ENVIRONMENTAL CHEMISTRY of SELENIUM

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MARCEL DEKKER, INC. NEW YORK • BASEL • HONG KONG

Library of Congress Cataloging-in-Publication Data

Environmental chemistry of selenium/edited by William T. Frankenberger, Jr., Richard A. Engberg.
p. cm. — (Books in soils, plants, and the environment; v.64)
Includes bibliographical references and index.
ISBN 0-8247-0136-4
1. Selenium—Environmental aspects. I. Frankenberger, W. T. (William T.). II. Engberg, R. A. III. Series.
QH545.S45E58 1998
577.27'5724—dc21 97-44122
CIP

This book is printed on acid-free paper.

Headquarters
Marcel Dekker, Inc.
270 Madison Avenue, New York, NY 10016
tel: 212-696-9000; fax: 212-685-4540

Eastern Hemisphere Distribution
Marcel Dekker AG
Hutgasse 4, Postfach 812, CH-4001 Basel, Switzerland
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World Wide Web
http://www.dekker.com

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Current printing (last digit):
10 9 8 7 6 5 4 3 2 1

PRINTED IN THE UNITED STATES OF AMERICA

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Mass Balance Approach to Selenium Cycling Through the San Joaquin Valley: From Source to River to Bay

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I. INTRODUCTION

Surface and ground waters of the Central Valley of California (e.g., rivers, dams, off-stream storage reservoirs, pumping facilities, irrigation and drinking water supply canals, agricultural drainage canals) are part of a hydrologic system that makes up a complex ecosystem extending from the riparian wetlands of the Sacramento and San Joaquin Rivers through the San Francisco Bay/Delta Estuary to the Pacific Ocean (Fig. 1). Water quality concerns center on elevated selenium (Se) and salt concentrations in irrigation drainage water discharged into the waterways of the relatively arid San Joaquin Valley (SJV), including the San Joaquin River (SJR). These waters are made unique by dissolved Se, weathered from marine sedimentary rocks of the Coast Ranges to the west, being ultimately concentrated to toxic levels in aquatic wildlife in the wetlands of the SJV/SJR trough (Figs. 1 and 2) (Presser and Ohlendorf, 1987; Presser, 1994). Scientific and environmental concerns focus on the bioreactive properties of Se and its partitioning among biota, water, and sediment, and on whether simple dilution models can be applied to an element that bioaccumulates. Because of state and federal commitments to provide water for irrigation, as well as drainage of irrigation wastewater by the year 2000 drainage from over 180,000 ha of seleniferous, salinized farmland within the western SJV will create approximately 387 million cubic meters of potentially toxic drainage water annually (i.e., "problem water," as defined by the San Joaquin Valley Drainage Program, 1990), thus lending urgency to an understanding of the biogeochemistry of Se in this environment.

