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Ecosystem-Scale Selenium Model for the San Francisco Bay-Delta Regional Ecosystem Restoration Implementation Plan (DRERIP)

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ABSTRACT

Environmental restoration, regulatory protections, and competing interests for water are changing the balance of selenium (Se) discharges to the San Francisco Bay–Delta Estuary (Bay–Delta). The model for Se described here as part of the Delta Regional Ecosystem Restoration Implementation Plan (DRERIP) draws both from the current state of knowledge of the Bay–Delta and of environmental Se science. It is an ecosystem-scale methodology that is a conceptual and quantitative tool to (1) evaluate implications of Se contamination; (2) better understand protection for fish and aquatic-dependent wildlife; and (3) help evaluate future restoration actions. The model builds from five basic principles that determine ecological risks from Se in aquatic environments: (1) dissolved Se transformation to particulate material Se, which is partly driven by the chemical species of dissolved Se, sets dynamics at the base of the food web; (2) diet drives bioavailability of Se to animals; (3) bioaccumulation differs widely among invertebrates, but not necessarily among fish; (4) ecological risks differ among food webs and predator species; and (5) risk for each predator is driven by a combination of exposures via their specific food web and the species' inherent sensitivity to Se toxicity. Spatially and temporally matched data sets across media (i.e., water, suspended particulate material, prey, and predator) are needed for initiating modeling and for providing ecologically consistent predictions. The methodology, applied site-specifically to the Bay–Delta, includes use of (1) salinity-specific partitioning factors based on empirical estuary data to quantify the effects of dissolved speciation and phase transformation; (2) species-specific dietary biodynamics to quantify foodweb bioaccumulation; and (3) habitat use and life-cycle data for Bay–Delta predator species to illustrate exposure. Model outcomes show that the north Bay–Delta functions as an efficient biomagnifier of Se in benthic food webs, with the greatest risks to predaceous benthivores occurring under low flow conditions. Improving the characterization of ecological risks from Se in the Bay–Delta will require modernization of the Se database and continuing integration of biogeochemical, ecological, and hydrological dynamics into the model.

KEY WORDS

Selenium, biodynamics, bioaccumulation, food webs, ecotoxicology, ecology.

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INTRODUCTION

The Delta Regional Ecosystem Restoration Implementation Plan (DRERIP) process focuses on construction of conceptual models that describe and define the relationships among the processes, habitats, species, and stressors for the Bay-Delta (DiGennaro and others 2012). The models use common elements and are designed to interconnect to achieve the goals of evaluating and informing Bay-Delta restoration actions. Selenium is recognized as an important stressor in aquatic environments because of its potency as a reproductive toxin and its ability to bioaccumulate through food webs (Chapman and others 2010; Presser and Luoma 2010a). Selenium's role is well documented in extirpation (i.e., local extinctions) of fish populations (Lemly 2002) and in occurrences of deformities of aquatic birds in affected habitats (Skorupa 1998). For Se, exposure is specific to a predator species' choice of food web and physiology, making some predators more vulnerable and, thus, more likely than others to disappear from moderately contaminated environments (Lemly 2002; Luoma and Presser 2009; Stewart and others 2004).

Concern about Se as a stressor in the Bay-Delta watershed originates from the damage to avian and fish populations that resulted when an agricultural drain to alleviate subsurface drainage conditions in the western San Joaquin Valley released Se into the Kesterson National Wildlife Refuge in the 1980s (Presser and Ohlendorf 1987). Later it was recognized that (1) some aquatic predators in the Bay-Delta were bioaccumulating sufficient Se to threaten their reproductive capabilities (SWRCB 1987, 1988, 1989, 1991) and; (2) primary Se sources included not only organic enriched sedimentary deposits in the San Joaquin Valley and elsewhere, but also their anthropogenic by-products such as oil (Cutter 1989; Presser 1994; Presser and others 2004). Proposals in 1978 and 2006 to extend an agricultural drain from the western San Joaquin Valley directly to the Bay-Delta as a way of removing Se from the valley were found both times to present substantial and broad ecological risks (e.g., USBR 1978, 2006; Presser and Luoma 2006).

Currently, Se contamination is spatially distributed from the Delta through the North Bay (Suisun Bay, Carquinez Strait, and San Pablo Bay) to the Pacific Ocean, mainly from oil-refining discharges internal to the estuary, and agricultural drainage discharges exported via the San Joaquin River. Regulatory and planning processes have intervened in the cases of both existing Se sources resulting in a decline in contamination since 1986-1992 when concentrations were maximal (SWRCB 1987, 1988, 1989, 1991; Presser and Luoma 2006; USBR 1995, 2001, 2009). However, the North Bay, the Delta, and segments of the San Joaquin River and some of its tributaries and marshes remain designated as impaired by Se (SWRCB 2011). More recently, the State initiated a Se Total Maximum Daily Load (TMDL) process to target both agricultural and oil refinery sources of Se (SFBRWQCB 2007, 2011) in coordination with development and implementation of site-specific water quality Se criteria for the protection of fish and wildlife by the U.S. Environmental Protection Agency (USEPA 2011a). The presence of a major oil-refining industry in the North Bay, and the substantial accumulated reservoir of Se in the soils and aquifers of the western San Joaquin Valley suggest that the potential for ecological risk from Se within the Bay-Delta watershed will continue into the foreseeable future as Se management and mitigation efforts take place (Presser and Luoma 2006; Presser and Schwarzbach 2008; USBR 2008; Appendix A.1).

Historic and more recent data show that certain predator species are considered most at risk from Se in the Bay-Delta (e.g., white and green sturgeon, scoter, scaup) because of high exposures obtained when they consume the estuary's dominant bivalve, *Corbula amurensis*, an efficient bioaccumulator of this metalloid (Stewart and others 2004; Presser and Luoma 2006). The latest available surveys of Se concentrations in *C. amurensis* and white sturgeon (*Acipenser transmontanus*) that were feeding (based upon isotopic evidence) in Carquinez Strait, Suisun Bay, and San Pablo Bay (Stewart and others 2004; Linares and others 2004; Kleckner and others 2010; Presser and Luoma 2010b; SFEI 2009) continue to show concentrations exceeding U.S. Fish and Wildlife Service (USFWS) dietary and tissue toxicity guidelines (Skorupa and others 2004; Presser and Luoma 2010b). Sturgeon contain higher concentrations of Se than any other fish species, reflecting their position as a top benthic predator (Stewart and others 2004). Surveys of surf scoter (*Melanitta perspicillata*) and greater scaup (*Aythya marila*) that feed voraciously on *C. amurensis* as they overwinter in Suisun Bay (SFEI 2005; De La Cruz and others 2008; De La Cruz 2010; Presser and Luoma 2010b) show Se has bioaccumulated to levels in muscle and liver tissue that may affect their ability to successfully migrate and breed (Heinz 1996; USDOI 1998; Ohlendorf and Heinz 2011).

Endangered Species Act requirements led to a number of species being determined as jeopardized by Se in the Bay-Delta under a proposed chronic aquatic life Se criterion of 5 $\mu g\ L^{-1}$ (USFWS and NOAA Fisheries 2000), including delta smelt (*Hypomesus transpacificus*); longfin smelt (*Spirinchus thaleichthys*); Sacramento splittail (*Pogonichthys macrolepidotus*); Sacramento perch (*Archoplites interruptus*); tidewater goby (*Eucyclogobius newberryi*); green sturgeon (*Acipenser medirostris*) and its surrogate white sturgeon (*Acipenser transmontanus*); steelhead trout (*Oncorhynchus mykiss*); Chinook salmon (*Oncorhynchus tshawytscha*); California clapper rail (*Rallus longirostris obsoletus*); California least tern (*Sterna antillarum browni*); bald eagle (*Haliaeetus leucocephalus*); California brown pelican (*Pelecanus occidentalis californicus*); marbled murrelet (*Brachyramphus marmoratus*); and giant garter snake (*Thamnophis gigas*). Recent analysis by the USFWS (2008a) of 45 species assumed the species most at risk depended on benthic food webs: greater scaup; lesser scaup (*Aythya affinis*); white-winged scoter (*Melanitta fusca*); surf scoter; black scoter (*Melanitta nigra*); California clapper rail; Sacramento splittail; green sturgeon; and white sturgeon. Not enough species-specific information is currently available for consideration of Se exposures for the giant garter snake, an endangered aquatic predator (USFWS 2006, 2009); the Dungeness crab (*Cancer magister*), an invertebrate that consumes *C. amurensis* (Stewart and others 2004); or for species that are within the Dungeness-crab food webs.

Human health advisories currently are posted for the Bay-Delta for the consumption of scoter, greater scaup, and lesser scaup based on elevated Se concentrations in their muscle and liver tissue (CDFG 2012, 2013). Selenium was found to be below the level of human health concern for consumption of edible tissue in certain species of fish, including white sturgeon, from the estuary (OEHHA 2011). White sturgeon contained the highest levels of Se among species of fish surveyed. Some individual white sturgeon sampled from North Bay locations had Se concentrations that exceeded Se advisory levels, based on specific consumption rates (see later detailed discussion under "Human Health" on page 23). Additionally, white sturgeon recreational fishing is limited, based on a decreasing species population (CDFG 2012).

It was recently suggested that the traditional regulatory approach to managing Se contamination is deeply flawed (Reiley and others 2003; Luoma and Presser 2009; Chapman and others 2010), and that a new conceptual model of the processes that control its toxicity is needed for regulatory purposes, especially in estuarine environments like the Bay-Delta. In recognition of the issues with the traditional approach to deriving a criterion for Se, the USEPA is leading a cooperative effort to develop site-specific fish and wildlife Se criteria for habitats affected by Se in California. Specifically for the Bay-Delta, the effort includes protection of Federally listed species and designated critical habitat (USFWS and NOAA Fisheries 2000; USEPA 2011a). Development of Se criteria for the Bay-Delta is proceeding first in this effort because the estuary is considered a sensitive hydrologic system and habitat in terms of Se and it was thought that protection here would elicit regulatory compliance upstream (USEPA 2011a). On the broader scale, Se is considered a general stressor of the estuary, and a constituent that should be analyzed as part of management and restoration planning and implementation (USEPA 2011b; NRC 2010, 2011, 2012).

The cooperative regulatory effort specifically recognizes that the new conceptual model must consider (1) the inaccuracies of deriving toxicity from waterborne Se concentrations; (2) the bioaccumulative nature of Se in aquatic systems; (3) Se's long-term persistence in aquatic sediments and food webs; and (4) the importance of dietary pathways in determining toxicity (USEPA 1992, 2000a; USFWS and NOAA Fisheries 2000; Luoma and Presser 2009; Presser and Luoma 2006, 2010a, 2010b). Revisions by USEPA also are occurring at the national level to incorporate into the basis for regulation recent advances in the environmental science of Se. For example, a fish tissue Se criterion and implementation plan are being proposed to better integrate dietary exposure pathways into regulatory frameworks, and ensure an adequate link to toxicity (USEPA 2004, 2011b). During this transitional period when species may be jeopardized and while Se criteria are being revised, USEPA has applied the national chronic freshwater Se criterion of 5 $\mu g\ L^{-1}$ to the estuary (USEPA 1992, 2000a).

We present here an ecosystem-scale Se conceptual model for the Bay-Delta that addresses the needs of both the DRERIP process and the USEPA. Quantitative applications of the model are also possible. Quantification provides an opportunity to evaluate site-specific Se risks under different circumstances, using field data combined with a systematic quantification of each of the influential processes that link source inputs of Se to toxicity. The methodology is presented in terms of specified DRERIP components (i.e., drivers, linkages, and outcomes). As an example of how quantitative applications can be used, we calculate the dissolved ambient Se concentrations that would result in compliance with a chosen fish or bird tissue guideline under different assumptions or environmental conditions. Uncertainties and model sensitivities are illustrated by comparing outcomes of different exposure scenarios. The scenario approach could facilitate the model's use by decision-makers for quantitative evaluation of restoration alternatives for ecosystem management and protection.

MODEL OVERVIEW

The DRERIP Ecosystem-Scale Selenium Model for the Bay-Delta (Figure 1) has five interconnected modules that depict drivers (sources and hydrology), linkages (ecosystem-scale processes), concentration outcomes (Se concentrations in water, particulates, and organisms), and food web exposure outcomes (effects on fish, wildlife, and human health). Model outcomes in Figure 1 are further refined to critical choices for modeling and species-specific risk scenarios for the Bay-Delta. Together the five modules consider the essential aspects of environmental Se exposure: biogeochemistry, food web transfer, and effects. They also take into account the estuary's ecology and hydrology as well as the functional ecology, physiology and ecotoxicology of the most vulnerable predator species. The modules define relationships that are important to conceptualizing and quantifying how Se is processed from water through diet to prey and predators, and the resulting effect on components of the food web. Thus, the DRERIP Ecosystem-Scale Selenium Model combines fundamental knowledge of Se behavior in ecosystems (Se drivers, linkages, and outcomes) with site-specific knowledge of the Bay-Delta (Bay-Delta drivers, linkages, and outcomes) to define site-specific Se risk (Figure 1).

The DRERIP Se submodels provide details for

- Sources and Hydrology (submodel A, Figure 2);
- Ecosystem-Scale Se Modeling (submodel B, Figure 3);
- Exposure: Food Webs, Seasonal Cycles, Habitat Use (submodels C, D; Figures 4, 5);
- Fish and Wildlife Health: Ecotoxicology and Effects (submodels E, F; Figures 6, 7); and
- Human Health (submodel G, Figure 8).

A human health pathway is designated, but emphasis here is on Se pathways to fish and wildlife health. The North Bay and the Delta are emphasized because the important Se sources have the potential to most affect those habitats and ecosystems (submodel A, Figure 2).

