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Viewpoint

Emerging Opportunities in Management of Selenium Contamination[1]

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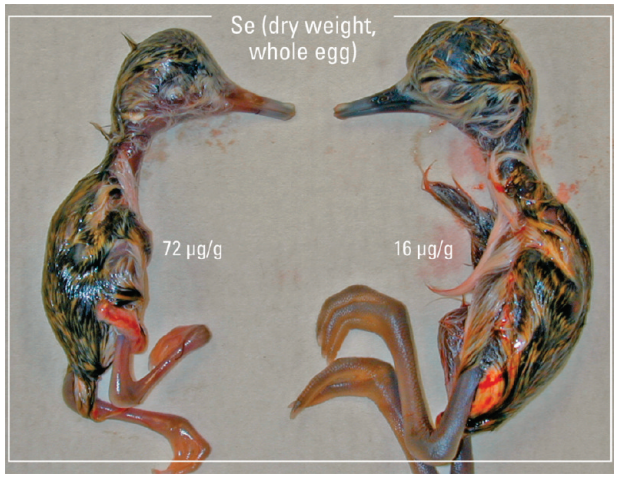
Integrating the chemistry of selenium with its biology and ecotoxicology gives indications on how to regulate its environmental levels.



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There probably is no chemical contaminant for which there are more contradictions about ecological risks in aquatic environments than selenium (Se). The detrimental effect on policy is evidenced by wide differences in regulations among jurisdictions and environments. In Europe, Se is not considered an ecological threat. It is not listed among chemicals of concern in the European Commission's Dangerous Substance Directive. Nor is it among the 41 chemicals for which Environmental Quality Standards are applicable (*1*). Although revisions are being proposed, U.S. Se guidelines for marine waters allow a maximum concentration of 300 µg/L Se and a continuous concentration of 71 µg/L Se (*2, 3*). What evidence is available from estuarine environments suggests that these guidelines are seriously under-protective for at least some predator species (*4*−*6*). In contrast, Canada's marine and freshwater guidelines are 2 µg/L (*7*). The EPA's freshwater criterion is 5 µg/L, with a lower guideline of 2 µg/L for some wetland environments in California (*2, 8*).

Reducing such disparities and internationally harmonizing management of ecological risks from Se is important. Selenium contamination is often of regional scale (*9*) and/or threatens ecological resources, like migratory birds, on scales that cross international boundaries (*10*). The costs of managing Se risks increase where regulations are not based upon convincing scientific evidence. There is also a likelihood that Se issues will grow in the years ahead with the exploitation of coal and similar fossil fuels, irrigation in semiarid regions, and mining of phosphate ore (*9*). Finally, Se is a bioaccumulative pollutant of substantial toxicity, but only if toxicity is determined from diet, not dissolved exposure (*11*).

The purpose of this Viewpoint is to suggest that a globally consistent regulatory approach to Se is feasible. Such an approach will require accepting advances in knowledge that question some traditional regulatory paradigms for metals and metalloids. Better recognition of the science underlying these conclusions could be a positive precedent for reconsidering management guidelines for other contaminants where controversies are common.

Ecosystem-Scale Selenium Model

Uncertainties in protective criteria for Se derive from a failure to systematically link biogeochemistry to trophic transfer and toxicity (Figure 1). In nature, adverse effects from Se are determined by a sequence of processes (*12*). Dilution and redistribution in a water body determine the concentrations that result from mass inputs. Speciation affects transformation from dissolved forms to living organisms (e.g., algae, microbes) and nonliving particulate material at the base of the food webs. The concentration at the base of the food web determines how much of the contaminant is taken up by animals at the lower trophic levels. Transfer through food webs determines exposure of higher trophic level animals such as fish and birds. The degree of internal exposure in these organisms determines whether toxicity is manifested in individuals. Se is first and foremost a reproductive toxicant (both a gonadotoxicant and a teratogen): the degree of reproductive damage determines whether populations are adversely affected. Adverse effects on reproduction usually occur at lower levels of exposure than acute mortality, but such effects can extirpate a population just as effectively as mortality in adults (*4, 13*).