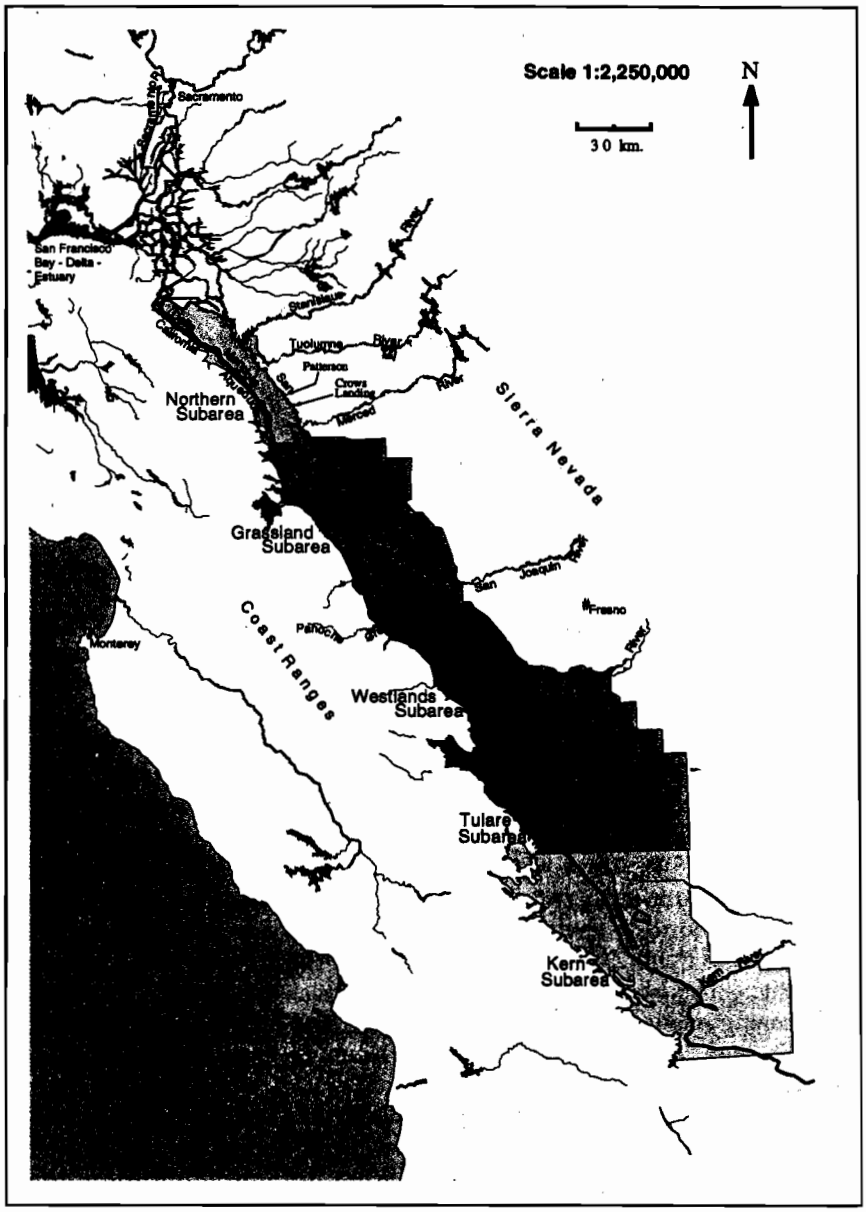

FIGURE 1 The San Francisco Bay/Delta Estuary and San Joaquin Valley of California, showing the major waterways and the five agricultural drainage management subareas (Northern, Grassland, Westlands, Tulare, and Kern).

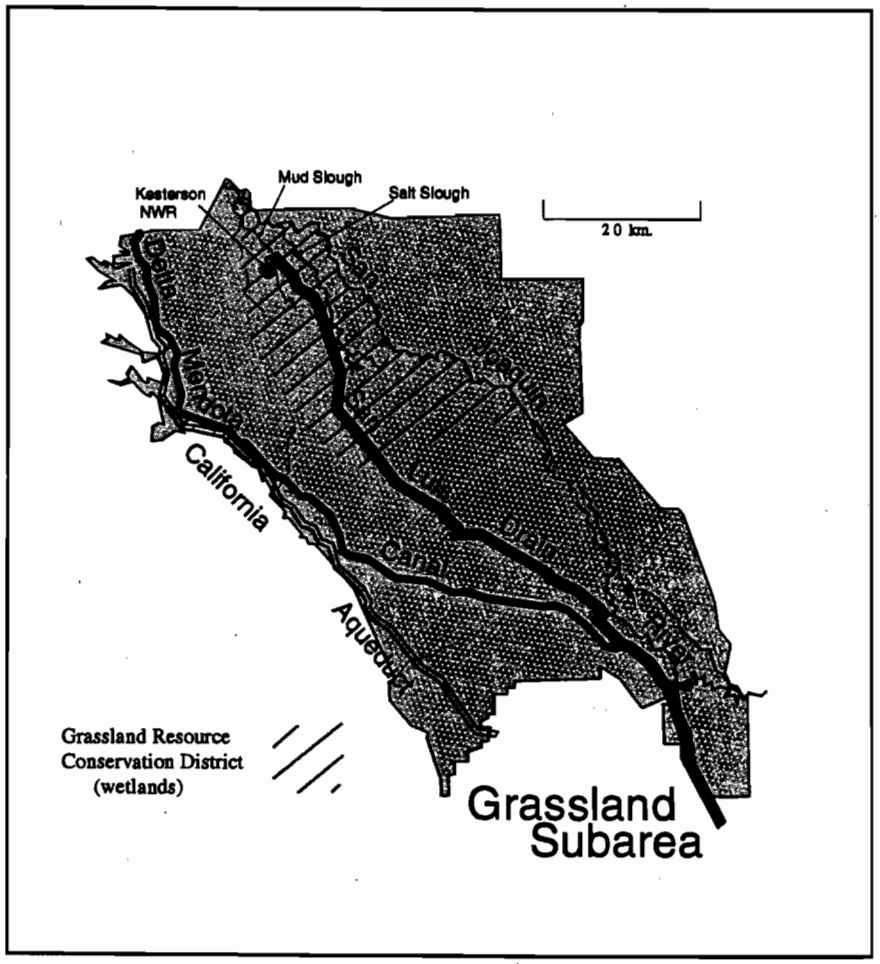

FIGURE 2 The Grasslands drainage management subarea showing the San Joaquin River, riparian wetlands, and drainage system, including the San Luis Drain.

