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A Methodology for Ecosystem-Scale Modeling of Selenium

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ABSTRACT

The main route of exposure for selenium (Se) is dietary, yet regulations lack biologically based protocols for evaluations of risk. We propose here an ecosystem-scale model that conceptualizes and quantifies the variables that determine how Se is processed from water through diet to predators. This approach uses biogeochemical and physiological factors from laboratory and field studies and considers loading, speciation, transformation to particulate material, bioavailability, bioaccumulation in invertebrates, and trophic transfer to predators. Validation of the model is through data sets from 29 historic and recent field case studies of Se-exposed sites. The model links Se concentrations across media (water, particulate, tissue of different food web species). It can be used to forecast toxicity under different management or regulatory proposals or as a methodology for translating a fish-tissue (or other predator tissue) Se concentration guideline to a dissolved Se concentration. The model illustrates some critical aspects of implementing a tissue criterion: 1) the choice of fish species determines the food web through which Se should be modeled, 2) the choice of food web is critical because the particulate material to prey kinetics of bioaccumulation differs widely among invertebrates, 3) the characterization of the type and phase of particulate material is important to quantifying Se exposure to prey through the base of the food web, and 4) the metric describing partitioning between particulate material and dissolved Se concentrations allows determination of a site-specific dissolved Se concentration that would be responsible for that fish body burden in the specific environment. The linked approach illustrates that environmentally safe dissolved Se concentrations will differ among ecosystems depending on the ecological pathways and biogeochemical conditions in that system. Uncertainties and model sensitivities can be directly illustrated by varying exposure scenarios based on site-specific knowledge. The model can also be used to facilitate site-specific regulation and to present generic comparisons to illustrate limitations imposed by ecosystem setting and inhabitants. Used optimally, the model provides a tool for framing a site-specific ecological problem or occurrence of Se exposure, quantify exposure within that ecosystem, and narrow uncertainties about how to protect it by understanding the specifics of the underlying system ecology, biogeochemistry, and hydrology. Integr Environ Assess Manag 2010;6:685–710. © 2010 SETAC

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Original Research

INTRODUCTION

Effects from Se toxicity have proven dramatic because of extirpations (i.e., local extinctions) of fish populations and occurrences of deformities of aquatic birds in impacted habitats (Skorupa 1998; Chapman et al. 2010). The large geologic extent of Se sources is connected to the environment by anthropogenic activities that include power generation, oil refining, mining, and irrigation drainage (Presser, Piper, et al. 2004). Toxicity arises when dissolved Se is transformed to organic Se after uptake by bacteria, algae, fungi, and plants (i.e., synthesis of Se-containing amino acids de novo) and then passed through food webs. Biochemical pathways, unable to distinguish Se from S, substitute excess Se into proteins and alter their structure and function (Stadtman 1974). The impact of these reactions is recorded most importantly during hatching of eggs or development of young life stages. Thus, the reproductive consequences of maternal transfer are the most direct and sensitive predictors of the effects of Se (Heinz 1996).

Each step in this sequence of processes is relatively well known, but the existing protocols for quantifying the linkage between Se concentrations in the environment and effects on animals have orders of magnitude of uncertainties. Conventional methodologies relate dissolved or water-column Se concentrations and tissue Se concentrations through simple ratios (i.e., bioconcentration factor, BCF; bioaccumulation factor, BAF), regressions, or probability distribution functions (DuBowy 1989; Peterson and Nebeker 1992; McGeer et al. 2003; Toll et al. 2005; Brix et al. 2005; DeForest et al. 2007). None of these approaches adequately accounts for each of the important processes that connect Se concentrations in water to the bioavailability, bioaccumulation, and toxicity of Se.

In this paper, we present an ecosystem-scale methodology that reduces uncertainty by systematically quantifying each of the influential processes that links source inputs of Se to toxicity. In particular, we emphasize a methodology for relating dissolved Se to bioaccumulated Se. The methodology allows us to 1) model Se exposure with greater certainty than previously achieved through traditional approaches that skip steps, 2) explain or predict Se toxicity (or lack of toxicity) in site-specific circumstances, and 3) translate proposed Se guidelines among media under different management or regulatory scenarios.

Important components of the methodology are 1) empirically determined environmental partitioning factors between water and particulate material that quantify the effects of dissolved speciation and phase transformation, 2) concentrations of Se in living and nonliving particulates at the base

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of the food web that determine Se bioavailability to invertebrates, 3) Se biodynamic food web transfer factors that quantify the physiological potential for bioaccumulation from particulate matter to consumer organisms and prey to their predators, and 4) critical tissue values that relate bioaccumulated Se concentrations to toxicity in predators. We compile data from 1) laboratory experiments that measured physiological biodynamic parameters for the dietary pathways of invertebrates and fish, and 2) field studies that simultaneously collected particulate, prey, and predator Se concentrations to develop species-specific trophic transfer factors. Additionally, we compiled data from field studies that simultaneously collected dissolved and particulate Se concentrations to evaluate partitioning into the base of the food web. Alternative approaches for modeling of aquatic birds are illustrated because biodynamic data for wildlife are limited. We show that enough data exist, or can be derived site specifically, to address food web transfer in many types of ecosystems. Finally, we test the predictions derived from the ecosystem-scale methodology against observations from nature and compare the outcomes of alternative exposure choices to assess implications for ecosystem management and protection.

Regulatory aspects

Persistent toxicants such as Hg and xenobiotic organic substances are among the most hazardous of contaminants because they efficiently bioaccumulate or biomagnify in food webs and put fish, wildlife, and humans at risk (Thomann 1989; Gobas 1993). Early in the history of pollution by these types of chemicals, a measure of bioaccumulative potential (or trophic transfer potential) was deemed necessary ''because acute toxicity is low (water pathway) and, once chronic effects appear, corrective actions such as terminating the addition of chemical to an ecosystem may not take hold soon enough to alleviate the situation before irreparable damage has been done'' (Neely et al. 1974). Selenium shares many attributes with bioaccumulative chemicals when toxicity is determined from diet, not dissolved exposure (Sappington 2002). Classification of Se as a hazard equivalent to other bioaccumulative chemicals has been contentious (Luoma and Presser 2009).

Regulating agencies such as the US Environmental Protection Agency (USEPA) have recognized that development of water quality Se criteria for the protection of aquatic life and wildlife require consideration of exposures other than solely dissolved Se to understand and assess environmental protection with certainty (USEPA 1998; US Fish and Wildlife Service [USFWS] and National Marine Fisheries Service [NMFS] 1998, amended 2000; Reiley et al. 2003). As of 2010, the USEPA has under consideration a national fish-tissue criterion and other state-, region-, or site-specific approaches for managing Se contamination (USEPA 1997, amended 2000, 2004). In general, this type of criterion would help fill the need to connect effects from a dietary exposure pathway into a regulatory framework. However, such regulations do not yet reflect the current state of knowledge concerning the transfer of Se through ecosystems (Sappington 2002; Reiley et al. 2003), nor do they formalize the knowledge necessary to understand the basis of protective criteria for Se. Furthermore, implementation of a fish-tissue criterion would require translation to a dissolved Se concentration to satisfy other regulatory requirements, such as permit and load limits. An important purpose of this paper is to demonstrate how a step-by-step ecosystem-scale methodology can address these problems and facilitate translation across steps to harmonize regulation.

Overview of modeling approach

A conceptual model (Figure 1) illustrates the linked factors (Table 1) that determine the effects of Se in ecosystems. Figure 1 also shows the data needed (e.g., Se speciation) for optimally modeling or fully understanding these linkages. The first 8 variables (source loads to health effects; Table 1) are considered systematically in developing and implementing an ecosystem-scale methodology. Predator life cycle (constraining the model in time and space) and demographics are listed as components of a comprehensive site-specific assessment but are not covered in detail in this paper. Emphasis in this paper is on protection of fish and birds, but similar modeling techniques could be used to evaluate amphibians and mammals.

The organizing principle for the methodology is the progressive solution of a set of simple equations or models, each of which quantifies a process important in Se exposure (Figure 2). Environmental partitioning between dissolved and particulate phases (K_d) is used here to characterize operationally the uptake and transformation (commonly termed bioconcentration) of dissolved Se into the base of the food web (Figure 2). K_d is environment specific (i.e., dependent on site hydrology, dissolved speciation, and type of particulate material) and is the ratio of the particulate material Se concentration (in dry weight, dw) to the dissolved Se concentration observed at any instant. The base of the food web, as sampled in the environment and characterized by K_d, can include phytoplankton, periphyton, detritus, inorganic suspended material, biofilm, sediment, or attached vascular plants. For simplicity, in our discussion we define this mixture of living and nonliving entities as particulate material. Dissolved or total Se can be specified in the derivation of K_d for modeling to accommodate use of existing data sets, but this substitution is a possible source of variability. Consideration of the amount of suspended particulate material and its contribution to the total Se measurement gives an indication of the difference incurred by this substitution. In our discussions, we refer to a generalized water-column Se concentration, but the preferred parameter to measure and model would be dissolved Se.

Kinetic bioaccumulation models (i.e., biodynamic models; Luoma and Fisher 1997; Luoma and Rainbow 2005) account for the now well-established principle that Se bioaccumulates in food webs principally through dietary exposure. Tissue Se attributable to dissolved exposure makes up less than 5% of overall tissue Se in almost all circumstances (Fowler and Benayoun 1976; Luoma et al. 1992; Roditi and Fisher 1999; Wang and Fisher 1999; Wang 2002; Schlekat et al. 2004; Lee et al. 2006). Biodynamic modeling (Figure 2) further shows that the extent of Se bioaccumulation (the concentration achieved by the organism) is driven by physiological processes that are specific to each species (Reinfelder et al. 1998; Baines et al. 2002; Wang 2002; Stewart et al. 2004). Experimental protocols for measuring parameters such as assimilation efficiency (AE), ingestion rate (IR), and the rate constant that describes Se excretion or loss from the animal (k_e) are

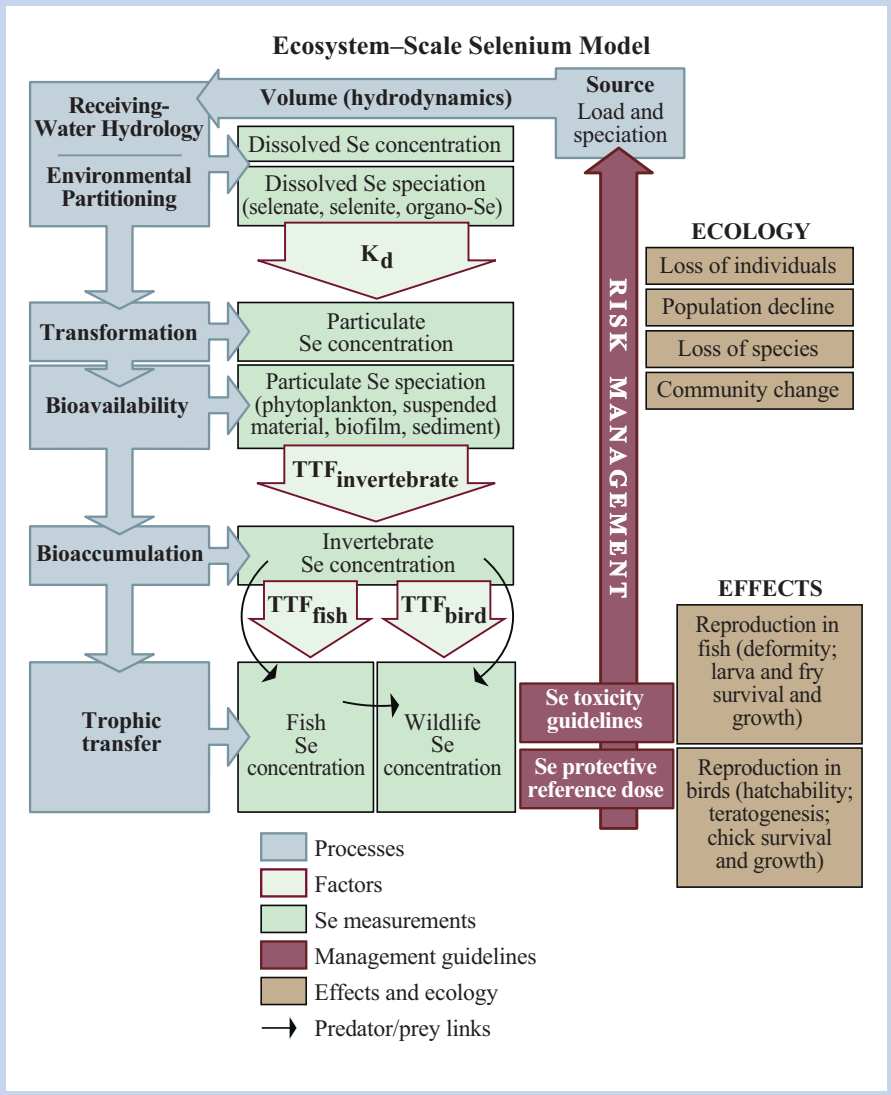

Figure 1. Ecosystem-scale Se model. The model conceptualizes processes and parameters important for quantifying and understanding the effects of Se in the environment. The model can be applied to forecast exposure and to evaluate the implications of management or regulatory choices. K_d = empirically determined environmental partitioning factor between water and particulate material; TTF = biodynamic food web transfer factor between an animal and its food.

now well developed (Wang et al. 1996; Luoma and Rainbow 2005).

Biodynamic models have the further advantage of providing a basis for deriving a simplified measure of the linkage between trophic levels: trophic transfer factors (TTFs; Figure 2; Reinfelder et al. 1998). TTFs are species-specific and link particulate, invertebrate, and predator Se concentrations (e.g., TTF_{clam} or $TTF_{sturgeon}$). They can be derived from laboratory experiments or from field data. $TTF_{invertebrate}$ and $TTF_{predator}$ differ from traditional BAFs in that they are the ratio of the Se concentration in each animal to the Se concentration in its food (Figure 2), whereas BAFs almost always are implemented as the Se concentration in an animal to the Se concentration in the water of its environment. Biodynamic model calculations and ratios derived here employ dw for media (particulate material and tissue). Variability or uncertainty in processes such as AEs or IRs can be directly accounted for in sensitivity analysis as shown for Se by Wang et al. (1996). This is accomplished by considering the range in the experimental observations for the specific animal in the model. Field-derived factors require some knowledge of feeding habits and depend upon available data for that species. Laboratory and field factors for a species can be compared and refined to improve levels of certainty in modeling. Hence, both physiological TTFs derived from kinetic experiments for a species and ecological TTFs derived either from data for a species across different field sites (global) or from one site (site-specific) are of value in modeling and understanding an ecosystem.

