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Critical Review

Biokinetic Food Chain Modeling of Waterborne Selenium Pulses into Aquatic Food Chains: Implications for Water Quality Criteria

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ABSTRACT

We evaluated the use of biokinetic models to predict selenium (Se) bioaccumulation into model food chains after short-term pulses of selenate or selenite into water. Both periphyton- and phytoplankton-based food chains were modeled, with Se trophically transferred to invertebrates and then to fish. Whole-body fish Se concentrations were predicted based on 1) the background waterborne Se concentration, 2) the magnitude of the Se pulse, and 3) the duration of the Se pulse. The models were used to evaluate whether the US Environmental Protection Agency's (USEPA's) existing acute Se criteria and their recently proposed intermittent Se criteria would be protective of a whole-body fish Se tissue-based criterion of 8.1 $\mu g\,g^{-1}$ dry wt. Based on a background waterborne Se concentration of 1 $\mu g\,L^{-1}$ and pulse durations of 1 d and 4 d, the Se pulse concentrations predicted to result in a whole-body fish Se concentration of 8.1 $\mu g\,g^{-1}$ dry wt in the most conservative model food chains were 144 and 35 $\mu g\,L^{-1}$, respectively, for selenate and 57 and 16 $\mu g\,L^{-1}$, respectively, for selenite. These concentrations fall within the range of various acute Se criteria recommended by the USEPA based on direct waterborne toxicity, suggesting that these criteria may not always be protective against bioaccumulation-based toxicity that could occur after short-term pulses. Regarding the USEPA's draft intermittent Se criteria, the biokinetic modeling indicates that they may be overly protective for selenate pulses but potentially underprotective for selenite pulses. Predictions of whole-body fish Se concentrations were highly dependent on whether the food chain was periphyton- or phytoplankton-based, because the latter had much greater Se uptake rate constants. Overall, biokinetic modeling provides an approach for developing acute Se criteria that are protective against bioaccumulation-based toxicity after trophic transfer, and it is also a useful tool for evaluating averaging periods for chronic Se criteria. *Integr Environ Assess Manag* 2016;12:230–246. © 2015 SETAC

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INTRODUCTION

Selenium (Se) is a naturally occurring, essential element that bioaccumulates in aquatic systems. Bioavailable forms of Se include selenate (SeO_4^{2-}), selenite, (SeO_3^{2-}), and organic Se compounds (e.g., seleno-L-methionine) (Lemly and Smith 1987; Maher et al. 2010). Selenate is the predominant form of Se mobilized into aquatic systems from the weathering or oxidation of seleniferous substrates, which can be facilitated by anthropogenic activities such as mining and agriculture, and selenite may enter aquatic systems from sources such as oil refinery effluents and fly ash disposal from coal-fired power plants (Maher et al. 2010; Young et al. 2010). Once selenate enters an aquatic system, it may be bioconcentrated by organisms at the base of the food chain, such as microbes, algae, and macrophytes, or reduced to selenite, which may then be bioconcentrated. The proportion of selenate reduced to selenite depends on site-specific conditions, such as the redox conditions of the water body. In general, well-oxygenated flowing streams (lotic waters) tend to be dominated by selenate, and lentic waters such as ponds and lakes tend to be dominated by selenite and also can have high proportions of organic Se (Ponton and Hare 2013). Once bioconcentrated into the base of the food chain, the inorganic Se species may be further reduced to organic Se compounds that are then efficiently transferred through the food chain. Diet is the predominant Se exposure pathway for consumer organisms. At sufficiently high diet-borne Se concentrations, oviparous organisms such as fish and birds can be particularly sensitive, with Se being maternally transferred to the eggs. Toxic effects can include mortality, deformities, and edema in larval fish and reduced hatchability and deformities in bird embryos (Janz et al. 2010).

Because Se speciation and trophic transfer potential is highly site-specific due to factors such as pH, redox, and biological productivity (Lemly and Smith 1987; Brix et al. 2005; Presser and Luoma 2010), a wide range of waterborne Se concentrations are seen that could ultimately result in adverse effects to fish and birds via dietary Se exposure. Accordingly, the applicability of ambient water quality criteria for Se based on waterborne concentrations is highly uncertain across sites, and regulatory fish tissue–based Se

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criteria have been recommended (Payne 2013; USEPA 2004, 2014). Because Se toxicity is primarily manifested via long-term exposures to food chain Se concentrations, most criteria and guidelines have focused on chronic exposures. However, acute exposures also can be environmentally important, such as those resulting from Se pulses into receiving waters during storm events or spring freshets. An important question, therefore, is whether acute waterborne Se criteria can be developed that would be protective against dietborne Se toxicity that could potentially result from Se pulses.

In its most recent draft ambient water quality criteria for Se, the USEPA proposed chronic water-based Se criteria of 4.8 and 1.3 μg/L for lotic and lentic waters, respectively, expressed as 30-d average concentrations. The USEPA did not recommend an acute criterion based on short-term waterborne Se toxicity, but rather a criterion equation for intermittent exposures was recommended (USEPA 2014). The draft intermittent-exposure criterion is solved for mathematically by determining what Se pulse concentration is allowable, for a given pulse duration and background waterborne Se concentration, such that the 30-d average waterborne concentration does not exceed 4.8 μg/L (lotic) or 1.3 μg/L (lentic). Thus, the USEPA's (2014) draft intermittent-exposure Se criterion equation is not based on short-term waterborne toxicity or whether a short-term Se pulse of a given magnitude and duration may result in exceedance of a chronic fish tissue–based toxicity threshold.

One approach for addressing whether existing acute waterborne Se criteria or the draft intermittent-exposure criterion equation are appropriately protective is biokinetic modeling. Biokinetic models can be used to estimate chemical concentrations in organisms as a function of the chemical concentration in the water and diet to which the organism is exposed, while also accounting for the time-course (i.e., uptake and elimination) of the chemical exposure (Reinfelder et al. 1998; Wang 2002; Luoma and Rainbow 2005). Brix and DeForest (2008) previously developed a biokinetic food chain model consisting of periphyton, mayflies, and minnows to evaluate the concentrations and durations of Se pulses that would be required to potentially achieve whole-body fish Se concentrations of interest (e.g., a tissue-based criterion). Inputs to the model were the background waterborne Se concentration, the waterborne pulse Se concentration, and the duration of the pulse. The overall objective of the current evaluation was to assess whether such biokinetic food chain Se models could inform whether acute or intermittent-exposure Se criteria are likely to be protective against bioaccumulation-based Se toxicity in fish.

This evaluation is specific to exposure scenarios in which surface water is the primary point of Se entry into the base of the food chain. Sediment- or detritus-based food chains were not evaluated because of the more complex biogeochemical cycling of Se at the sediment–water interface, particularly in lentic waters with long residence times. In general, we assumed that a periphyton-based food chain will generally be more applicable to lotic (flowing) waters, although not necessarily all lotic sites, and a periphyton-based food chain could be applicable to certain lentic sites as well. We also assumed that a phytoplankton-based food chain will generally be more applicable to lentic (standing) waters, although, again, not necessarily all lentic sites and a phytoplankton-based food chain could be applicable to certain lotic sites.

METHODS

Existing model

Brix and DeForest (2008) developed a standard biokinetic Se model to predict Se bioaccumulation and trophic transfer along a 3-step food chain consisting of periphyton, mayflies, and minnows. The model was parameterized with data from Riedel and Cole (1999), which was later finalized as Riedel and Cole (2001), and Bertram and Brooks (1986). The model inputs were 1) a baseline waterborne Se concentration, 2) the concentration of an Se pulse, and 3) the duration of the Se pulse.

Baseline (steady-state) tissue Se concentrations in periphyton were calculated using Equation 1 and Se concentrations in mayflies and minnows, from both waterborne and dietborne Se exposures, using Equation 2:

$$C_{Se,\,producer} = \frac{k_{u,\,water} \times C_{Se,\,water}}{k_e + g} \quad (1)$$

$$C_{Se,\,consumer} = \frac{\left(k_{u,\,water} \times C_{Se,\,water}\right) + \left(AE + IR \times C_{Se,\,diet}\right)}{k_e + g} \quad (2)$$

Tissue Se concentrations during and after the waterborne Se pulses were then calculated for periphyton using Equation 3 and for mayflies and minnows using Equation 4:

$$C_{Se,\,producer} = \frac{k_{u,\,water} \times C_{Se,\,water}}{k_e + g} \times \left(1 - e^{-(k_e+g)\times t}\right) + C_{Se,\,tissue} \times e^{-(k_e+g)\times t} \quad (3)$$

$$C_{Se,\,consumer} = \frac{\left(k_{u,\,water} \times C_{Se,\,water}\right) + \left(AE \times IR \times C_{Se,\,diet}\right)}{k_e + g} \times \left(1 - e^{-(k_e+g)\times t}\right) + C_{Se,\,tissue} \times e^{-(k_e+g)\times t} \quad (4)$$

Where: $k_{u,water}$ = uptake rate constant from water ($L^{-1}\ g^{-1}\ h^{-1}$); IR = ingestion rate (h^{-1}); AE = assimilation efficiency (fraction); k_e = elimination rate constant (h^{-1}); g = growth rate constant (h^{-1}); t = time (h); and C = concentration (mg kg^{-1} dry wt). The model parameters originally used in Brix and DeForest (2008) are included in Table 1.

Updates to existing model

The potential to develop model food chains in addition to that described in Brix and DeForest (2008) was evaluated based on a review of the scientific literature. Potentially relevant studies were identified in which biokinetic Se parameters (Equations 1–4) were measured in model organisms. Although the focus of this evaluation was food chains in freshwater systems, biokinetic Se data for saltwater organisms were also compiled and compared with biokinetic data for freshwater organisms. If Se uptake and elimination rates in saltwater fish overlapped with rates measured in freshwater fish, for example, the saltwater data were deemed appropriate for incorporation into model food chains to more fully encompass the range of Se biokinetics in freshwater food chains.

Table 1. Waterborne Se biokinetic parameters used in the current analysis

Se Form	Species	Habitat type	$k_{u,water}$ (L g^{-1} h^{-1})	$k_{e,water}$ (h^{-1})	g (h^{-1})	$k_e + g$ (h^{-1})	Steady-state EF (L kg^{-1} dw)[1]	Data source
Primary Producers								
Selenate	Periphyton	FW	0.0045	0.0033	0.004	0.0073	616	Riedel and Cole 2001
	Periphyton	FW	0.0028	–	–	0.0081	346	Conley et al. 2013
	Algae (*C. reinhardtii*)	FW	0.17[a]	–	–	0.42	405	Besser et al. 1993
Selenite	Periphyton	FW	0.0112	0.0028	0.004	0.0068	1647	Riedel and Cole 2001
	Periphyton	FW	0.015	–	–	0.0041	3659	Conley et al. 2013
	Algae (*C. reinhardtii*)	FW	0.24[a]	–	–	0.26	923	Besser et al. 1993
Invertebrates								
Selenate	Mayfly (*C. triangulifer*)	FW	0.0006	0.015	0.0075	0.023	–	Riedel and Cole 2001
	Cladoceran (*D. magna*)	FW	0.021[b]	–	–	0.10	–	Besser et al. 1993
Selenite	Mayfly (*C. triangulifer*)	FW	0.0008	0.019	0.0075	0.027	–	Riedel and Cole 2001
	Cladoceran (*D. magna*)	FW	0.14[b]	–	–	0.28	–	Besser et al. 1993
Fish								
Selenate[2]	Fathead minnow (*P. promelas*)	FW	0.000095	0.0011	–	0.0011	–	Bertram and Brooks 1986
	Bluegill (*L. macrochirus*)	FW	0.000015[c]	0.0017	–	0.0017	–	Cleveland et al. 1993
Selenite	Bluegill (*L. macrochirus*)	FW	0.000054	0.0015	–	0.0015	–	Besser et al. 1993
	Mangrove snapper (*L. argentimaculatus*)	SW	0.000033	0.0011	–	0.0011	–	Xu and Wang 2002
	Glassfish (*A. jacksoniensis*)	SW	0.000022	0.0017	–	0.0017	–	Creighton and Twining 2010

[1]Steady-state EF = $k_{u,water}$ / ($k_e + g$) × 1000.
[2]A 6:1 selenate:selenite mixture was tested by Cleveland et al. (1993) but was treated as a selenate exposure in our analysis.
[a]Uptake rate constants ($k_{u,water}$) could also be derived as a function of the waterborne Se concentration ($C_{Se,water}$): $k_{u,water} = 0.2449(C_{Se,water})^{-0.077}$ for selenate and $k_{u,water} = 0.3037(C_{Se,water})^{-0.122}$ for selenite.
[b]Uptake rate constants ($k_{u,water}$) could also be derived as a function of the waterborne Se concentration ($C_{Se,water}$): $k_{u,water} = 0.121(C_{Se,water})^{-0.564}$ for selenate and $k_{u,water} = 0.1999(C_{Se,water})^{-0.187}$ for selenite.
[c]Uptake rate constants ($k_{u,water}$) could also be derived as a function of the waterborne Se concentration ($C_{Se,water}$): $k_{u,water} = 0.0002(C_{Se,water})^{-0.418}$ for selenate.
FW = freshwater; SW = saltwater; EF = enrichment factor.