Commencing in 1968, a 137 km section of the San Luis Drain (SLD) was built to Kesterson National Wildlife Refuge, in what was then seen as the first step of a plan to transport agricultural drainage to the San Francisco Bay/Delta Estuary (Fig. 1). To minimize the cost of agricultural drainage disposal in this interim project (i.e., prior to completion of the drain), wastewater that was drained from surface and subsurface agricultural lands and transported by drainage canals, including the SLD, was used as water supplies for aquatic wildlife habitat on the Pacific Flyway in the SJV (San Joaquin Valley Interagency Drainage Program,

1979). However, questions were raised beginning in 1983 about the practice of disposal of irrigation drainage in wetlands, owing to the appearance of deformities among embryos and hatchlings of waterfowl at Kesterson National Wildlife Refuge (Ohlendorf et al., 1986), the main recipient of SLD wastewater (Fig. 2). Selenium was found to bioaccumulate in the food chain and hence, in the proteins of higher level species, causing teratogenicity in aquatic birds. In 1985, the U.S. Department of the Interior (USDOI) shut down the SLD. In 1988 Kesterson Reservoir, representing approximately one-fourth of the refuge and its most contaminated part, was filled and graded by the U.S. Bureau of Reclamation (USBR, 1986), as ordered by the state of California, as a type of what some consider "on-site disposal." Today, Kesterson Reservoir remains a terrestrial habitat monitored for return of Se to the surface, Se accumulation in plants and biota, and Se seepage to groundwater.

The SJR, the only natural outlet from the SJV, has been and continues to be used as a de facto drain for agricultural wastewater to the San Francisco Bay/Delta Estuary distribution system, despite the closure of the SLD. The SJR is California's largest river south of the San Francisco Bay/Delta Estuary. Its headwaters are in the Sierra Nevada; in its lower reaches, the river flows northward through the SJV trough for 110 miles to the Delta (Fig. 1). Currently, 98% of the water is diverted for irrigation purposes. This leaves the lower reach of the river at certain times of the year as a "dry reach" that is totally dependent on disposal of agricultural drainage for its flow. This usage of the SJR water is the subject of a lawsuit filed in 1988 by The Natural Resources Defense Council in the U.S. District Court in Sacramento, of recent complaints (Smith, 1995; Bard, 1996) to the California State Water Resources Control Board (CSWRCB), and of congressional legislation (The Central Valley Project Improvement Act of 1992) because of purported lack of protection (1) of fish, wildlife, and habitat of the river, (2) of the river as a public trust resource, (3) of endangered species using the river, and (4) of water quality (due to disposal of agricultural drainage). Its riparian wetlands contain the largest tract of natural wetlands remaining in the SJV, the Grassland Resource Conservation District (Fig. 2). Nearly 95% of wetland habitat in the SJV has been lost. Historically, varying amounts of drainage have been used to supplement contracted water supplies in these wetlands tributary to the SJR, and varying lengths of the complex channel system within the wetlands have been employed to convey agricultural drainage to the river.

The SJR has been monitored for Se concentrations since 1985, mainly by the California Central Valley Regional Water Quality Control Board (CCVRWQCB, 1996a, 1996b). In 1991 and 1992 the state acknowledged elevated levels of Se in the SJR and parts of the San Francisco Bay/Delta Estuary. It declared the lower reach of river "impaired" (CCVRWQCB, 1991) and the Se levels in the bay "of concern" (CSFBRWQCB, 1992). The major source of Se to the river is agricultural drainage; sources to the San Francisco Bay/Delta Estuary include both agricultural drainage under certain flow conditions and oil refinery waste that originates from

oil refineries around the bay. Flow within the SJR is complex owing to climatic variability (i.e., alternating drought and flood conditions) and agricultural management variability (i.e., preirrigation, irrigation, drainage). The juncture of the SJR and the estuary is further complicated by the need to (1) maintain a balance between water supply and demand that permits achievement of salinity standards in the estuary and (2) recycle a certain percentage of the SJR back to the south via supply canals (e.g., the Delta Mendota Canal, Fig. 2) for irrigation purposes.

