to shifts in diets of redear sunfish from an open-water–based food source (zooplankton) that was higher in Se to a near-shore–based food source (amphipods) that was lower in Se, while the reverse was true for Inland silversides (Lucas and Stewart 2005). Zhang and Wang (2007) modeled the Se accumulation in the marine juvenile fish *Acanthopagrus schlegeli* and showed that the Se concentration decreased exponentially with an increase in fish length. They also demonstrated that TTF values for these fish decreased (from 1.5 to 0.5) with increasing fish size. The driving force for the observed decreased in TTFs with size appeared to be the decrease in ingestion rates, because the assimilation efficiency of Se increased with increasing fish size (over a size range of 1 to 3 cm) (Zhang and Wang 2007). Currently, the biokinetic parameters available for Se in fish are generally limited to small-sized individuals. This limitation is because these parameters are derived through radiotracer experiments, and the space limits of the gamma detectors used to measure Se radioactivity make it difficult to study larger fish.

5.2.7.2.3   Marine vs. Freshwater

The speciation of trace metals and the permeability of biological membranes change with salinity. For this reason it might be expected that Se toxicity, uptake from water, assimilation from food, and elimination from both exposure routes may be different in marine and freshwater systems. This is the reasoning typically given for the pronounced differences between Se guidelines in freshwater and saline waters. Studies that systematically compare tissue levels in marine and freshwater fish are lacking, but several studies have examined the effects of changes in salinity on Se accumulation and toxicity. For example, Schlenk et al. (2003) showed that increasing salinity (from 0.5 to 13.4 psu) resulted in significantly lower mortality rates in rainbow trout (*Oncorhynchus mykiss*) exposed to dietary seleno-L-methionine. But Ni et al. (2005) showed that salinity affected aqueous, but not dietary, uptake of Se in the intertidal mudskipper (*Periophthalmus cantonensis*). For example, varying the salinity from

10 to 30 psu had no effect on the dietary assimilation of Se or on the efflux rates in these fish. However, concentration factors from aqueous exposure were higher at lower salinities (10 to 20 psu) than at higher salinity (30 psu). Much remains to be learned about this important subject, but at this point it is difficult to support a greater than 10-fold difference in Se guidelines between fresh and salt water based upon Se toxicity differences in fish alone. Indeed, competition from sulfate at uptake sites on membranes in marine systems may be an important factor (Section 5.2.2).

5.2.7.3   Selenium Turnover in Fish Tissues

As noted previously, aqueous Se uptake in fish is so slow as to be negligible ($k_u <$ 0.01 L g^{-1} d^{-1}) (Zhang and Wang 2007). In addition, efflux rates in fish from aqueous exposure are significantly higher than from dietary exposure (Ni et al. 2005), highlighting the importance of dietary exposure in contributing to Se body burdens in fish. Biological half-lives ($t_{1/2}$) for Se in fish can be as short as 7 days, but are more typically on the order of 3 to 4 weeks (Presser and Luoma in press). Zhang and Wang (2007) showed that the biological half-life of Se in the intertidal mudskipper was affected by salinity and exposure route, with higher salinity and dietary exposure leading to the longest $t_{1/2}$ (38.5 d). Trophic transfer studies by Bennett et al. (1986) and Dobbs et al. (1996) showed that, after about 1 week of exposure to Se-enriched rotifers (*Brachionus calyciflorus*), juvenile fathead minnow (*Pimephales promelas*) had Se body burdens approximating that of their diet. Juvenile bluegill consuming Se-laden worms also showed increased tissue Se levels within 1 week, but steady-state equilibration with diet took approximately 100 days (McIntyre et al. 2008). These data suggest that tissue Se levels in fish rapidly begin to reflect dietary levels (e.g., within 1 week), although a steady-state relationship may not be achieved for a period of weeks or months.

5.2.7.4   Periods of Vulnerability

Selenium effects in fish are manifest through maternal transfer to eggs and effects among progeny, so fish are most vulnerable during the period when they are actively developing eggs. This period varies widely in duration and season among fish species (Table 5.7). Many fish species, particularly larger ones, exhibit synchronous

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TABLE 5.7

Ovarian Development Periods Relative to Spawning Habitats (Environment Canada 2009)

Reproduction Type	Ovary Development
Synchronous spawners	Starts in late fall for spring spawners. Early to mid-summer for fall spawners.
Multiple spawners, few spawns	Starts 2+ months prior to spawning with maximum development in last 4 weeks.
Multiple spawners, many spawns	Rapid development approximately 4 weeks prior to spawning.
Asynchronous spawners	May occur in as few as 2 weeks prior to initiation of spawning, sometimes longer.
Asynchronous development (year off)	Development only in years when spawning will occur.

