

Aquatic selenium pollution is a global environmental safety issue

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Abstract

Selenium pollution is a worldwide phenomenon and is associated with a broad spectrum of human activities, ranging from the most basic agricultural practices to the most high-tech industrial processes. Consequently, selenium contamination of aquatic habitats can take place in urban, suburban, and rural settings alike--from mountains to plains, from deserts to rainforests, and from the Arctic to the tropics. Human activities that increase waterborne concentrations of selenium are on the rise and the threat of widespread impacts to aquatic life is greater than ever before. Important sources of selenium contamination in aquatic habitats are often overlooked by environmental biologists and ecological risk assessors due to preoccupation with other, higher priority pollutants, yet selenium may pose the most serious long-term risk to aquatic habitats and fishery resources. Failure to include selenium in the list of constituents measured in contaminant screening/monitoring programs is a major mistake, both from the hazard assessment aspect and from the pollution control aspect. Once selenium contamination begins, a cascade of bioaccumulation events is set into motion which makes meaningful intervention nearly impossible. However, this cascade of events need not happen if adequate foresight and planning are exercised. Early evaluation and action are key. Prudent risk management based on environmentally sound hazard assessment and water quality goals can prevent biological impacts.

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1. Introduction

Selenium is a naturally occurring trace element that can be released in the waste materials from certain mining, agricultural, petrochemical, and industrial manufacturing operations. Once in the aquatic environment, it can rapidly attain levels that are toxic to fish and wildlife because of bioaccumulation in food chains and resultant dietary exposure (Fig. 1). This rapid bioaccumulation causes the response curve for selenium poisoning to be very steep. For example, a transition from no effect to complete reproductive failure in fish can occur within a range of only a few $\mu\text{g/L}$ (parts per billion) waterborne selenium (Fig. 2). Thus, activities that cause even slight increases in the water concentration of selenium pose a major ecological risk and, much too often, leave natural resource managers trying to deal with selenium problems after they happen rather than anticipating and preventing them in the first place (Lemly, 2002a).

Selenium pollution is a worldwide phenomenon and is associated with a broad spectrum of human activities,

ranging from the most basic agricultural practices to the most high-tech industrial processes. Consequently, selenium contamination of aquatic habitats can take place in urban, suburban, and rural settings alike--from mountains to plains, from deserts to rainforests, and from the Arctic to the tropics. Few environmental contaminants have the potential to affect aquatic resources on such a broad scale, and even fewer exhibit the complex aquatic cycling pathways and range of toxic effects that are characteristic of selenium. For many years, selenium has been a largely unrecognized pollutant, particularly in developing nations, and has been overshadowed by issues involving contaminants such as industrial chemicals, heavy metals, pesticides, and air pollutants--just to name a few. However, during the past decade, aquatic pollution surveillance and monitoring programs have expanded markedly in terms of both the areal extent of coverage and the range of substances measured. As a result, selenium has emerged as an important environmental contaminant, and has gained the attention of natural resource managers and water quality regulators around the world (e.g., Jawaharlal Nehru University [JNU], 2000; Moscow Lomonosov State University [MLSU], 2001; New South Wales Environmental Protection Agency

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MAJOR ECOLOGICAL RISKS FROM SELENIUM

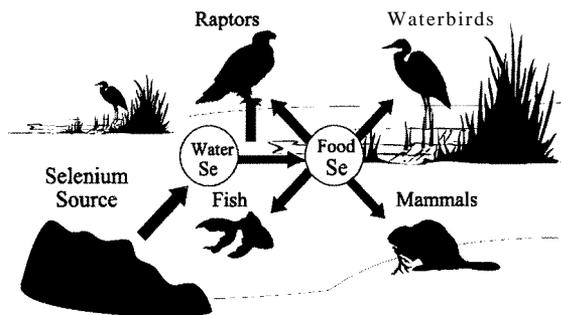


Fig. 1. Pathways for selenium movement, bioaccumulation in food chains, and dietary exposure of fish and wildlife populations in aquatic habitats. These basic principles of selenium ecotoxicology are consistent around the world and make aquatic selenium pollution a major environmental safety issue.

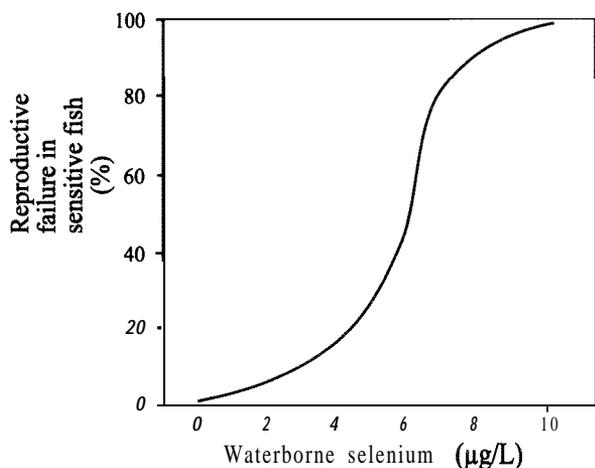


Fig. 2. Relationship between the concentration of selenium in habitats favorable for bioaccumulation (e.g., wetlands, lakes and impoundments, off-channel bays along rivers), and degree of reproductive failure in sensitive fish species (e.g., bluegill, *Lepomis microchirus*; data from Cumbie and Van Horn, 1978; Gillespie and Baumann, 1986; Lemly, 1985a; Woock et al., 1987). A small increase in waterborne selenium can result in catastrophic impacts on reproductive success. Recent escalation in human activities that promote the mobilization of selenium into aquatic ecosystems threatens to impact fish populations on a widespread scale in the USA and other countries around the world.