By modeling different exposure scenarios, it is possible to differentiate consumer species and food webs in terms of bioaccumulative potential, an important step in reducing uncertainties in predicting ecological risks (Stewart et al. 2004). To translate exposure into toxicity, we employ results from dietary toxicity studies in predators that correlate the two. There has been considerable discussion about choices of protective levels for fish and wildlife (Skorupa 1998; DeForest et al. 1999; Hamilton 2004; Lemly 2002; Adams et al. 2003; Ohlendorf 2003). Nevertheless, tissue guidelines are being proposed to be nationally promulgated by USEPA,

Table 1. Variables considered for ecosystem-scale modeling of Se

Variable	Ecosystem-scale modeling
Source load	Coal fly ash disposal, agriculture drainage, oil refinery effluent, phosphate and coal mining waste leachate, mining discharge
Dissolved speciation	Selenate, selenite, organo-Se
Receiving-water partitioning and/or transformation environment	Wetland and/or marsh, pond, backwater and/or oxbow, stream, river, estuary, ocean, freshwater or saltwater
Particulate speciation	Elemental Se, adsorbed selenite and/or selenate, organo-Se
Bioavailability	Sediment, detritus, phytoplankton, periphyton, biofilm
Invertebrate specific bioaccumulation	Species-specific physiological parameters (ingestion rate, assimilation efficiency, efflux rate, growth), field derived factors
Trophic transfer to fish or aquatic birds[a]	Species-specific physiological parameters (ingestion rate, assimilation efficiency, efflux rate, growth), field derived factors, dose–response curves
Health effect endpoints	Reproduction, teratogenesis, decreased growth, decreased survival (especially in winter), disease (immunosuppression), sublethal (chronic effects)
Predator life cycle	Species-specific energetics (body weight and ingestion rate), life stage (breeding, larval, adult), distribution (resident, mobile, migratory), timing (route, duration), feeding behavior (prey availability and preference, foraging pattern, background intake)
Demographics	Loss of individuals (threatened or endangered species), population reduction, community change, loss of species

[a]Modeling can be extended to terrestrial birds, amphibians, and mammals.

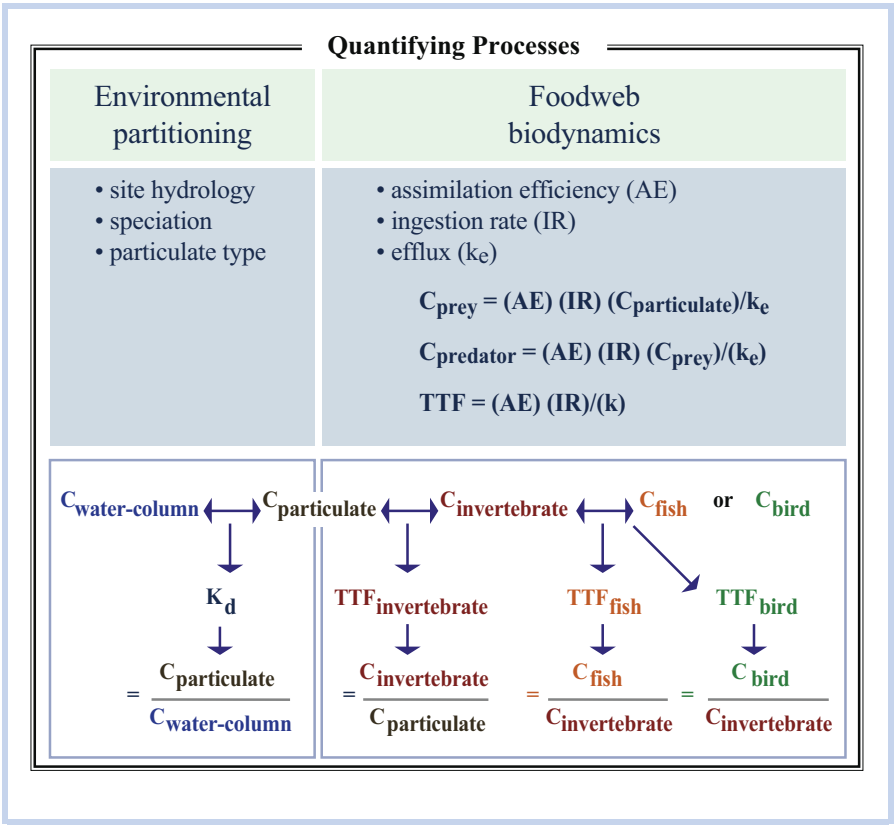

Figure 2. Critical factors for linked steps in ecosystem-scale Se modeling. Environmental partitioning and biodynamic physiological parameters quantify dietary pathways in nature. For modeling, the physiological parameters are combined into a TTF, which characterizes the bioaccumulation potential for each specific particulate–invertebrate pair or prey–predator pair.

recommended by USFWS as part of Endangered Species Act consultation, or stipulated for watershed or regional regulation based on a review of existing toxicity literature (USFWS and NMFS 1998, amended 2000; USEPA 2004). Steps in wildlife criteria development (e.g., ingestion models that use rate of consumption, body weight, and reference dose to calculate a dietary limitation or wildlife criterion) are also delineated here to illustrate that our approach is compatible with a more traditional regulatory approach to the protection of wildlife.

Another use of the model is in understanding the environmental concentrations and conditions that would result in a predetermined Se concentration in the tissues of a predator. Assuming that the tissue guideline is generic for all fish or birds (for example), the choice of the predator species in which to assess that concentration is still important because it determines the $TTF_{invertebrate}$. That specific predator's feeding habits drive the choice of invertebrate, for which a species-specific TTF is used to calculate particulate Se concentrations. A K_d feasible for that ecosystem (or a range of K_ds) is then used to determine the allowable water-column Se concentration, which is ultimately the concentration in that specific type of environment and food web that would result in the specified Se concentration in the predator (i.e., the applied criterion). Thus the allowable water-column concentration can differ among environments, an outcome that reflects the realities of nature. This biologically explicit approach also forces consideration of the desired uses and benefits in a watershed (i.e., which species of birds and fish are the most threatened by Se and/or are the most important to protect).

In the absence of detailed knowledge of the watershed, choices can be made based on rudimentary knowledge about prey and predator pairs; however, the more rudimentary the choices, the greater the uncertainty. Thus, implicitly, the modeling approach creates incentives to understand ecosystems better for which enough is at stake to invest in data collection. Explicitly, it points toward critical choices for data collection. As the knowledge necessary for a full conceptual ecosystem-scale model for Se is developed at a selected site, uncertainties about effects of Se are progressively narrowed. A strength of this approach is that Se bioaccumulation and trophic transfer predicted by the methodology (Figure 1) can be used to validate or estimate uncertainties through comparison of predicted invertebrate, fish, and bird Se concentrations with independent observations of those concentrations from field studies.

MODEL COMPONENTS

Sources of selenium

Knowledge of a dissolved Se concentration in a water body is a crucial first step in understanding the potential for adverse ecological effects. Documenting how different sources and processes contribute to that concentration is also essential (Figure 1). Potential sources of Se in the environment have been well described elsewhere (Seiler et al. 2003; Presser, Piper, et al. 2004). In brief, organics-rich marine sedimentary rocks, especially black shales, petroleum source rocks, and phosphorites, are major sources of Se. In terms of Se as a commodity, Se's source is in igneous Cu deposits. The interface of aquatic systems with waste products or overburden from coal, phosphate, and metals mining; oil refining; fossil fuel combustion; and irrigation in arid regions can deliver Se to the environment on a large scale.

Each of the above sources typically can release Se with a different speciation. Selenate is often dominant in agricultural drainage, mountaintop coal mining and/or valley fill leachate, and Cu mining discharge (Presser and Ohlendorf 1987; Naftz et al. 2009; West Virginia Department of Environmental Protection 2009). Selenite is frequently found in oil refinery and fly-ash-disposal effluents (Bowie et al. 1996; Cutter and Cutter 2004). Combinations of selenite and organo-Se are common in pond-treated agricultural drainage (Amweg et al. 2003) and the oceans (Cutter and Bruland 1984). Speciation in phosphate mining overburden leachate in streams depends on season and flow conditions: selenate during maximum flow, selenite and organo-Se during minimum flow (Presser, Hardy, et al. 2004).

Hydrologic environment

How inputs (source loads) of Se interact in a specific hydrologic environment determines receiving-water Se concentrations (Figure 1). Comprehensive hydrodynamic models can be used to represent Se transport and smaller scale effects such as elevated concentrations near sources of inflow or detailed distribution within receiving waters. Models have been used successfully to describe Se concentrations in complex environments by incorporating basic physical and geochemical processes involved in determining how load and volume interact (Meseck and Cutter 2006; Diaz et al. 2008; Naftz et al. 2009). Simpler approaches can be used to estimate regional scale effects. For example, Se concentrations in San Francisco Bay were estimated by quantifying mass inputs, broadly differentiating seasonal flow regimes, and characterizing source signatures to understand the overall response of the ecosystem to several sources of Se contamination (Presser and Luoma 2006). Regional scale estimates agreed with observations from the use of this abbreviated approach.

Modeling of interactions of Se loading and hydrodynamics initiates the ecosystem-scale approach by developing an understanding of dissolved Se concentrations in a given environment (Figure 1). However, complex physical modeling is not sufficient to determine the ultimate effects of Se in an ecosystem (Wrench and Measures 1982), nor is a detailed understanding of physical processes or dissolved Se distributions adequate to unravel questions about Se effects or its regulation compared with understanding and incorporating phase transformation, biological reactions, and the influences of ecology into modeling.

Partitioning and transformation environments: Speciation and bioavailability

Phase transformation reactions from dissolved to particulate Se are of toxicological significance because particulate Se is the primary form by which Se enters food webs (Figure 1) (Cutter and Bruland 1984; Oremland et al. 1989; Luoma et al. 1992). The different biogeochemical transformation reactions also result in different forms of Se in particulate material: organo-Se, elemental Se, or adsorbed Se. The resulting particulate Se speciation, in turn, affects the bioavailability of Se to invertebrates depending on how an invertebrate samples the complex water, sediment, and particulate milieu that composes its environment.

Given this sequence (Figure 1), the first requirement for reducing the uncertainty in tying dissolved Se to effects on

predators is quantification of the linkage between dissolved Se and Se concentrations in particulate material at the base of the food web. In a data-rich environment, biogeochemical models might be able to capture at least some of the processes that drive phase transformation (see, e.g., Meseck and Cutter 2006), but even sophisticated models, to some extent, rely in their development on empirical observations of partitioning between dissolved and particulate Se.

With the present state of knowledge, it is feasible to use field observations to quantify the relationship between particulate material and dissolved Se as expressed by

$$K_d = C_{particulate} \div C_{water-column}. \quad (1)$$

This operationally defined ratio is an instantaneous observation in which $C_{particulate}$ is the particulate material Se concentration in μg/kg dw and $C_{water\text{-}column}$ is the water-column Se concentration in μg/L. Use of a partitioning descriptor can be controversial because K_d formally implies an equilibrium constant. Indeed, thermodynamic equilibrium does not govern Se distributions in the environment (Cutter and Bruland 1984; Oremland et al. 1989), and partitioning coefficients for Se are known to be highly variable (McGeer et al. 2003; Brix et al. 2005), but K_d can be a useful construct if it is recognized that the instantaneous ratio is not intended to differentiate processes or to be predictive beyond the specific circumstance in which it is determined. The sole intention is to describe the particulate to water ratio at the moment when the sample is taken.

Experience shows that repeated observations of this operational K_d can narrow uncertainties about local conditions. However, K_d will vary widely among hydrologic environments (i.e., in parts of a watershed such as wetlands, streams, or estuaries) and potentially among seasons. Consideration of the characteristics of the environment such as speciation, residence time, and/or particle type can also be used to narrow this potential variability, but K_d remains a large source of uncertainty in the model if translation to a water-column Se concentration is required. Initiation of modeling with a particulate Se concentration (see below under *Validation*) eliminates this step and the associated uncertainty and points to the importance of particulate phases in determining Se toxicity. If required, performing calculations with several alternative, but plausible, site-specific choices for K_d can elucidate and constrain the uncertainty around the introduction of K_d.

Speciation. Dissolved Se can exist as selenate, selenite, or organo-Se (+6, SeO_4^{-2}; +4, SeO_3^{-2}, −2, Se-II, respectively). The dissolved species that are present will influence the type of phase transformation reaction that creates particulate Se. Examples of types of reactions include 1) uptake by plants and phytoplankton of selenate, selenite, or dissolved organo-Se and reduction to particulate organo-Se by assimilatory reduction (see, e.g., Sandholm et al. 1973; Riedel et al. 1996; Wang and Dei 1999; Fournier et al. 2006); 2) sequestration of selenate into sediments as particulate elemental Se by dissimilatory biogeochemical reduction (e.g., Oremland et al. 1989); 3) adsorption as coprecipitated selenate or selenite through reactions with particle surfaces; and 4) recycling of particulate phases back into water as detritus after organisms die and decay (see, e.g., Reinfelder and Fisher 1991; Velinsky and Cutter 1991; Zhang and Moore 1996). Selenate is the least reactive of the 3 forms of Se, and its uptake by plants is slow. If all other conditions are the same, K_d will increase as selenite and dissolved organo-Se concentrations increase (even if that increase is small). Experimental data support this conclusion. Calculations using data from laboratory microcosms and experimental ponds show speciation-specific K_ds of 140 to 493 when selenate is the dominant form, 720 to 2800 when an elevated proportion of selenite exists, and 12 197 to 36 300 for 100% dissolved seleno-methionine uptake into at least some algae or periphyton (Besser et al. 1989; Kiffney and Knight 1990; Graham et al. 1992).

Residence time. The conditions in the receiving-water environment are also important to phase transformation. When selenate is the only form of Se and residence times are short (e.g., streams and rivers), the limited reactivity of selenate means that partitioning of Se into particulate material tends to be low. Similarly, dissimilatory reduction does not seem efficient unless water residence times are extended. Longer water residence times, in sloughs, lakes, wetlands, and estuaries, for example, seem to allow greater uptake by plants, algae, and microorganisms. This is accompanied by greater recycling of selenite and organo-Se back into solution, further accelerating uptake (Bowie et al. 1996; Lemly 2002; Meseck and Cutter 2006). Neither selenite nor organo-Se is easily reoxidized to selenate, because the reaction takes hundreds of years (Cutter and Bruland 1984). Therefore, the net outcome in a watershed that flows through wetland areas or estuaries is a gradual build-up of selenite and organo-Se in water and higher partitioning into particulate material (Lemly 1999; Presser and Luoma 2009). Environments downstream in a watershed can also have higher concentrations of selenite and organo-Se, and higher K_ds, reflecting the cumulative contributions of upstream recycling in a hydrologic system.

Differences in Se bioaccumulation have been described between lentic (stream) and lotic (lake) environments (Hamilton and Palace 2001; Brix et al. 2005; Orr et al. 2006). This could at least partially reflect the observations described above: if other conditions are similar, environments with longer residence times, such as lakes, tend to have greater recycling, a higher ratio of particulate and/or dissolved Se, and higher concentrations of Se entering the food web. Exceptions also occur, however. For example, flow period or season might be a consideration even within individual segments of a watershed.