Since the closure of Kesterson Reservoir, management and treatment options have been researched and debated for disposal of the potentially toxic soil leachate mobilized by irrigation. With finite water supplies, however, environmental effects and benefit/cost ratios have prevented the achievement of an effective balance between maintaining agricultural production and supporting environmental resources. Legal challenges to the use and/or disposal of agricultural drainage and regulatory efforts at the federal and state levels generally come under the Clean Water Act (1972), including the National Pollutant Discharge Elimination System permit program, as well as under the Endangered Species Act (1973), the National Environmental Policy Act (1969), the Resource Conservation and Recovery Act (1988), the Porter–Cologne Water Quality Act (California State Water Resources Control Board, 1969), the California Toxic Pits Cleanup Act (California Health and Safety Code, 1984), the California Environmental Quality Act (California Public Resources Code, 1970), and the Public Trust Doctrine (Dunning, 1980). The Migratory Bird Treaty Act of 1918 (Margolin, 1979), which might address concerns about bird deaths at Kesterson Reservoir, has not been the subject of a specific legal action. An exhaustive review of enacted statutes and legal actions is beyond the scope of this chapter. Particular concerns, however, have centered on (1) protection of aquifers, human health, and aquatic life, (2) definition and disposal of hazardous waste, (3) definition of toxicity on a functional basis, (4) evidence of risk and potential harm, (5) application of a dilution credit for bioaccumulable substances, (6) adoption of waste discharge requirements, and (7) exemption of agricultural drains and waters from regulation. Regulation of agricultural drainage is hampered by the lack of authority on the part of the U.S. Environmental Protection Agency (USEPA) to enforce water quality standards for either point source or non–point source pollution from irrigated agriculture. This is because agricultural runoff (irrigation return flow) has been exempted from point source regulation through the Clean Water Act, and adherence to federal non–point source regulation programs is voluntary (Environmental Defense Fund, 1994).

A cooperative project among agricultural, government, and environmental parties enacted by the USBR (1995) reopened the SLD on an interim 5-year basis to transport drainage to the SJR. Renamed the Grassland Bypass Channel Project, the project focuses on the Grassland drainage management subarea of the western SJV (Figs. 1 and 2). This project is a regional management effort to improve

water quality by regulating Se loads, to protect wildlife habitat by assuring the wetlands of an adequate supply of clean water through removal of drainage from the wetlands and, at the same time, to examine possible adverse effects that may result from this more direct routing of drainage through the SLD and Mud Slough to the SJR (Fig. 2). As we discuss below, drainwater entering the river will now be deprived of the effects of dilution by wetland flows and loss of Se to sediment and biota due to bioaccumulation.

The Grassland Bypass Channel Project proposes the following goals: regulation of Se based on total loads (rather than water quality standards), commitment to meet and further define environmental concerns for wetlands and the SJR, creation of a regional drainage entity to assign responsibility for pollution, agreement on monetary penalties for exceedence of loads, and development of a long-term management strategy to achieve water quality objectives. Although load targets have been developed mainly through a simple averaging of data from 1986 to 1994, as a requirement for reuse of the SLD, conditions of the SJR "will not worsen" over yet-to-be-defined historical input loads (USBR, 1995). Recent adoption by the state of a water quality objective of less than 2 micrograms per liter (μg/L) Se for the Grassland wetland channels (CCVRWQCB, 1996c), has essentially removed these channels as alternative flow paths for drainage water (approximate average 62 μg/L Se). This regulation will make it difficult to reuse the wetland channels, for example, during flood runoff events as a means of circumventing project objectives, even if loads to the SLD are exceeded.

A decision by the U.S. District Court in Fresno, California, announced on December 16, 1994, also addresses agricultural drainage relief through use of the SLD. The court order calls for the USBR to explore the possibility of obtaining a state permit to discharge agricultural drainage directly into the San Francisco Bay/Delta Estuary (Fig. 1) by extending the SLD to the bay as originally designed in 1968. The decision is under appeal. During the 1950s, agriculturalists and water purveyors proposed a master drain to the San Francisco Bay, and this proposal was enacted as part of the federal San Luis Act in 1960. More recently, the state (CCVRWQCB, 1994a, 1995; CSWRCB, 1995) has emphasized that an extension of an export drain is the only "technically feasible solution" for management of agricultural drainage in the western SJV, although no recipient of the drainage has been officially selected. Some proponents envision expansion of the drainage facilities to include other types of discharge (e.g., municipal and industrial). If these out-of-valley disposal plans are enacted, Se-enriched agricultural drainage from Grassland, Westlands, and Tulare drainage management subareas (Fig. 1) could be collected in the future in a valley-wide agricultural drain, transferring the waste load from the SJV directly to the San Francisco Bay/Delta Estuary or the Pacific Ocean.

