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MODELING SELENIUM BIOACCUMULATION THROUGH ARTHROPOD FOOD WEBS IN SAN FRANCISCO BAY, CALIFORNIA, USA

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Abstract—Trophic transfer is the main process by which upper trophic level wildlife are exposed to selenium. Transfers through lower levels of a predator's food web thus can be instrumental in determining the threat of selenium in an ecosystem. Little is known about Se transfer through pelagic, zooplankton-based food webs in San Francisco Bay ([SFB], CA, USA), which serve as an energy source for important predators such as striped bass. A dynamic multipathway bioaccumulation model was used to model Se transfer from phytoplankton to pelagic copepods to carnivorous mysids (*Neomysis mercedis*). Uptake rates of dissolved Se, depuration rates, and assimilation efficiencies (AE) for the model were determined for copepods and mysids in the laboratory. Small (73–250 μm) and large (250–500 μm) herbivorous zooplankton collected from SFB (*Oithona*/*Limnoithona* and *Acartia* sp.) assimilated Se with similar efficiencies (41–52%) from phytoplankton. Mysids assimilated 73% of Se from small herbivorous zooplankton; Se AE was significantly lower (61%) than larger herbivorous zooplankton. Selenium depuration rates were high for both zooplankton and mysids (12–25% d^{-1}), especially compared to bivalves (2–3% d^{-1}). The model predicted steady state Se concentrations in mysids similar to those observed in the field. The predicted concentration range (1.5–5.4 μg g^{-1}) was lower than concentrations of 4.5 to 24 μg g^{-1} observed in bivalves from the bay. Differences in efflux between mysids and bivalves were the best explanation for the differences in uptake. The results suggest that the risk of selenium toxicity to predators feeding on *N. mercedis* would be less than the risk to predators feeding on bivalves. Management of selenium contamination should include food webs analyses to focus on the most important exposure pathways identified for a given watershed.

Keywords—Selenium Trophic transfer Bioaccumulation Mysid Copepod

INTRODUCTION

A wide range of abiotic and biotic factors affect the exposure of organisms to selenium (Se). Selenium loading dictates the dissolved Se concentrations to which organisms are exposed. Processes involved in transforming dissolved Se to particulate Se play an important role in controlling Se exposure to consumer organisms because dietary uptake is the most important exposure route for the bioaccumulation of Se by lower trophic level aquatic animals [1–4]. For example, biogenic Se that results from assimilatory transformations (e.g., the uptake of dissolved selenite by phytoplankton) is more available to bivalves than is elemental Se that results from microbial dissimilatory reductive transformations [3]. The role of assimilatory processes in introducing Se into the base of pelagic food webs is less well known, however. In addition, the importance of biotic factors such as prey type in determining Se exposure to pelagic predators is poorly understood. In this paper we develop parameters for a dynamic bioaccumulation model and use the model to determine how geochemical (e.g., dissolved and particulate selenium concentrations) and biotic (e.g., feeding rate, diet composition) factors can affect trophic transfer and steady state selenium bioaccumulation in zooplankton and one of their predators in San Francisco Bay, the mysid *Neomysis mercedis*.

The uncertainty about trophic transfer of Se to pelagic predators is of importance from an environmental management perspective. Selenium can accumulate through trophic levels, a process that makes predators especially susceptible to Se toxicity [5,6]. Incidents of Se toxicity to upper-level wildlife (e.g., fish and wildfowl) are documented in freshwater systems (e.g., Kesterson Reservoir, CA, USA and Belews Lake, NC, USA) that have experienced increased Se concentrations due to anthropogenic activities. On the other hand, bioaccumulation data show that Se exposures can vary widely among predators in an ecosystem, suggesting all predators are not equally vulnerable to this element (e.g., [7]).

Understanding the processes determining Se bioaccumulation in prey can help identify predators that are at risk for Se toxicity. This is important in San Francisco Bay, where Se contamination of food webs occurs [7,8]. Stable isotope data have shown that at least two separate food chains occur in San Francisco Bay [9]. Diving ducks (e.g., surf scoter and greater scaup) and bottom-feeding fish (e.g., white sturgeon and starry flounder) exhibit stable isotope signatures indicative of diets that include the bivalve *Potamocorbula amurensis* [9]. Isotopic signatures of pelagic fish like striped bass, however, indicate that these top-predators largely feed on crustaceans, such as shrimp and mysids [9]. Selenium concentrations in white sturgeon are approximately twice those in striped bass [9]. Differences in prey concentrations could help explain these differences.

A well-established basis exists for why predators that ingest *P. amurensis* may be at risk for Se toxicity. This invasive bivalve is distributed widely and densely in San Francisco Bay, is preyed on extensively by some wildfowl and fish, and exhibits elevated Se concentrations in portions of this system. Selenium concentrations for *P. amurensis* collected in the Carquinez Straits can exceed 18 μg Se g^{-1} dry weight during some times of year (S.N. Luoma, unpublished data). When

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using dissolved and particulate Se concentrations measured from the Carquinez Straits, physiological-based bioaccumulation models predict tissue Se concentrations that range from 8 to 24 μg Se g^{-1} body weight [10]. Controlled experiments show that developmental toxicity occurs at relatively high frequency in wildfowl that consume diets containing ≥8 μg Se g^{-1} dry weight [6], and teratogenic effects can occur in fish at dietary concentrations >5 μg g^{-1} [7]. The agreement of independent measured and modeled Se concentrations for *P. amurensis* suggests that predators of this clam receive Se exposure that is sufficiently high to cause adverse developmental effects.