[NSWEPA], 1999). This paper presents an overview of the wide variety of selenium sources that can lead to pollution of aquatic habitats, and gives a sample of the many locations where aquatic life has been contaminated.

2. Sources and impacts of selenium contamination

2.1. Coal mining and combustion

One of the primary human activities responsible for mobilizing selenium in the environment is the procurement, processing, and combustion of coal for electric

power production (Lemly, 1985b). Although burning fossil fuels offers a cheaper and perhaps seemingly safer alternative to nuclear power production, especially in the aftermath of the Three Mile Island and Chernobyl reactor incidents, it does not necessarily constitute an environmentally clean alternative—there are numerous contaminant problems associated with both raw coal and its waste byproducts. Virtually all categories of solid waste and liquid effluents from the power industry are highly enriched with selenium as compared to the Earth’s crust and surface waters (Table 1). Enrichment factors for selenium in coal (ratio of selenium in coal to selenium in surrounding soils and mineral layers) can exceed 65 and are among the highest of all trace elements (Ensminger, 1981). When coal is burned to produce electricity, the ash that remains is further enriched with selenium, perhaps by as much as 1250 times (Table 1, coal vs. precipitator ash). Thus, the potential for enrichment of selenium in wastes arising from the power industry is compounded due to the fact that the raw materials have already undergone natural mineral concentration processes during their formation.

Selenium in freshly mined coal can be leached out of storage piles as rainwater percolates through, or when the coal is washed prior to being transported to power plants. Solid wastes from coal combustion (fly ash,

Table 1
Concentrations of selenium present in raw material used by the electric power industry and in various wastes produced during processing and utilization”

Material or waste	Selenium concentration
Earth’s crust	0.2 µg/g ^{b,c}
Surface waters	0.2 µg/L ^b
Coal	0.4–24 µg/g ^c
Coal storage pile leachate	1–30 µg/L
Coal cleaning process water	15–63 µg/L
Coal cleaning solid waste	2.3–31 µg/g ^c
Coal cleaning solid waste leachate	2–570 µg/L
Coal burner ash (bottom ash)	7.7 µg/g ^c
Precipitator ash (fly ash)	0.2–500 µg/g ^c
Scrubber ash (fly ash)	73–440 µg/g ^c
Fly ash leachate	40–610 µg/L
Flue gas desulfurization process water	1–2700 µg/L
Flue gas desulfurization sludge	0.2–19 µg/g ^d
Boiler cleaning water	5–151 µg/L
Coal ash slurry	50–1500 µg/L
Ash settling ponds	87–2700 µg/L
Ash pond effluents	2–260 µg/L
Ash disposal pit leachate	40–950 µg/L
Coal gasification process water	5–460 µg/L
Coal gasification solid wastes	0.7–17.5 µg/g ^d
Gasification solid waste leachate	0.8–100 µg/L
Coal liquifaction process water	100–900 µg/L
Coal liquifaction solid wastes	2.1–22 µg/g ^d

“Table adapted from Lemly (1985b).

^aRepresentative values.

^bExpressed on a dry weight basis.

^cExpressed on a wet weight basis.

Table 2

A sample of locations where selenium pollution has contaminated fish and wildlife populations (refer to Fig. 3 for map locations)

Map #	Location	Cause of selenium pollution	Major aquatic life contaminated	Reference
2	North Carolina, USA	Coal combustion waste	Reservoir fish	Lemly (2002b)
3	Pennsylvania, USA	Coal landfill waste	Stream fish	Pennsylvania Bulletin (I 992)
4	West Virginia, USA	Coal mining waste	Stream and lake fish	USFWS (2003)
5	Minnesota, USA	Municipal landfill leachate	Stream fish	MPCA (2000)
6	Texas, USA	Coal combustion waste	Reservoir fish	Sorensen (1988)
7	Louisiana, USA	Oil refinery waste	Aquatic birds	LWRRRI (2000)
8	Utah, USA	Irrigation drainage	Fish, aquatic birds	Lemly (1995)
9	Idaho, USA	Phosphate mining waste	Fish, aquatic birds	Lemly (1999)
10	California, USA	Irrigation drainage	Aquatic birds, fish	Lemly et al. (1993)
11	Yukon, Canada	Gold mining waste	Stream fish	DINA (2000)
12	British Columbia, Canada	Coal mining waste	Stream fish	McDonald and Strosher (1998)
13	Ontario, Canada	Metal smelting waste	Stream and lake fish	Nriagu and Wong (1983)
14	Chihuahua, Mexico	Irrigation drainage	Stream and river fish	Contreras-Balderas and Lozano-Vilano (1994)
15	Quito, Ecuador	Gold & silver mining waste	Stream fish	CDSC (1999)
16	Tefe, Brazil	Gold mining waste	Stream fish	MCP (2000)
17	Buenos Aires, Argentina	Gold mining waste	Stream fish	FSNR (2001)
18	London, United Kingdom	Municipal landfill leachate	Stream fish	RCEP (2001)
19	Stockholm, Sweden	Municipal landfill leachate	Stream fish	SWA (2000)
20	Torun, Poland	Nickel & silver mining waste	Stream fish	WUM (2001)
21	Perrier Vittel, France	Gold & nickel mining waste	Stream fish	INRA (1999)
22	Cairo, Egypt	Irrigation drainage	Fish, aquatic birds	ENRC (1998)
23	Niamey, Niger	Gold mining waste	Stream fish	NDEP (2000)
24	Capetown, South Africa	Gold mining waste	Fish, aquatic birds	UC (1999)
25	Jerusalem, Israel	Irrigation drainage	Fish, aquatic birds	NNPPA (2001)
26	Gorkiy, Russia	Coal combustion waste	Stream, river fish	MLSU (2001)
27	New Delhi, India	Oil refinery waste	Fish, aquatic birds	JNU (2000)
28	Wan Chai, Hong Kong	Municipal landfill leachate	Fish, aquatic birds	HKG (2001)
29	Vladivostok, Russia	Metal smelting waste	Stream, estuarine fish	FESU (1998)
30	Tokyo, Japan	Municipal landfill leachate	Fish, aquatic birds	NFRI (2001)
	New South Wales, Australia	Coal combustion waste	Lake, estuarine Fish	NSWEPA (1999)