This chapter presents a retrospective view of Kesterson Reservoir as it applies to a mass balance approach for current and future monitoring of Se

loadings in the SJV due to agricultural drainage. Table 1 provides Se concentrations and loads in the western SJV where man-induced perturbations have enhanced or diminished natural levels. These concentrations are compared to primary source, background, and concern levels in soil, sediment, water, and wildlife. We discuss the status of drainage disposal after 10 years of management, regulation, and legal challenges in two drainage management areas of the SJV, Grassland, and Tulare subareas (Fig. 1). Our main focus, however, is on the reopened SLD in the Grassland subarea and the relation of the Se load from this subarea to the SJR (Fig. 2). The areas from which data are reported represent essentially two types of environment, differentiated by flow. The described Kesterson and Tulare systems, consisting of basin evaporation ponds, are static regimes. The Grassland system, consisting of many miles of wetland channels in addition to Mud and Salt Sloughs, is a flow-through regime. The San Francisco Bay/Delta Estuary may be an example of a system that is intermediate in terms of flow. This estuary system now has a clear and significant Se load due to oil refinery waste and some agricultural waste and may have an additional Se load due to extension of the SLD.

Whether the detrimental effects of Se observed in closed systems will develop in open or intermediate systems remains to be proven for different Se pathways (i.e., SJR or SLD) and repositories (bay or ocean). Our mass balance calculations from the small amount of available data, however, suggest long-term Se mass loading in the SJR and in the highly productive San Francisco Bay/Delta Estuary. Monitoring protocols must be developed to evaluate the exact magnitude and rate of loss/gain of Se from the water column and the precise mechanisms that drive Se's pathway from source rock through biota to its accumulation in bed sediment. As opposed to historical data, data collected during current (e.g., Grassland Bypass Channel Project) and future projects may allow improvement in these types of mass balance calculations.

II. DRAINAGE SUBAREAS

Five drainage management subareas (Fig. 1) have been designated by the joint federal–state San Joaquin Valley Drainage Program (1990) that developed recommendations for a management plan for agricultural subsurface drainage from 1985 to 1990. The subareas are Northern, Grassland, Westlands, Tulare, and Kern. These subareas are important for determining management options, which include source control, drainage reuse, evaporation systems, land retirement, groundwater management, discharge to the San Joaquin River, and institutional change (e.g., tiered water pricing). The main disposal option in each subarea is:

1. Grassland subarea drains irrigation subsurface wastewater into the SJR.

TABLE I Se Concentrations, Levels of Concern, and Loads for Environmental Components (Source Rock, Soil, Sediment, Water, and Biota) in the San Joaquin Valley and Selected Areas[a]

Environmental components		Se content (mean/range)	Ref.[b]
SJV source rock (μg/g)	Seleniferous rocks (e.g., Kreyenhagen, Monterey, and Moreno Formations)	8.9	1
	Nonseleniferous rocks (e.g., Panoche and Lodo Formations)	1.1	1
Soil (μg/g)	San Joaquin Valley (western slope)	0.14	2
	San Joaquin Valley (Panoche Fan)	0.68	2
	Western United States	0.34	3
	Conterminous U.S.	0.26	3
Sediment (μg/g)	Kesterson Reservoir		
	Top 15 cm	5.0	4
	Top 5 cm, "muck"	55	4
	Organic detritus	165	4
	Cleanup criterion	4.0	4
	San Luis Drain	84	4
	Tulare evaporation ponds	0.05–15	5
	Grassland wetlands	<2.0	6
	San Francisco Bay	0.1–0.6	7
	Deep sea	0.17	8
Water (μg/L)	Westlands drainage sumps	140–1400	9
	Grassland drainage sumps	8–4200	9
	San Luis Drain (inflow to pond 2)	330	4, 9
	Tulare evaporation ponds	<1–6300	5
	Mud and Salt Sloughs	16/2–100	10
	Panoche Creek	2–60	1
	Coast Ranges (seeps/ephemeral streams)	<2–3500	1
	U.S. rivers	0.2	11