The disparities among regulations result from different approaches to linking toxicity and dissolved Se. The lack of regulation in Europe and some regulations in the U.S., such as those for the marine environment, rely upon toxicity tests that directly expose animals to dissolved contaminants. Other approaches, such as freshwater regulations, consider field data but do not take into account important, but variable, ecosystem processes. Differences in assumptions about those

[1] Editor's Note: To our delight at *ES&T*, we have started to receive Features and Viewpoints by independent author(s) coincidentally overlapping both in topic and review schedule. Within days of this paper's acceptance another concerning metals in the environment was accepted. The choice was thus made to present both manuscripts in the same issue (November 15, 2009; *43* [22]). Readers of this piece by Luoma and Presser are therefore encouraged to read that by Menzie et al. (DOI 10.1021/es9006405).

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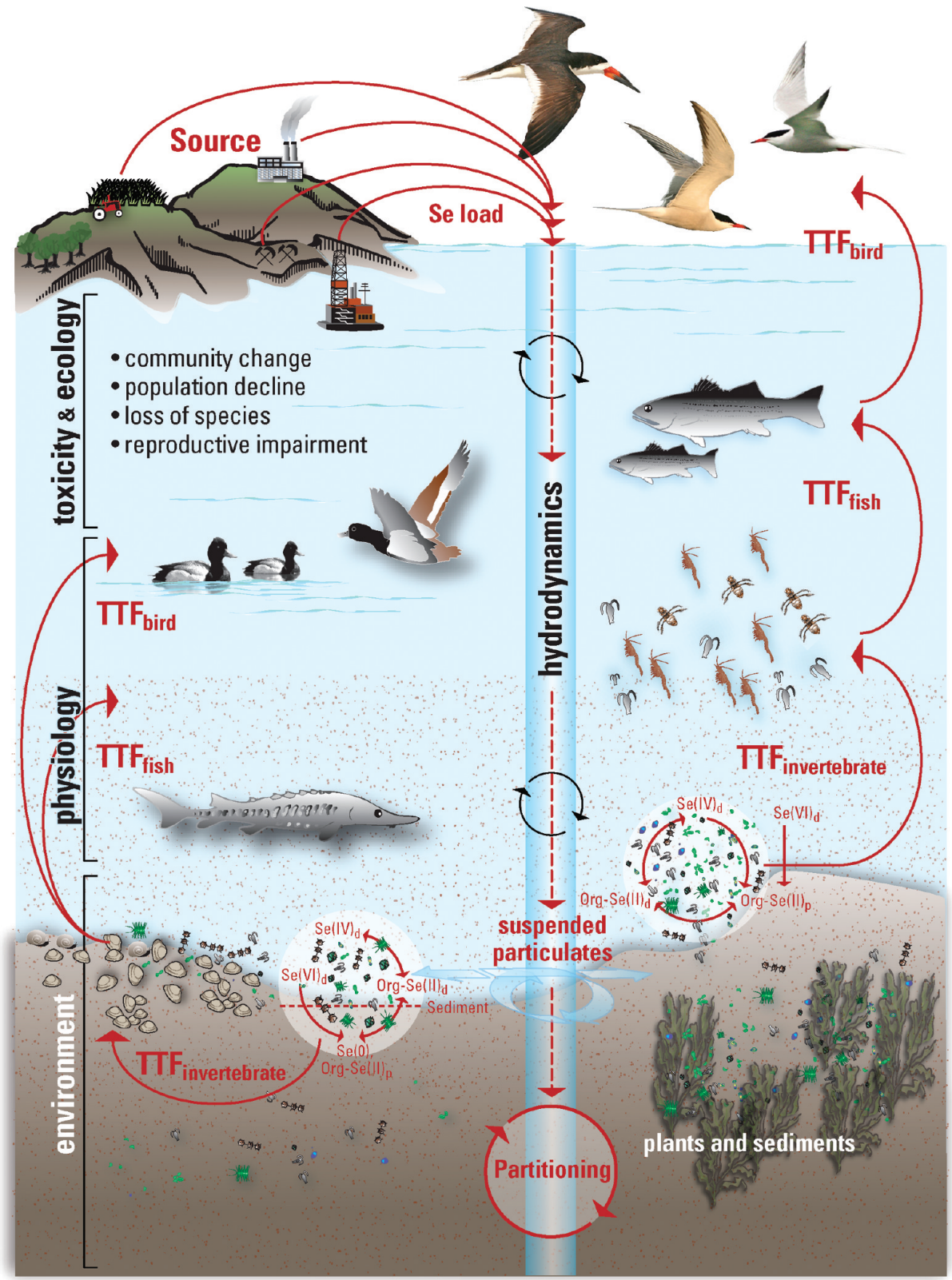