The quantitative DRERIP Ecosystem-Scale Selenium Model is based upon concepts and parameters developed elsewhere for a wide variety of aquatic systems and their food webs (submodel B, Figure 3; submodel E, Figure 6) (Luoma and Rainbow 2005; Luoma and Presser 2009; Chapman and others 2010; Presser and Luoma 2010a). To quantitatively apply the rela-

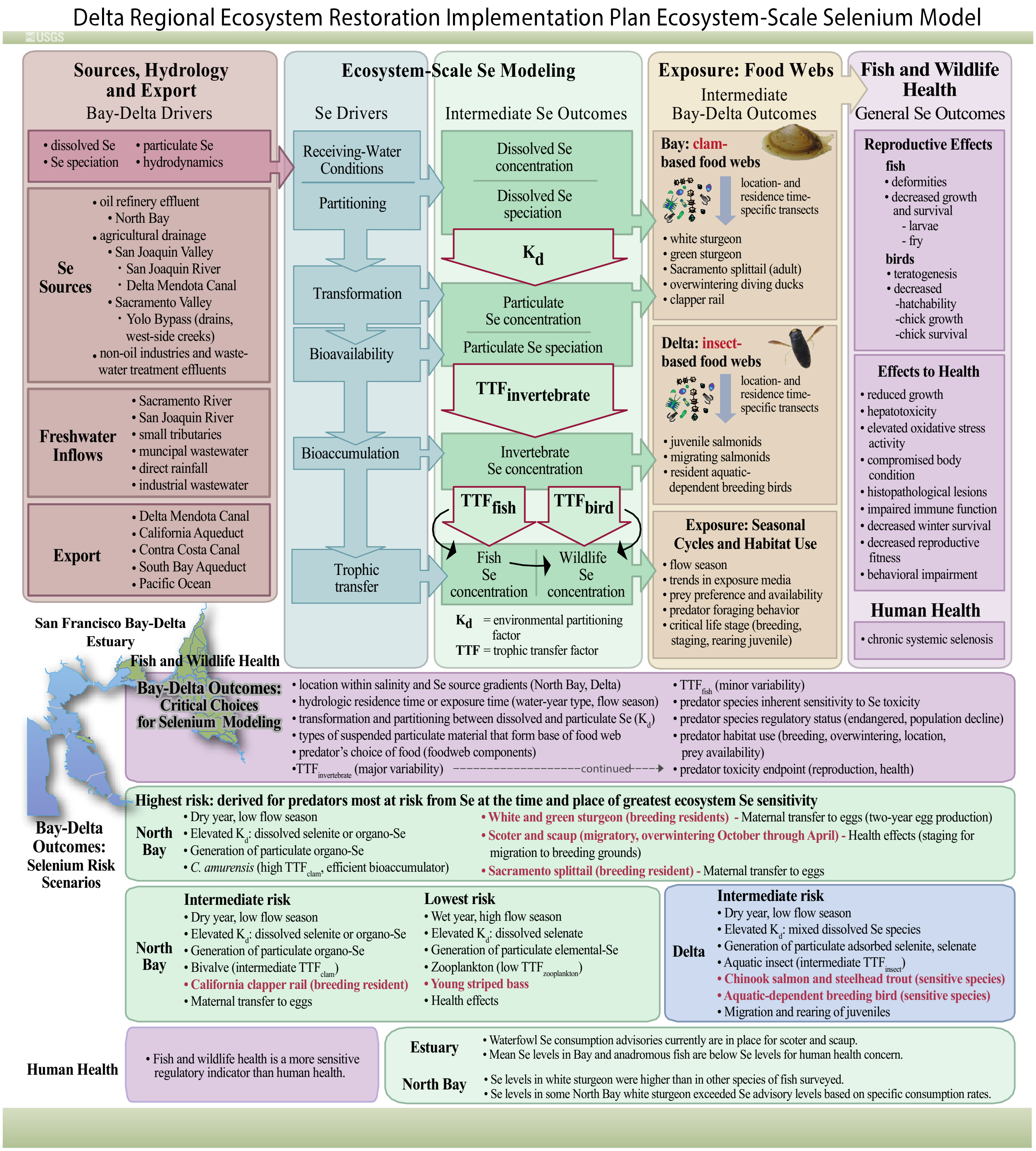

Figure 1 The DRERIP Ecosystem-Scale Selenium Model illustrates five interconnected modules that depict essential aspects of the Bay-Delta's hydrology, biochemistry, and ecology and of the exposure and ecotoxicology of predators at risk from selenium. These modules, and the detailed sub-models that follow, conceptualize (1) how selenium is processed from water through diet to predators and (2) its effects on ecosystems. Critical choices for modeling are summarized, and a quantitative application of the model for the estuary is derived for predators most at risk from Se at the time and place of greatest ecosystem Se sensitivity.

tionships in the conceptual model, we use empirical data from the Bay-Delta (e.g., Cutter and Cutter 2004; Presser and Luoma 2006, 2010b) to (1) help define environmental partitioning factors (K_ds) that quantify transformation of dissolved Se into particulate forms; and (2) help define biodynamic trophic transfer factors (TTFs) that quantify uptake by consumer species and their predators (submodel C, Figure 4; submodel D, Figure 5; submodel F, Figure 7). The broader, ecosystem-scale Se modeling approach was validated by comparing model forecasts with field data, across both a range of common food webs and hydrologic environments (Luoma and Rainbow 2005; Presser and Luoma 2010a) and specifically for the Bay-Delta and Newport Bay (Presser and Luoma 2006, 2009, 2010b).

The organizing principle for quantification is the progressive solution of a set of simple equations, each of which quantifies a process important in Se exposure (submodel B, Figure 3). The interaction of Se loading from different sources, hydrology, and hydrodynamics determine dissolved Se concentrations in the Bay-Delta. Transformation of Se from its dissolved form to a particulate form (represented here operationally as K_d) ultimately determines bioavailability to the food web. In a given environment, Se is taken up much faster from food than from solution by animals. Thus, the entry of Se into the food web can be estimated by a TTF for each trophic level. $TTF_{invertebrate}$ defines dietary uptake by a consumer species, which occurs when invertebrates (or herbivorous fish), feed on primary producers, detritus, microbes, or other types of particulate materials. Selenium bioaccumulation differs widely among invertebrate species because of different physiologies (Luoma and Rainbow 2005). These differences are captured by employing species-specific TTFs (Luoma and Presser 2009). Species-specific TTFs for predaceous fish and birds ($TTF_{predator}$) also are applied to the transfer of Se from invertebrate prey species to their predators (Presser and Luoma 2010a).

For the Bay-Delta, Stewart and others (2004) showed that Se concentrations differ widely among predators that live in the same environment. The main reason for those differences lies in the prey preferences of predators. For example, bass eating from the water-column food web consume invertebrates with much lower Se concentrations than sturgeon eating benthic invertebrates, especially bivalves (Stewart and others 2004). The differences in Se uptake among predator species ($C_{predator}$) can be captured only if the correct prey species (or class of prey species) is included in the equation (submodel B, Figure. 3) and the conceptualization (submodel C, Figure 4). This also means that the choice of predator species is critical in assessing risks from Se contamination.

Selenium concentrations in predators can be predicted with surprisingly strong correlation to observations from nature if particulate Se concentrations are known and an appropriate food web is used for the predator (Luoma and Presser 2009; Presser and Luoma 2010a). One use of these calculations might be to quantify the degree to which different species of birds and fish might be threatened by Se in a specified environment, for example. The correspondence between observed $C_{predator}$ and predictions of $C_{predator}$ from the series of equations that begins with dissolved concentrations (submodel B, Figure 3) depends upon how closely the partitioning between dissolved and particulate Se used in the model matches that occurring in the ecosystem of interest. One use of quantification in this instance is to run the model in the reverse direction to determine the dissolved Se concentration in a specific type of hydrologic environment and food web that would result in a specified Se concentration in the predator. Later, we present a detailed example of how the latter might be applied to real-world issues.

In the final step, effects on the reproduction and health of predaceous fish and birds are determined from bioaccumulated Se concentrations. Selenium is one of the few trace elements for which tissue concentrations have been correlated to these adverse effects in both dietary toxicity tests and field studies. The toxicity data for some of the key species in the Bay-Delta are limited or non-existent. The necessity of establishing effects thresholds from surrogate species adds some uncertainty to assessments of risk. Therefore, in our examples, we use different possible choices for such thresholds.

Additionally, modeling here is within a specified location and flow condition to provide context for exposure and to help narrow the uncertainties in quantifying the ecological and physiological potential for bioaccumulation (Presser and Luoma 2010b).

MODULES

Sources, Hydrology, and Export

Estuary Mass Balance

The major portion of the estuary from the rivers to the Golden Gate Bridge is termed the Northern Reach, with Suisun Bay near the head of the estuary (submodel A, Figure 2). Selenium sources and their hydraulic connections within that reach have been documented in a number of publications (Cutter 1989; Cutter and San Diego–McGlone 1990; Cutter and Cutter 2004; Meseck and Cutter 2006; Presser and Luoma 2006, 2010b; SFBRQWCB 2011) (Figure 1; submodel A, Figure 2). In brief, the most important regulated estuarine sources of Se are (1) internal inputs of oil refinery wastewaters from processing of crude oils at North Bay refineries; and (2) external inputs of irrigation drainage from agricultural lands of the western San Joaquin Valley conveyed mainly through the San Joaquin River. (submodel A, Figure 2). These and other potential Se sources are described in detail in Appendix A.1. These details reflect the depth of history for Se management within the Bay-Delta watershed and the continuing tradeoffs that accompany their presence.

The Sacramento and San Joaquin rivers are the main sources of freshwater inflow to the Bay-Delta, with the Sacramento River being the dominant inflow under most conditions (Conomos and others 1979; Peterson and others 1985). The rivers provide 92% of the freshwater inflows to the Bay-Delta, with small tributaries and municipal wastewater providing approximately 3% each (McKee and others 2008).

In general, Se concentrations in the Sacramento River (above tidal influence, e.g., at Freeport) are low and relatively constant (1998 to 1999 average: 0.07 $\mu g\ L^{-1}$; range 0.05 to 0.11 $\mu g\ L^{-1}$) (Cutter and Cutter 2004). Dissolved Se concentrations in the San Joaquin River (above tidal influence, e.g., at Vernalis) were about an order-of-magnitude higher than those in the Sacramento River in 1999 (1998 to 1999 average: 0.71 $\mu g\ L^{-1}$; range 0.4 to 1.07 $\mu g\ L^{-1}$) (Cutter and Cutter 2004) and are much more variable. In the late 1980s and early 1990s concentrations above 5 $\mu g\ L^{-1}$ were observed occasionally in the San Joaquin River (Presser and Luoma 2006), but in-valley source control efforts have reduced Se loads and concentrations (Appendix A.1).

In the present configuration of the Bay-Delta, the San Joaquin River is predominantly re-routed and exported back to the San Joaquin Valley (submodel A, Figure 2; Appendix A.1). Hence, for the purposes of evaluating Se contamination sources, the simplest assumption is that the “baseline” Se concentrations (undisturbed by human activities) in the Delta would be close to the Se concentrations in the Sacramento River. The pre-disturbance baseline Se concentrations in the Bay or tidal reaches of the rivers would be concentrations in the Sacramento River mixed with concentrations in coastal waters, as reflected by the salinity of the sampling location. Deviations from that baseline reflect inputs of Se internal to the Bay (industrial or local streams) (Cutter and San Diego-McGlone 1990; Cutter and Cutter 2004) or input of Se to the Bay from the San Joaquin River.

The current San Joaquin River contributions to the Bay, thought to be minimal during most flow conditions, are especially difficult to measure (Appendix A.1). However, that could change. Under some proposals for modifications in water infrastructure, increased diversion of the Sacramento River through tunnels or canals would be accompanied by greater inflows from the San Joaquin River to the Delta and the Bay. In simulations available of the implications of such a change, Meseck and Cutter (2006) found that Se concentrations doubled in particulate material in the Bay.

The conceptual model described above suggests that parameters critical in determining the mass balance model for Se inputs for the Bay-Delta are (1) total river discharge (Sacramento River and San Joaquin River); (2) water diversions or exports (i.e., pumping at Tracy and Clifton Court Forebay south to the Delta–Mendota Canal and the California Aqueduct); (3) proportion of the San Joaquin River directly

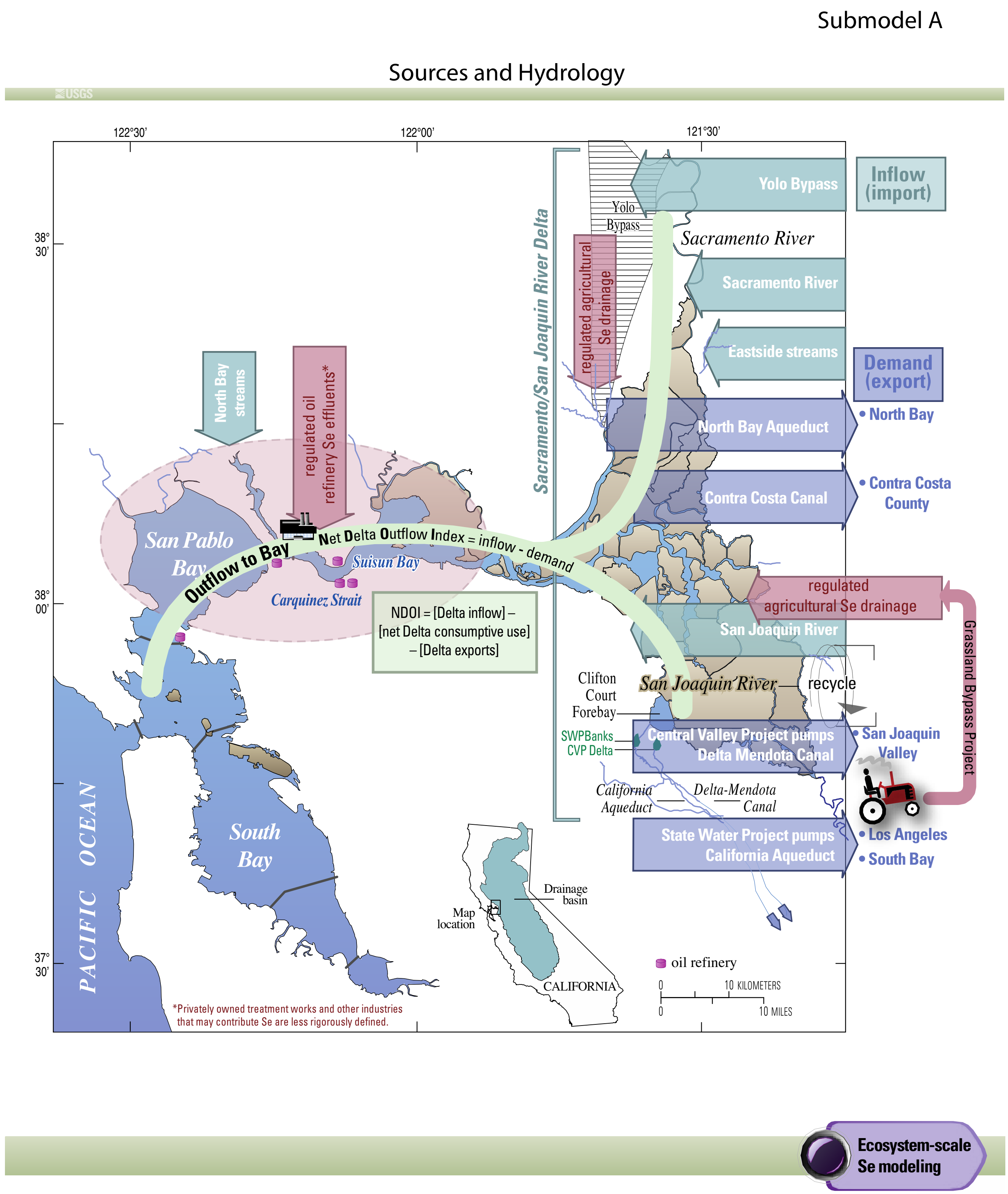

Figure 2 Submodel A. Sources and Hydrology

recycled south before it enters the Bay; 4) Se concentrations in each of the internal and external sources; and 5) total outflow of the rivers to the Bay or Net Delta Outflow Index (NDOI).