spawning based on specific temperature or flow cues (e.g., catastomids, salmonids) and initiate ovarian development well in advance (e.g., months) of spawning (Table 5.7). Species exhibiting asynchronous development (e.g., some Arctic char populations) may also show prolonged ovarian development, but only in the years in which spawning occurs. Other species, particularly those that spawn multiple times per year (multiple spawners) or asynchronously, exhibit relatively rapid ovarian development just prior to spawning (e.g., within weeks; Table 5.7). Therefore, the period of vulnerability with respect to maternal uptake of Se and transfer to eggs is highly species dependent.

5.2.7.5 Fish Movements

Many types of fish migrate on a regular basis, on time scales ranging from daily to annual, and over distances ranging from a few meters to thousands of kilometers. This migration is often to satisfy dietary or reproductive needs, although the reasons for fish movement are not always known. Such migrations can confound interpretation of dietary contaminant uptake, because measured contaminant body burdens may relate to sources located somewhere other than where the fish are collected. In Se studies, linking tissue Se levels to sources of exposure can be particularly problematic because it is not unusual for migration to occur from preferred forage areas to spawning areas that may be quite distant. Fish may move closer to or farther away from Se sources during the period when eggs are being actively developed. Therefore, characterization of Se risks to fish necessitates an understanding of whether sensitive aquatic species are occupying Se-rich habitats at times when eggs are rapidly developing. Species are relatively less vulnerable outside of this period, although juvenile and adult life stages could be affected through direct dietary exposure if Se concentrations are sufficiently high.

Residency of fish can be assessed in various ways. Radiotelemetry allows for movements of individuals to be tracked over time, but this approach tends to be highly labor intensive and expensive (Brenkman et al. 2007). Comparison of the stable isotope signatures of fish tissues relative to other abiotic and biotic samples collected within an area can also assist in determining site fidelity (Orr et al. 2006). More recently, analysis of life history exposure to Se was assessed by laser ablation–inductively coupled–mass spectrometry of Se in fish otoliths (Palace et al. 2007); concentrations of Se in annual growth zones of the otoliths suggested that fish from a mine-impacted system were recent immigrants from nearby reference streams. Implementation of these or alternative techniques can be highly beneficial in interpretation of data for species for which duration of occupancy in Se-rich areas is uncertain.

5.2.7.6 Tissue Allocations

Relationships among Se concentrations in different fish tissues (e.g., whole body, muscle) can vary widely among fish species within locations and sometimes within species among locations (GEI Consultants et al. 2008). Tissue Se relationships have typically been strong (based on high r^2) for most species within studies, but there have been many exceptions (e.g., almost one-fourth of relationships presented by GEI Consultants et al. (2008) had $r^2 \leq 0.5$). Of 10 fish species for which data were presented, rainbow trout demonstrated the highest concentrations of Se in eggs

relative to muscle, while brook trout showed the lowest egg concentrations relative to muscle, indicating that generalizations respecting relative tissue Se allocations cannot be assumed, even between closely related species. Additional data from a study conducted in the Elk River (BC, Canada) gave similar results in that pre-spawning westslope cutthroat trout showed very strong correlations between muscle plug, muscle fillet, ovary, and whole-body Se concentrations, but muscle Se concentrations in pre-spawning mountain whitefish did not strongly correspond to concentrations in either ovary or whole body (Minnow Environmental Inc. et al. 2007). Differences in factors such as the habitats (and therefore diet) utilized during spawning-related migration or the precise stage of egg development among sampled individuals may affect the strength of tissue Se relationships. The rapid uptake of Se (Section 5.2.7.3) from diet and the relatively longer period of time over which Se is redistributed among tissues may influence apparent tissue Se relationships, particularly in settings where there are sharp spatial and temporal gradients.

5.2.7.7 Interactions between Se and Mercury

Significant interaction between Se and Hg was recognized as early as the 1960s (Parizek and Ostadalova 1967; Koeman et al. 1973). It has been known that Se can protect mammals against Hg intoxication (Augier et al. 1993; Glynn et al. 1993; Schlenk et al. 2003), and thus most studies on the interactions between Hg and Se have been conducted in mammalian and fish systems, with few studies on invertebrates. Interaction of Se and Hg may occur in the external environment by complexation or within the metabolic sites after metals are accumulated intracellularly (Amiard-Triquet and Amiard 1998). Possibilities of the protection of Se against Hg toxicity include the redistribution of Hg in the tissues, the competition for binding sites, and the formation of an Hg–Se complex (Cuvin-Aralar and Furness 1991). In addition, the formation of an equimolar Hg–Se complex binding to selenoprotein P may lead to a positive correlation between Hg and Se (Luten et al. 1980; Sasakura and Suzuki 1998).

