Research Article

Selenium in Aquatic Birds From Central California

FRED L. PAVEGLIO,[1] *United States Fish and Wildlife Service, Division of Natural and Cultural Resources, Branch of Refuge Biology, 1211 SE Cardinal Court, Suite 100, Vancouver, WA 98683, USA*

KEVIN M. KILBRIDE, *United States Fish and Wildlife Service, Division of Natural and Cultural Resources, Branch of Refuge Biology, 1211 SE Cardinal Court, Suite 100, Vancouver, WA 98683, USA*

ABSTRACT After mostly freshwater replaced agricultural drainage water used for wetland management in 1985, Selenium (Se) concentrations in 3 wintering waterfowl species and black-necked stilts (*Himantopus mexicanus*) from the North and South Grasslands of central California, USA, declined in the years from 1986 to 1988 and 1989 to 1994. However, Se concentrations were still above the threshold for potential reproductive impairment and exceeded background levels for some species. Consequently, we measured Se concentrations in aquatic birds in 2005 after long-term use (20 yr) of predominately freshwater for wetland management in the Grasslands. As in 1986–1994, Se concentrations in 2005 were higher for birds from the South Grasslands, which historically received more undiluted drainage water compared with the North Grasslands. Liver Se concentrations for stilts from the South Grasslands were at levels associated with potential reproductive impairment. All species from the South Grasslands, as well as mallards (*Anas platyrhynchos*), northern pintails (*A. acuta*), and American coots (*Fulica americana*) from the North Grasslands, were above species-specific background levels. From 1994 to 2005, Se levels in some aquatic birds stabilized above background levels likely indicating long-term cycling within the Grasslands. We recommend Se-contaminated drainage water ($\geq$2 ppb Se) not be used for management or allowed as an input into arid wetlands throughout the western United States. (JOURNAL OF WILDLIFE MANAGEMENT 71(8):2550–2555; 2007)

DOI: 10.2193/2006-250

KEY WORDS adaptive management, aquatic birds, California, drainage water, irrigation, selenium, shorebirds, waterfowl, water quality, wetlands.

The Central Valley of California, USA, which is composed of the Sacramento and San Joaquin valleys, provides habitat for the largest concentrations of wintering waterfowl in the world (Heitmeyer et al. 1989). An estimated 20–40 million waterfowl historically used wetlands within the Central Valley as wintering habitat during the 1980s (Ducks Unlimited 2005). Approximately 60% of the waterfowl within the Pacific Flyway depend upon the Central Valley for wintering habitat, and about 25% of those birds use the San Joaquin River (SJR) Basin (Central Valley Joint Venture 2006). There are only 36,423 ha of wetlands (collectively known as the Grasslands [Merced County]) remaining in the SJR Basin, and most occur within the Grassland Water District (GWD). The Grasslands, which includes the North and South Grasslands portions (Fig. 1), represents the largest remaining tract of contiguous waterfowl habitat within the San Joaquin Valley (Gilmer et al. 1982).

The major land use (70%) for the SJR Basin is agriculture that requires irrigation to grow crops in an arid environment. Soils in the SJR Basin are marine in origin and have high levels of salts. As a result of salts (including Selenium [Se]) leaching through the soil profile during irrigation, shallow groundwater (subsurface drainage) must be removed from the root zone with tile drains to prevent crop damage (Presser and Barnes 1985, Presser and Ohlendorf 1987). Soils and shallow groundwater in the SJR Basin with the highest Se concentrations are located within the 39,255 ha of farmland south of the GWD that is referred to as the Drainage Project Area (DPA; Chilcott 2000; California Regional Water Quality Control Board [CRWQCB], Central Valley Region 2001; McCarthy and Grober 2001). Monitoring at tile drainage sites indicated that 82% of the water samples in the DPA had Se concentrations ranging from 11 ppb to 500 ppb (Chilcott 1988).

