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Life Cycle of the Phosphoria Formation: From Deposition to the Post-Mining Environment

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Chapter 11

THE PHOSPHORIA FORMATION: A MODEL FOR FORECASTING GLOBAL SELENIUM SOURCES TO THE ENVIRONMENT

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ABSTRACT

Mining of the Permian Phosphoria Formation – a marine, oil-generating, phosphatic shale – provided the selenium (Se) source implicated in the recent deaths of livestock in southeast Idaho. Field studies and the geohydrologic balance of Se in southeast Idaho confirm risk to animals from exposure to Se through leaching of mined waste shale into streams, discharge of regional drainage, and impoundment of drainage in wetland areas. Forage grown to stabilize waste rock contoured into hills or used as cross-valley fill provides an additional mechanism of Se exposure for the environment (Mackowiak et al., Chapter 19). The average Se concentration of the Meade Peak Member of the Phosphoria Formation is an order of magnitude higher than those of other exploited marine shales that have been linked to incidences of Se toxicosis via oil refining and irrigation in the western United States.

The Phosphoria Formation accumulated in an environment that preserved organic matter and contributed to the formation of economic-grade phosphate and oil deposits. The addition of this phosphate-mining case study enables a comprehensive approach to the identification of marine sedimentary Se sources and a more complete range of ecotoxic field studies on which to establish the conditions and anthropogenic connections that determine uptake, release, and recycling of Se in food webs. A constructed conceptual model of Se pollution indicates that ancient organic-rich depositional marine basins, unrestricted by age, are linked to the contemporary global distribution of Se source rocks. A global plot shows (a) the areal association of major basins hosting phosphate deposits and petroleum source rocks and (b) the importance of paleo-latitudinal setting in influencing the composition of the deposits. Given the geographic patterns, Se emerges as a contaminant within specific regions of the globe that may limit phosphate mining, oil refining, and drainage of agricultural lands because of potential ecological risks to vulnerable food webs. Selenium also may serve as a geochemical exploration tool that signals an ancient productive biological environment.

INTRODUCTION

The initial accumulation and elevated concentrations of phosphate and other trace nutrients in organic-rich marine sedimentary rocks, specifically black shales, petroleum source rocks, and phosphorites, depend on the role of these elements in the primary productivity of the oceans (Sheldon, 1981; Cutter and Bruland, 1984; Piper, 1994). For Se, these fundamental processes extend further to the ability of bacteria, algae, fungi, and plants to synthesize Se-containing amino acids *de novo* (Stadtman, 1974). Once Se-containing biological compounds are established in food webs, they are consumed by progressively more complex species (Presser et al., 1994). Dietary levels exceeding those necessary for nutrition affect the reproductive system, immune system, and growth, including embryo deformities in higher-level predators (US Department of the Interior, 1998).

These processes of primary productivity in the Permian Phosphoria sea led to selected trace-element deposition, largely as organic detritus, on the sea floor under denitrifying conditions (Piper, 2001). Elevated concentrations of phosphate, Se, and other trace nutrients (e.g. Cd, Ni, Mo) in the rocks resulted from the loss of roughly 90% of the host organic matter, mostly during early diagenesis via bacterial respiration, retention of nutrients by the sediment, and an extremely low-accumulation rate of otherwise diluting phases. Concentrations of phosphate of up to 40% (as P_2O_5) were achieved. The Phosphoria Formation currently is still highly organic-rich (up to 15% total organic carbon) based on amounts (> 1.5–2% residual organic carbon) necessary to qualify for petroleum exploration, as well as phosphorite exploitation (McKelvey et al., 1959; Claypool et al., 1978).

In this chapter, we present data from field studies of Se pollution in the western United States, including those for southeast Idaho, to illustrate the biogeochemical pathways of Se in the environment. Concentrations of Se in geologic sources, receiving waters, food webs, and vulnerable species show the range and severity of ecological impacts from such anthropogenic activities as irrigation of agricultural land, refining of petroleum, and mining of phosphate when applied to Se source rocks. The addition of phosphorites as a category of Se-containing rocks to that of other carbon-rich source rocks enable a forecast of global Se sources. Although black shales and their recoverable organic fractions are widely recognized as sources of trace elements, the implications of worldwide reservoirs, site-specific fluxes, and persistent biologic cycling of Se are not. However, enough is known in terms of guidelines for health and risk to establish a first-order understanding of effects, should Se be discharged into vulnerable environments.

METHODS AND SOURCES OF DATA

Selenium guidelines

Compilations of Se health and risk criteria are available for: (a) nutrition, adequate/chronic toxicity (Puls, 1988; US Department of Health and Human Services, 1989, 1996); (b) protection of aquatic life (US Environmental Protection Agency, 1987; US Department of Health and Human Services, 1996); (c) protection of animal life (Puls, 1988); (d) human health advisory, consumption of fish (Fan et al., 1988); and (e) human health advisory, drinking water (US Department of Health and Human Services, 1996).

Guidelines for risk to aquatic life (i.e. ecological thresholds) take into account food webs in that they were derived for water, sediment, diet, fish tissue, and bird eggs (Stanley et al., 1996; US Department of Interior, 1998). The criterion for a hazardous Se waste is designed to protect ground water from the leaching of toxic substances based on an extraction procedure of solid wastes (US Department of Health and Human Services, 1996). Values for solids are given in dry weight, except as noted.

Western United States (Colorado River watersheds, San Joaquin Valley, and San Francisco Bay-Delta Estuary, California)

Seawater Se concentrations for the North Pacific are reported in Bruland (1983) and in Cutter and Bruland (1984). Selenium source-rock data are taken from compilations in Presser (1994) and Piper and Isaccs (1995). Extensive data sets (e.g. 2055 bird eggs) for drainage, receiving waters, food webs, and predator species of concern from the western United States are non-random representing contaminated sites only, except for coot and duck eggs (Presser and Ohlendorf, 1987; Saiki and Lowe, 1987; Ohlendorf and Hothem, 1994; Presser, 1994; Hamilton, 1998; Skorupa, 1998; US Department of Interior, 1998; Luoma and Presser, 2000). Where avian eggs were collected regionally, including uncontaminated reference sites, the minimum-to-maximum range was used. Where only contaminated sites were sampled, the regional minimum is unconfirmed and only the maximum was used (i.e. ?–maximum). It is expected, however, that regional minima are $< 1\ \mu g\, g^{-1}$ Se for coot and duck populations (Skorupa, 1998).