The interaction of Se and Hg is far from consistent in different studies. For example, there can be either no correlation (Cappon 1981; Lyle 1986; Barghigiani et al. 1991) or a negative correlation (Paulsson and Lundbergh 1991; Chen et al. 2001) between the concentrations of Se and Hg in fish. Sheline and Schmidt-Nielsen (1977) found little effect of Se on the overall body retention of MeHg in the fish *Fundulus heteroclitus*, while Turner and Swick (1983) showed that addition of Se can effectively reduce Hg concentrations in pike (*Esox lucius*) and perch (*Perca flavescens*) with appropriate doses and addition periods. In other field studies, Southworth et al. (2000) found a long-term increase in Hg concentrations in the largemouth bass with a reduction in waterborne Se. A significantly negative correlation between the total Hg concentrations in perch and walleye muscle with the Se concentrations collected from 9 Sudbury (ON, Canada) lakes was also documented (Chen et al. 2001). In the rainbow trout *Oncorhynchus mykiss*, exposure to Se(IV) or Se(VI) in the external medium at 0.075 to 0.75 µM or 5.9 to 59 µg/L did not affect the uptake of MeHg across the perfused gills or its liberation from the gills (Pedersen et al. 1998). However, a Se(IV) or Se(VI) concentration of 7.5 µM or 590 µg/L augmented the MeHg uptake across the gills and internal Se(IV) also increased the efflux of MeHg.

In a more recent study, Mailman (2008) conducted a mesocosm experiment to evaluate the effectiveness of low Se concentrations to lower Hg concentrations in yellow perch. After 8 weeks of exposure, the concentrations of spiked Hg in muscle and liver of fish inversely correlated with Se concentrations in water. Increasing the Se concentrations from about 0.2 to 1.0 µg/L resulted in Hg concentrations in muscle of fish that were 54% lower relative to controls.

Fewer studies have addressed the interaction of Hg and Se in invertebrates (e.g., crabs, starfish, and bivalves; Pelletier 1986; Micallef and Tyler 1987; Sorensen and Bjerregaard 1991; Bjerregaard and Christensen 1993; Larsen and Bjerregaard 1995; Wang et al. 2004) and phytoplankton (Gotsis 1982). Starfish *Asterias rubens* exposed simultaneously to 75 µg/L Se(IV) and 10 µg/ L Hg accumulated more Hg and Se in the tube feet and body wall than did starfish exposed to the two alone, suggesting a synergistic interaction between Se and Hg (Sorensen and Bjerregaard 1991). In the shore crabs *Carcinus maenas*, exposure to Se(IV) either increased the assimilation of MeHg from the food (Bjerregaard and Christensen 1993) or did not consistently alter the AE of MeHg (Larsen and Bjerregaard 1995). In the shrimp *Pandalus borealis*, the biologically incorporated Se in the mussel prey did not apparently affect Hg uptake (Rouleau et al. 1992).

Pelletier (1986) found that Se bioaccumulation in the mussel *Mytilis edulis* increased in the presence of Hg, but Hg bioaccumulation was not affected by various concentrations and chemical species of Se. A synergistic interaction of Se with Hg was documented by Micallef and Tyler (1987). In their study, simultaneous additions of a high concentration of Se were more toxic to the mussel *M. edulis* than the Hg-alone treatment. Patel et al. (1988) found that Se did not offer any protection against the toxic effects of Hg in marine mollusks, and Siegel et al. (1991) demonstrated that there is no consistent difference in the protection against Hg poisoning in a wide variety of organisms (invertebrates, fish, and vascular plants) by different S and Se derivatives. Based on these limited studies, consistent conclusions regarding the interaction of Se and Hg in marine invertebrates are not possible. Reasons for this inconsistency may be the use of different Se species and concentrations in these earlier studies and/or because of the differences in the exposure history of the animals. For phytoplankton, Gotsis (1982) indicated that Se(IV) and Hg(II) interacted in an antagonistic way on the cell growth of alga *Dunaliella minuta* when both were added simultaneously at the beginning of the growth period.