bottom ash, scrubber ash, etc.) present an even greater risk of generating contaminated leachate because of their oxidation state and alkaline pH, which promote dissolution of selenium anions (selenate, selenite) on contact with water. Moreover, selenium can accumulate to high concentrations in process and disposal waters in a very short period of time. For example, using feed water with $< 10 \mu\text{g Se/L}$, a power plant's FGD (flue gas desulfurization) once-through cleaning stream may acquire as much as $2700 \mu\text{g Se/L}$ during its passage through the system, and a coal ash slurry stream may pick up over $1000 \mu\text{g Se/L}$ within 15 min (Cumbie, 1980; Santhanam et al., 1979). The power industry produces numerous waste materials that contain high concentrations of selenium. This selenium is readily mobilized during all phases of waste collection, treatment, and disposal that involve aqueous processes or subsequently bring dry ash materials into contact with water. These two factors, along with the potential for bioaccumulation and toxic effects in aquatic life at very low waterborne concentrations ($2\text{--}5 \mu\text{g Se/L}$), combine to make coal a highly hazardous source of selenium, with serious implications for industrial waste management

and environmental safety. As society's need for electric power increases, so does the volume of seleniferous coal wastes that is produced. In the United States alone, over 120 million tons of fly ash is produced annually, and the disposal of this material is creating a new selenium issue because of contaminated landfill leachate.

Episodes of selenium pollution associated with power production wastes have taken place around the world (Table 2, Fig. 3), and some of the most serious impacts to aquatic life have occurred as a result of this type of selenium contamination. In the United States, for example, entire populations of reservoir fish have been eliminated due to selenium poisoning that resulted from power plant waste discharges (Lemly, 2002b). Severe reproductive effects are the hallmark of chronic selenium toxicity, and the insidious nature of these effects can make selenium poisoning an elusive, yet devastating threat to aquatic life. The widespread, expanding use of coal for electric power production makes the associated risk of selenium contamination a global issue. Because it is a trace element, selenium does not biodegrade or otherwise break down into harmless

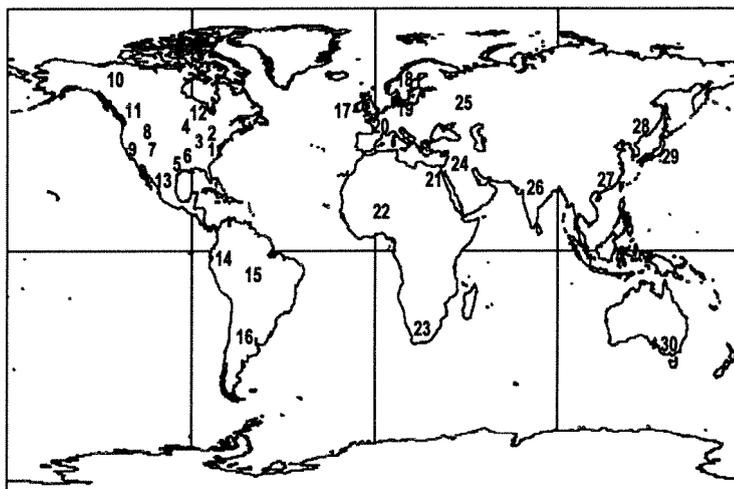


Fig. 3. Aquatic selenium pollution is a worldwide phenomenon. Numbers indicate locations where fish and/or wildlife populations have been contaminated. (1) North Carolina, USA, (2) Pennsylvania, USA, (3) West Virginia, USA, (4) Minnesota, USA, (5) Texas, USA, (6) Louisiana, USA, (7) Utah, USA, (8) Idaho, USA, (9) California, USA, (10) Yukon, Canada, (11) British Columbia, Canada, (12) Ontario, Canada, (13) Chihuahua, Mexico, (14) Quito, Ecuador, (15) Tefe, Brazil, (16) Buenos Aires, Argentina, (17) London, United Kingdom, (18) Stockholm, Sweden, (19) Torun, Poland, (20) Perrier Vittel, France, (21) Cairo, Egypt, (22) Niamey, Niger, (23) Capetown, South Africa, (24) Jerusalem, Israel, (25) Gorkiy, Russia, (26) New Delhi, India, (27) Wan Chai, Hong Kong, (28) Vladivostok, Russia, (29) Tokyo, Japan, (30) New South Wales, Australia. (Refer to Table 2 for causes of selenium pollution at these sites.)

materials. Rather, it moves and cycles from one environmental compartment to another (Fig. 1) and the toxicity it causes can persist for decades. This makes state-of-the-art waste management a necessity in the development of an environmentally compatible coal industry. While major advances have been made in reducing the particulate air pollution emanating from power plants, relatively little has been accomplished in dealing with the solid waste that is produced, other than to bury it in landfills. In fact, the same technology that improved air quality has exacerbated threats to aquatic life by producing increased volumes of seleniferous fly ash (Clean Air Task Force [CATF], 2000). At this time, there is no treatment technology that eliminates serious environmental risks associated with disposal of this coal industry waste.