Idaho

Selenium source-rock data are taken from compilations in McKelvey et al. (1986) and Piper et al. (2000). The methodology for measuring Se concentrations in bird eggs from Idaho that are reported here is a fluorescence-based micro-digestion (Fan et al., 1997). Collection methodologies and extent and duration of sampling for other environmental media in southeast Idaho have evolved since 1997 under cooperative agreements between mining companies and federal agencies, with the most impacted area monitoring in accordance with a federal Comprehensive Environmental Response, Compensation, and Liability Act (TRC, 1999; Montgomery Watson, 1998, 1999, 2000, 2001a,b). The number of samples in each category for Idaho varies (rocks, $n = 378$; waste-rock seeps and drains, $n = 35$; receiving waters, $n = 231$; benthic invertebrates, $n = 67$; avian eggs, $n = 74$ including 27 from American coot; forage fish, $n = 53$; gamefish, $n = 61$). Samples of sheep liver are limited due to conditions of carcasses ($n = 7$) (Piper et al., 2000). Selenium concentrations in water samples collected in association with bird egg samples that are shown here graphically were analyzed by fluorescence-based micro-digestion (Fan et al., 1997).

Global distribution of phosphate deposits and petroleum basins

The distribution of world phosphate deposits was compiled from Notholt et al. (1989) and the distribution of world productive petroleum (oil and gas) basins was adapted from Klemme and Ulmishek (1991). Klemme and Ulmishek (1991) divided petroleum source rocks into those with dominantly types I and II kerogen (oil prone) and those containing dominantly type III kerogen and coal (gas prone). Thirty-one of the 47 petroleum basins considered in the analysis are of type II kerogen (marine oil shales). However, 13 are of type III kerogen and/or coal (continental deposits) and three are of type I kerogen (mainly lacustine deposits). In the future, it may be productive to expand our coverage to include coal deposits and power production that uses seleniferous coal because local extinctions of fish populations have occurred from contamination from fly ash that was elevated in soluble Se (Lemly, 1996; Skorupa, 1998).

The temporal distribution of major phosphate deposits was based on data from Cook and Shergold (1986) and Notholt et al. (1989). Identified phosphate resources (in million tonnes) were compiled by country, distributed by age, and normalized to a total tonnage for the United States, Latin America and Mexico, Asia and the Pacific, Africa, the Middle East, Europe, and Central Eurasia. Time distribution of effective petroleum source rocks was adapted from Klemme and Ulmishek (1991). They normalized the data as percentages of the original global petroleum reserves generated by these rocks. Grouping by age of percentages of petroleum source rocks is different in two instances from those shown by Klemme and Ulmishek (1991) to accommodate depiction with phosphate resources: the Oligocene and Miocene originally grouped together as 12.5% are represented as 6.25% in both the Oligocene and Miocene; the Pennsylvanian–Early Permian originally grouped together as 8.0% are represented as 4% in both the Pennsylvanian and Early Permian. These generalizations affect individual percentages for phosphate and petroleum, but not the overall conclusions shown by the time distributions.

CONCEPTUAL MODEL

The marine pathway through the environment accounts for the largest natural flux of Se (Haygarth, 1994). The marine system is also the major sink in the global cycle of Se. However, the current release of Se to the environment shows that the mobilization through anthropogenic activities is larger than the total flux of natural marine, terrestrial, and atmospheric sources on an annual basis (Haygarth, 1994). Haygarth (1994) concluded that this escalated rate of release over natural transfer in the environment indicates human interference is a major factor in the distribution, fate, and transport of Se.

We introduce here a conceptual model of Se pollution, annotated with environmental concentrations of Se, which illustrates specific biogeochemical pathways connected to irrigation, petroleum refining, and mining in the western United States. Overall the model shows the Se cycle from sources through food chain pathways to vulnerable predators. Processes important for Se cycling and defining the toxicity of Se in the environment, Se enrichment, Se mobilization, and establishment of Se-containing biological compounds, form the basis for the model. The model shows the diversity of environments that are affected including wetlands, rivers, estuaries, and forage lands. Several important ecosystems in the western United States are documented including those of the Colorado River basins, the San Francisco Bay-Delta Estuary, the San Joaquin Valley, California, and the Blackfoot River watershed, Idaho. The model encompasses:

- oceanic depositional environments;
- organic carbon-rich marine sediments that are source rocks for petroleum and phosphate ores;
- specific Se source rocks;
- anthropogenic activities that facilitate transfer to the environment;
- source waters or pollutant streams that reflect concentrated Se leachates or effluents;
- affected receiving water bodies;
- food webs that have bioaccumulated Se to toxic dietary levels; and
- predator species (birds, fish, and livestock) whose tissue Se concentrations exceed toxic risk thresholds.

Selenium effects, in order of increasing sensitivity as toxic endpoints, are: adult mortality, juvenile mortality, teratogenesis, mass wasting in adults, embryo mortality, reduced juvenile growth, and immuno-suppression (Skorupa, 1998). Regulated public health effects presently are related to consumption of fish and wild bird tissue in California, Colorado, Utah, and Texas (US Department of Health and Human Services, 1996). In general, issues of public safety also arise concerning subsistence lifestyles and consumption of wild fish and game and, in the long-term, deterioration of groundwater aquifers.

Selenium biochemistry and guidelines

Selenium is an essential micronutrient in bacteria and animals (Stadtman, 1974). Beneficial effects in humans stem mainly from the role of Se as an antioxidant. However, Se is the most toxic of all biologically essential elements in mammals (Venugopal and Luckey, 1978). Toxic effects occur via biochemical pathways unable to distinguish Se from S, thus substituting Se-containing amino acids in structural and functional proteins during critical stages of development and growth (Stadtman, 1974). Hence, dramatic effects such as congenital anomalies (monstrosities) occur in embryos of aquatic birds (Presser and Ohlendorf, 1987; Skorupa, 1998).

