Appendix A: Selected Case Studies of Ecosystem Contamination by Se

Terry F. Young, Keith Finley, William J. Adams, John Besser, William A. Hopkins, Dianne Jolley, Eugenia McNaughton, Theresa S. Presser, D. Patrick Shaw, Jason Unrine

CONTENTS

A1.0 Belews Lake, North Carolina 259
A1.1 Selenium Source 259
A1.2 Fate and Transformation 259
A1.3 Effects 259
A1.4 Lessons Learned 260
A1.5 References 262
A2.0 Hyco Lake, North Carolina 262
A2.1 Selenium Source 262
A2.2 Fate and Transformation 262
A2.3 Effects 263
A2.4 Lessons Learned 263
A2.5 References 263
A3.0 Martin Creek Reservoir, Texas 264
A3.1 Selenium Source 264
A3.2 Fate and Transformation 264
A3.3 Effects 264
A3.4 Lessons Learned 265
A3.5 References 265
A4.0 D-Area Power Plant, Savannah River, South Carolina 265
A4.1 Selenium Source 265
A4.2 Fate and Transformation 266
A4.3 Effects 267
A4.4 Lessons Learned 267
A4.5 References 267
A5.0 Lake Macquarie, New South Wales, Australia 269
A5.1 Introduction 269
A5.2 Selenium Sources 269

A5.3 Fate and Transformation 270
A5.4 Effects 270
A5.5 Lessons Learned 270
A5.6 References 270
A6.0 Elk River Valley, Southeast British Columbia, Canada 271
A6.1 Selenium Sources 271
A6.2 Fate and Transformation 272
A6.3 Effects 272
A6.4 Lessons Learned 273
A6.5 References 273
A7.0 Areas of the Appalachian Mountains Affected by Mountaintop Mining and Valley Fills 274
A7.1 Selenium Sources 274
A7.2 Fate and Transformation 274
A7.3 Effects 274
A7.4 Lessons Learned 275
A7.5 References 275
A8.0 Kesterson Reservoir, San Joaquin Valley, California 275
A8.1 Selenium Source 275
A8.2 Fate and Transformation 276
A8.3 Effects 277
A8.4 Lessons Learned 278
A8.5 References 278
A9.0 Terrestrial and Aquatic Habitats, San Joaquin Valley, California 279
A9.1 Selenium Sources 279
A9.2 Fate and Transformation 280
A9.3 Effects 280
A9.4 Lessons Learned 281
A9.5 References 282
A10.0 Grassland Bypass Project (San Joaquin Valley), California 282
A10.1 Selenium sources 282
A10.2 Fate and Transformation 283
A10.3 Effects 283
A10.4 Lessons Learned 284
A10.5 References 285
A11.0 San Francisco Bay-Delta Estuary, California 286
A11.1 Selenium Sources 286
A11.2 Fate and Transformation 287
A11.3 Effects 287
A11.4 Lessons Learned 287
A11.5 References 288
A12.0 Phosphate Mining in the Upper Blackfoot River Watershed, Idaho 288
A12.1 Selenium Sources 288
A12.2 Fate and Transformation 289

A12.3 Effects..290
A12.4 Lessons Learned...291
A12.5 References 291

A1.0 BELEWS LAKE, NORTH CAROLINA

A1.1 Selenium Source

In the 1970s, Se was introduced into the newly impounded Belews Lake, a 1560-ha coal-burning power plant cooling reservoir, via water from an ash settling basin. Coal ash collected from power plant flue gases was transported to the ash basin, where the coarse (bottom ash) and fine (fly ash) particulates settled from the water column. Clarified ash sluice water was returned to Belews Lake, an impoundment having limited natural surface water inflows. As an unforeseen result of this design, highly concentrated Se-laden wastewater (100 to 200 μg/L) was introduced into the lake over several years, leading to increased Se loading, elevated Se concentrations in the water column, and ultimately elevated Se concentrations in the sediment and biota. In 1985, the primary Se source was terminated with the installation of a dry fly ash collection system at the power plant, and the rerouting of the NPDES-permitted ash basin effluent (which continued to receive minor Se contributions from power plant bottom ash) to the nearby Dan River.

A1.2 Fate and Transformation

Selenium from coal combustion wastes occurred primarily as selenite (Cutter 1991). Lakewide water-column Se concentrations averaging 10 μg/L were observed in the late 1970s, with rapidly declining concentrations by the early 1980s as various control measures were implemented (Figure A.1). Sediment Se concentrations ranged mostly from about 4 to near 30 mg/kg dw, with a few samples having concentrations considerably greater (up to 100 mg/kg; Duke Energy 2006). During the contamination episode, the entire lake was affected with the Se-laden effluents except for a small remote headwater region of the reservoir.

Monitoring conducted a year before the impoundment showed that Belews Lake supported a diverse warm-water fishery typical of the ecoregion (Figure A.2). The lake's fish community included several trophic levels, including typical warm-water reservoir fish such as shad (*Dorosoma* spp.; Clupeidae) and blueback herring (*Alosa aestivalis;* Clupeidae), common carp (*Cyprinus carpio;* Cyprinidae) and minnows (Cyprinidae), largemouth bass (*Micropterus salmoides;* Centrarchidae), crappie (*Pomoxis* spp.; Centrarchidae), and a variety of sunfish (Centrarchidae) as well as several catfish (Ictaluridae). When maximal Se inputs occurred, Se concentrations ranged from 41 to 97 mg/kg dw in zooplankton and phytoplankton; 15 to 57 mg/kg dw in benthic macroinvertebrates; and 40 to 159 mg/kg dw in fish egg/ovary tissue (Lemly 1997a).

A1.3 Effects

Adverse impacts were initially observed in 1976, with a widespread reproductive failure of the fishery, except at the remote uplake headwater area (Cumbie and

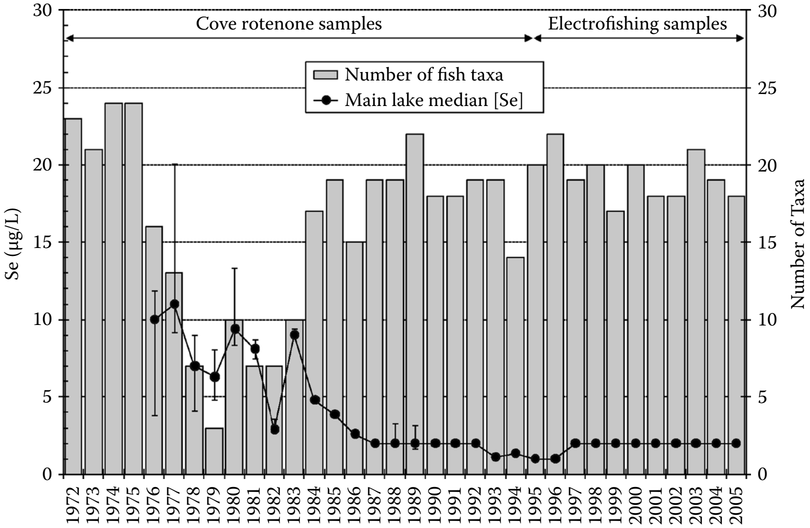

FIGURE A.1 Belews Lake monitoring data characterizing the decline and recovery of the warm-water fish community, quantified by the number of fish taxa collected annually in rotenone (1972–1994) and electrofishing samples (post-1994). In the years prior to 1977, a total of 29 fish taxa were collected. Water-column Se concentrations after 1986 primarily reflect variability in the analytical laboratory reporting limit. (Data from Van Horn 1978; Barwick and Harrell 1997; Duke Energy 2006.)

Van Horn 1978). Out of as many as 29 resident species documented prior to contamination, by 1977 only common carp, catfish, and fathead minnows (*Pimephales promelas*) were found in the remaining downlake fish community. Piscivore and insectivore species were virtually absent from the downlake area.

In addition to reproductive failure, adult mortality was hypothesized to have affected downlake fish populations at the height of the Se exposure, although no notable adult fish kills were reported. As the lakewide Se contamination diminished over the next 2 decades, populations of the more sensitive fish species migrating from the upper watershed gradually became reestablished in Belews Lake (Barwick and Harrell 1997). As the fish community was reestablished, green sunfish (*Lepomis cyanellus*) were notable among centrarchids in their apparent relative tolerance to higher environmental Se exposures, and in their slightly lower propensity to bioaccumulate Se. By the mid-1990s, the Belews Lake fishery once again represented a diverse warm water community, including sensitive fish species, although marginally elevated rates of deformities in larval fish were reported as late as 1996 (Barwick and Harrell 1997; Lemly 1997a).

A1.4 Lessons Learned

Waterborne Se concentrations in the lake never reached the then-applicable USEPA chronic Se criterion for the protection of aquatic life (35 µg/L Se as selenite, dissolved

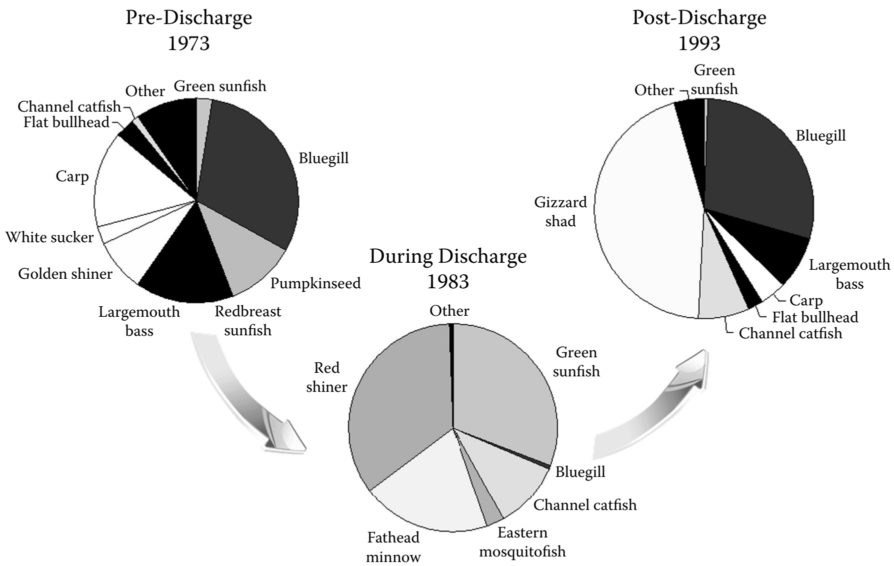

FIGURE A.2 Changes in Belews Lake warm-water fish community composition observed in samples collected at selected 10-year intervals, including sampling prior to, during, and after termination of a coal ash pond discharge to the lake. (Adapted from Barwick and Harrell 1997.)

exposure only), yet the fish community was decimated as a result of food web Se bioaccumulation. USEPA revised the chronic Se criterion for the protection of aquatic life to 5 µg/L using data from Belews Lake. Use of field data implicitly incorporated protection based on dietary exposure. Both Belews Lake and Hyco Lake (see next case study) demonstrated that discharging effluent from coal ash settling ponds into lentic systems can produce undesirable outcomes, due in part to prolonged retention of Se within the system.

Embryolarval stages of fish were clearly more sensitive to Se when compared to adults, as evidenced by the lack of adult fish kills and population structures missing young-of-year classes (Lemly 2002). Monitoring annual recruitment and fish population structure helped to establish the date of the onset and progression of this particular contamination episode. Toxic effects on benthic invertebrates were not documented. Se-related deformities were observed in field-collected specimens, and the development of a standard index of malformations was explored as an ecosystem monitoring tool (Lemly 1997b).

A 1996 retrospective comparison of lake conditions, ten years after waste disposal had ceased, showed a largely recovered but changed community structure (Figure A.2) and higher-than-normal incidence of deformed fry in some species due to the recycling of legacy Se from sediments into food webs (Lemly 1997a). Even as fish populations have recovered, Se concentrations in fish tissues, sediments, and the benthic food web remain substantially elevated with respect to reference sites.

A1.5 References

Barwick DH, Harrell RD. 1997. Recovery of fish populations in Belews Lake following selenium contamination. *Proc Ann Conf SE Assoc Fish Wildl Agencies* 51:209–216.

Cumbie PM, Van Horn SL. 1978. Selenium accumulation associated with fish mortality and reproductive failure. *Proc Ann Conf SE Assoc Fish Wildl Agencies* 32:612–624.

Cutter GA. 1991. Selenium biogeochemistry in reservoirs. Volume 1: Time series and mass balance results. Research Project 2020-1. Charlotte (NC, USA): Electric Power Research Institute.

Duke Energy. 2006. Assessment of balanced and indigenous populations in Belews Lake for Belews Creek Steam Station: NPDES No. NC0024406. Huntersville (NC, USA): Duke Energy Corporate EHS Services.

Lemly AD. 1997a. Ecosystem recovery following selenium contamination in a freshwater reservoir. *Ecotoxicol Environ Saf* 36:275–281.

Lemly AD. 1997b. A teratogenic deformity index for evaluating impacts of selenium on fish populations. *Ecotoxicol Environ Saf* 37:259–266.

Lemly AD. 2002. Symptoms and implications of selenium toxicity in fish: the Belews Lake example. *Aquat Toxicol* 57:29–49.

Van Horn SL. 1978. Development of the sport fishing potential of an industrial cooling lake. Federal Aid in Fish Restoration Project F-23. Raleigh (NC, USA): North Carolina Wildlife Resources Commission.