Potentially relevant studies from the primary literature were gathered through several search methodologies. The Web of Science and Google Scholar were searched for potentially useful studies, published between 1975 and January 2014, using terms such as "biokinetic," "selenium" "biokinetic selenium modeling," "selenium uptake," and "selenium assimilation efficiency." Once potentially relevant studies were identified, the reference sections were reviewed for additional papers. Finally, supporting material in Presser and Luoma (2010) was reviewed for potentially relevant papers because they included a synthesis of studies that reported biokinetic Se parameter data.

A total of 46 potentially relevant studies were identified through our literature search. Of the 46 papers reviewed, 32 papers provided 1 or more parameters that could possibly be used to develop models. This initial set of 32 papers included the 2 papers (Bertram and Brooks 1986; Riedel and Cole 2001) that were used to generate the original model developed by Brix and DeForest (2008), leaving 30 papers with potentially new data. The remaining 14 papers, although not specific to the biokinetic model, provided additional information and insight on general Se bioaccumulation, trophic transfer, biomagnification, and biogeochemical cycling.

In compiling biokinetic modeling data from the additional studies identified, 2 data-handling procedures should be noted. First, in Equations 2 and 4, the product of AE × IR equals the uptake rate constant from the diet ($k_{u,diet}$; h^{-1}). In some studies, $k_{u,diet}$ was measured and reported directly. Thus, the $k_{u,diet}$ data compiled in our evaluation were sometimes based on direct measurements and sometimes as the product of AE × IR. Second, although uptake rate and elimination rate constants were generally derived from experiments using radiolabeled Se, we also calculated uptake rate and elimination rate constants from empirical measurements of Se concentrations in organism tissues and the corresponding Se exposure medium (i.e., waterborne or

dietborne Se) at various time points. Furthermore, in some studies, Se uptake was evaluated (from which an uptake rate constant could be derived), but Se elimination was not. In those cases, the ($k_e + g$) term was solved for by rearranging Equation 1 or 2 if steady-state was demonstrated at the end of the exposure period or by rearranging Equation 3 or 4 if steady-state was not demonstrated. This approach allowed us to expand our database of biokinetic Se data for potential model food chains; details of the approach are presented in Section S1 of Supplemental Data.

As discussed in Luoma and Rainbow (2005), k_u should be determined based on short-term exposures to estimate unidirectional metal influx rates. In other words, metal efflux is assumed to be negligible over the short term. If longer-term exposures are used, k_u will likely be underestimated because the amount of metal bioconcentrated from water represents the balance between uptake and efflux (Luoma and Rainbow 2005). The assumption that k_u is a constant over a range of Se exposure concentrations, however, can be conservative for elements such as Se, which generally show saturable uptake rates. For example, decreasing Se AEs with increasing Se concentrations in the diet have been observed in a cladoceran (*Daphnia magna*) fed algae (*Chlamydomonas reinhardtii*, *Scenedesmus obliquus*) (Yu and Wang 2002a), and in brine shrimp (*Artemia*) fed diatoms (*Dunaliella viridis*) (Grosell 2008). This strongly suggests that intestinal Se uptake is mediated by specific transport pathways that are saturable at higher dietary selenium concentrations. Similarly, in an alga (*C. reinhardtii*), Fournier et al. (2006) reported that Se uptake rates (picograms $[10^5$ cells$]^{-1}$ h^{-1}) decreased significantly with increasing waterborne selenate (and selenomethionine) exposures (nominal added Se concentrations of 0 to 2000 $\mu g\,L^{-1}$), but not for waterborne selenite exposures up to the maximum concentration of 2000 $\mu g\,L^{-1}$. If the inverse relationship between k_u values and Se exposure concentrations is a general phenomenon, then the uptake rate constants used in the present evaluation are likely conservative for the pulse concentrations of interest (where the pulse Se concentrations are higher than the Se concentrations in the experiments from which the k_u values were derived), and developing concentration-dependent values for k_u (or for AE and IR) may be more appropriate. We evaluated the influence of concentration-dependent k_u values on modeling outcomes where sufficient data were available.

Background Se concentrations in the organisms constituting the model food chains is also important to consider. This was especially important for modeling the steady-state Se concentrations before modeling the pulse Se scenarios. The uptake and elimination rate constants compiled were typically based on Se exposure concentrations that were in the 10 to greater than 100 $\mu g\,L^{-1}$ range for waterborne exposures and greater than 10 $\mu g\,g^{-1}$ for dietborne exposures. When these uptake and elimination rate constants were applied to a background waterborne Se concentration of 1 $\mu g\,L^{-1}$, for example, the predicted steady-state whole-body fish Se concentrations were less than 0.5 $\mu g\,g^{-1}$ for most model food chains, which is generally less than would be expected based on field observations. For the objectives of the current paper, this was nonconservative and hence problematic, because it would inappropriately suggest that fish could bioaccumulate a greater concentration of Se before reaching or exceeding a tissue-based toxicity threshold. Accordingly, we defined baseline Se concentrations in primary producers, invertebrates, and whole-body fish by considering Se concentrations in control and reference area organisms and then modeled "added Se" from the Se pulses. This approach for modeling "added Se" was conceptually similar to that used by Borgmann and Norwood (1995) in modeling excess Cu and Zn in an amphipod. We set the background Se concentration in primary producers equal to 1 $\mu g\,g^{-1}$ dry wt, which was based on a median particulate (e.g., algae, detritus) concentration of 0.8 $\mu g\,g^{-1}$ dry wt (rounded upward) at colocated waterborne Se concentrations of 1 $\mu g\,L^{-1}$ or less as compiled in Supplemental Data S3; Table S13. The median was used to minimize the influence of unusually low or high particulate Se concentrations. Background Se concentrations in invertebrates and fish can vary severalfold, but for the purposes of our evaluation we assumed background Se concentrations of 2 $\mu g\,g^{-1}$ for both invertebrates and fish (i.e., a trophic transfer factor $[TTF]_{invert}$ of 2 and TTF_{fish} of 1).

The final step was then to define model food chains based on the additional biokinetic data compiled. Model food chains were developed for both waterborne selenate and selenite exposures. Both periphyton- and phytoplankton-based model food chains were defined, with invertebrates in periphyton-based food chains consisting of mayflies and phytoplankton-based food chains consisting of daphnids. The 2 freshwater fish species in the models were fathead minnows and bluegill, because these were the only 2 freshwater species for which biokinetic Se data were available. We also evaluated "mean combined" and "maximum combined" model food chains, which also considered data for saltwater invertebrate taxa and fish species (which were found to not be unique relative to freshwater species, as shown in later sections).

Validate updated models

Pulse exposure data from mesocosm or field studies were not identified, but Se bioaccumulation predictions under steady-state conditions were compared with field data to evaluate the representativeness of the food chain models. Biokinetic Se model outputs were validated based on comparisons with Se bioconcentration (net Se uptake from waterborne exposure) and trophic transfer (net Se uptake from dietborne exposure) data from laboratory and field studies. Net Se uptake by primary producers (i.e., periphyton, phytoplankton) was defined using enrichment factors (EFs), which were derived from the model parameter:

$$EF = \frac{C_{ss}}{C_w} \times 1000 \quad (5)$$

By rearranging Equation 1 and substituting Equation 5, the EF can be derived as:

$$EF = \frac{k_u}{(k_e + g)} \times 1000 \quad (6)$$

Where: EF = enrichment factor (L kg^{-1} dry wt); C_{ss} = steady-state Se concentration in tissue (μg g^{-1} dw); C_w = Se concentration in water (μg L^{-1}); 1000 = conversion factor (g kg^{-1}); k_u, k_e, and g were previously defined.

Similarly, net Se uptake from dietborne exposure was defined using TTFs, which were derived for invertebrates and fish as follows:

$$TTF = \frac{k_u}{(k_e + g)} \quad (7)$$

For each of the model food chains, the EF for particulates (Eqn. 6) and TTFs for invertebrates and fish (Eqn. 7) can be used to derive the bioaccumulation factors (BAFs) for fish, which related fish Se concentrations to water Se concentrations, as follows:

$$BAF_{fish} = EF_{part} \times TTF_{invert} \times TTF_{fish} \quad (8)$$

The EFs for particulates and BAFs for fish were compared with EFs and BAFs from field datasets. Because field-based EFs and BAFs are not constants, but instead inversely related to waterborne Se concentration, the field-based EFs and BAFs were plotted versus waterborne Se concentration. The EFs and BAFs predicted from the biokinetic models, therefore, could be compared with EFs and BAFs as a function of waterborne Se concentration, which then allowed for interpretation of whether they were conservative for the pulse Se concentrations of interest.

Acute water quality criteria for selenium

The US Environmental Protection Agency (USEPA) has developed several draft and final acute water quality criteria (WQC) for Se since the 1980s (USEPA 1987, 1999, 2004), and most recently, in lieu of acute toxicity based on direct waterborne exposures, has developed draft criteria for intermittent exposures based on chronic exposure and toxicity data (USEPA 2014). The USEPA initially recommended an acute freshwater Se criterion of 20 μg/L (USEPA 1987), which is still the acute Se criterion in the water quality standards of most states. This acute criterion is based on the USEPA's current chronic Se criterion of 5 μg/L, with an acute–chronic ratio "applied in reverse" (USEPA 1987). This is a technically problematic approach because the chronic Se criterion is based on fish population data from Belews Lake (NC, USA), in which the primary exposure route was dietborne organic Se, whereas the acute–chronic ratio is based on paired acute and chronic toxicity data for inorganic Se from waterborne laboratory studies (Canton 1999). The USEPA's currently recommended acute Se criterion, although it has not been adopted in most states, is based on direct waterborne toxicity data and the proportional relationship of selenate and selenite in a water body, where the acute selenite criterion is 185.9 μg/L and the acute selenate criterion is 12.82 μg/L (USEPA 1999):

$$\text{Current Acute Se Criterion} = 1/[f_{selenate}/CMC_{selenate} + f_{selenite}/CMC_{selenite}] \quad (9)$$

Where: $f_{selenate}$ = fraction of total Se concentration present as selenate; $CMC_{selenate}$ = criterion maximum concentration or acute selenate criterion (12.82 μg/L); $f_{selenite}$ = fraction of total Se concentration present as selenite; $CMC_{selenite}$ = criterion maximum concentration or acute selenite criterion (185.9 μg/L). This draft criterion equation is questionable because the draft selenite criterion is more than an order of magnitude greater than the draft selenate criterion, although selenite is more acutely toxic than selenate.