There are several uncertainties in quantification of the Se mass balance. One is the difficulty of precisely defining the contribution of the San Joaquin River to the NDOI, and hence the agricultural component of Se inputs to the Bay. Diversions and Delta hydrodynamics are sufficiently complex that every method available to determine that contribution has serious uncertainties (e.g., subtracting Sacramento River flow at Rio Vista from NDOI). Simple water accounting suggests minimal potential for flow from the San Joaquin River to enter the Bay (i.e., as measured by the percent by which river flow at Vernalis exceeds total export) during many months of the year (USBR 2012). Inputs are possible during spring months (April and May), wet and above normal years, and times of low capture efficiency (e.g., when river barriers are in-place) or when the ratio of the Sacramento River and San Joaquin River discharges is lowest in the fall.

A second uncertainty is that the strong tidal circulation in the Bay and the Delta mixes dissolved and particulate Se through the entire tidal reach, distorting spatial patterns that might otherwise help identify important sources of Se input (Ganju and others 2004). The three-dimensional nature of tidally driven hydrodynamics dissociates distributions of dissolved and particulate Se as well, adding complexity. One important outcome of this is that particulates contaminated with Se from industrial sources in Suisun Bay could feasibly be found throughout the full tidal range in both rivers, including otherwise uncontaminated segments of the Sacramento River. Riverine endmember concentrations of particulate Se, therefore, must be defined from landward of the reach of the tides, although river discharge at those locations does not necessarily represent riverine outflow to the Bay. Collecting an adequate mass of suspended particulate material for Se analysis in non-tidal freshwaters is challenging; therefore, few such data exist for the Sacramento River and even for some of the areas possibly affected by agricultural drainage. Hydrodynamic models of varying complexity are available that can approximate water movements in this complex situation (e.g., Delta Simulation Model II). But modeling the distribution of particulate material (crucial for understanding implications of Se) is much more difficult (Ganju and others 2004).

Links Between Source Inputs and Water Inflows

Both Sacramento River and San Joaquin River discharges vary dramatically during the year depending on runoff, water management, and diversions. Residence (or retention) time is affected by river discharges (e.g., Cutter and Cutter 2004), but the strong tidal influences make that difficult to precisely define. Nevertheless, even a coarse differentiation of seasonal periods (low flow and high flow) and classification by water year (critically dry, dry, below normal, normal, above normal and wet) can be useful in evaluating influences on processes important to the fate and bioavailability of Se (Presser and Luoma 2006). Empirical data suggest processes such as dilution of local inputs and phase transformations that incorporate Se into organic particulate material appear to be affected by changes in retention time in the estuary, at least to some extent (Cutter and Cutter 2004; Doblin and others 2006; Presser and Luoma 2006, 2010a, 2010b). For example, Cutter and San Diego-McGlone (1990) found that a peak in selenite concentrations was centered around the area of inputs from oil refineries during low riverine inflows to the Bay in the 1980s; but that peak disappeared during periods of high riverine discharge. They used a one-dimensional model of the water and a Se mass balance to show that the mass of Se discharged by the refineries was the dominant source of selenite during low flows, but that it was insignificant compared to the mass of Se input from the Sacramento River during high flows. The selenite peak was reduced and replaced by a different pattern of dissolved Se speciation when Se discharges from the refineries were reduced by about half in 1999 (Cutter and Cutter 2004). Similarly, high Se concentrations in the southernmost Delta (Stockton) reflect San Joaquin River inputs, but concentrations seaward of this location decline as they are diluted by the large volumes of Se-poor Sacramento River water channeled into the Delta for export (Lucas and Stewart 2007). Local tributaries could be an internal source of Se to the Bay, but these inputs occur almost entirely during high riverine inflow periods when their Se loads are insignificant compared to the large mass of Se carried into the Bay by high discharge from the Se-poor Sacramento River.

The NDOI, essentially inflow minus demand, is often used to indicate hydrologic influences on Se concentrations, including differences in retention time of a parcel of water in the Bay and Delta (Cutter and Cutter 2004). Increased exposure time (i.e., the cumulative amount of time a particle spends within a domain, taking into consideration repeated visits over multiple tidal cycles; L. Doyle, W. Fleenor, and J. Lund, University of California, Davis, pers. comms.; 2012) at the lowest inflows may explain why NDOI is a relevant indicator of the effect of flow on processes such as conversion of Se from dissolved to particulate forms.

Exports

The Delta–Mendota Canal, California Aqueduct, Contra Costa Canal, and South Bay Aqueduct all export water from the Delta. Thus, all are secondary recipients of the Se sources considered here (submodel A, Figure 2). The Delta–Mendota Canal also receives agricultural drainage directly, with that source proposed to be under regulatory control (USFWS 2009; USBR 2011). In general, however, few data are available to assess a mass balance for Se through the State Water Project, Central Valley Project, and other water-delivery systems.

In terms of export of Se to the Pacific Ocean from the Bay, some data are available for seaward locations in the Bay. Dissolved concentrations at these locations are among the lowest observed in the system when not under flood flows (Cutter 1989; Cutter and San Diego–McGlone 1990; Cutter and Cutter 2004); particulate concentrations are occasionally high, however. Under shorter residence times during high flows, increased dissolved concentrations near the Golden Gate Bridge (Cutter and Cutter 2004) suggest sources internal to the Bay affect ocean-dissolved Se concentrations. Outflows to the sea have been estimated in simple mass balance models (Cutter and San Diego-McGlone 1990) although there are some uncertainties in such estimates. Ocean disposal was considered as one of the alternatives for comprehensive agricultural drainage management from the western San Joaquin Valley (USBR 2006). However, efficient Se recycling within productive ocean ecosystems and the opportunities for Se biomagnification in complex marine food webs suggest serious risks are likely (Cutter and Bruland 1984); hence, there are reasons for careful study before such options are considered.

Ecosystem-Scale Selenium Modeling

Dissolved Selenium Concentrations, Speciation, and Transformation

Total dissolved Se concentrations within the Bay range from 0.070 to 0.303 $\mu g\ L^{-1}$, with a mean of 0.128 ± 0.035 $\mu g\ L^{-1}$ and a median of 0.125 $\mu g\ L^{-1}$ across 128 samples collected since 1997 (Doblin and others 2006; Lucas and Stewart 2007). The mean concentration is only approximately two times higher than Se concentrations in the dominant freshwater endmember (the Sacramento River). In all surveys since the 1980s, Se concentrations in the tidal Bay and Delta are highest in Suisun Bay, with a downward spatial trend from Carquinez Strait toward the ocean. The latter suggests that dissolved concentrations in the ocean endmember are about the same as those in the Sacramento River.

The dissolved gradients of Se concentration are not necessarily the best indicators of the distribution of Se effects. Ecological implications depend upon the biogeochemical transformation from dissolved to particulate Se. Phase transformation of Se is of toxicological significance because particulate Se is the primary form by which Se enters food webs (Figures 1, 3 and 4) (Luoma and others 1992). Speciation of dissolved Se into its three dominant oxidation states is an important component in many conceptual models. In the Bay-Delta, speciation of dissolved Se is important because it influences the type and rate of phase transformation reaction that creates particulate Se. Examples of phase transformation reactions include (1) uptake by plants and phytoplankton of selenate, selenite, or dissolved organo-Se and transformation to particulate organo-Se by

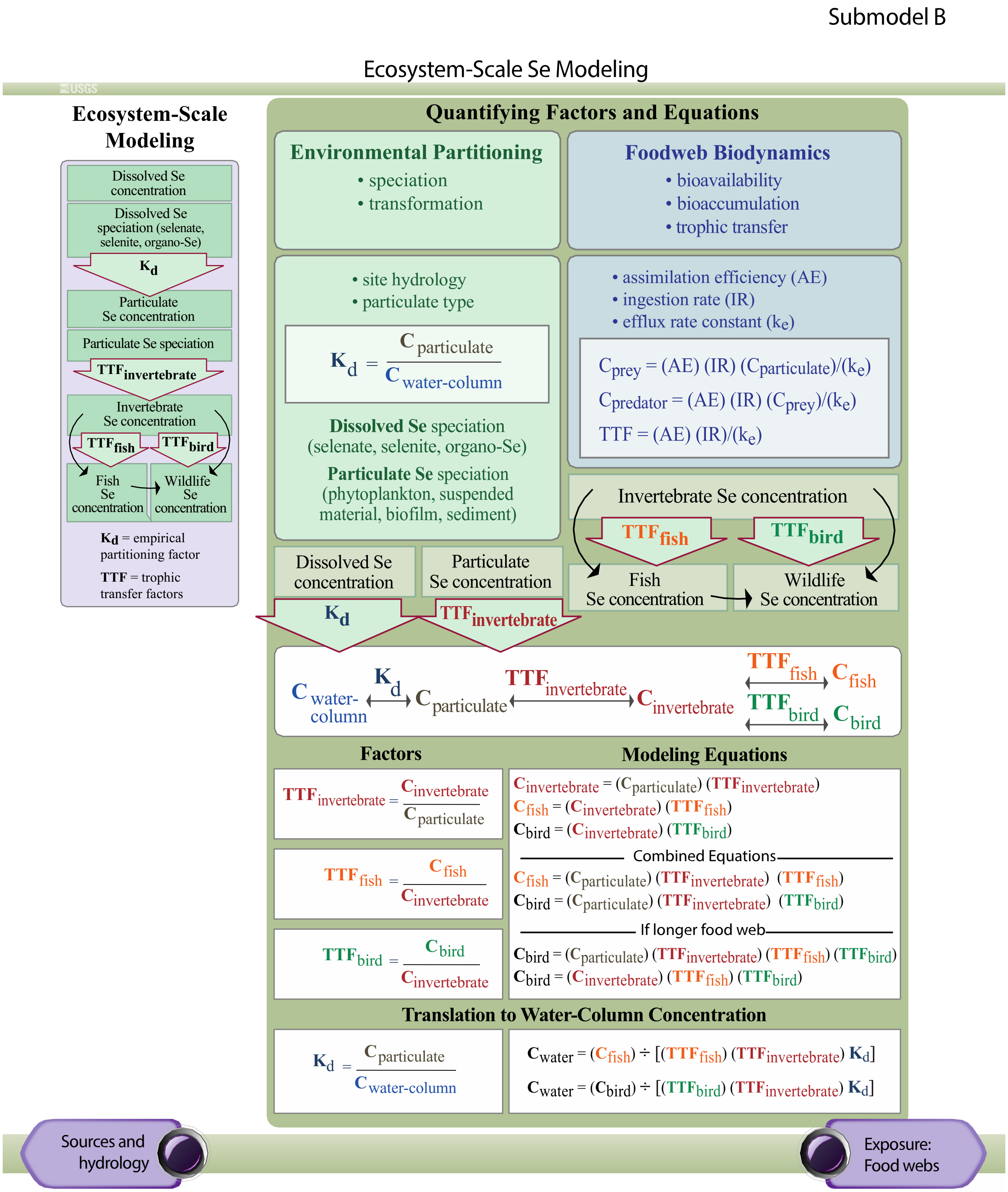

Figure 3 Submodel B. Ecosystem-Scale Se Modeling

assimilatory reduction, where uptake of selenate is considerably slower than uptake of the other two forms (e.g., Sandholm and others 1973; Riedel and others 1996; Wang and Dei 1999; Fournier and others 2006); (2) sequestration of selenate into sediments as particulate elemental Se by dissimilatory biogeochemical reduction (e.g., Oremland and others 1989); (3) adsorption as co-precipitated selenite through reactions with particle surfaces; and (4) recycling of particulate phases back into water as detritus or as dissolved organo-Se, after organisms die and decay (e.g., Velinsky and Cutter 1991; Reinfelder and Fisher 1991; Zhang and Moore 1996).

These different biogeochemical transformation reactions result in different forms of Se in particulate material: organo-Se, adsorbed Se, or elemental Se. Although only a few studies have determined speciation of particulate Se (e.g., Doblin and others 2006), such data can greatly aid in understanding bioavailability. Experimental studies show that particulate organo-Se is the most bioavailable form when it is eaten by a consumer species (Luoma and others 1992). Detrital or adsorbed Se is also bioavailable when ingested by animals, although to a lesser extent than organo-Se (Wang and others 1996). Non-particle associated elemental Se is not bioavailable (Schlekat and others 2000).

Concentrations of Se in particulate materials (per unit mass material) within the Bay and tidal freshwaters range widely from 0.1 to 2.2 $\mu g\ g^{-1}$ dry weight (dw), with a mean of $0.56 \pm 0.32\ \mu g\ g^{-1}$ dw and a median of 0.45 $\mu g\ g^{-1}$ dw (n = 128) since 1997 (Doblin and others 2006; Lucas and Stewart 2007). The 15-fold range in particulate concentrations contrasts sharply with the 4-fold range in dissolved concentrations, as do the contrasts in standard deviations. Not only are particulate concentrations much more dynamic than dissolved concentrations, but they also are about four times higher if expressed in common units. Both reflect biogeochemical transformation processes and, perhaps, inorganic adsorption. The latter is probably more important in soils than in the aquatic environment. Given the different dynamics and the variability of dissolved and particulate Se, it is not surprising that the ratio of the two also is quite variable.