	San Joaquin River water quality objective	5.0	12
	San Francisco Bay	0.07–0.4	13
	Pacific Ocean	0.13	14
	Aquatic maximum (drinking water standard)	50	15
Concern level—solids ($\mu g/g$)[c]	Sediment	2.0–4.0	6, 16
	Aquatic vegetation and invertebrates	3.0–7.0	6, 16
	Fish (whole body)	4.0–12.0	6, 16
	Avian eggs	3.0–8.0	6, 16
Concern level—liquids ($\mu g/L$)[c]	Aquatic level (for protection of wildlife)	<2.3–5.0	17
Hazardous waste	Solid ($\mu g/g$)	100	4
	Liquid ($\mu g/L$)	1000	4
Load level (kst)[a]	San Luis Drain (bed sediment)	0.26–0.85	4, 18
	San Luis Drain (reuse annual target)	0.38[d]	19
	San Joaquin River (model calculation)	0.067–0.15	20
	San Joaquin River (measured, WY 1995)	0.90	10
	San Joaquin River (total, 1986–1995)	5.85	10
	Kesterson Reservoir (total, 1981–1985)	1.0	4
	Grassland wetlands (cumulative loss, 1986–1995)	0.95	18, 19
	Annual human dietary intake	10^{-8}–$10^{-8.6}$	21

[a]Concentrations for solids are reported on a dry weight basis. Load levels are in Kestersons (kst): 1 kst = 7900 kg, or 17,400 lb, Se. See discussion in Section IV.
[b]Numbers designate the following references, as listed at the end of the chapter: 1, Presser et al. (1990); 2, Tidball et al. (1989); 3, Shacklette and Boerngen (1984); 4, USBR (1986); 5, CCVRWQCB (1990); 6, Henderson et al. (1995); 7, Luoma (personal communication, 1997); 8, Turekian and Wedepohl (1961); 9, Presser and Barnes (1985); 10, CCVRRWQCB (1996a, 1996b); 11, Wedepohl (1969–1978); 12, CCVRWQCB (1996c); 13, Cutter (1989, 1990); 14, Bruland (1983); 15, USEPA (1992b); 16, Skorupa et al. (1996); 17, Skorupa and Ohlendorf (1991), Peterson and Nebeker (1992), Lemly (1993); 18, Presser et al. (1996); 19, USBR (1995); 20, Environmental Defense Fund (1994); 21, National Research Council (1980).
[c]Toxicity levels, although not listed, are represented by the upper limit of the concern levels.
[d]This amount (i.e., 0.38 kst; = 6600 lb) represents the agreed-on annual load limit at compliance point B (USBR, 1995).

2. Westlands subarea, prior to 1986, drained to Kesterson Reservoir, but since has a "no discharge" policy, that is, storage of drainage in a ground water aquifer and use of the aquifer for dilution.
3. Tulare and Kern subareas, as hydrologically closed basins, continue to drain to evaporation ponds.
4. No action was recommended for drainage originating in the Northern subarea.

The natural landscape dictated, to some extent, which option was implemented in each subarea. This subdivision has allowed for mitigation of some drainage problems (e.g., migration of drainage from upslope to downslope) by assigning ownership of subsurface drainage to regional drainage entities such as that instituted within the Grassland Bypass Channel Project.

Identification of contaminated lands that produce a high percentage of the overall Se load has been listed as a priority step in determining a long-term, in-valley solution for drainage management (National Research Council, 1989). A memorandum of understanding was signed by state and federal agencies and agricultural water managers in 1991, to implement the in-valley recommendations of San Joaquin Valley Drainage Program (CCVRWQCB,1994a). This agreement was reinforced in the 1995 Water Quality Control Plan for the San Francisco Bay/Sacramento–San Joaquin Delta Estuary, which called for implementation of the program to help achieve water quality objectives (CSWRCB, 1995). A coordinated effort to oversee implementation of the management plan was instituted in 1991, but the program was never funded (SJVDIP, 1994). No comprehensive monitoring has been done to document the overall effectiveness of steps taken to manage drainage after the baseline studies during the late 1980s. Pilot land retirement programs on both Federal and State levels have been funded (the federal Central Valley Project Improvement Act of 1992 and the California State San Joaquin Valley Drainage Relief Act of 1992), but delays in the development of guidelines for the project have slowed acquisition.