The potential for predators to experience Se toxicity in crustacean-based food webs is less clear, largely because few accurate measurements of tissue Se concentrations exist for crustaceans in San Francisco Bay. Copepods and mysids are important ecologically in estuaries like San Francisco Bay because they act as a trophic link between zooplankton and higher trophic levels [11,12] and they are preyed upon by important fish species (e.g., juvenile striped bass in San Francisco Bay). Purkerson et al. [13] measured Se concentrations within several operationally defined size classes of zooplankton in San Francisco Bay. Selenium concentrations in the largest size class (>2,000 μm), which included mysids, isopods, and shrimp, were low (<2 μg Se g^{-1} dry wt) in comparison with *P. amurensis* [13]. These results suggest that consumers of crustaceans should be less threatened by Se toxicity than consumers of bivalves. The mechanistic explanation for the different Se concentrations in crustaceans and bivalves, however, is unclear. The objective of the present paper was to develop a rate-based, physiological bioaccumulation model for planktonic crustaceans in San Francisco Bay so that the mechanisms of uptake can be compared to similar physiological data for bivalves. Bioaccumulation models also offer the opportunity to evaluate how abiotic (e.g., Se loads, water flow) and biotic (species composition and abundance of copepod prey) factors affect bioaccumulation and trophic transfer. Such factors can vary spatially and temporally on scales that are impractical to sample in biomonitoring programs.

MATERIALS AND METHODS

Overview of model

The dynamic multipathway bioaccumulation model [10,14–16] was used to determine steady state selenium concentrations in mysids. This model uses kinetics of uptake from dissolved and dietary pathways and the kinetics of physiological turnover (i.e., depuration) to predict steady state concentrations, and has been field-validated for bivalves [2,4] and copepods [17,18]. A two-step model was developed in the present study. The first step of the food web determined the trophic transfer of Se from phytoplankton to copepods; the second step, from copepods to predatory mysids. Within each step, the kinetics of selenium uptake from both dissolved and dietary pathways were determined, as were depuration kinetics. For the first step, dietary uptake was determined by measuring the efficiency with which two operationally defined copepod size classes (73–250 μm and 250–500 μm mesh) assimilated Se associated with planktonic diatoms. For the second step, the dietary pathway considered assimilation of Se by the mysid *N. mercedis* from the two copepod groups. All assimilation efficiencies were measured with radiolabeled ^{75}Se using modified pulse-chase methods. Dissolved uptake for both copepods and mysids were conducted using short (4 h) exposures to selenite ($^{75}SeO_3^{2-}$), which has been demonstrated to be the most bioavailable form of dissolved inorganic selenium [19].

Experimental animals

Copepods were collected in October 1999 and April 2000 from San Pablo Bay (CA, USA, a portion of northern San Francisco Bay) using a 73-μm mesh ring net. Copepods were separated into two operationally defined size classes, 73 to 250 μm and 250 to 500 μm. The composition of copepods within each size class varied depending on the time of sampling. In October 1999, the 73 to 250 μm size class was composed of adult *Oithona* and *Limnoithona*, whereas the 250- to 500-μm size class was composed of immature life stages of *Tortanus* sp. In April 2000, the 73- to 250-μm size class was composed of immature *Acartia* sp., whereas the 250- to 500-μm size class was composed of adult *Acartia* sp. Assimilation efficiency of Se from diatoms to copepods was measured for both size classes at both sampling periods. Additionally, copepods of both size classes from the April 2000 sampling period were used to measure the efficiency with which mysids assimilated Se from copepod prey.

Mysids (*N. mercedis*) were collected from nearshore sediments in Lake Merced (San Francisco, CA, USA) using a dipnet. *Neomysis mercedis* is described as a brackish-water species that inhabits coastal rivers and near-shore marine environments [12]. As Lake Merced is a freshwater system, animals were acclimated to the test salinity (12‰) by increasing salinity at a rate that did not exceed 5‰ d^{-1}. No mortality was observed during the acclimation period, and mysid feeding activity was not affected by the increase in salinity.

After acclimation, all animals were maintained in aerated 12‰ seawater (prepared by diluting fresh seawater [34‰] with Milli Q® water [Millipore, Billerica, MA, USA]) at 15°C. Each day, copepods received a suspension of diatoms (*Phaeodactylum tricornutum*), and mysids were fed cultured brine shrimp (*Artemia* sp.).

Assimilation efficiency measurements

Copepod assimilation efficiency measurements. Radiolabeled diatoms (*P. tricornutum*) were used as food in copepod assimilation efficiency experiments. Radiolabeling was accomplished by adding radiolabeled selenite ($^{75}SeO_3^{2-}$) to log-phase cultures of *P. tricornutum* f/2 media [20] at 12‰. Cultured algae were grown under 24-h light for 4 to 6 d, and were shaken 2 to 3 times/d. Then, cells were filtered over a 0.45-μm membrane filter, washed with 10 ml of 0.2-μm filtered seawater, and resuspended in 200 ml 0.2-μm filtered seawater. Subsamples (10 ml) were taken, filtered (0.45 μm), and rinsed with 0.2-μm filtered seawater to determine the partitioning of selenium between algal cells and the dissolved phase. Greater than 95% of the activity was associated with filters, indicating that the majority of the selenite had been assimilated by diatoms.