In 2004, the USEPA released a draft acute selenate criterion that was dependent on the sulfate concentration in the water body (279 $\mu g\,L^{-1}$ at a sulfate concentration of 50 $mg\,L^{-1}$, for example) and a draft acute selenite criterion of 258 $\mu g\,L^{-1}$ (USEPA 2004). However, these draft criteria were never finalized. Most recently, the USEPA released draft intermittent water Se criteria for fractions of a 30-d exposure period (USEPA 2014). Although the draft acute Se criteria released in 2004 were never finalized and are not considered in the USEPA's latest draft criteria (USEPA 2014), they were used as acute benchmarks in our current evaluation because they are the most robust acute criteria that have been developed to date based on direct acute waterborne toxicity to aquatic organisms and are therefore useful for answering the question of whether potential waterborne Se criteria based on short-term toxicity from uptake of Se directly from water are also protective against dietborne and bioaccumulation-based Se toxicity.

Chronic whole-body fish selenium toxicity threshold

The objective of this evaluation was to predict combinations of Se pulse concentrations and durations that would be protective of a whole-body fish Se toxicity threshold. The critical endpoint for Se toxicity is generally considered larval mortality, deformities, or edema resulting from the maternal transfer of Se to the eggs; fish egg Se concentration is considered the most relevant predictor of whether Se toxicity is likely (Janz et al. 2010). However, toxicokinetic data on the maternal transfer of Se from the diet to fish eggs are limited and could not be incorporated into the biokinetic models developed here. Accordingly, a whole-body Se toxicity threshold was used in this evaluation. Various whole-body fish Se toxicity thresholds have been recommended, including 4 $\mu g\,g^{-1}$ dry wt (Hamilton 2002; Lemly 1996), 8.1 $\mu g\,g^{-1}$ dry wt (DeForest and Adams 2011), and 9 $\mu g\,g^{-1}$ dry wt (DeForest et al. 1999). In addition, the State of Kentucky adopted a whole-body fish Se criterion of 8.6 $\mu g\,g^{-1}$ dry wt (Payne 2013), and the USEPA released a draft whole-body fish Se criterion of 8.1 $\mu g\,g^{-1}$ dry wt (USEPA 2014). A whole-body fish Se toxicity threshold of 8.1 $\mu g\,g^{-1}$ dry wt was used in the current evaluation (although any whole-body fish Se toxicity threshold of interest could be used in the model).

Selenium pulse scenarios

We first evaluated whether single Se pulses equivalent to acute criteria (279 $\mu g\,L^{-1}$ selenate or 258 $\mu g\,L^{-1}$ selenite) would result in a predicted whole-body fish Se concentration of ≥8.1 $\mu g\,g^{-1}$ dry wt in any of the model food chains. Pulse durations of 24 and 96 h were evaluated, with the latter considered a conservatively long pulse duration that was still consistent with the standard duration of acute toxicity tests with fish. The biokinetic model was developed such that Se step functions were instantaneous. For example, for a 24-h pulse, the background Se concentration immediately increased to the desired pulse Se concentration, and then the pulse Se concentration immediately decreased to the background Se concentration at 24 h.

In our second evaluation, we determined the magnitudes of the Se pulses into the model food chains that would be predicted to 1) equal the whole-body Se threshold of 8.1 $\mu g\,g^{-1}$ dry wt and 2) exceed the whole-body Se threshold for 7 d, which we considered a conservatively short chronic duration. The latter was somewhat arbitrary but used as a means for evaluating water Se pulse concentrations that would be required for a whole-body Se concentration greater than the toxicity threshold to persist for several days rather than the maximum modeled whole-body Se concentration to briefly equal the whole-body Se toxicity threshold.

In a third evaluation, we considered the influence of higher background waterborne Se concentrations (5 and 10 μg/L) on uptake and elimination kinetics of Se in model food chains. This was conducted for phytoplankton-based food chains and for both selenate and selenite. The evaluation provided an understanding of not only how higher background waterborne Se concentrations may influence the magnitudes of predicted whole-body fish Se concentrations under various scenarios, but also estimates of the duration required for whole-body Se concentrations to return to the baseline steady-state concentration after an Se pulse exposure.

The first 3 evaluations focused on single-pulse exposure scenarios. In the 4th evaluation, we considered how multiple Se pulses of varying magnitudes, durations, and intervals could influence predictions of whole-body Se concentrations in fish. Of particular interest was evaluating scenarios in which a single pulse of a given magnitude and duration did not result in a whole-body Se concentration of 8.1 $\mu g\,g^{-1}$ dry wt or greater, but where multiple pulses of the same or similar magnitudes perhaps could.

In the final, 5th evaluation, we considered the use of uptake rate constants that varied as a function of exposure concentration in the biokinetic model. For those studies in which Se uptake was evaluated at multiple Se exposure concentrations, k_u values were plotted versus corresponding Se exposure concentrations, and regression models were fit to the data. The regression equations were then inserted into the biokinetic models, as available, such that k_u varied with Se exposure concentration. These modeling results with variable k_u values were then compared with results from the initial models, where uptake rates were treated as constants regardless of exposure concentrations.

RESULTS

Biokinetic modeling data

Primary producers. Riedel and Cole (2001) was the only study we identified in which waterborne Se uptake, elimination, and growth rate constants were all reported for periphyton (Table 1). For comparison, Conley et al. (2013) measured Se bioconcentration in periphyton at various time points during 192-h exposures to either selenate or selenite. We derived waterborne uptake rate constants of 0.0028 and 0.015 $L\,g^{-1}\,h^{-1}$ for selenate and selenite, respectively, based on the short-term bioconcentration data that they reported (Table 1; see Supplemental Data S1 for details). Riedel and Cole (2001) reported comparable uptake rate constants of 0.0045 and 0.0112 $L\,g^{-1}\,h^{-1}$ for selenate and selenite, respectively. Conley et al. (2013) did not measure Se elimination and periphyton growth, but we estimated the combined $(k_e + g)$ term for selenate and selenite based on the derived uptake rate constants and the Se bioconcentration data reported after different exposure periods in the original study (the biokinetic modeling approach used in this evaluation did not require that k_e and g be separately defined). We derived $(k_e + g)$ values of 0.0081 and 0.0041 h^{-1} for selenate and selenite, respectively (Table 1; see Supplemental Data S1 for details). These estimates from Conley et al. (2013) were again comparable in magnitude to the $(k_e + g)$ values of 0.0073 and 0.0068 h^{-1} for selenate and selenite from Riedel and Cole (2001).

Although several studies have evaluated Se bioconcentration by various phytoplankton species, few have reported sufficient data for deriving biokinetic parameters. Besser et al. (1993) measured selenate and selenite bioconcentration into the alga *Chlamydomonas reinhardtii* after 3-, 8-, 24-, and 48-h exposures. We derived mean waterborne uptake rate constants of 0.17 and 0.24 $L\,g^{-1}\,h^{-1}$ for selenate and selenite, respectively, based on the short-term bioconcentration data that they reported (Table 1; see Supplemental Data S1 for details). The uptake rate constant for selenite in *C. reinhardtii* was therefore 41% greater than for selenate. Following the same approach as described above for the Conley et al. (2013) dataset, we also derived mean combined $(k_e + g)$ terms of 0.42 and 0.26 h^{-1} for selenate and selenite, respectively (Table 1; see Supplemental Data S1 for details).

The selenate and selenite uptake rate constants for *C. reinhardtii* were approximately 50-fold and 18-fold greater than those for periphyton, which clearly has an important influence on modeling Se pulses (i.e., *C. reinhardtii* would be able to take up much more Se than periphyton during a short-term pulse). Selenium uptake rate constants for *C. reinhardtii* and other phytoplankton species were identified or derived, but elimination rate data were either lacking or the combined $(k_e + g)$ term could not be derived because Se concentrations in the algae were not measured or reported. This precluded consideration of these data in one of our model food chains. However, additional Se uptake rate constants for phytoplankton are provided here as a point of comparison with those values derived from Besser et al. (1993). Selenite uptake rate constants for *C. reinhardtii* were derived from the data reported in Yu and Wang (2004a), which averaged 0.62 (range, 0.013–4.5) $L\,g^{-1}\,h^{-1}$ over a range of different nutrient regimens. This range brackets the selenite uptake rate constant of 0.24 $L\,g^{-1}\,h^{-1}$ that we derived from Besser et al. (1993). It also should be emphasized that Yu and Wang (2004a) observed a greater than 300-fold variation in uptake rate constants, demonstrating how different nutrient conditions can influence selenite uptake rates in the same species. Riedel et al. (1991) and Fournier et al. (2006) also evaluated selenate and selenite uptake by *C. reinhardtii* in short-term exposures. Selenium concentrations in algae were reported based on cell counts, so a mean dry weight of 68.3 pg $cell^{-1}$ from Yu and Wang (2002a) was assumed. The mean uptake rate constants for selenate and selenite derived from these studies were, respectively, 0.016 and 0.11 $L\,g^{-1}\,h^{-1}$ based on Riedel et al. (1991) and 0.0036 and 0.0016 $L\,g^{-1}\,h^{-1}$ based on Fournier et al. (2006). The selenate uptake rate constants were 10-fold and 50-fold less than those derived from Besser et al. (1993), and the selenite uptake rate constants were 2-fold and 150-fold less than those derived from Besser et al. (1993). This suggest high variability in Se uptake rate constants for phytoplankton and that those derived from Besser et al. (1993) may be conservative. This could be related, in part, to differences in nutrient concentrations in the tests, which could influence algae growth rates and therefore Se uptake rate constants (i.e., higher growth rates would result in lower uptake rate constants). The nitrogen (N) and phosphorus (P) concentrations in the experiments conducted by Besser et al. (1993) were less than the concentrations in the experiments conducted by Riedel et al. (1991): 3.5 mg N/L and 0.4 mg P/L versus 14 mg N/L and 1.5 mg P/L. In the Fournier et al. (2006) experiments, the N concentration was higher than in the Besser et al. (1993) experiment (7 mg N/L), and P concentrations were lower (0.15 mg P/L).

Overall, sufficient data were identified to evaluate selenate and selenite bioconcentration from pulse exposures into model food chains comprising either periphyton or phytoplankton (as represented by C. *reinhardtii*). The mean uptake rate constants for selenate were 38-fold to 61-fold greater for C. *reinhardtii* than for periphyton and 16-fold to 21-fold greater for selenite. However, the mean ($k_e + g$) term for C. *reinhardtii* was also greater than for periphyton, because this term was 52-fold to 58-fold greater for selenate and 38-fold to 63-fold greater for selenite.

Invertebrates. For freshwater species, the most complete biokinetic data for both waterborne and dietborne Se exposures were identified for a mayfly (*Centroptilum triangulifer*) (Riedel and Cole 2001; Tables 1 and 2). In addition, a complete set of biokinetic parameters for waterborne and dietborne Se uptake was compiled from multiple studies for the planktonic cladoceran *D. magna* (Besser et al. 1993; Guan and Wang 2004; Yu and Wang 2002a, 2002b, 2004b). A complete biokinetic parameter data set was also available for dietborne, but not waterborne, Se uptake by the alderfly *Sialis velata* (Dubois and Hare 2009) (Table 2). For comparison with freshwater invertebrates, biokinetic Se data were compiled for saltwater copepods, mysids, and brine shrimp exposed to dietborne Se via seston, algal, or copepod prey diets (Wang and Fisher 1998; Schlekat et al. 2004; Mathews and Fisher 2008) (Table 2). No clear differences were seen between the freshwater and saltwater invertebrates in terms of dietborne uptake and combined elimination and growth rate constants (Figure 1A), with steady-state trophic transfer factors (TTFs) ranging from 0.3 to 1.9 (Table 2). These TTFs fall within the range of typical values for arthropods based on measurements in field and laboratory studies (Presser and Luoma 2010; Stewart et al. 2010).