A2.0 HYCO LAKE, NORTH CAROLINA

A2.1 Selenium Source

Hyco Lake was impounded in 1964 to provide a cooling water supply for a coal-fired electric generating station. Similar to nearby Belews Lake, Hyco Lake received Se-laden effluent from an ash settling pond associated with disposal of fly ash extracted from power plant flue gas, as well as boiler bottom ash. As increased generation capacity was added to the power plant in the 1970s, Hyco Lake began receiving significantly increased loading of Se via ash pond effluent. Fly ash–associated Se inputs to the reservoir were eventually eliminated with the 1990 installation of a dry fly ash collection system at the power plant.

A2.2 Fate and Transformation

Selenium was predominantly in the soluble selenite form as it entered Hyco Lake (Cutter 1991). The degree of Se contamination varied within the lake, with headwater areas and portions of the lake most distant from the effluent outfall being less impacted, as compared to areas closer to the ash pond discharge. Water-column Se concentrations in areas near the effluent source were as high as 7 to 14 μg/L, to near 1 μg/L or less elsewhere. Sediment concentrations ranged over an order of magnitude from 3.6 to 35 mg/kg dw, depending on proximity to the effluent source.

Selenium concentrations in phytoplankton during the height of the contamination ranged from about 5 to slightly above 60 mg/kg dw. Selenium concentrations in benthic invertebrates ranged from 30 to a maximum of 88 mg/kg dw. Fish tissue concentrations were monitored in bluegill (*Lepomis macrochirus*) and largemouth bass

(*Micropterus salmoides*) during the maximal Se inputs into the reservoir. Bluegill muscle concentrations at the peak of the contamination episode ranged between 22 and 68 mg/kg dw, and liver concentrations ranged between 27 and 239 mg/kg dw. Largemouth bass tissues, sampled after dry fly ash collection methods were adopted at the power plant and effluent Se loading to the reservoir was curtailed, were lower, in part reflecting lower lakewide environmental concentrations of Se. Largemouth bass muscle Se ranged from 7 to 24 mg/kg dw, with liver concentrations ranging between approximately 10 and 35 mg/kg dw.

A2.3 Effects

Fish community surveys documented declines in the Hyco Lake fishery in the late 1970s and early 1980s (Crutchfield 2000). Following start-up of an additional large power plant generating unit in September 1980, a month-long fish kill occurred in the reservoir (Carolina Power and Light Corporation 1981). Whereas Hyco Lake had previously supported a diverse warm-water fishery, comprising sunfish (*Lepomis* spp.), largemouth bass, crappie (*Pomoxis* spp.), yellow perch (*Perca flavescens*), and sucker species (Catostomidae*)*, fish recruitment failure and the massive fish kill had by 1980 led to a decimated fishery. As a result of Se bioaccumulation via food web exposures, an assemblage of more Se-tolerant species, including green sunfish (*L. cyanellus*), satinfin shiner (*Cyprinella analostana*), gizzard shad (*Dorosoma cepedianum*), mosquito fish (*Gambusia affinis*), and introduced redbelly tilapia (*Tilapia zillii*) became dominant in the reservoir. Selenium concentrations in the reservoir were reduced beginning in the late 1980s and 1990s with the implementation of a dry fly ash collection system at the power plant. Gradual reductions in Se exposure via the food web led to the reestablishment of a diverse Hyco Lake fish community similar to the period prior to Se impact.

A2.4 Lessons Learned

As in the closely parallel Belews Lake case, the primary exposure of fish to Se in Hyco Lake occured via the food web, and reduced fish population recruitment for sensitive species, due to early life stage susceptibility, was the first observed impact. Laboratory studies subsequently confirmed the importance of maternal transfer via ovary/egg to larvae in fish reproductive failure (Baumann and Gillespie 1986; Woock et al. 1987). Based on fish monitoring data from areas of Hyco Lake having successful recruitment, a warm-water fish muscle Se threshold of 8 mg/kg dw and fish Se liver threshold of 12 mg/kg dw were proposed for protection of reproductive impairment (Crutchfield 2000).

A2.5 References

Baumann PC, Gillespie RB. 1986. Selenium bioaccumulation in gonads of largemouth bass and bluegill from three power plant cooling reservoirs. *Environ Toxicol Chem* 5:695–701.

Carolina Power and Light Corporation 1981. Hyco Reservoir environmental report 1979–1980. Volume III: Chemical and biological studies. New Hill, NC, USA.

Crutchfield JU Jr. 2000. Recovery of a power plant cooling reservoir ecosystem from selenium bioaccumulation. *Environ Sci Policy* 3:S145–S163.
Cutter GA. 1991. Selenium biogeochemistry in reservoirs. Volume 1: Time series and mass balance results. Research Project 2020-1. Charlotte (NC, USA): Electric Power Research Institute.
Woock SE, Garrett WR, Partin WE, Bryson WT. 1987. Decreased survival and teratogenesis during laboratory selenium exposures to bluegill, *Lepomis macrochirus*. *Bull Environ Contam Toxicol* 39:998–1005.

A3.0 MARTIN CREEK RESERVOIR, TEXAS

A3.1 Selenium Source

Martin Creek Reservoir is a large (2000 ha) reservoir used by a coal-fired power plant for cooling water. In 1978, the reservoir received surface water discharge for 8 months from 2 fly ash settling ponds associated with the power plant. Whereas most fly ash–contaminated sites receive contaminant input for years or even decades, Martin Creek Reservoir provided the unique opportunity to examine the impacts of a relatively brief input of Se into an aquatic system. Fish in the system were monitored during the year prior to effluent discharge, and for several years after discharge ceased.

A3.2 Fate and Transformation

As soon as effluent discharge started, dissolved Se concentrations rose rapidly in the fly ash ponds, and discharges from the ponds into the reservoir reached concentrations as high as 2700 µg/L (Garrett and Inman 1984). As a result, concentrations in redear (*Lepomis microlophus*) liver rose to greater than 10 mg/kg ww (40 mg/kg dw if 75% moisture is assumed) (Sorenson et al. 1982a,b). Despite the fact that the discharge only lasted 8 months, Se continued to cycle within aquatic food webs for years thereafter. For example, Se concentrations in fish muscle exceeded 7–9 mg/kg ww (28–36 mg/kg dw if 75% moisture is assumed) following one year of recovery, declining to approximately 3–4 mg/kg ww (12–16 mg/kg dw if 75% moisture is assumed) after 3 years (Garrett and Inman 1984). However, in some cases (e.g., redear sunfish), tissue concentrations still exceeded 7 mg/kg ww (28 mg/kg dw if 75% moisture is assumed) 7 years after discharge ceased.

A3.3 Effects

Numerous studies in Martin Creek Reservoir have documented histopathologic abnormalities in fish tissues following the discharge of power plant effluent into the system. In all cases, authors concluded that abnormalities were attributable to Se because it was the only coal-derived trace element that was accumulated by fish in the reservoir (Sorenson et al. 1983a; Garrett and Inman 1984). Liver, kidney, heart, and gonadal abnormalities were the most commonly documented aberrations (Sorensen et al. 1982a,b, 1983a,b, 1984; Sorenson 1988). For some species (e.g., redear sunfish) overall health was compromised (reduced condition factor) for more than 8 years after discharge ceased (Sorenson 1988). More important, population decline was documented in several fish species, drastically altering the aquatic community in Martin Creek Reservoir. Planktivorous and carnivorous species were most affected, with gizzard shad populations experiencing some of the most drastic declines, from 890 individuals/ha in 1977 to 182 individuals/ha in 1979. Recovery of this species was slow, reaching only 264 individuals/ha in 1981 (Garrett and Inman 1984). For several species, small size classes were reduced for years thereafter, providing indirect evidence of reproductive and/or recruitment problems.

A3.4 Lessons Learned

What we learned from the Martin Creek Reservoir study is that, under certain circumstances, ecological damage can occur quickly once Se is discharged into an aquatic system, but recovery tends to be slow after discharge has ceased. Similar observations were made in Belews Lake. Numerous histopathologic changes were identified that, when accompanied with tissue residue data, build a compelling case that Se is the causative agent contributing to population declines.

A3.5 References

Garrett GP, Inman CR. 1984. Selenium-induced changes in fish populations in a heated reservoir. *Proc Ann Conf SE Assoc Fish Wildl Agencies* 38:291–301.

Sorensen EMB. 1988. Selenium accumulation, reproductive status, and histopathological changes in environmentally exposed redear sunfish. *Arch Toxicol* 61:324–329.

Sorensen EMB, Harlan CW, Bell JS. 1982a. Renal changes in selenium-exposed fish. *Amer J Forensic Med Pathol* 3:123–129.

Sorensen EMB, Bauer TL, Bell JS, Harlan CW. 1982b. Selenium accumulation and cytotoxicity in teleosts following chronic, environmental exposure. *Bull Environ Contam Toxicol* 29:688–696.

Sorensen EMB, Bauer TL, Harlan CW, Pradzynski AH, Bell JS. 1983a. Hepatocyte changes following selenium accumulation in a freshwater teleost. *Amer J Forensic Med Pathol* 4:25–32.

Sorensen EMB, Bell JS, Harlan CW. 1983b. Histopathological changes in selenium exposed fish. *Amer J Forensic Med Pathol* 4:111–123.

Sorensen EMB, Cumbie PM, Bauer TL, Bell JS, Harlan CW. 1984. Histopathological, hematological, condition-factor, and organ weight changes associated with selenium accumulation in fish from Belews Lake, NC. *Arch Environ Contam Toxicol* 13:152–162.

A4.0 D-AREA POWER PLANT, SAVANNAH RIVER, SOUTH CAROLINA

A4.1 Selenium Source

The D-Area power plant has been supplying electricity to the Savannah River Site for more than 50 years. The 70 MW power plant utilizes a wet waste handling system, where slurried fly ash is deposited in a series of large settling basins before surface waters are expelled into Beaver Dam Creek, a tributary of the Savannah River. The configuration of the basins has changed over the decades, with several basins being filled and capped. At one point in the 1950s, the ash slurry was pumped directly into the Savannah River Floodplain, where it settled across a 40-ha natural depression up to 2.7 m deep (Roe et al. 2005). These historical practices resulted in significant surface contamination that persists today. Because the site (both the active basins and the legacy floodplain contamination) is located in an area with rich invertebrate and vertebrate biodiversity, a wide variety of organisms are exposed to the waste materials.

A4.2 Fate and Transformation

Selenium concentrations in the ash have fluctuated over the years, but dissolved concentrations as high as 100–110 μg/L have been documented in portions of the drainage system from 1973 to 1979 (Cherry et al. 1976, 1979a,b; Guthrie and Cherry 1979; Cherry and Guthrie 1977; Rowe et al. 2002). Typical aqueous concentrations at the outfall of the settling basin system are presently much lower, in the range of 2 μg/L. Concentrations are rapidly diluted in Beaver Dam Creek before reaching the Savannah River, but total loading of Se may be an important consideration given the duration of continuous discharge. Selenium in the coal ash is predominately Se (IV) (Jackson and Miller 1998). Se speciation in the aqueous phase has not been investigated at this site.

From an ecological perspective, the D-area site is among the best-studied coal ash disposal sites in the world. Since the 1970s, numerous studies have documented the accumulation of Se and other coal-derived elements in flora and fauna. At the base of the aquatic food chain, algal and plant resources contain concentrations ranging from 1 mg/kg in leaves of trees and emerging macrophytes to 6 mg/kg (all concentrations dry weight) in filamentous algae and 12 mg/kg in submerged macrophytes (Unrine unpublished data). The periphyton, an important food resource for grazing species in the system, contains Se concentrations reaching 7 mg/kg (Unrine unpublished data). Concentrations in aquatic invertebrates have been documented as high as 20 mg/kg ranging from 0.7 mg/kg in chironomids to 20 mg/kg in bivalves (Unrine et al. 2007; Nagle et al. 2001; Guthrie and Cherry 1979). At higher trophic levels, Se is clearly bioavailable to most species of fish, bird, amphibian, and reptile studied to date. For example, studies have documented whole-body concentrations of Se from 15 mg/kg in fish and 25 mg/kg in amphibian larvae at the site (Unrine et al. 2007; Rowe et al. 2002). The highest concentrations of Se have been found in individual organs from higher trophic level predators such as water snakes (exceeding 100 mg/kg in liver) that feed upon fish and amphibians in the basins (Hopkins et al. 2002). Some of these prey species have whole-body concentrations of Se that also exceed 100 mg/kg (Hopkins et al. 2006). When Se concentrations in whole bodies of other animals were compared across trophic levels using stable isotopes, there was no evidence that Se had biomagnified in this system (Unrine et al. 2007). Concentrations of other trace elements such as As, Cd, Sr, and Cu are also present at elevated concentrations in food webs at the site, but the interactions of these elements with Se have not been rigorously studied in this system.

Many of the species studied to date (amphibians, fish [*Gambusia*], turtles, alligators, and birds [green herons and grackles]) maternally transfer Se to their eggs (Nagle et al. 2001; Bryan et al. 2003; Roe et al. 2004; Staub et al. 2004; Hopkins et al. 2006). Of particular interest are species such as birds and amphibians that move into the site seasonally to breed. For example, narrow-mouth toads transfer

53% of their total body burden of Se to their eggs, resulting in concentrations as high as 100 mg/kg dw in eggs (Hopkins et al. 2006).