2.2. Gold, silver, and nickel mining

Mining for precious and semiprecious metals has a long history of environmental problems, primarily associated with surface disposal of waste rock and the water used to process ore (Lemly, 1994a). Increasing values for gold, silver, and nickel have pushed exploration for new deposits to the northern limits of the Canadian Arctic in North America. In addition, new technologies have emerged that make extraction of these metals, particularly gold, a profitable endeavor using ore grades that were of little or no interest just a few decades ago. For example, the heap-leach process, which percolates cyanide-laden water through ore piles and dissolves/leaches out the gold, is a widely used

practice in the western United States at locations that were previously "mined out" using traditional deep shaft and open pit methods. However, there are serious environmental risks and numerous episodes of aquatic pollution associated with this practice. Many of the mines in North America have left a legacy of environmental damage to lakes and fish populations because of contaminants that leach from improperly disposed tailings and other surface residuals (Lemly, 1994a). Selenium is an important elemental component of the mineral matrix of ore deposits. Although present in deceptively low concentrations relative to other constituents (low parts-per-million level for selenium vs. high parts-per-hundred or -thousand for the metals being mined), it has the potential to rapidly affect aquatic life because of its propensity to bioaccumulate and increase in concentration as it moves up the food chain (Fig. 1). Any mining operation that mobilizes selenium from the ore and brings it into contact with water activates this risk. Selenium has contaminated surface waters and fish and wildlife populations near mine sites at locations ranging from the Klondike in Yukon, Canada to the Tobe near Capetown, South Africa (see Table 2, Fig. 3; Department of Indian and Northern Affairs [DINA], 2000; University of Capetown [UC], 1999). The best way to minimize the potential for selenium issues in the mining industry is to minimize surface disposal of tailings and wastewater. Practices such as backfilling of solids, recycling of process water, and in situ leaching can dramatically reduce risks and improve the environmental performance of mines (Lemly, 1994a).

2.3. Metal smelting

Metal ores contain some amount of selenium, and the physical/chemical treatment of this ore to extract the desired metal often releases selenium and other constituents into the process water or solid waste that is left. These wastes often contaminate local aquatic habitats (Lemly, 1994a). However, some ores are also heated (smelted) in order to mobilize and separate the desired metal, in particular, copper, nickel, and zinc. When heating occurs, selenium is readily volatilized and can be emitted into the air as a vapor. Once released, this selenium cools and can coalesce or adhere to atmospheric dust particles (some of which are produced by the smelters themselves), subsequently reaching terrestrial and aquatic systems by either dry or wet deposition (Germani et al., 1981; Small et al., 1981). In some situations, these processes can be a substantial factor in the cycling of selenium near smelting facilities. One such example occurred near Sudbury, Ontario, Canada (Table 2, Fig. 3). Selenium is quite common in copper ore and may actually be more concentrated than in coal (20–82 $\mu\text{g Se/g}$ for copper ore vs. 0.4–24 $\mu\text{g Se/g}$ for coal, Table 1, Nriagu and Wong, 1983). On a total mass basis, the Sudbury ore deposits north of Lake Huron in Canada are the largest source of selenium in North America (Shamberger, 1981). Large-scale copper smelting at Sudbury began in the early 1900s, and sampling conducted in the late 1970s showed that selenium discharges had contaminated freshwater lakes for a distance of at least 30 km downwind of the smelter (Nriagu and Wong, 1983). The aerial plume was also implicated as the primary cause of elevated concentrations of selenium in fish and other biota of Georgian Bay in Lake Huron, some 100–200 km away (Hodson et al., 1984). It is important to recognize this source of selenium because in addition to contaminating local habitats, smelting can contribute to selenium inputs in distant aquatic systems due to the mechanism by which it is transported in the atmospheric vapor/particle phase (Small et al., 1981). This aspect of selenium pollution operates on the same principle as the acid rain phenomenon, that is, emission of gas phase pollutants that eventually reach aquatic systems and threaten aquatic life and that form deposition/pollution corridors downwind from major sources. Large-scale metal smelting operations should be viewed as an important contributor to this phenomenon for selenium.

2.4. Municipal landfills

Although not currently recognized as a widespread cause of selenium pollution, municipal landfills can generate leach water that contains elevated concentrations of the trace element (5–50 $\mu\text{g Se/L}$) if seleniferous materials have been disposed there. Noteworthy

examples have occurred in the United States, the United Kingdom, Sweden, Hong Kong, and Japan (see Table 2, Fig. 3; Hong Kong Government [HKG], 2001; Minnesota Pollution Control Agency [MPCA], 2000; National Fisheries Research Institute [NFRI], 2001; Royal Commission on Environmental Pollution [RCEP], 2001; Stockholm Water Authority [SWA], 2000). The source material for selenium in these landfills seems to be similar and involves large amounts of photoelectronic components (rectifiers, capacitors, photocopy printer/toner products, etc., which require selenium to operate properly) that were disposed of from local computer and electronics manufacturing facilities (MPCA, 2000; SWA, 2000). Selenium is widely used in electronics because of its photosensitive and semiconducting properties (Sharma and Singh, 1983). The disposal history of these landfills suggests that selenium-laden leachate could have been released for a number of years, but was only detected recently due to expanded pollution screening programs mandated by local water quality authorities. Because of the global distribution of electronics and computer/copier industries, coupled with the practice of landfill disposal of their solid wastes, this source of selenium poses an important localized threat of selenium contamination. The lesson to be learned from these examples is that contaminant surveillance programs need to monitor landfill leachate for possible selenium contamination. This leachate monitoring can be done by simply including selenium in the list of constituents designated for chemical analysis.