Fish. For freshwater species, the most complete biokinetic data for waterborne and dietborne Se exposures were identified for fathead minnows (*Pimephales promelas*) exposed to waterborne selenate (biokinetic data for waterborne selenite exposures by fathead minnows were not identified) (Bertram and Brooks 1986; Tables 1 and 2). In addition, we derived waterborne and dietborne biokinetic parameters for bluegill (*Lepomis macrochirus*) based on Besser et al. (1993) and Cleveland et al. (1993) (Tables 1 and 2). Waterborne and dietborne uptake, elimination, and growth rate parameters were also identified for several saltwater fish species (Baines et al. 2002; Xu and Wang 2002; Zhang and Wang 2007; Mathews and Fisher 2008; Creighton and Twining 2010) (Tables 1 and 2), which were similar to those observed in freshwater fish species (Figure 1B). The steady-state TTFs ranged from 0.3 to 1.8 across all fish species, with an overall mean of 0.8 (Table 2). As seen with invertebrates, these TTFs fall within the range of typical values for fish based on measurements in field and laboratory studies (Presser and Luoma 2010; Stewart et al. 2010).

Model food chains

To evaluate waterborne Se pulse concentrations that could result in whole-body fish tissue Se concentrations that exceed chronic toxicity thresholds, we developed model food chains based on the biokinetic Se data compiled for primary producers, invertebrates, and fish. We considered multiple model food chains, including some that were specific to the species for which biokinetic data were available, as well as "combined" food chains in which biokinetic parameters were averaged or combined in different ways across multiple species within each step of the model food chain. Model food chains were developed for both selenate and selenite pulses.

The first set of model food chains developed was based on systems comprising periphyton, mayflies, and fish (Models 1–6 in Table 3). Periphyton Se concentrations were modeled based on the biokinetic data derived from either Riedel and Cole (2001; Models 1, 3, 5) or Conley et al. (2013; Models 2, 4, 6). Because of data limitations, only selenate pulses could be modeled for the fathead minnow, but both selenate and selenite pulses could be modeled for bluegill. The predicted steady-state bioaccumulation factors (BAFs) for fish, which represent an integration of EF and TTFs ($BAF = EF \times TTF_{invert} \times TTF_{fish}$), are provided as an indication of which models may be more conservative, although the most conservative steady-state model may not necessarily be the most conservative model for evaluating Se pulses. From this set of periphyton- and mayfly-based models, models 1 and 6 for selenate and selenite, respectively, were initially used in our evaluations because these had the highest BAFs.

The second set of model food chains developed was based on phytoplankton, daphnids, and fish (models 7–9 in Table 3). Dietborne biokinetic parameter values for daphnids, fathead minnows, and bluegill were averages from 2 or 3 studies. Based on the steady-state BAFs for the model food chains, models 7 and 9 for selenate and selenite, respectively, were initially used in our evaluations, because these had the highest BAFs. This phytoplankton- and daphnid-based food chain resulted in steady-state Se bioaccumulation in fish that was approximately 2 times greater than in the periphyton- and mayfly-based food chain based on waterborne selenate, whereas the 2 types of models predicted similar levels of steady-state Se bioaccumulation for selenite exposure scenarios.

The 3rd set of model food chains developed was based on different statistics for combining biokinetic data for primary producers (periphyton and phytoplankton), invertebrates, and fish (herein called "combined"). For invertebrates and fish, data from freshwater and saltwater species were pooled because no significant differences were seen between the 2 ($p \geq 0.53$ for invertebrates and fish for both k_e and $[k_e + g]$). These model food chains were based on arithmetic mean biokinetic parameter values for waterborne uptake by primary producers, invertebrates, and fish, and then we considered arithmetic mean, geometric mean, minimum, and maximum biokinetic values for dietborne Se exposures by invertebrates and fish. As shown in Figure 1, an overall positive relationship is seen between $k_{u,diet}$ and ($k_{e,diet} + g$). In other words, species with higher Se uptake rates also generally have higher Se elimination rates. Accordingly, we did not develop model food chains based on unlikely extremes of each (e.g., the maximum Se uptake rate paired with the minimum Se elimination rate). The geometric mean and minimum models were the least conservative and not considered further. The final combined model food chains evaluated, based on arithmetic mean and maximum biokinetic parameter values for invertebrates and fish (models 10–17), are listed in Table 3.

Model validation

Although field data characterizing pulse waterborne Se exposures and resulting concentrations in primary producers were not identified, we were able to compare the steady-state

Table 2. Dietborne Se biokinetic parameters used in the current analysis

Species	Habitat type	Diet	IR (h^{-1})	AE (%)	$k_{u,diet}$ (h^{-1})	$k_{e,diet}$ (h^{-1})	g (h^{-1})	k_e+g (h^{-1})	Steady-state TTF (dw)[1]	Data source
Invertebrates										
Mayfly (*C. triangulifer*)	FW	Periphyton	0.030	39	0.012	0.018	0.0075	0.026	0.5	Riedel and Cole 2001
Alderfly (*S. velata*)	FW	Worm	0.0064	70	0.0045	0.0067	–	0.0067	0.7	Dubois and Hare 2009
		Midge	0.0042	62	0.0026	0.0018	–	0.0018	1.4	Dubois and Hare 2009
Cladoceran (*D. magna*)	FW	*C. reinhardtii*	–	–	0.0098[a]	–	–	0.013	0.8	Besser et al. 1993
		C. reinhardtii	0.054	45	0.024	0.0080	–	0.0080	1.9	Yu and Wang 2002a; Guan and Wang 2004
		S. obliquus	0.067	31	0.021	0.0057	–	0.0057	3.7	Yu and Wang 2002a, 2004b; Guan and Wang 2004
Copepod (*T. longicornis*)	SW	Seston	0.018	50	0.0090	0.0065	0.0038	0.010	0.9	Wang and Fisher 1998
		T. weissflogii	0.018	59	0.011	0.0065	0.0038	0.010	1.0	Wang and Fisher 1998
		T. pseudonana	0.018	58	0.010	0.0065	0.0038	0.010	1.0	Wang and Fisher 1998
Copepods (73–250 μm)	SW	*P. tricornutum*	0.018	50	0.0090	0.0065	0.0038	0.010	0.9	Schlekat et al. 2004
(250–500 μm)		*P. tricornutum*	0.018	52	0.0094	0.0065	0.0038	0.010	0.9	Schlekat et al. 2004
Mysid (*N. mercedis*)	SW	Copepods	0.019	67	0.013	0.01	–	0.010	1.3	Schlekat et al. 2004
Brine shrimp (*A. salina*)	SW	*I. galbana*	0.013	60	0.0079	0.025	–	0.025	0.3	Mathews and Fisher 2008
Fish										
Fathead minnow (*P. promelas*)	FW	*Daphnia*	0.00125	55	0.00069	0.00058	–	0.00058	1.2	Bertram and Brooks 1986
		Rotifer	–	–	0.0077	0.0010	0.0047	0.0057	1.4	Bennett et al. 1986
Bluegill (*L. macrochirus*)	FW	*Daphnia*	–	–	0.00037	0.0015	–	0.0015	0.3	Besser et al. 1993
		Synthetic	–	–	0.0011[b]	0.0021	–	0.0021	0.5	Cleveland et al. 1993
Striped bass (*M. saxatilis*)	SW	Brine shrimp	0.014	33	0.0046	0.0038	–	0.0038	1.2	Baines et al. 2002
		Copepods	0.014	42	0.0059	0.0033	–	0.0033	1.8	Baines et al. 2002
Mangrove snapper (*L. argentimaculatus*)	SW	Copepods	0.0023	65	0.0015	0.0013	–	0.0013	1.1	Xu and Wang 2002
Black sea bream (*A. schlegeli*)	SW	Ghost shrimp	0.0092	28	0.0025	0.0018	0.0013	0.0031	0.8	Zhang and Wang 2007
Sea bream (*S. auratus*)	SW	Brine shrimp	0.0023	77	0.0018	0.0054	–	0.0054	0.3	Mathews and Fisher 2008
Sea bass (*D. labrax*)	SW	Brine shrimp	0.0023	64	0.0015	0.0025	–	0.0025	0.6	Mathews and Fisher 2008
Glassfish (*A. jacksoniensis*)	SW	Brine shrimp	0.0021	23	0.00048	0.0018	–	0.0018	0.3	Creighton and Twining 2010

[1]Steady-state TTF = $k_{u,diet}$ / (k_e+g).
[a]Uptake rate constants ($k_{u,diet}$) could also be derived as a function of the dietborne Se concentration ($C_{Se,diet}$): $k_{u,diet} = 0.0111(C_{Se,diet})^{-0.238}$.
[b]Uptake rate constants ($k_{u,diet}$) could also be derived as a function of the dietborne Se concentration ($C_{Se,diet}$): $k_{u,diet} = 0.0023(C_{Se,diet})^{-0.376}$.
FW = freshwater; SW = saltwater; TTF = trophic transfer factor.

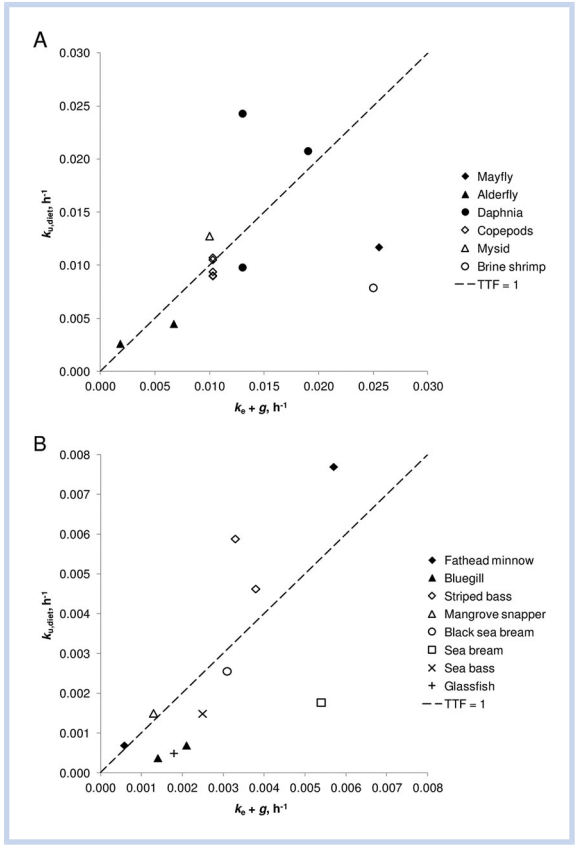

Figure 1. Relationship between dietborne Se uptake rate constants ($k_{u,diet}$) and elimination + growth rate constants ($k_e + g$) for freshwater (filled symbols) and saltwater (open symbols) invertebrates (**A**) and fish (**B**). Diagonal dashed line represents a steady-state TTF of 1.

Se bioconcentration potential of periphyton and phytoplankton based on the uptake, elimination, and growth rate constants compiled from Riedel and Cole (2001) and derived from Conley et al. (2013) and Besser et al. (1993) with periphyton and algal Se bioconcentration potential measured at field sites.