Nutritional guidelines and national guidelines for risk have been developed (Fig. 11-1). The guidelines for food webs show the narrow difference between concentrations

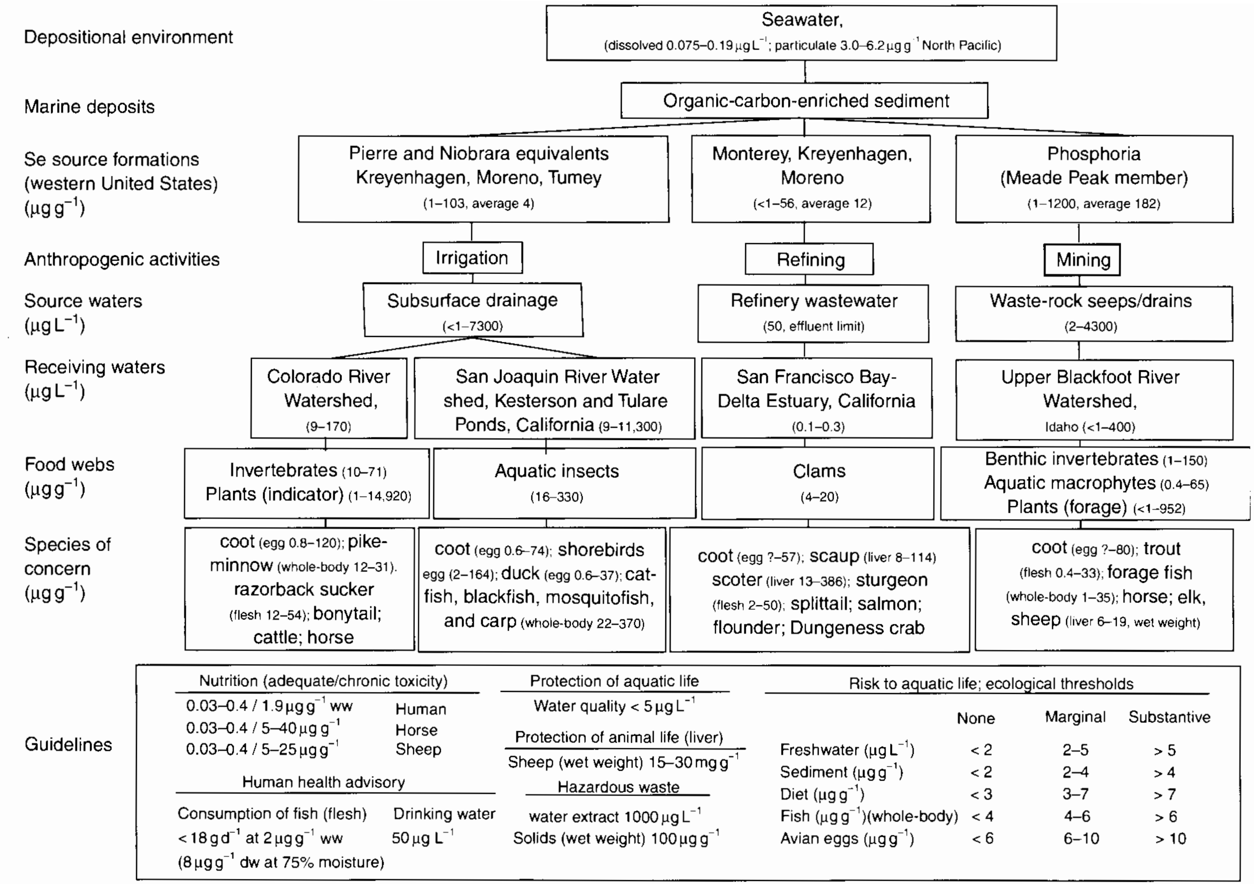

Fig. 11-1. Conceptual model of Se pollution based on Se concentrations in the environment from examples in the western United States. Guidelines for protection from Se toxicity, ecological risk thresholds, and hazardous wastes are listed for comparison. Food webs focus on vulnerable species. Selenium concentration ranges (in dry weight, dw, except as noted; ww = wet weight) are given in parentheses, together with averages for the source-rock shales. Sources of data are in the Methods and Sources of Data Section.

considered safe and those considered harmful. Nutritional guidelines may not be directly comparable across classes or within species because Se toxicity is dependent on the sensitivity of the animal, the chemical form of the Se, and the dose and duration of exposure. For example, the threshold for chronic toxicity in humans (wet weight, whole diet) is based on a longer exposure time than that for horses and sheep (Puls, 1988). Despite these complexities, five western states at 11 sites have human-health advisories for fish consumption because of Se (US Department of Health and Human Services, 1996). Children (less than age 15) and pregnant women are advised not to consume fish or game from a posted area, whereas adult males and non-pregnant women should consume no more than one meal each 2-week period of approximately 120 g of fish or game flesh (i.e. muscle) (Fan et al., 1988).

Ecological risk threshold ranges are indicative of the endpoints used to measure adverse biological effects (US Department of Interior, 1998). Thresholds for marginal and substantive risk are well established for water, sediment, diet, fish tissue, and bird eggs (Fig. 11-1). Because the difference between essential and toxic levels for Se is narrow, concern of marginal risk levels, which are between levels considered safe (no effect) and those considered harmful (substantive risk or the toxicity threshold), are intended to provide protection for the environment. The equality of the criterion for the protection of aquatic life and the ecological threshold at which substantive risk occurs (i.e. 5 $\mu g\,L^{-1}$ Se) demonstrates a need to establish a set of criteria that fully encompasses both aquatic and semi-aquatic food web components (US Environmental Protection Agency, 1998).

Selenium ocean chemistry

The dissolved concentration of Se currently in the North Pacific Ocean ranges from 0.075 $\mu g\,L^{-1}$ Se in surface water to 0.19 $\mu g\,L^{-1}$ Se in deep water (Cutter and Bruland, 1984). The depth-profile of Se parallels those of phosphate and nitrate (Bruland, 1983), essential and limiting nutrients to primary productivity (Codispoti, 1989). Organic selenide makes up 80% of the total dissolved Se in surface water (Cutter and Bruland, 1984). The reduced-state organic selenide maximum, supposedly consisting of seleno-amino acids, coincides with the maxima of primary productivity, suggesting entrance into food-chain organisms. The downward flux of particulate Se, found primarily in the −2 oxidation state, decreases with depth. Sediment trap material for the North Pacific (100–970 m) ranged in Se concentration from 3.0 to 6.2 $\mu g\,g^{-1}$ Se (Cutter and Bruland, 1984).