FIGURE 1. Conceptual model of Se fate and effects emphasizing the roles of speciation, biogeochemical transformation, and trophic transfer factors in modeling two aquatic food webs: a water column food web and a benthic food web. TTF = trophic transfer factor. Subscript d means dissolved, subscript p means particulate.

processes are usually at the heart of the controversies over what Se concentration is protective in any given environment. Progressively considering each step in the ecosystem sequence described above provides a systematic protocol for evaluating Se risks at any location.

Biogeochemistry

Speciation. As with all trace elements, Se speciation has important influences on the fate of the element (Figure 1). Selenium is a metalloid with anionic speciation in water, so

the primary species are selenate (SeO_4^{2-} or Se[VI]), selenite (SeO_3^{2-}, or Se[IV]) and organo-selenide (e.g., selenomethionine or org-Se[II]). Unlike most trace elements, the distribution of Se among dissolved species cannot be predicted from thermodynamics alone. Biological (kinetically driven) processes are just as important as geochemical processes in determining the forms of Se that are present (*14*). Biological processes are difficult to predict from environmental characteristics, so conventional speciation modeling is problematic for Se. On the other hand, Se is one of the few elements for which the different species can be directly analyzed at environmental concentrations (*14, 15*). These data show that geologic and anthropogenic sources often release mostly SeO_4^{2-} (*8*), which is not reactive with particle surfaces, although some types of bacteria convert SeO_4^{2-} to elemental Se in sediments (Figure 1; (*16*)). SeO_4^{2-} in the water column is taken up only slowly, especially if competition with sulfate (SO_4^{2-}) is involved. SeO_3^{2-} and organo-selenide are much more reactive. If any form of Se is taken up at the base of the food web by plants and microbes, it is converted to organo-selenide (Figure 1; (*17*)). Organo-selenide is released back to the water column as these cells die or are consumed (Figure 1; (*18*)), where some SeO_3^{2-} is formed. But neither SeO_3^{2-} nor organo-selenides are reconverted to SeO_4^{2-} because the back reaction has a half time of hundreds of years (*14*). The result is a build-up of proportionately more organo-selenides and SeO_3^{2-} as Se is recycled through the base of food webs, and proportionately less SeO_4^{2-}. For example, Se is nearly 100% SeO_4^{2-} in streams and irrigation water in the San Joaquin River watershed in California. Downstream in the delta of the San Joaquin River, SeO_3^{2-}, organo-selenide, and SeO_4^{2-} are in equal abundance (*15*). In the Pacific Ocean the metalloid is nearly 100% SeO_3^{2-} and organo-selenide (*14*). This unidirectional build-up of potentially reactive forms, especially in environments where water residence times are extended (e.g., wetlands, estuaries) is a key factor in the ecological risks posed by Se.

Transformation to Particulate Forms. Speciation has a very important influence on the concentration of Se accumulated in algae, microbes, seston (particulate matter in seawater), or sediments (*5*), although other complex biogeochemical processes are also involved. In general, Se concentrations in algae, microbes, sediments, or suspended particulates are 100−500 times higher than dissolved concentrations in SeO_4^{2-} dominated environments such as streams and rivers. But when SeO_3^{2-} or organo-selenide are proportionately more abundant, the ratio can be 1000−10,000, such as in wetlands, some estuaries, the oceans, and pure phytoplankton cultures. This variability of particulate concentrations relative to dissolved concentrations is a major cause of the variability in the correlation between Se in water and Se in organisms (*19*).