Wang et al. (2004) examined the influences of different concentrations and species of Se (selenite, selenate, seleno-L-methionine) in the ambient environment on the accumulation of Hg(II) and (MeHg) by the diatom *Thalassiosira pseudonana* and the green mussel *Perna viridis*. Aqueous uptake and dietary assimilation of both Hg species were not significantly affected by the different Se(VI) and Se(IV) concentrations (<500 µg/L). In contrast, seleno-L-methionine significantly inhibited the uptake of MeHg and enhanced the uptake of Hg(II) by the diatoms and the mussels at a relatively low concentration (2 µg/L), but did not affect assimilation from the ingested diatoms. One possible reason for the increasing Hg(II) uptake with seleno-L-methionine could be complexation of the Hg(II). The complex may be transported across the membrane at a faster rate because Hg(II) has one of the highest binding affinities

with sulfur-containing compounds. The green mussels were exposed to Se(IV) and selenomethionine for different time periods (1 to 5 weeks) to allow the build up of different tissue body burdens of Se, and the accumulation of Hg(II) and MeHg was then quantified. Tissue Se concentrations did not significantly affect the dietary assimilation of Hg, but the influences on the aqueous uptake were variable. These data thus indicated the specificity of the Se–Hg interaction in marine mussels for different Se and Hg species. Heinz and Hoffman (1998) also found that selenomethionine and MeHg interacted in opposite ways in adult and young mallards (*Anas platyrhynchos*). Selenomethionine protected against MeHg toxicity to adult males, but it worsened the effects of MeHg to the young individuals (hatching, survival, and growth).

5.2.8 BIRDS

Birds have been shown to be highly sensitive to Se exposure. Many of the processes that modify exposures in fish apply to birds, but there are important differences that can lead to variable Se exposures in nature. There is limited information on the biodynamics of Se in birds due to the difficulties of conducting laboratory exposures of large organisms. Thus, the vast majority of estimates of uptake and loss have been inferred from field assessments, dietary toxicity tests, or captive breeding studies. Selenium accumulation in birds was not a primary focus of this chapter but is examined in detail relative to toxic effects in Chapter 6. Here we highlight a few of the critical mechanisms known to influence Se accumulation in birds.

5.2.8.1 Feeding Behavior Influences Se Enrichment

In comparing birds from the same geographical region, breeding and developmental stage Se concentrations often vary the most among those species with different diets. In the northern reach of San Francisco Bay (CA, USA), diving ducks feeding on bivalves (surf scoters, scaup) had higher liver Se values than shorebirds feeding on invertebrates in tidal mud flats (avocets, *Recurvirostra americana*) and higher yet than shorebirds feeding on invertebrates in vegetated edge marsh habitats (black-necked stilts, *Himantopus mexicanus*) or Bay piscivorous species (Forester's tern, *Sterna forsteri* and Caspian terns, *Hydroprogne caspia*) (Ackerman and Eagles-Smith 2009). Ackerman and Eagles-Smith (2009) suggest that differences in exposure likely originate from site-specific Se concentrations determined by the habitat and Se concentrations of the prey items known to vary in the region (Stewart et al. 2004).

Bioenergetic models suggest that the relative caloric content of a bird's diet and the bird's metabolic requirements may further play a role in determining Se uptake. DuBowy (1989) used field Se values for a variety of bird diets and estimated ingestion rates based on data in Heinz et al. (1987) to calculate relative exposures from different diets. He predicted that birds consuming vascular plants and algae, which typically have low Se levels relative to invertebrates or fish, are expected to have the highest exposures, due to the higher intake rates of plant material to meet caloric requirements. These patterns appear to be supported to some degree by field data

from a closed system that show the highest Se levels in herbivorous marsh birds (e.g., American coots) and lower levels in insectivorous ducks and shorebirds (Ohlendorf et al. 1986).

5.2.8.2   Time Scales of Exposure

Uptake rates and tissue turnover times appear to be substantially higher in bird tissue and eggs than in fish tissues. When birds fed on Se-contaminated diets during the laying season, the exposure was quickly reflected in elevated levels of Se in eggs (Latshaw et al. 2004). Similarly, when the birds were switched to a clean diet, Se concentrations in eggs declined quickly. When mallard hens were fed a diet containing Se at 15 mg/kg dw (as selenomethionine), levels peaked in eggs (to about 43 to 66 mg/kg dw) after about 2 weeks on the treated diet and leveled off at a relatively low level (<16 mg/kg dw) about 10 days after switching to an untreated diet (Heinz 1993).