Selenium in animal tissues from the site has primarily been shown to consist of Se (-II) in proteinaceous forms or as selenomethionine, supporting the notion that uptake, reductive metabolism, and assimilation of Se at the base of food webs is an important factor in determining bioavailability. High concentrations of Se (-II) were present in deformed mouth parts in amphibian larvae (Punshon et al. 2005). Another study indicated that Se in amphibian larvae primarily consisted of selenomethionine and proteinaceous forms of Se with a relatively small amount of selenite present (Jackson et al. 2005).

A4.3 Effects

Accumulation of Se and other coal-derived elements has adverse effects on a variety of fauna in D-area. Sublethal effects include changes in endocrinology, metabolism, performance, predator–prey interactions, behavior, reproductive success, and histological aberrations (Rowe et al. 2002; Bryan et al. 2003; Ganser et al. 2003; Hopkins et al. 2003, 2004, 2005, 2006; Roe et al. 2004, 2006; Snodgrass et al. 2003, 2004, 2005; Staub et al. 2004). In several cases, direct lethality in amphibian larvae (*Bufo terrestris*) and juvenile lake chubsucker (*Erimyzon sucetta*) has been observed. Indirect effects appear to be extremely common in the system, particularly for higher trophic-level species that suffer from reduced food resources in the site. In one of the more interesting studies, microbial communities in downstream areas were also affected by the effluent (Stepanauskas et al. 2005). Specifically, coevolution of metal resistance and antibiotic resistance was documented downstream from D-area as well as downstream from other coal-fired power plants.

A4.4 Lessons Learned

Studies in D-area suggest that benthic feeding species (e.g., certain amphibian larvae and benthic feeding fish) and fossorial species (e.g., adult burrowing amphibians) may be particularly at risk, accumulating as much or more Se in their tissues than higher trophic level species. The D-area studies also highlight connections between aquatic and terrestrial Se exposure pathways from disposal of coal ash in settling basins. Some limited information on Se transformation from inorganic forms in fly ash to amino acid and proteinaceous forms in vertebrates also exists for D-area (Punshon et al. 2005; Jackson et al. 2005), which is lacking for most sites.

Like many other sites, the presence of other contaminants in the effluent has complicated the process of ascribing adverse effects to Se alone. The indirect effects of the waste stream, including cascading food web effects, further complicate the risk assessment process.

A4.5 References

Bryan L, Hopkins WA, Baionno JA, Jackson BP. 2003. Maternal transfer of contaminants to eggs in common grackles (*Quiscalus quiscala*) nesting on coal fly ash basins. *Arch Environ Contam Toxicol* 45:273–277.

Cherry DS, Guthrie RK. 1977. Toxic metals in surface waters from coal ash. *Water Resour Bull* 13:1227–1236.

Cherry DS, Guthrie RK, Rogers JH Jr, Cairns J Jr, Dixon KL. 1976. Responses of mosquitofish (*Gambusia affinis*) to ash effluent and thermal stress. *Trans Amer Fish Soc* 105:686–694.

Cherry DS, Larrick SR, Guthrie RK, Davis EM, Sherberger FF. 1979a. Recovery of invertebrate and vertebrate populations in a coal ash-stressed drainage system. *J Fish Res Board Can* 36:1089–1096.

Cherry DS, Guthrie RK, Sherberger FF, Larrick SR. 1979b. The influence of coal ash and thermal discharges upon the distribution and bioaccumulation of aquatic invertebrates. *Hydrobiologia* 62:257–267.

Ganser LR, Hopkins WA, O'Neil L, Hasse S, Roe JH, Sever DM. 2003. Liver histopathology of the southern watersnake, *Nerodia fasciata fasciata*, following chronic exposure to trace element-contaminated prey from a coal ash disposal site. *J Herpetol* 37:219–226.

Guthrie RK, Cherry DS. 1979. Trophic level accumulation of heavy metals in a coal ash basin drainage system. *Water Resour Bull* 15:244–248.

Hopkins WA, Roe JH, Snodgrass JW, Staub BP, Jackson BP, Congdon JD. 2002. Trace element accumulation and effects of chronic dietary exposure on banded water snakes (*Nerodia fasciata*). *Environ Toxicol Chem* 21:906–913.

Hopkins WA, Snodgrass JW, Staub BP, Jackson BP, Congdon JD. 2003. Altered swimming performance of benthic fish (*Erimyzon sucetta*) exposed to contaminated sediments. *Arch Environ Contam Toxicol* 44:383–389.

Hopkins WA, Staub BP, Snodgrass JW, Taylor BE, DeBiase AE, Roe JH, Jackson BP, Congdon JD. 2004. Responses of benthic fish exposed to contaminants in outdoor microcosm—examining the ecological relevance of previous laboratory toxicity test. *Aquat Toxicol* 68:1–12.

Hopkins WA, Snodgrass JW, Baionno JA, Roe JH, Staub BP, Jackson BP. 2005. Functional relationships among selenium concentrations in the diet, target tissues, and nondestructive tissue samples of two species of snakes. *Environ Toxicol Chem* 24: 344–351.

Hopkins WA, DuRant SE, Staub BP, Rowe CL, Jackson BP. 2006. Reproduction, embryonic development, and maternal transfer of contaminants in an amphibian *Gastrophryne carolinensis*. *Environ Health Persp* 114:661–666.

Jackson BP, Miller W. 1998. Arsenic and selenium speciation in coal fly ash extracts by ion chromatography-inductively coupled plasma mass spectrometry. *J Analyt Atom Spectrom* 13:1107–1112.

Jackson BP, Hopkins WA, Unrine J, Baionno J, Punshon T. 2005. Selenium speciation in amphibian larvae developing in a coal fly ash settling basin. In: Holland JG, Bandura DR, editors, Plasma source mass spectrometry, current trends and future developments. Special Publication No. 301. Cambridge (UK): The Royal Society of Chemistry. p 225–234.

Nagle RD, Rowe CL, Congdon JD. 2001. Accumulation and selective maternal transfer of contaminants in the turtle *Trachemys scripta* associated with coal ash deposition. *Arch Environ Contam Toxicol* 40:531–536.

Punshon T, Jackson BP, Lanzirotti A, Hopkins WA, Bertsch PM, Burger J. 2005. Application of synchrotron x-ray microbeam spectroscopy to the determination of metal distribution and speciation in biological tissues. *Spectros Lett* 38:343–363.

Roe JH, Hopkins WA, Baionno JA, Staub BP, Rowe CL, Jackson BP. 2004. Maternal transfer of selenium in *Alligator mississippiensis* nesting downstream from a coal burning power plant. *Environ Toxicol Chem* 23:1969–1972.

Roe JH, Hopkins WA, Jackson BP. 2005. Species- and stage-specific differences in trace element tissue concentrations in amphibians: implications for the disposal of coal-combustion wastes. *Environ Pollut* 136:353–363.

Roe JH, Hopkins WA, Durant SE, Unrine JM. 2006. Effects of competition and coal combustion wastes on recruitment and life history characteristics of salamanders in temporary wetlands. *Aquat Toxicol* 79:176–184.
Rowe CL, Hopkins WA, Congdon JD. 2002. Ecotoxicological implications of aquatic disposal of coal combustion residues in the United States: a review. *Environ Monit Assess* 80:207–276.
Snodgrass JW, Hopkins WA, Roe JH. 2003. Effects of larval stage, metamorphosis, and metamorphic timing on concentrations of trace elements in bullfrogs (*Rana catesbeiana*). *Environ Toxicol Chem* 22:1597–1604.
Snodgrass JW, Hopkins WA, Broughton J, Gwinn D, Baionno JA, Burger J. 2004. Species-specific responses of developing anurans to coal combustion wastes. *Aquat Toxicol* 66:171–182.
Snodgrass JW, Hopkins WA, Jackson BP, Baionno JA, Broughton J. 2005. Influence of larval period on responses of overwintering green frog (*Rana clamitans*) larvae exposed to contaminated sediments. *Environ Toxicol Chem* 24:1508–1514.
Staub BP, Hopkins WA, Novak J, Congdon JD. 2004. Respiratory and reproductive characteristics of Eastern mosquitofish (*Gambusia holbrooki*) inhabiting a coal ash settling basin. *Arch Environ Contam Toxicol* 46:96–101.
Stepanauskas R, Glenn TC, Jagoe CH, Tuckfield RC, Lindell AH, McArthur JV. 2005. Elevated microbial tolerance to metals and antibiotics in metal-contaminated industrial environments. *Environ Sci Technol* 39:3671–3678.
Unrine JM, Hopkins WA, Romanek CS, Jackson BP. 2007. Bioaccumulation of trace elements in omnivorous amphibian larvae: implications for amphibian health and contaminant transport. *Environ Pollut* 149:182–192.

A5.0 LAKE MACQUARIE, NEW SOUTH WALES, AUSTRALIA

A5.1 INTRODUCTION

Lake Macquarie is a 125-km^2 barrier estuary south of the city of Newcastle on the central coast of New South Wales, Australia. The lake catchment has an area of approximately 622 km^2. It is shallow with an average depth of about 6.7 m. The estuary extends 22 km in a north-south direction with a maximum width of 9 km and is the largest coastal lake in eastern Australia. The lake's narrow entrance results in poor tidal flushing and an intertidal range of approximately 6–15 cm. As a result, most contaminants in the catchment are expected to accumulate in the lake. Lake Macquarie is characteristically marine given the minimal freshwater contribution from the 2 main fluvial inflows.

Lake Macquarie once supported a large commercial and recreational fishery. Approximately 280 species of fish are known to inhabit the waters of Lake Macquarie. Prior to 2006, sea mullet caught commercially had an estimated market value of AU$ 1.0 million per annum, with a catch in 1991/92 of about 108 tonnes (NSW Fisheries 1995). The lake is now encompassed within a marine park and fishing is limited to recreational licenses.

A5.2 SELENIUM SOURCES

Industrial sources of contamination in the northern section of the lake include the discharges from the lead-zinc smelter that commenced operation in 1897, a steel foundry, collieries (underground coal mines), and sewage-treatment works. The southern section of the lake includes 2 coal-fired power plants at Eraring and Vales Point. For the best part of a century, the ash produced during coal combustion was placed into dams located on the foreshore of the lake. The ash dams and stack emissions from the coal-fired power stations produced large amounts of seleniferous fly ash. The emissions and ash contained Se concentrations of 50–300 mg/kg dw. Peters et al. (1999) showed that Se contamination from fly ash dams has been occurring for a long period, but significant Se contamination of the lake is a phenomenon of the last 30 years. Sediment Se concentrations measured at reference sites at depth (to 30 cm) average 0.3 mg/kg dw, and surficial sediments range from 0.9 to 5.6 mg/kg dw (<100 μm fraction) (Kirby et al. 2001). The highest concentration, 14 mg/kg dw at depth (Batley 1987), was found adjacent to the Vales Point coal-fired power station. Elevated Se concentrations occur at depths well within the reach of common bioturbating organisms.

Lake Macquarie is a marine seagrass–dominated system, which is predominantly lentic due to the poor flushing of the waters with minor currents in the system generated by wind activity. The lake has low turbidity due to the high salinity, low movement, and high iron content in the water. Dissolved Se concentrations (using a 0.45 μm filter) are below detection limits (<0.25 μg/L), and the dominant species is selenite (Jolley unpublished data).

A5.3 Fate and Transformation

Barwick and Maher (2003) provide a detailed food web with associated Se concentrations. Based on these data, the authors conclude that Se biomagnification has occurred and that the elevated Se concentrations in the top carnivores resulted from uptake of Se through benthic food chains. Uptake of Se from sediments by Lake Macquarie benthic species has been confirmed in laboratory studies (Peters et al. 1999).

A5.4 Effects

Selenium concentrations in a number of species exceeded those allowable for human consumption (Barwick and Maher 2003). Effects on the lake's inhabitants have not been confirmed.

A5.5 Lessons Learned

Elevated Se concentrations occur in the food webs of Lake Macquarie. Further research at this site is needed to determine the cumulative effects of Se on higher trophic individuals, populations, and communities. Future studies should consider incorporating aquatic birds into the monitoring regime.

A5.6 References

Barwick M, Maher W. 2003. Biotransference and biomagnification of selenium, copper, cadmium, zinc, arsenic and lead in a temperate seagrass ecosystem from Lake Macquarie Estuary, NSW, Australia. *Mar Environ Res* 56:471–502.

Batley GE. 1987. Heavy metal speciation in waters, sediments and biota from Lake Macquarie, New South Wales. *Austr J Mar Freshw Res* 38:591–606.

Kirby J, Maher W, Krikowa F. 2001. Selenium, cadmium, copper, and zinc concentrations in sediments and mullet (*Mugil cephalus*) from the southern basin of Lake Macquarie, NSW, Australia. *Arch Environ Contam Toxicol* 40:246–256.
NSW Fisheries. 1995. A review of the information on the factors affecting the fisheries of Lake Macquarie. Fisheries Research Institute, Australia.
Peters GM, Maher WA, Jolley D, Carroll BI, Gomes VG, Jenkinson AV, McOrist GD. 1999. Selenium contamination, redistribution and remobilisation in sediments of Lake Macquarie, NSW. *Organic Geochem* 30:1287–1300.