Se in subsurface drainage bioaccumulated in the food chain at Kesterson Reservoir (situated within the North Grasslands, formerly located within the Kesterson National Wildlife Refuge) and caused poor reproductive success and overt teratogenesis in aquatic birds during 1983–1985 after storage of agricultural drainage started during 1978 (Ohlendorf et al. 1986*a*, *b*; Hoffman et al. 1988; Ohlendorf and Hothem 1995). As with Kesterson Reservoir, elevated concentrations of Se occurred in nesting aquatic birds and their eggs in the South Grasslands during 1984 (Ohlendorf et al. 1987, Ohlendorf and Hothem 1995). Because Se-contaminated drainage water affected avian reproduction, the California State Water Resources Control Board ordered the GWD to reduce Se concentration in its supply water used for wetland management (California State Water Resources Control Board 1985).

Modifications were made to the GWD conveyance system so water supplied to the wetlands was switched from agricultural drainage to predominantly freshwater (<2.0 ppb of Se) during autumn 1985 (Grassland Water District and Grassland Water Task Force 1986; CRWQCB, Central Valley Region 1998). From 1985 to 1996, water supply channels of the GWD were alternately used to convey agricultural drainage and freshwater (flip-flop system) in order to keep freshwater supplies separated from subsurface agricultural drainage water. However, residual Se in water supply channels contaminated freshwater delivered to GWD wetlands (CRWQCB, Central Valley Region 2000). To improve the delivery of freshwater, the Grasslands Bypass was implemented during September 1996 so