Because it is the Se in the egg, rather than in the parent bird, that causes developmental abnormalities and death of avian embryos, Se in the egg gives the most sensitive measure for evaluating hazards to birds (Skorupa and Ohlendorf 1991). Given the rapid accumulation and loss patterns of Se in birds (Heinz et al. 1990; Heinz 1993; Heinz and Fitzgerald 1993; Latshaw et al. 2004), Se concentrations in eggs also probably best represent contamination of the local environment. Additional advantages of measuring Se in eggs are that eggs are frequently easier to collect than adult birds, the loss of one egg from a nest probably has little effect on a population, and the egg represents an integration of exposure of the adult female during the few days or weeks before egg laying.

5.2.9   Reptiles and Amphibians

There is limited information on the accumulation of Se by reptiles and amphibians. However, available data suggest that amphibians, in particular, accumulate Se efficiently and transfer it to reproductive tissues where reproductive effects have been observed.

In a study of Se accumulation in the food web of a swamp located near a power generation facility in South Carolina (USA), bullfrog larvae (*Rana catesbeiana*) had the highest Se burden (~28 mg/kg dw) of all species examined, followed by clams (*Corbicula fluminea*; 20 mg/kg dw) and other taxa (~5 to 15 mg/kg dw), including snails, aquatic insects, and fish (Unrine et al. 2007). It is unclear why the bullfrog larvae were enriched relative to the other taxa. Bullfrog larvae are thought to be omnivorous feeding on sediments, biofilms (bacteria, diatom, algae, and detritus), and animal tissues, diets that would have been shared to some degree with other species. Presently, there are no biodynamic data that could help determine whether the higher accumulation rates in the bullfrog larvae are due to their foraging ecology or physiology. Other studies on adult anurans from the same site show that not only do adult toads accumulate high levels of Se but they also transfer it efficiently to their eggs (Hopkins et al. 2006). Toads collected from reference and contaminated sites were brought in from the field and placed in experimental uncontaminated mesocosms to document the effects of Se exposures on the hatching success and development of toad larvae (*Gastrophryne carolinensis*). Hopkins et al. (2006) found that

Se concentrations in the tissues of the female toads (up to 42 mg/kg dw) strongly influenced their egg Se concentrations (Log $[Se]_{eggs} = 1.0255 \times$ Log $[Se]_{female} - 0.0448$, $r^2 = 0.94$). Further, the females transferred roughly 53% of their Se body burden to their eggs upon oviposition. This pattern of partitioning was independent of exposure history and was roughly equivalent to the proportion of reproductive tissue to whole-body mass. The maternal transfer of Se by *G. carolinensis* far exceeded that observed for other reptiles, birds, and fish from the same site. Slightly lower percentages (~33%) were observed in female fence lizards (*Sceloporus occidentali*) relative to their ovaries (eggs were not measured) in experimental exposures (Hopkins et al. 2005). As with the bullfrog larvae, it is unclear why the adult toads had such high Se concentrations relative to other species. *Gastrophryne carolinensis* are predaceous, feeding on terrestrial insects, including ants and beetles, which may lead to a more efficient trophic transfer of Se, if these insects accumulate substantial amounts of Se. In another high-Se area (Elk River, BC, Canada), Columbia spotted frog eggs had Se concentrations (12 to 38 mg/kg dw) that were comparable to or lower than concentrations measured in sediments (62 mg/kg dw) or other biota (composited benthic invertebrates 21 mg/kg dw, whole-body longnose sucker 9 to 80 mg/kg dw, red-winged black bird eggs 18 to 20 mg/kg dw) collected from the same area (Minnow Environmental Inc. et al. 2007).

Selenium concentrations appear to be relatively consistent among life stages of anuran species collected from contaminated sites and show patterns that are unlike many other trace elements (Snodgrass et al. 2004; Roe et al. 2005). Selenium concentrations of the southern toad (*Bufo terrestris*) showed slight (but not significant) increases in concentrations moving from larval to metamorph to adult stages, despite shifts in feeding behavior among life stages. Selenium concentrations in southern leopard frog (*Rana sphenocephala*) were similar for larvae and metamorphs and then significantly declined to reference site levels in adults. It is unknown what drives these species-specific differences in Se accumulation among life stages.