A6.0 ELK RIVER VALLEY, SOUTHEAST BRITISH COLUMBIA, CANADA

A6.1 Selenium Sources

The Elk Valley and surrounding Rocky Mountains are rich in high-grade coal deposits that have been mined since the late 1800s. With the introduction of open-pit mining techniques in the 1950s, the greatly increased disturbance area and subsequent volumes of waste rock led to weathering and release of pyrite-associated Se. The waste rock is transported to extensive dump areas, often valley fills, which leach and drain to the Elk River. There are 5 large mines in the valley with a 2008 production of about 22 million tonnes of coal, and which together contributed in 2006 an estimated load of 6.2 tonnes of Se to the Elk River (Figure A.3).

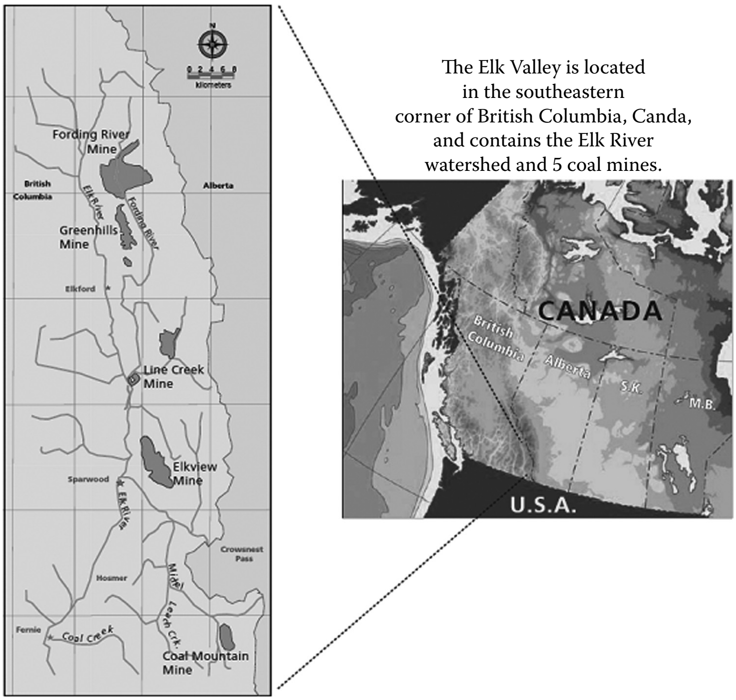

FIGURE A.3 Location of active coal mining areas in the Elk River watershed (from Teck Coal Ltd.).

A6.2 Fate and Transformation

Waste rock leachates drain directly to the Elk River or to the Fording River, which is the major upstream tributary, or may flow into small wetland areas before entering the main river. Selenium is released as selenate (Martin et al. 2008), with effluent concentrations ranging to more than 300 µg/L. Where effluents flow to ponds and marshes, dissolved Se concentrations typically range from 50 to 80 µg/L. Selenium levels in the main Elk River in 2008 ranged from 9.6 µg/L near the mines to 5.8 µg/L at a long-term water quality monitoring site roughly 60 km downstream. Se concentrations in the Elk River have been increasing at about 6% to 8% per year for the past decade (Elk Valley Se Task Force 2008a).

The elevated water-column Se concentrations have translated to elevated concentrations in biota. In 2002, Se concentrations in periphyton in lentic receiving waters averaged about 5 mg/kg dw, and ranged from 3.9 to 12.3 mg/kg dw in rooted macrophytes (Orr et al. 2006). Benthic invertebrates range from 26 to 96 mg/kg dw in lentic habitats and from 2.7 to 9.6 mg/kg dw in lotic habitats. Levels in vertebrates have been measured as well, with concentrations in Columbia spotted frog (*Rana luteiventris*) eggs in Se exposed areas ranging from 10 to 38 mg/kg dw, in eggs of shorebirds (spotted sandpiper, *Actitis macularia*) from 3 to 4 mg/kg dw, and in eggs of marsh birds (red-winged blackbird, *Agelaius phoeniceus*) from 5 to 23 mg/kg dw (Minnow Environmental 2007). Fish tissues (westslope cutthroat trout, *Oncorhyncus clarki lewisi*) are likewise elevated, with muscle Se concentrations in exposed lentic areas up to 76 mg/kg dw and in exposed lotic areas from 4 to 15 mg/kg dw compared to reference area concentrations of 3 to 5 mg/kg dw. Higher levels in lentic areas of the watershed are postulated to be due to production of organo-Se by the detrital microbial community, with subsequent uptake by biota (Orr et al. 2006).

A6.3 Effects

Studies have been conducted in both lentic and lotic environments and species to examine effects of elevated Se and to establish regional toxicity thresholds. Studies of waterbirds (American dipper [*Cinclus mexicanus*] and spotted sandpiper; Harding et al. 2005) showed decreased hatchability in the sandpiper at average egg Se concentrations of 2.2 mg/kg ww. Differences in measured endpoints in American dipper (1.1 mg/kg ww egg Se) were not statistically significant (p = 0.056). Amphibian studies showed a positive relationship between egg Se content and development of deformities (Elk Valley Se Task Force 2008). Three attempts (Kennedy et al. 2000; Rudolph et al. 2008; Nautilus Environmental and Interior Reforestation 2009) have been made to establish site-specific Se effects thresholds in cutthroat trout. The first attempt was by Kennedy et al. (2000), which showed no effect even at high Se concentrations (~80 mg/kg dw egg Se). Subsequent work was conducted to address a critique of this study by Hamilton and Palace (2001). The 2 subsequent studies (Rudolph et al. 2008; Nautilus Environmental and Interior Reforestation 2009) showed similar results, with effect thresholds (inferred either as an “effect level” or a calculated EC10) of 19 to 22 mg/kg dw Se. Both of these studies also indicated reproductive failure, through either unviable embryos or unfertilizable eggs, at Se concentrations greater than about 35 mg/kg dw egg Se. Selenium in trout in the most exposed areas of the Elk Valley are at risk of Se toxicity, while levels elsewhere in the valley are currently (2009) lower than the foregoing effect levels.

A6.4 Lessons Learned

The studies conducted in the Elk River Valley highlight the challenge of conducting field-based research on Se-contaminated sites. Apart from the logistical difficulties, there are potential confounding factors related to water chemistry, weather, or hydrology that make it difficult to isolate the effects attributable solely to Se. Selenium accumulation in biota in lentic and lotic environments has been well demonstrated in studies of wetland areas adjacent to the river.

Based on studies conducted to date, current levels of Se in the Elk River Valley are resulting in only localized adverse effects (Elk Valley Se Task Force 2008; Canton et al. 2008).

A6.5 References

Canton SP, Fairbrother A, Lemly AD, Ohlendorf H, McDonald LE, MacDonald DD. 2008. Experts workshop on the evaluation and management of selenium in the Elk Valley, British Columbia, Workshop summary report. http://www.env.gov.bc.ca/eirs/epd

Elk Valley Selenium Task Force. 2008. Selenium status report 2007—Elk River Valley, BC. Sparwood, BC, Canada.

Hamilton SJ, Palace VP. 2001. Assessment of selenium in lotic ecosystems. *Ecotox Env Safet* 50:161–166.

Harding LE, Graham M, Paton D. 2005. Accumulation of selenium and lack of severe effects on productivity of American dippers (*Cinclus mexicanus*) and spotted sandpipers (*Actitis macularia*). *Arch Environ Contam Toxicol* 48:414–423.

Kennedy CJ, McDonald LE, Loveridge R, Strosher MM. 2000. The effect of bioaccumulated selenium on mortalities and deformities in the eggs, larvae, and fry of a wild population of cutthroat trout (*Oncorhynchus clarki lewisi*). *Arch Environ Contam Toxicol* 39: 46–52.

Martin AJ, Wallschläger D, London J, Wiramanaden CIE, Pickering IJ, Belzile N, Chen YW, Simpson S. 2008. The biogeochemical behaviour of selenium in two lentic environments in the Elk River Valley, British Columbia. Technical Paper 8, Proceedings of the 32nd Annual British Columbia Mine Reclamation Symposium, September 15–18, 2008. 2008. Kamloops, BC, Canada.

Minnow Environmental. 2007. Selenium monitoring in the Elk River Watershed 2006. Sparwood (BC, Canada): Elk Valley Selenium Task Force.

Nautilus Environmental and Interior Reforestation. 2009. Evaluation of the effects of selenium on early lifestage development of westslope cutthroat trout from the Elk Valley, BC. Elkford (BC, Canada): Elk Valley Selenium Task Force.

Orr PL, Guiguer KR, Russel K. 2006. Food chain transfer of selenium in lentic and lotic habitats of a western Canadian watershed. *Ecotoxicol Environ Saf* 63:175–188.

Rudolph BL, Andreller I, Kennedy CJ. 2008. Reproductive success, early life stage development, and survival of westslope cutthroat trout (*Oncorhynchus clarki lewisi*) exposed to elevated selenium in an areas of active coal mining. *Environ Sci Technol* 42:3109–3114.

A7.0 AREAS OF THE APPALACHIAN MOUNTAINS AFFECTED BY MOUNTAINTOP MINING AND VALLEY FILLS

A7.1 Selenium Sources

Large-scale land disturbance is associated with waste rock management at coal mines in the southern and central Appalachian Mountains. Tops of mountain ridges are sheared off, and waste rock is deposited in adjacent valleys (valley fills) and back-stacked to preserve landscape contours. Over 4.8 million hectares, mainly in West Virginia, are scheduled for mining through this technique during the next several years because low-sulfur coal resources are dwindling, forcing mining of near-surface, thin-layered coals of Appalachia. These coal layers are unique in that they are enriched in Se and do not generate as much acid drainage as other coals in the area.

Surface coal mining production (million tonnes) for 1998 was as follows: southern West Virginia, 44.1; eastern Kentucky, 45; Virginia, 7.7; and Tennessee, 1.5. Ninety-five percent of the surface mining in southern West Virginia would be classified as mountaintop mining. Estimated remaining years of surface production in West Virginia is about 50 and in Kentucky is about 100.

A7.2 Fate and Transformation

Most major rivers and tributaries east of the Mississippi River originate in the mountains of the Appalachian regions. Ecoregions in the mountaintop mining area are unique because they combine characteristically northern species with their southern counterparts, and thus boast enormous richness and diversity. Headwater stream populations have the greatest potential for natural selection processes that may result in development of new species/subspecies. The southern Appalachians have one of the richest salamander fauna in the world. Many species of birds, such as the cerulean warbler (*Dendroica cerulea*), Louisiana waterthrush (*Seiurus motacilla*), and Acadia flycatcher (*Empidonax virescens*), depend on large areas of relatively unbroken forest (93% forest cover) and headwater stream habitats. The mountaintop mining area also is unique and important in the evolution and speciation of North American freshwater fishes. Fifty-six species of fish are present in the watersheds, with small headwater streams harboring populations with unique genetic diversity.

A review of available environmental data from Appalachia reveals leaching of Se into streams below valley fills (median, 11.7 μg/L) when compared to streams in non-mined areas (median, 1.5 μg/L) (USEPA 2005). Ponds located at the toes of fills, which provide mitigation habitat for birds and fish, had the highest concentrations (up to 42 μg/L). This mobilization of Se is expected because, as mined materials are exposed, Se is 1) oxidized into mobile selenate; 2) transported regionally within watersheds; 3) biochemically transformed to bioavailable Se; and 4) eventually accumulates in prey, which serve as diet for higher trophic level predators (Presser et al. 2004a,b).

A7.3 Effects

Concentrations of Se in streams exceed Se water-quality criteria for protection of aquatic life (USEPA 2005). Fish tissue Se concentrations exceed toxicity criteria for fish and dietary criteria for protection of wildlife. The Upper Mud River Reservoir in West Virginia, downstream from one of the largest mountaintop removal operations in the United States, recently came under scrutiny because of the identification of deformed juvenile fish (Appalachian Center for the Economy and the Environment et al. 2009). Selenium concentrations in bluegill averaged 28 mg/kg dw (USGS 2008). Streams affected by waste material had lower numbers of total species and benthic species than unmined streams, and mayfly populations have been decimated (Pond et al. 2008).

A7.4 Lessons Learned

The problems in the Appalachians are arising not from coals extraordinarily enriched in Se, but from the mining practices. Fish in reservoirs below valley fills are vulnerable, along with food webs in ponds at toes of valley fills. Conclusions of studies in the phosphate fields of southeast Idaho concerning processes of Se mobilization from waste rock piles are relevant to processes occurring in waste overburden deposited in valley fills (Presser et al. 2004a,b).

A7.5 References

Appalachian Center for the Economy and the Environment, Save Our Cumberland Mountains, Ohio Valley Environmental Coalition, Coal River Mountain Watch, Sierra Club. 2009. Toxic selenium: how mountaintop removal coal mining threatens people and streams. Lewisburg (WV, USA) http://www.sierraclub.org/coal/downloads/Seleniumfactsheet.pdf.

Pond GJ, Passmore ME, Borsuk FA, Reynolds I, Rose CL. 2008. Downstream effects of mountaintop coal mining: comparing biological conditions using family- and genus-level macroinvertebrate bioassessment tools. *J N Am Benthol Soc* 27:717–737.

Presser TS, Piper DZ, Bird KJ, Skorupa JP, Hamilton SJ, Detwiler SJ, Huebner MA. 2004. The Phosphoria Formation: a model for forecasting global selenium sources to the environment. In: Hein JR, editor, Life cycle of the Phosphoria Formation: from deposition to the post-mining environment. New York (NY, USA): Elsevier. p 299–319.