Feeding chambers (100-ml glass beakers) were prepared by adding 40 ml seawater (T = 15°C, S = 12‰). Aliquots of a suspension of copepods within each size class were then added to each chamber (four–six/treatment). Feeding was initiated by adding 50 ml of radioactive algae. Copepods were fed for 40 min, and feeding was terminated by pouring the contents of feeding chambers over a sieve (73 or 230 μm). Copepods were rinsed thoroughly with clean seawater and placed in scintillation vials. The activity of ^{75}Se ingested by copepods was measured for 2 min at 75 to 450 keV using a gamma counter.

This measurement represented the quantity of diatom-associated activity that was ingested by copepods. Copepods were then placed in beakers containing fresh seawater and a suspension of unlabeled *P. tricornutum*.

Copepods were gamma counted at either T = 4, 12, 24, and 72 h, (October 1999 experiment) or at T = 4, 24, and 48 h (April 2000 experiment). The time point when activity stabilized was designated final activity ($A_{t=F}$), which represented the quantity of selenium assimilated across the gut wall.

Mysid assimilation efficiency measurements. Copepods were radiolabeled by exposing them to unfiltered cultures of *P. tricornutum* that contained radiolabeled selenite ($^{75}SeO_3^{2-}$) for 3 to 4 d. Copepods were exposed to dietary and dissolved forms of selenium, as they would be in nature. On the day of the experiment, copepods were poured over sieves (either 73 or 230 μm), rinsed with clean seawater, and provided with unlabeled phytoplankton for 4 to 5 h before allowing mysids to feed. This ensured that activity associated with copepods truly was assimilated, rather than occurring as ingested algae within copepod digestive tracts.

Mysid feeding chambers consisted of 250-ml beakers that contained 175 ml of seawater (T = 15°C, S = 12‰). Six mysids, which were starved for 12 h prior to test initiation, were added to each beaker (6 beakers per copepod size class) via wide bore pipette. Feeding was initiated by adding an aliquot of radiolabeled copepods to each beaker. Mysids were allowed to feed for 1 h, after which time they were added to wide-mouth scintillation vials and gamma-counted as described previously. Mysids were then placed in beakers containing fresh seawater, and were provided with unlabeled *Artemia* nauplii. Mysids were gamma-counted at T = 4, 8, 12, 24, 48, 72, and 96 h. The time point when activity stabilized was designated final activity ($A_{t=F}$), which represented the quantity of selenium assimilated across the gut wall. Assimilation efficiency was calculated using the following formula:

$$AE = (A_{T=F}/A_{T=0}) \cdot 100 \quad (1)$$

where $A_{T=F}$ = final measured tissue activity and $A_{T=0}$ = initial tissue activity.

Dissolved uptake measurements

Influx rates (k_u) for copepods and mysids were measured by exposing animals to radiolabeled solutions of selenite at concentrations of 0.11, 0.25, 0.50, 1.00, and 5.00 μg Se L^{-1}. This concentration range covers the dissolved Se concentration in San Francisco Bay ([8], G.A. Cutter, Old Dominion University, Norfolk, VA, USA, unpublished data). Solutions were prepared by adding $^{75}SeO_3^{2-}$ to 0.2 μm of filtered seawater at a concentration of 0.11 μg Se L^{-1}. The lowest concentration received only radiolabeled selenite, and higher concentrations were achieved by adding appropriate quantities of nonlabeled Na_2SeO_3.

Both size classes of copepods from the April 2000 collection were exposed to $^{75}SeO_3^{2-}$ in 100-ml glass beakers. Approximately 60 to 80 copepods from each size class were added to each of three replicate beakers per concentration. After 4 h, the contents of each beaker were washed over a sieve, rinsed with clean seawater, placed in a scintillation vial, and gamma-counted for 2 min. Contents were then filtered onto preweighed glass fiber filters, dried at 70°C until dry (36–48 h), and measured for dry weight.

For *N. mercedis*, mysids were exposed to 150 ml of dissolved selenite in 250-ml beakers. Six mysids were added to each of three replicate beakers per concentration, and were exposed as described above for copepods.

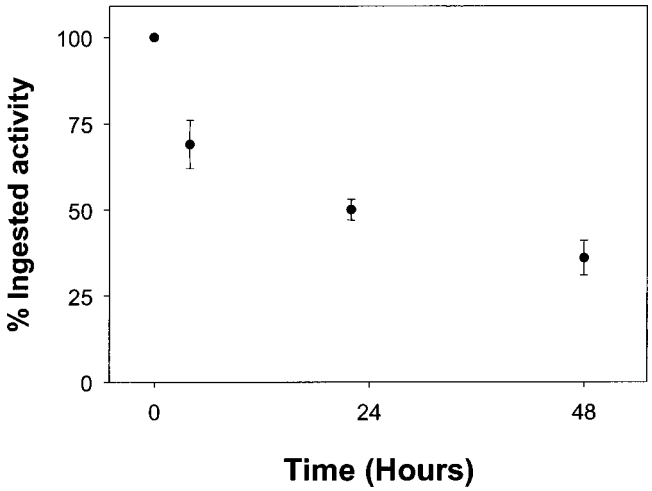

Fig. 1. Time course showing ^{75}Se activity in copepods after ingesting radiolabeled diatoms (*Phaeodactylum tricornutum*). Copepods were collected on a 73-μm screen after passing through a 250-μm mesh. Error bars represent one standard deviation from the mean.