Geochemical models that attempt to capture phase transformations of Se under different conditions are problematic. In fact, no models are available that can predict particulate Se concentrations based solely upon dissolved concentrations and biogeochemical conditions. One reason is that conventional thermodynamic equilibrium-partitioning models are inadequate for Se. Critical Se transformation processes are biological, and not predictable from thermodynamics. Some model approaches predict the particulate Se added on to a pre-existing particulate concentration, using a combination of phytoplankton productivity and re-suspension (Meseck and Cutter 2006; SWRCB 2011; Tetra Tech, Inc. 2010). While such models provide interesting estimates of temporal and spatial distributions of particulate Se, their major limitations lie in the basis upon which the pre-existing concentration is chosen and their inability to comprehensively account for all the processes involved in transformation.

The choice of the (pre-existing) baseline particulate Se concentration is critical to the questions models can address. Local data can be used for choosing pre-existing Se concentrations at the seaward and landward boundaries in the Bay-Delta. But the data used to date are from tidally affected reaches of the river, and are likely to be biased by redistribution of already contaminated particles from tidal pumping. As noted above, few data exist for particulate Se concentrations above the tidal reach of the Sacramento River; nor are there adequate determinations of Se concentrations on particulates from the coastal zone. In such a case, answers to questions about changing the internal Se inputs to the Bay are biased in that the boundary condition already includes such inputs (SWRCB 2011; Tetra Tech, Inc. 2010). On the other hand, this modeling approach appears to be well suited to test the influence of changing inputs from one boundary or from primary production alone (Meseck and Cutter 2006; Tetra Tech, Inc. 2010).

Observations of environmental partitioning of Se between dissolved and particulate phases can be employed to estimate transformation efficiencies in lieu of a comprehensive approach to modeling biogeochemical phase transformation for Se. Presser and Luoma (2006) first used field observations to quantify partitioning, which they described by the somewhat controversial term K_d. Luoma and Presser (2009) were careful to emphasize that their K_ds represented conditional observations from the Bay-Delta at a specific time and place; and were not meant to be equilibrium constants. Thermodynamic equilibrium constants would be inappropriate to describe an inorganic to organic transformation. They pointed out that no single constant could be expected to apply to all environmental conditions either in the Bay-Delta or elsewhere. Site hydrology, dissolved speciation, and the type of particulate material are all influential, although specific influences were not necessarily predictable in quantitative terms. An operational approach was therefore chosen to try to estimate influences of such processes.

They defined K_d as the ratio of particulate material Se concentration (in dw) to the dissolved Se concentration observed at any instant in simultaneously collected samples. The specific equation is

$$K_d = (C_{\text{particulate material}}, \mu g\ kg^{-1}\ dw) \div (C_{\text{water}}, \mu g\ L^{-1}) \quad (1)$$

Of interest here is the particulate matter at the base of the food web. As sampled in the environment that can include suspended particulate Se (which is a physically inseparable mix of phytoplankton, periphyton, detritus and inorganic suspended material), biofilm, sediment and/or attached vascular plants. Feeding characteristics of the organisms in question and data availability dictate the best choice among these. For example, for a filter-feeding bivalve in the Bay-Delta, Se concentrations determined in suspended particulate material (in $\mu g\ g^{-1}$ dw) are the preferred parameter for modeling because these animals filter their food from the water-column.

Some broad generalizations are possible about K_ds for Se (Presser and Luoma 2010a). For example, if all other conditions are the same, K_d will increase as selenite and dissolved organo-Se concentrations increase relative to selenate. Calculations using data from laboratory microcosms and experimental ponds show speciation-specific K_ds of 140 to 493 where selenate is the dominant form; 720 to 2,800 when an elevated proportion of selenite exists; and 12,197 to 36,300 for 100% dissolved seleno-methionine uptake into algae or periphyton (Besser and others 1989; Graham and others 1992; Kiffney and Knight 1990). Compilations of K_ds also show different general ranges for rivers, streams, lakes, ponds, wetlands, and estuaries that are affected by Se inputs (Presser and Luoma 2010a), although with some overlap. Exposure time for phase transformation is probably an important factor driving differences among such systems. Estuaries are among the sites with the highest values (range of medians from 4,000 to 21,500) indicating efficient conversion of dissolved Se to particulate Se. Finally, although the influence of exposure time for a particle within an estuary is challenging to understand precisely, especially in the Bay-Delta because of the dominance of tidally driven circulation, K_ds seem to be higher during conditions where more time is available for transformation reactions to occur (Presser and Luoma 2010b).

The most recent transects of the Bay that provide spatially and temporally matched data for derivation of K_ds from dissolved and particulate Se concentrations were from June 1998 to November 1999 (Cutter and Cutter 2004; Doblin and others 2006). In these studies, samples were collected at 1 meter below the surface, and included dissolved Se concentrations, suspended particulate material Se concentrations, dissolved Se speciation, suspended particulate Se speciation, salinity, and total suspended material. These data were collected in four different transects across the salinity gradient in the Northern Reach under a variety of river discharge and presumed residence time conditions. The full range of dissolved Se concentrations in these transects was 0.070 to 0.303 $\mu g\ L^{-1}$. The suspended particulate material Se concentrations were more variable: 0.15 to 2.2 $\mu g\ g^{-1}$ dw. Calculated K_ds ranged from 712 to 26,912. The degree of variability across this whole data set is large. However, the largest part of the variability was driven by very high values in the landward-most and seaward-most samples, where dissolved concentrations were very low. Such ratios can be artificially inflated when values become very low in the denominator, if the numerator does not decline as rapidly. Tidal pumping of contaminated particles from the Bay upstream into the less contaminated Sacramento River water is a possible cause of such an effect.

Downstream transport of highly contaminated particles from the San Joaquin River into Bay or Delta water could also be a cause. Finally, seaward, where residence times are elevated in Central and San Pablo bays, biological transformation could enrich Se in particles while depleting it from the water column. If the goal is to find conditions where there is sufficient linkage between dissolved and particulate Se to be useful in forecasts of one from the other, none of these conditions would apply. Presser and Luoma (2010b) avoided such biases and thereby constrained variability by restricting K_ds geographically to the middle range of the salinity zone in Suisun Bay. This also focused the modeling on the most contaminated segment of the estuary.

If location is restricted to Carquinez Strait–Suisun Bay—eliminating freshwater and ocean interfaces—then the range of dissolved Se concentrations is narrowed to 0.076 to 0.215 µg L^{-1} and the range of suspended particulate material Se concentrations is narrowed to 0.15 to 1.0 µg g^{-1} dw. The variation of K_d is narrowed to a range of means of 1,180 to 5,986 (or of individual measurements, 712 to 7,725). Because this data set is still large, median or mean concentrations, or a given percentile, can be used as viable indicators of partitioning in modeling scenarios.

Seasonality also is important, and restrictions to specific flow regimes also can be used to constrain variability. For example, the highest mean K_ds occur during periods of the lowest river inflows (and highest residence times). Constrained to Suisun Bay, the mean K_d was 1,180 ± 936 in June 1998. This was a high flow season wherein Cutter and Cutter (2004) estimated a residence time of 11 days. The mean K_d was 5,986 ± 1,353 in November 1999. This was a low flow season with an estimated residence time of 70 days. The mean K_d among all constrained samples was 3,317, and the mean for low flow seasons was 4,710.

Transects in the Delta were also conducted between 1998 and 2004 in different flow regimes (Doblin and others 2006; Lucas and Stewart 2007). Dissolved Se concentrations among all these samplings ranged from 0.083 to 1.0 µg L^{-1}, with a mean of 0.25 ± 0.24 (n = 72). Particulate concentrations ranged from 0.27 to 6.3 µg g^{-1} dw, with a mean of 0.98 ± 0.94 (n = 71). As in the Bay transects, the range in particulate concentrations (23-fold) exceeds the range in dissolved concentrations (12-fold). Concentrations and variability, thus, were even greater in the Delta, overall, than in the Bay. In the Delta, K_ds ranged from 554 to 38,194, with the range of means from 1,886 ± 1,081 in January 2003 (a high flow season) to 7,712 ± 3,282 in July 2000 (a low flow season). Sets of dissolved and particulate Se concentrations determined as part of focused research for the Delta in September 2001, the low flow season of a dry year, yielded some especially elevated K_ds (>10,000) (Lucas and Stewart 2007). In general, these elevated K_ds may reflect tidal pumping, or represent times and areas where Se is concentrating in particulate material because of differing hydrologic environments (e.g., slow-moving backwaters with high productivity). Constraining variability is more difficult in the Delta, hence, quantifying phase transformation from empirical data is more uncertain in this system.

Given the degree of variability in both the Bay and the Delta, modeling that requires linking dissolved Se to particulate Se should include several scenarios using different K_ds that are within a range of values constrained, as described above.

Uptake Into Food Webs

Kinetic bioaccumulation models (i.e., biodynamic models, Luoma and Fisher 1997; Luoma and Rainbow 2005, 2008) account for the now well-established principle that Se bioaccumulates in food webs principally through dietary exposure. Uptake attributable to dissolved exposure makes up less than 5% of bioaccumulated Se in almost all circumstances (Fowler and Benayoun 1976; Luoma and others 1992; Roditi and Fisher 1999; Wang and Fisher 1999; Wang 2002; Schlekat and others 2004; Lee and others 2006). Biodynamic modeling (submodels B and C, Figures 3 and 4) shows that Se bioaccumulation (the concentration achieved by the organism) is driven by physiological processes specific to each species (Reinfelder and others 1998; Wang 2002; Baines and others 2002; Stewart and others 2004). Biodynamic models have the further advantage of providing a basis for deriving a simplified measure of the linkage between trophic levels: TTFs. For each species, a TTF can be derived from either experimental studies or field observations.

Experimental derivation of TTFs is based on the capability of a species to accumulate Se from dietary exposure as expressed in the biodynamic equation (Luoma and Rainbow 2005):

$$dC_{species}/dt = (AE)\ (IR)\ (C_{food}) - (k_e + k_g)\ (C_{species}) \quad (2)$$

where $C_{species}$ is the contaminant concentration in the animals (µg g^{-1} dw), t is the time of exposure in days (d), AE is the assimilation efficiency from ingested particles (%), IR is the ingestion rate of particles (g g^{-1} d^{-1}), C_{food} is the contaminant concentration in ingested particles (µg g^{-1} dw), k_e is the efflux rate constant (d^{-1}) that describes Se excretion or loss from the animal, and k_g is the growth rate constant (d^{-1}). Key determinants of Se bioaccumulation are the ingestion rate of the animal, the efficiency with which Se is assimilated from food, and the rate constant that describe Se turnover or loss from the tissues of the animal (Luoma and Rainbow 2005; Presser and Luoma 2010a). Experimental protocols for measuring such parameters as AE, IR, and k_e are now well developed for aquatic animals (Luoma and others 1992; Wang and others 1996; Luoma and Rainbow 2005). 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 and others 1996).

In the absence of rapid growth, a simplified, resolved biodynamic exposure equation for calculating a Se concentration in an invertebrate (submodel B, Figure 3) is

$$C_{invertebrate} = [(AE)(IR)(C_{particulate})] \div [k_e] \quad (3)$$

For modeling, these physiological parameters can be combined to calculate a $TTF_{invertebrate}$, which characterizes the potential for each invertebrate species to bioaccumulate Se. $TTF_{invertebrate}$ is defined as

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

Similarly, foodweb biodynamic equations for fish or birds are

$$C_{fish\ or\ bird} = [(AE)\ (IR)\ (C_{invertebrate})] \div k_e \quad (5)$$

and

$$TTF_{fish\ or\ bird} = [(AE)\ (IR)] \div k_e \quad (6)$$

Where laboratory data are not available, TTFs can be defined from field data, where the TTF defines the relationship between Se concentrations in an animal and in its food in dw. The field $TTF_{invertebrate}$ must be defined from spatially and temporally matched data sets (in dw or converted to dw) of particulate and invertebrate Se concentrations (submodel B, Figure 3) as

$$TTF_{invertebrate} = C_{invertebrate} \div C_{particulate} \quad (7)$$

A field derived species-specific TTF_{fish} is defined as

$$TTF_{fish} = C_{fish} \div C_{invertebrate} \quad (8)$$

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 µg g^{-1} dw (submodel B, Figure 3).

Whether the TTFs are determined from the laboratory or the field, the modeling approach is sufficiently flexible to represent complexities such as mixed diets. For example, a diet that includes a mixed proportion of prey in the diet can be addressed using the equation

$$C_{fish} = (TTF_{fish})\ [(C_{invertebrate\ a})\ (\text{prey fraction}) + (C_{invertebrate\ b})\ (\text{prey fraction}) + (C_{invertebrate\ c})\ (\text{prey fraction})] \quad (9)$$

Equations are combined to represent step-wise bioaccumulation from particulate material through invertebrates to fish (submodel B, Figure 3) as

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

Similarly, for birds, the combined equation is

$$C_{bird} = (TTF_{invertebrate})\ (C_{particulate})\ (TTF_{bird}) \quad (11)$$

Modeling can 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 (submodel B, Figure 3) is

$$C_{predator\ fish} = (TTF_{invertebrate})\ (C_{particulate})\ (TTF_{forage\ fish})\ (TTF_{predator\ fish}) \quad (12)$$

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

$$C_{bird} = (TTF_{invertebrate})\ (C_{particulate})\ (TTF_{fish})\ (TTF_{bird}) \quad (13)$$

Variability or uncertainty in processes that determine AEs or IRs can be directly accounted for in sensitivity analysis (Wang and others 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 on available data for that species. Laboratory and field factors for a species can be compared and refined to reduce uncertainties in modeling (Presser and Luoma 2010a).

A substantial number of species-specific TTFs are available (Luoma and Presser 2009; Presser and Luoma 2010a). These are enough data at least to begin to model important food webs. Across invertebrate species, TTFs range from 0.6 to 23. Of the 29 species studied, 27 species have TTFs > 1. Thus, most invertebrate species bioaccumulate as much as or more Se than concentrated in the trophic level below them. In other words, the concentration of Se biogeochemically transformed into algae, microbes, seston, or sediments is preserved and/or (bio)magnified as Se passes up food webs. In general, TTFs for bivalves (clams, mussels, oysters) and for barnacles are the highest among species of invertebrates (i.e., an experimentally determined TTF range of approximately 4 to 23) (Presser and Luoma 2010a).