Presser TS, Hardy M, Huebner MA, Lamothe PJ. 2004. Selenium loading through the Blackfoot River watershed: linking sources to ecosystems. In: Hein JR, editor, Life cycle of the Phosphoria Formation: from deposition to post-mining environment. New York (NY, USA): Elsevier. p 437–466.

USEPA (U.S. Environmental Protection Agency). 2005. Programmatic environmental impact statement on mountaintop mining and associated valley fills in Appalachia (http://www.epa.gov/region3/mtntop/eis2005.htm).

USGS. 2008. Annual report for West Virginia, Mud River Reservoir data. Charleston (WV, USA): U.S. Geological Survey.

A8.0 KESTERSON RESERVOIR, SAN JOAQUIN VALLEY, CALIFORNIA

A8.1 Selenium Source

The arid San Joaquin Valley in the southern Central Valley of California has undergone extensive agricultural development since the 1950s. Regional water supplies were increasingly diverted to agricultural and urban uses and away from natural wetlands within the valley. More than 90% of wetlands in the valley disappeared, severely limiting Pacific Flyway waterfowl use during annual migrations (Ohlendorf et al. 1990).

Beginning in 1949, as part of the Central Valley Project under the direction of the U.S. Bureau of Reclamation, plans were developed to build a large-scale subsurface drainage system to alleviate potential salinization of irrigation croplands. Funding was obtained in the 1970s, and planning and construction began on the San Luis Drain (SLD). The SLD was a canal intended to collect subsurface (tile) irrigation drainwater containing high levels of mineral salts and transport it to a yet-to-be determined discharge point in the San Francisco Bay (California).

Kesterson Reservoir, a series of a dozen shallow interconnected ponds totaling approximately 500 ha, was constructed adjacent to the SLD. As originally envisioned, the reservoir would have controlled flows within the completed drain system. Located at the temporary endpoint of SLD construction, the reservoir became, in effect, a series of terminal flow evaporative ponds. Although using agricultural drainage to supply wetlands in the valley was controversial because of mineral contaminants, the Kesterson National Wildlife Refuge (NWR) was established by cooperative agreement between the U.S. Fish and Wildlife Service and the U.S. Bureau of Reclamation to benefit wildlife populations and related recreational users.

In 1975, funding limitations and environmental concerns stopped construction of the SLD. Kesterson Reservoir was managed as a series of interconnected evaporation ponds and surrounding native grassland (Presser and Ohlendorf 1987; Ohlendorf et al. 1990; Schuler et al. 1990).

A8.2 Fate and Transformation

Elevated concentrations of Se in irrigation drainage entering Kesterson Reservoir were not initially detected because of a flawed sample preparation procedure performed prior to analysis (Presser and Ohlendorf 1987). Without the correct digestion, some forms of Se were lost in the analysis procedure. This delayed the identification of Se as a possible contaminant in drainage and allowed its discharge to continue, loading the ecosystem with an estimated 7900 kg of Se during the period from 1981 to 1985 (Presser and Piper 1998). By 1983, Se concentrations measured in mosquitofish ranged up to 247 mg/kg dw.

Water-column Se concentrations entering Kesterson Reservoir from the SLD in 1983 ranged from 140 to 1400 μg/L, averaging 340 μg/L. These Se concentrations were far in excess of concentrations (<2 μg/L) measured in the nearby Volta Wildlife Management Area, which was not impacted by agricultural drainage (Presser and Barnes 1984; Presser and Ohlendorf 1987). In terms of speciation, 98% of dissolved Se was selenate in the SLD and pond 2, but 20%–30% of dissolved Se was selenite in pond 11, the terminal pond in the evaporation pond series. Sediment Se concentrations in the SLD were exceptionally elevated (up to 210 mg/kg dw). Kesterson Reservoir aquatic organisms consumed by waterfowl, as well as species as diverse as amphibians, reptiles, and mammals utilizing the site, bioaccumulated elevated Se concentrations from incoming drainwater (Ohlendorf et al. 1988). Initial sampling showed Se concentrations moving through the food webs: filamentous algae, rooted plants, and net plankton, 35–85 mg/kg dw; insects and mosquitofish, 22–175 mg/kg dw. Highest mean Se concentrations occurred in midge (Diptera) larvae (139 mg/kg dw), dragonfly (Odonata) nymphs (122 mg/kg dw), damselfly nymphs (175 mg/kg dw), and mosquitofish (170 mg/kg dw) (Ohlendorf et al. 1986). These means were approximately 12 to 130 times those found at Volta Wildlife Management Area (a reference area). Sampling in 1984 showed species mean Se concentrations ranging from 1.5 to 170 mg/kg dw for Kesterson aquatic macrophytes, and from 18.6 to 102 mg/kg dw for aquatic insects (Schuler et al. 1990).

A8.3 Effects

In 1983, a local fish extirpation occurred involving up to 8 warm-water species, with only mosquitofish, a species that is relatively Se tolerant, remaining in the SLD and refuge (Saiki and Lowe 1987; Skorupa 1998). The SLD mosquitofish population, analyzed in 1984–1985, experienced impaired reproductive success, as documented by increased rates of stillborn fry with unabsorbed yolk sacs, and a 70% to 77% survival rate, compared to 97% to 99% survival rate for reference site fish (Saiki and Ogle 1995).

Deformity and death in embryos and hatchlings of aquatic bird populations were widespread; toxicity and immune deficiency contributed to the death of adult aquatic birds (Ohlendorf 1989; Skorupa 1998). Kesterson NWR waterfowl populations exhibited severe reproductive impairment, with over 40% of nests having one or more dead embryos, and nearly 20% having a malformed embryo or chick. Species affected initially included mallard ducks (*Anas platyrhyncos*), American coots (*Fulica americana*), avocets (*Recurvirostra avosetta*), eared grebes (*Podiceps nigricollis*), and black-necked stilts (*Himantopus mexicanus*). Subsequently, malformed young were observed in additional duck species. Developmental abnormalities were of types linked to excessive Se exposure, and included missing or abnormal eyes, wings, legs, feet, and beaks, with frequently more than one abnormality observed per specimen (Ohlendorf 1989; Skorupa 1998). Additionally, malformed major organs such as heart, brains, and liver were documented (Ohlendorf et al. 1986; Ohlendorf et al. 1988; Hoffman et al. 1988). Eared grebe eggs averaged 69.7 mg/kg dw and coot eggs 30.9 mg/kg dw. These 2 species contained the highest frequency of embryotoxicity, with 64% of nest affected. Ducks and stilts had lower frequencies of embryotoxicity (24% of nests affected). Mean egg Se from these species ranged from 6.85 to 28.2 mg/kg dw. By comparison, mean Se concentrations in eggs from the reference Volta Wildlife Management Area were generally less than 2 mg/kg dw, and no abnormal embryos were found.

By 1986, agricultural irrigation inputs were stopped, the SLD closed, and Kesterson NWR was designated as a contaminated site to be remediated. The ponds were filled and capped with clean soil in 1988, substantially limiting the wildlife exposures. The Kesterson experience subsequently led the U.S. Department of Interior to initiate screening at wildlife refuges associated with agricultural irrigation in 13 western U.S. states (Presser et al. 1994; Seiler et al. 2003).

A8.4 Lessons Learned

The Kesterson Reservoir case history greatly expanded our understanding of the geologic origin of Se, the analytical methods necessary for the complete reduction of Se species, and the importance of speciation in determining outcomes in Se-contaminated ecosystems. Specifically, in terms of the San Joaquin Valley, documentation at Kesterson Reservoir led to understanding the ecological risks associated with irrigation practices in arid environments containing seleniferous soils or source rock strata such as marine shales. At Kesterson Reservoir, the following basic steps were identified: 1) Se lost from the water column of the ponds entered the food chain through uptake by biota; 2) biological processes, rather than thermodynamic processes, determined the reduction of Se and its consequent entry into the food web; and 3) the probability of embryo death or deformity was statistically related to Se concentrations in the egg, with both of these factors understood to be influenced by dietary Se levels.

The culmination of Se-associated avian reproductive impairment and abnormalities came to be known as the "Kesterson Syndrome" (Skorupa 1998). The associated phenomenon of biogeochemical translocation of toxic Se levels from source (sedimentary rock formations) via irrigation drainage conveyance to the aquatic ecosystem and ultimately to waterfowl came to be termed the "Kesterson Effect" (Presser 1994). Identification of the components in this biogeochemical pathway led to a reconnaissance effort within the western United States to look for areas where seleniferous agricultural wastewater was being discharged into wetland areas (Presser et al. 1994; Seiler et al. 2003).

Selenium exposures triggering reproductive impairment in waterfowl vary from site to site, which is explained in part by species differences in migration patterns, feeding preferences, and wildlife site fidelity (i.e., the tendency to remain in an area over an extended period or return to an area previously occupied). Site assessments should include relatively sedentary species (e.g., coots and grebes), and sampling should be performed near the end of the nesting season to ensure appropriate consideration of worst-case ecological risk (Ohlendorf et al. 1990; Fairbrother et al. 1999).

A8.5 References

Fairbrother A, Brix KV, Toll JE, McKay S, Adams WJ. 1999. Egg selenium concentrations as predictors of avian toxicity. *Human Ecol Risk Assess* 5:1229–1253.

Hoffman DJ, Ohlendorf HM, Aldrich TW. 1988. Selenium teratogenesis in natural populations of aquatic birds in central California. *Arch Environ Contam Toxicol* 17:519–525.

Ohlendorf HM. 1989. Bioaccumulation and effects of selenium in wildlife. In: Jacobs LW, editor, Selenium in agriculture and the environment. Special Publication 23. Madison (WI, USA): American Society of Agronomy and Soil Science Society of America. p 133–177.

Ohlendorf HM, Hoffman DJ, Saiki MK, Aldrich TW. 1986. Embryonic mortality and abnormalities of aquatic birds: apparent impacts of selenium from irrigation drainwater. *Sci Total Environ* 52:49–63.

Ohlendorf HM, Kilness AW, Simmons JL, Stroud RK, Hoffman DJ, Moore JF. 1988. Selenium toxicosis in wild aquatic birds. *J Toxicol Environ Health* 24:67–92.

Ohlendorf HM, Hothem RL, Bunck CM, Marois KC. 1990. Bioaccumulation of selenium in birds at Kesterson Reservoir, California. *Arch Environ Contam Toxicol* 19:495–507.

Presser TS. 1994. "The Kesterson Effect." *Environ Manage* 18:437–454.
Presser TS, Barnes I. 1984. Selenium concentrations in waters tributary to and in the vicinity of the Kesterson National Wildlife Refuge, Fresno and Merced Counties, California. USGS Water-Resources Investigation Report 84-4122. Menlo Park (CA, USA): U.S. Geological Survey.
Presser TS, Ohlendorf HM. 1987. Biogoechemical cycling of selenium in the San Joaquin Valley, California. *Environ Manage* 11:805–821.
Presser TS, Piper DZ. 1998. Mass balance approach to selenium cycling through the San Joaquin Valley: from source to river to bay. In: Frankenberger WT Jr, Engberg RA, editors, Environmental chemistry of selenium. New York (NY, USA): Marcel Dekker. p 153–182.
Presser TS, Sylvester MA, Low WH. 1994. Bioaccumulation of selenium from natural geologic sources in the Western States and its potential consequences. *Environ Manage* 18:423–436.
Saiki MK, Lowe TP. 1987. Selenium in aquatic organisms from subsurface agricultural drainage water, San Joaquin Valley, California. *Arch Environ Contam Toxicol* 16:657–670.
Saiki MK, Ogle, RS. 1995. Evidence of impaired reproduction by western mosquitofish inhabitating seleniferous agricultural drainwater. *Trans Amer Fish Soc* 124:578–587.
Seiler RL, Skorupa JP, Naftz DL, Nolan BT. 2003. Irrigation-induced contamination of water, sediment, and biota in the Western United States—synthesis of data from the National Irrigation Water Quality Program: U.S. Geological Survey Professional Paper 1655. 123 p.
Schuler CA, Anthony RG, Ohlendorf HM. 1990. Selenium in wetlands and waterfowl foods at Kesterson Reservoir, California, 1984. *Arch Environ Contam Toxicol* 19:845–853.
Skorupa JP. 1998. Selenium poisoning of fish and wildlife in nature: lessons from twelve real-world examples. In: Frankenberger WT Jr, Engberg RA, editors, Environmental chemistry of selenium. New York (NY, USA): Marcel Dekker. p 315–354.

A9.0 TERRESTRIAL AND AQUATIC HABITATS, SAN JOAQUIN VALLEY, CALIFORNIA

Kesterson National Wildlife Refuge (NWR) ephemeral pools (1988 to the present) and Reuse Areas (1995 to present)

A9.1 Selenium Sources

Salt and Se in the soils, subsurface drainage, and groundwater aquifers of the western San Joaquin Valley accumulate as a result of the combination of arid climate, natural and agricultural runoff, and erosion from the marine sedimentary rocks of the California Coast Ranges (Presser and Luoma 2006).

Perhaps the best-known case of Se poisoning in a field environment was found at Kesterson NWR in the San Joaquin Valley of California (Presser and Ohlendorf 1987). There, deformity and death in embryos and hatchlings of aquatic bird populations were widespread, toxicity and immune deficiency contributed to the death of adult aquatic birds, multispecies warm-water fish assemblages disappeared, and a high incidence of still-born fry occurred in tolerant mosquitofish (Ohlendorf 1989; Skorupa 1998).