Trophic Transfer

Bioaccumulation. Dissolved Se uptake is slow by animals, whatever the form (*20*). Therefore, dissolved Se makes little or no direct contribution to bioaccumulation and toxicity in animals (Supporting Information (SI); *1, 6, 13*), and only influences the concentration of Se in particulate matter. It is this particulate matter, both abiotic and biotic, that is the port of entry of Se at the base of the food web when consumed at the second trophic level. Concentrations of Se associated with particulate matter (in μg/g) determine the degree of bioaccumulation by the animal consuming the particle.

Passage through the food web becomes predictable once concentrations of Se at the base of the food web are known. For each species a trophic transfer factor (TTF) can be derived from either experimental studies or field observations, where the TTF defines the relationship between Se concentrations in an animal and in its food. Experimental derivation of TTFs is based upon the capability of a species to accumulate Se from dietary exposure as expressed in the biodynamic equation (*21*):

$$dC/dt = (AE \times IR \times C_{food}) - (k_e + k_g) \times C \qquad (1)$$

where C is the contaminant concentration in the animals (μg/g), t is the time of exposure (d), AE is the assimilation efficiency from ingested particles (%), IR is the ingestion rate of particles (g/g·d), C_{food} is the contaminant concentration in ingested particles (μg/g), k_e is the efflux rate constant (/d), and k_g is the growth rate constant (/d). The equation shows that key determinants of Se bioaccumulation are the ingestion rate of the animal, the efficiency with which Se is assimilated from food, and the rate constant describing Se turnover or loss from the tissues of the animal. All three can be determined experimentally (*21*). AEs of Se from living material (e.g., phytoplankton) are typically >50% and for some feeding relationships may be >80% (*22*). The high AEs also help explain the dominance of Se uptake from food over that from water. Rate constants of loss vary depending upon the species, from approximately 0.2 to 0.02/d (*21, 22*).

The species-specific TTF is then (*23, 24*):

$$TTF = (AE \times IR)/(k_e + k_g) \qquad (2)$$

Steady state concentrations of Se in the species tissues ($C_{ss\text{-}species x}$) can be predicted from:

$$(C_{ss\text{-}species x}) = TTF_{species x} \times C_{food\ of\ species x} \qquad (3)$$

Experimental data deriving TTFs are available for a number of invertebrates and fish species (Figure 2, SI 2). To validate the TTFs, predictions of Se bioaccumulation can be compared to independent determinations of Se concentrations in that same species in the field. Strong agreement is usually found in such comparisons (*6, 21*). The TTF can also be derived from field data by comparing Se concentrations in a consumer or predator and its specific food at the site of interest. Uncertainties about feeding relationships and/or the complexity of feeding in some species add to the uncertainty of the field-derived values, however.

Once trophic transfer factors are known, Se at higher trophic levels can be modeled by combining the biogeochemically derived concentration at the base of the food web with trophic transfer factors at each trophic level:

$$(C_{ss\text{-}predator2}) = (C_{particulate} \times TTF_{consumer}) \times TTF_{predator1} \times TTF_{predator2} \qquad (4)$$

Particulate (base of food web) concentrations can be linked to dissolved Se by determining the site-specific ratio of the two directly, or by estimates based upon the dissolved concentrations alone and consideration of the hydrologic character of the water body (e.g., lentic [still] or lotic [flowing] environment) and/or speciation data, if available. However, the less data, the more uncertain is the estimate of particulate concentration. Thus eq 4 allows determination of site-specific predator concentrations from dissolved concentrations. One value of such a model lies in its ability to address implications to the food web of changes in concentration, speciation, or biogeochemical conditions that might affect particulate concentrations. Dissolved concentrations can also be back-calculated from the bioaccumulated Se in a predator or prey organism, to address questions about dissolved concentrations necessary to achieve a targeted concentration in a given trophic level organism (e.g., a predator).