Trophic transfer factors from the available data for fish have a median of approximately one, and vary much less than among invertebrates: from 0.5 to 1.8 (Presser and Luoma 2010a). Compilations show that TTFs derived from laboratory biodynamic experiments range from 0.51 to 1.8; TTFs for different fish species derived from field studies are similar, ranging from 0.6 to 1.7.

Trophic transfer factors for aquatic birds (diet to bird egg) are less well developed, and laboratory data are limited (Presser and Luoma 2010a). The most robust data from the laboratory relate Se concentrations in the diet (as seleno-methionine) to egg Se concentrations from controlled feeding of captive mallards (*Anas platyrhynchos*). The range of $TTF_{bird\ egg}$ calculated from the compilation of nominal experimental diet Se concentrations and mean egg Se data given in Ohlendorf (2003) for mallards is 1.5 to 4.5. Using the detailed data from Heinz and others (1989) narrows this range to 2.0 to 3.9, with a mean of 2.6. Field data could be used to refine $TTF_{bird\ egg}$ on a site-specific basis, but variability in food sources and habitat use may add uncertainty to such data, and limits applications among habitats.

Exposure: Food Webs, Seasonal Cycles, and Habitat Use

Selenium is at least conserved and usually biomagnified at every step in a food web (Presser and Luoma 2010a). Selenium toxicity is generally assumed to be observed first in specific predator species as differences in food web exposure are propagated up trophic pathways (Luoma and Rainbow 2005; Stewart and others 2004). Some invertebrate species also may be susceptible to environmentally relevant Se concentrations (Conley and others 2009, 2011). Selenium is usually not detoxified in animal tissues by conjugation with metal-specific proteins or association with non-toxic inclusions (Luoma and Rainbow 2008). Hence, general mechanisms that semi-permanently sequester metals in non-toxic forms and lead to progressive accumulation with size or age probably are less applicable to the metalloid Se than to metals in general (Luoma and Presser 2009).

Predator population distribution, feeding preference, prey availability, life stage, gender, physiology, and species sensitivity are all variables that influence how a predator is affected by Se. Field factors such as varying weather, water depth, human disturbance, and food dispersion also affect foraging energetics, and accessibility of contaminants in foods on a localized level. Despite these complexities, some generalizations are possible at the present state of understanding. Predator species for the Bay-Delta, their food webs, and potential exposure are shown in submodels C and D (Figures 4 and 5), with further supporting information compiled in Appendix A.2 and A.3.

Based upon studies of invertebrate bioaccumulation the greatest exposures to Se will occur in predators that ingest bivalves in the Bay-Delta (Stewart and others 2004; Presser and Luoma 2006, 2010b). The estimated maximum percentages of diet that are clam-based for various benthic predators were estimated by the USFWS (2008a) (submodel C, Figure 4): lesser scaup 96%; surf scoter 86%; greater scaup 81%; black scoter 80%; white-winged scoter 75%; California clapper rail 64%; bald eagle 23%; white sturgeon (and assumed for green sturgeon) 41%; and Sacramento splittail (2-year olds) 34%. Dietary estimates are not specific to *C. amurensis*, but a bivalve component to diet in general. Bald eagles are an example of a predator with a diet wherein 23% are those waterfowl (scaups and scoters) that primarily feed on benthic mollusks (USFWS 2008a). Clapper rails feed on benthic food webs, but are littoral feeders that usually do not eat *C. amurensis*, which is mostly subtidal. Figure 4 (submodel C) also shows potential food webs for Dungeness crab. Diet component data and kinetic loss rates are not documented for life stages of this crustacean, but isotopic data indicate that clams such as *C. amurensis* would be expected to be an important food for this species (Stewart and others 2004). Selenium concentration data, in turn, indicate that predators of this crab would be subjected to elevated dietary Se concentrations (submodel C, Figure 4).

Food webs illustrated for Delta inhabitants include aquatic insects to salmonids (submodel C, Figure 4). The diets of salmon and steelhead trout are dominated by species with TTFs lower than bivalves. These species thereby incur less dietary Se exposure than molluscivores. Field data for Se concentrations are limited to 1986 to 1987 for Chinook salmon (Saiki and others 1991) and absent for steelhead trout that inhabit the estuary and migration corridors. Although their exposures are not exceptionally high, these species may be vulnerable because of their toxicological sensitivity to Se (USFWS 2008a, 2008b; Janz 2012). Delta smelt are endemic to the estuary and are included here because population numbers for the Delta smelt are alarmingly low. Thus, the USFWS (2008a) concluded that this species is particularly vulnerable to any adverse effect. It should be noted, however, that the feeding habits of Delta smelt would not suggest high exposures compared to other species, and sensitivity or bioaccumulation data are not available.

Not all predators reside in the estuary throughout their lives. When a predator is present across flow seasons and during critical life stages may influence Se exposure and effects. Predator seasonal cycle diagrams are shown for migratory birds (scoter and scaup); breeding birds (California clapper rail, bald eagle); migrating/rearing juveniles (Chinook salmon, steelhead trout); and breeding fish (green sturgeon, white sturgeon, and Sacramento splittail) (submodel D, Figure 5). The North Bay is part of the migration corridor and feeding ground for anadromous fish such as white sturgeon, Chinook salmon, and striped bass. The estuary also serves seasonally as a nursery area for species that spawn either in freshwater (e.g., Sacramento splittail) or in the ocean (e.g., Dungeness crab). Migrating diving ducks on the Pacific flyway winter and feed in the estuary as they stage for breeding in the freshwater ecosystems of the boreal forests of Canada and Alaska (De La Cruz and others 2009). As migratory waterfowl move north to breed in the spring, there is the potential for depuration of Se (USFWS 2008a; Appendix A.2 and A.3).

Some of the highest *C. amurensis* Se concentrations of the annual cycle occur when overwintering scoter and scaup actively feed in Suisun Bay and San Pablo Bay during the fall and early winter, (Linville and others 2002; Kleckner and others 2010) (submodel D, Figure 5). Long-lived white sturgeon feed predominantly on *C. amurensis* and have a two-year internal egg maturation that makes them particularly vulnerable to loading of Se in eggs and reproductive effects (Linville 2006). As an indication of this potential, Linares and others (2004) found Se concentrations as high as 47 µg g^{-1} dw in immature gonads of 39 white sturgeon captured in the estuary. In earlier studies, Kroll and Doroshov (1991) reported that Se concentrations in developing ovaries

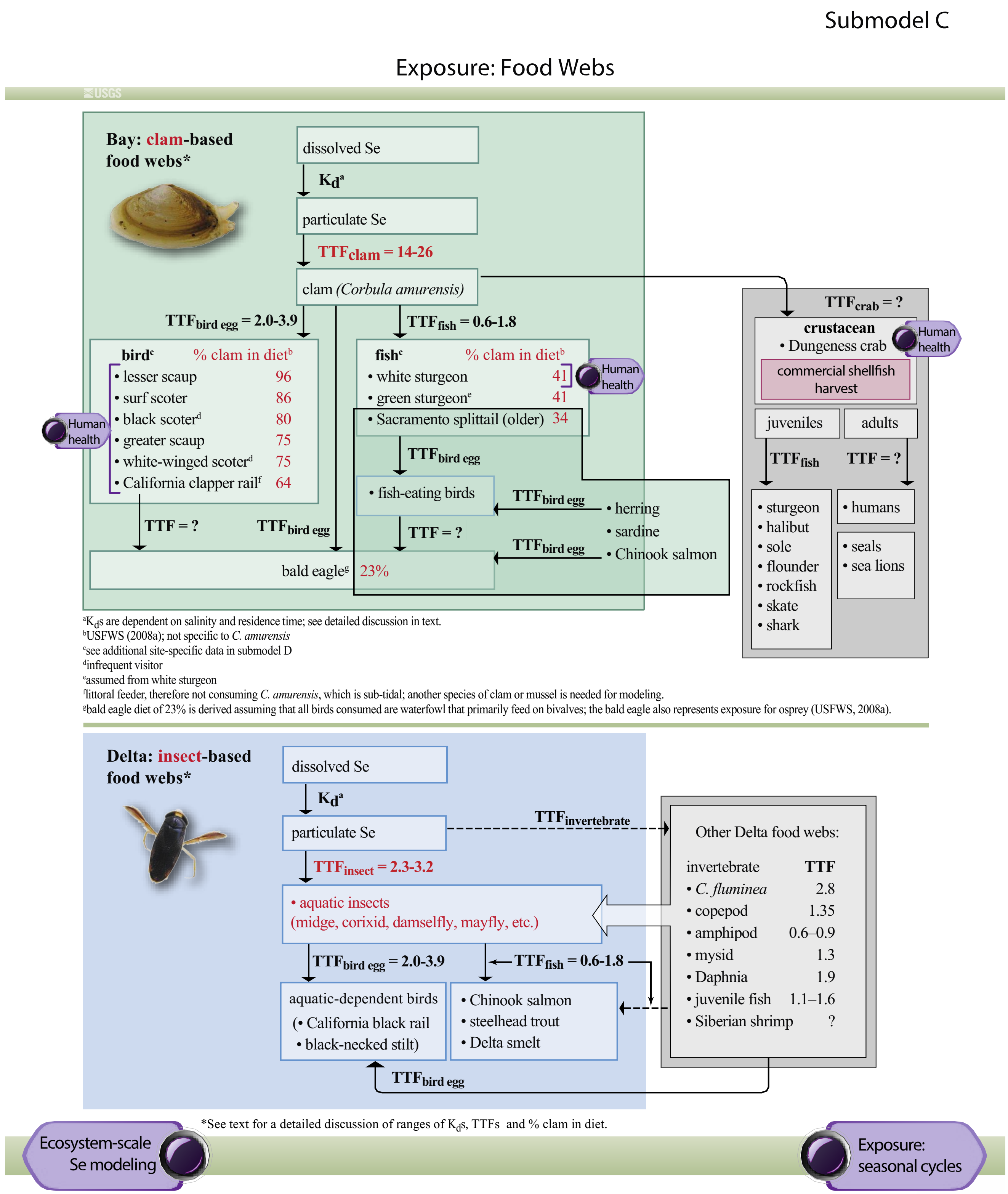

Figure 4 Submodel C. Exposure: Food Webs

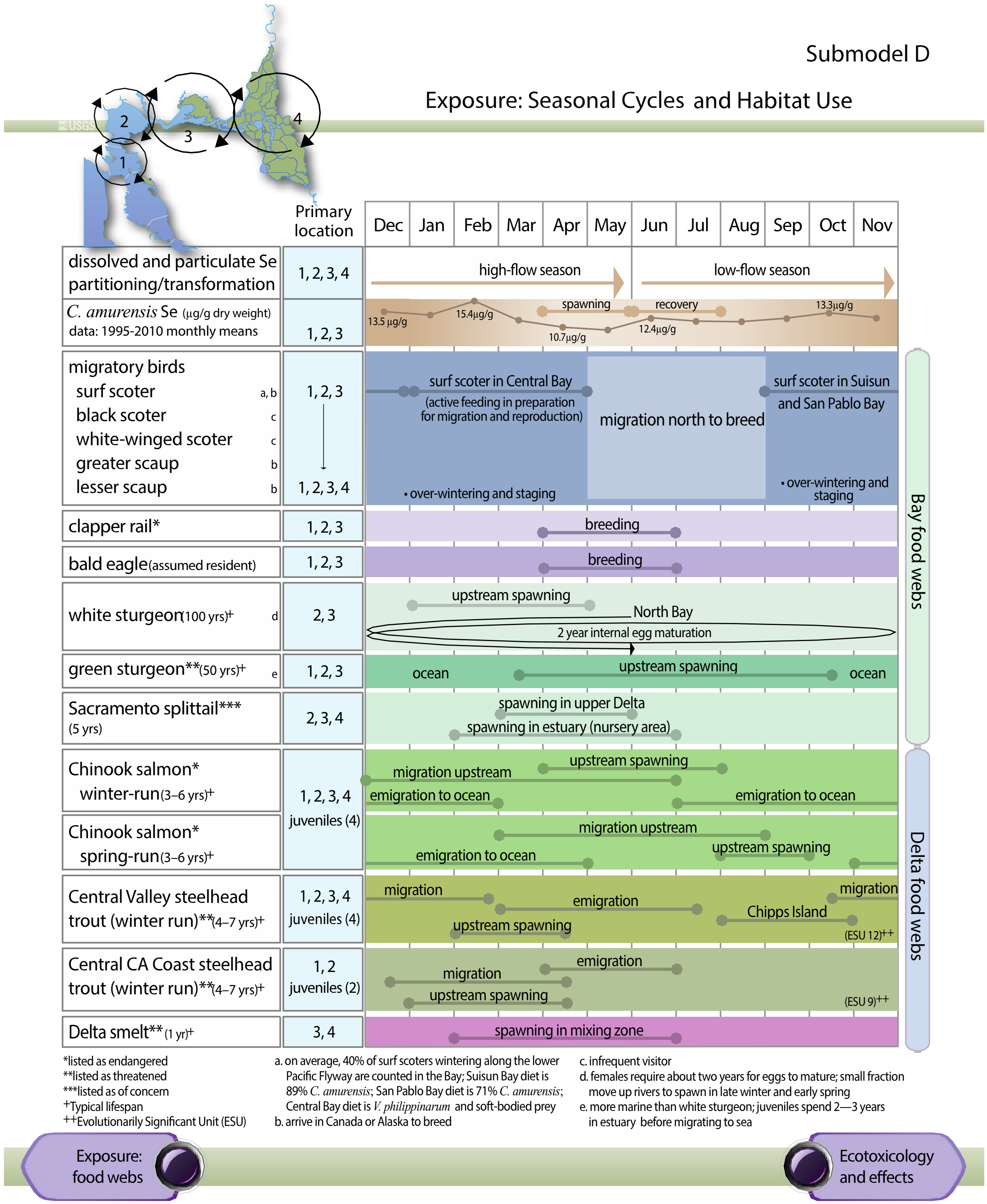

Figure 5 Submodel D. Exposure: Seasonal Cycles and Habitat Use

of white sturgeon from the Bay contained maxima of 72 µg $g^{-1}$and 29 µg g^{-1}. This range of wild white sturgeon reproductive tissue Se concentrations approach or exceed levels that cause severe deformities and mortalities in newly hatched larvae (Lemly 2002; Linville 2006). Larger, older Sacramento splittail also feed on *C. amurensis* and they are known to spawn both in the upper Delta and estuary (Stewart and others 2004). Modeling for species such as clapper rail would need specifics of diet composition (i.e., which species of clam, mussel, or crab is consumed), and whether prey species are efficient bioaccumulators of Se. Formalized, detailed knowledge such as this (submodel D, Figure 5), in turn, helps set choices in comparative modeling scenarios.