Particle type. The K_d can also be influenced by the type of material in the sediment. For example, field data for Luscar Creek in Alberta, Canada, show a hierarchy of Se concentrations: 2.4 μg/g in sediment, 3.2 μg/g biofilm, and 5.5 μg/g for filamentous algae (Casey 2005). Using these concentrations with a field-measured water-column Se concentration of 10.7 μg/L yields K_ds of 224, 299, and 514, respectively, with an average K_d of 346. Similarly, field data for a slough tributary to the San Joaquin River, California, USA, show a hierarchy of particulate Se concentrations: 0.47 μg/g in sediment, 2.4 μg/g in algae, and 7.9 μg/g in detritus (Saiki et al. 1993). Using these concentrations with a field measured water-column Se concentration of 13 μg/L yields K_ds of 36, 185, and 608, respectively, with an average K_d of 276. In these instances, the influence of particle type is not as great as that of speciation and residence time.

Calculation of K_d. Knowing the range of K_ds in nature for a specific category of site (e.g., ponds, rivers, estuaries) allows some generalization about the potential range of particulate Se concentrations that could occur at a site under different modeled receiving-water conditions. We compiled data from 52 field studies in which both water-column Se concentrations and particulate Se concentrations were determined and calculated K_ds (Supplemental Data Table A). The K_ds across the complete variety of ecosystems vary by as much as 2 orders of magnitude (100–10 000) and measure up to 40 000 (Table 2). Even higher K_ds have been measured in experimental studies using cultured phyoplankton (Reinfelder and Fisher 1991; Baines and Fisher 2001).

There is, however, some consistency among types of environments. Most rivers and creeks show K_ds of greater than 100 and less than 300 (Table 2). For example, K_ds for the Fording River, British Columbia, Canada, and San Joaquin River are 122 and 146, respectively. Lakes and reservoirs are mainly greater than 300, with many being in the 500 to 2000 range. The K_ds for Salton Sea, California, USA, and the Great Salt Lake, Utah, USA, are 1196 and 1759 respectively. The K_ds for Hyco Reservoir, North Carolina, USA, and Belews Lake, North Carolina, USA, based on data from the 1980s are approximately 3000. Those K_ds greater than 5000 are usually associated with estuary and ocean conditions (e.g., seaward San Francisco Bay and Newport Bay, California, >10 000). Exceptions from this categorization of streams included a set of streams in southeastern Idaho receiving runoff from phosphate mining waste characterized by a majority of selenite plus organo-Se under certain flow conditions (Presser, Hardy, et al. 2004). The overall K_d average for these streams is 1708, with the range among individual streams showing considerable variability (494–3000). These data were for partitioning into mainly attached algae.

Modeling and data requirements. Data collected in site-specific field situations for particulate phases can include benthic or suspended phytoplankton, microbial biomass, detritus, biofilms, and nonliving organic materials associated with fine-grained (<100 μm) surficial sediment (Luoma et al. 1992). For modeling, if the data are available, averaging concentrations of Se in sediment, detritus, biofilm, and algae to define K_d may help to take into account partitioning in different media and best represent the dynamic conditions present in an aquatic system. At a minimum, interpretation and modeling of particulate Se concentration data should take into consideration the nature of the particulate material. In that regard, collection of one consistent type of material that can be compared among locations is an option. Bed sediments are the least desirable choice for calculating K_d, especially if the sediments vary from sand to fine-grained among the samples. In general, sandy sediments dilute concentrations with a high mass of inorganic material and may yield K_ds that are anomalously low (Luoma and Rainbow 2008).

Bioaccumulation: Invertebrates

Biodynamics and kinetic trophic transfer factors. A key aspect of Se risk is bioaccumulation (i.e., internal exposure) in prey and predators (Figure 1; Luoma and Rainbow 2005). Bioaccumulation of Se is modeled here through a biodynamic quantification of the processes that lead to bioaccumulation. These pathway-specific bioaccumulation models (e.g., the dynamic multipathway bioaccumulation [DYMBAM] model) quantify Se tissues concentrations through consideration of 1) the form and concentration of Se in food (i.e., particulate material) and water, and 2) the physiology (AE, IR, k_e, and growth) of invertebrates (Luoma et al. 1992; Wang et al. 1996; Schlekat et al. 2002a) as expressed by

$$C_{species}/dt = [(k_u)(C_w) + (AE)(IR)(C_f)] - (k_e + k_g)(C_{species}), \quad (2)$$

where $C_{species}$ is the contaminant concentration in the animal (μg/g dw); t is the time of exposure (d), k_u is the uptake rate constant from the dissolved phase ($L \cdot g^{-1} d^{-1}$), C_w is the contaminant concentration in the dissolved phase (μg/L), AE is the assimilation efficiency from ingested particles (%) or the proportion of ingested Se that is taken up into tissues, IR is the ingestion rate of particles ($g \cdot g^{-1} d^{-1}$), C_f is the contaminant concentration in ingested material (μg/g dw), k_e is the efflux rate constant (/d), and k_g is the growth rate constant (/d). The differential equation describing these processes can be solved to determine metal concentrations at steady state as

$$C_{species} = [(k_u)(C_w) + (AE)(IR)(C_f)] \div [k_e + k_g]. \quad (3)$$

The physiological components of the model are species-specific, and each can be determined experimentally for any given species (see, e.g., Luoma et al. 1992; Wang et al. 1996). The mathematics state that bioaccumulation in an organism results from a combination of gross influx rate as balanced by the gross efflux rate (i.e., biodynamics). Gross efflux is an instantaneous function of the concentration in tissues and the rate constants of loss. Gross influx can come from water or from food. The uptake rate from each is a function of the concentration of Se in that phase.

Biodynamic experiments (Figure 2) mimic dietary pathways in nature by using radiolabeled dissolved selenite to radiolabel food (i.e., particulate material) that is then fed to invertebrates (Luoma and Fisher 1997). A large body of evidence shows that uptake rates of dissolved Se are almost always sufficiently slow in invertebrates that uptake from the dissolved phase is irrelevant compared with uptake from particulate sources such as phytoplankton, detritus, or sedimentary material (Fowler and Benayoun 1976; Luoma et al. 1992; Wang and Fisher 1999; Wang 2002; Schlekat et al. 2004; Lee et al. 2006). For example, the calculated tissue component attributable to dissolved selenite uptake using experimentally determined physiological parameters for the large copepods *Tortanus* sp. and *Acartia* sp. is 1.7% and for the clam *Corbula amurensis* is 1.3% (Schlekat et al. 2002b, 2004; Lee et al. 2006). Thus, a simplification to exposure from only food is justified. The rate constant of growth is significant only when it is comparable in magnitude to the rate constant of Se loss from the organism. Consideration of the complications of growth can usually be eliminated if the model is restricted to a long-term, averaged accumulation in adult animals (Wang et al. 1996).

In the absence of rapid growth, a simplified, resolved exposure equation for invertebrates is

$$C_{invertebrate} = [(AE)(IR)(C_{particulate})] \div [k_e]. \quad (4)$$

To simplify modeling, these physiological parameters can be combined to calculate a $TTF_{invertebrate}$, which characterizes

Table 2. Calculated K_ds based on field studies (supporting data and references for each site are shown in Supplemental Data Table A)

K_d	Ecosystem
107	San Diego Creek, California
110	Alamo River, California
122	Fording River, British Columbia (sediment)
146	San Joaquin River, California
>200	
255	San Diego Creek, constructed pond, California
256	New River, California
269	Tulare Basin, evaporation ponds, California (range 109–500)
272	Upper Newport Bay, California (range 101–776)
276	Mud Slough, California
340	Benton Lake (pool 2), Montana
346	Luscar Creek, Alberta, Canada (range 220–514)
355	Kesterson Reservoir (SLD/pond 2), California (range 200–500)
359	Salt Slough, California
494	Sage Creek, Idaho
≥500	
500	Benton Lake, Montana, pool 5
512	Benton Lake, Montana, pool 1 channel
591	Elk River, British Columbia
611	Lower Great Lakes, Lake Ontario
625	East Allen Reservoir, Wyoming
657	Crow Creek at Toner, Idaho
667	Meeboer Lake, Wyoming
750	Diamond Lake, Wyoming
762	Chevron Marsh (constructed), California (range 214–1241)
767	Miller's Lake, Colorado
784	San Diego Creek constructed marsh, California
818	Mac Mesa Reservoir, Colorado
968	Sweitzer Lake, Colorado
968	Desert Reservoir, Colorado
>1000	
1104	Mud River at Spurlock, West Virginia
1196	Salton Sea, California
1224	Twin Buttes Reservoir, Wyoming
1312	Galett Lake, Wyoming
1341	Angus Creek, Idaho
1388	Lower Great Lakes, Hamilton Harbor
1436	Tulare Basin, evaporation ponds, California
1498	Big Canyon Wash (sites 1 and 2), California
1579	Cobb Lake, Colorado
1619	Timber Lake, Colorado
1717	Larimer Hwy. 9 pond, Colorado
1759	Great Salt Lake, Utah
1800	Upper Mud River Reservoir at Palermo, West Virginia
1818	Crow Creek above Sage Creek, Idaho
1941	Wellington State Pond, Colorado
1943	Thompson Creek, Idaho
>2000	
2143	Highline Reservoir, Colorado
2250	Deer Creek, Idaho
2798	Belews Lake, North Carolina
2902	Kesterson Reservoir (pond 8), California
>3000	
3044	Hyco Reservoir, North Carolina
3150	Big Canyon Wash (site 3), California
3556	Kesterson Reservoir (pond 11), California
4000	Delaware River (tidal freshwater), Delaware
>5000	
6500	Great Marsh, Delaware
7800	San Francisco Bay (1998–1999) (range 3198–26 912)
9456	Salton Sea estuary, Alamo River
12 000	Salton Sea estuary, Whitewater River
13 800	Seaward San Francisco Bay (1998–1999) (range 8136–26 912)
15 000	Xiamen Bay, Fujian Province, China
17 400	Salton Sea estuary, New River, California
18 900	Lower Newport Bay, California (range 6933–42 715)
21 500	San Francisco Bay (1986; 1995–1996) (range 3000–40 000)

the potential for each invertebrate species to bioaccumulate Se. $TTF_{invertebrate}$ is defined as

$$TTF_{invertebrate} = (AE)\,(IR) \div k_e. \quad (5)$$

For clams and mussels, AEs as low as 20% have been found for sediments containing elemental Se (Luoma et al. 1992; Roditi and Fisher 1999; Lee et al. 2006). Assimilation efficiencies of about 40% are typical for experiments in which mussels are exposed to Se adsorbed to particulate materials (see, e.g., Wang and Fisher 1996). However, both elemental and adsorbed Se are probably minor components of the food of most organisms. Assimilation of Se is more efficient when animals ingest living food or detritus, both of which are dominated by organo-Se. From these materials, AEs vary from 55 to 86% among species, with smaller differences among living food types such as different species of algae (see, e.g., Reinfelder et al. 1997; Roditi and Fisher 1999; Schlekat et al. 2004; Lee et al. 2006). If data on particulate speciation are available (see, e.g., Doblin et al. 2006; Meseck and Cutter 2006), then a composite AE may be employed. In this case, the AE for each form of the particulate Se is applied to its fraction of the total Se in sediments. However, particulate speciation data are rarely available. Because most particulate feeders seek organic material in their food, AEs of >50% are probably the best generic representation of assimilation efficiency in nature. Use of species-specific data may result in a more precise value, but validation studies suggest that use of a generic AE, determined for the species of interest with an average-type food, does not add great uncertainty to the calculations (see, e.g., Luoma et al. 1992; Luoma and Rainbow 2005).

Schlekat et al. (2004) determined physiological parameters for the copepods *Tortanus* sp. and *Acartia* sp. of AE = 52% and $k_e = 0.155$. They assumed an IR = 42% from the literature. If the copepods consume diatoms containing 0.5 μg/g Se, then bioaccumulated Se at steady state is

$$\begin{aligned} C_{copepod} &= (0.52)(0.42)(0.5\,\mu g/g) \div 0.155 \\ &= 0.72\,\mu g/g. \end{aligned} \quad (6)$$

Combining the physiological parameters gives a $TTF_{copepod}$ of 1.4. In contrast, Lee et al. (2006) determined physiological parameters for the bivalve C. *amurensis* of AE = 45%, IR = 25%, $k_e = 0.025$. If C. *amurensis* consumed phytoplankton containing 0.5 μg/g Se, then bioaccumulated Se at steady state is

$$C_{clam} = (0.45)(0.25)(0.5\mu g/g) \div 0.025 = 2.36\mu g/g, \quad (7)$$

and the TTF_{clam} is 4.5. The difference in Se concentrations between the copepod and the clam is primarily driven by the slower rate constant of loss in the bivalve compared with the copepod (i.e., 0.155 vs. 0.025). In both cases, Se concentrations increased from one trophic level to the next (TTF >1), but much more so in the bivalve.

Uncertainties about generic constants are least if species-specific and site-specific information is available for 1) assimilation efficiencies of different types of particulate matter, 2) concentrations of Se in particulate phases (such as suspended particulate material), and 3) proportions of different foods likely to be eaten by that species. Then, a concentration of Se in food can be calculated that takes into account site-specific bioavailability of particulate material to invertebrates. The generalized equation is

$$\begin{aligned} C_{particulate} = {} & (AE)(C_{particulate\,a})(\text{sediment fraction}) \\ & + (AE)(C_{particulate\,b})(\text{detritus fraction}) \\ & + (AE)(C_{particulate\,c})(\text{algae fraction}). \end{aligned} \quad (8)$$

Hypothetically, let us assume that particulate material is composed of 20% sediment, 40% detritus, and 40% algae and that Se particulate concentrations are 0.5 μg/g in sediment, 2.0 μg/g in detritus, and 4.0 μg/g in algae. From the literature, reasonable assimilation efficiencies for these phases are 15% for sediment, 35% for detritus, 60% for algae. Consequently, the particulate Se concentration for use in modeling is

$$\begin{aligned} &0.02\mu g/g \text{ from sediment} + 0.28\mu g/g \text{ from detritus} \\ &\quad + 0.96\mu g/g \text{ from algae} = 1.3\mu g/g. \end{aligned} \quad (9)$$

We compiled physiological parameters for invertebrates available in the literature in which AE, IR, and k_e data were determined for an identified test species (Supplemental Data Table B). Sufficient species-specific data, although mainly from marine species, are available from kinetic experiments to calculate $TTF_{invertebrate}$ for a number of species from different feeding guilds. These are enough data at least to begin to model important food webs. A summary of the available laboratory data for the marine environment used for modeling shows that TTFs for invertebrates vary from 0.6 for amphipods to 23 for barnacles (Table 3). The vast majority of TTFs are >1. The TTFs vary 38-fold among species, but increasing Se concentrations from the base of the food web into invertebrates is the rule, rather than the exception, for the available data. This 38-fold variability is propagated up food webs by subsequent trophic transfer steps. The result is that some predators are exposed to much higher Se concentrations than other predators.