Reptiles have also been shown to accumulate high levels of Se from their diet (Hopkins et al. 2004, 2005) and to transfer it to their eggs. In a long-term laboratory exposure study, seleno-D,L-methionine–spiked diets had a significant influence on tissue Se levels of exposed brown house snakes (Hopkins et al. 2004). At the highest Se exposure levels (20 mg/kg dw), snakes had Se concentrations up to 20 mg/kg dw in liver and ovary and up to 30 mg/kg dw in kidney. Selenium content of the eggs was significantly related to dietary exposures and Se tissue levels of the females (Hopkins et al. 2004). Gopher snakes collected from the Se-enriched area of the Kesterson Reservoir (CA, USA) had Se concentrations in their livers ranging from 4.7 to 32 mg/kg dw (mean 11.4), levels significantly higher than those from the nearby reference site in the Volta Wildlife Area (range 1.3 to 3.6 mg/kg dw, mean 2.14) (Ohlendorf et al. 1988). The site-specific differences in Se concentrations of the snakes reflected the site-specific differences in Se concentrations in the bird eggs, a known prey item (Ohlendorf et al. 1988). Selenium concentrations were not significantly correlated with body size, sex, or date of collection. Further, it is unclear whether the large range in Se concentrations was in response to the movement of the snakes between reference and contaminated environments.

Until biodynamic information is obtained for a variety of reptile and amphibian species, it will be difficult to resolve critical mechanisms (i.e., physiology vs. foraging

ecology) driving inter- and intra-specific patterns in accumulation. The elevated concentrations observed in this group of organisms highlights the need for further study.

5.3 BIODYNAMIC MODELING OF Se

5.3.1 MODEL IMPROVEMENTS

The biodynamic modeling approach for predicting and understanding trace element accumulation is powerful and accurate when employed with appropriate model parameters (Luoma and Rainbow 2005; Wang and Rainbow 2008). Even simplified model versions predicting trophic Se transfer from IR and AE and/or field-derived data are relatively successful (Presser and Luoma in press). Nevertheless, advances in our understanding of Se uptake from the aqueous phase and from diets as well as dietary relationships (prey selectivity), present an opportunity to further refine biodynamic modeling of Se. In particular, non-linear relationships between dissolved Se and accumulation in microorganisms, non-linear relationships between dissolved Se and uptake in invertebrates, and finally concentration-dependent AEs must be studied further. In particular, such refinements could improve site-specific application of models, or at least should be evaluated with regard to whether they do result in such improvements.

The ubiquitous essentiality of Se is associated with high-affinity transport systems for cellular Se uptake (Section 5.2.2), which effectively ensures sufficient Se uptake even at low ambient or dietary Se concentrations. High-affinity Se carrier systems are also characterized by a limited capacity for uptake which, at least in theory and over a narrow concentration range, results in hyperbolic relationships between uptake and concentration. These qualities of Se uptake pathways may contribute to observed negative correlations between BAFs and exposure concentrations and between BCFs and exposure concentrations (McGeer et al. 2003; DeForest et al. 2007).

5.3.1.1 Uptake Terms K_d and K_u

Uptake of dissolved Se by algae is traditionally described by a K_d relating the ambient and accumulated Se concentrations. This approach assumes a constant enrichment of Se in microorganisms regardless of dissolved Se concentration. At very low Se concentrations, perhaps similar to uncontaminated conditions, this assumption may not accurately reflect Se entry into the base of food webs, one of the most significant parameters for Se accumulation at higher trophic levels. Algae display a hyperbolic (Michaelis-Menten) relationship with higher apparent "K_d" at low concentrations than at higher concentrations (Table 5.1; Riedel et al. 1991; Fournier et al. 2006), illustrating the potential error associated with the concept of constants describing the enrichment of Se by microorganisms.

Similar considerations apply to the uptake of dissolved Se (and most other trace elements) by invertebrates. Although ingestion and assimilation of dietary Se sources dominates Se accumulation in most invertebrates and aquatic vertebrates, some exceptions may exist. In these cases, uptake of dissolved Se by invertebrates has typically been described by a rate constant (K_u), which may not accurately reflect Se accumulation over broad concentration ranges. Indeed, saturation kinetics

(hyperbolic, Michaelis-Menten relationships) seems to accurately describe uptake from the water at least by some invertebrates (Martin Grosell, University of Miami, personal communication). For metals such non-linearities typically occur at concentrations that exceed those expected in even contaminated environments (Luoma and Rainbow 2008), but no such systematic evaluation is available for Se.

It is recommended that, when available information allows, an EF rather than a constant K_d is employed to characterize the relationship between ambient Se and that accumulated by microorganisms, and that an uptake rate function rather than a constant K_u is used to describe uptake of dissolved Se at higher trophic levels.