Fish and Wildlife Health: Ecotoxicology and Effects

Toxicity arises when dissolved Se is transformed to organic-Se by bacteria, algae, fungi, and plants (i.e., synthesis of Se-containing amino acids *de novo*) and then passed through food webs. It is generally thought that animals are unable to biochemically distinguish Se from sulfur, and therefore excess Se is substituted into proteins and alters their structure and function (Stadtman 1974). Other biochemical reactions also can determine and mediate toxicity (Chapman and others 2010). The effect of these reactions is recorded, most importantly in birds and fish, as failures in hatching or proper development (teratogenesis or larval deformities) (submodel E, Figure 6). Other toxicity endpoints include growth, winter survival, maintenance of body condition, reproductive fitness, and susceptibility to disease (submodel E, Figure 6; Appendix A.3). Specifically, Se can alter hepatic glutathione metabolism to cause oxidative stress (Hoffman and others 1998, 2002; Hoffman 2002) and diminished immune system function (Hoffman 2002).

Details of general ecotoxicological pathways of Se for fish and birds and effects of concern for Se are shown in submodel E (Figure 6). As represented here, birds and fish differ in how Se taken up from diet distributes among tissues (submodel E, Figure 6). Physiological pathways shown here for birds emphasize an exogenous dietary pathway and for fish an endogenous liver pathway. Species-specific Se effect models for the Bay-Delta are shown for breeding clapper rail; migratory scoter and scaup; white sturgeon; downstream-migrating juvenile salmonids; and upstream-migrating adult salmonids (submodel F, Figure 7). Details of Se-specific toxicological information for predator species considered here are compiled in Appendix A.3.

Such health effects are important to the overall ability of birds and fish to thrive and reproduce. But the consequences of Se transfer from the mother to her progeny via each reproductive stage are the most direct and sensitive predictors of the effects on birds and fish (Heinz 1996; Lemly 2002; Chapman and others 2010). Ultimately, it would be expected that effects on reproduction, especially in slowly reproducing, demographically vulnerable species (e.g., sturgeon), could lead to effects on populations and community changes.

To translate exposure into toxicity, effects levels are needed for predator species. Traditionally, guidelines relate Se concentrations in water to effects. But it is increasingly recognized that the concentrations of Se bioaccumulated in fish and bird tissues are more strongly related to signs of toxicity in nature, and would provide less ambiguous guidelines (Chapman and others 2010). The best correlations occur between Se in reproductive tissue and effects on reproductive processes. To assess implications of Se contamination in water from such relationships a bioaccumulation model is, then, necessary.

Experimental determination of tissue Se concentrations at which adverse effects occur is influenced by choice of endpoint, life-stage, dietary form, route of transfer, and choice of effect concentration. Another consideration in determining the guideline is the steepness of the Se dose-response curves and the choice of mathematical models to describe the curve (Skorupa 1998; Ohlendorf 2003; Lemly 2002; Environment Canada 2005; Beckon and others 2008; Chapman and others 2010). Effect guidelines that focus on a combination of the most sensitive assessment measures might include, for example, a selenomethionine diet, parental exposure, and embryonic or larval life-stage effect (Presser and Luoma 2006).

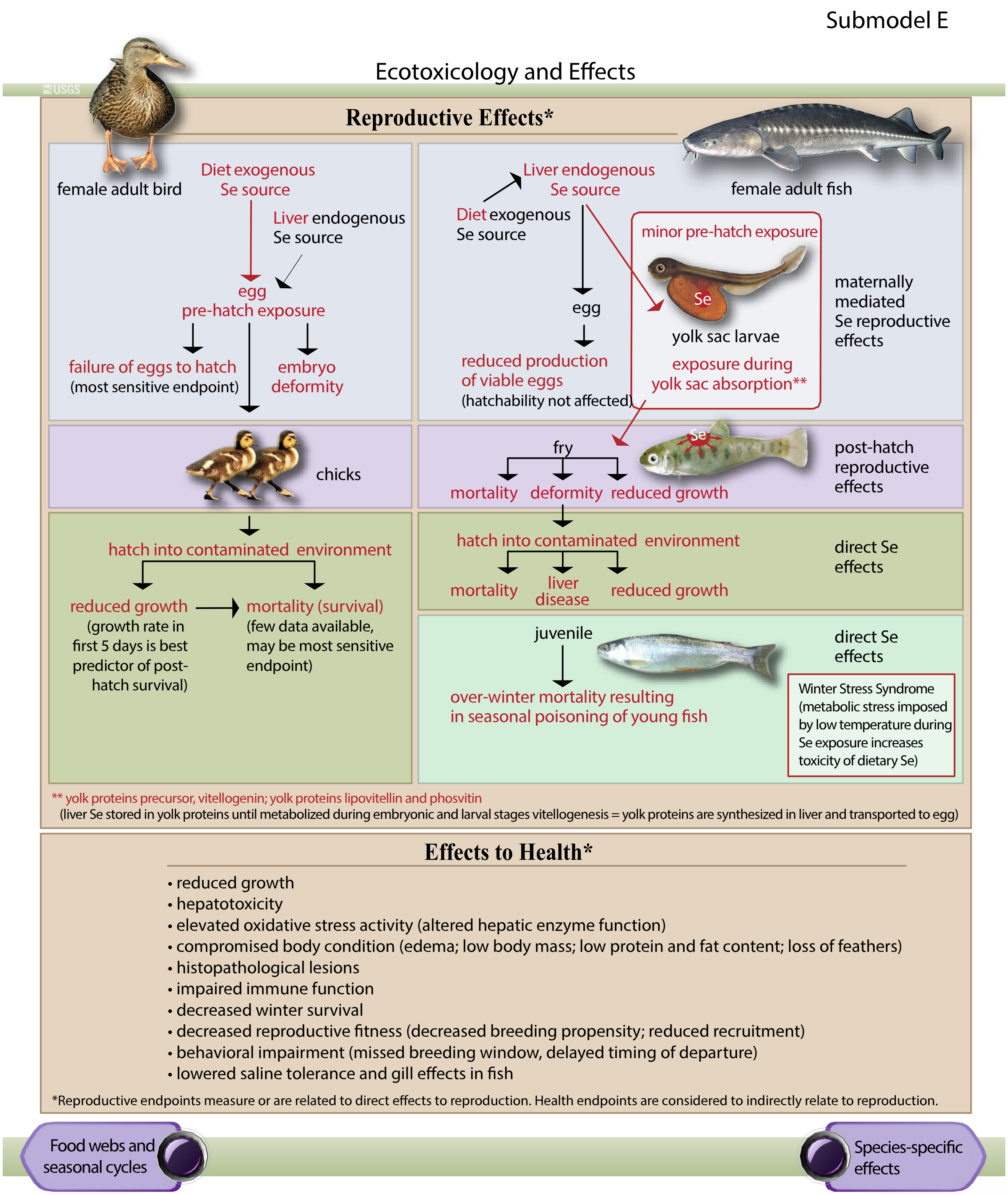

Figure 6 Submodel E. Ecotoxicology and Effects

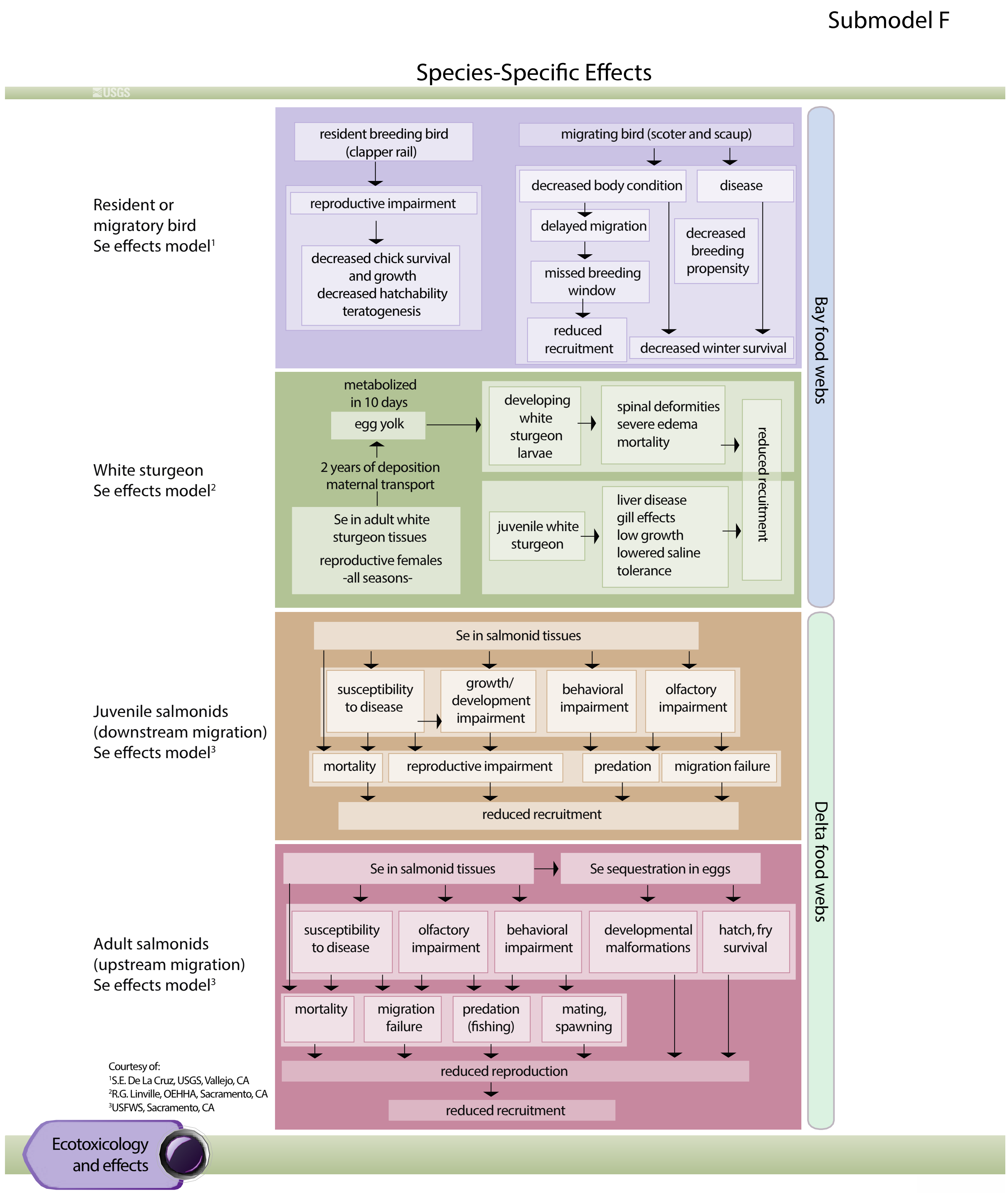

Figure 7 Submodel F. Species-Specific Effects

Even then the choice of statistical analysis and effect level can lead to disagreement about effect guidelines.

Human Health

A number of species from the Bay-Delta are consumed by humans (submodel G, Figure 8). Human health advisories against consumption of greater scaup, lesser scaup, and scoter because of elevated Se levels have been in effect since 1986 (Presser and Luoma 2006) for Suisun Bay, San Pablo Bay, Central Bay, and South Bay (CDFG 2012, 2013). The health warning states that no one should eat more than four ounces of scaup meat per week or more than four ounces of scoter meat in any two week period. Further, no one should eat the livers of ducks from these areas.

Fish consumption advisories, including for white sturgeon, exist for the Bay because of the effect of mercury and PCBs (OEHHA 2011, 2012). Pesticides, flame retardants, and Se also were tested, but a mean concentration calculated for each fish species collected from locations throughout the Bay-Delta over a range of years was found to be below that chemical's advisory tissue level (OEHHA 2011, 2012). Specifically for Se, concentrations in white sturgeon (n = 56 during 1997 to 2009, or 4.3 fish per year) were higher than other species of fish tested; and some Se concentrations for white sturgeon collected in North Bay locations (maximum 18.1 µg g^{-1} dw) exceeded Se advisory levels (e.g., 10.4 µg g^{-1} dw or 2.5 µg g^{-1} wet weight based on consumption of three 8-ounce meals per week (OEHHA 2011, 2012). Length restrictions (117 to 168 cm) and a bag limit of one fish per day are in effect for legal fishing of white sturgeon in the Bay, with a mean of 134 cm measured in fish collected for advisories.

A median per angler consumption rate of 16 g d^{-1} was determined specifically for Bay fish during 1998 and 1999 (SFEI 2000). This site-specific rate can be compared to a national recreational fisher consumption rate of 17.5 g d^{-1} and a national per capita rate of 7.5 g d^{-1} (USEPA 2000b).

Nutritional guidelines, toxicity symptoms, and national guidance concerning human health risk for consumption of fish are shown in submodel G (Figure 8). The details of how guidelines shown in Figure 8 were determined and how they might be linked to regulation of Se in wildlife and to fish health are presented in Appendix A.4.

QUANTITATIVE MODELING

This section presents an example of an application of the quantitative DRERIP Ecosystem-Scale Selenium Model. The questions addressed in this example are: What are the implications for ecosystem concentrations of Se if a fish tissue and/or wildlife Se guideline is implemented (a guideline based upon Se concentrations in a predator)? More specifically, what changes in dissolved or particulate Se concentration in the Bay-Delta would be necessary to achieve the selected tissue concentrations in predators? Agencies have traditionally regulated contaminants on the basis of dissolved concentrations, and managed inputs from different sources based upon their implications for dissolved concentrations (e.g., total mass daily loadings). This example shows a methodology that ties the new concept of tissue guidelines to the traditional concept of dissolved-concentration-based management. Inherent in every regulatory guideline are assumptions about the environment being regulated. The model allows an explicit evaluation of the implications of different assumptions.