The resulting steady-state selenate EFs predicted for periphyton were 616 and 346 L kg^{-1} dry wt based on Riedel and Cole (2001) and Conley et al. (2013), respectively, and 405 L kg^{-1} dry wt for C. *reinhardtii*. For selenite, the resulting steady-state EFs predicted for periphyton were 1647 and 3659 L kg^{-1} dry wt based on Riedel and Cole (2001) and Conley et al. (2013), respectively, and 923 L kg^{-1} dry wt for C. *reinhardtii*. These EFs were compared with co-located EF and water Se concentrations for lotic and lentic sites compiled in Supplemental Data S3; Table S13. A distinct inverse relationship occurs between EFs and water Se concentrations, and the predicted steady-state EFs for periphyton and C. *reinhardtii* are generally associated with waterborne Se concentrations of less than approximately 20 μg/L (Figure 2), which is less than the pulse exposure concentrations of interest in this evaluation. Accordingly, the model food chains based on the periphyton and C. *reinhardtii* used in this evaluation appear to be reasonably conservative.

As for primary producers, field data characterizing pulse waterborne Se exposures and resulting concentrations in fish were not identified, but we were able to compare the steady-state Se bioaccumulation potential of fish based on the uptake, elimination, and growth rate constants compiled from conservative model food chains for selenate and selenite with fish Se bioaccumulation potential measured at field sites.

Models 1 and 6 for periphyton-based food chains resulted in whole-body fish Se BAFs of 455 and 739 L kg^{-1} dry wt for selenate and selenite, respectively, and models 7 and 9 for phytoplankton-based food chains resulted in whole-body fish Se BAFs of 1009 and 1310 L kg^{-1} dry wt for selenate and selenite, respectively (Table 3). These BAFs were compared with field-based BAFs based on a database of colocated whole-body and water Se data for lotic and lentic waters that were compiled from government and industry reports and published literature (Supplemental Data S3; Table S14). Selenate was likely the dominant Se form present in lotic waters, but the steady-state selenite BAF is still provided for comparative purposes. As observed for Se EFs (Figure 2), whole-body fish Se BAFs are inversely related to the water Se concentration and are highly variable, ranging from greater than 1000 L kg^{-1} dry wt at lower water Se concentrations to less than 100 L kg^{-1} dry wt at higher water Se concentrations (Supplemental Data S2; Figure S6). The modeled steady-state BAFs are generally greater than the field-based BAFs when water Se concentrations are greater than 30 μg L^{-1}, which are of greatest interest in this evaluation of Se pulse concentrations. As such, this provides support that these models appear to be reasonably conservative.

Are acute water quality benchmarks for selenium protective against chronic fish tissue–based selenium toxicity?

In the first and second sets of model food chains, whole-body fish Se concentrations predicted from selenate or selenite pulses equal to acute benchmarks of 279 μg L^{-1} or 258 μg L^{-1}, respectively, were evaluated. For selenate, 1-d Se pulses of 279 μg L^{-1} into either the periphyton→mayfly→fathead minnow food chain or the phytoplankton→daphnid→fathead minnow food chain resulted in a predicted whole-body fish Se concentration less than 8.1 μg g^{-1} dry wt (Figure 3A, 3C). However, a 4-d pulse resulted in a predicted whole-body Se concentration of approximately 8.1 μg g^{-1} dry wt in the periphyton→mayfly→fathead minnow food chain and a predicted exceedance of 8.1 μg g^{-1} dry wt for 33 d in the phytoplankton→daphnid→fathead minnow food chain (Figure 3B, 3D). For selenite, 1-d pulses did not result in predicted whole-body fish Se concentrations greater than 8.1 μg g^{-1} dry wt in either the periphyton- or phytoplankton-based food chains, but 4-d pulses resulted in Se concentrations greater than 8.1 μg g^{-1} dry wt that persisted for approximately 30 d (Figure 4).

In the third set, "combined" food chains based on either mean or maximum uptake and elimination rates in invertebrates and fish, 4-d selenate pulses of 279 μg L^{-1} in the "mean combined" food chain, and both 1-d and 4-d pulses in the "maximum combined" food chain resulted in predicted whole-body fish Se concentrations greater than 8.1 μg g^{-1} dry wt for both the periphyton- and phytoplankton-based food chains (Supplemental Data S2; Figures S7 and S8). For selenite, both 1-d and 4-d pulses of 258 μg L^{-1} into both the "mean" and "maximum" food chains resulted in predicted whole-body Se concentrations greater than 8.1 μg g^{-1} dry wt for both the periphyton- and phytoplankton-based food chains (Supplemental Data S2; Figures S9 and S10).

An acute selenate criterion of 279 μg L^{-1} (at a sulfate concentration of 50 mg L^{-1}) and acute selenite criterion of

Table 3. Model food chains evaluated

			Primary producer		Invertebrate				Fish				
			Waterborne Se		Waterborne Se		Dietborne Se		Waterborne Se		Dietborne Se		
No.	Model Food Chain	Se Form	$k_{u,water}$ (L g^{-1} h^{-1})	k_e+g (h^{-1})	$k_{u,water}$ (L g^{-1} h^{-1})	k_e+g (h^{-1})	$k_{u,diet}$ (h^{-1})	k_e+g (h^{-1})	$k_{u,water}$ (L g^{-1} h^{-1})	k_e+g (h^{-1})	$k_{u,diet}$ (h^{-1})	k_e+g (h^{-1})	Fish BAF[1]
1	Periphyton→Mayfly→FHM	Selenate	0.0045	0.0073	0.0006	0.023	0.012	0.026	0.000095	0.0011	0.00069	0.00058	455
2	Periphyton→Mayfly→FHM	Selenate	0.0028	0.0081	0.0006	0.023	0.012	0.026	0.000095	0.0011	0.00069	0.00058	307
3	Periphyton→Mayfly→Bluegill	Selenate	0.0045	0.0073	0.0006	0.023	0.012	0.026	0.000015	0.0017	0.00053	0.00180	134
4	Periphyton→Mayfly→Bluegill	Selenate	0.0028	0.0081	0.0006	0.023	0.012	0.026	0.000015	0.0017	0.00053	0.00180	83
5	Periphyton→Mayfly→Bluegill	Selenite	0.0112	0.0068	0.0008	0.027	0.012	0.026	0.000054	0.0015	0.00053	0.00180	359
6	Periphyton→Mayfly→Bluegill	Selenite	0.015	0.0041	0.0008	0.027	0.012	0.026	0.000054	0.0015	0.00053	0.00180	739
7	Phytoplankton→Daphnid→FHM	Selenate	0.17	0.42	0.021	0.10	0.018	0.0089	0.000095	0.0011	0.00069	0.00058	1310
8	Phytoplankton→Daphnid→Bluegill	Selenate	0.17	0.42	0.021	0.10	0.018	0.0089	0.000012	0.0017	0.00074	0.00180	430
9	Phytoplankton→Daphnid→Bluegill	Selenite	0.24	0.26	0.14	0.28	0.018	0.0089	0.000054	0.0015	0.00074	0.00180	1009
10	Periphyton→Invert→Fish (mean)	Selenate	0.0037	0.21	0.011	0.061	0.012	0.015	0.000055	0.0014	0.0022	0.0028	192
11	Periphyton→Invert→Fish (max)	Selenate	0.0037	0.21	0.011	0.061	0.018	0.026	0.000055	0.0014	0.0053	0.0054	228
12	Phytoplankton→Invert→Fish (mean)	Selenate	0.17	0.42	0.011	0.061	0.012	0.015	0.000055	0.0014	0.0022	0.0028	435
13	Phytoplankton →Invert→Fish (max)	Selenate	0.17	0.42	0.011	0.061	0.018	0.026	0.000055	0.0014	0.0053	0.0054	491
14	Periphyton→Invert→Fish (mean)	Selenite	0.013	0.0055	0.070	0.15	0.012	0.015	0.000036	0.0014	0.0022	0.0028	1878
15	Periphyton→Invert→Fish (max)	Selenite	0.013	0.0055	0.070	0.15	0.018	0.026	0.000036	0.0014	0.0053	0.0054	2090
16	Phytoplankton→Invert→Fish (mean)	Selenite	0.24	0.26	0.070	0.15	0.012	0.015	0.000036	0.0014	0.0022	0.0028	973
17	Phytoplankton →Invert→Fish (max)	Selenite	0.24	0.26	0.070	0.15	0.018	0.026	0.000036	0.0014	0.0053	0.0054	1111

[1]Steady-state fish bioaccumulation factor (BAF) = EF × TTF_{invert} × TTF_{fish}

FHM = fathead minnow.

Studies used to develop each model:

Model #1: Periphyton parameters from Riedel and Cole (2001); mayfly parameters from Riedel and Cole (2001); fathead minnow parameters from Bertram and Brooks (1986).

Model #2: Periphyton parameters from Conley et al. (2013); mayfly parameters from Riedel and Cole (2001); fathead minnow parameters from Bertram and Brooks (1986).

Model #3: Periphyton parameters from Riedel and Cole (2001); mayfly parameters from Riedel and Cole (2001); bluegill parameters from Besser et al. (1993) and Cleveland et al. (1993).

Model #4: Periphyton parameters from Conley et al. (2013); mayfly parameters from Riedel and Cole (2001); bluegill parameters from Besser et al. (1993) and Cleveland et al. (1993).

Model #5: Periphyton parameters from Riedel and Cole (2001); mayfly parameters from Riedel and Cole (2001); bluegill parameters from Besser et al. (1993) and Cleveland et al. (1993).

Model #6: Periphyton parameters from Conley et al. (2013); mayfly parameters from Riedel and Cole (1999); bluegill parameters from Besser et al. (1993) and Cleveland et al. (1993).

Model #7: Phytoplankton parameters from Besser et al. (1993); daphnid parameters from Besser et al. (1993), Yu and Wang (2002, 2004), Guan and Wang (2004); fathead minnow parameters from Bertram and Brooks (1986).

Models #8 & 9: Phytoplankton parameters from Besser et al. (1993); daphnid parameters from Besser et al. (1993), Yu and Wang (2002, 2004), Guan and Wang (2004); bluegill parameters from Besser et al. (1993) and Cleveland et al. (1993).

Models #10-17: Primary producer parameters from Riedel and Cole (2001), Conley et al. (2013), Besser et al. (1993); mean invertebrate parameters from Besser et al. (1993), Wang and Fisher (1998), Riedel and Cole (2001), Yu and Wang (2002, 2004), Guan and Wang (2004), Schlekat et al. (2004), Mathews and Fisher (2008); fish parameters from Bennett et al. (1986), Bertram and Brooks (1986), Besser et al. (1993), Cleveland et al. (1993), Baines et al. (2002), Xu and Wang (2002), Zhang and Wang (2007), Mathews and Fisher (2008), Creighton and Twining (2010).

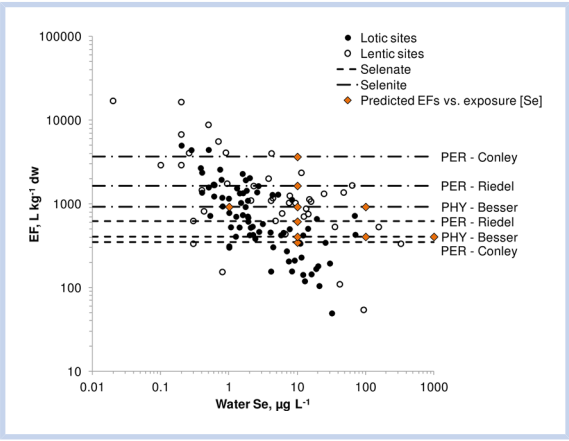

Figure 2. Relationship between Se enrichment factors (EFs) and co-located water Se concentrations from lotic (flowing water) and lentic (standing water) sites and comparison with biokinetic model-based EFs for periphyton (PER) and phytoplankton (PHY). Horizontal dashed lines show predicted steady-state EFs, and orange diamonds show the water Se concentrations in the tests from which the biokinetic parameters were derived. Field data from DeForest et al. (In Review); Besser = Besser et al. (1993); Conley = Conley et al. (2013); Riedel = Riedel and Cole (2001).