Field-derived trophic transfer factors. The kinetic experiments cited above focused mainly on marine species; the freshwater invertebrate kinetic database is weak. However, many field studies are conducted at freshwater sites. When laboratory data are not available, a field $TTF_{invertebrate}$ can be defined from matched data sets (in dw or converted to dw) of particulate and invertebrate Se concentrations as

$$TTF_{invertebrate} = C_{invertebrate} \div C_{particulate}. \quad (10)$$

We calculated freshwater TTFs from field studies documented in the literature (Supplemental Data Table C) and summarized the TTFs by species of invertebrate for modeling (Table 3). We narrowed uncertainties inherent in the field-data approach by constraining the compilation to real-time data that have clearly defined particulate phases and food webs. Either 1) field averages of multiple matched data sets (Se concentrations in particulate material and invertebrates that is time-specific) from sites with similar food webs or 2) regressions of particulate to invertebrate Se concentrations for a series of individual sites with similar food webs were used. Nevertheless, the field TTFs are likely to be more uncertain than the laboratory-derived TTFs. The availability of additional field observed TTFs surely will be improved upon in the future.

Table 3. Summary of selected TTFs for invertebrates, fish, and birds used in modeling and validation (TTFs are derived from data and references shown in Supplemental Data Tables A, B, and C)

Invertebrate	TTF
Amphipod (marine) (*Leptocheirus plumulosus*)	0.6
Amphipod (freshwater) *(Hyalella azteca, Gammarus fasciatus, Corophium* spp.)	0.9
Mysid (marine) (*Neomysis mercedis*)	1.3
Euphausiid (marine) (*Meganyctiphanes norvegica*)	1.3
Copepod (marine) (*Acartia tonsa, Temora longicornis, Tortanus* sp., *Oithona, Limnoithona*)	1.35
Zooplankton (freshwater composite)	1.5
Crayfish (*Procambarus clarki*, Astacidae, *Orconectes* sp.)	1.6
Brine fly (*Ephydra gracilis*)	1.65
Daphnia (Daphnia magna)	1.9
Oyster (*Crassostrea virginica*)	2.05
Corixid (*Cenocorixa* sp.)	2.14
Cranefly (Tipulidae)	2.3
Brine shrimp (young) (*Artemia franciscana*)	2.4
Stonefly (Perlodidae/Perlidae, Chloroperlidae)	2.6
Damselfly (Coenagrionidae)	2.6
Mayfly (Baetidae, Heptageniidae, Ephemerellidae)	2.7
Chironomid (*Chironomus* sp.)	2.7
Clam (*Corbicula fluminea*)	2.8
Aquatic insect (average)[a]	2.8
Caddisfly (Rhyacophilidae, Hydropsychidae)	3.2
Aquatic insect composite	3.2
Brine shrimp (adult)	4.2
Clam (*Macoma balthica*)	4.5
Mussel (*Dreissena polymorpha*)	6.0
Clam (*Corbula amurensis*)	6.25
Mussel (*Mytilus edulis*)	6.3
Clam (*Puditapes philippinarum*)	11.8
Barnacle (*Elminius modestus*)	15.8
Barnacle (*Balanus amphitrite*)	20.3
Clam (*Mercenaria mercenaria*)	23
Fish (whole-body or muscle)	
Leopard shark (*Triakis semifasciata*)	0.52
Gilthead sea bream (*Sparus auratus*)	0.6
Brook trout (*Salvelinus fontinalis*)	0.77
Smooth toadfish (*Tetractenos glaber*)	0.8
Chinese mudskipper (*Periophthalmus cantonensis*)	0.84
Striped bass (juvenile) (*Morone saxatilis*)	0.89
Sucker (*Catostomus* sp.) (Utah and mountain suckers are common in Idaho)	0.97
Rainbow trout (*Oncorhynchus mykiss*)	0.98
Fathead minnow (larval and adult) (*Pimephales promelas*)	1.0
Largemouth bass (*Micropterus salmoides*)	1.0
Cutthroat trout (*Oncorhynchus clarkii*)	1.0
Bluegill (*Lepomis macrochirus*)	1.06
Mangrove snapper (*Lutjanus argentimaculatus*)	1.1
European sea bass (*Dicentrarchus labrax*)	1.1
Chub (*Gila* sp.) (Utah chub is common in Idaho)	1.2
Yellowfin goby (*Acanthogobius flavimanus*)	1.2
Western mosquitofish (*Gambusia affinis*)	1.25
White sturgeon (*Acipenser transmontanus*)	1.3
Brown trout (*Salmo trutta*)	1.3
Mountain whitefish (*Prosopium williamsoni*)	1.3
Sailfin molly (*Poecilia latipinna*)	1.4
Mottled sculpin (*Cottus bairdi*)	1.4
Longnose dace (*Rhinichthys cataractae*)	1.5
Redside shiner (*Richardsonius balteatus*)	1.5
Starry flounder (*Platichthys stellatus*)	1.6
Bird (egg)	
Mallard (*Anas platyrhynchos*)	1.8

[a]Mean of mayfly, caddisfly, crane fly, stonefly, damselfly, corixid, and chironomid.

Freshwater invertebrate TTFs compiled for modeling range from 0.9 for amphipods to 6.0 for zebra mussels (Table 3). Invertebrate TTFs fall into several broad categories in terms of bioaccumulative potential that include means of $\leq$1 for amphipods, 1.3 to 1.9 for crustaceans, 2.8 for aquatic insects, and $\geq$2.8 to 6.0 for clams and mussels. To illustrate the level of uncertainty for one group of organisms, the value for $TTF_{aquatic\ insect}$ used in modeling (2.8) can be compared with several sets of data for insects that include mayfly, caddisfly, cranefly, stonefly, damselfly, corixid, and chironomid (TTF range 2.3–3.2; Supplemental Data Table C and Table 3; Birkner 1978; Saiki et al. 1993; Casey 2005; Harding et al. 2005). Few species-specific comparisons of physiologically derived TTFs with comprehensively derived field TTFs are available (Supplemental Data Tables B and C). However, the range of values for freshwater invertebrates is remarkably

similar to that for marine invertebrates determined in the laboratory, as are the values for comparable taxa (Table 3).

TTFs are species-specific because of the influence of the physiology of the animal. They may vary to some extent as a function of the concentration in food, or if AE or IR vary (Besser et al. 1993; Luoma and Rainbow 2005). For modeling here, TTFs from laboratory studies are calculated using a chosen set of physiological or kinetic parameters, usually a mean from the range of experimental data, presented for a specific species. TTFs from field studies are calculated from averages or regressions for specific particulate material–prey pairs. These approaches lead to consideration of a single TTF to quantify trophic transfer from particulate material to invertebrate for each species. If enough data are available to develop diet–tissue concentration regressions specific to inhabitants of a watershed, then use of those regressions would provide more detailed TTFs than single determinations. Additionally, in nature, if it is assumed that organisms regulate a constant minimum concentration of Se, then the observed TTF will increase when the concentration in food is insufficient to maintain the regulated concentration. Data sets from which TTFs are derived for use in modeling here were collected from sites exposed to Se contamination and identified as problematic because of Se bioaccumulation. As noted previously, the relatively small variation of TTF within taxonomically similar animals is evidence that these potential sources of uncertainty may be classified as small (less than 2-fold; see Landrum et al. 1992).

Trophic transfer: Fish

Biodynamics and kinetic trophic transfer factors. Biodynamics can also be applied to fish that feed on invertebrates (Figures 1 and 2). Laboratory test systems extend water–particulate–invertebrate food webs by feeding radiolabeled invertebrates to fish (Reinfelder and Fisher 1994; Baines et al. 2002; Xu and Wang 2002). The mechanistic equations for modeling of Se bioaccumulation in fish tissue are the same as for invertebrates, if whole body concentrations in fish are the endpoint. The choice of C_f (i.e., the contaminant concentration in the ingested food) for fish should reflect the preferred foods of the specific species. Thus, modeling is specific for each fish species in terms of both physiology and food choices.

Uptake of selenite from solution contributes even less to bioaccumulation in fish than it does in invertebrates. For example, the calculated tissue component attributable to dissolved selenite using experimentally determined physiological parameters for mangrove snapper (*Lutjanus argentimaculatus*) is <0.16% (Xu and Wang 2002).

In the absence of rapid growth, the exposure equation for a fish that eats aquatic insects, for example, simplifies to

$$C_{fish} = [(AE)(IR)(C_{invertebrate})] \div [k_e]. \quad (11)$$

A TTF_{fish} characterizes the potential for each fish species to bioaccumulate Se and is defined as

$$TTF_{fish} = (AE)\,(IR) \div k_e. \quad (12)$$

Complete species-specific information (i.e., AE, IR, k_e) from kinetic experiments is available for few fish species (Supplemental Data Table D). To expand the limited kinetic database for fish species, entries that contain some measured values and some assumed parameters (e.g., 5% ingestion rate, 50% assimilation efficiency) are included. For modeling, we compiled TTF_{fish} by combining these physiological parameters for each fish species for which some experimental data are available (Table 3).

Selenium concentration in whole-body fish is calculated in modeling because that type of data is experimentally available, routinely collected, and proposed for Se regulation. Transfer to fish ovaries or egg tissue is more meaningful in terms of a direct connection to reproductive endpoints, but available data are scant (North America Metals Council 2008). Additional conversion factors could be derived to link to ovary or egg Se concentrations (Lemly 2002).

Xu and Wang (2002) determined physiological parameters for mangrove snapper (AE = 69%, IR = 5%, $k_e = 0.027$). To calculate a TTF_{fish}, if a snapper consumes brine shrimp larvae with an Se concentration of 5 μg/g, then the calculated snapper tissue Se concentration is

$$C_{snapper} = (0.69)(0.05)(5\mu g/g) \div 0.027 = 5.6\mu g/g. \quad (13)$$

Some increase in snapper Se concentration is shown in this example, insofar as the $TTF_{snapper}$ is 1.1. For comparison, Baines et al. (2002) determined physiological parameters for juvenile striped bass (*Morone saxatilis*; AE = 42%, IR = 17%, $k_e = 8\%$). If a bass consumes brine shrimp with an Se concentration of 5.0 μg/g, the calculated bass tissue Se concentration is

$$C_{striped\,bass} = (0.42)(0.17)(5.0\mu g/g) \div 0.08 = 4.46\mu g/g. \quad (14)$$

The $TTF_{striped\ bass}$ is 0.89, signifying efficient food web transfer but an accumulated body burden slightly less than that occurring in the invertebrate diet.

Field-derived trophic transfer factors. Given the paucity of experimental kinetic data for fish, we reviewed field data to obtain species-specific TTFs relevant to freshwater and marine fish (Supplemental Data Table D). A field derived species-specific TTF_{fish} is defined as

$$TTF_{fish} = C_{fish} \div C_{invertebrate}, \quad (15)$$

where $C_{invertebrate}$ is for a known prey species, C_{fish} is reported as muscle or whole-body tissue, and both Se concentrations are reported in dw. The calculations were constrained as described above for field-derived $TTF_{invertebrate}$ by using real-time data and those studies that have clearly defined food webs (i.e., matched data sets of invertebrate and fish Se concentrations in dw). Derived freshwater TTF_{fish} are summarized by species for modeling (Table 3). For example, a species-specific $TTF_{white\ sturgeon}$ of 1.3 was calculated from field studies of San Francisco Bay using matched data sets for clams and sturgeon. Species-specific TTFs of 1.04 and 0.91 (mean 0.98) were calculated for rainbow trout from field studies in southeast Idaho, USA, and Alberta, Canada, using matched data sets for aquatic insects (mainly mayflies) and trout (Supplemental Data Table D and Table 3). The range of TTFs derived for fish from laboratory experiments and field data is remarkably similar, with a mean TTF of 1.1 for 25 fish species. TTFs for all fish species fall within a relatively narrow range (0.5–1.6, or less than a 4-fold variation) compared with those among

invertebrate species (38-fold variation; Table 3). Consequently, variability in bioaccumulated Se among fish species and among food webs is driven more by a fish species' dietary choice of invertebrate and the bioaccumulation kinetics of that invertebrate than by differences in dietary transfer to the fish itself.

Most fish, of course, eat a mixed diet, with tendencies toward certain types of foods. Modeling of Se bioaccumulation can represent a diet that includes a mixed proportion of prey in the diet through use of the equation

$$\begin{aligned} C_{fish} = (TTF_{fish})[&(C_{invertebrate\,a})(\text{prey fraction}) \\ &+ (C_{invertebrate\,b})(\text{prey fraction}) \\ &+ (C_{invertebrate\,c})(\text{prey fraction})]. \end{aligned} \quad (16)$$

For example, using a hypothetical, but typical, TTF_{fish} of 1.1, a mixed invertebrate diet of 50% amphipods at 1.8 μg/g, 25% daphnids at 3.8 μg/g, and 25% chironomids at 5.6 μg/g, the equation yields

$$\begin{aligned} 1.1[&(1.8\mu g/g)(50\%) + (3.8\mu g/g)(25\%) \\ &+ (5.6\mu g/g)(25\%)] \\ &= 3.6\mu g/g. \end{aligned} \quad (17)$$

This Se concentration is in contrast to a concentration of 6.2 μg/g if a single component diet of chironomids is considered.

Modeling of fish tissue can also represent stepwise or sequential bioaccumulation from particulate material through invertebrate to fish by combining the equations

$$\begin{aligned} C_{invertebrate} &= (TTF_{invertebrate})(C_{particulate}) \text{ and } C_{fish} \\ &= TTF_{fish}(C_{invertebrate}). \end{aligned} \quad (18)$$

to give

$$C_{fish} = (TTF_{invertebrate})(C_{particulate})(TTF_{fish}). \quad (19)$$

For example, if a stream contains a particulate Se concentration of 2 μg/g and is inhabited by trout (TTF 1.0) that are eating a single invertebrate diet of mayflies (TTF 2.8), then the fish-tissue Se concentration, C_{trout}, derived from the particulate material Se concentration is 5.6 μg/g.

Modeling can also accommodate longer food webs that contain more than one higher-trophic-level consumer (e.g., forage fish being eaten by predatory fish) by incorporating additional TTFs. One equation for this type of example is

$$\begin{aligned} C_{predator\,fish} = (TTF_{invertebrate})(C_{particulate})(TTF_{forage\,fish}) \\ (TTF_{predator\,fish}). \end{aligned} \quad (20)$$

Trophic transfer: Birds

Trophic transfer factors. A link to wildlife, as illustrated here for aquatic-dependent birds, is not as straightforward as in the case for fish (Figure 1). Little information is available for a biodynamic approach to modeling exposure of birds through water and diet. Theoretically, the biodynamic exposure equation for a selected bird species would be similar to that for fish. The equation for calculating a bird tissue Se concentration for a single invertebrate diet is

$$C_{bird} = (AE)(IR)(C_{invertebrate}) \div (k_e). \quad (21)$$

A TTF_{bird} can be defined either as

$$TTF_{bird} = (AE)(IR) \div k_e \quad (22)$$

or

$$TTF_{bird} = C_{bird} \div C_{invertebrate} \quad (23)$$

to give

$$C_{bird} = (TTF_{bird})(C_{invertebrate}). \quad (24)$$

Selenium concentration in bird tissue can be for muscle if desired, but transfer to egg tissue is more meaningful in terms of a direct connection to reproductive endpoints.