The generalized equations for prediction of a dissolved Se concentration from a tissue Se concentration are given in submodel B (Figure 3). Table 1 gives the specific combinations of choices for food web, guideline, location, hydrologic condition, K_d, and TTFs used for the Bay-Delta application. In this example, several alternatives for a tissue guideline were chosen from among those that have been discussed in the regulatory context. Then, the invertebrate, particulate, and dissolved Se concentrations were calculated that would be expected if the tissue concentrations were in compliance with each choice of a guideline. Calculations also were conducted under different assumptions about K_d, food web, and TTFs. Finally, the calculated dissolved, particulate,

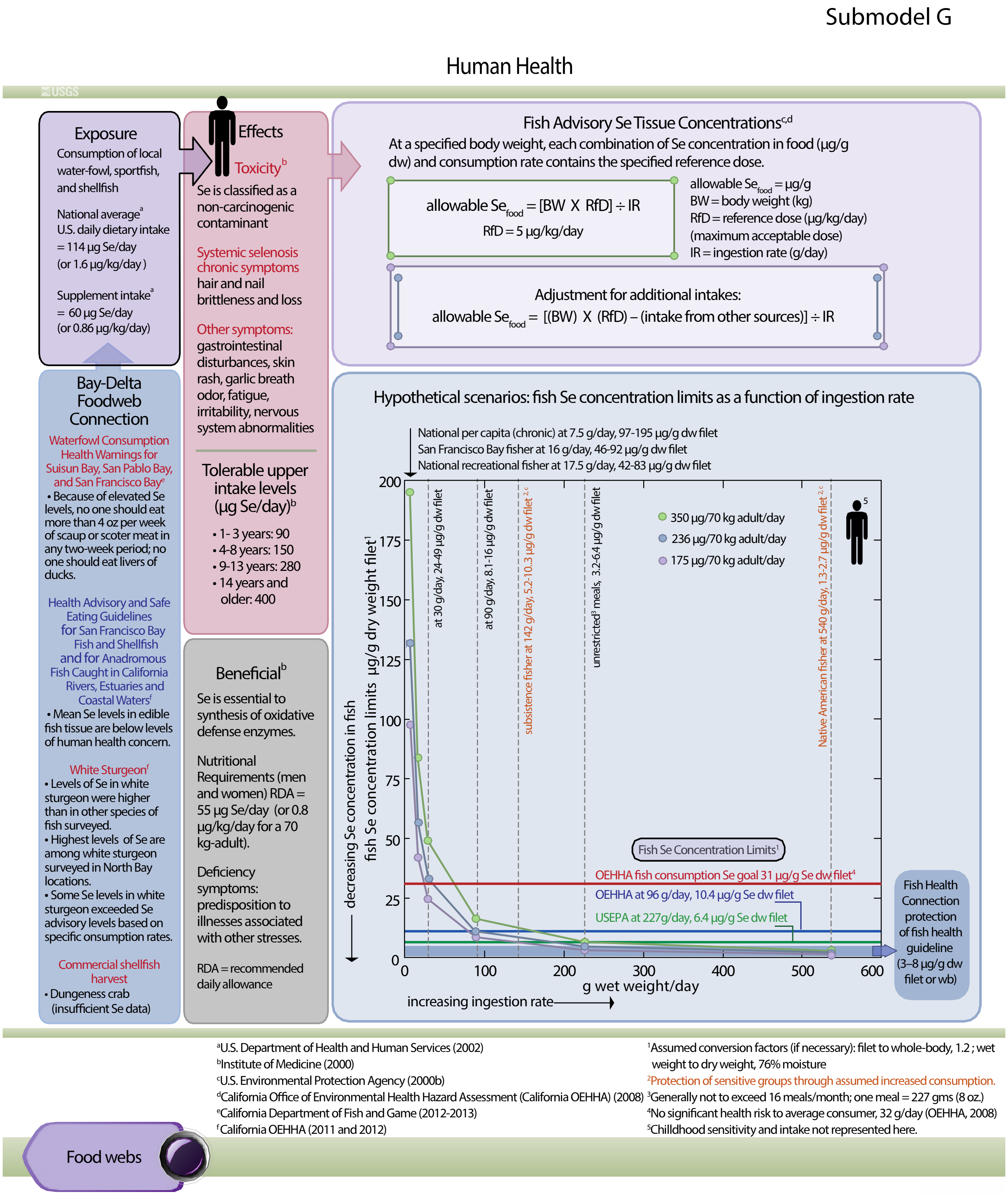

Figure 8 Submodel G. Human Health. See additional explanation in Appendix A.4.

Table 1 Locations, food webs, and model parameters for quantitative modeling examples

Location	Predator	Food web	Predator tissue target ($\mu g\ g^{-1}$ Se, dw)	$TTF_{predator}$	Prey	TTF_{prey}	Particulate phase as base of food web	K_d	Flow condition
San Francisco Bay (Carquinez Strait – Suisun Bay)	sturgeon	clam-based	5 or 8 whole-body	1.3	50% *C. amurensis* 50% [amphipods plus other crustaceans]	9.2	suspended particulate material	5,986	low flow (Nov 1999)
	sturgeon	clam-based	5 or 8 whole-body	1.3	50% *C. amurensis* 50% [amphipods plus other crustaceans]	9.2	suspended particulate material	3,317	average condition
	young striped bass	zooplankton-based	8 whole-body	1.1	zooplankton	2.4	suspended particulate material	3,317	average condition
	bird	clam-based	7.7, 12.5, or 16.5 egg	2	50% *C. amurensis* 50% [amphipods plus other crustaceans]	9.2	suspended particulate material	5,986	low flow (Nov 1999)
	bird	clam-based	7.7, 12.5, or 16.5 egg	2	50% *C. amurensis* 50% [amphipods plus other crustaceans]	9.2	suspended particulate material	3,317	average condition
Sacramento–San Joaquin Delta	fish	insect-based	5 or 8 whole-body	1.1	aquatic insects	2.8	suspended particulate material	3,680	average condition
	bird	insect-based	7.7, 12.5, or 16.5 egg	2	aquatic insects	2.8	suspended particulate material	3,680	average condition
San Joaquin River (main stem at Vernalis)	fish	insect-based	5 or 8 whole-body	1.1	aquatic insects	2.8	suspended particulate material	1,212	generalized (July 2000)

and invertebrate Se concentrations were compared with observations of those values from the Bay-Delta to assess how much existing conditions would be need to change to achieve compliance with the chosen guidelines (Table 2). Implicitly, comparisons of outcomes with data from nature tests how well model predictions match reality (Luoma and Rainbow 2005). Comparisons under different assumed conditions test the sensitivity of the model to changes within a few critical parameters.

The method, as indicated in the conceptual model (Figures 3 and 4, especially) includes the following steps: (1) selection of tissue guidelines to test; (2) selection of places and times of interest; (3) derivation of K_d using spatially and temporally matched dissolved and particulate Se concentrations constrained within the selected place and time; (4) selection of a food web of interest to each locality; (5) determination of species-specific TTFs for invertebrates and their specific predators that are relevant to the place and food web; (6) prediction of invertebrate, particulate and dissolved Se concentrations; (7) comparison of predicted values to field observations of Se concentrations in these media in the Bay-Delta; and (8) conclusions about implications for compliance.

Modeling Parameters and Variables

Guidelines

The effect guidelines chosen for evaluation were 5 and 8 $\mu g\ g^{-1}$ dw fish whole-body; as well as 7.7, 12.5, and 16.5 $\mu g\ g^{-1}$ dw for bird eggs (Presser and Luoma 2010b) (Table 1). The regulatory community is debating appropriate critical tissue values that relate bioaccumulated Se concentrations and toxicity in predators (see previous discussion). We are not

Table 2 Predicted dissolved and particulate Se concentrations and percent exceedances for example scenarios

Location	Flow condition and tissue guideline ($\mu g\ g^{-1}$ Se, dw fish whole-body or bird egg)	Predicted invertebrate concentration ($\mu g\ g^{-1}$ Se, dw)	Predicted particulate concentration ($\mu g\ g^{-1}$ Se, dw)	Percent particulate Se exceedance in ecosystem	Predicted dissolved concentration ($\mu g\ L^{-1}$ Se)	Percent dissolved Se exceedance in ecosystem
San Francisco Bay: Carquinez Strait – Suisun Bay						
Bay sturgeon	low flow – 5.0	3.8	0.42	59	0.070	100%
	average – 5.0	3.8	0.42	59	0.126	47%
	low flow – 8.0	6.2	0.67	27	0.112	66%
	average – 8.0	6.2	0.67	27	0.202	3%
Bay striped bass	average – 8.0	7.3	3.0	0	0.914	0%
Bay birds	low flow – 7.7	3.9	0.42	59	0.070	100%
	average – 7.7	3.9	0.42	59	0.126	47%
	low flow – 12.5	6.3	0.68	25	0.113	64%
	average – 12.5	6.3	0.68	25	0.205	2%
	low flow – 16.5	8.3	0.90	11	0.150	23%
	average – 16.5	8.3	0.90	11	0.270	1%
Sacramento–San Joaquin Delta						
Delta fish	average – 5.0	4.5	1.6	7	0.441	19%
	average – 8.0	7.3	2.6	3	0.706	10%
Delta birds	average – 7.7	3.9	1.4	16	0.374	19%
	average – 12.5	6.3	2.2	3	0.607	11%
	average – 16.5	8.3	2.9	3	0.801	6%
San Joaquin River (main stem at Vernalis)						
River fish	July 2000 – 5.0	4.5	1.6	No data	1.3	16%
	July 2000 – 8.0	7.3	2.6	No data	2.1	3%

suggesting these are the best choices for guidelines; but they are within the range of those that are being discussed. In particular, the fish whole-body target of 5 $\mu g\ g^{-1}$ and a bird egg target of 7.7 $\mu g\ g^{-1}$ have been derived to provide additional protection for endangered species (Skorupa and others 2004; Skorupa 2008). The illustrated scenarios also considered the differences in the changes required if a bird egg-based guideline were used instead of a whole-body fish-based guideline.

Place and Time

The modeling scenarios compared two locations: a brackish-water Bay environment and a tidal freshwater Delta environment. For the Bay, we constrained consideration to the geographic area of Carquinez Strait and Suisun Bay (Presser and Luoma 2010b) (Table 1). In terms of drivers, this location is affected by oil-refinery effluents that contain Se, and also could be influenced by inputs from the San Joaquin Valley. As noted previously, Se concentrations in at least some predators (sturgeon and diving ducks) at this location now exceed USFWS Se guidelines (Presser and Luoma 2010b). For the Delta, the area considered was from Stockton westward through the Delta, and was constrained to the freshwater environment. We also compared scenarios for average conditions across the year(s) in the Bay, to a specific example of conditions for one low flow season

(November 1999). An average condition for the Delta was modeled.

Partitioning and K_ds

The approach of Presser and Luoma (2006, 2010b) was used to select two K_ds for the scenarios from the Bay and one for the Delta (Table 1). The data for the Bay were narrowed to a Carquinez Strait–Suisun Bay location (Cutter and Cutter 2004; Doblin and others 2006; Presser and Luoma 2010b) to focus on the most contaminated area in the estuary, and to exclude the extreme K_ds at the ocean and freshwater interfaces. We selected the mean of co-collected dissolved and particulate Se concentrations from a transect for November 1999 (K_d = 5,986) to represent low flow conditions. Average conditions in the Bay across all seasons and several years were represented by the grand mean of all transects through the Carquinez Strait–Suisun Bay area during 1998-1999 (K_d =3,317) and the freshwater Delta during 2003-2004 (K_d = 3,680). For comparison, the Delta grand mean K_d for low flow transects was 2,613 and for high flow transects 5,283. As discussed earlier, the value that describes transformation, even when constrained, is the most variable of any of the model parameters. The uncertainty associated with the choice of this value could be avoided if environmental guideline were based upon empirically determined particulate Se, but cannot be avoided if it is necessary to relate tissue Se to dissolved Se.

Food Webs and TTFs

For the Bay, the food web used was for suspended particulate material to *C. amurensis* to clam-eating fish or aquatic-dependent clam-eating bird (submodel C, Figure 4 and Table 1). The diet for both predators was assumed to be 50% clam and 50% benthic crustaceans. The bivalve food web is the most efficient at accumulating Se in the system, in both the field and in the quantitative model; therefore, it is the most environmentally protective to use in evaluating a tissue guideline. Different assumptions, of course, could be used for the percentage of diet that is clam-based (e.g., 75% to 96% for scoter and scaup, submodel C, Figure 4). Data on variability of benthic assemblages with time, Bay location, and hydrologic condition also can be used to adjust dietary considerations (Peterson and Vayssieres 2010). If migrating scoter and scaup were modeled, a guideline based on body-condition endpoint, rather than a direct reproductive guideline, would be appropriate. To test the sensitivity of the choice of predator, one comparative simulation was calculated for a pelagic food web in the Bay: suspended material to zooplankton to young striped bass. The food web for the Delta was suspended particulate material to aquatic insects to juvenile salmon or steelhead trout.

Only a few recent data sets from the Bay-Delta are available that analyze Se concentrations across a reasonably complete food web (e.g., Stewart and others 2004). Some important food webs have not been assessed at all (e.g., aquatic insects and Chinook salmon or steelhead trout) (Presser and Luoma 2010b). However, studies of Se concentrations in enough individual predator and prey species are available to assess the predictions from the model and to derive, in a few instances, some critical trophic transfer relationships (e.g., Linville and others 2002; Stewart and others 2004; Schwarzbach and others 2006; Lucas and Stewart 2007; De La Cruz and others 2008; De La Cruz 2010). For the Bay, the dominant bivalve in the Carquinez Strait–Suisun Bay area is *C. amurensis*. This species strongly bioaccumulates Se (Linville and others 2002). A species-specific $TTF_{C.\ amurensis}$ of 17 (a range of 14 to 26 over different estuary conditions) was used here based on the field calibration that Presser and Luoma (2010b) describe. Benthic crustaceans, like amphipods and isopods, are much less efficient than clams in bioaccumulating Se; TTFs can range from 0.8 for amphipods to 2.0 for other crustaceans (Presser and Luoma 2010a). Under the assumption of a mixed diet of *C. amurensis* ($TTF_{C.\ amurensis}$ = 17) and benthic crustaceans ($TTF_{\text{benthic crustacean}}$ = 0.8 and 2.0), the combined diet TTF used here is 9.2.