By the end of 1988, Kesterson Reservoir had been dewatered and the low-lying areas within the evaporation pond system filled with soil to at least 15 cm above the expected average seasonal rise of groundwater. The created terrestrial habitat at Kesterson NWR is used by such bird species as kestrel (*Falco sparverius*), owl (*Tyto alba*), shrike (*Lanius ludovicianus*), stilt (*Himantopus mexicanus*), and killdeer (*Charadrius vociferous*).

Current active management projects in the Valley include 1) conveyance of agricultural drainage to the San Joaquin River (see Grassland Bypass Project Case Study); and 2) pumping of stored drainage to the surface landscape (i.e., collectively called Reuse Areas). Most options present opportunities for wildlife use and human exposure. Over 42 species of birds have been found to use drainwater pilot Reuse Areas.

A9.2 Fate and Transformation

Kesterson NWR is now a mosaic of primarily terrestrial habitats that are less contaminated than the aquatic habitat they replaced (Ohlendorf and Santolo 1994). However, ephemeral pooling creates aquatic habitat in wet years. Agricultural drainage Reuse Areas exist on a pilot-scale level in the valley but are an important component of recently proposed management plans (Presser and Schwarzbach 2008). Planned Reuse Area expansion in the valley ranges from 3000 to 7700 ha. This would represent up to a 10-fold scale-up from the existing pilot project of 730 ha. The Reuse Areas integrate Se-contaminated drainage with terrestrial habitats by exposing the landscape to an agricultural waste stream. In addition to concern about day-to-day management of such large-scale operations, there is also the potential for adverse effects related to Se-contamination with ponding and creation of transitory aquatic habitats 1) during rainfall events and 2) when management actions call for maintaining flow.

Because these habitats are transitory in nature, data sets characterizing the ecosystem are not complete. Monitoring of bird eggs does take place, and data for water-column Se concentrations are collected from time to time, driven mainly by rainfall events. In 2000, ephemeral pools at Kesterson NWR showed water-column Se concentrations from 15 to 247 µg/L (USBR 2000). Available food items appearing in these temporary pools and their Se concentrations included the following: aufwuchs (biofilm), 11 to 190 mg/kg dw; *Daphnia* (*Cladocera*), 35 to 77 mg/kg dw; corixids (*Heteroptera*), 8 to 21 mg/kg dw; beetles (*Coleoptera*) 14 to 149 mg/kg dw; and backswimmers (*Notonectidae*), 2.3 to 24 mg/kg dw.

The Red Rock Ranch integrated drainage management pilot project, a Reuse Area, includes traditional cropland, tree plantations, halophyte cropland, and a solar evaporator basin (Skorupa 1998). In 1996, a sample of the water impounded in the solar evaporator contained more than 11,000 µg/L Se. Water entering the halophyte plot during the spring of 1996 averaged approximately 1,600 µg/L. In 2004, the Panoche Drainage District included an accidentally flooded pasture within the Reuse Area (Presser and Schwarzbach 2008). Here, concentrated agricultural drainage (60 to 200 µg/L Se) was being managed to reduce the amount of Se discharged to the San Joaquin River.

A9.3 Effects

Aquatic dietary items for birds at Kesterson NWR exceeded 6 mg/kg dw, a level considered a high risk for reproductive impairment (USDOI 1998). Risk assessments took into account such factors as 1) birds being able to feed on a mixture of aquatic invertebrates, terrestrial invertebrates, or terrestrial plants; 2) the transitory nature of ponding; and 3) the proportion of aquatic habitat to terrestrial habitat available for bird use. Bird egg Se concentrations ranged from 1.6 to 7.4 mg/kg dw for kestrel, swallow (*Hirundinidae*), starling (*Sturnidae*), killdeer, king bird (*Tyrannidae*), and shrike (*Laniidae*) (USBR 2000). No evidence of toxicological impact on these species of birds was observed at Kesterson Reservoir during monitoring from 1988 to 2000.

In 1996, ponding of drainage water inflow at the solar evaporator and adjacent halophyte plot at the Red Rock Ranch pilot project was great enough to attract breeding shorebirds (Skorupa 1998). During the short period of ephemeral ponding and spring nesting, a viable food web was formed, birds nested and fed on contaminated dietary items, and eggs developed. Nonviability of eggs was 67% and the level of teratogenicity (56.7%) surpassed the level found at Kesterson Reservoir during the 1980s.

In 2004, in the Panoche Drainage District pilot project, the average Se concentration in avocet and stilt eggs was 58 mg/kg dw. A reduction of hatchability and deformities of bird embryos were expected to occur at these concentrations (USDOI 1998; Skorupa 1998). From a compilation of data from 2003 through 2006 from the Panoche Drainage District Reuse Area, Se concentrations in bird eggs were consistently above concentrations associated with Se toxicity to embryos during those 4 years (Presser and Schwarzbach 2008). Selenium concentrations in avocets and stilts in 2006 exceeded 90 mg/kg dw, higher than during the flooding event of 2003.

A9.4 Lessons Learned

Ephemeral pools and aquatic habitats form efficiently in agricultural areas affected by a high water table. Data taken during accidental flooding events illustrate the fact that even small ponds are inviting to aquatic birds in the San Joaquin Valley given the limited habitat opportunities. To put the magnitude of contamination in context, Table A.1 compares the mean bird egg Se concentrations for the Panoche Reuse

TABLE A.1
Comparison of the Mean Egg Se Concentrations (mg/kg dw bird egg) at the Panoche Reuse Area to Those at Kesterson Reservoir (1983–1985)

	Panoche *Reuse Area*			
Species	2003	2004	2005	2006
Killdeer	12.5	13.1	15.9	22.8
Avocets & Stilts	39.0	15.3	35.3	23.0
Blackbirds	5.9	6.0	N/A	8.8
	Kesterson Reservoir			
Species	1983	1984	1985	
Killdeer	N/A	33.1	46.4	
Avocets & Stilts	16.1	20.9	34.6	
Blackbirds	N/A	6.0	N/A	

Area, 2003–2006, to the mean bird egg Se concentrations for Kesterson Reservoir, 1983–1985 (Ohlendorf et al. 1986; Presser and Schwarzbach 2008).

Note that, except for killdeer, the results for the Panoche Reuse Area are effectively no different from the results for Kesterson Reservoir (see Kesterson Reservoir, California, case study). The timing of appearance of food webs in the ponds and immediate nesting also illustrate the need for vigilance on the part of management for this type of habitat. Selenium concentrations in bird eggs from the majority of reference sites sampled were also highly elevated, suggesting a landscape effect larger than the Reuse Area as management and storage of concentrated drainwater takes place over several years.

A9.5 References

Ohlendorf HM. 1989. Bioaccumulation and effects of selenium in wildlife. In: Jacobs LW, editor, Selenium in agriculture and the environment. Special Publication 23. Madison (WI, USA): American Society of Agronomy and Soil Science Society of America. p 133–177.

Ohlendorf HM, Santolo GM. 1994. Kesterson Reservoir—Past, present, and future: an ecological risk assessment. In: Frankenberger WT Jr, Engberg RA, editors, Environmental chemistry of selenium. New York (NY, USA): Marcel Dekker, p 69–117.

Ohlendorf HM, Hoffman HJ, Saiki MK, Aldrich TW. 1986. Embryonic mortality and abnormalities of aquatic birds: apparent impacts of selenium from irrigation drainwater. *Sci Total Environ* 52:49–63.

Presser TS, Ohlendorf HM. 1987. Biogeochemical cycling of selenium in the San Joaquin Valley, California. *Environ Manage* 11:805–821.

Presser TS, Luoma SN. 2006. Forecasting selenium discharges to the San Francisco Bay-Delta Estuary: ecological effects of a proposed San Luis drain extension. Professional Paper 1646. Menlo Park (CA, USA): U.S. Geological Survey. Available at http://pubs.usgs.gov/pp/p1646.

Presser TS, Schwarzbach SE. 2008. Technical analysis of in-valley drainage management strategies for the Western San Joaquin Valley, California: Open-File Report 2008–1210. Menlo Park (CA, USA): U.S. Geological Survey.

Skorupa JP. 1998. Selenium poisoning of fish and wildlife in nature: lessons from twelve real-world examples. In: Frankenberger WT Jr, Engberg RA, editors, Environmental chemistry of selenium. New York (NY, USA): Marcel Dekker. p 315–354.

[USBR] U.S. Bureau of Reclamation. 2000. Ecological risk assessment for Kesterson Reservoir. Report prepared by CH2MHill and Lawrence Berkeley Laboratory, San Francisco, CA, USA.

[USDOI] U.S. Department of the Interior. 1998. Guidelines for interpretation of the biological effects of selected constituents in biota, water, and sediment. Irrigation Water Quality Program Report 3. Denver (CO, USA): National Bureau of Reclamation, Fish and Wildlife Service, Geological Survey, Bureau of Indian Affairs.

A10.0 GRASSLAND BYPASS PROJECT (SAN JOAQUIN VALLEY), CALIFORNIA

A10.1 Selenium sources

Sources of Se in the San Joaquin Valley, California, are ancient marine sediments of the Coast Ranges to the west of the valley (Presser et al. 1994; Schwartz et al. 2003). Selenium in the alluvium is mobilized via the naturally eroding lithology during rain events in the wet season (October–May). Selenium moves with the flood water through the few streams, such as Panoche Creek, of the arid foothills to the hydrologically altered agricultural fields, and into ditches, canals, and sloughs, finally draining into the San Joaquin River.

The 38,800-ha Grassland Drainage Area is to the west of the Kesterson National Wildlife Refuge (see Kesterson Reservoir case study, Section A8) and to the north of the agricultural area that disposed of drainage into the San Luis Drain and consequently Kesterson Reservoir. Irrigated agriculture in the Grassland Drainage Area requires the use of subsurface drains to move water away from water-logged crop root zones.

Prior to 1995, drainage from the agricultural fields was sent into the Grassland Ecological Area (GEA), a wetland of worldwide importance, part of the San Luis National Wildlife Refuge complex in the vicinity of the San Joaquin River. The wastewater provided a source of water for the wetlands, saving irrigation water for other uses. The wastewater was alternated with fresh water flowing through the wetland channels (e.g., Mud and Salt Sloughs). Selenium bioaccumulation and trophic transfer were documented in organisms inhabiting the GEA (USBR et al. 2004-2005).

In 1995, the discharge was consolidated into a 45-km segment of the original San Luis Drain (renamed the Grassland Bypass) in order to reduce contaminated water supplies, but discharge to the San Joaquin River via Mud Slough remains (Figure A.4) (CSWQCB 2001). Drainage is greatest throughout the long growing season (January through October).

A10.2 Fate and Transformation

The San Joaquin Valley is an important region for migratory birds, although most of the wetland areas in the valley have been drained and converted to agricultural and urban uses. Duck (hunting) clubs and wildlife refuges provide habitat for birds on the Pacific Flyway. As the Grassland Bypass Project is near to the Kesterson National Wildlife Refuge, it is understood that species affected include aquatic and aquatic-dependent species.

Selenium in this system is predominantly selenate (Presser and Luoma 2006). As a flowing water system, the San Joaquin River may be less sensitive to Se effects (especially if selenate dominates inputs) than adjacent riparian wetlands, where residence times and biogeochemical transformations of selenate are more likely. Wherever there is ponded water, there is the possibility of the accumulation of inorganic Se in a more biologically available form.

A10.3 Effects

Since the Grassland Bypass Project began in 1995, physical parameters (pH, conductivity, temperature, and flow) and Se have been monitored in the San Luis Drain, Mud and Salt Slough, the channels leading into the GEA, and the San Joaquin River (Figure A.4) (USBR et al., 1998 and ongoing). Selenium is also measured in sediment accumulating in the drain and in organisms (invertebrates, fish, bird eggs, and vascular plants). Toxicity tests (short-term chronic testing of 4 or 7 days using survival,

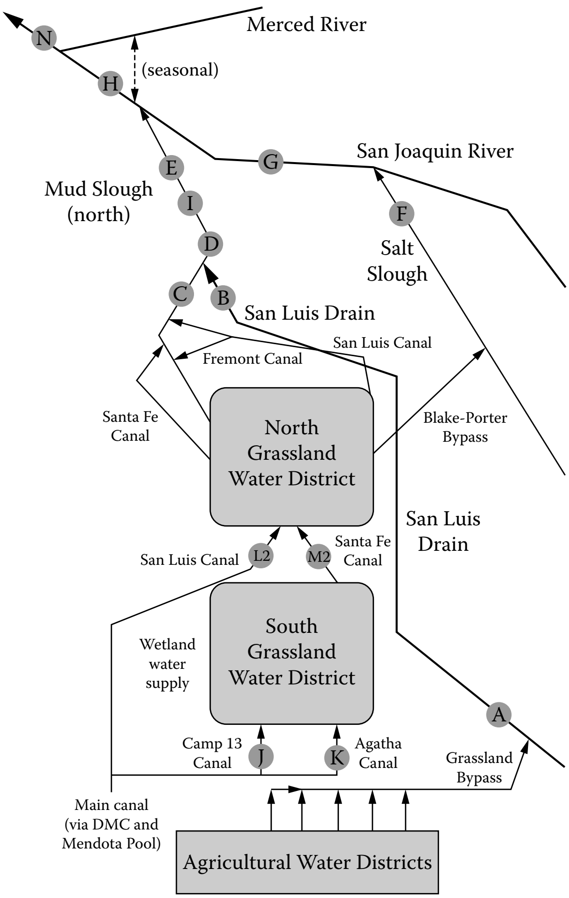

FIGURE A.4 Schematic diagram of Grassland Bypass Project moving agricultural drainwater to the San Joaquin River, CA (Adapted from USBR et al. 1998 and ongoing). Letters indicate sampling locations throughout the project area.

growth, or reproduction endpoints) are conducted with water from all sampling sites using an alga, an invertebrate, and a fish. Selenium concentrations in water in the inlet channels to the GEA and in water and organisms in Salt Slough have decreased to a "moderate hazard to wildlife" Se level (Lemly 1993), but water and organisms in Mud Slough and downstream to the San Joaquin have risen to above a "hazard to wildlife" Se level (USBR et al. 1998 and ongoing, 2004–2005).