Modeling of bird tissue can represent stepwise or sequential bioaccumulation from particulate material through invertebrate to bird by combining the equations

$$\begin{aligned} C_{invertebrate} &= (TTF_{invertebrate})(C_{particulate}) \text{ and } C_{bird} \\ &= TTF_{bird}(C_{invertebrate}) \end{aligned} \quad (25)$$

to give

$$C_{bird} = (TTF_{invertebrate})(C_{particulate})(TTF_{bird}). \quad (26)$$

Modeling for bird tissue can also represent Se transfer through longer or more complex food webs (e.g., additional TTFs for invertebrate to fish and fish to birds) by combining the equations

$$\begin{aligned} C_{invertebrate} &= (TTF_{invertebrate})(C_{particulate}); C_{fish} \\ &= TTF_{fish}(C_{invertebrate}) \end{aligned} \quad (27)$$

and

$$C_{bird} = (TTF_{bird})(C_{fish}) \quad (28)$$

to give

$$C_{bird} = (TTF_{invertebrate})(C_{particulate})(TTF_{fish})(TTF_{bird}). \quad (29)$$

Modeling approach. Laboratory data relating dietary Se concentrations to egg Se concentrations are used for modeling and derivation of TTFs of birds. A synthesis of data from controlled feeding of captive mallards (*Anas platyrhynchos*) exposed to known dietary Se concentrations showed the relationship of egg hatchability and egg tissue Se concentration (i.e., a dose–response curve; Ohlendorf 2003). Ohlendorf (2003) conducted logistic regressions on a set of pooled results from different studies to be able to calculate mean Se concentrations that are associated with different percentages of reduction in the hatchability of mallard eggs (e.g., the 10% effect concentration or EC10 is associated with a 10% reduction in hatchability). The range of $TTF_{bird\ egg}$ calculated from the compilation given by Ohlendorf (2003) for mallards is 1.5 to 4.5. Although mallards are believed to be a sensitive species based on reproductive endpoints in the laboratory, chickens and quail were shown to be more sensitive than mallards (Detwiler 2002). An order that reflects the effects of field factors present at Kesterson

Reservoir, California, USA, and is based on the number of dead or deformed embryos or chicks is (coot = grebe) > (stilt = duck = killdeer) > avocet (Ohlendorf 1989; Skorupa 1998).

The model can be run using any chosen $TTF_{bird\ egg}$, but a $TTF_{bird\ egg}$ of 1.8 (near the lower limit from the captive mallard studies) will be assumed here for modeling purposes (Table 3). Generalized species-specific or site-specific, species-specific TTFs for birds may also be derived from field studies, as was suggested for fish, which would take into account variables intrinsic to bird behavior and habitat use. Resident bird species nesting in a contaminated area may be the best choice for such a compilation.

TOXICITY: EFFECTS

Linking modeling to effects requires knowledge of species toxicological sensitivity through 1) effect guidelines for diet or tissue based on chronic Se exposure of predators; 2) toxicity reference values (TRV) specific to target receptor groups, endpoints, exposure routes, and uncertainty levels; or 3) national, state, or local regulatory guidance on diet or tissue Se concentrations. The chosen guideline can link diet, fish tissue, or bird tissue to toxicity.

Several authors give comprehensive compilations of Se guidelines (USDOI 1998; Lemly 2002; Presser and Luoma 2006; Luoma and Rainbow 2008). The controversy over choice of protective levels of Se for fish and birds is intense in part as a result of the steepness of the Se dose–response curves and the use of different models for quantifying those relationships (Skorupa 1998; Lemly 2002; Ohlendorf 2003; Beckon et al. 2008). Specificity in several variables based on experimental conditions when referencing a Se guideline is desirable. These variables include 1) endpoint (e.g., toxicity, reproductive, survival, growth, immunosuppression); 2) life stage (e.g., larvae, fry, adult); 3) form (e.g., selenate, selenite, selenomethionine, selenized yeast); 4) route of transfer (e.g., dietary, maternal); 5) definition of protection (e.g., threshold, toxicity level, criterion, target); and 6) toxicity basis (e.g., EC10). In general, for Se, reproductive endpoints are more sensitive than toxicity and mortality in adult birds and fish (Skorupa 1998; Lemly 2002; Chapman et al. 2010). Within reproductive endpoints, larval survival in fish and hatchability (i.e., embryo survival) in birds are considered the most sensitive endpoints. Effects guidelines that focus on a combination of the most sensitive assessment measures might include, for example, a seleno-methionine diet, parental exposure, and embryonic or larval life stage (Presser and Luoma 2006).

Any criterion, guideline, or target may be used in modeling to predict effects on predators, and, whatever the choice, the model can give its implications. For illustration purposes, we use a single value for each type of effects guideline (dietary = 4.5 μg/g dw, fish whole body = 5 μg/g dw, and bird egg = 8 μg/g dw), while recognizing that debate is still occurring about determining critical tissue values that relate bioaccumulated Se concentrations to toxicity in predators.

VALIDATION AND APPLICATION OF METHODOLOGY

Validation

Validation is necessary to establish sufficient confidence that the predictions from a model can be usefully applied to the environment. Advantages of the ecosystem-scale approach are that some aspects of the model are built from observations from natural systems, and the predictions from the biodynamic model center around bioaccumulated Se in a specific species. Thus, predictions from the model can be unambiguously compared with independent observations of Se concentrations in that same species resident in the environment of interest. The comparison of these 2 independent values illustrates both validity and uncertainty.

We tested the proposed methodology by comparing predictions and observations from 29 locations that were either historically, or are presently, affected by Se (Table 4 and Supplemental Data Tables E and F). The case studies include several types of hydrologic regimes, streams, rivers, ponds, lakes, reservoirs, wetlands, and estuaries, and many species of invertebrates, fish, and birds (see Supplemental Data). Sources of Se and food webs represented at sites used for the validation are also shown in Table 4. All sites are relatively well-known for associated Se contamination, and many are still in remediation or being mitigated because of ecosystem bioaccumulation of Se. In all case studies, reasonable food webs were identified and sufficient high-quality field data were available across media (particulate material, invertebrates, fish and/or bird tissue) and during a constrained time period (i.e., data were temporally and spatially matched; Supplemental Data Tables E and F). In 3 study area investigations (Kesterson Reservoir, McLeod River/Luscar Creek watershed, San Joaquin River), sites identified as reference sites are included to help illustrate the prediction capability of the model at the lower end of the concentration gradient.

The equations used for validation begin with a particulate material Se concentration, and thus do not incorporate the uncertainties associated with dissolved and/or particulate transformations (K_d), which we address below. We progressively calculate 1) invertebrate Se concentrations from particulate material, and 2) fish or bird tissue Se concentrations from the predicted invertebrate Se concentrations. Combining the progressive equations

$$C_{invertebrate} = (C_{particulate})(TTF_{invertebrate}), \quad (30)$$

$$C_{fish} = (C_{invertebrate})(TTF_{fish}), \quad (31)$$

and

$$C_{bird\ egg} = (C_{invertebrate})(TTF_{bird}) \quad (32)$$

yields

$$C_{fish} = (C_{particulate})(TTF_{invertebrate})(TTF_{fish}) \quad (33)$$

and

$$C_{bird\ egg} = (C_{particulate})(TTF_{invertebrate})(TTF_{bird}). \quad (34)$$

Thus, this approach tests whether bioaccumulation at the invertebrate and predator trophic levels can be predicted accurately if particulate Se concentrations are known.

For the predictions of Se concentrations in invertebrates, the observed particulate Se concentration at a site is multiplied by a species-specific TTF for the species of invertebrate in the identified food web (Supplemental Data Table E). The TTFs selected for use in the validation are a subset of those given in Table 3. The case studies allow 101 paired predicted

Table 4. Site locations, associated Se sources, and available prey and predator data for case studies used in model validation (see Supplemental Data Tables E and F for data sets)

Location or watershed	Sources	Available prey data	Available predator data
Belews Lake, North Carolina	Coal fly-ash disposal	Phytoplankton + zooplankton, insect, mollusk, crustacean, annelid	Bluegill, warmouth, redear sunfish, pumpkinseed, largemouth bass
Cienega de Santa Clara, Colorado River Delta	Agricultural drainage	Brine shrimp, crayfish	Sailfin molly, largemouth bass, striped mullet, common carp
Converse County, Wyoming	Uranium mining	Grasshopper	Red-winged blackbird
Elk River and Fording River watersheds, British Columbia, Canada	Coal mining	Insect, composite benthic invertebrate, mayfly, stonefly, caddisfly, cranefly	Cutthroat trout, mountain whitefish, American dipper, spotted sandpiper
Goose Lake, Kendrick Reclamation Project, Wyoming	Agricultural drainage	Composite insect	Eared grebe
Great Salt Lake, California	Copper mining	Brine shrimp, brine fly	American avocet, black-necked stilt, California gull
Hyco Reservoir, North Carolina	Coal fly-ash disposal	Benthic insects	Bluegill
Illco Pond, Kendrick Reclamation Project, Wyoming	Agricultural drainage	Composite insect	Common carp
Imperial National Wildlife Refuge, Lower Colorado River watershed, Arizona and Colorado	Agricultural drainage	Clam, crayfish	Lesser nighthawk, green heron, pied-billed grebe, least bittern
Kesterson National Wildlife Refuge, California	Agricultural drainage	Net plankton, corixid, chironomid, dragonfly, damselfly, beetle, diptera	Western mosquitofish (die-off of other fish species); pied-billed and eared grebe, American coot, mallard, gadwall, cinnamon teal, northern pintail, redhead, ruddy duck, black-necked stilt, American avocet, killdeer, western meadowlark, tri-colored blackbird, cliff and barn swallow
McClean Lake area, Saskatchewan, Canada	Uranium mining	Chironomid, caddisfly, dragonfly, leech, snail	Northern pike, white sucker, stickleback, burbot
McLeod River/Luscar Creek watersheds, Alberta, Canada	Coal mining	Insect	Rainbow, brook, and bull trout, mountain whitefish
Miller's Lake, Colorado	Agricultural drainage	Chironomid, corixid, crayfish	Fathead minnow
Newport Bay, California	Agricultural drainage	Amphipod, bivalve, clam, mussel, isopod, clam, snail	Topsmelt, diamond turbot, deep body anchovy, California halibut, striped mullet, California killifish, shadow, arrow and cheekspot goby, barred and spotted sand bass, staghorn sculpin, black and pile surfperch, American avocet, black-necked stilt, killdeer, clapper rail, pied-billed grebe, least tern, black skimmer
Rasmus Lee Lake, Kendrick Reclamation Project, Wyoming	Agricultural drainage	Composite insect	American avocet
Red Draw Reservoir, Big Spring, Texas	Refinery waste	Chironomid, snail	Inland silverside, sheepshead minnow, gulf killifish

TABLE 4. (*Continued*)

Location or watershed	Sources	Available prey data	Available predator data
Salton Sea, California	Agricultural drainage	Amphipod, corixid, pileworm	Largemouth bass, sargo, redbelly and Mozambique tilapia, Gulf croaker, orangemouth corvina, channel catfish, Caspian tern, white-faced ibis, snowy egret, black skimmer, great egret, black-crowned night heron
San Diego Creek watershed, California	Urban drainage	Zooplankton, corixid, crayfish, clam, snail, backswimmer, chironomid	Western mosquitofish, common carp, American avocet, black-necked stilt, killdeer, pied-billed grebe, American coot, clapper rail
San Francisco Bay–Delta Estuary, California	Oil refinery effluent agricultural drainage	Clam, zooplankton, amphipod, isopod, shrimp	White sturgeon, striped bass, starry flounder, yellowfin goby, leopard shark, Sacramento splittail
San Joaquin River watershed, California	Agricultural drainage	Zooplankton, amphipod, chironomid, crayfish	Bluegill, largemouth bass
Savage River watershed (Blacklick Run), Maryland	Coal stack emissions	Crayfish, mayfly, caddisfly, cranefly, stonefly, dragonfly, dobsonfly	Mottled sculpin, blacknose dace, brook trout
Savannah River (D-area Power Plant), South Carolina	Coal fly-ash disposal	Composite, benthic invertebrates	Lake chubsucker
Sweitzer Lake, Colorado	Agricultural drainage	Damselfly, chironomid, crayfish	Plains killifish
Thompson Creek, Idaho	Molybdenum mining	Composite insect	Slimy sculpin, cutthroat/rainbow trout
Tulare Basin Ponds, California	Agricultural drainage	Brine shrimp, brine fly larvae, corixid, damselfly	American avocet, black-necked stilt, eared grebe
Twin Buttes Reservoir, Wyoming	Agricultural drainage	Plankton, amphipod, corixid, damselfly, chironomid	Plains killifish, Iowa darter, fathead minnow
Uncompahgre River watershed, Colorado	Agricultural drainage	Invertebrates with some insects, crayfish	Bluehead flannelmouth and white sucker, speckled dace, roundtail chub, green sunfish
Upper Blackfoot River watershed, Idaho	Phosphate mining	Insect, composite benthic invertebrate	Cutthroat, brook, and brown trout, mountain whitefish, longnose dace, mottled sculpin, common snipe, American coot, killdeer, eared grebe
Upper Mud Reservoir/Mud River watershed, West Virginia	Coal mining	Dragonfly, crayfish, clam, snail	Bluegill, green sunfish, crappie

and observed data points for invertebrates (Figure 3). The data range across the entire data set probably covers the full extent of Se concentrations that might be expected from the most to the least contaminated environments. The agreement is remarkable, with a calculated correlation coefficient (r^2) for predicted and observed invertebrate Se concentrations of 0.917 ($p < 0.0001$) (Figure 3).

The second correlation compares observed Se concentrations in fish with concentrations predicted from observed particulate concentrations, the previously predicted invertebrate Se concentrations using the most likely food choice of that particular species of fish, and the universal choice of a TTF_{fish} of 1.1 (Supplemental Data Table E). In some cases, when several invertebrate Se concentrations were predicted, an average invertebrate Se concentration was used to predict a fish Se concentration. In cases in which Se concentrations in diet were elevated enough to cause fish die-offs (e.g., Belews Lake, Hyco Reservoir, Kesterson Reservoir, Sweitzer Lake; Skorupa 1998), trophic transfer of Se in fish may be additionally affected by poor feeding efficiency and food avoidance (Hilton et al. 1980; Finley 1985). The case studies allow 46 paired predictions and observations for fish (Figure 4). Again, the agreement is remarkable, with $r^2 = 0.892$ ($p < 0.0001$). These strong regressions show that, if particulate Se concentrations are known and food webs are considered in an ecologically based way, bioaccumulation in the different food webs of an ecosystem can be reliably predicted.