Depuration rate measurements

Depuration rates were calculated for copepods and mysids using time course data from assimilation efficiency experiments. In addition, a separate experiment was conducted for mysids in which mysids were exposed to radiolabeled copepods and dissolved Se for 4 d. Depuration was initiated by sieving animals from their exposure chambers, dividing animals into three groups of five, and then monitoring activity in each group for up to 88 h.

RESULTS

Assimilation efficiency measurements

Copepods. Time course measurements showed that egestion by copepods was completed within 24 h. In the 73- to 250-μm size class that was sampled in October 1999, copepods appeared to have egested radiolabeled food by 12 h (Fig 1). However, as later experiments were not measured between 4 and 24 h, the 24-h time point was chosen as a consistent measure of final activity ($A_{t=F}$). Mean assimilation efficiencies from *P. tricornutum* were significantly different among the four groups of copepods tested ($F_{3,15} = 37.22$, $p < 0.001$). Specifically, copepods in the 250- to 500-μm range that were collected in October 1999 (immature *Tortanus* sp.) assimilated Se at a significantly lower efficiency (mean Se AE = 7.0 ± 2.9%) than the other three groups (Table 1). Mean Se assimilation efficiency among the three other groups ranged from 41.0 ± 13.5% for the *Oithona*/*Limnoithona* sp. assemblage to 52.3 ± 5.9% for the adult *Acartia* sp. assemblage (Table 1). *Tortanus* sp. are carnivorous copepods, whereas the remaining species (*Acartia*, *Oithona*, and *Limnoithona*) are herbivorous and omnivorous throughout their life cycles. The mean assimilation efficiency for herbivorous copepods taken as a group was 48.4 ± 8.7%. These values agree well with those of Wang and Fisher [18], who showed that the marine calanoid copepod *Temora longicornis* assimilated 59% of Se from the diatom *Skeletonema costatum*.

Mysids: Neomysis mercedis. Copepod assemblages used in the mysid assimilation efficiency experiments were composed

Table 1. Mean selenium assimilation efficiencies (AE) of copepods feeding on ^{75}Se-labeled diatoms (*Phaeodactylum tricornutum*). Copepods were collected in October 1999 and April 2000, and separated into operational-size classes, based on sieve mesh size, ranging from 73 to 250 μm and 250 to 500 μm. The species composition of copepods from each size class/collection date combination are reported

Copepod size class	Collection date	Species composition	AE (± standard deviation)
73–250 μm	October 1999	*Oithona*/*Limnoithona*	41.0 (13.5)
250–500 μm	October 1999	*Tortanus* sp.	7.9 (2.9)
73–250 μm	April 2000	Immature *Acartia* sp.	49.5 (4.2)
250–500 μm	April 2000	Adult *Acartia* sp.	52.3 (5.9)

of immature (73–250-μm size class) and adult (250–500-μm) forms of *Acartia* sp. Time course measurements of mysids showed that ^{75}Se activity stabilized after 8 h (all unassimilated ^{75}Se was egested; Fig. 2). Mysids that consumed copepods from the 73–250-μm assemblage assimilated ^{75}Se with significantly higher efficiency (mean Se AE = 73.4% ±3.4) than mysids that consumed copepods from the 250–500-μm assemblage (mean Se AE = 61.0% ± 2.3) ($t_{5,0.05}$ = 5.45, p = 0.001).

Dissolved uptake experiments

Determination of dissolved $^{75}SeO_3^{2-}$ by copepods was not possible because copepod dry weights were too small to be quantified.

Influx rate of selenite by *N. mercedis* was related linearly to dissolved Se concentrations that ranged from 0.1 to 1.0 μg L^{-1} (Fig. 3). The influx rate at 5.0 μg L^{-1} was lower than that at 1.0 μg L^{-1}. For the 0.1 to 1.0 μg L^{-1} concentration range, the relationship between dissolved concentration and influx rate was $k_u = 0.204(C_w)^{1.41}$ (r^2 = 0.978, p = 0.001), where C_w = the dissolved selenium concentration.

Efflux rate determinations

The efflux rate of assimilated ^{75}Se calculated for the 73- to 250-μm size class of copepods that was sampled in October 1999 was 0.30 d^{-1} (Fig. 1). This rate is within the range of selenium depuration rate constants observed by Wang and Fisher [18] for *T. longicornus* that fed on diatoms and natural seston (see Table 1 from Wang and Fisher [18]).

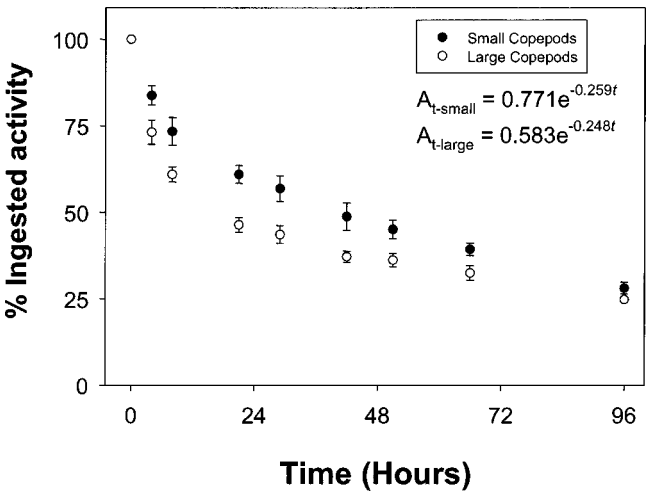

Fig. 2. Time course showing ^{75}Se activity in mysids (*Neomysis mercedis*) after ingesting radiolabeled copepods from two operationally defined size classes. Copepods that were collected on a 73-μm screen after passing through a 250-μm screen were defined as small, whereas those retained on a 250-μm screen after passing through a 500-μm mesh were defined as large. Error bars represent one standard deviation from the mean.