Field case-studies and environmental selenium concentrations

The sources and biogeochemistry of Se combine to make contamination by this element an ecological issue of concern (Fig. 11-1). Environmental Se concentrations from ecotoxic field case-studies in the western United States provide comparison for dispersal of Se investigated in Idaho (Trelease and Beath, 1949; Presser, et al., 1994; Hamilton, 1998; Skorupa, 1998). Illustrated examples from California and the watersheds of the Colorado River also include a range of processing activities that call attention to anthropogenic connections (disposal of oil refining effluents and subsurface drainage into wetlands and estuaries), in addition to surface processes (weathering, erosion, and runoff) that can ultimately mediate contamination.

Selenium source rocks in the western United States encompass a wide range of sedimentary deposits, from marine shales mildly enriched in organic carbon to oil shales strongly enriched in organic matter, biogenic silica, phosphate, and trace elements (Fig. 11-1) (Presser, 1994; Piper and Isaccs, 1995; Piper et al., 2000). The resource extraction histories of shales demonstrate how sedimentary rocks exposed to weathering and erosion at basin margins may be buried deeply enough in the central part of a basin to produce oil. The marine shales of the Colorado River watersheds and those that provided source sediment for the alluvial fans of the San Joaquin Valley of California provide enriched, but disseminated Se sources (Fig. 11-1). Selenium transport is by both mass wasting and delivery of Se in dissolved load from surface runoff and groundwater throughflow. These watershed transport mechanisms provide soluble selenate and a secondary solid-source Se usually of large mass, but of a comparatively low-level concentration, which acts as a continuously renewed source. The Moreno and Kreyenhagen Formations of the Coast Ranges of California also provide oil for nearby refineries surrounding the San Francisco Bay-Delta Estuary. Here, a more concentrated source of Se is processed as reflected in effluent loads discharged to the estuary (Luoma and Presser, 2000). Restrictions for aquatic discharges recently have been enacted under regulatory permits necessitating a partitioning of Se into a solid waste for disposal on land as part of the refining process.

A model developed in the 1940s (Trelease and Beath, 1949) and refined in the 1980s for the western United States (Presser et al., 1994; Luoma and Presser, 2000) shows that Se is mainly oxidized to soluble selenate. Consequently, in areas of semi-arid to arid climates where evaporation greatly exceeds precipitation and where drainage is impeded (i.e. in areas of net negative annual water budgets), Se accumulates as salts in soils or in aquifers. The affected lands support agriculture only through massive irrigation, which leaches salts and Se, and management of subsurface drainage flows (Fig. 11-1). Installation of subsurface drains increases the speed, volume, and control of the drainage of shallow groundwater that impedes agricultural production. Collection of drainage from irrigated soils in drainage canals enables efficient discharge into surface waters. In the San Joaquin Valley and the Colorado River basins (Fig. 11-1), Se concentrations in agricultural drains exceeded the criterion for a water-extracted hazardous Se waste (1000 $\mu g\,L^{-1}$ Se).

Selenium released to aquatic systems can result in Se being bioaccumulated to toxic levels in plants, fish, bird eggs, and livestock (Presser and Piper, 1998; Skorupa, 1998). The general term bioaccumulation can be applied to all of the biological levels of Se transfer through the food web. Linked biological and geochemical reactions affect how readily Se enters food webs, initiates food-web transfer, and cycles through particulate matter, sediments, consumer organisms, and predators (Luoma and Presser, 2000). Because Se concentrations can be magnified at each step of food-web transfer, upper trophic level species are most vulnerable to adverse effects from Se contamination.

Beginning in the 1930s, seleniferous open-range forage plants associated with the Pierre and Niobrara Formations (or their equivalents) were found to poison livestock mainly in Wyoming, Nebraska, and South Dakota (Fig. 11-1) (Trelease and Beath, 1949). Lands were withdrawn from use by livestock and leaching through subsurface drains was proposed as a means to remediate saline and seleniferous soils.

The most well-known case of Se poisoning in an aquatic ecosystem was at Kesterson National Wildlife Refuge in the San Joaquin Valley, California (Fig. 11-1) (Presser and Ohlendorf, 1987; Presser, 1994). Widespread fish mortality and deformities in ducks, shorebirds, grcbcs, and coots occurrcd in wetlands fed by agricultural irrigation drainage. The deformities most frequently observed in birds were defects of eyes, feet or legs, beak, brain, and abdomen (Ohlendorf and Hothem, 1994). Further south in the San Joaquin Valley, a higher level of tetratogenicity (56.7%) occurred in shorebirds inhabiting ponds where accelerated evaporation was taking place as part of a management program (Skorupa, 1998). Levels of Se in the San Joaquin Valley wetlands, streams, and rivers that support beneficial uses for fish and birds exceeded levels for protection of aquatic life ($>5\ \mu g L^{-1}$ Se) (Fig. 11-1). Although food chains are specific to each water body, food-web biota exceeded ecological thresholds for dietary Se toxicity ($>7\ \mu g g^{-1}$ Se) (Fig. 11-1) (Saiki and Lowe, 1987; US Department of Interior, 1998). Levels of Se in tissues of fish, mostly non-native, exceeded ecological thresholds for substantive risk ($>6\ \mu g g^{-1}$ Se), as did Se concentrations in bird eggs ($>10\ \mu g g^{-1}$ Se) (Skorupa, 1998). Agricultural drainage canals are posted with human-health advisories against consumption of fish because of Se contamination (Fan et al., 1988).

Selenium contamination in the upper and lower Colorado River basins (Fig. 11-1) has contributed to the decline of native fish (i.e. pikeminnow, *Ptychocheilus lucius*; bonytail, *Gila elegans*; and razorback sucker, *Xyrauchen texanus*) and now represents a high hazard for effects in fish from Se exposure (Hamilton, 1998; Hamilton et al., 2002). A recovery program has been enacted in an effort to stabilize and enhance populations of endangered fish, especially razorback suckers, in the upper Colorado River. Eggs from American coot (*Fulica americana*) collected in wetlands affected by irrigation drainage in the Green River watershed showed an average Se concentration of $50\ \mu g g^{-1}$ Se (Skorupa, 1998). The level of teratogenicity was approximately 10% in eggs that survived to full term and the level of egg inviability (failed-to-hatch eggs) was $>85\%$.