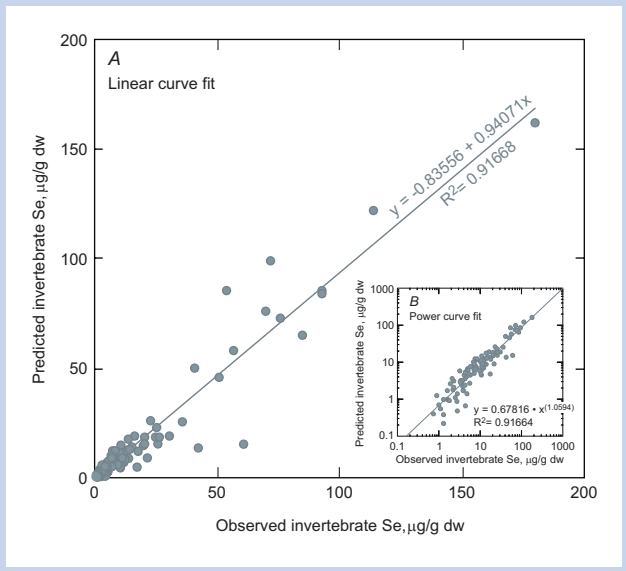

Figure 3. Linear regression and correlation of observed invertebrate Se concentrations from selected field studies and those predicted through ecosystem-scale modeling. Inset shows a power curve fit of data. See Supplemental Data Table E for data and references.

In the same manner, predictions are made of Se concentrations in birds that consume a diet of invertebrates or fish using a TTF_{bird} of 1.8 (Supplemental Data Table F). Because of the severity of exposure at several historical sites (e.g., Kesterson Reservoir, Tulare Basin Ponds, Rasmus Lee Lake, Goose Lake), factors such as food avoidance and poor physical condition might have affected feeding and hence trophic transfer of Se in birds (Ohlendorf et al. 1988; Heinz and Sanderson 1990; Heinz and Fitzgerald 1993; Ohlendorf 1996; Skorupa 1998). At these sites, predicted egg Se concentrations were above observed concentrations. At other sites, predicted bird egg Se concentrations were in the range of observed Se concentrations. The comparison for birds is hampered by the lack of data compared with data for fish, but it is illustrative of a comparable methodology for wildlife. Application of a TTF_{bird} of 1.8 may be useful under certain conditions, but selective regressions of data over a narrow range to represent site-specific conditions or a wildlife criterion methodology (discussed below) may better represent Se transfer at specific sites. This is an area in which greater understanding of the prey-to-predator kinetics in birds is needed.

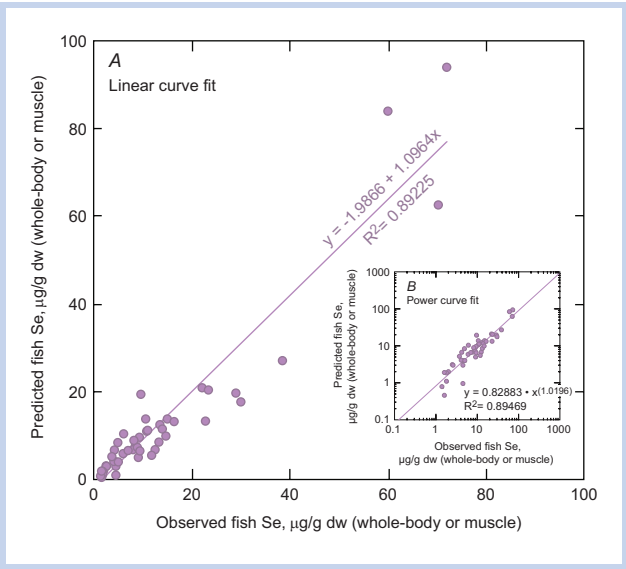

Figure 4. Linear regression and correlation of observed fish Se concentrations from selected field sites and those predicted through ecosystem-scale modeling. Inset shows a power curve fit of data. See Supplemental Data Table E for data and references.

Application

The value of the ecosystem-scale methodology lies in its explanation of how a predator might be accumulating an Se concentration that, for example, exceeds the choice of criterion, guideline, or target concentration in its tissues. The step-by-step approach of the methodology (Figure 1) provides a means of linking water-column Se concentrations to Se bioaccumulation with much more certainty that does the traditional correlation approach. The methodology can also describe implications of different choices of dietary or tissue guidelines. For example, a water-column concentration responsible for an observed bioaccumulated Se concentration can be determined in any specific environment for which some data are available (or a reasonable scenario can be defined). Similarly, it is possible to calculate water-column Se concentrations that might be allowable under a given set of conditions if the environment is to comply with a chosen fish tissue guideline.

Translations to water-column Se concentration and load. The discussions and equations given above address the complexity associated with each major variable listed in Table 1 and quantify the major contributors to Se bioaccumulation within an ecosystem. The complexity of nature is viewed by some as deterring use of such models in simpler applications of effects guidelines. However, even in the absence of site-specific data, simplified choices of model factors can be based on rudimentary knowledge of a watershed and its species-specific food webs, and outputs can be used for the purposes of establishing a perspective on management decisions. For example, one application of the model might be to translate bioaccumulated Se in a predator (observed or established by a model scenario) to the water-column concentration that might be responsible for that body burden, in that specific environment. This could be an instructive exercise for facilitating implementation of a fish tissue or wildlife guideline by allowing visualization of the change in water-column concentration that would be necessary to achieve the tissue guideline.

Several important choices (Table 5) based on information about the watershed or water body must be made to initiate an exercise such as translation.

1. The choice of a predator food web is the basis for derivation of an allowable water-column concentration and allowable load. Several fish species or the most Se-sensitive fish species may be considered as starting points. It should be remembered that sensitivity of a fish species is defined by both potential for exposure (does the fish eat an

Table 5. Steps in ecosystem-scale Se methodology for translation of a tissue Se guideline to a water-column Se concentration for protection of fish

Translation of Fish Tissue Guideline or Criterion to Water-Column Concentration
Develop a conceptual model of food webs in watershed
Choose toxicity guideline for fish in watershed
Choose fish species to be protected in watershed
Choose species-specific TTF_{fish} or use default TTF_{fish} of 1.1
Identify appropriate food web for selected fish species based on species-specific diet
Choose $TTF_{invertebrate}$ for invertebrates in selected food web or use default $TTF_{invertebrate}$ for taxonomic group of invertebrate
Choose K_d indicative of 1) generalized source of Se and receiving water conditions, or 2) site-specific hydrologic type and speciation; or use a default K_d of 1000
Solve equation(s) for allowable water-column concentration for protection of fish
If assume single invertebrate diet · $C_{water} = (C_{fish}) \div (TTF_{fish})(K_d)(TTF_{invertebrate})$
If assume a mixed diet of invertebrates · $C_{water} = (C_{fish}) \div (TTF_{fish})(K_d)[(TTF_{invertebrate\ a})(\text{prey fraction})] + [(TTF_{invertebrate\ b})(\text{prey fraction})] + [(TTF_{invertebrate\ c})(\text{prey fraction})]$
If assume sequential bioaccumulation in longer food webs · $C_{water} = (C_{fish}) \div (TTF_{fish})(K_d)(TTF_{invertebrate\ a})(TTF_{forage\ fish})$ · $C_{water} = (C_{fish}) \div (TTF_{fish})(K_d)(TTF_{TL2\ invertebrate})(TTF_{TL3\ invertebrate})(TTF_{TL3\ fish})$

invertebrate that is a strong bioaccumulator?) and its response in dietary toxicity tests.

2. A TTF must be chosen for invertebrate-to-fish transfer. If a TTF_{fish} specific to the local food web is not available, then a value of 1.1 can be assumed based on the mean value from 25 fish species (Table 3).
3. The choice of a fish species sets the choice of dietary prey; in general, what species of prey does this fish consume?
4. Particulate-to-prey kinetics are incorporated via TTFs for major species of invertebrates, such as those chosen in our validation exercise. These TTFs can then be used to represent a set of common food webs (Table 3).
5. The choice of a value to link water-column concentration to particulate concentration (our K_d) is an exacting challenge. Local data can narrow the range of choices, as long as they are high-quality analytical data. In the absence of a rich data set, the range can be narrowed based on hydrologic and speciation conditions, for example, using the data in Table 2. A K_d of 1000 is a default case that may be an environmentally conservative choice for environments other than reservoirs, estuaries, and the oceans. In any case, it is critical that the assumptions behind the choice of K_d be made explicit, and the potential variability in this crucial factor be recognized. In the absence of well-developed site models, the choice of K_d is usually the greatest source of uncertainty among model parameters.

Once these choices are made, the generalized equation for translation of a fish tissue Se concentration to water-column Se concentration is

$$C_{water} = (C_{fish}) \div (TTF_{fish})(TTF_{invertebrate})K_d, \quad (35)$$

where $(K_d)(C_{water})$ is substituted for $C_{particulate}$ and the equation is solved for C_{water} (Table 5). An analogous equation for translation of a bird egg Se concentration is

$$C_{water} = (C_{bird\,egg}) \div (TTF_{bird})(TTF_{invertebrate})K_d. \quad (36)$$

As an illustration, predators are consuming a diet exclusively composed of one invertebrate species. For example, if the effects guideline is an Se concentration of 5 μg/g in whole-body fish tissue and the selected site is a lake (hypothetical K_d of 1000) inhabited by sunfish (TTF of 1.1) that are eating a diet of mayfly larvae (TTF of 2.8), then the allowable water-column concentration for the lake is

$$C_w = 5\mu g/g \div [1.1 \times 2.8 \times 1000] = 1.6\mu g/L. \quad (37)$$

Under a food web scenario in which a fish with a similar TTF eats *Daphnia* (TTF of 1.9), the allowable Se water-column concentration is

$$C_w = 5\mu g/g \div [1.1 \times 1.9 \times 1000] = 2.4\mu g/L. \quad (38)$$

Table 5 also shows an equation that considers longer food webs. Despite some uncertainty at every biological step and even greater uncertainty with regard to transformation, the predicted allowable values fall across the range of values characteristic of contaminated situations.

Model sensitivity. To test the sensitivity of the predictions to differences in invertebrate species, dissolved concentrations of Se are predicted across a range of invertebrate species [mysid, *Daphnia*, mayfly, clam (*C. amurensis*), and barnacle (*E. modestus*)] using species-specific TTFs (Figure 5). Assumptions are 1) a guideline for whole-body fish tissue of 5 μg/g, 2) a hypothetical K_d of 1000, and 3) a TTF_{fish} of 1.1. The allowable water-column Se concentrations associated with the 5 specific food web exposures that would protect predators under the specified assumptions range from 3.5 μg/L for an invertebrate diet of exclusively mysids to 0.28 μg/L for an invertebrate diet of barnacles.

If 5 μg/g represents a whole-body Se guideline for fish and the TTF_{fish} is relatively constant (i.e., averaging 1.1 among all species of fish for which data were available), then an alternative strategy is a dietary guideline for fish. For the purposes of illustration, we employ a dietary guideline of 4.5 μg/g under these assumptions. Using a paired 8 μg/g bird egg Se guideline and a TTF_{bird} of 1.8 gives 4.4 μg/g for an allowable diet for birds. This similarity in allowable dietary Se concentrations for both fish and birds reinforces the hypothesis that fish and birds are of similar sensitivity in a general sense. Because the dietary guidelines are similar, the graph depicting protective concentrations for fish would apply to the protection of birds (Figure 5). If this were not the case, 2 graphs would be necessary to depict predictive protective Se concentrations for fish and birds. The difference in protection for fish and birds may also diverge in site-specific instances in which detailed predator-specific data are available to determine TTFs across a range of concentrations.

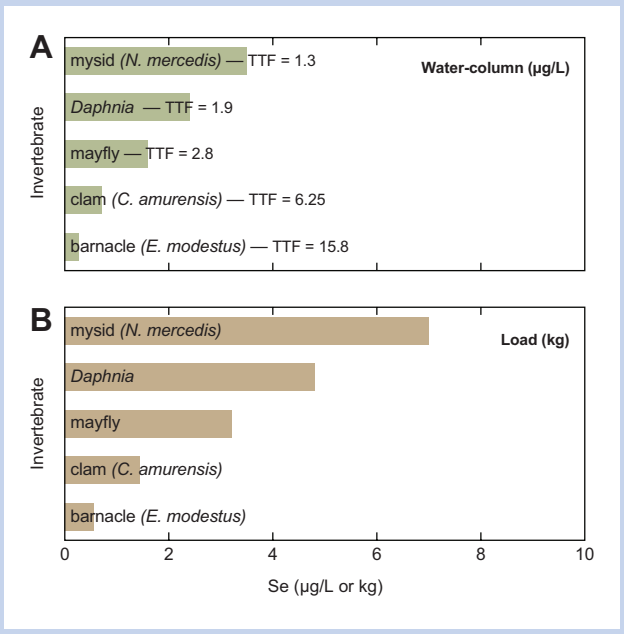

Figure 5. Predicted allowable water-column Se concentrations and Se loads based on choices of invertebrates in food webs. Assumptions are TTF_{fish} of 1.1, whole-body fish guideline of 5.0 µg/g dw, K_d of 1000, and stream flow of 1.2 Mm^3. See Table 3 for TTFs for invertebrates and Equation 39 for consideration of load.

Regulatory considerations such as NPDES permits and TMDLs for 303d listed water bodies put limits on loads. A fundamental equation to calculate load is

$$(C_{water-column})(volume)(10^{-6}) = load, \qquad (39)$$

where the water-column concentration is in µg/L, volume is in cubic meters (m^3), and load is in kilograms (Presser and Luoma 2006). We use this exceptionally simplified approach to consider Se loading at a site to calculate the hypothetical loads associated with the different food webs illustrated in Figure 5A. These loads (Figure 5B) are calculated based on the predicted allowable water-column Se concentrations (Figure 5A) and an assumed waste stream flow of 1.2 million m^3 (Mm^3). Under the different exposure scenarios for fish, loads vary from 0.56 to 7.0 kg depending on the choice of the invertebrate that is consumed by fish in the selected food web (Figure 5B). Of course, this is only an illustration of the ultimate linkage to source loads that modeling can provide (Figure 1). More sophisticated load models are recommended when calculating loads from concentrations and volumes, and, again, it is critical that predictions be explicit about why a specific K_d was chosen and the potential variability in that choice.