III. HISTORICAL PERSPECTIVE FOR WETLAND AND SAN JOAQUIN RIVER PROTECTION

A significant regulatory action for subsurface drainage was taken in 1985 by the California State Water Resources Control Board when it adopted Order No. WQ 85-1 (CSWRCB, 1985). This order was passed to protect the habitat of the Grassland Resource Conservation District and the SJR from a fate similar to that of Kesterson Reservoir. The order required development of plans for (1) cleanup and abatement of Kesterson Reservoir, (2) regulation of agricultural drainage to the San Joaquin River, including waste discharge requirements, and (3) control

of agricultural subsurface drainage in the San Joaquin Basin (CSWRCB, 1987). Included in these plans were extensive monitoring, adoption and implementation of improved irrigation practices and drainage reduction strategies, and the development, recommendation, and implementation of water quality objectives for Se. In 1988 the state adopted Se water quality objectives for the San Joaquin Basin, calling for compliance by 1991 for the lower reaches of the SJR and compliance by 1993 for the upper reaches. To date, no waste discharge requirements or permits for disposal of agricultural drainage in the SJR have been issued by the state, and full compliance to state objectives is now not required until the year 2010 (CCVRWQCB, 1996c).

In an effort to increase protection of the SJR under the federal and state antidegradation policy, the USEPA in 1992 rejected part of the state-adopted Se water quality objective for protection of aquatic life (USEPA, 1992a). The USEPA promulgated lower allowable water concentrations (5 μg/L Se instead of 8–10 μg/L; 4-day average instead of a monthly mean) in some tributaries and reaches of the SJR. The lower standards were based on national data from field observations of impacts to aquatic life. Research based on ecological risk assessment to wildlife, mainly avian egg bioaccumulation, suggests the need for a level even lower, namely, less than 2.3 μg/L Se for water (1.0 μg/L dissolved Se, or 2.3 μg/L total recoverable Se) to protect wildlife (Skorupa and Ohlendorf, 1991; Peterson and Nebeker, 1992; Lemly, 1993). However, federal and state water quality objectives for the lower SJR and some of its tributaries were exceeded more than 50% of the time from water years 1986 to 1995 (a water year begins in October), and for some months continuously (CCVRWQCB, 1996a, 1996b).

Because the lower reach of the SJR is a quality-impaired water body (CCVRWQCB, 1991), the federal Clean Water Act requires that water quality standards be translated into total maximum daily loads (TMDLs) through modeling that focuses on sources (Environmental Defense Fund, 1994). The model developed for the SJR, named the Total Maximum Monthly Load (TMML) model, is a conservative element dilution model for assimilative capacity (i.e., dilution capacity) of the river that does not take into account bioaccumulation (CCVRWQCB, 1994b). Additional assumptions used in the model to derive loads result in calculated SJR annual loads significantly higher (an additional 1817–1449 kg) than that derived using more stringent, hence more protective criteria (Table 1). However, load targets for the reuse of the SLD to deliver drainage to the SJR were eventually negotiated among federal and state agencies, farmers, and environmentalists with only an environmental commitment that the input loads to the SJR "will not worsen" over historical loads (USBR, 1995). Annual load targets for the 5-year SLD reuse project are 3000 kg for each of the first two years (Table 1), with at least a 5% load reduction for each succeeding year of a 3-year period (USBR, 1995). This level essentially maintains a status quo that includes extensive violation of USEPA Se standards, since the targets

were based on the greater of either a historical average of limited data collected between 1986 and 1994 or the TMML calculation.

The compliance point for the reuse of the SLD is the drain terminus at Mud Slough, located at Kesterson Reservoir terminal ponds (Fig. 2). Although the former Kesterson Reservoir ponds no longer support aquatic habitat, the area remains as a grim reminder of the loss of California's natural resources, at a time when Se has once again advanced to elevated levels in the drainage water of the SLD. An additional compliance point for state regulators is the SJR at Crows Landing (Fig. 1). A possible extension of the SLD to bypass Mud Slough and the lower reach of the SJR above Crows Landing has been discussed (CCVRWQCB, 1996c). This alternative would avoid having drainage in these parts of the slough and river in the future. Such planning again provides for more direct routing of drainage to the SJR and more control by management to comply with objectives that would be dependent mainly on dilution by the Merced River.

Recent management and regulatory approach strategies in the Grassland subarea have lacked a scientific conceptual basis. For example, in the past 6 years, no causal connection between drainage management (i.e., pollution load reduction) and improved water quality has been documented by monitoring efforts (Presser et al., 1996; Westcot et al., 1996). Source control efforts such as improvements in irrigation efficiency and recycling of surface and subsurface drainage may have resulted in reduction of deep percolation, but not in an overall reduction in water quality loads. The reuse of the SLD is being adopted by the USBR as an effort for long-term drainage management despite the lack of data and conceptualization just indicated.