To describe both uptake of dissolved Se by microorganisms and higher trophic levels (μg/g/h), the following relationship is recommended:

$$\text{Dissolved Se uptake} = \frac{a \times [\text{ambient Se}]}{b + [\text{ambient Se}]} \qquad (6)$$

where a and b denote maximal uptake rate (μg/g/h) and affinity (μg/L), respectively, of the Se uptake pathway. It is important to apply EFs and uptake rate functions only to a concentration range for which they have been derived. It follows from this recommendation that laboratory experiments to assess the relationship between ambient concentrations and uptake rates should be designed to span the concentrations relevant to the environmental situation of interest.

5.3.1.2 Assimilation from the Diet (AE) and Ingestion Rate (IR)

Limited information is available regarding the relationship between AE and prey Se concentration. However, expectation of interactions between AE and prey Se concentration is dictated by the transport kinetics of intestinal Se transport pathways leading to non-linearity at the lowest (environmentally relevant) concentrations. In theory, at low dietary Se concentrations, high affinity uptake pathways could result in high AE. In contrast, as dietary Se concentrations increase and intestinal carrier systems become saturated, overall AE could decrease. Nevertheless, non-linear relationships between Se concentrations in prey organisms and dietary uptake are not captured in biodynamic modeling efforts that assume AE is a simple constant regardless of exposure concentration. The inverse, non-linear, relationship between dietary Se concentration and AE, predicted from saturable intestinal Se uptake pathways, was first demonstrated for *Daphnia* feeding on 2 different algae species (Guan and Wang 2004). In addition, a recent study of Se assimilation by *A. fransiscana* fed a green algal diet revealed very high AEs (~95% at low algal Se concentration), which gradually declined to a minimum (~75%) as dietary Se concentrations increased (Martin Grosell, University of Miami, personal communication).

In addition to the influence of prey Se concentrations, IR and AE are likely to show interactions. Specifically, for constant prey Se concentrations, it can be expected that higher IRs, which may lead to shorter gut passage time, may impose a limitation on Se assimilation from the diet. Limited information is available about the interactions between AE and IRs, which clearly points to an area in need of further attention. The most important research needs with regard to model refinements lie in understanding the concentration ranges over which differences occur relative to concentrations in

nature (contaminated and uncontaminated waters) and in considering the magnitude of the differences with regard to how they might affect model predictions.

5.3.2 MODEL OUTCOMES: HYPOTHETICAL SCENARIOS ILLUSTRATE PRINCIPLES

One value of any modeling is to illustrate principles in quantitative terms. Figure 5.3 contrasts Se uptake in 2 food webs: one in which the phytoplankton are purely made up of a species of chlorophyte and the other in which the phytoplankton are purely a species of dinoflagellate. Using data from Baines and Fisher (2001), the concentration of Se in the chlorophyte would be 0.2 mg/kg dw and in dinoflagellate would be 20 mg/kg dw at a selenite concentration of 2 µg/L. In general chlorophytes have among the lowest concentration factors for Se and some dinoflagellates have among the highest concentration factors. In one case, we employ a bivalve with a TTF of 6 (similar to zebra mussels and marine mussels) as the invertebrate and use the average fish TTF of 1.1 (typical of many marine and freshwater fish that have been studied). The model suggests that Se concentrations in mussels could range from 1.2 to 120 mg/kg dw for different algal community situations and in the fish they would range from 1.3 to 132 mg/kg dw. The difference is driven by biological differences in the predominant algal species.

Figure 5.3 also contrasts a mussel-based marine/estuarine food web with a copepod-based food web. The scale is log–log, so the difference between these two is minimized visually. But the calculations show that at 2 mg/kg dw in the dinoflagellate, one would expect 13 mg/kg dw in the estuarine fish feeding on mussels and 4.4 mg/kg dw in the estuarine fish feeding on copepods. These differences are similar to those seen in San Francisco Bay (CA, USA; Stewart et al. 2004).

These simple simulations show that at similar Se concentrations in water, outcomes for fish can differ widely, driven by differences in enrichment at the base
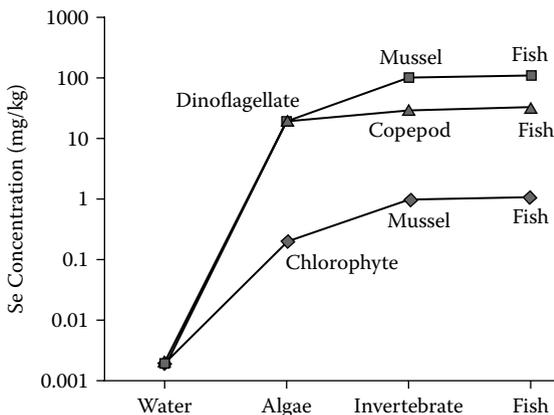

FIGURE 5.3 Selenium accumulation in different species of algae, invertebrates, and fish. Data (TTFs) are for a chlorophyte food web in fresh waters and a dinoflagellate food web in an estuary. Both food webs have a bivalve as the invertebrate and use an average fish TTF of 1.1. The estuarine food web also illustrates the outcome for a copepod with a lower TTF from algae than a mussel.

of the food web and differences in trophic transfer to invertebrates rather than any change in Se concentrations. A choice of a single, universal water quality guideline for Se in these situations would under-protect some aquatic environments and over-protect others in terms of food web exposure to Se.