Among the 21 invertebrates and fish species for which TTFs are available from laboratory studies, values range from 0.6 to 23 (Figure 2). About 76% of the species studied have TTFs ≥ 1 under typical environmental conditions. Most

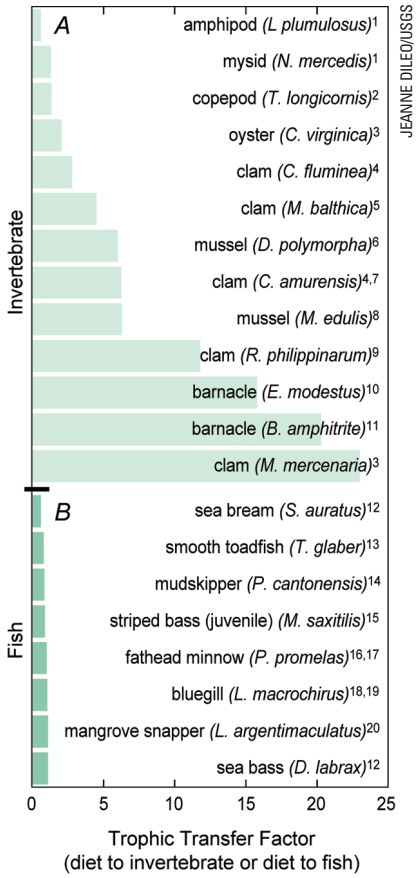

FIGURE 2. Trophic transfer factors for (a) invertebrates and (b) fish that were derived from laboratory studies that define the crucial model components described in eq 1. (Reference citation is denoted with species name; see SI 2 for references).

species bioaccumulate as much as or more Se than that of the trophic level below them; many bioaccumulate considerably more. Thus the concentration of Se biogeochemically transformed into algae, microbes, seston, or sediments is preserved and/or (bio)magnified as Se passes up food webs. From the viewpoint of managing risks, Se therefore qualifies as a bioaccumulative chemical, one of the criteria for substantial potential for ecological risk. To reach this conclusion, however, one must accept the primacy of trophic transfer in evaluating ecological risks.

TTFs appear to be more variable among invertebrate species at the second trophic level than among the fish species that have been studied to date (Figure 2). The 38-fold variability among invertebrate species is driven by physiological differences in assimilation efficiency and the rate constant of loss of Se from different species (*22*). Trophic transfer factors from the available data for fish, on the other hand, have a median of ~1. Thus, biogeochemical transformation determines the concentration of Se available to the food web, but variability in the TTF at the consumer trophic level is very influential in determining how much Se different predators accumulate.

Although not yet thoroughly studied, it is likely that there is variability in TTF within species as food sources change and perhaps as concentrations change. This variability is probably smaller than the variability among species in the most common environmental conditions. It is certainly smaller than the variability found when comparing Se concentrations in an animal to that of water (*25*).

Selenium concentrations differ among predator species in the same environment, but, where studied, those differences are driven by differences in choice of prey (*26*). Identifying food web relationships is thus extremely important to understanding, predicting, and managing ecological risks from Se. For example, a long-standing source of confusion in San Francisco Bay was the observation that some fish and bird species important to the bay (e.g., sturgeon) are sufficiently contaminated with Se to suggest risk to their reproduction while others (e.g., striped bass) show little contamination in their tissues. It is now clear that partitioning of ecological risk into some food webs but not into others, driven by a difference in uptake by prey species, could be typical of Se in many environments and should be expected by risk assessors.