The San Joaquin River is now being restored, but the degraded conditions as a result of agricultural drainage discharges to the river over time have led to a predominance of invasive fish species over native fish species.

A10.4 Lessons Learned

Once Se-laden inputs were removed from the GEA, the associated wetlands began to recover. Elevated Se concentrations occur in the surrounding area, however, including Mud Slough. By the time the Grassland Bypass Project ends, considerable data will be available regarding the rates of recovery of this wetland-and-slough system.

The Grassland Bypass Project pioneered a new regulatory structure for agricultural drainage in the United States. The Se load discharged through the Grassland Bypass Project is regulated both by a contract with the Bureau of Reclamation and by a Waste Discharge Requirement from the California Central Valley Regional Water Quality Control Board (CSWQCB 1998a). This is the first case in the United States where quantitative load limits have been imposed on contaminants contained in agricultural drainage (a "nonpoint source discharge"). As a result of this project and its associated regulatory structure, Se loads from the Grassland Bypass Project have decreased from approximately 3636 kg/yr to 1818 kg/yr. Future load restrictions are designed to meet the water-quality criteria for the protection of aquatic life for the San Joaquin River (5 μg/L Se) and for the GEA (2 μg/L; CSWQCB 1998b, 2001; USEPA 1992).

A10.5 References

[CSWQCB] California State Water Quality Control Board. 1998a. Waste discharge requirements for San Luis and Delta-Mendota Authority and US Department of Interior Bureau of Reclamation Grassland Bypass Channel Project. Order No. 98-171. Sacramento (CA, USA): Central Valley Regional Water Quality Control Board.

[CSWQCB] California State Water Quality Control Board. 1998b. The water quality control plan (Basin Plan) for the Sacramento River Basin and San Joaquin River Basin. 4th edition. Sacramento (CA, USA): Central Valley Regional Water Quality Control Board.

[CSWQCB] California State Water Quality Control Board. 2001. Waste discharge requirements for San Luis and Delta-Mendota Authority and US Department of Interior Bureau of Reclamation Grassland Bypass Channel Project. Order No. 5-01-234. Sacramento (CA, USA): Central Valley Regional Water Quality Control Board.

Lemly AD. 1993. Guidelines for evaluating selenium data from aquatic monitoring and assessment studies *Environ Monitor Assess* 28:83–100.

Presser TS, Luoma SN. 2006. Forecasting selenium discharges to the San Francisco Bay-Delta Estuary: ecological effects of a proposed San Luis drain extension. Professional Paper 1646. Menlo Park (CA, USA): US Geological Survey. Available at http://pubs.usgs.gov/pp/p1646.

Presser TS, Sylvester MA, Low WH. 1994. Bioaccumulation of selenium from natural geologic sources in the Western States and its potential consequences. *Environ Manage* 18:423–436.

Schwartz H, Sample J, Weberling KD, Minisini D, Moore JC. 2003. An ancient linked fluid migration system: cold-seep deposits and sandstone intrusions in the Panoche Hills, California, USA. *Geo-Mar Lett* 23:340–350.

[USBR] United States Bureau of Reclamation et al. 1998 and ongoing. Grassland Bypass Project monthly, quarterly, and annual reports. Mid-Pacific Region, Sacramento, CA, USA. http://www.sfei.org/grassland/reports/gbppdfs.htm.

[USBR] United States Bureau of Reclamation et al. 2004-2005. Grassland Bypass Project annual report for 2004-2005. Mid-Pacific Region, Sacramento, CA, USA. http://www.sfei.org/grassland/reports/gbppdfs.htm.

[USEPA] United States Environmental Protection Agency. 1992. Rulemaking, water quality standards, establishment of numeric criteria for priority toxic pollutants, States' compliance: Final Rule, 57 FR 60848 (December 22, 1992).

A11.0 SAN FRANCISCO BAY-DELTA ESTUARY, CALIFORNIA

A11.1 Selenium Sources

Major sources of Se in the San Francisco Bay-Delta Estuary (Bay-Delta) (Figure A.5) are 1) discharges of irrigation drainage conveyed from agricultural lands of the western San Joaquin Valley into the San Joaquin River; 2) effluents from North Bay refineries, which refine crude oil from the western San Joaquin Valley, along with crude oil from other sources; and 3) Sacramento River inflows that dominate the freshwater contribution (high water volume) to the estuary (Presser and Luoma 2006).

The volume of water flowing into the Bay-Delta is determined by climate and water management. On a broad scale, the Bay-Delta watershed is characterized by a distinct seasonal cycle of high inflows from the Sacramento and San Joaquin rivers in January through June (high flow season), followed by lower inflows through the last

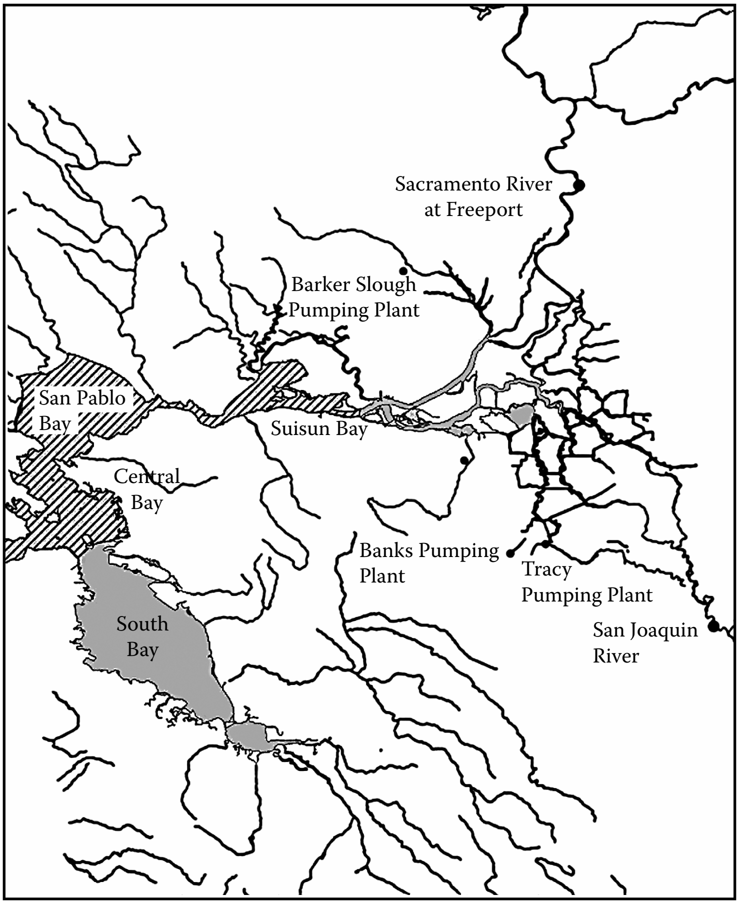

FIGURE A.5 Map of North San Francisco Bay. (From Tetra Tech 2008.)

6 months of the calendar year (low flow season). Riverine influences also depend on water year type (wet year or dry year).

A11.2 Fate and Transformation

The San Joaquin-Sacramento River system and the internal refinery inputs move into an estuarine environment. In the Bay-Delta in the 1980s, speciation differed among source waters (Cutter and San Diego-McGlone 1990). The Sacramento River inflow was 30% to 70% selenate, depending on season; organo-Se was the other main component. The San Joaquin River inflow was 70% selenate and 22% organo-Se. Refinery wastewaters averaged 62% selenite. In the late 1980s, during low flow in the North Bay, as much as 50% of the Se was selenite, reflecting the predominance of refinery inputs. In the late 1990s, studies showed less selenite in the North Bay after refinery inputs were reduced because of regulatory limits on both the Se concentration and load and the installation of additional treatment technology. However, organo-Se increased in abundance, reflecting recycling of the metalloid in the estuary. Selenite plus organo-Se constituted 60% of the mass of Se (Cutter and Cutter 2004).

A11.3 Effects

Selenium contamination documented from 1982 to the mid-1990s was sufficient to threaten reproduction in key species within the Bay-Delta estuary ecosystems (Presser and Luoma 2006). The aquatic or aquatic dependent wildlife species in San Francisco Bay with the greatest potential to have been affected included white sturgeon (*Acipenser transmontanus*), starry flounder (*Platichthys stellatus*), Dungeness crab (*Cancer magister*), diving ducks (scoters [*Melanitta* spp.], and scaups [*Aythya* spp.]).

Human health advisories were posted based on Se concentrations in tissues of diving ducks. From 1989 to 1990 in the North Bay, average Se concentrations in surf scoter liver tissue and sturgeon flesh exceeded reproductive toxicity guidelines (Heinz 1996; Lemly 2002; Presser and Luoma 2006). Analyses from 1982 through 1996 showed that the animals with the highest Se tissue concentrations from the North Bay ingested bivalves (*Corbicula fluminea* prior to 1986 and *Potamocorbula amurensis* in subsequent samplings) as a major component of their diet. Selenium concentrations in the predominant bivalve in the Bay-Delta were higher in the mid-1990s than in 1977 through 1990 (Linville et al. 2002; Presser and Luoma 2006). Selenium concentrations in *P. amurensis* reached 20 mg/kg dw in the North Bay in October 1996, exceeding by 6-fold the USDOI (1998) dietary guideline (>3 mg/kg dw) of concern.

A11.4 Lessons Learned

Prior to refinery cleanup, Se concentrations in the Bay-Delta were well below the most stringent recommended water quality criterion (1 μg/L). Enhanced biogeochemical transformation to bioavailable particulate Se and efficient bioaccumulation by bivalves characterize the Bay-Delta ecosystem (Luoma et al. 1992; Stewart et al. 2004; Presser and Luoma 2006). The results of this research are being incorporated into the regulatory limits for Se discharges to the estuary (http://www.waterboards.ca.gov/sanfranciscobay/water_issues). A first-of-its-kind aquatic-dependent wildlife criterion for Se also is under development for this region as a result of the risk Se poses to estuarine systems (Beckon and Maurer 2008).

A11.5 References

Beckon WN, Maurer TC. 2008. Species at risk from selenium exposure in the San Francisco estuary. Final Report to the U.S. Environmental Protection Agency. Inter-Agency Agreement No. DW14922048-01-0. Sacramento (CA, USA): US Fish and Wildlife Service.

Cutter GA, San Diego-McGlone MLC. 1990. Temporal variability of selenium in fluxes in San Francisco Bay. *Sci Total Environ* 97/98:235–250.

Cutter GA, Cutter LS. 2004. Selenium biogeochemistry in the San Francisco Bay estuary: changes in water column behavior: *Estuar Coast Shelf Sci* 61:463–476.

Heinz GH. 1996. Selenium in birds. In: Beyer WN, Heinz GH, Redmon-Norwood AW, editors, Environmental contaminants in wildlife: interpreting tissue concentrations. New York (NY, USA): Lewis. p 447–458.

Lemly AD. 2002. Selenium assessment in aquatic ecosystems: a guide for hazard evaluation and water quality Criteria. New York (NY, USA): Springer-Verlag.

Linville RG, Luoma SN, Cutter LS, Cutter GA. 2002. Increased selenium threat as a result of invasion of the exotic bivalve *Potamocorbula amurensis* into the San Francisco Bay-Delta. *Aquat Toxicol* 57:51–64.

Luoma SN, Johns C, Fisher NS, Steinberg NA, Oremland RS, Reinfelder J. 1992. Determination of selenium bioavailability to a benthic bivalve from particulate and solute pathways. *Environ Sci Technol* 26:485–491.

Presser TS, Luoma SN. 2006. Forecasting selenium discharges to the San Francisco Bay-Delta Estuary: ecological effects of a proposed San Luis drain extension. Professional Paper 1646. Menlo Park (CA, USA): U.S. Geological Survey. Available at http://pubs.usgs.gov/pp/p1646.

Stewart RS, Luoma SN, Schlekat CE, Doblin MA, Hieb KA. 2004. Food web pathway determines how selenium affects ecosystems: a San Francisco Bay case study. *Environ Sci Technol* 38:4519–4526.

Tetra Tech. 2008. Technical memorandum #4: Conceptual model of Se in North San Francisco Bay. Prepared for the California Regional Water Quality Control Board. Alameda, CA, USA.

[USDOI] U.S. Department of the Interior. 1998. Guidelines for interpretation of the biological effects of selected constituents in biota, water, and sediment. Irrigation Water Quality Program Report 3. Denver (CO, USA): National Bureau of Reclamation, Fish and Wildlife Service, Geological Survey, Bureau of Indian Affairs.