258 $\mu g\,L^{-1}$ may not be protective against a whole-body Se toxicity threshold of 8.1 $\mu g\,g^{-1}$ dry wt for all pulse durations and model food chains. This is consistent with the observation that 1-d pulses of 279 or 258 $\mu g\,L^{-1}$ would result in 30-d average Se concentrations of 11 and 10 $\mu g\,L^{-1}$, respectively (assuming a background Se concentration of 1 µg/L), which exceed the draft lentic and lotic criteria of 1.3 and 4.8 µg/L. A pulse duration of 1 d versus 4 d can have an important influence on not only whether a fish whole-body Se concentration greater than 8.1 $\mu g\,g^{-1}$ dry wt is predicted, but also the duration over which an exceedance is predicted. The duration of a whole-body Se toxicity threshold exceedance is also influenced by the nature of the food chain, because periphyton have a slower elimination rate constant.

We also evaluated whether the USEPA's (2014) draft intermittent criteria for Se are appropriately protective when considering biokinetic modeling. For comparison with the biokinetic modeling results presented, we considered pulse durations of 1 d and 4 d, with a background waterborne Se concentration of 1 $\mu g\,L^{-1}$ and a lotic Se criterion of 4.8 $\mu g\,L^{-1}$ or a lentic Se criterion of 1.3 $\mu g\,L^{-1}$. The USEPA's draft intermittent Se criteria for lotic systems under these 2 scenarios are 115 $\mu g\,L^{-1}$ for a 1-d pulse and 30 $\mu g\,L^{-1}$ for a 4-d pulse. For lentic systems, the USEPA's draft intermittent Se criteria under these scenarios are 10 $\mu g\,L^{-1}$ for a 1-d pulse and 3.3 $\mu g\,L^{-1}$ for a 4-d pulse. Assuming that the periphyton-based model food chains were more representative of lotic systems, we then modeled a 1-d pulse of 115 $\mu g\,L^{-1}$ and a 4-d pulse of 30 $\mu g\,L^{-1}$ into each of 6 periphyton-based model food chains (3 each for selenate and selenite). We also assumed that the phytoplankton-based model food chains were more representative of lentic systems and modeled a 1-d pulse of 10 $\mu g\,L^{-1}$ and a 4-d pulse of 3.3 $\mu g\,L^{-1}$ into each of 6 phytoplankton-based model food chains (3 each for selenate and selenite). The predicted whole-body fish Se concentrations were less than the whole-body fish Se toxicity threshold of 8.1 $\mu g\,g^{-1}$ dry wt in 11 of the 12 model food chains (Supplemental Data Figure S11). The only exception was the maximum periphyton-based model food chain for selenite, which resulted in maximum whole-body fish Se concentrations of greater than 14 $\mu g\,g^{-1}$ dry wt in both pulse scenarios. Overall, the draft intermittent Se criteria appear to be protective for selenate pulses into lotic and lentic systems and selenite pulses into lentic systems but potentially underprotective for selenite pulses into lotic systems.

Which selenium pulse scenarios result in exceedance of a chronic fish tissue–based benchmark?

Depending on the food chain model used, selenate and selenite pulses predicted to result in the whole-body fish Se threshold of 8.1 $\mu g\,g^{-1}$ dry wt varied considerably. For the periphyton→mayfly→fathead minnow model (model 1), the 1-d selenate pulse predicted to result in the fish tissue threshold of 8.1 $\mu g\,g^{-1}$ dry wt was 1470 $\mu g\,L^{-1}$, and the 4-d pulse was 270 $\mu g\,L^{-1}$ (Table 4). The 1-d and 4-d selenate pulses required to exceed the tissue threshold for 7 d (a conservative duration for chronic toxicity) using the same model were 1633 $\mu g\,L^{-1}$ and 294 $\mu g\,L^{-1}$, respectively. For the phytoplankton→daphnid→fathead minnow model (model 7), the 1-d selenate pulse predicted to result in the fish tissue threshold was 613 $\mu g\,L^{-1}$, and the 4-d pulse predicted to result in this threshold was 143 $\mu g\,L^{-1}$. Exceedances of the fish tissue threshold for 7 d using the same model required 1-d and 4-d selenate pulses of 813 $\mu g\,L^{-1}$ and 167 $\mu g\,L^{-1}$, respectively. The higher uptake rate constants for Se in phytoplankton resulted in lower pulse selenate concentrations necessary to obtain a predicted whole-body fish Se concentration equal to the threshold of 8.1 $\mu g\,g^{-1}$ dry wt compared with the periphyton-based model.

For selenite, 1-d and 4-d pulses predicted to result in a whole-body fish Se concentration of 8.1 $\mu g\,g^{-1}$ dry wt using the periphyton→mayfly→bluegill model (model 6) were 578 $\mu g\,L^{-1}$ and 104 $\mu g\,L^{-1}$, respectively (Table 4). The 1-d and 4-d selenite pulses predicted to exceed the fish tissue threshold for 7 d using this model were 621 $\mu g\,L^{-1}$ and 111 $\mu g\,L^{-1}$, respectively. For the phytoplankton→daphnid→fathead minnow model (Model 9) the 1-d and 4-d selenite pulses predicted to result in the fish tissue threshold were 313 $\mu g\,L^{-1}$and 82 $\mu g\,L^{-1}$, respectively, and the 1-d and 4-d selenite pulses needed to exceed the tissue threshold for 7 d were 397 $\mu g\,L^{-1}$ and 103 $\mu g\,L^{-1}$, respectively. The high uptake and elimination rate constants for Se in phytoplankton mean that the difference between a 1-d and a 4-d pulse can be significant in terms of Se bioaccumulation at higher levels of the food chain in lentic systems.

We also determined the pulse selenate and selenite concentrations that would result in the whole-body fish Se threshold of 8.1 $\mu g\,g^{-1}$ dry wt based on the "combined" model food chains, which were either periphyton-based or phytoplankton-based. These model food chains were also based on average and maximum biokinetic parameters for invertebrates and fish, including freshwater and saltwater species. Overall, depending on the food chain model, 1-d Se pulse concentrations predicted to result in a whole-body fish Se threshold of 8.1 $\mu g\,g^{-1}$ dry wt ranged from 142 to 1470 µg/L for selenate and from 56 to 578 µg/L for selenite (Table 4). The 4-d pulse Se concentrations predicted to result in the whole-body fish Se threshold ranged from 34 to 270 µg/L for selenate and from 16 to 104 µg/L for selenite (Table 4). The pulse selenate and selenite concentrations predicted to exceed the whole-body Se toxicity threshold for 7 d are also provided in Table 4.

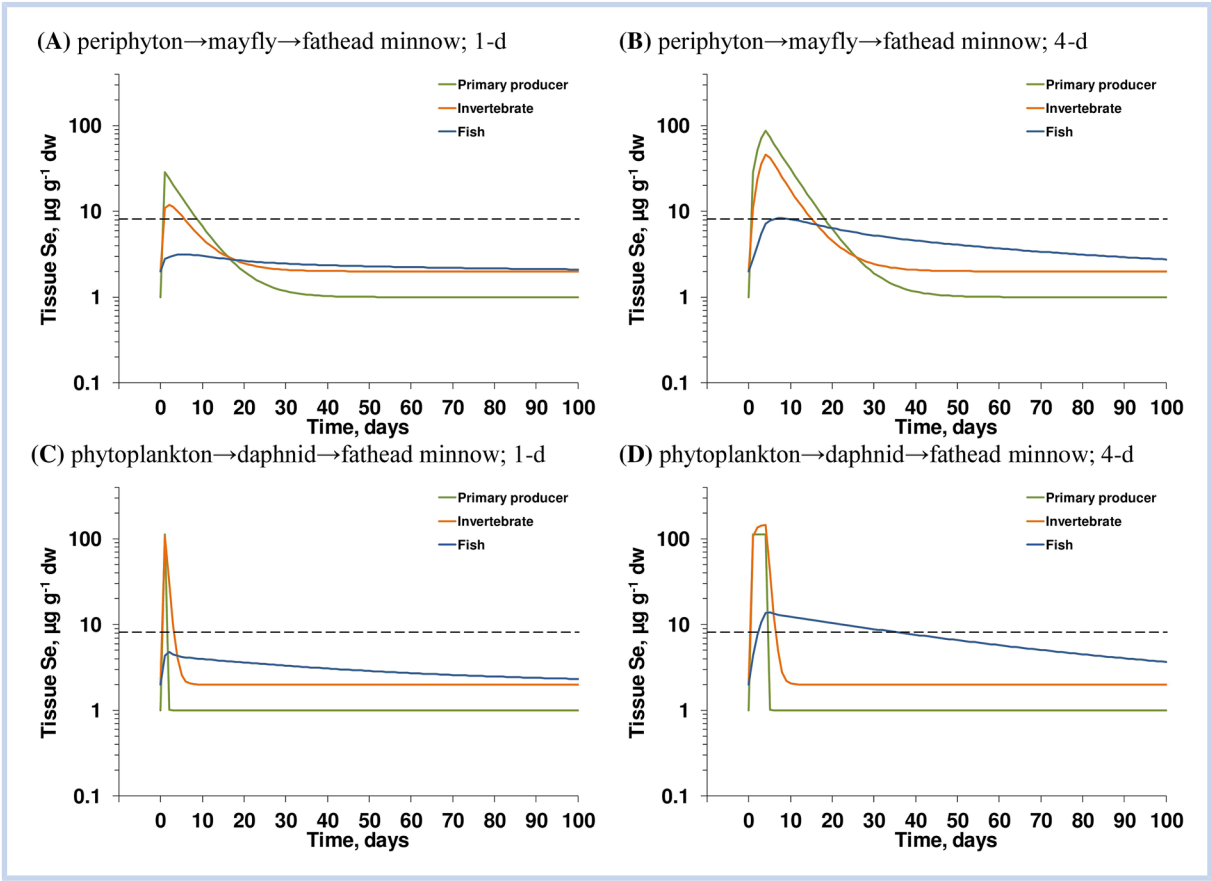

Figure 3. Selenate pulses into a periphyton→mayfly→fathead minnow food chain (**A** and **B**; Model 1 in Table 3) and a phytoplankton→daphnid→fathead minnow food chain (**C** and **D**; Model 7 in Table 3). Waterborne selenate pulse = 279 µg L^{-1} (draft acute selenate criterion at 50 mg SO_4 L^{-1}); background water selenate = 1 µg L^{-1}. Horizontal dashed lines note whole body fish Se guideline of 8.1 µg g^{-1} dw. Panels **A** and **C** are based on 1-d pulses; Panels **B** and **D** are based on 4-d pulses.

What is the influence of the background water selenium concentration on predicted whole-body fish selenium concentrations?