One reason that bioaccumulated Se is a valuable piece of data for Se ecotoxicology, is that it can be correlated (as a measure of dose) with signs of toxicity in birds and fish (SI 1). Se is a strong reproductive toxicant and a teratogen, as graphically shown in the lead picture for this article. In that case, sibling black-necked stilt (*Himantopus mexicanus*) embryos were collected from a single nest on the same day from a Tulare Basin evaporation pond in California in 2001. The overtly teratogenically affected embryo on the left, exhibiting stunted growth, no eyes, and deformed bones (in right foot), contained 72 μg/g whole-egg content Se dry weight (dw). The normal sibling, on the right, contained 16 μg/g whole-egg content Se dw. There is some discussion as to what exact Se concentrations in tissue would best protect fish and birds (*5, 19, 27, 28*), but the discussions center around differences that are orders of magnitude smaller than the differences among regulations in dissolved concentrations. Because Se harm manifests primarily on reproductive pathways, processes like fecundity are also influential in determining its ultimate effect(s) on populations. Thus, ecological risk assessment for a specific predator species must consider all three factors involved in toxicity:

(1) the likelihood of high exposures of the organism in the environment as determined by its feeding habits (*viz* does its prey efficiently bioaccumulate Se?);
(2) the inherent sensitivity of the species relative to concentrations in its reproductive tissues as accumulated from diet; and
(3) the demographics of the organism in terms of susceptibility to a reproductive toxicant.

The Path Forward

Regulatory guidelines for Se will differ greatly as long as different jurisdictions rely on upon different types of data. Traditional dissolved toxicity testing, dietary and/or reproductive toxicity testing, and field observations yield very different conclusions about toxicity of Se (see also SI 1). Similarly, the lack of a simple and direct linkage between dissolved Se and Se toxicity adds difficulty in evaluating risks from site to site. Unfortunately, no one universal concentration of dissolved Se can be predictive of toxicity across environments. But if biogeochemical transformation of Se is considered, and linked to trophic transfer through the food web via TTFs, the uncertainties about toxicity and site-specificity can be greatly reduced. More importantly, simple models that link these factors allow new opportunities for evaluating implications of guideline choices. For any specific environment, the most important data include the biogeochemical partitioning ratio within the system, rudimentary knowledge of feeding relationships in the local food webs, TTFs from the base of the food web to the most common consumer organisms, and TTFs from consumers to predators. For modeling, a growing database is available to supply the TTFs. Concentrations at the base of the food web should probably be determined at the site of interest. However, in the absence of site-specific data, generalizations about the values that describe each linkage are possible, although the more general the model the more uncertain will be the assessment.

Perhaps the key observation from nature for any environment is the bioaccumulated/biomagnified concentration of Se either in a predator or its prey. As we show, guidelines based upon bioaccumulated Se (*11, 29*) can be used to derive allowable Se concentrations in water with much less ambiguity than presently exists. The allowable water values would change from environment to environment, but the bioaccumulated Se guidelines would not. Implementation of such an approach initially will be more complex than a simple dissolved Se guideline, in that it would require biological and ecological considerations that are not necessarily within the skill set of all of today's regulators. Perhaps this would be the most important step forward. It could signal the beginning of a new era in management of environmental contamination in which ecology finally becomes as important as toxicity testing in deciphering environmental risks of contaminants (*13*).

Author Biographical Statement. Samuel N. Luoma is a research scientist with the John Muir Institute of the Environment at the University of California Davis, and Emeritus Senior Scientist at the U.S. Geological Survey. The analysis in the present viewpoint partly stemmed from work on the text "Trace Metal Contamination in Aquatic Environments: Science and Lateral Management" by Luoma and coauthor Philip Rainbow (The Natural History Museum, London), published by Cambridge University Press. Theresa Presser is a chemist with the National Research Program of the U.S. Geological Survey. She has conducted research on selenium sources and exposure since her initial investigations at Kesterson National Wildlife Refuge in California in 1983. Luoma and Presser are currently collaborating with the U.S. Environmental Protection Agency and the U.S. Fish and Wildlife Service to develop wildlife selenium criteria for California and in implementing the national aquatic life selenium water quality criterion. Please address correspondence regarding this article to snluoma@usgs.gov.

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Supporting Information Available

SI 1 is a short description of Se toxicity including the limitations of dissolved toxicity testing. SI 2 provides the references from which Figure 2 was derived. (Reference citation is denoted with species name in Figure 2). This information is available free of charge via the Internet at http://pubs.acs.org.

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