2.5. Oil transport, refining, and utilization

Similarly to the coal industry, procurement and refining of oil produces a variety of selenium-laden wastes (Table 3). The source of selenium in oil is also the same as for coal—natural selenium contained in the fossil raw material that formed over a geologic time scale. However, crude oil contains much higher concentrations of selenium than coal (500–2200 $\mu\text{g Se/L}$ vs.

Table 3
Concentrations of selenium present in oil shale, crude oil, and various products and wastes^a

Material or waste	Selenium concentration
Oil shale	1.3–5.2 $\mu\text{g/g}^b$
Crude shale oils	92–540 $\mu\text{g/L}$
Shale oil retort water	3–100 $\mu\text{g/L}$
Retort solid waste leachate	10–30 $\mu\text{g/L}$
Crude oil	500–2200 $\mu\text{g/L}$
Refined oils	5–258 $\mu\text{g/L}$
Refinery wastewater	15–75 $\mu\text{g/L}$
Oil burner ash (fly ash)	3–10 $\mu\text{g/g}^b$

^a Table compiled from API (1978), Lemly (1985b), and Ohiendorf and Gala (2000).

^b Expressed on a dry weight basis.

0.4–24 $\mu\text{g Se/g}$), thus the potential for hazardous amounts to be released in process waters and effluents is relatively high. Once in the aquatic environment, selenium in these wastes can rapidly bioaccumulate and cause reproductive failure in fish and aquatic birds (Ohlendorf and Gala, 2000), and I list two examples where aquatic life has been contaminated (Table 2, Fig. 3). In most cases, selenium pollution from refinery wastes is overlooked because of concerns over other constituents that receive higher priority; for example, total suspended solids, polyaromatic hydrocarbon compounds (PAHs), oil and grease, and heavy metals (Ridlington et al., 1982; Rowe et al., 1983a, b; United States Environmental Protection Agency [USEPA], 1974; Woodward et al., 1981, 1983). These constituents also get most of the attention when accidental spills of crude oil occur in marine or freshwater habitats (Mielke, 1990; Schmitt, 1999). Notable examples include the 1978 Amoco Cadiz spill off the coast of France and the 1989 Exxon Valdez spill near the south shore of Alaska. Extensive, long-term studies of these pollution episodes show that primary concerns are for heavy oil coating wildlife and beaches and the aquatic toxicity of the hydrocarbon fraction (Haensly et al., 1982; Mielke, 1990; Schmitt, 1999) rather than recognizing dangers of trace elements such as selenium which may, in fact, pose a substantial long-term risk because of bioaccumulation and persistence in the environment. The lack of attention to selenium associated with oil transport and refining is widespread and even pervades university research conducted to develop treatment methods for reducing ecological risks from refinery effluents (e.g., Hawkins et al., 1997). The oil industry transports and disposes huge volumes of selenium-laden materials on a global scale. At any point in this process it can become a major contributor to elevated selenium concentrations in aquatic ecosystems.

2.6. Agricultural irrigation

In the early 1980s a new selenium threat to fish and wildlife emerged—subsurface irrigation drainage. This drainage water usually contains elevated concentrations of soil trace elements and other constituents and has contaminated fish and aquatic birds at several locations in the USA and Middle-East (Table 2; Fig. 3; Egyptian National Research Center [ENRC], 1998; Lemly et al., 1993; Nature and National Parks Protection Authority [NNPPA], 2001). The mechanism underlying this phenomenon is simple, yet almost insidious. Agricultural irrigation practices in arid and semiarid regions typically use water applications in the range 60–80 cm/yr. The amount of water applied is far in excess of what is needed to support crops, but the excess is used to flush away salts that tend to accumulate in crop root zones as evaporation occurs and inhibit plant growth. Subsurface

irrigation drainage is produced due to a specific set of soil conditions. Shallow subsurface (3–10 m) layers of clay impede the vertical movement of irrigation water as it percolates downward. If not removed, this results in waterlogging of the crop root zone and subsequent buildup of salts as excess water evaporates from the soil surface—exactly the same problem that irrigation is intended to solve in the first place (Moore et al., 1990).

Several methods of removing excess shallow groundwater can be employed, including the use of wells and surface canals to forcefully pump and drain the water away. The method of choice in the western USA is to install rows of permeable clay tile or perforated plastic pipe 3–7 m below the surface of agricultural fields (Letey et al., 1986). Once these drains are installed, irrigation water can be applied liberally, thus satisfying the water needs of crops while also flushing away excess salts. The resultant subsurface wastewater is pumped or allowed to drain into ponds for evaporative disposal, or into creeks and sloughs that are tributaries to major wetlands, streams, and rivers (Moore et al., 1990). Subsurface irrigation drainage is characterized by alkaline pH, elevated concentrations of salts, trace elements, and nitrogenous compounds, and low concentrations of pesticides. The natural biological and chemical filter provided by the soil effectively degrades and removes most pesticides as irrigation water percolates downward to form subsurface drainage. At the same time, naturally occurring trace elements in the soil, such as selenium (up to 1400 $\mu\text{g Se/L}$), are leached out under the alkaline, oxidizing conditions prevalent in arid climates and are carried in solution in the drainwater (Presser and Ohlendorf, 1987).