[1] *E-mail: fred_paveglio@fws.gov*

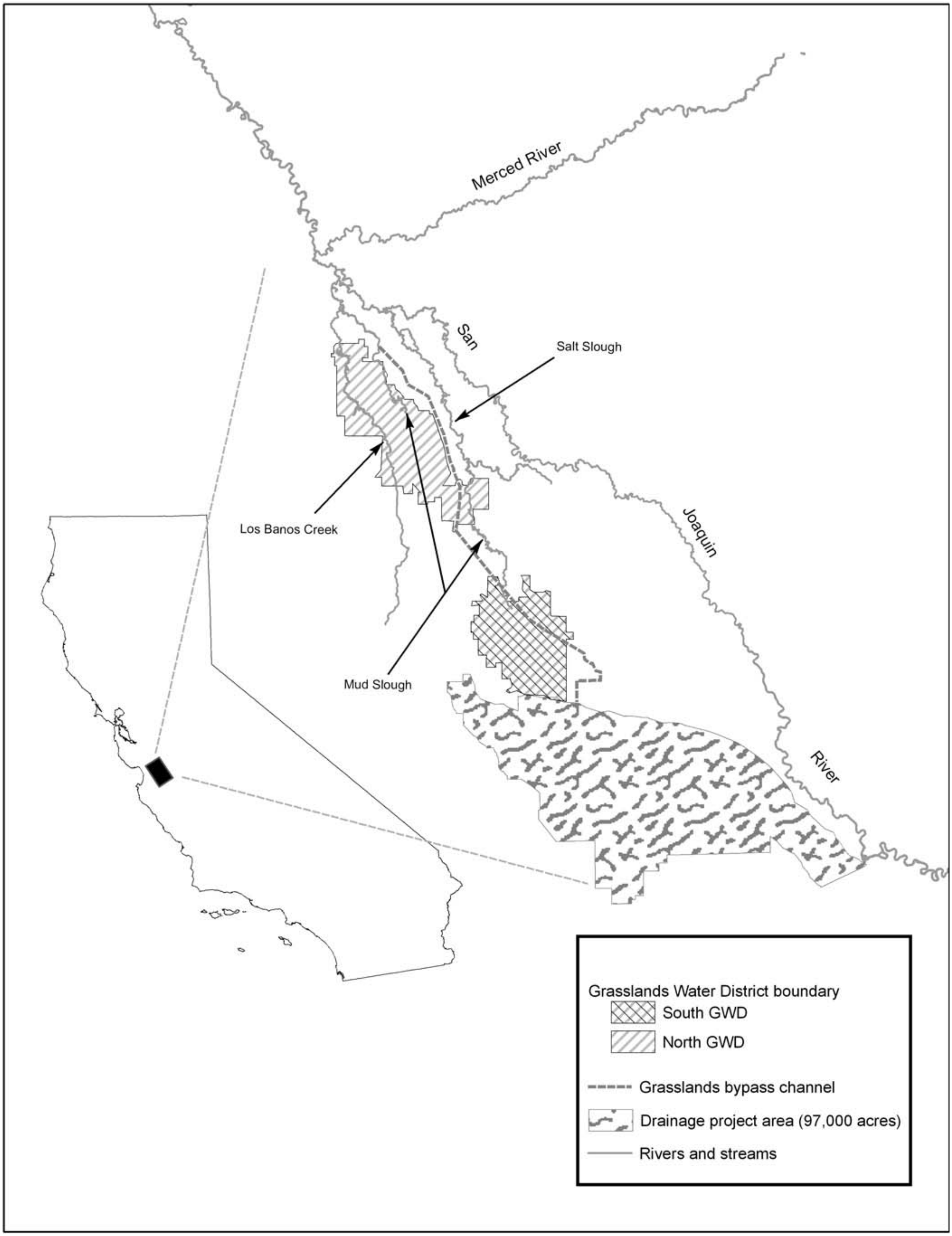

Figure 1. North and South Grasslands within the Grasslands Watershed of Central California, USA, where we studied selenium in aquatic birds in 2005. GWD = Grassland Water District.

subsurface drainage from the DPA was collected and routed around the GWD into the SJR. The Grasslands Bypass removed most of Se load from the wetland supply channels and, in turn, the Grasslands wetlands.

After wetland management of the North and South Grasslands was switched from agricultural drainage to predominantly freshwater during autumn 1985 using the flip-flop system, Paveglio et al. (1992) collected American coots (*Fulica americana*), black-necked stilts (*Himantopus mexicanus*), mallards (*Anas platyrhynchos*), and northern shovelers (*A. clypeata*) during February 1986 that contained Se concentrations 1.3 to 4.6 times higher than birds taken as they arrived in the Grasslands during autumn 1985 (Paveglio et al. 1992). After 9 years of flip-flop freshwater management, Paveglio et al. (1997) found Se concentrations decreased in wintering aquatic birds collected from the Grasslands; however, some of these concentrations remained above levels associated with impaired reproduction in birds from laboratory and field studies (Ohlendorf et al. 1987, Heinz et al. 1989). In addition, only northern pintails (*Anas acuta*) were at background levels in the North and South Grasslands by 1994 (Paveglio et al. 1997).

Our objectives for a follow-up to these studies from 1986 through 1988 (Paveglio et al. 1992) and 1989 through 1994 (Paveglio et al. 1997) were to 1) evaluate the long-term effectiveness (20 yr) of freshwater management as remediation for Se contamination in wintering aquatic birds of the North and South Grasslands; 2) determine if the South Grasslands, which received more undiluted drainage water than the North Grasslands, remained more contaminated; and 3) assess whether freshwater management in the Grasslands had reduced Se concentrations in wintering aquatic birds to species-specific background levels.

STUDY AREA

We used 4 drainage areas in the North Grasslands and 6 drainage areas in the South Grasslands for collection of aquatic birds during February 2005. These drainage areas were delineated in accordance with the canal systems historically used to irrigate waterfowl food plants and pastures during summer, as well as to flood marshes with varying amounts of fresh and drainage water during autumn (Paveglio et al. 1992).

METHODS

We attempted to collect equal numbers of males and females for mallards, shovelers, pintails, coots, and stilts from each drainage area using methods described by Paveglio et al. (1992). As in previous collection years, we shot all birds within a 14-day period.

After collection, we used a chemically cleaned stainless steel scalpel and forceps to remove livers that were then frozen (4° C) in chemically cleaned jars until we analyzed them for Se. We quantified concentrations of Se using hydride-generation atomic-absorption spectroscopy with methods described by Paveglio et al. (1992). The detection limit for Se determinations was 0.05 ppm dry mass (DM). Recovery rates from tissue samples spiked with Se averaged 96% (1986–1989), 99% (1989 and 1994), and 100% (2005), respectively.