A12.0 PHOSPHATE MINING IN THE UPPER BLACKFOOT RIVER WATERSHED, IDAHO

A12.1 Selenium Sources

The Meade Peak Member of the Phosphoria Formation extends throughout southeast Idaho, and adjacent areas of Wyoming, Montana, and Utah (McKelvey et al. 1959, 1986; Presser et al. 2004a). 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 20th century, mining in Idaho provided approximately 4.5% of world demand for phosphate, used mainly in fertilizer (USDOI and USGS 2000). About 49% of the total production has occurred since 1985. This tonnage represents approximately 15% of the estimated 1 billion tonnes accessible to surface mining within the Phosphoria Formation (USDOI and USDA 1977). Out of 19 mining sites in Idaho, 4 are presently active (Dry Valley Mine, Enoch Valley Mine, Rasmussen Ridge Mine, and Smoky Canyon Mine) and 2 are categorized as existing mine operations (Maybe Canyon Mine and Lanes Creek Mine) (Presser et al. 2004a). The Phosphoria Formation also is estimated to have generated about 3×10^{10} tonnes of oil.

The Meade Peak Member contains Se concentrations of up to 1200 mg/kg dw. Average Se concentrations range from 48 to 560 mg/kg dw in westernmost Wyoming and in southeast Idaho (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 2 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 (Herring and Grauch 2004). 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.

The upper Blackfoot River watershed in southeast Idaho receives drainage from 11 of 16 phosphate mines that have extracted ore from the Phosphoria Formation (Presser et al. 2004a,b). Ten of the active and legacy mines are now Superfund sites (http://www.greateryellowstone.org/media/pdf/phosphate-superfund-map.pdf).

A12.2 Fate and Transformation

Mining removes phosphate-rich beds and exposes organic carbon-rich waste rock to subaerial weathering (Presser et al. 2004a). Waste rock is generated at a rate of 2.5 to 5 times that of mined ore (USDOI and USDA 1977). Individual dumps contain 5-65 million tonnes 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 atmosphere and surface and groundwater, Se is oxidized from relatively insoluble selenide and elemental Se to soluble oxyanions of selenite and selenate (Piper et al. 2000).

The cross-valley fills at the Smoky Canyon mine (45 million tonnes) and South Maybe Canyon mine (27 million tonnes) are stabilized with under-drains (Presser et al. 2004a). Discharges from these drains are source waters for Pole Creek and Maybe Creek. Concentrations of Se in these 2 drains, as well as in a dump seep at the inactive Conda Mine, were equal to or exceeded 1000 µg/L.

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 µg/L. Waste-rock dump seeps and surface streams exhibit annual cycles in Se concentration that peak during the spring period of maximum flow (Montgomery Watson 1998, 1999, 2000, 2001a,b; Presser et al. 2004a,b). In 1998, the stream Se concentration maximum for all samples collected in May was 260 µg/L, whereas it was 32 µg/L in September. In May 2000, the Se concentration in East Mill Creek was 400 µg/L and was 19 µg/L in September 1999.

Samples collected in 2001 at 2 mining areas (Mackowiak et al. 2004) showed mean Se concentrations in forage plants (legume and grass) grown on waste-rock dumps exceeded thresholds of dietary toxicity for horses (5–40 mg/kg dw) and sheep (5–25 mg/kg dw). Location within a dump site, as well as the species of plant, were factors in determining Se concentrations in vegetation. For example, in 2001, alfalfa bioaccumulated Se to a greater extent (mean 150 mg/kg dw, maximum 952 mg/kg dw) than grasses (mean 27 mg/kg dw, maximum 160 mg/kg dw). 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 mg/kg ww, or 143 mg/kg dw at 30% moisture) (USDHHS 1996).

A12.3 Effects

Livestock deaths from Se toxicosis have been documented, including deaths of horses and sheep (Presser et al. 2004a). Permits for grazing have been suspended for some mine-disturbed areas (Idaho Department of Environmental Quality 2002). Embryo deformities in birds have occurred, most notably in the American coot and the Canada goose; a Se concentration of 80 mg/kg dw is the highest reported Se concentration among coot eggs (Presser et al. 2004a; Skorpa et al. 2002). Aquatic invertebrate samples in the area also contained record elevated amounts of Se (up to 788 mg/kg dw) (Skorupa et al. 2002).

Deer, elk, and moose populations also may be at risk based on studies of Se concentrations in livers donated by hunters in the areas near the phosphate waste dumps (there is a direct correlation between elevated Se concentrations in the liver versus distance of the harvested elk from the nearest mine site) (Idaho Department of Environmental Quality 2002).

Selenium concentrations in submerged macrophytes reached a maximum of 56 mg/kg dw in spring and 44 mg/kg dw in fall (Montgomery Watson 1998, 1999, 2000, 2001a,b). Benthic macroinvertebrates showed a maximum Se concentration of 150 mg/kg dw in spring and 63 mg/kg dw in fall. Based on tissue, whole-body Se concentrations in forage fish (suckers, sculpins, minnows, and salmonids <15 cm) exceeded the USDOI (1998) risk threshold of 6 mg/kg dw for growth and survival during both seasons (maxima: 35 mg/kg dw in spring and 11 mg/kg dw in fall). These values also exceeded the USDOI (1998) risk threshold for diet, if these fish were eaten by larger fish. Concentrations of Se in gamefish (>15 cm) showed a maximum skin-on fillet concentration of 33 mg/kg dw in spring and 17 mg/kg dw in fall. Depending on the conversion factor used (Piper et al. 2000), whole-body Se concentrations in gamefish would reach 55–77 mg/kg dw in spring. These included Yellowstone cutthroat trout (*Oncorhynchus clarki bouvieri*), brook trout (*Salvelinus fontinalis*), and rainbow trout (*Oncorhynchus mykiss*). Trout have disappeared from the most Se-contaminated streams (e.g., East Mill Creek, dissolved Se > 20 ug/L; whole-body cutthroat trout 52 mg Se/kg dw) (Montgomery Watson 2001a,b; Hamilton and Buhl 2004). The proportion of trout above the 2 mg/kg ww Se guideline for human consumption of fish flesh (USDHHS 1996; USDOI 1998) increased from <1% in fall to 30% in spring.

In 1999, a significant larval salamander die-off (at least 250 individuals) at a pit lake at the Gay Mine was confirmed as Se poisoning (Green 2001). A Se concentration of 126 mg/kg dw measured in salamander tail tissue is a record for that type of tissue. Samples of dead larval salamanders from the Smoky Canyon Mine were collected in 2000. Two important diseases were diagnosed: chronic selenosis and iridovirus infection (Green and Miller 2001). It was concluded that Se contributed directly to their deaths by poisoning or indirectly by causing damage to the immune system.

Two human health advisories for Se have been issued for activities in the phosphate mining areas (Idaho Department of Environmental Quality 2003). The first was a hunter's advisory that recommended limited consumption of elk liver by area hunters (Idaho Department of Fish and Game 2000; Idaho Bureau of Environmental Health and Safety 2001). The second advisory recommended limited consumption of fish from East Mill Creek by children based on elevated Se concentrations observed in edible fish tissue from this stream (ATSDR 2002).

A12.4 Lessons Learned

Large-scale land disturbance in southeast Idaho leaves behind waste rock that provides many routes of Se exposure for fish, birds, and livestock. 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 addition of phosphorites as a category of Se-containing rocks to that of other carbon-rich source rocks enabled a forecast of global Se sources (Presser et al. 2004b).

A12.5 References

[ATSDR] Agency for Toxic Substances and Disease Registry. 2002. Health consultation: Selenium in fish streams of the upper Blackfoot River watershed, southeast Idaho selenium project, Soda Springs, Caribou County, Idaho. Atlanta, GA, USA.

Green DE. 2001. Final diagnostic report for Case #16322, 001-022: Gay Mine tiger salamander larvae. Madison (WI, USA): National Wildlife Health Center, Biological Resources Division, U.S. Geological Survey.

Green DE, Miller KJ. 2001. Final diagnostic report for Case #16947, 001-003: Smoky Canyon Mine tiger salamander larvae and garter snake. Madison (WI, USA): National Wildlife Health Center, Biological Resources Division, U.S. Geological Survey.

Hamilton SJ, Buhl KJ. 2004. Selenium in water, sediment, plants, invertebrates and fish in the Blackfoot River drainage. *Water Air Soil Pollut* 159:3–34.

Herring JR, Grauch RI. 2004. Lithogeochemistry of the Meade Peak Phosphatic Shale Member of the Phosphoria Formation, southeast Idaho. In: Hein JR, editor, Life cycle of the Phosphoria Formation: from deposition to the post-mining environment. New York (NY, USA): Elsevier p 321–366.

Idaho Bureau of Environmental Health and Safety. 2001. Health consultation: evaluation of selenium in beef, elk, sheep and fish in the Southeast Idaho Phosphate Resource Area. Pocatello (ID, USA): Idaho Department of Health and Welfare.

Idaho Department of Environmental Quality. 2002. Area wide human health and ecological risk assessment and related memorandum. Report prepared by R Clegg. Boise (ID, USA): Tetra Tech EM Inc.

Idaho Department of Environmental Quality. 2003. Area wide risk management plan, area wide investigation: Southeast Idaho Phosphate Mining Resource Area. Soda Springs, ID, USA.

Idaho Department of Fish and Game. 2000. Elk liver consumption advisory, Unit 76. Pocatello, ID, USA.

Mackowiak CL, Amacher MC, Hall JO, Herring JR. 2004. Uptake of selenium and other elements into plants and implications for grazing animals in Southeast Idaho. In: Hein JR, editor, Life cycle of the Phosphoria Formation: from deposition to the post-mining environment. New York (NY, USA): Elsevier. p 527–555.

McKelvey VE, Williams JS, Sheldon RP, Cressman ER, Cheney TM, Swanson RW. 1959. The Phosphoria, Park City, and Shedhorn Formations in the western phosphate field. Professional Paper 313-A. Denver (CO, USA): U.S. Geological Survey.

McKelvey VE, Strobell JD, Slaughter AL. 1986. The Vanadiferous Zone of the Phosphoria Formation in western Wyoming and southeastern Idaho. Professional Paper 1465. Denver (CO, USA): U.S. Geological Survey.

Montgomery Watson. 1998. Fall 1997 interim surface water survey report, Southeast Idaho phosphate resource area, Selenium Project. Steamboat Springs, CO, USA.

Montgomery Watson. 1999. Final 1998 Regional investigation report, Southeast Idaho phosphate resource area, Selenium Project. Steamboat Springs, CO, USA.

Montgomery Watson. 2000. 1999 Interim investigation data report, Southeast Idaho phosphate resource area, Selenium Project. Steamboat Springs, CO, USA.

Montgomery Watson. 2001a. Draft 1999–2000 regional investigation data report for surface water, sediment and aquatic biota sampling activities, May–June 2000, Southeast Idaho phosphate resource area, Selenium Project. Steamboat Springs, CO, USA.

Montgomery Watson. 2001b. Draft 1999–2000 regional investigation data report for surface water, sediment and aquatic biota sampling activities, September 1999, Southeast Idaho Phosphate resource area, Selenium Project. Steamboat Springs, CO, USA.

Piper DZ, Skorupa JP, Presser TS, Hardy MA, Hamilton SJ, Huebner M, Gulbrandsen RA. 2000. The Phosphoria Formation at the Hot Springs Mine in southeast Idaho: a source of trace elements to ground water, surface water, and biota. Open-File Report 00-050. Menlo Park (CA, USA): U.S. Geological Survey.

Presser TS, Piper DZ, Bird KJ, Skorupa JP, Hamilton SJ, Detwiler SJ, Huebner MA. 2004a. The Phosphoria Formation: a model for forecasting global selenium sources to the environment. In: Hein JR, editor, Life cycle of the Phosphoria Formation: from deposition to the post-mining environment. New York (NY, USA): Elsevier, p 299–319.

Presser TS, Hardy MA, Huebner MA, Lamothe P. 2004b. Selenium loading through the Blackfoot River watershed: linking sources to ecosystems. In: Hein JR, editor, Life cycle of the Phosphoria Formation: from deposition to the post-mining environment. New York (NY, USA): Elsevier. p 437–466.

Skorupa JP, Detwiler SJ, Brassfield R. 2002. Reconaissance survey of selenium in water and avian eggs at selected sites within the Phosphate Mining Region near Soda Springs Idaho: May–June 1999. Sacramento (CA, USA): U.S. Fish and Wildlife Service. Available at http://wwwrcamnl.wr.usgs.gov/Selenium/library.htm.

[USDHHS] United States Department of Health and Human Services. 1996. Toxicological profile for selenium. Altanta (GA, USA): Agency for Toxic Substances and Disease Registry.

[USDOI] United States Department of the Interior. 1998. Guidelines for interpretation of the biological effects of selected constituents in biota, water, and sediment. Irrigation Water Quality Program Report 3. Denver (CO, USA): National Bureau of Reclamation, Fish and Wildlife Service, Geological Survey, Bureau of Indian Affairs.

[USDOI and USDA] United States Department of the Interior and US Department of Agriculture. 1977. Final environmental impact statement: development of phosphate resources in southeastern Idaho. Vol. I. Washington (DC, USA): US Government Printing Office.

[USDOI and USGS] United States Department of the Interior and US Geological Survey. 2000. Minerals yearbook, metals and minerals. Vol. I. Washington (DC, USA): US Government Printing Office.