The translation approach of the ecosystem-scale model, of course, can start with any media (dissolved, particulate, diet, tissue) and translate to any other media, as long as the food web is known (or assumed; Figure 1). In all cases, it is important to connect the appropriate fish species to the appropriate food (i.e., biologically correct or observed knowledge of prey–predator pairs) to illustrate the potential for bioaccumulation within a watershed. Uncertainties can be greatly narrowed if part of the risk management strategy is for an agency or stakeholders to decide which predators are the most important to protect.

Table 5 formalizes the steps in a fish tissue water-column translation. Following these steps would facilitate risk management for Se based on a tissue guideline. As shown above, equations can be included that are appropriate for mixed invertebrate diets and longer food webs (e.g., forage fish being eaten by predatory fish). The steps in this approach (Table 5) are simple enough to be widely used in a management context but address the complexity of a specified ecosystem sufficiently to reduce uncertainty well below that of conventional approaches.

Hypothetical case studies and site-specific conceptualization. One outcome of the application of the ecosystem-scale model is explicit recognition that allowable dissolved Se concentrations and loads will vary among environments. The degree of such variability that is possible can be shown by predictions of allowable dissolved concentrations for different watershed types and food web scenarios. To illustrate a full range of possible conditions, we modeled realistic scenarios based on the previously compiled field case sites and ecosystem habitats (Figure 6). The illustrated K_d categories are broadly indicative of 1) an estuary, 2) a reservoir, 3) a mainstream river, 4) a backwater, 5) a saline lake or pond, and 6) a wetland (Table 2). Species-specific TTFs are employed based on Table 3. To illustrate the discussion here, translation is for a fish tissue guideline of 5 µg/g dw whole body and an avian egg guideline of 8.0 µg/g dw (see also under *Toxicity*). These targets are applied to starry flounder, white sturgeon, Sacramento blackfish, redear sunfish, bluegill, cutthroat trout, and largemouth bass as examples of fish species and black-necked stilt, American dipper, eared grebe, and greater scaup as examples of bird species. Some of the illustrations reflect food webs of historically contaminated sites (e.g., Kesterson Reservoir, Belews Lake, San Francisco Bay–Delta Estuary), and others reflect food webs of current areas of contamination (e.g., mountain streams in Idaho and British Columbia, Great Salt Lake).

A range of Se water-column concentrations from 0.24 to 34 µg/L is predicted as protective of the different predators that are the targets of the assumed guidelines in the illustrated exposure scenarios (Figure 6). For fish, an exposure scenario that has a very low K_d (mainstream river, 150) and low food web potential (bluegill eating amphipods, $TTF_{fish} = 1.1$, $TTF_{invertebrate} = 0.9$) predicts a water-column Se concentration of up to 34 µg/L (Figure 6A). If the river is transported through a watershed into a hydrologic area of differing K_d, for example, into a backwater where the flow is decreased ($K_d = 350$), then trout consuming insects would require a much lower Se concentration in the water column (4.6 µg/L; Figure 6B).

An exposure scenario for a reservoir with a K_d of 1800 that is reflective of more opportunities for transformation and a food web that contributes to significant accumulate of Se in prey and predators (redear sunfish eating freshwater clams, $TTF_{fish} = 1.1$, $TTF_{invertebrate} = 2.8$) predicts a water-column Se concentration of less than 1 µg/L (Figure 6C). However, if Sacramento blackfish in the reservoir are consuming only zooplankton ($TTF_{fish} = 1.1$, $TTF_{invertebrate} = 1.5$), then modeling predicts a water-column Se concentration of 1.7 µg/L. Estuaries require the lowest water-column Se concentrations

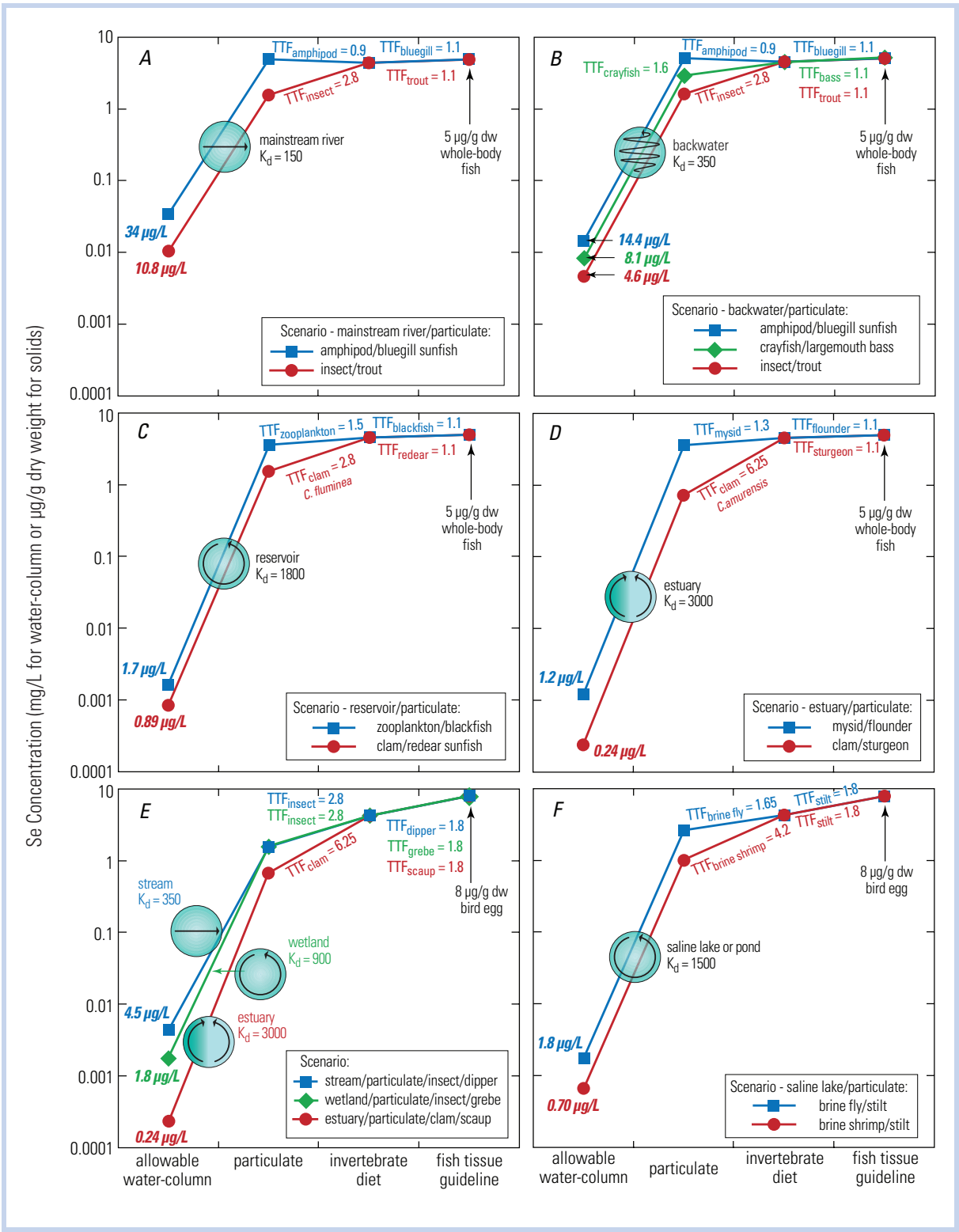

Figure 6. Range of predicted allowable water-column Se concentrations for various environmental exposure scenarios using ecosystem-scale modeling. Hydrologic environment types include an estuary, reservoir, mainstream river, backwater, saline lake, and a wetland. Food webs illustrate invertebrates as prey and fish or birds as predators. Additional food web steps can be added to illustrate more complex food webs (e.g., invertebrate through fish to bird or to include forage fish to predatory fish).

(0.24 µg/L) because of the potential for very high K_ds (Table 2) and the presence of clam-based food webs (sturgeon or scaup eating C. *amurensis*, $TTF_{fish} = 1.1$, $TTF_{invertebrate} = 6.25$; Figure 6D).

For birds, an exposure scenario similar to that at Kesterson Reservoir ($K_d = 900$) where eared grebes are feeding on aquatic insects ($TTF_{bird} = 1.8$, $TTF_{invertebrate} = 2.8$) predicts a water-column Se concentration of 1.8 µg/L (Figure 6E). A

scenario for a saline lake or pond (K_d of 1500) inhabited by black-necked stilts that are eating brine flies ($TTF_{bird} = 1.8$, $TTF_{invertebrate} = 1.65$) leads to a 1.8 μg/L water-column Se concentration, or 0.70 μg/L if stilts consume a diet of brine shrimp ($TTF_{bird} = 1.8$, $TTF_{invertebrate} = 4.2$; Figure 6F). A scenario for a mountain stream ($K_d = 350$) where American dippers are eating a diet of mayflies predicts a water-column Se concentration of 4.5 μg/L (Figure 6E).

An additional factor would be necessary to illustrate a scenario, for example, in which birds in an estuary are feeding on fish that prey on aquatic insects. If the selected fish species possesses a low food web potential ($TTF_{fish} = 1.1$) as found here, then the predicted allowable water-column Se concentration would not differ substantially from that predicted from invertebrates alone.

This exercise illustrates both the strengths and the limits of the model. Even when feeding relationships and TTFs are known, potential exists for variability in the translation from water to particulate phase. The model can provide perspective by illustrating that variability around reasonable scenarios for that watershed, but the model is not suitable for explicitly defining one number that will be protective in any habitat. Documenting all decisions, whether mathematical or policy choices, throughout modeling will record all considered pathways between dissolved Se and tissue Se and their outcomes.

Limitations and uncertainties. No model can incorporate all the complexities of nature or make exact predictions of outcomes. The approach presented in this paper is no exception. However, models can provide new insights that advance understanding of value to both science and management. The greatest values of the present model are that it shows why allowable water-column concentrations differ among aquatic environments and that it advances our ability to explain food web bioaccumulation of Se. The combined mechanistic and empirically based approach provides a unified methodology for evaluating how interactions of hydrology, biogeochemistry, biology, ecology, and toxicology affect ecological risks from Se at any given location. However, as with every model, forecasts from the model have limitations and uncertainties, most of which were detailed above.

Sensitivity analyses in earlier work compared the influence of uncertainty on different terms used in kinetic biodynamic modeling (see, e.g., Wang et al. 1996). Variability in TTFs reflects the outcome of those uncertainties when summed for an individual species. Experimentally determined TTFs appear to have low uncertainties judged by repeatable results in different studies. For example, TTFs for estuarine or marine zooplankton range from 1.3 to 1.5 in repeated experiments; TTFs for barnacles range from 15.8 to 20.3 (Table 3). We might expect the most uncertainty in TTFs derived from field observations given the complexity of field variables, but field- and laboratory-derived TTFs for individual species also appear to agree well (within 2-fold) in the few cases in which comparisons are possible. For example, TTFs calculated from Conley et al. (2009) for mayflies (combined mean 2.2) are very similar to the average TTF of 2.8 derived here for larvae of aquatic insects in general (Table 3).

Such conclusions are consistent with the strong correspondence between model-predicted Se concentrations for a specific environment and independent determinations of bioaccumulated Se concentrations in the same species from that environment (Figures 3 and 4). The approximately 2-fold or lower difference between predictions and independent observations for individual species of invertebrates or fish 1) is similar to the degree of uncertainty found with biodynamic modeling of a variety of metals and metalloids (including Se) in earlier studies (Luoma and Rainbow 2005) and 2) is given by Landrum et al. (1992) as sufficient accuracy to define a useful relationship within aquatic modeling. Much greater uncertainties are found in the conventional BAF approaches to modeling Se bioaccumulation at least because they are not typically species, food web, or habitat specific. The 38-fold variability in TTFs observed among invertebrate species illustrates one reason for the poorer performance of the conventional approaches than the present model. The mechanistic reasons for the similarities within taxa and the differences among some taxa are not fully known and deserve further investigation.

The relatively low uncertainty in TTFs and the validation comparisons at least partially result from recognition that such values are species specific, require the appropriate predator–prey match-ups, and should be made within the same or similar environments. The methodology recognizes that modeling of Se partitioning from the dissolved phase into the particulate material phase (transformation) and Se distribution among particulate phases (bioavailability) must mimic adequately the conditions typical of an environmental site to yield results that can be widely extrapolated to nature. Thus, if particulate Se concentrations are known for an environment and trophic transfer pathways are carefully chosen to match nature, then predictions of Se bioaccumulation can be expected that are within an acceptable uncertainty for toxicokinetic modeling (Landrum et al. 1992). Similarly, if tissue concentrations in a fish predator are known, reasonable predictions of the particulate-material Se concentrations in that environment should be feasible (recognizing the caveats described above in defining particulate material).

The concentration dependence of TTFs, as a source of uncertainty, remains largely unstudied. However, the large database of TTFs reported here was derived from a variety of habitats with different degrees of contamination, so this limitation may not normally be of concern for model application except at the extremes of possible system status for Se. Uncontaminated situations and their inhabitants are underreported in our compilation and, as noted above, elevation of TTFs in uncontaminated circumstances might be expected if Se is physiologically regulated at low environmental concentrations. Hence, further direct investigation of this premise is needed to be able to apply the model with certainty across the full spectrum of investigated sites and predators. Use of TTFs and K_ds developed from studies of only systems that fall into the same order-of-magnitude range of Se contamination as the one that someone wants to model may further mitigate this uncertainty.

The greatest potential for variability in predictions and forecasts is the choice of a factor to describe transformation of Se from dissolved to particulate phase (K_d). Representing a hydrologic system in terms of the dynamics of transformation is complex. Geochemical models (equilibrium-based) cannot describe transformation outcomes well because transformation processes are biogeochemically driven. Meseck and Cutter (2006) incorporated hydrodynamic processes, redis-

tribution from sediment to the water column, and the influence of primary productivity in describing the fate and speciation of Se in San Francisco Bay. However, the complexity of this type of modeling, uncertainties about boundary conditions, and lack of consideration of multifaceted but influential aspects of hydrodynamics limit the applications of such models to date and the questions even such admirable efforts can address. For the present model, we chose a more parsimonious approach, relying on empirical knowledge of the site or watershed to limit uncertainties. Collection of sets of well-matched samples for analysis of dissolved and particulate Se concentrations can document variability within an ecosystem, especially if hydrologic characteristics and speciation are taken into account in the interpretation. For example, data collection that divides modeling efforts into subareas and temporal cycles of rainfall or flow might be employed to reduce uncertainties, even without complex modeling. It is also possible to illustrate potential variability by computing predictions using alternative choices of K_d bracketed by the variability empirically observed in the environment of choice. The database of K_ds derived here from matched data sets shows less variability within broad categories of aquatic systems (lotic, lentic, estuaries) than across the entire data set. Information on speciation may also be another way to constrain the choice of K_d in the absence of empirical data (see above under *Partitioning and transformation environments*). However, the database of K_ds suggests that uncertainties in the transformation coefficient could range from 2-fold to 10-fold in the absence of local data.