We used 3-factor analysis of variance (ANOVA) to assess the effects of location (North vs. South Grasslands), years (1986–2005), and sex on Se concentrations. If an interaction was present, we ran ANOVAs on subsets of the data so that results were not confounded. For example, if there was an interaction between year and location, we used separate ANOVAs for the North and South Grasslands to compare Se concentrations among years. Where there were no interactions between factors (e.g., yr and location), we calculated averages of cell means for the primary factor (e.g., yr; Neter and Wasserman 1974). We used Bonferroni and Tukey's tests to separate means where we found differences for ANOVAs with and without interactions, respectively. We transformed Se concentrations to common logarithms to satisfy assumptions for homogeneity of variance. We converted logarithmic means to the ppm scale by the inverse of the logarithmic function (10^x where x is a logarithmic value) that resulted in geometric means. We used SAS Institute Incorporated (1985) to run ANOVAs and compute test statistics at $\alpha = 0.05$.

We calculated 95% confidence intervals to assess Se concentrations in wintering birds from 2005 relative to ranges of potential reproductive impairment and background levels. We calculated separate 95% confidence intervals for the North and South Grasslands but combined data from males and females because ANOVAs indicated Se varied between locations, but there were no interactions between sex and location. J. Skorupa (U.S. Fish and Wildlife Service, unpublished data) found 20 ppm to 30 ppm DM of Se in the liver was associated with possible (14–79%) adverse biological effects to breeding waterbirds. This threshold range was based upon exposure-response relationships in breeding aquatic birds from 9 populations during 1983–1989 in the San Joaquin Valley. Background levels for each species were derived from birds collected immediately upon or shortly after arrival to the North Grasslands during autumn 1985 (Paveglio et al. 1992). Because there were lower concentrations of Se in the North Grasslands, along with minimal exposure time prior to this collection, these values best represent background levels for birds arriving in the northern San Joaquin Valley during the autumn migration.

RESULTS

We collected 250 birds from the North and South Grasslands during February 2005 (Table 1). For all study years ($n = 6$) from 1986 to 2005, we collected a total of 1,499 birds during late January and early February from the Grasslands. We detected Se in all liver samples from birds collected from 1986 to 1994 (Paveglio et al. 1992, 1997) and 2005. Selenium concentrations in 2005 were 40–93% higher for shovelers, coots, and stilts from the South Grasslands compared with the North Grasslands (Table 2). For 2005, there were no differences between sexes for any

Table 1. Sample sizes of aquatic birds collected from the North and South Grasslands, California, USA, February 2005.

Species	Sex	North Grasslands	South Grasslands
Mallard	F	9	13
	M	11	17
Northern shoveler	F	7	13
	M	10	20
Northern pintails	F	7	11
	M	10	22
American coot	F	12	21
	M	8	9
Black-necked stilt	F	11	17
	M	9	13
Total		94	156

bird species. Selenium concentrations were lower during 2005 compared with 1986–1987 for aquatic birds except pintails from the North Grasslands where there was no difference between 1987 and 2005 (Table 3). Selenium concentrations for mallards, pintails, shovelers, coots, and stilts declined 38% (pintails [South Grasslands]) to 68% (shovelers [North and South Grasslands combined]) throughout our 20-year study. Only Se concentrations for shovelers from the North and South Grasslands declined (33%) between 1994 and 2005.

By 2005, only stilts from the South Grasslands had Se levels that overlapped the threshold range for possible reproductive impairment (Table 4). In contrast, no 2005 birds from the North Grasslands had 95% confidence intervals within or above the potential impairment range. All birds collected from the South Grasslands during 2005 had a 95% confidence interval above the species-specific background level (Table 4). For the North Grasslands, shovelers and stilts had a 95% confidence interval at or below the species-specific background level.