When subsurface irrigation drainage is discharged into surface waters a variety of serious biological effects can take place. The immediate impact is degradation of surface and groundwater quality through salinization and contamination with toxic or potentially toxic trace elements (e.g., selenium, arsenic, boron, molybdenum, chromium, etc.). Long-term impacts can occur if selenium enters aquatic food chains. A landmark case example of this type of impact occurred in 1985 at Kesterson National Wildlife Refuge, California, USA (Table 2, Fig. 3; Lemly et al., 1993), where thousands of fish and waterfowl were poisoned. Selenium and other trace elements were leached from soils on the west side of the San Joaquin Valley and carried to the refuge in irrigation return flows that were used for wetland management (Zahm, 1986). Selenium bioaccumulated in aquatic food chains and contaminated 500 ha of shallow marshes. Elevated selenium was found in every animal group inhabiting these wetlands, from fish and birds to insects, frogs, snakes, and mammals (Clark, 1987; Ohlendorf et al., 1988a; Saiki and Lowe, 1987). Selenium-induced reproductive impairment was documented in a variety of species, and teratogenic

deformities (a biomarker of chronic selenosis) were evident as well. Congenital malformations in young waterbirds were severe and consisted of missing eyes and feet, protruding brains, and grossly deformed beaks, legs, and wings (Hoffman et al., 1988; Ohlendorf et al., 1986a, b, 1988a, b). Several species of fish were eliminated and a high frequency (30%) of stillbirths occurred in the single remaining species (Saiki and Ogle, 1995). Laboratory studies conducted by the US Fish and Wildlife Service confirmed the field assessment that irrigation drainage was the source of elevated selenium and toxic effects (Lemly et al., 1993).

The biogeochemical conditions leading to the production of seleniferous subsurface irrigation drainage, culminating in death and deformities in wildlife, have been termed the "Kesterson Effect" and are prevalent throughout the western USA (Presser, 1994; Presser et al., 1994; Seiler et al., 1999). These conditions include (1) a marine sedimentary basin that contains soils formed during the Cretaceous period, which have relatively high natural concentrations of selenium, (2) alkaline, oxidized soils that promote the formation of water-soluble forms of selenium (especially selenate), (3) a dry climate in which evaporation greatly exceeds precipitation, leading to salt buildup in soils, (4) subsurface layers of clay that impede downward movement of irrigation water and cause waterlogging of the crop root zone, and (5) subsurface drainage, by natural gradient or buried tile/pipe drainage networks, into wetlands and aquatic habitats. Knowing the key factors that contribute to hazardous subsurface drainage, it is important that existing and planned agricultural irrigation projects be reviewed for possible selenium contamination. Anticipating and evaluating potential problem areas will allow changes to be made in irrigation practices for the benefit of both agriculture and wildlife (Lemly, 1994b, c; Lemly et al., 2000).

3. Emerging selenium threats

3.1. Constructed wetlands

In the mid-1980s, the agricultural irrigation selenium issue emerged in central California. A variety of treatment options for removing selenium from subsurface irrigation drainage and reducing hazards to fish and wildlife in downstream waters were examined. One method tested experimentally in the late 1980s, and promoted during the 1990s, was the use of constructed wetlands. In addition to treating irrigation drainage, this "phytoremediation" approach has also been advocated for removing selenium from oil refinery effluents (Terry and Zayed, 1998). However, it is important to recognize that serious ecological risks may accompany this treatment technology (Lemly and Ohlendorf, 2002).

The major objective of treatment wetlands is to remove materials that could threaten the health and biological integrity of down-gradient receiving waters. If that goal is achieved, ecological benefits result. However, if the wastewater being treated contains selenium, the apparent benefits to downstream water quality can be more than offset by toxic hazards created within the wetlands because of bioaccumulation. Moreover, wetlands constitute attractive habitat for fish and wildlife, which increases the likelihood that they will be exposed to hazardous levels of selenium. The end result can be a net loss of benefits and creation of an ecological liability that did not previously exist. Treatment wetlands may thus create selenium problems rather than solve them. That result did take place at the Chevron USA Oil Refinery in Richmond, California in the mid-1990s. A 40-ha constructed wetland intended for "water enhancement" of conventional pollutants (biological oxygen demand, total organic carbon, total suspended solids, ammonia, etc.) was also effective in removing selenium from the waste stream, which was initially viewed as an unanticipated net benefit. The habitat feature it provided attracted large numbers of migratory waterfowl and shorebirds, which was also promoted as a benefit of the wetland. However, bioaccumulation caused selenium levels to exceed toxic thresholds for wildlife, and waterbirds were poisoned. In 1995, selenium concentrations in birds were "high enough to reduce hatchability of eggs and cause some reduction of post-hatch survival among chicks" (Ohlendorf and Gala, 2000). That finding prompted the implementation of an alternative management plan designed to reduce wildlife exposure by manipulating vegetation and water levels in areas of highest selenium concentrations to make them less attractive to birds. After several years under this new management plan, selenium levels in bird eggs were reduced, but still exceeded thresholds for reproductive toxicity (Chevron, 2000). This example illustrates the difficulty of meeting water quality treatment objectives without creating toxic hazards to wildlife. In the USA, there are also important legal issues associated with creation of such hazards; for example, federal statutes such as the Migratory Bird Treaty Act and the Endangered Species Act prescribe strict penalties (monetary fines and/or imprisonment) for killing wildlife by these means, whether or not the owner/operator knowingly allows this "take" to occur (e.g., Lemly and Ohlendorf, 2002; Margolin, 1979).

The underlying problem with constructed wetlands is the failure of those who develop wetland selenium treatments to adequately evaluate risks to fish and wildlife. For example, researchers developing treatment methods typically seek to establish how effective wetlands can be in removing selenium from water, but make little effort to document or reveal ecological hazards (e.g., Hansen et al., 1998; Terry and Zayed, 1998).

Consequently, the methods have inherent dangers that are not readily apparent to potential users. These oversights are a major shortcoming that is pervasive in the wetland treatment technology field. Many wetland treatment methods are being marketed on a broad scale in the USA and other countries without full knowledge or disclosure of the risks they pose to fish and wildlife. Constructing a wetland to treat selenium-laden wastewater may result in selenium poisoning wherever this practice is used.