The San Francisco Bay-Delta Estuary (Fig. 11-1) is characterized by enhanced biogeochemical transformations to bioavailable particulate Se (Luoma and Presser, 2000). Efficient Se uptake to toxic levels occurs in clams and then diving ducks and bottom-feeding fish, even though waterborne concentrations in the estuary are more than fivefold below the freshwater criterion for the protection of aquatic life and the ecological threshold at which substantive risk occurs (Fig. 11-1) (Luoma and Presser, 2000). Selenium in food webs is sufficient to be a threat to listed or endangered species such as the Sacramento splittail (*Pogonichthys macrolepidotus*) and a concern to human health if those species are consumed. Resources that show declining populations such as Dungeness crab (*Cancer magister*) and chinook salmon (*Oncorhynchus tshawytsch*) also may be at risk from Se, in addition to other causative factors.

IDAHO CASE STUDY

Phosphate production and shale exposures

The Meade Peak Member of the Phosphoria Formation extends throughout southeast Idaho, and adjacent areas of Wyoming, Montana, and Utah (McKelvey et al., 1959). Outcrops occur over a vast part of that area as a result of folding, faulting, uplift, and subsequent erosion of younger deposits. The area supports phosphate mining, livestock grazing, fishing, and hunting. Over the last half of the twentieth century, mining in Idaho provided approximately 4.5% of world demand for phosphate, used mainly in fertilizer (US Department of Interior, 2000; Jasinski et al., Chapter 3; Jasinski, Chapter 22). About 49% of the total production has occurred since 1985. This tonnage represents approximately 15% of the estimated one billion tons accessible to surface mining within the Phosphoria Formation (US Department of Interior and US Department of Agriculture, 1977). Out of 19 mining sites in Idaho, four are presently active (Dry Valley Mine, Enoch Valley Mine, Rasmussen Ridge Mine, and Smoky Canyon Mine) (Causey and Moyle, 2001) and two are categorized as existing mine operations (Maybe Canyon Mine and Lanes Creek Mine). Expansion at five existing mining operations and development of five new sites is expected during the next 15 years (US Department of Interior et al., 2000). The Phosphoria Formation also is estimated to have generated about 3×10^{10} metric tons of oil (Claypool et al., 1978).

The Meade Peak Member contains up to 1200 $\mu g\, g^{-1}$ Se, a value exceeding a solid Se hazardous waste (100 $\mu g\, g^{-1}$ Se, wet weight; or 111 $\mu g\, g^{-1}$ Se, dry weight at 10% moisture), if this criterion was applied to mining waste (Fig. 11-1) (McKelvey et al., 1986; US Department of Health and Human Services, 1996). Average concentrations range from 48 to 560 $\mu g\, g^{-1}$ Se in westernmost Wyoming (Lakeridge core, subsurface depth of 4200 m) and in southeast Idaho (Hot Springs Mine, Enoch Valley Mine; Vanadiferous Zone of Bloomington Canyon) (McKelvey et al., 1986; Piper et al., 2000). Selenium is dispersed throughout the deposit, but achieves its highest concentration in a waste-shale zone between two major phosphate-ore zones of the Meade Peak Member. The waste-shale beds are phosphate lean, but enriched in organic carbon compared to the ore zones (Claypool et al., 1978; Herring and Grauch, Chapter 12). The lower-ore zone is about 12 m thick, the waste zone 27 m thick, and the upper-ore zone 5 m thick, each of which approximately maintains its thickness over 21,500 km^2 (McKelvey et al., 1959).

Geochemical mechanism of dispersal and selenium discharges

Mining removes phosphate-rich beds and exposes organic carbon-rich waste rock to subaerial weathering. Waste rock is generated at a rate of 2.5–5 times that of mined ore (US Department of Interior and US Department of Agriculture, 1977). Individual dumps contain 6–70 million tons of waste-rock that is either contoured into hills, used as cross-valley fill, or used as back-fill in mine pits. In terms of Se chemistry, when Se hosted by organic matter in source rocks is exposed to the oxic atmosphere and surface and ground water, Se is oxidized from relatively insoluble selenide (Se^{2-}) and elemental Se^0 to soluble oxyanions, selenite (SeO_3^{2-}) and selenate (SeO_4^{2-}) (Presser, 1994; Piper et al., 2000). Organic Se (operationally defined as organic selenide) also can exist in the dissolved phase.

The cross-valley fills at the Smoky Canyon mine (50 million tons) and South Maybe Canyon mine (30 million tons) are stabilized with under-drains (TRC, 1999; US Department of Interior and US Department of Agriculture, 2002). Discharges from these drains are source waters for Pole Creek and Maybe Creek. Concentrations of Se in these two drains, as well as in a dump seep at the inactive Conda Mine, were equal to or exceeded the criterion for a water-extracted hazardous waste of 1000 $\mu g\,L^{-1}$ Se (Fig. 11-1) (US Department of Health and Human Services, 1996; TRC, 1999; US Department of Interior and US Department of Agriculture, 2002).

In the upper Blackfoot River watershed, where the majority of mines are located, Se concentrations in streams draining both active and inactive mines contained up to 400 $\mu g\,L^{-1}$ Se (Fig. 11-1) (Montgomery Watson, 2001a), exceeding the protective guidelines of 2–5 $\mu g\,L^{-1}$ Se for freshwater (US Department of Health and Human Services, 1996; US Department of Interior, 1998). These concentrations compare in order of magnitude to those discharged from subsurface drains to reservoirs and rivers in field case studies from the western United States (Presser, 1994; Presser et al., 1994; Skorupa, 1998).

Temporal stream sampling in Idaho showed that waste-rock dump seeps and surface streams exhibit annual cycles in Se concentration that peak during the spring period of maximum flow (Fig. 11-2) (Montgomery Watson, 1999; Presser et al., Chapter 16).

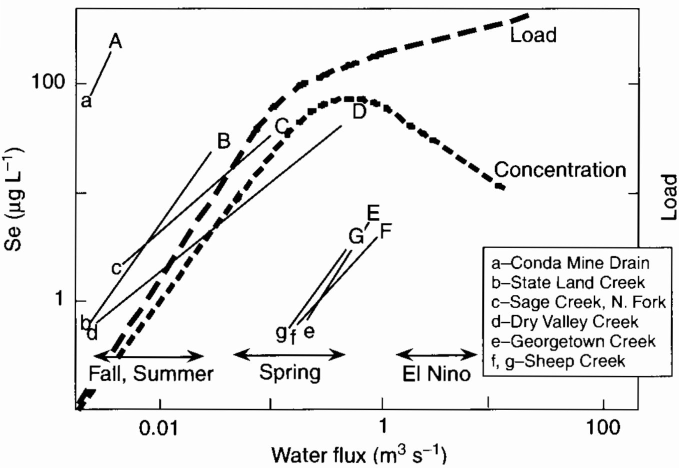

Fig. 11-2. Relation between surface flow and Se concentrations in streams from southeast Idaho. Solid curves connect data collected from drains and streams in the Blackfoot River watershed in May (upper case) and again in September (lower case) of 1998 (Montgomery Watson, 1999). Broken lines represent generalized trends of flow, concentration, and load data from the San Joaquin Valley in California (Luoma and Presser, 2000).