DISCUSSION

After 20 years of freshwater management, Se continued to recycle in the Grasslands wetlands as indicated by liver concentrations we evaluated, especially in stilts from the South Grasslands. Similarly, Ohlendorf et al. (1990) found that sedentary, insectivorous species (i.e., stilts and grebes [*Podiceps* spp.]) had the highest liver concentrations at Kesterson Reservoir during 1983. Se concentrations in aquatic invertebrates, which are the primary forage for stilts, typically were 2 to 6 times the levels in rooted plants and algae. At Kesterson Reservoir during 1983, aquatic invertebrates had mean concentrations of Se >100 ppm DM (Ohlendorf et al. 1986*a*, *b*; Saiki 1986*a*, *b*; Saiki and Lowe 1987). In contrast with stilts, mallards and pintails in the Grasslands had lower Se levels during 2005 (Table 3) likely as a result of their mobility and dietary preference. Mallards and pintails typically foraged over wide areas within the Grasslands on a more omnivorous diet, which likely included seeds and vegetative matter (low Se levels) as well as invertebrates. In 1983 at Kesterson Reservoir, the mean Se concentration in anatids (including mallards and pintails) was 20 ppm DM compared with 63 ppm DM for stilts (Ohlendorf 1989).

Se cycling within Grasslands wetlands likely is attributable to the following 3 factors: historic use of agricultural

Table 2. Average (cell $\bar{x}$)[a] concentrations (ppm, dry mass) of selenium in livers of aquatic birds collected during February from the North and South Grasslands, California, USA, 2005.

Species	North	South	*P*-value
Mallard	6.8	8.0	0.141
Northern shoveler	6.6	9.7	0.003
Northern pintail	7.0	6.8	0.802
American coot	5.0	7.0	0.006
Black-necked stilt	8.8	17	<0.001

[a] Values are averages of cell (M and F) means.

Table 3. Average (cell $\bar{x}$)[a,b] concentrations (ppm, dry mass) of selenium in livers of aquatic birds collected during February from the North and South Grasslands, California, USA, 1986 to 2005.

Species	1986	1987	1988	1989	1994	2005
Mallard	14A[c]	10A	6.9B	7.2B	7.1B	7.3B
Northern shoveler	26A	15B	13B	15B	12B	8.0C
Northern pintail[d,e]						
North		6.3A	6.1A	6.5A	5.3A	6.8A
South		11A	14A	13A	6.1B	6.8B
American coot[e]						
North	12A	6.2B	5.4B	4.8B	4.5B	4.9B
South	24A	14B	15B	9.3C	9.1C	7.3C
Black-necked stilt	32A	19B	13BC	14BC	11C	12BC

[a] Values, except for northern pintail and American coot, are averages of cell (North and South Grasslands) means. We combined sexes for all species for statistical analyses.

[b] Data for yr 1986–1994 were previously reported in Paveglio et al. (1992, 1997).

[c] Means with the same letter did not differ ($P > 0.05$) among yr for a species.

[d] Because northern pintails departed before the Feb collection during 1986, we excluded these data for comparisons among yr.

[e] Because a yr-by-location interaction ($P \leq 0.05$) was found, we analyzed comparisons among yr separately for the North and South Grasslands.

Table 4. Confidence intervals (95%) for selenium concentrations (ppm, dry mass [DM]) in livers of aquatic birds[a] collected from the North and South Grasslands, California, USA, February 2005.

Species	Background level[b]	North Grasslands	South Grasslands
Mallard	4.1	5.5–8.2	7.1–8.9
Northern shoveler	8.1	5.5–7.6	8.5–11
Northern pintail	5.5	5.7–8.0	6.2–7.5
American coot	3.2	4.1–5.9	6.3–8.4
Black-necked stilt	9.5	7.1–11	15–20[c]

[a] Because results for 2-factor (location and sex) analyses of variance for each species during 2005 indicated differences among locations without interactions between location and sex, we combined M and F to derive 95% CI separately for the North and South Grasslands.

[b] Background levels for each species were derived from birds we collected immediately upon or shortly after arrival to the North Grasslands during autumn 1985 (Paveglio et al. 1992).