3.2. Disposal of fly ash

Treatment technologies to reduce airborne particulate emissions from coal-fired power plants have reached a high level of efficiency, sometimes achieving in excess of 99.5% removal. However, this impressive protection of air quality belies other environmental risks associated with large-scale burning of coal. Huge volumes of seleniferous fly ash (50–300 $\mu\text{g Se/g}$) and other combustion wastes are generated in the process. The current annual production of coal ash in the USA is about 120 million tons and is projected to steadily increase in the coming decades (USEPA, 1998). Most fly ash is disposed in landfills that are generally built on clay soils (to impede downward movement of contaminants or upward movement of groundwater), capped with a layer of clay (to impede infiltration of rainwater) and topsoil, and revegetated. The problem with this disposal method is that over time, landfills can become unstable so that either the surface clay cap or the underlying clay develops cracks, rainwater or groundwater infiltrates, and leaching of selenium begins to occur. If that happens, selenium-laden seepage (50–200 $\mu\text{g Se/L}$) can be transported off-site, where it may ultimately reach streams or other surface water, bioaccumulate, and threaten the health of fish and wildlife populations. In fact, the design specifications for fly-ash landfills acknowledge that even under the best conditions, some contaminated leachate will result (Murtha et al., 1983).

One example of this problem occurred in 1991 in eastern Pennsylvania, USA, where plans were being made to construct a 65-ha landfill to dispose of fly ash from five different power plants. Concerns were voiced by local wildlife conservation groups regarding the possibility that selenium-laden leachate from the landfill would threaten populations of native brook trout (*Salvelinus fontinalis*), which is a sport fish highly valued in the region. This potential threat to brook trout prompted an investigation by the Pennsylvania Department of Environmental Resources (PDER) into the leaching behavior of selenium in fly ash. Evidence from the initial investigation, which found that selenium leaching was a legitimate concern, led the PDER to revoke the disposal permit for two of the five facilities identified in the original application (Pennsylvania

Bulletin, 1992) and call for strict controls on the physical and chemical characteristics of ash materials allowed in the landfill (Commonwealth of Pennsylvania, 1991). Additional investigations revealed more potential problems with selenium in leachate from the site and resulted in the landfill being re-permitted to handle only construction and demolition waste--no fly ash was allowed. The events in this case example represent major adjustments to Pennsylvania laws brought about by environmental concerns over selenium and fly ash in municipal landfills. Moreover, the actions taken by PDER set an important precedent by establishing very rigid requirements for fly-ash landfills that are proposed in the future.

As coal-fired power production continues in the new millennium the number of fly-ash landfills will steadily increase, as will the threat of selenium-laden leachate contaminating aquatic habitats and impacting fish populations. When the large number of existing waste dumps is factored in, it becomes clear that the risk of serious ecological consequences is on the rise. Every new landfill is a potential selenium source to down-gradient aquatic habitats, and every new landfill increases the extent of the threat on a regional, national, and international scale.

3.3. Feedlot wastes

Selenium is widely used as a nutritional supplement to livestock diets and it is not uncommon for the liquid manure associated with swine or cattle feedlots to contain 50–150 $\mu\text{g Se/L}$ (Oldfield, 1998). A primary reason for these relatively high levels is that livestock feeds are typically supplemented with selenium to enhance growth; thus, higher intake means higher concentrations in wastes. Because excreted selenium has been physiologically processed by the animal, the chemical forms present in this matrix likely include various organic metabolites or other organic compounds. Importantly, organic selenium has a much greater bioaccumulation potential in aquatic ecosystems than the inorganic selenium that is associated with other pollution sources (e.g., coal-fired power plants, subsurface agricultural irrigation drainage). For example, waterborne inorganic selenate and selenite typically bioaccumulate 1004,000 times in aquatic food chains, but organic selenoamino acids can produce bioaccumulation factors in excess of 350,000 (Besser et al., 1993). This magnitude of bioaccumulation means that a waterborne concentration of only 0.1 $\mu\text{g Se/L}$ organic selenium, in the right chemical form, is sufficient to elevate residues in food-chain organisms to levels that are toxic in the diet of fish (5–15 $\mu\text{g Se/g}$).

The threat of selenium contamination from intensive feedlot operations becomes apparent when one considers the size and number of these operations in

combination with the magnitude of pollution events that have occurred due to drainage or spills from manure pits. For example, in the coastal plain region of eastern North Carolina, USA, modern swine-rearing farms are known as “hog factories” or “confinement facilities,” each with 5000–20,000 animals. Hog production in North Carolina nearly tripled during the 5-yr period from 1990 to 1995, increasing from 5 million to 14 million animals. The large volume of liquid manure produced is stored in multimillion-gallon lagoons until it is removed and sprayed onto fields. Spills or overflows from these sewage lagoons, or pollution from runoff of manure from excessively sprayed fields, is a common occurrence (Schildgen, 1996). In 1995, a 25-million-gallon spill entered North Carolina’s New River and killed fish for 20 miles downstream. Hog waste was also implicated in massive pollution of the state’s Neuse River, which was quarantined for a 35-mile stretch in 1995 (Schildgen, 1996), and likely contributed to outbreaks of a toxic dinoflagellate (*Pfiesteria piscidia*) in the Pamlico River Estuary (Glasgow et al., 1995).

Intensive livestock feeding operations generate a large volume of seleniferous waste that has the potential to severely impact nearby aquatic ecosystems as well as downstream habitats such as wetlands and estuaries. This seleniferous waste is an escalating threat that could affect many areas of the USA and other countries. Although there is a pressing need to evaluate this threat, there has been no monitoring for acute or residual selenium contamination of aquatic life in any of the pollution events associated with feedlot operations, and there is no monitoring of selenium movement off fields sprayed with large amounts of liquid manure. Concerns for aquatic impacts of livestock wastes are focused on nutrient enrichment, bacterial contamination, and depression of dissolved oxygen—there is no recognition of selenium issues.