5.4   SUMMARY

Understanding bioaccumulation and trophic transfer is central to managing ecological risks from Se. The dietary route of exposure generally dominates bioaccumulation processes. This fact has practical implications because the traditional ways of predicting bioaccumulation in animals on the basis of exposure to water concentrations do not work for Se. Further, the predominance of dietary Se exposure pathways mandates that we understand fundamental aspects of Se bioaccumulation in key components of the ecosystems we are trying to protect, from primary producers to top predators. Biodynamic modeling provides a unifying basis for understanding and quantifying dietary uptake and the linkages among food web components.

The single largest step in the bioaccumulation of Se occurs at the base of food webs (Figure 5.1). Primary producers generally concentrate Se from 10^2- to 10^6-fold above ambient dissolved concentrations. We have termed this initial concentrating process the "enrichment function" (EF) because thermodynamic or equilibrium-based constants are not appropriate for describing Se bioaccumulation at the base of food webs. Concentration-dependent EFs are specific to each plant or microbe (particulate material). Uptake of Se by phytoplankton is unlike uptake of trace metals (or organic contaminants). The fact that dead cells do not accumulate or appreciably sorb Se implies that Se bioaccumulation is a non-passive, carrier-mediated process.

Potential to bioaccumulate Se in consumer and predatory animals can be described by a trophic transfer function (TTF; Figure 5.1). TTFs can be derived from established laboratory experimental protocols (biodynamics) or, perhaps with more uncertainty, by using field data to calculate a ratio of the Se concentrations in an animal to Se concentrations in its assumed food. Further, it should be recognized that the TTF can vary with the concentration of Se in the diet due to transport processes in the gastrointestinal tract.

Selenium bioaccumulation by primary producers, invertebrates, and predators varies widely among species. This variation, for animals, is a function of food choice and physiological processes, which can be fundamentally different among taxonomic groups (Figure 5.3). Selenium accumulated by consumer organisms is passed on efficiently to their predators. This finding implies that higher-trophic organisms could be at greater risk in Se-contaminated environments. However, relative to the initial large Se incorporation step at the base of the food web, subsequent transfers to higher trophic levels tend to be smaller. Depending on relative sensitivity to effects, protection of top predators may not guarantee protection of all biota situated lower in the food web.

In light of all of these factors, a single, universal water quality criterion cannot be derived for Se that will protect all aquatic environments with any degree of certainty. Aqueous concentrations of Se that are considered protective in one system may not be protective or attainable in another.

The following knowledge gaps were identified:

1) TTFs in freshwater environments have a relatively high degree of uncertainty because biodynamic parameters for invertebrates and vertebrates are lacking. Therefore, the application of established experimental protocols for dominant freshwater groups (insects and fish) would be highly beneficial. Additionally, there is relatively little information available for fish-to-fish TTFs in both freshwater and marine environments.

2) The variability of TTFs as a function of taxonomy is unclear. Some trends have been identified in marine species, but no such understanding occurs for freshwater taxa. Additional data representing a broad taxonomic range from different ecosystems are required.

3) We need to better understand enrichment at the base of food webs. Specific areas of weakness include our understanding of kinetic processes, particularly saturation kinetics at environmentally relevant concentrations in a wide variety of basal species. Additionally, data for Se uptake into and trophic transfer from bacteria are practically absent for both freshwater and marine systems. Finally, protocols for isolating biotic from abiotic components of suspended particles and bottom sediments would improve model inputs representing Se concentrations at the base of the food web.

4) The bioavailability of selenate to freshwater primary producers deserves more study. In marine systems, the relative abundance of sulfate makes selenate uptake into primary producers relatively unimportant. In freshwaters, this may not be the case.

5) Inter-organ transfers and thus distributions of Se in fish are obviously key mediators of toxicity, but inter-species differences in inter-organ distributions, their variability, and their relevance to reproductive toxicity, remain poorly understood.

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