[c] CI overlapped with the range (20–30 ppm DM) of possible reproductive impairment to aquatic birds (J. Skorupa, U.S. Fish and Wildlife Service, unpublished data).

drainage resulting in a reservoir of Se in wetlands and supply channel sediments, storm-water inflows, and unregulated inflows of subsurface drainage directly into wetlands or indirectly into their supply channels. From 1986 through 1994, water quality monitoring found a 30% mean loss in Se levels as drainage water flowed through the Grasslands supply channels likely indicating the possible deposition into channel sediments (River Discharge Technical Committee 1999). Since 1996, there also have been infrequent, short-term instances where agricultural drainage flows (Se water-borne concentrations ranging from 3.5 ppb to 44 ppb) within the Grasslands Bypass have been diverted into Grasslands supply channels during winter storm events (Grassland Area Farmers 2005). High flow rates have been associated with storm events during water years 1995, 1997, 1998, and 2005 resulting in spikes of Se concentrations in the Grasslands supply channels (Luoma and Presser 2000, Grassland Area Farmers 2005). There were several sources of agricultural drainage water outside the DPA ($\geq$39,255 ha) affecting the Grasslands that were not regulated by the discharge restrictions (Chilcott 2000). Unregulated drainage water inputs from these areas have or continue to commingle with freshwater used for wetland management, especially within the South Grasslands (L. Ruport, U.S. Fish and Wildlife Service, personal communication).

Most of the Se dissolved in water, which is present as inorganic selenite and selenate in central California (Cooke and Bruland 1987, Presser et al. 1994), can become incorporated in sediments through natural processes of chemical and microbial reduction followed by adsorption, co-precipitation, or settling (Lemly and Smith 1987). Even if water concentrations are low as they typically are for current Grasslands supplies, organic and inorganic Se can be taken up (mobilized) by aquatic plants (via roots), benthic invertebrates, and detrital-feeding fish and wildlife. Dissolved Se also can be adsorbed onto sediment particles that can be ingested, absorbed, and transformed by benthic organisms. In addition, Se incorporated into supply channel sediments may become remobilized during freshwater deliveries for wetland management (Byron et al. 2003). The dissolved Se can be mobilized by producers (e.g., algae, bacteria) biotransforming it into organic Se, which is then biomagnified from consumers (e.g., zooplankton, insect larvae) into top predators such as aquatic birds (River Discharge Technical Committee 1999). Most Se in animal or plant tissues is eventually deposited as detritus.

Although chemical, physical, and biological processes move Se into and out of the sediments in aquatic habitats, most (90%) of the Se usually accumulates in the top few cm of sediment and detritus (Lemly and Smith 1987). Selenium concentrations were likely elevated in some aquatic birds from the Grasslands because the sediments have functioned as a sink and reservoir. Rooted aquatic plants and detrital food uptake with food-chain transfer represent a recognized route for Se accumulation for wildlife within the SJR ecosystem (Ohlendorf et al. 1993, Maier and Knight 1994, River Discharge Technical Committee 1999).

MANAGEMENT IMPLICATIONS

For Se concentrations in aquatic birds to reach background levels (indicative of full ecosystem recovery), Se inputs need to be reduced in order to deplete the reservoir of Se remaining in the Grasslands thereby, reducing or eliminating Se cycling. To protect Grasslands wetlands and its breeding and wintering waterfowl from Se-contaminated drainage water originating from the DPA, the Se water quality objective (monthly $\bar{x} \leq 2$ ppb) established under section 303 (d) of the Clean Water Act during 1996 must be maintained. In addition, eliminating unrestricted inflows of subsurface drainage from outside the DPA reaching wetlands and supply channels of the Grasslands is necessary for all migratory birds to reach background levels.

ACKNOWLEDGMENTS

We thank D. Marciochi and board members of the Grassland Water District for their cooperation, as well as duck club owners and managers of the Grasslands for access to their wetlands for bird collections. Staff of the San Luis National Wildlife Refuge Complex provided logistical support. We especially thank L. Ruport and D. Woolington, who coordinated and assisted with collecting and processing birds. S. Milar prepared the figure. J. Heyd and P. Crader (CRWQCB) provided reports for Se monitoring in the Grasslands associated with the Grasslands Bypass. J. Skorupa and J. Winckel reviewed and provided helpful suggestions to improve the manuscript.

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Associate Editor: Hupp.