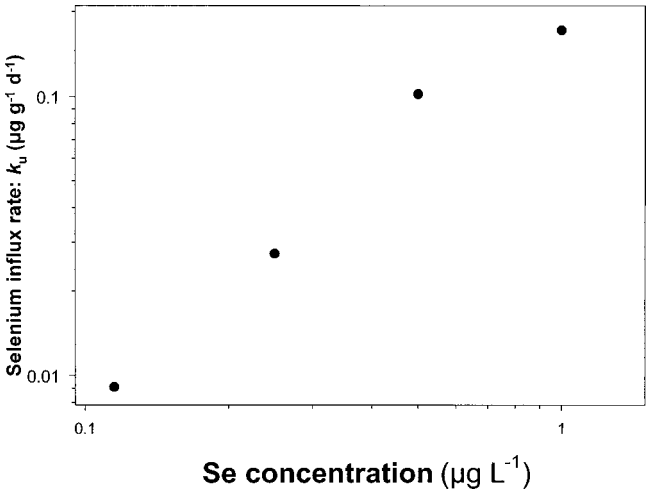

Fig. 3. Uptake rates (k_u) of dissolved Se(IV) by *Neomysis mercedis*.

The efflux rates of assimilated ^{75}Se calculated for mysids after feeding on the two size classes of radiolabeled copepods for 1 h were not significantly different (*t*-test on slopes: t_0 = 0.088, $p > 0.9$; Fig. 2). Taken together, k_e is shown to be 0.25 d^{-1}. Mysids that fed on radiolabeled copepods for 4 d exhibited a two-phase loss (Fig. 4). The rate of loss from the slow phase was 0.23 d^{-1} (Fig. 4). Thus, efflux rates of selenium from mysids do not appear to be related to duration of feeding.

Model determinations

Experimentally determined kinetics of selenium uptake and loss for copepods and mysids were incorporated into a bioenergetic-based model [10,14–16] to estimate steady state selenium concentrations for copepods and mysids under conditions present in San Francisco Bay. As shown in previous studies, steady state selenium concentrations (C_{ss}, μg g^{-1}) can be described by

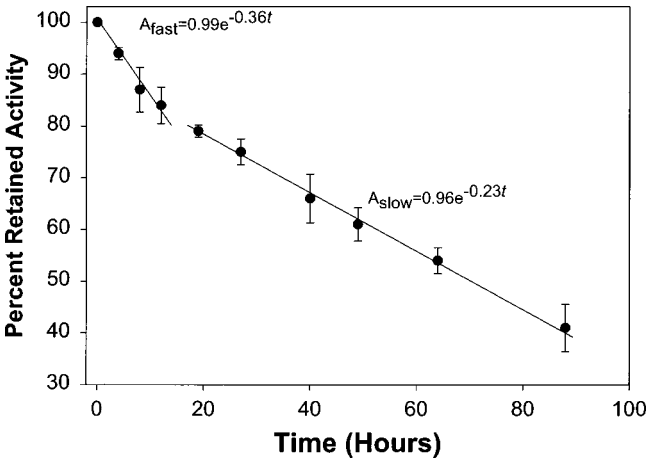

Fig. 4. Time course showing ^{75}Se depuration from *Neomysis mercedis* after mysids had fed on radiolabeled copepods for 4 h. Error bars represent one standard deviation from the mean.

Table 2. Parameters used in the dynamic multipathway bioaccumulation model for estimating steady state selenium tissue concentrations (μg g^{-1}) for *Neomysis mercedis*. IR = ingestion rate; AE = assimilation efficiencies

	Dissolved uptake		Dietary uptake				Efflux
Species	k_u (L g^{-1} d^{-1})	C_W (μg L^{-1})	Food type	C_{food} (μg g^{-1})	IR (g g^{-1} d^{-1})	AE	k_e (d^{-1})
Small copepods	0.024[a]	0.24[b]	Diatoms	1–3[b]	0.42[a]	0.50[c]	0.155[a]
Large copepods	0.024[a]	0.24[b]	Diatoms	1–3[b]	0.42[a]	0.52[c]	0.155[a]
Neomysis mercedis	0.027[c]	0.24[b]	Small copepods	Model dependent	0.45[d]	0.73[c]	0.25[c]
Neomysis mercedis	0.027[c]	0.24[b]	Large copepods	Model dependent	0.45[d]	0.61[c]	0.25[c]

[a] Wang and Fisher [18].
[b] G. Cutter (Old Dominion University, Norfolk, VA, USA, unpublished data).
[c] This study.
[d] Johnston and Lasenby [12].