The methodology here uses partitioning and food web scenarios to combine variables and illustrate uncertainty. For example, under conditions of an assumed global TTF_{fish} of 1.1 and a backwater K_d of 350 (Figure 6B), a high degree of certainty exists that fish eating an exclusive diet of amphipods will require a less stringent water-column Se concentration (14 μg/L) than if fish are exclusively eating aquatic insects (5 μg/L), given the magnitude of the difference in trophic transfer at the prey level (0.9 vs. 2.8). If a K_d of 500 were chosen for the example, the allowable water-column Se concentrations would be 10 μg/L and 3.2 μg/L, respectively. The exact number may differ in these examples, but the tenets remain unchanged.

A requirement to measure dissolved-phase Se concentrations rather than total water-column Se concentrations would rectify the geochemical inaccuracy of including a suspended-particulate-material Se fraction in a dissolved-phase modeling parameter. Further development of methods for differentiation of particulate material type and for dissolved and particulate speciation is also important to improving the accuracy of this final step in translation.

Quantitative modeling does produce quantitative outcomes, leading to the potential for overexpectations from a model. Given the uncertainties described above, the present model is more suitable for illustrating the implications of different choices of, for example, a site-specific water quality guideline for Se than it is for choosing any specific number for that guideline, but realistically the outcomes of guideline development depend on decisions in addition to mathematical ones. Policy choices based on what scenario or food web the regulator wishes to manage toward are also important decision points. Additional detailed analysis of ecological and hydrological variations for the site (i.e., site-specific conceptualization) could address uncertainty within mathematical choices or ranges but at a level of reasoning different from mathematics (Table 1). For example, 1) clearly defining food webs in conceptual models of fauna and their feeding relationships from empirical knowledge of the investigated site can identify details of species-specific exposure, 2) life cycles of habitat species can be displayed on a yearly basis to identify details of spatial and temporal exposure, 3) identifying feeding areas for wildlife can help determine what percentage of diet comes from the polluted site, 4) dissolved- and particulate-material Se speciation can be related to hydrologic conditions (e.g., high- or low-flow season or residence time), and 5) bioaccumulation dynamics can be related to particulate material characterization. As development of Se protection proceeds, a compilation of site-specific derivations of water-column Se concentrations from diverse sites and their validation through monitoring could ultimately address the sufficiency of data requirements for ecosystem-scale modeling.

Further work is needed to expand the database available for use in quantitative models. Continued work on quantitatively modeling transformation from dissolved to particulate Se under different circumstances is essential. More data are needed on physiological TTFs for invertebrates, fish, and bird species derived from kinetic experiments. Comparisons are also needed for experimental vs. field-derived TTFs (with the latter derived from matched data sets across different field sites). Few biodynamic studies are available for different fish species, so determining the range of TTFs from experimental studies would further assess the importance of the role of fish physiology in understanding food webs. Biodynamic kinetic studies are not available for avian species, and data available for derivation of TTF for different bird species in different dietary settings are limited, so further experiments to develop egg–diet relationships are needed with particular attention to mimicking the bioavailability of a diet found in nature. Inclusion of a database of factors for translation to fish ovary Se concentrations would be an important addition to allow connection of modeling of fish directly to reproductive effects. Developing TTFs specific to the dietary exposure concentration being modeled would require systematic experimental studies of common food web species to generate a set of generalized TTF equations as a function of dietary Se.

In the end, if we are to protect ecosystems with defensible assessment procedures, then the only choice is to incorporate the complexity of multiple route exposures, whatever the challenges. Thus, ecosystem-scale modeling offers a major step forward in terms of confronting and defining uncertainty by formalizing the knowledge necessary to understand the basis of protective criteria for Se. This formalization of knowledge, including choices used to initiate or limit modeling scenarios, thus clearly documents pathways that connect dissolved and tissue Se concentrations and provides a record of supporting data throughout decision-making phases.

Complementary approach: Wildlife criteria

A wildlife criterion (sometimes referred to as a wildlife value or tissue residue guideline, TRG) is the dietary concentration of an element necessary to keep the daily ingested amount of a contaminant at or below a level at which no adverse effects are expected (USEPA 1989; Sample et al. 1996; CCME 1999; USFWS 2003). The use of dietary

toxicity testing is one common link with the ecosystem-scale approach. In regulatory terminology, a wildlife criterion is analogous to a tissue residue concentration (TRC) for human health criterion. A common focus for these types of criteria is consumption of fish either by wildlife or by humans (USEPA 2001). The steps for deriving this type of wildlife criterion and applying it in modeling are shown in Table 6 and discussed further in the Supplemental Data. This approach to deriving a wildlife criterion uses body weight (BW, kg wet weight), food ingestion rate (IR, g food/d), and a reference dose (RfD, $\mu g \cdot kg^{-1} d^{-1}$) determined by dietary toxicity testing (Nagy 1987; USEPA 1993; Sample et al. 1996). In effect, the wildlife criterion converts an RfD into a species-specific allowable dietary uptake rate, if 100% assimilation efficiency is assumed, or into an allowable Se concentration in food for each species. In modeling here for birds, an Se wildlife criterion is referred to as an allowable C_{food} ($\mu g/g$) and is defined by the equation

$$\text{allowable } C_{food} = (\text{RfD})(\text{BW}) \div \text{IR}. \quad (40)$$

An allowable Se dose, or exposure rate, is defined by the equation

$$\text{allowable dose} = (\text{RfD})(\text{BW}). \quad (41)$$

An allowable Se concentration in food for predators (i.e., wildlife criterion) can be written in terms of allowable dose as

$$\text{allowable } C_{food} = \text{dose} \div \text{IR}. \quad (42)$$

If a Se RfD is assumed for modeling of effects to birds, then an allowable C_{food} for various species of birds can be calculated (see Supplemental Data). For watershed evaluation, the allowable C_{food} is used as a dietary target and compared with 1) existing Se concentrations in dietary items in biologically appropriate food webs, or 2) predicted concentrations as a result of food web modeling. Equations can be added to consider mixtures of food (Table 6).

The wildlife criteria approach and the ecosystem-scale approach could easily be combined by adding values for assimilation efficiency and considering K_d, for example, in the translation to dissolved Se. Validation would be important; uncertainties in the relationship of body weight and ingestion rate, for example, would have to considered, but the combination might be helpful in assessing a watershed in terms of threatened and endangered avian species. A list of species can be developed, wildlife criteria calculated, and species-specific dietary guidelines applied in modeling (USFWS 2003). Steps such as this in the methodology could also serve to harmonize regulation, a goal long sought in obtaining consensus and understanding (Reiley et al. 2003).

Table 6. Steps in Wildlife Value derivation (aquatic birds) and dietary application (invertebrate or fish diet for aquatic birds) for ecosystem-scale Se methodology

Wildlife Value and Dietary Modeling (acquatic bird example)
Develop a conceptual model of food webs in watershed
Choose avian RfD, endpoint, and uncertainty factor · RfD = NOEC or LOEC ÷ uncertainty factor
Choose bird species
Choose body weight and ingestion rate for selected bird species
Calculate allowable concentration in food of selected bird species (i.e., allowable Se C_{food} or species-specific RfD or Wildlife Value) · Wildlife Value = (RfD)(BW) ÷ IR
Identify species-specific diet
Choose dietary items
1. Compare to available food in ecosystem
2. Compare to predicted Se concentrations in invertebrate diet for aquatic birds
Identify food web(s)
Solve equation(s) for dietary Se concentration in invertebrates
If single invertebrate species diet and known particulate Se concentration or K_d and C_{water} · $C_{invertebrate} = (TTF_{invertebrate})(C_{particulate})$ or $C_{invertebrate} = (TTF_{invertebrate})(K_d)(C_{water})$
If sequential bioaccumulation in longer food webs contributes to diet · $C_{invertebrate\ b} = (C_{particulate})(TTF_{invertebrate\ a})(TTF_{invertebrate\ b})$
3. Compare to predicted Se concentrations in fish diet for aquatic birds
Identify food web(s)
Solve equation(s) for dietary Se concentration in fish
If a single invertebrate species and known particulate Se concentration or K_d and C_{water} · $C_{fish} = (TTF_{invertebrate})(C_{particulate})(TTF_{fish})$
If several invertebrate species contribute to diet · $C_{fish} = TTF_{fish}$ $(C_{particulate})[(TTF_{invertebrate\ a})$ (prey fraction)] + [$(TTF_{invertebrate\ b})$ (prey fraction)] + [$(TTF_{invertebrate\ c})$ (prey fraction)]
If assume sequential bioaccumulation in longer food webs contribute to diet · $C_{fish} = (C_{particulate})(TTF_{TL2\ invertebrate})(TTF_{TL3\ invertebrate})$ $(TTF_{TL3\ fish})(TTF_{TL4\ fish})$

NOEC = no observable effect level; LOEC = lowest observable effect level.

CONCLUSIONS

Consideration of each step in the sequence that links environmental Se concentrations to Se toxicity is fundamental to deriving effective Se criteria or guidelines for the protection of aquatic life and aquatic-dependent wildlife (Figures 1 and 2). Ecosystem-scale Se modeling provides a context for establishing these linkages and a set of model parameters for common food webs that can be used to predict species-specific responses. A high degree of correlation ($r^2 = 0.9$) is shown between observed bioaccumulation in invertebrates and fish from 29 field locations and bioaccumulation predicted based on particulate-material Se concentration and our compiled TTFs (Figures 3 and 4). This model validation illustrates how variability in food webs result in widely different Se concentrations in different predators in a contaminated ecosystem, but those differences can be explained and quantified using this relatively simple protocol.

The validation also establishes the adequacy of the type of knowledge compiled to represent a specific occurrence of Se.

Analysis from the model shows that 1) a crucial factor ultimately defining Se toxicity is the link between dissolved and particulate phases at the base of the food web (i.e., K_d); 2) collection of particulate material phases and analysis of their Se concentrations are key to representing the dynamics of the system; 3) bioaccumulation in invertebrates is a major source of variability in Se exposure of predators within an ecosystem, although that variability can be explained by invertebrate physiology (i.e., $TTF_{invertebrate}$; Figure 5); 4) TTF_{fish} is relatively constant across all species considered here; and 5) Se concentrations are at least conserved and usually magnified at every step in a food web (Figure 6).

Application of the model to habitat-specific and species-specific exposure scenarios illustrates how, if a desired Se concentration is chosen to protect predators, allowable dissolved Se concentrations will vary among sites depending on how phase transformation and food webs are linked (Figure 6). Much of the controversy about a proper dissolved Se guideline for regulating the chemical, therefore, stems from unavoidable biogeochemical and food web differences within and among environments. The mechanistic aspects of the model and the flexibility of model components in terms of portraying the realities of exposure in nature all increase the reliability of model predictions over traditional approaches that tie water-column concentrations directly to tissue concentrations. Details of hydrology and ecology added to modeling through conceptualization of seasonal hydrologic cycles, food webs, life cycles of predators, and feeding possibilities create several levels of confidence in model outcomes based on mathematics and realistic ecology. Thus, the model can confront complexity to account directly for critical sources of variability and uncertainty in assessing Se effects. The model can run either backward or forward to verify choices and develop scenarios based on knowledge of food webs, hydrology, or proposed management.

The methodology also shows the need for a better understanding of the aspects of ecosystems, such as water residence time and dissolved and particulate speciation, that contribute to the environmental partitioning and bioavailability of Se. In lieu of this, determining Se concentrations in the suspended particulate material phase is the preferred measure of the complex water, sediment, and particulate milieu that forms the base of the food web and is consumed as food by invertebrates. Monitoring invertebrate Se concentrations in food webs that are the most likely to be heavily contaminated may be a practical initial step in a monitoring plan, because the first and second most variable aspect of Se dynamics (i.e., K_d and $TTF_{invertebrate}$) are integrated into invertebrate bioaccumulation. Policy choices such as 1) the predator species to represent an ecosystem (e.g., toxicologically sensitive, ecologically vulnerable based on food web, resident or migratory, commercially or esthetically valuable) and 2) the food web to represent an ecosystem (e.g., potentially restored food webs in addition to current food webs) also serve as important initial inputs into the development of protective scenarios for a site or watershed.

Currently, within USEPA's Clean Water Act programs, aquatic life criteria and wildlife criteria are separate and are derived independently (see, e.g., USEPA 1995, 2004). The USEPA in 1989 identified the need for criteria to protect wildlife as an outgrowth of Se-induced deformities of aquatic birds at Kesterson Reservoir (USEPA 1989) but has not acted nationally to develop a wildlife Se criterion. The USEPA started considering development of a fish tissue aquatic-life criterion for Se in 1998 and proposed a national fish whole-body Se criterion of 7.9 μg/g dw to protect freshwater fish in 2004 (USEPA 1998, 2004). That criterion is now under revision. Our model can be a useful tool in determining scientifically integrated protection for both aquatic life (such as fish) and aquatic-dependent wildlife (such as waterfowl). For example, based on typical TTFs for Se, USEPA's proposed whole-body fish tissue criterion of 7.9 μg/g dw (USEPA 2004) would also allow Se concentrations in aquatic invertebrates that, when eaten by breeding waterbirds, would pose a substantively higher hazard (see, e.g., Ohlendorf 2003; EC50) for avian toxicity than the designed level of protection for fish (USEPA 2004; EC20).

Our ecosystem-scale model for Se is applicable to connecting fish and bird tissue to environmental concentrations in a rigorous way and to providing perspective when deriving site-specific or broader Se guidelines. We now have the knowledge necessary to understand the basis of protective water-quality criteria for Se for fish and birds. Species-specific diets and reference doses for wildlife can also be used to determine an allowable Se concentration in food (i.e., a wildlife criterion or value) using a few outlined supplemental steps. As we noted above, the set of choices to initiate ecosystem-scale modeling implicitly suggests that management of Se requires consideration of biology, ecology, biogeochemistry, and hydrology along with ecotoxicology. Intuitively, this seems an obvious requirement. In practice, it provides a means to move beyond the traditional objections (see, e.g., Cairns and Mount 1990) that we can never understand enough about ecology and hydrology to include them in chemical regulation.

SUPPLEMENTAL DATA

Methodology for ecosystem-scale modeling of selenium: Data and references.

Supplemental Data Table A. Water-column Se concentrations, particulate Se concentrations (dw), and calculated K_ds from field studies.

Supplemental Data Table B. Experimental data for invertebrate physiological parameters and calculated kinetic TTFs for invertebrates (particulate to invertebrate in dw).

Supplemental Data Table C. Calculated TTFs from field studies for invertebrates (particulate to invertebrate in dw).

Supplemental Data Table D. Calculated kinetic or field TTFs for fish (invertebrate to fish in dw except where noted as fish to fish in dw).

Supplemental Data Table E. Model validation for prediction of invertebrate and fish (whole-body or muscle) Se concentrations.

Supplemental Data Table F. Model validation for prediction of invertebrate and bird egg Se concentrations.

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