Concentration data are also available without accompanying flow data for Idaho (Montgomery Watson, 1998, 1999, 2000, 2001a,b). For example, in 1998, the stream Se concentration maximum for all samples collected in May was 260 $\mu g L^{-1}$ Se, whereas it was 32 $\mu g L^{-1}$ Se in September. In May 2000, the Se concentration in East Mill Creek was 400 $\mu g L^{-1}$ Se and was 19 $\mu g L^{-1}$ Se in September 1999. The observation that increased ground- and surface-water flows in the mining area result in increased Se concentrations and, by inference, increased loads is similar to that seen in the San Joaquin Valley, California (Luoma and Presser, 2000). Only during periods of exceptional runoff in California (e.g. an El Niño year) did the high flow achieve a diluting effect of the large internal reservoir of Se that influences water quality (Fig. 11-2). Although the Idaho data sets for flow and concentration were not adequate to extrapolate to Se loads on an annual basis, the similarity in mobility trends in the two regions suggests massive Se storage in Idaho that is now subject to transport, as has occurred in California.

Biological reactions and selenium concentrations in biota

Mass balance is important in assessing ecosystem-level Se contamination (Presser and Piper, 1998). Biological reactions dominate Se partitioning once Se enters aquatic environments, leading to Se transfer through food webs (bioaccumulation). Pathway bioaccumlation models consider food as the main route of transfer and link environmental Se concentrations to biological effects in upper trophic level animals (Luoma and Presser, 2000; Piper et al., 2000). Hence, Se toxicity depends not only on exposure via aquatic loading, but also on the processes that influence Se bioavailability in food webs and Se trophic transfer to vulnerable higher-level predators.

Plants, invertebrates, and fish

In Idaho, Se concentrations in biota showed a similar seasonal trend to that of drainwater and surface streams (Montgomery Watson, 1998, 1999, 2000, 2001a,b). Submerged macrophytes reached a maximum of 56 $\mu g g^{-1}$ Se in spring and 44 $\mu g g^{-1}$ Se in fall. Benthic macroinvertebrates showed a maximum of 150 $\mu g g^{-1}$ Se in spring and 63 $\mu g g^{-1}$ Se in fall (Fig. 11-1). Both these food-webs bioaccumulate Se to an extent that they can provide a diet above 7 $\mu g g^{-1}$ Se, which is defined as causing substantive risk for higher trophic level species (US Department of Interior, 1998). Based on tissue, whole-body Se concentrations in forage fish (suckers, sculpins, minnows, and salmonids < 15 cm) exceeded the substantive risk threshold of 6 $\mu g g^{-1}$ Se for growth and survival during both seasons (maxima: 35 $\mu g g^{-1}$ Se in spring and 11 $\mu g g^{-1}$ Se in fall) (Fig. 11-1) (US Department of Interior, 1998). These values also exceeded the substantive risk threshold for diet, if these fish are eaten by larger fish. Concentrations of Se in gamefish (> 15 cm) showed a maximum skin-on fillet concentration of 33 $\mu g g^{-1}$ Se in spring and 17 $\mu g g^{-1}$ Se in fall (Fig. 11-1). Depending on the conversion factor used (Piper et al., 2000), whole-body

Se concentrations in gamefish would reach 55–77 $\mu g\, g^{-1}$ Se in spring. These included Yellowstone cutthroat trout (*Oncorhynchus clarki bouvieri*), brook trout (*Salvelinus fontinalis*), and rainbow trout (*Oncorhynchus mykiss*). The proportion of trout above the 2 $\mu g\, g^{-1}$ Se wet-weight guideline for human consumption of fish flesh (Fig. 11-1) (US Department of Health and Human Services, 1996; US Department of Interior, 1998) increased from < 1% in fall to 30% in spring.

Birds and mammals

Eggs of a common water bird, American coot (*Fulica americana*), collected at three impoundments down-gradient of mine-waste dumps (i.e. high-risk sites based on Se concentrations in ponds and wetlands) showed a trend of increasing Se concentration with increasing Se in pond waters (Fig. 11-3). Selenium-contaminated impoundments appear to present greater risks to wildlife than Se-contaminated streams and rivers (Seiler, 1995; Skorupa, 1998). Samples were collected in spring when ephemeral vernal wetlands provide habitat and breeding birds are present. Coot eggs reached 80 $\mu g\, g^{-1}$ Se, above the 10 $\mu g\, g^{-1}$ Se embryo viability threshold and the 65 $\mu g\, g^{-1}$ Se concentration above which 100% teratogenesis in coot embryos has been observed (Figs. 11-1 and 11-3) (Skorupa, 1998; US Department of Interior, 1998). Reproductive impairment was found at one impoundment (Fig. 11-4) in spite of the fact that egg collection was limited (i.e. a population-level

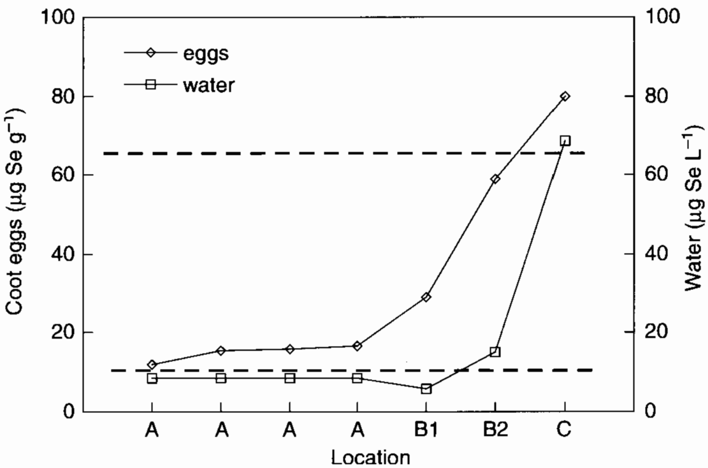

Fig. 11-3. Selenium in coot eggs and associated aquatic habitats sampled in spring 1999 in south-east Idaho. Sites A and C are in the upper Blackfoot River watershed and site B is in the Salt River watershed, all influenced by the Meade Peak Member of the Phosphoria Formation. The upper broken line gives the Se concentration above which 100% teratogenesis is observed for coots; the lower broken line gives the avian embryo viability threshold (i.e. threshold of substantive risk) (Fig. 11-1) (Skorupa, 1998; US DOI, 1998).