These evaluations assumed that the background waterborne Se concentration was 1 µg L^{-1}. Using the "average combined" phytoplankton-based models for selenate and selenite, we compared the model predictions based on an assumed background concentration of 1 µg L^{-1} versus background concentrations of 5 and 10 µg L^{-1} (which may represent some reference streams in naturally high seleniferous regions). Although the background waterborne Se assumption obviously controls predicted steady-state Se concentrations in fish, it has a small influence on maximum predicted whole-body fish Se concentrations after pulse exposures, especially based on a 4-d pulse (Supplemental Data Figure S12). For example, a 5-fold increase in the background water Se concentration in the "average combined" phytoplankton-based model for selenate (i.e., 1–5 µg L^{-1}) results in a 3% increase in the maximum predicted whole-body Se concentration after a 1-d pulse and essentially a 0% increase after a 4-d pulse. The phytoplankton-based food chain for selenite predicts a background whole-body fish Se concentration greater than 8.1 µg g^{-1} dry wt when a background water Se concentration of 10 µg L^{-1} is assumed (Supplemental Data Figure S12).

The above suggests that the background waterborne Se concentration assumed in the model is not important to the magnitude of the pulse, at least when considering background waterborne Se concentrations that are less than or equal to the current chronic criterion of 5 µg L^{-1}. However, the background waterborne Se concentration can have a greater influence on the duration over which a tissue-based toxicity threshold is exceeded (Supplemental Data Figure S12). This could influence whether the tissue Se concentration persists for a duration such that chronic toxicity may be expected.

How do predicted whole-body fish selenium concentrations compare between single- and multiple-pulse scenarios?

These evaluations focused on single-pulse Se exposures. We also evaluated the influence of multiple Se pulses on the biokinetic model and predicted Se concentrations in whole-body fish tissue. Of particular interest was whether individual pulse scenarios not resulting in predicted whole-body Se concentrations greater than 8.1 µg g^{-1} could result in an exceedance of this concentration if multiple instances of the same pulse scenario occurred. The key term in the biokinetic model for this evaluation is the combined ($k_e + g$) term, which defines the rate at which Se is eliminated from the fish and food chain organisms. If the duration for Se to reach steady-state in fish tissue is shorter than the duration between Se pulses, the baseline Se concentration in fish will be greater, and whole-body Se concentrations in the subsequent pulse may be greater. This is demonstrated in Figure 5, in which a single Se pulse of 200 µg L^{-1} for 4 d was insufficient to achieve a predicted whole-body fish Se concentration of greater than 8.1 µg g^{-1} dry wt, but when the same pulse occurred every 30 d, the 3rd event did result in a predicted whole-body Se concentration greater

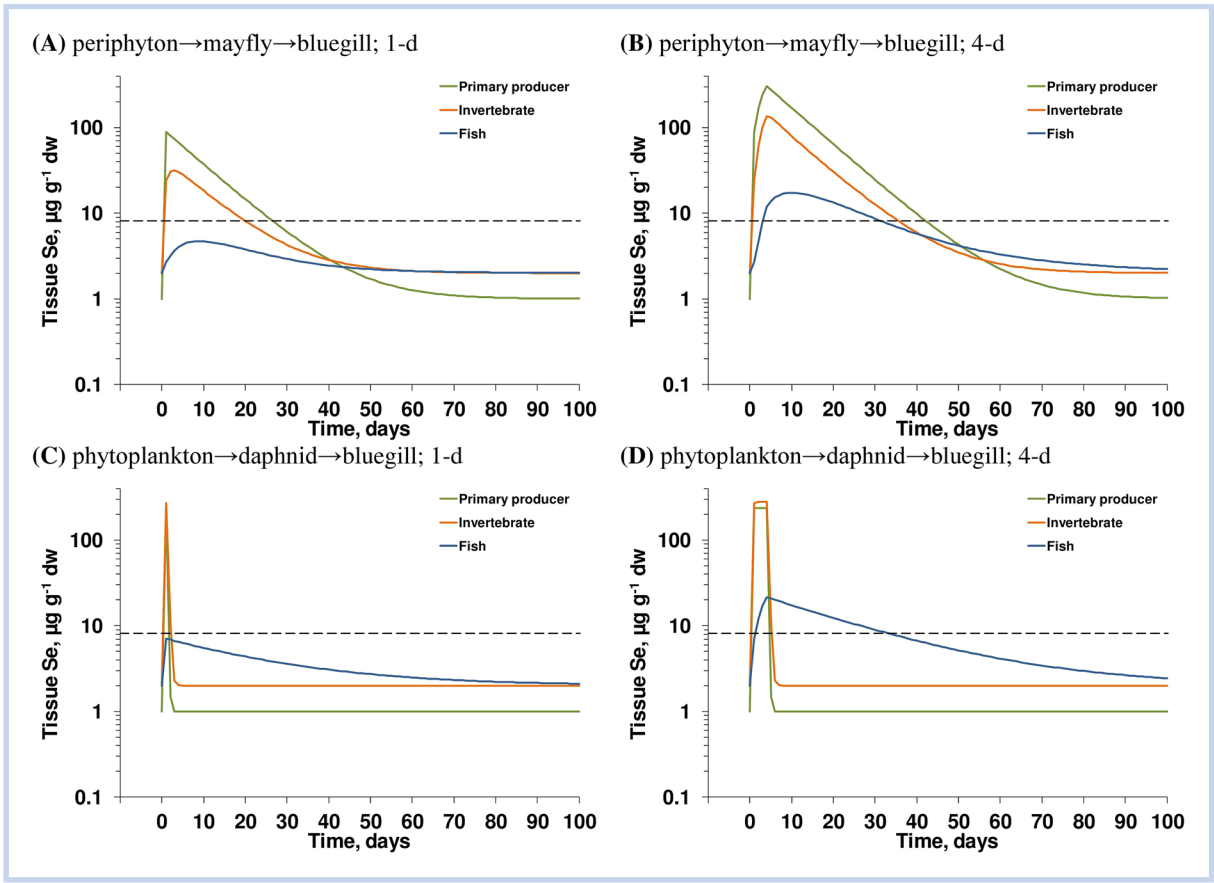

Figure 4. Selenite pulses into a periphyton→mayfly→bluegill food chain (**A** and **B**; Model 6 in Table 3) and a phytoplankton→daphnid→bluegill food chain (**C** and **D**; Model 9 in Table 3). Waterborne selenite pulse = 258 µg L^{-1}; background water selenite = 1 µg L^{-1}. Horizontal dashed lines note whole body fish Se guideline of 8.1 µg g^{-1} dw. Panels **A** and **C** are based on 1-d pulses; Panels **B** and **D** are based on 4-d pulses.

than 8.1 µg g^{-1} dry wt. Even though predicted Se concentrations in periphyton and mayflies returned to steady-state within 30 d, the much slower Se elimination rate from fish precluded whole-body Se concentrations from reaching steady-state before the next pulse.

What is the potential influence of concentration-dependant uptake rate constants on predicted food chain selenium concentrations?

A 5th objective was to evaluate the influence of concentration-dependent uptake rate constants (k_u) on the biokinetic model predictions. Inverse relationships between k_u and exposure concentration could be derived for phytoplankton (*C. reinhardtii*) exposed to selenate and selenite, *D. magna* exposed to waterborne selenate and selenite and dietborne Se, and bluegill exposed to waterborne selenate and dietborne Se (Tables 1 and 2; Figures S1–S5 in Supplemental Data S1). Thus, we modeled an Se pulse into a phytoplankton→daphnid→bluegill food chain using k_u values that were treated as constants across all exposure concentrations versus concentration-dependent values. We assumed a pulse selenate concentration of 200 µg L^{-1} for 4 d. The use of concentration-dependent k_u values had a negligible influence on predicted Se concentrations in phytoplankton, but a large influence on predicted Se concentrations in daphnids and bluegill (Figure 6). Using the concentration-dependent k_u values, the maximum predicted Se concentrations in *D. magna* and bluegills were 27 and 3.8 µg g^{-1} dry wt, respectively, compared with 90 and 13 µg g^{-1} dry wt, respectively, when the k_u was held constant. It is possible the k_e could also be concentration-dependent, but no clear patterns were observed based on the available data sets. This example highlights the potential importance for measuring k_u values as a function of exposure concentration.

DISCUSSION

Model uncertainties and data gaps

Overall, robust biokinetic Se data are only available for a limited number of primary producers, invertebrates, and fish species. The greatest uncertainty is perhaps associated with the limited data available for primary producers, which is the key point of Se uptake into aquatic food chains. Biokinetic Se data for periphyton are available from 2 separate studies, which showed good agreement in Se uptake and elimination rates (i.e., varied by less than a factor of 2). However, biokinetic Se data were only identified for 1 freshwater phytoplankton species (*C. reinhardtii*), which had very high uptake and elimination rate constants (likely because of the higher surface-area-to-volume ratio of unicellular phytoplankton compared with periphyton). As such, the model food chains consisting of phytoplankton predicted higher Se concentrations in invertebrates and fish in pulse exposure scenarios than model food chains consisting of periphyton (even though periphyton were predicted to have higher EFs than phytoplankton under steady-state conditions; Table 1). Overall, Se uptake and elimination rate constants were much less variable between invertebrate species and between fish species.

Table 4. Selenate and selenite pulse concentrations predicted to result in the whole-body fish Se threshold of 8.1 μg/g dw or exceed it for 7 days. A background water Se concentration of 1 μg L^{-1} was assumed

			Se Pulse Concentration (μg L^{-1})			
			1-d Pulse		4-d Pulse	
Se Form	Model No.	Model Food Chain	WB Fish Se = 8.1 μg g^{-1}	WB Fish Se > 8.1 μg g^{-1} for 7 days (Max. WB Fish Se, μg g^{-1})	WB Fish Se = 8.1 μg g^{-1}	WB Fish Se > 8.1 μg g^{-1} for 7 days (Max. WB Fish Se, μg g^{-1})
Selenate	1	Periphyton→Mayfly→FHM	1470	1633 (8.8)	270	294 (8.7)
	7	Phytoplankton→Daphnid→FHM	613	813 (10.1)	143	167 (9.2)
	10	Periphyton→Invert→Fish	453	777 (12.5)	99	139 (10.7)
	11	Periphyton→Invert→Fish	226	450 (14.3)	53	80 (11.3)
	12	Phytoplankton→Invert→Fish	329	570 (12.6)	72	101 (10.7)
	13	Phytoplankton→Invert→Fish	142	285 (14.4)	34	51 (11.4)
		Current selenate acute criterion[1] = 12.2 μg L^{-1}				
		Draft selenate acute criterion[2,3] = 279 μg L^{-1}				
		Previous total Se acute criterion[4] = 20 μg L^{-1}				
Selenite	6	Periphyton→Mayfly→Bluegill	578	621 (8.6)	104	111 (8.5)
	9	Phytoplankton→Daphnid→Bluegill	313	397 (9.7)	82	103 (9.8)
	14	Periphyton→Invert→Fish	136	175 (9.9)	33	40 (9.6)
	15	Periphyton→Invert→Fish	61	85 (10.6)	16	20 (10.3)
	16	Phytoplankton→Invert→Fish	128	187 (11.0)	33	43 (10.0)
	17	Phytoplankton→Invert→Fish	56	95 (12.4)	16	23 (11.5)
		Current selenite acute criterion[1] = 185.9 μg L^{-1}				
		Draft selenite acute criterion[2] = 258 μg L^{-1}				
		Previous total Se acute criterion[4] = 20 μg L^{-1}				

[1]USEPA (1999).
[2]USEPA (2004), never finalized.
[3]Based on a sulfate concentration of 50 mg L^{-1} (USEPA 2004).
[4]USEPA (1987).
FHM = fathead minnow; WB = whole-body.