An important benthic predator, white sturgeon, was chosen for the example, because the Se biomagnifier *C. amurensis* is an important food source for this species in the Bay. White sturgeon accumulate higher concentrations of Se than any other fish in the Bay (Stewart and others 2004; OEHHA 2011), making it the environmentally conservative choice for evaluating a guideline. From studies in the late 1980s, field TTFs derived specifically for white sturgeon from the Bay that used bivalves as prey, showed a range from 0.6 to 1.7, with a mean of 1.3 (Presser and Luoma 2006); similar to the value of 1.1, which is the mean among all fish species studied. Calculations from more recent data sets for *C. amurensis* at Carquinez Strait, and seaward white sturgeon, showed a somewhat lower TTF of 0.8 (Presser and Luoma 2010b).

For the Delta food web, Se TTFs for freshwater aquatic insects were selected from data from literature sources (submodel C, Figure 4). For example, Presser and Luoma (2010a) derived a mean Se TTF_{insect} of 2.8 (range 2.3 to 3.2) based on matched field data sets for particulate and insect Se concentrations in freshwater environments for several species of aquatic insect larvae including mayfly, caddisfly, dragonfly, midge, and waterboatman. These values generally compare well to laboratory-derived TTFs for aquatic insect larvae (Conley and others 2009). TTFs for other potential invertebrates in Delta food webs (range 0.6 to 2.8) also are shown in submodel C, Figure 4 (Presser and Luoma 2010a).

Much less data are available to evaluate bioaccumulation in avian food webs. Data from the study of toxicity in mallards (Heinz and others 1989, 1990) are the most comprehensive studies available to use for modeling dietary exposure. From these studies, the laboratory-derived $TTF_{bird\ egg}$ of 2.6 was assumed for transfer of Se from prey to bird eggs (which correlate best with toxicity). For the model, this choice of TTF for bird species was lowered to 2.0 to illustrate the possible effect of field variables on exposure factors that encompass habitat use and feeding behavior. A diet of 50% clams and 50% crustaceans was assumed for a clam-eating bird.

Implications of Model Choices and Estuary Conditions

Details of the calculations to evaluate implications of different guidelines, under different conditions, are summarized in Table 2. To compare the implications of these choices, we determined the percentage Se concentrations in dissolved and particulate form that exceeded the value predicted to be necessary to meet the tissue guideline. All published dissolved (n = 168) and particulate Se (n = 168) data from the Bay and from the Delta, collected after 1997, are employed in this estimate. Together, the scenarios depict a Bay for which there is ecological risk from Se contamination, but the degree of risk, judged by the degree of compliance with the guidelines, depends heavily upon assumptions about toxicity (the guideline), transformation, and choice of food web.

The occurrence of 8 µg g^{-1} dw Se in sturgeon muscle from the contaminated area of San Francisco Bay (Linares and others 2004) is one of several lines of evidence that ecological risks from Se are occurring in the Bay. When this concentration was used for a predator guideline (Table 2), the model predicted Se concentrations in invertebrates and suspended particulate material and a dissolved Se concentration that were within the range typical of the Bay-Delta (Table 2). Thus, the model results appear to successfully capture the links between Se concentrations in different ecosystem components of the Bay, in general [also see Presser and Luoma (2010b) for further validation details]. This also suggests that the use of calibrated mean K_ds to reduce uncertainties about transformation adequately captures and constrains the variability in these processes. The agreement between ecosystem observations and the predicted Se concentrations in invertebrates and predators similarly points to the validity of the TTFs.

The most remarkable conclusion from the calculations is that fish tissue Se concentrations typical of risks to reproductive toxicity (the selected guideline examples) occur in the Bay at dissolved Se concentrations more than ten times less than the traditional water quality regulatory guideline of 5 µg L^{-1} (Table 2). At least some food webs in the Bay and the Delta are particularly vulnerable to small changes in bioavailable Se concentrations. The very high K_ds consistently observed in both the Bay and the Delta, compared to many other ecosystems (Presser and Luoma 2010a), may be one reason for this sensitivity. Also influential is the strong ability of invertebrates such as *C. amurensis* to bioaccumulate Se when compared to other prey species. It appears that ecosystems wherein dissolved Se is efficiently transformed to particulate Se, and in which particulate Se is propagated up a food web to predators, will amplify relatively small changes in concentrations of dissolved Se concentrations to levels that could affect predators.

Under low flow conditions, 23 to 66% of dissolved Se determinations in the Bay exceeded the value predicted to be necessary to meet the higher sturgeon-based guideline or the higher bird-based guidelines (Table 2). Under guidelines chosen to protect endangered species, 100% exceedance occurs at low flow conditions. Clearly, low flow conditions, like those in November 1999, are the time of greatest ecosystem sensitivity to Se inputs (as suggested by Presser and Luoma 2006). It is notable that the example presented here does not represent the most extreme condition of a low flow season of a dry year or critically dry year.

If annual average conditions are assumed (the mean of spatially constrained K_ds), compliance is much more sensitive to the choice of guideline. Few if any exceedances (1 to 3%) are observed if the higher fish or bird egg guidelines are implemented under that assumption. For endangered species protection under an average condition, exceedance is approximately 47% for both the fish and bird guidelines. Of course, regulations based upon average conditions run the risk of under-protecting species sensitive to Se exposure during the protracted time in every year (especially drier years) when Se is most bioavailable.

Considering the choice of different guidelines, if a 5 µg g^{-1} guideline is implemented that uses sturgeon as the target organism, the entire Bay would be out of compliance. The model calculation suggests nearly all anthropogenic Se would have to be removed to drive sturgeon tissues to concentrations as low as 5 µg g^{-1}, especially during a low flow condition. The projected dissolved Se concentration necessary to reach that level in sturgeon tissue is approximately the value for the Sacramento River, and hence the pre-disturbance baseline condition for the Bay. The modeling results suggest that if it is assumed that 5 µg g^{-1} represents the toxicity threshold for sturgeon, and if it were applied using concentrations in sturgeon from the field, then there is no room for any deviation from concentrations in the Sacramento River without risk to the species. It is important to remember, however, that this toxicity guideline was derived for the most sensitive fish species. So, the use of the most sensitive surrogate in the toxicity guideline combined with field determinations from the fish with the greatest exposure results in an ultra-sensitive outcome.

These model results also illustrate how sensitive the implementation of a tissue guideline can be to the choice of predator. For example, many of the differences between sturgeon-based guidelines and bird egg-based guidelines are relatively small. Both appear to be sensitive indicators of ecological risks. However, the outcomes of guidance based upon striped bass, a water-column predator, are quite different from outcomes based upon bird eggs or sturgeon. The model showed that while aquatic birds and sturgeon are at risk under most assumptions, few or no exceedances of Se concentrations occur if the choice of regulatory indicator is based upon striped bass tissues. The differences are the result of the different invertebrate prey of the two species. Sturgeon eat a diet that includes strong Se bioaccumulator species (bivalves); striped bass eat from prey that live in the water-column and do not strongly bioaccumulate Se.

Selenium concentrations in the water column or particulate material of the Delta are higher and more variable than in the Bay. Average K_ds are similar between the Delta and the Bay. Nevertheless, few exceedances of dissolved and particulate Se concentrations (3% to 19%) are predicted in the Delta, even when the most sensitive fish guideline is used. This is consistent with the observation of low Se concentrations in the few fish that have been sampled from the Delta (e.g., Foe 2010). Use of the local food web is extremely influential in this outcome. Bioaccumulation of Se in the aquatic insect larvae (and other arthropods) that are the primary prey species of most Delta fish and birds is much lower than bioaccumulation by bivalves. As a result, it appears that the Delta food webs are easier to protect from adverse effects of Se than benthic food webs in the Bay, even if it is assumed that the most sensitive fish guideline applies. Nevertheless, the actual concentrations of dissolved Se predicted to be necessary to meet the tissue guidelines range from 0.37 to 0.80 μg L^{-1}, far below the Se concentrations typical of most existing dissolved guidelines for Se (Luoma and Presser 2009). This reflects the unusually high K_ds consistently observed in this freshwater environment.

Few determinations of Se concentrations in particulate material in the incoming rivers to the Bay are available outside the tidal range. Lucas and Stewart (2007) reported matched dissolved and particulate Se concentrations from which one K_d could be calculated (a value of 1,212) for the San Joaquin River during transect sampling in 2000. The example in Table 2 shows that if that were typical of the river, and the food web was mainly based upon arthropods, then compliance with a tissue guideline could occur at dissolved Se concentrations ten times higher than would be the case in the Bay. This river simulation is based on very limited data; it is given here for comparative purposes to show the sensitivity of the model to the choice of hydrologic setting. Comprehensive modeling of the San Joaquin River system would require data collection and analysis specific to the river's settings, predator species, food webs, and habitats. Percentage exceedance (Table 2) is based on weekly sampling of total Se for the river at Vernalis from water year 1995 through water year 2010 (SWRCB 2012)

CONCLUSIONS

The DRERIP Ecosystem-Scale Selenium Model outcomes for the Bay-Delta show critical choices for Se modeling, and derived risk scenarios that illustrate varying degrees of risk, depending on those choices (Figure 1; Tables 1 and 2). In general, the conceptual model for Se shows that the focus of concern for this contaminant is the top of the food web. Quantitative model calculations show that enough is known to adequately characterize the distribution of Se through the Bay-Delta ecosystem, although the available data from which to validate the outcomes is dated and does not include conditions within a low flow season of a dry year or critically dry year. Presser and Luoma (2010b) give additional specifics for updated data collection and model refinements.

Selenium concentrations in fish or bird tissues alone appear to be good indicators of ecological risks from Se. Key invertebrates (e.g., the bivalve *C. amurensis* in the Bay) may be a more pragmatic indictor for frequent monitoring. Given that (1) suspended particulate material Se concentrations are key to accurate prediction of prey and predator Se concentrations; and (2) dissolved Se concentrations are constrained to a narrow dynamic range within the estuary, a suspended particulate material Se concentration also may be a sensitive parameter on which to assess change. Dissolved Se concentrations appear to be the variable of choice for regulatory agencies, however, because of links to total maximum daily loads.

The ability to quantitatively characterize distributions among all these ecosystem components from field determination of only one component allows great flexibility in future monitoring whatever the choice of indicator. The detailed site-specific conceptual model, and the ability to quantitatively apply that model, also provide perspective on the processes that are most influential in determining Se contamination in the predators of this Se-sensitive environment (Figure 1).

The quantitative example (Tables 1 and 2) provides some lessons for implementing regulations to manage Se in this system. First, it is notable that extremely small changes in dissolved Se concentrations, in absolute terms, have strong implications for compliance with the tissue guidelines. A regulatory program that focuses on dissolved Se would require an extremely rich data set to reliably detect the differences between compliance and non-compliance, based upon the translation from tissue to dissolved Se. This is another reason why regulation of suspended particulate material Se concentration may be a more sensitive parameter on which to assess change.

Second, if compliance is determined from tissue concentrations in a predator, the choice of that predator is crucial. Predators of bivalves in benthic food webs are much more at risk than predators from pelagic food webs. The former should be the basis of tissue monitoring in the Bay.

Third, any decision as to whether reductions in ambient concentrations of Se would be required to comply with the tissue guidelines depends upon the choice of guideline and assumed environmental conditions. For example, the modeling suggests that a fish tissue guideline of 5 µg g^{-1} would ultimately require essentially all enriched Se inputs to the Bay to be eliminated if the guideline were applied using Se concentrations in sturgeon. According to the calculations, dissolved Se concentrations in the Bay would have to decline to nearly those in the Sacramento River to comply with such a guideline. If a guideline of 8 µg g^{-1} was used, the Bay would be near compliance under average conditions; but 66% out of compliance in a situation like November 1999 (i.e., low flow). Calculating in the opposite direction from a traditional dissolved Se concentration guideline, allowing dissolved concentrations of Se in the Bay to reach 5 µg L^{-1} (the current regulatory guideline) or even 2 µg L^{-1} would result in tissue concentrations (potentially greater than 100 µg g^{-1} in *C. amurensis*) that could threaten many of the predators in the Bay, if other conditions stay as they are.

Fourth, the current food webs in the Delta are less at risk from Se than the benthic food webs of the Bay, because of the differences in food webs. The differences between the Delta and the Bay are not the result of the freshwater versus brackish water nature of the systems of interest because, on average, transformation efficiencies are similar in the two. Where transformation processes are greatly different between two ecosystems, then a different outcome from implementing the same tissue guideline might be expected. The San Joaquin River example shows how a less efficient transformation of dissolved Se to particulate Se in the river can result in less sensitivity of the ecosystem to changes in Se concentrations.

Finally, the more specificity added to the model, the less uncertainty in predictions. If, for example, the geographic range is narrowed by using data only from Carquinez Strait–Suisun Bay, then freshwater and ocean interfaces are avoided. If the temporal range is narrowed to low flow seasons of dry years (i.e., high residence time or high exposure time), then focus can be on times when the transformative nature of the estuary is elevated. Juxtaposition of times when suspended particulate material or prey species achieve maximum Se concentrations with critical life stages of species at risk being present allows regulatory considerations to focus on times that govern Se's ecological effects (i.e., ecological bottlenecks) (Figure 1).

The greatest strength of the analytical and modeling processes is that it is an orderly, ecologically consistent approach for assessing different aspects of the fate and effects of Se. Assessments such as the examples shown here can represent a starting point for initiating management decisions. Application of the DRERIP Ecosystem-Scale Selenium Model shows that management of Se requires incorporation of the complexity of dietary exposures and the systematic consideration of critical aspects of hydrology, biogeochemistry, physiology, ecology, and ecotoxicology to define ecosystem protection. Although this is complex, scenarios can be developed from specific questions that arise in the planning and implementation of restoration actions for the Bay-Delta. Quantitative evaluation of those scenarios is feasible. However, the Se database and monitoring program need to be modernized (e.g., refocused and expanded). Specifically, monitoring should include (1) representation of conditions in dry and critically dry years; and (2) collection of spatially and temporally matched data sets across media (i.e., water, suspended particulate material, prey, and predator) to ensure that derived site-specific factors are current for the ecological and hydrological dynamics of the Bay-Delta. Only then will predictions from the model remain relevant and realistic to a constantly evolving estuary.

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