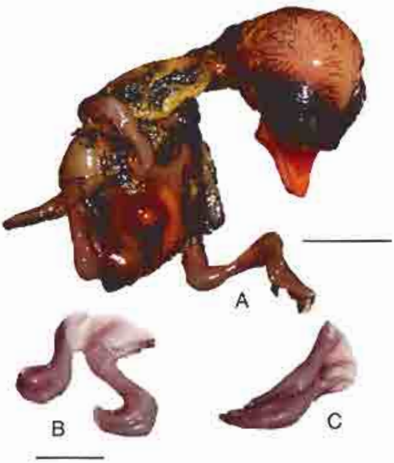

Fig. 11-4. Deformed American coot (*Fulica americana*) embryo from a nest in the vicinity of a southeast Idaho phosphate mine tailings reservoir. The deformity exhibited here, "curly toe," is similar to that induced by Se in chickens (Detwiler, 2002) (B, deformed; C, normal). The scale bar represents 10 mm in each image. This coot egg was artificially incubated and analyzed using a fluorescence-based micro-digestion (Fan et al., 1997).

exposure assessment would necessitate the collection of more eggs). The egg tissue contained 12 $\mu g\,g^{-1}$ Se, a value just above the threshold (10 $\mu g\,g^{-1}$ Se) for substantive risk to embryo viability (Skorupa, 1998; US Department of Interior, 1998). In all, of the 27 coot eggs collected, nine embryos were assessable for presence or absence of overt deformities. One deformity in nine embryos is a factor of 75 above the background rate for overt deformities. This deformity is considered "mild" and, as such, is considered a suggestive, not definitive, endpoint for Se toxicity. When considered with the sets of data for tissue, water, and diet from Idaho (Fig. 11-1), it represents additional evidence of risk to resident birds and those migrating through southeast Idaho.

Because acute dietary exposure led to the death of eight horses and approximately 250–300 sheep since 1996 at six sites in the mining district, hunter-killed elk are being evaluated for public-health risks and permits for grazing have been suspended for some mine-disturbed areas (Idaho Department of Environmental Quality, 2002). The elk survey shows a direct correlation between elevated concentrations of Se in liver versus the distance of the harvested elk from the nearest phosphate mine. Samples in 2001 at two mining areas (Mackowiak et al., Chapter 19) showed mean Se concentrations in forage plants (legume and grass) grown on waste-rock dumps exceed thresholds of dietary toxicity for horses (5–40 $\mu g\,g^{-1}$ Se) and sheep (5–25 $\mu g\,g^{-1}$ Se) (Fig. 11-1). Location within a dump site, as well as species of plant, were factors in determining Se concentrations in vegetation (Piper et al., 2000; Mackowiak et al., Chapter 19). For example, in 2001, alfalfa bioaccumlated Se to a greater extent (mean 150 $\mu g\,g^{-1}$ Se, maximum 952 $\mu g\,g^{-1}$ Se) than grasses (mean 27 $\mu g\,g^{-1}$ Se, maximum 160 $\mu g\,g^{-1}$ Se) (Mackowiak et al., Chapter 19).

Maximum Se concentrations in grass and mean and maximum Se concentrations in legume would qualify the plant material itself, regardless of dietary considerations, as hazardous based on the criterion for a hazardous Se solid waste (100 $\mu g\, g^{-1}$ Se, wet weight; or 143 $\mu g\, g^{-1}$ Se, dry weight at 30% moisture) (Fig. 11-1) (US Department of Health and Human Services, 1996).

GLOBAL OCCURRENCE OF PHOSPHORITES AND PETROLEUM

Prediction of selenium sources

Selenium emerges as an ecological issue of more widespread concern than illustrated by our case studies (Fig. 11-1) when possible candidates for Se sources are extrapolated from major basins hosting phosphate and petroleum source rocks. From the combined global distribution of phosphate deposits and petroleum-generating basins, it is possible to produce a world-wide map that shows the distribution of organic-carbon enriched sedimentary basins (Fig. 11-5) (Notholt et al., 1989; Klemme and Ulmishek, 1991). This map presents a base on which to predict environments that may be affected by Se loading. It is notable that 68% of the global petroleum reserves and more than 70% of phosphate resources were deposited at low latitudes in the Tethyan oceanic realm

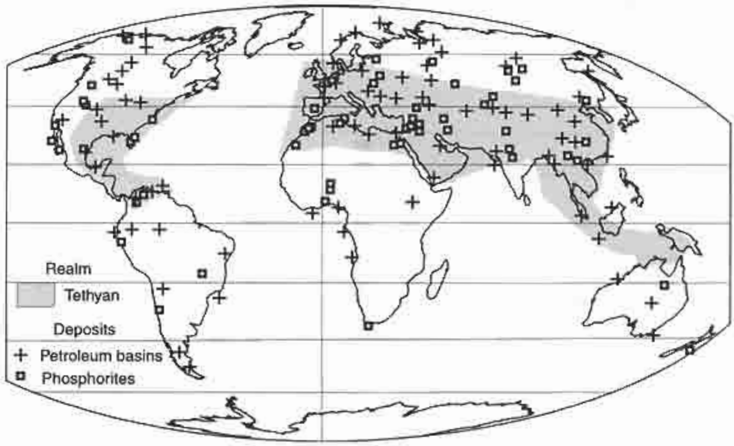

Fig. 11-5. The distribution of phosphate deposits (Notholt et al., 1989) is overlain onto that of productive petroleum (oil and gas) basins (Klemme and Ulmishek, 1991) to generate a global plot of organic carbon-rich sedimentary basins. The Tethyan basins, which are emphasized, far outweigh the productivity of other defined realms encompassing much greater areas (i.e. Boreal or northern group of basins, the Pacific accreted terrains, and Gondwana or southern group of basins) (Klemme and Ulmishek, 1991). The Tethys was a progression of seaways subjected to many tectonic openings and closings that separated North America, Europe, and Asia to the north from South America, Africa, India, Australia, and Antarctica to the south.