$$C_{ss,w} = I_w/(k_{ew} + g) \quad (2)$$

$$C_{ss,f} = I_f/(k_{ef} + g) \quad (3)$$

$$C_{ss} = C_{ss,w} + C_{ss,f} \quad (4)$$

where $C_{ss,w}$ is the selenium concentration obtained from the dissolved phase (μg g^{-1}), $C_{ss,f}$ is the concentration obtained from food (μg g^{-1}), I_w is the influx rate from the dissolved phase (μg g^{-1} d^{-1}), I_f is the influx rate from food (μg g^{-1} d^{-1}), $k_{ew,f}$ are efflux rates following uptake from the dissolved and dietary pathways, respectively (d^{-1}), and g is the growth rate constant (d^{-1}). Both I_w and I_f are calculated as

$$I_w = k_u C_w \quad (5)$$

$$I_f = AE \cdot IR \cdot C_f \quad (6)$$

where k_u is the uptake rate constant from the dissolved phase (L g^{-1} d^{-1}), C_w is the dissolved concentration (μg L^{-1}), AE is assimilation efficiency from ingested food (%), IR is ingestion rate (mg dry wt g^{-1} d^{-1}), and C_f is selenium concentration in food (μg g^{-1}). In the present study, AE and k_e were determined for copepods, and AE, k_u, and k_e were determined for mysids. Mean values for these parameters appear in Table 2. The remaining parameters were obtained from the literature.

Kinetic parameters of Se uptake and loss by copepods that were not determined directly in this study were taken from Wang and Fisher [18]. For example, they determined that Se influx rates for *T. longicornus* followed the relationship $I_u = 0.024(C_w)^{0.850}$. These investigators also used an IR of 0.42 g g^{-1} d^{-1}. Finally, Wang and Fisher [18] used a depuration rate constant of 0.155 d^{-1}, that represented the slow loss phase of Se after copepods had fed for 2 d. At this rate of physiological loss, effects of growth rate constants become insignificant [17]. Ingestion rates for mysids were obtained from Johnston and Lasenby [12], who reported that *N. mercedis* ingested harpacticoid copepods at a rate of 0.45 g g^{-1} d^{-1}.

The model was used to estimate steady state Se concentrations in copepods and mysids using Se concentrations relevant for San Francisco Bay. We assumed that copepods ingested only phytoplankton, and that mysids ingested only herbivorous copepods. Therefore, assimilation efficiencies for predatory copepods (i.e., *Tortanus* sp.) were not used. For herbivorous copepods, dietary Se influx is dependent upon the Se concentration in phytoplankton. We defined the range of phytoplankton Se concentrations to be 1 to 3 μg g^{-1}, as this represents the observed particulate Se concentration range for San Francisco Bay (G. Cutter, personal communication). For mysids, dietary Se influx depends on copepod Se concentrations, as estimated by the model. We estimated effect of dissolved Se concentrations on steady state concentrations by using a range of dissolved Se concentrations of 0.024 to 0.24 μg L^{-1}, which represents the observed range for San Francisco Bay. We assumed that all dissolved Se was present as selenite (SeO_3^{2-}), as this species is the most bioavailable form of dissolved selenium [19].

Modeling results show that steady state Se concentrations for copepods and mysids responded to relevant particulate Se concentrations, but not to relevant dissolved Se concentrations. When particulate concentrations ranged from 1 to 3 μg Se g^{-1}, steady state Se concentrations increased approximately threefold for both copepods and mysids (Fig. 5A). Steady state concentrations in copepods and mysids remained unchanged when dissolved Se concentrations increased 10-fold, from 0.024 to 0.24 μg Se L^{-1} (Fig. 5B). To determine the relative importance of dietary and dissolved uptake routes, steady state Se concentrations were estimated for copepods and mysids using different combinations of dissolved and particulate concentrations. Within the range of dissolved (0.024–0.24 μg Se L^{-1}) and particulate (1–3 μg g^{-1}) Se concentrations measured for San Francisco Bay, dietary uptake routes accounted for >98% of the steady state concentrations for both copepods and mysids for all dissolved/particulate concentration combinations (Table 3). For example, dietary uptake accounted for >98% even under the combination of high dissolved concentration (0.24 μg Se L^{-1}) and low particulate concentration (1 μg Se g^{-1}) (Table 3).

To examine the consequences of worst-case conditions on the relative importance of dietary versus dissolved uptake routes, the model also was used to estimate steady state selenium concentrations in mysids using a dissolved Se concentration of 1.0 μg Se L^{-1}. At a $Se_{phytoplankton}$ concentration of 1 μg Se g^{-1}, mysid tissue concentrations were estimated to be 2.80 μg Se g^{-1}, with dietary uptake accounting for 70.9% of accumulated Se. Increasing $Se_{phytoplankton}$ to 3 μg g^{-1} resulted in mysid concentrations of 6.36 μg Se g^{-1}, and increased the dietary contribution to 87.2%. The contribution of dissolved Se at 1 μg Se L^{-1} was substantially higher than at concentrations relevant for San Francisco Bay (i.e., 0.024–0.24 μg Se L^{-1}), but dietary uptake was still the predominant pathway even under these worst-case conditions.