Only 1 study that explicitly evaluated the influence of pulse waterborne Se exposures on Se enrichment and trophic transfer in aquatic food chains was identified. Maier et al. (1998) monitored Se concentrations in water, aquatic plants, and aquatic invertebrates in a stream system (first- and second-order streams) that received a 1-time application of a commercial seleniferous fertilizer (Selcote) that contained 1% Se by weight (as sodium selenite). The water Se concentrations were less than 1 μg L^{-1} before treatment, 10.9 (±0.7) μg L^{-1} 3 h posttreatment, and then again less than 1 μg L^{-1} from 11 d through 11 months posttreatment. The mean (±SD) Se concentration in plants significantly ($p < 0.05$) increased from 0.62 (±0.11) μg g^{-1} dry wt before treatment to 1.16 (±0.32) μg g^{-1} dry wt at 11 d posttreatment, and then declined to 0.51 μg g^{-1} dry wt by approximately 4 months posttreatment. In invertebrates, the mean (±SD) Se concentration was 1.67 (±1.65) μg g^{-1} before treatment and then significantly ($p < 0.05$) increased to 4.74 (±1.73) μg g^{-1} at 11 d posttreatment. Mean Se concentrations from approximately 2 months through 11 months posttreatment ranged from 4.02 to 4.99 μg g^{-1} dry wt. The selenite biokinetic models considered in this evaluation would not have predicted that invertebrate Se concentrations would remain relatively unchanged from approximately 11 d through 11 months posttreatment; however, how relevant this particular formulation would be to short-term pulses of dissolved selenite is unclear, because current Selcote formulations are based on granules consisting of both slow- and fast-release forms, suggesting that this may have the potential to behave more like a long-term exposure than a pulse effect. No studies were

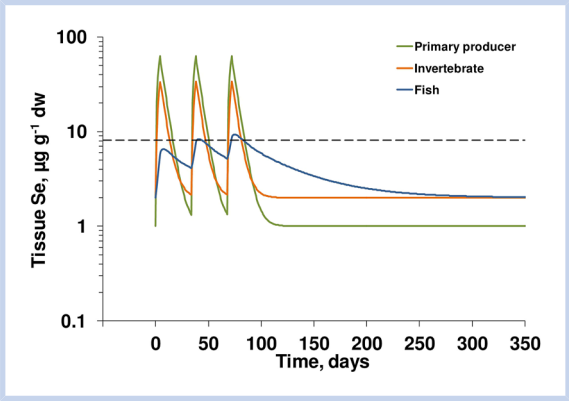

Figure 5. Example of 3 selenate pulses of equal magnitude (200 µg L^{-1}) and of equal duration (4 d) occurring with a frequency of every 30 d. Selenate pulses in a periphyton→mayfly→fathead minnow food chain (Model 1 in Table 3). Background water selenate = 1 µg L^{-1}; horizontal dashed line notes whole body fish Se guideline of 8.1 µg g^{-1} dw.

identified that explicitly evaluated the bioaccumulation of Se in an aquatic food chain after a pulse exposure of selenate.

Implications for acute waterborne selenium criteria

The food chains with phytoplankton as the primary producer required lower pulse selenate concentrations to reach the whole-body fish Se concentration of 8.1 µg g^{-1} dry wt, because phytoplankton have a greater k_u than periphyton. Of the model food chains evaluated, the "worst-case" model was the "maximum combined" food chain. The 1-d and 4-d pulse selenate concentrations of 144 and 35 µg L^{-1}, respectively, that were predicted to result in the whole-body fish Se threshold of 8.1 µg g^{-1} are greater than the current selenate criterion of 12.82 µg L^{-1} and the previous acute Se criterion of 20 µg L^{-1} (which did not differentiate for Se speciation).

As also observed for selenate, the food chains with phytoplankton as the primary producer also required lower pulse selenite concentrations to reach the whole-body fish Se concentration of 8.1 µg g^{-1} dry wt, because phytoplankton have a greater k_u than periphyton, and the "worst-case" model was the "maximum combined" food chain. The 1-d and 4-d pulse selenite concentrations of 57 and 16 µg L^{-1}, respectively, that were predicted to result in the whole-body fish Se threshold of 8.1 µg g^{-1} are less than the current selenite criterion of 185.9 µg L^{-1}, and the 4-d pulse concentration was also less than the previous acute Se criterion of 20 µg L^{-1} (which did not differentiate for Se speciation).

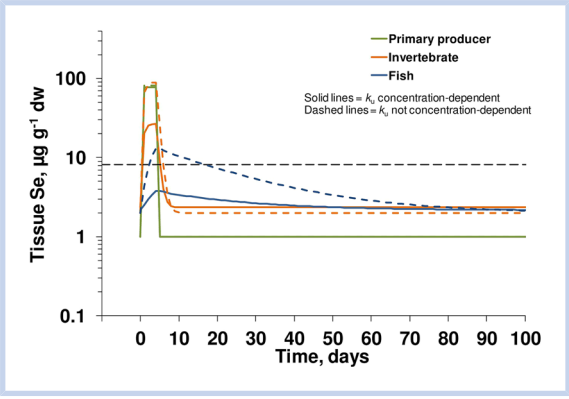

Figure 6. Comparison of phytoplankton→daphnid→bluegill food chain model where k_u was either a constant over all exposure concentrations or where it varied as a function of exposure concentration. Selenate pulse of 200 µg L^{-1}; pulse duration of 4 d; background water selenate = 1 µg L^{-1}; horizontal dashed line notes whole body fish Se guideline of 8.1 µg g^{-1} dw. The solid and dashed lines for primary producers are largely indistinguishable at the figure scale.

Overall, the modeling results indicate that the current acute selenate criteria are protective of both 1-d and 4-d pulse exposures that could result in a whole-body fish Se threshold of 8.1 µg g^{-1} dry wt. For selenite, the modeling results indicate that the current acute selenite criterion may not be protective of either 1-d or 4-d pulse exposures.

We also applied our biokinetic Se models to predict the whole-body fish Se concentrations from the USEPA's draft intermittent Se exposure criteria. Based on 1-d and 4-d pulse scenarios, and a background waterborne Se concentration of 1 µg L^{-1}, the USEPA's draft intermittent Se exposure criteria are 115 and 30 µg L^{-1}, respectively, for lotic systems and 10 and 3.3 µg L^{-1}, respectively, for lentic systems. With the exception of the "maximum combined" periphyton-based model food chain (model 15) for selenite, predicted whole-body fish Se concentrations were less than 8.1 µg g^{-1} dry wt (Supplemental Data Figure S11). This indicates that the draft intermittent exposure criterion for Se, under the pulse scenarios evaluated, would be protective against selenate pulses into both lotic and lentic systems and selenite pulses into lentic systems, but not always protective against selenite pulses into lotic systems.

Finally, we observed cases in which a single Se pulse scenario did not result in exceedance of the whole-body fish Se threshold of 8.1 µg g^{-1} dry wt but was exceeded when the same pulse scenario was repeated in successive 30-d intervals (Figure 5). This was driven by the relatively low elimination rate constants for fish, which did not allow for steady-state Se concentrations in fish to be achieved before the next pulse. This potentially has important implications for acute or intermittent Se criteria that are bioaccumulation-based rather than based on direct short-term toxicity.

Recommendations for future studies

Because primary producers are the important point of entry for Se into aquatic food chains, biokinetic studies on multiple primary producers are needed. Given the importance of periphyton at the base of food chains in many lotic systems, particularly mountainous systems that are often of interest for Se because of mountaintop coal and phosphate mining, studies of various periphyton assemblages would help to better understand potential variability in Se uptake and elimination rates. In addition, biokinetic studies with algal species, where the full range of biokinetic parameters were evaluated (k_u, k_e, g), are limited, and studies with macrophytes appear to be completely lacking. All of the current models assume the kinetics of Se transfer to fish are equivalent between the whole-body and egg-ovary compartment. Gaining an understanding of any potential differences in Se kinetics between these 2 compartments and how that might influence our understanding of toxicity from Se pulses would be of considerable value. Understanding the timing of Se pulse exposures relative to the timing of vitellogenesis in fish species of varying reproductive strategies, which is important for understanding the relationship between pulse exposure scenarios and potential effects on offspring after maternal transfer, also would be valuable.

The influence of water chemistry parameters, such as sulfate, on Se uptake rates in primary producers also should be a point of

emphasis in future studies. Sulfate has been shown to clearly reduce selenate bioavailability in algae and macrophytes under longer-term exposures (Williams et al. 1994; Lo et al. 2012; Nautilus Environmental 2013), but the influence of sulfate on selenate uptake rates has not been robustly evaluated. If biokinetic Se models are going to have increased utility in the future, the influence of parameters such as sulfate should be accounted for. Nitrate and phosphate also have been shown to have an influence on Se bioavailability (Yu and Wang 2004a).

In addition to nitrate and phosphate potentially influencing Se bioavailability, the concentrations of these nutrients in water also have an important influence on growth rates of algae and other primary producers. Highly productive systems would be likely to support much higher growth rates, which may result in lower Se concentrations because of growth dilution. Explicitly understanding how nitrate and phosphate influence the growth rate constant (g) also has important implications in biokinetic Se modeling.

The limited evaluation presented here on how Se uptake rate constants are concentration dependent suggested that this may be important in modeling over a wide range of Se exposure concentrations. This is particularly true when uptake rate constants are available from studies with intermediate Se concentrations. In such cases, the uptake rate constants may underestimate food chain Se concentrations under baseline conditions and overestimate food chain Se concentrations resulting from high pulse Se concentrations. The former can in part be accounted for by defining baseline Se concentrations in tissue, but the latter cannot be reasonably accounted for. We suggest that future biokinetic studies with Se be conducted over a range of Se exposure concentrations with a sufficient number of treatments to define concentration-dependent k_u and k_e parameters.

Mesocosm or field studies to validate the models presented here, or updated models as new biokinetic data become available, are critical for understanding whether these models are providing meaningful estimates of Se uptake, transfer, and elimination in aquatic food webs.

Finally, we emphasize that the models evaluated and presented here are intended to be representative of Se pulses primarily into aquatic food chains, where waterborne Se is the initial compartment. The periphyton-based model food chains were considered more representative of a lotic system with short residence times and minimal accumulation of fine sediments, which limit Se cycling, whereas the phytoplankton-based model food chains were considered more representative of a lentic system. For the latter, biogeochemical cycling of Se can be much more complex because of longer residences times and accumulation of fine sediments and detritus that can act as significant Se sources. In such systems, lower waterborne Se concentrations, including those from pulse events, can result in higher tissue Se concentrations. Along those same lines, the downstream fate of Se into lentic systems needs to always be considered (e.g., oxbows, lakes).

CONCLUSIONS

Biokinetic modeling of Se in model aquatic food chains provides a valuable tool for evaluating whether acute water quality criteria based on direct Se toxicity may be protective of bioaccumulation-based toxicity in fish. Biokinetic Se models also provide a promising tool for temporally colocating Se concentrations in multiple food chain components as part of field monitoring programs in support of Se bioaccumulation modeling and for assessing how Se concentrations in aquatic food chains respond to time-varying or seasonal changes in waterborne Se concentrations. Because uptake and elimination rate constants for Se at the base of the aquatic chain are limited to 2 periphyton assemblages and 1 phytoplankton species, biokinetic Se data for additional assemblages and species of primary producers would help broaden our understanding of how Se biokinetics may vary in different food chains. Future biokinetic Se studies should also focus on how Se uptake and elimination rates vary over a range of Se concentrations in water or diets. Additionally, water quality parameters such as sulfate are known to influence the bioavailability of selenate, but biokinetic studies conducted to date have not been conducted over a range of sulfate concentrations. Finally, validation of Se uptake, transfer, and elimination in aquatic model food chains using mesocosm or field studies are needed.

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SUPPLEMENTAL DATA

Supplemental Data S1. Supplemental information on studies reviewed for selenium biokinetic data and associated Figures S1-S5 and Tables S1-S10.

Supplemental Data S2. Supplemental Figures S6-S12.

Supplemental Data S3. Supplemental Tables S13 and S14.

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