(Notholt et al., 1989; Klemme and Ulmishek, 1991). Yet, the Tethyan realm constitutes less than one-fifth of the global land area and continental shelves (Fig. 11-5) (Klemme and Ulmishek, 1991). The Tethyan realm was an east-west corridor for oceanic circulation nearly parallel to the equator. The Tethyan basins were characterized by a warm, moist climate that sustained abundant organic richness in broad, shallow continental shelves or in epicontinental seas during transgressive oceanic events throughout the Mesozoic and into the Cenozoic.

Originally, source-rock age was hypothesized as controlling Se sources, with Cretaceous sedimentary rocks such as the Pierre and Niobrara Formations identified as important sources of Se (Trelease and Beath, 1949). However, formations selected for our case studies (Fig. 11-1) range in age from the Permian Phosphoria Formation to the Miocene Monterey Formation, with significant Cenozoic sources in the California Coast Ranges. A compilation by age of major phosphate resources and effective petroleum source rocks (normalized as a percentage of total global resources or of original petroleum reserves, respectively), show that some geologic ages are more important than others in determining productivity, but no apparent predictable periodicity can be discerned (Fig. 11-6) (Cook and Shergold, 1986; Notholt et al., 1989; Klemme and Ulmishek, 1991). Some 50% of phosphate resources were deposited in the Eocene and Miocene (Fig. 11-6) (Cook and

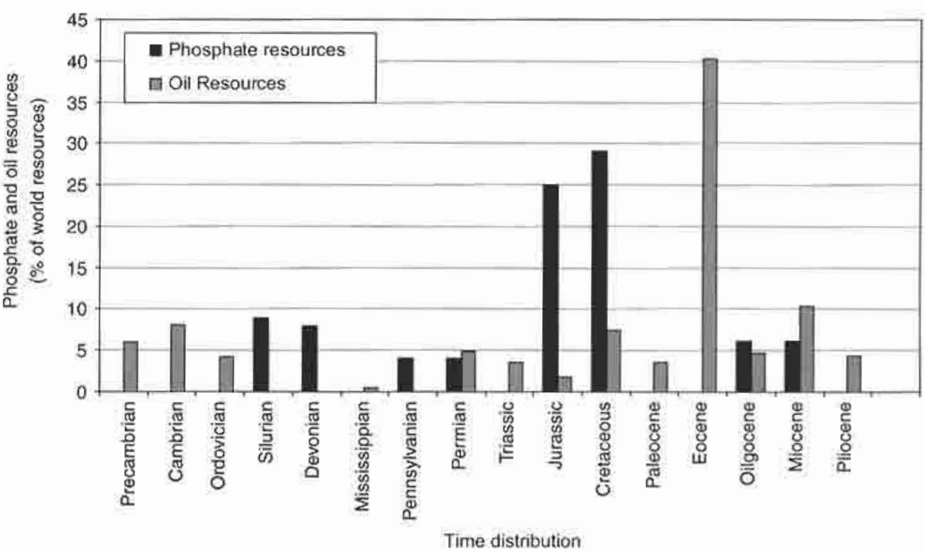

Fig. 11-6. Temporal distribution of major phosphate resources (Cook and Shergold, 1986; Notholt et al., 1989; Trappe, 1998) and of effective source rocks (Klemme and Ulmishek, 1991) normalized as percentages of total global resources and the original global petroleum reserves, respectively. Generalizations imposed on the data affect individual percentages for phosphate and petroleum, but not the overall conclusions shown by the time distributions (see Methods and Sources of Data Section).

Shergold, 1986; Notholt et al., 1989; Trappe, 1998). Ninety percent of the global discovered oil resources come from six stratigraphic intervals, with the middle Cretaceous and upper Jurassic accounting for 54% (Fig. 11-6) (Klemme and Ulmishek, 1991).

Commodities and exploration

Current anthropogenic activity, when combined with our forecasts based on distribution of organic carbon-rich rocks (Fig. 11-5), helps locate areas that may warrant investigations of Se dynamics during exploitation. The US has remained the world's largest producer of phosphate rock throughout most of the last century and into the twenty-first century (US Department of Interior and US Department of Agriculture, 1977; US Department of Interior, 2000). North Africa and the Middle East together produce a comparable amount. Major oil production is from the Middle East (6870 million barrels per year) with Latin America, Central Eurasia, Asia and the Pacific, the United States, and Europe each contributing in the range of 2500 million barrels per year (Oil and Gas Journal Energy Database, 1996). Areas of the Alaskan North Slope, North Africa, and Kazakhstan represent areas where both commodities are available or where industries possibly will expand (Bird and Magoon, 1987; US Geological Survey Energy Assessment Team, 2000). These enriched resource areas (Fig. 11-5) also now encompass most of the great deserts of the world, which may add severity to Se effects as evidenced by areas considered susceptible to Se contamination in the western United States (Presser et al., 1994; Seiler, 1995).

CONCLUSIONS

Further refinements in models for Se deposition, source-rock weathering, and efficiency of bioaccumulation need to be made to complete our understanding of site-specific factors that may exacerbate or ameliorate Se retention and bioavailability. For example, the Miocene through Holocene phosphate deposits in North Carolina have a range of 4–9 $\mu g\,g^{-1}$ Se with a correspondingly low organic carbon content (Riggs et al., 1985), which possibly reflect deposition under oxic conditions rather than denitrifying conditions identified for the Phosphoria basin. This Se concentration range is far lower than the average for Idaho, but is comparable to that of Se source rocks in the California Coast Ranges, where serious and enduring Se contamination problems are occurring from disposal of both agricultural and oil refinery waste effluents (Presser, 1994; Luoma and Presser, 2000). However, the problems in California arose more from irrigation and refinery practices than from source rocks extraordinarily enriched in Se. Hence, the magnitude of commodity production as a measure of anthropogenic activity represents a relevant factor. Our analysis here reveals that a broad range of Se source rocks exists that encompasses essentially all organic carbon-rich marine sedimentary rocks. Consequently, we predict that the development of protective criteria and remediation technologies for controlling Se pollution in many geographic regions will become increasingly critical to natural resource exploitation activities, as well as to fish and wildlife conservation efforts.

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