DISCUSSION

This paper reports a physiologically based selenium bioaccumulation model for the mysid *N. mercedis*. It is the first such model developed for predatory crustaceans, and it com-

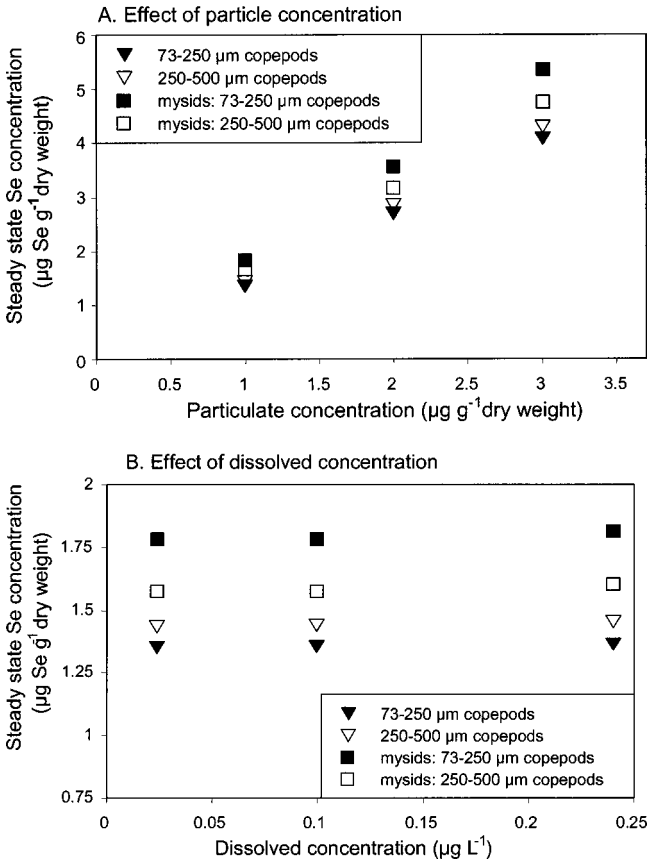

Fig. 5. Results of multipathway physiologically based selenium bioaccumulation model for copepods and mysids (*Neomysis mercedis*) showing the influence of (**A**) particulate (the diatom *Phaeodactylum tricornutum*) and (**B**) dissolved Se concentration on steady-state selenium concentration. It was assumed that copepods consumed only diatoms and that mysids consumed only copepods.

plements models that have been developed to predict metal and metalloid bioaccumulation by herbivorous bivalves [4] and copepods [18], deposit-feeding polychaetes [21], and larval fish [22,23]. The mysid bioaccumulation model showed that these predatory crustaceans bioaccumulate selenium almost exclusively through dietary uptake. Modeled steady state tissue concentrations were marginally lower than those of field-collected mysids, but the differences between model and the field data were not large enough to confound comparisons among species. Both the model and the field data show that selenium uptake by mysids was substantially lower than uptake by other San Francisco Bay invertebrates. The model's physiological components reveal that the rapid selenium depuration exhibited by *N. mercedis* is the main process that reduces bioaccumulation by mysids. Although mysids and bivalves both assimilate Se efficiently from their food, the bivalve *P. amurensis* exhibits almost a 10-fold slower selenium depuration rate than do mysids (S.N. Luoma, unpublished data), so the bivalves have much higher steady state concentrations of selenium. It follows that predators of the bivalves will be more threatened by selenium contamination than would predators of mysids.

This is the first report of the importance of dietary Se uptake for predatory crustaceans, but it is consistent with previous demonstrations of the importance of dietary uptake of Se for herbivorous copepods [24] and bivalves [2,4]. The importance of dietary Se uptake means that dissolved Se is not an accurate predictor of the dose for predatory wildlife. The fact that different food chains accumulate Se differently, for fundamental physiological reasons, further uncouples dissolved selenium from direct links to predator effects. The controversies over regulatory guidelines based upon dissolved selenium, therefore, are not surprising. Rather than using dissolved Se concentrations, evaluating effects of selenium contamination to a specific organism should be based on concentrations of selenium in the food of that organism. Both tissue and particulate selenium might offer some promise as a regulatory guideline, but knowledge of food webs and sensitivities of predators also will be important.

Bioaccumulation modeling can help identify factors that influence steady state trace element concentrations, but to be useful in environmental decision-making processes, the model projections need to be comparable to field measurements. Purkerson et al. [13] reported selenium concentrations of 3.5

Table 3. Proportions of selenium bioaccumulated through dietary pathways based on a physiologically based bioaccumulation model for a two-step food chain, from the diatom *Phaeodactylum tricornutum* to copepods and from copepods to the mysid *Neomysis mercedis.* Copepods were collected from San Francisco Bay (CA, USA) and represent those animals that were retained on a 73-µm sieve after passing through a 25-µm mesh. Dissolved and particulate Se concentrations represent the ranges measured in San Francisco Bay

Consumer/food	Se_{Phyto}[a] (µg g^{-1})	$Se_{dissolved}$ (µg L^{-1})	C_{SS} − diet (µg g^{-1})	C_{SS} − solution (µg g^{-1})	Contribution from diet (%)
Copepod/diatom[b]	1.0	0.024	1.35	<0.01	99.99
Copepod/diatom[b]	1.0	0.24	1.35	0.01	99.19
Copepod/diatom[b]	3.0	0.024	4.06	<0.01	100.00
Copepod/diatom[b]	3.0	0.24	4.06	0.01	99.73
Mysid/copepod[c]	1.0	0.024	1.78	<0.01	99.99
Mysid/copepod[c]	1.0	0.24	1.78	0.03	98.56
Mysid/copepod[c]	3.0	0.024	5.34	<0.01	100.00
Mysid/copepod[c]	3.0	0.24	5.34	0.49	99.51

[a] Se concentration in diet refers to the concentration in phytoplankton at the beginning of the food chain. For mysids, the influx rate from food was calculated using modeled copepod Se concentrations from the appropriate phytoplankton concentration.

[b] Copepods (*Acartia* sp.) from small size class (73–250 µm mesh) consuming the diatom *Phaeodactylum tricornutum* with an assimilation efficiency of 50%.