3.4. Open-pit phosphate mining

Open-pit phosphate mining is an emerging selenium contamination issue that poses serious risks to aquatic life in the western USA. As with gold, silver, and nickel ore, selenium is associated with the mineral matrix of phosphate deposits, some of which resemble low-grade coal with respect to their carbon content. Selenium is present at concentrations of 2–20 µg Se/g, which are similar to those of raw coal. Thus, many of the concerns about selenium contamination from the solid waste and surface residuals of phosphate mining parallel those of coal mining. Phosphate mining in the western USA occurs primarily in areas of low annual precipitation (<40 cm/yr). Consequently, the potential for large quantities of selenium to be leached from surface residuals by natural rainfall/snowmelt is not as

great as it would be in regions of high precipitation. For many years, these conditions prevented major selenium runoff from occurring. However, the immense size of mine tailings piles (up to 50 million m³) has changed subsurface hydrology so that groundwater has risen within them and created miniature aquifers, which seep laterally and exit the mine spoils as streams of selenium-laden leachwater containing up to 1500 µg Se/L (Desborough et al., 1999; Herring et al., 1999). Local fish, wildlife, and livestock have been poisoned, and a major recreational fishery is threatened (Lemly, 1999). Although there are currently no other well documented cases of this type of selenium pollution, natural resource managers around the world should understand that phosphate mining has the potential to severely impact aquatic life wherever the practice occurs. It is also important to recognize that local climate and hydrology will determine the rate and type of selenium leaching that takes place from surface residuals.

3.5. Electrolytically produced metals

Another important selenium issue involves the use of selenium as an additive in the production of electrolytic manganese metal. In this process, known as **electrowinning**, a cathode and anode are immersed in an aqueous slurry (electrolyte) made from manganese ore. Electric current is applied and soluble manganese is transformed to a chemically reduced (positively charged) state, moves to the cathode, and forms an accretion of pure metal. However, elemental manganese has a low reduction potential and the electrolytic process creates a hydrogen evolution reaction, both of which reduce the current efficiency of the process. This reduced efficiency means that a large amount of electricity is required to produce a small amount of metal. Suppressing the hydrogen evolution reaction improves current efficiency, increases yields, and results in a substantial saving in production costs. A simple and effective means of reducing hydrogen is to add selenium (as selenious acid) to the electrolyte. However, the majority of the added selenium will report to the cathode and mix with the depositing manganese, resulting in a product with a metal purity of about 99.7% Mn (selenium content about 0.15%). Selenium-free manganese has a metal purity of at least 99.9% Mn. About 75% of the world’s manganese is currently made using the selenium-addition method in order to cut production costs and maximize profits.

The environmental significance of selenium-contaminated metal becomes apparent when manganese is alloyed with steel or aluminum (to harden the end product), which is its major industrial use. Most of the selenium in manganese does not stay in the heated metal alloy but becomes incorporated into waste streams, i.e.,

dross and/or dusts generated and collected in the manufacturing process. These wastes may contain selenium at concentrations exceeding 1.0 mg Se/L or 50 µg Se/g (Manganese Metal Company [MMC], 2002a, b), which classifies them as hazardous material according to US Environmental Protection Agency criteria (USEPA, 2000). Under these criteria, disposal is only allowed in specially designed sites that contain/collect and monitor leachate. Since 1998, the selenium-manganese connection has been gaining recognition in the United States and is beginning to receive regulatory attention. However, prior to 1998 the selenium content of this waste was largely unknown and it was sent to nonhazardous municipal landfills for disposal. Leachate from these sites poses a major environmental risk due to the selenium-laden waste that was dumped there. The magnitude of this threat is just now being explored, as information is gathered from aluminum and steel manufacturers on their disposal sites and practices over the past several decades.

Of great significance globally is the fact that selenium-contaminated manganese continues to be produced in China (it produces about 75% of the world's manganese) and exported to buyers around the world, most of which likely have no knowledge of how the manganese they are using was produced, or of the potential for associated environmental impacts from selenium pollution (MMC, 2002a, b). It may be hoped that information gained from case examples in the United States will find its way, through papers such as this, to scientists and regulatory authorities in other countries in time to curtail the risk of widespread selenium pollution. Switching to selenium-free manganese in the aluminum and steel industries would immediately stem this threat around the world.

4. Conclusions

When the phenomenon of selenium pollution on a global scale is examined closely it becomes clear that the more we look, the more examples we find. Human activities that increase waterborne concentrations of selenium and provide conditions favorable for bioaccumulation are on the rise. The risk of widespread impacts from new selenium threats is greater than ever before. Important sources of selenium contamination in aquatic habitats are often overlooked by environmental biologists and ecological risk assessors due to preoccupation with other, higher priority pollutants, yet selenium may pose the most serious long-term threat to aquatic habitats and fishery resources. These oversights occur in experimental research as well as field management operations. Failure to include selenium in the list of constituents measured in contaminant screening/monitoring programs is a major mistake, both from

the hazard assessment aspect and the pollution control aspect. Once selenium contamination begins, a cascade of events is set into motion that can quickly lead to irreversible ecosystem disruption. However, this cascade of events need not happen if adequate foresight and planning are exercised. Recent advances in selenium assessment techniques (e.g., Lemly, 2002a) provide the means for rapid identification and evaluation of potential problems, thereby allowing early intervention by those responsible for pollution control. Environmentally sound hazard assessment and water quality goals coupled with prudent risk management can prevent significant biological impacts from taking place.

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