[c] Mysids (*Neomysis mercedis*) consuming copepods (*Acartia* sp.) from small size class (73–250 µm mesh) with an assimilation efficiency of 73%.

$\pm$ 0.9 $\mu g\ g^{-1}$ for zooplankton in the 73- to 250-μm size class, 3.1 $\pm$ 0.3 $\mu g\ g^{-1}$ for zooplankton in the 250- to 500-μm size class, and 1.4 $\pm$ 0.3 $\mu g\ g^{-1}$ for mysids that were collected in San Francisco Bay. Modeled concentrations for copepods ranged from 1.1 to 4.3 $\mu g\ g^{-1}$ (Fig. 5A), which is consistent with the field determinations of Purkerson et al. [13]. Model projections for mysid Se concentrations ranged from 1.5 to 5.4 $\mu g\ g^{-1}$ (Fig. 5A), depending on the initial particulate concentration. These concentrations generally are above the concentration range for field-collected mysids.

One possible explanation for why the concentrations in field-collected mysids were lower than model projections is that mysid diets are more complex in nature than the simple copepod diet used in the present study. *Neomysis mercedis* ingests copepods at night, and sediment and detrital particles during the day [12]. Selenium concentrations in San Francisco Bay sediments generally are $<1\ \mu g\ g^{-1}$ (G.A. Cutter, unpublished data). Also, particle feeding invertebrates generally assimilate sediment-associated selenium with lower efficiencies than biogenic selenium [2,3]. We used the following parameters to predict selenium concentrations for mysids that ingested both sediment and copepods in equal proportions: Copepod Se concentrations = 1.1 to 4.3 $\mu g\ g^{-1}$; sediment concentrations = 1 $\mu g\ g^{-1}$; and Se AE from sediment = 25%, a value consistent with other particle-ingesting invertebrates (C.E. Schlekat, unpublished data). Using these parameters, predicted steady state concentrations for mysids ranged from 1.0 to 2.4 $\mu g\ g^{-1}$, a range that is close to the concentrations reported by Purkerson et al. [13].

Selenium bioaccumulation models developed for the bivalve *P. amurensis* predict that it will reach higher selenium concentrations than will *N. mercedis*. For example, at a dissolved concentration of 0.24 $\mu g\ L^{-1}$ and a phytoplankton concentration of 3 $\mu g\ g^{-1}$, tissue Se concentrations are predicted to be 3.9 $\mu g\ g^{-1}$ for *N. mercedis* and 24.0 $\mu g\ g^{-1}$ for *P. amurensis*. Physiological parameters used in the bioaccumulation model might be useful to identify sources for these differences. Physiological parameters of selenium uptake were either higher for *N. mercedis* than the bivalve, or they were similar. For example, at a dissolved concentration of 0.24 μg Se L^{-1}, the influx rate (I_W, Eqn. 4) for *N. mercedis* is 6.5×10^{-3} μg Se $g^{-1}\ d^{-1}$ (this study), compared to 7.2×10^{-4} μg Se $g^{-1}\ d^{-1}$ for *P. amurensis* (S.N. Luoma, unpublished data). Both organisms assimilate Se from their food with high efficiency. *Potamocorbula amurensis* assimilated between 78 and 89% of Se associated with five phytoplankton species [25], compared with the Se AE of 61 to 73% for *N. mercedis* from copepods observed in this study. Mysid feeding rates (0.45 g $g^{-1}\ d^{-1}$) [11], however, are greater than those observed for *P. amurensis* (0.25 g $g^{-1}\ d^{-1}$, S.N. Luoma, unpublished data). Based on uptake kinetics alone, *N. mercedis* would be predicted to accumulate more selenium than *P. amurensis*. However, selenium depuration kinetics were nearly an order of magnitude higher for *N. mercedis* (0.23 d^{-1}, this study) than for *P. amurensis* (0.025 d^{-1}, S.N. Luoma, unpublished data). Thus, although *N. mercedis* was capable physiologically of accumulating selenium through dietary pathways as rapidly as *P. amurensis*, the rate of loss was so much greater that steady state concentrations remained below those of *P. amurensis*.

Lemly [6] reports that dietary Se concentrations greater than 3 $\mu g\ g^{-1}$ are considered to be in excess of nutritional requirements. Excess selenium can be deposited by parental fish into developing eggs, and when selenium concentrations in eggs are greater than 10 $\mu g\ g^{-1}$, the prevalence of teratogenic deformities increases rapidly. The dietary selenium concentration necessary to exceed this threshold concentration ranges from 5 to 20 $\mu g\ g^{-1}$. Effects of teratogenic deformities can affect feeding and escape behaviors and can lessen population fitness. Results of the present study suggest that in San Francisco Bay predators of mysids are at lower risk for Se toxicity than predators of *P. amurensis*. Selenium concentrations in different fish species support this notion. Liver and muscle tissue concentrations in striped bass collected in San Francisco Bay in fall 1999 consistently were lower than those of white sturgeon [9]. Stable isotopic signatures of striped bass and sturgeon were consistent with diets of pelagic crustaceans (including mysids) and benthic bivalves (including *P. amurensis*), respectively [9]. Monitoring and water management practices might best be designed to focus on food webs most likely to be affected by contaminants like Se. In San Francisco Bay, and perhaps in estuaries in general, the bivalve-based food webs would be a better focus for Se than would zooplankton-based food webs.

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