IV. ENVIRONMENTAL FRAMEWORK SELENIUM VALUES

The difference between essential and toxic levels for Se is quite narrow. Concern levels, which are between levels considered safe (no effect) and levels considered harmful (toxicity threshold), are intended to provide protection for the environment. These values are listed in Table 1 for comparison with ranges for primary geologic sources and background levels and with a compilation of Se concentration means and ranges in soil, sediment, and water for Kesterson Reservoir and the Tulare and Grassland subareas. Ranges of concentrations for sources of agricultural drainage (i.e., collector sumps) and drainage canals for 1985 are given; recent detailed data are not available. Until long-term studies have better defined contamination and cumulative risk due to Se, these ecological risk guidelines must be used in the assessment of environmental conditions. Historical loading to the SJR is also given, along with estimated load attenuation in the Grassland wetlands in units of Kestersons (kst), for which 1 kst equals 7900 kg of Se. The 7900 kg

amount is based on the mass loading at Kesterson Reservoir (USBR, 1986, see below). Thus, we propose the Kesterson as a unit to represent a measure of hazard to wildlife, where 1 kst was the cause of the ecotoxicity problem at Kesterson Reservoir.

V. SELENIUM LOADS AND FIELD EVIDENCE FOR LOAD ATTENUATION

A. Kesterson Reservoir

Beginning in 1978, agricultural subsurface drainage flowed through the SLD from the Westlands drainage management subarea into Kesterson National Wildlife Refuge (Figs. 1 and 2). Introduction of Se into the food chain from these waters was first demonstrated in 1983 at Kesterson Reservoir, a closed series of evaporation ponds that covered approximately one-fourth of the refuge (Presser and Barnes, 1985; Ohlendorf et al., 1986). Selenium in the inlet pond, as soluble selenate (SeO_4^{2-}) was at a concentration of 330 μg/L (Table 1). The water was classified as a sodium–sulfate water with a sulfate concentration of 5550 mg/L and sodium concentration of 2750 mg/L. The correlation between dissolved Se and both sodium and sulfate was +0.93 in water samples from agricultural drainage collector sumps that discharged into the SLD, and thus into the reservoir ponds.

Concentrations of these soluble constituents were expected to increase progressively as the water flowed through a series of 12 interconnected evaporation ponds. In the terminal evaporation pond at Kesterson Reservoir, however, the concentration of Se in water was very low (14 μg/L), whereas the sodium and sulfate concentrations, as expected, had increased (6250 and 11,500 mg/L, respectively) (Presser and Barnes, 1984, 1985). These data showed a significant loss of dissolved Se between input and terminal pond. Selenium was later found to have been taken into an algal mat that covered the almost dry terminal pond. The concentration of Se in the algal mat approached a level of 13 μg/g, dry weight in May 1983, and 24 μg/g in August 1983. These levels exceed the concern level for selenium in aquatic vegetation (Table 1) and thus were in the toxic range for the diet of birds.

In later studies, organisms showed extensive biomagnification of Se through the food chain (Sakai and Lowe, 1987). By contrast, salt crusts accumulating on the pond, identified as the mineral thenardite (sodium sulfate), contained an order of magnitude less Se, 1.8 μg/g. Soil Se averaged 55 μg/g, dry weight, in the depth range of 0 to 5 cm, with 76 to 96% of the Se present in this uppermost layer of sediment (USBR, 1986). Organic detritus from six of the ponds averaged 165 μg/g dry weight. Although this early sampling at Kesterson Reservoir was limited, the data demonstrated that (1) Se lost from solution in the ponds entered the food chain through uptake by biota and (2) organic processes were more

effective in removing Se from surface water than were inorganic processes (Presser and Ohlendorf, 1987).

Discrepancies between the chemical balances of Se versus those of sodium and sulfate elucidated the different processes undergone by a nonconservative element (Se) and a conservative element (sodium). A general Se mass balance for Kesterson Reservoir, for the years 1981 to 1985 (USBR, 1986), gives the total input of Se into the SLD and Kesterson Reservoir at 10,300 kg. Of that amount, 2400 kg was estimated to have been retained by the sediment of the SLD. The remaining 7900 kg, or 1 kst (Table 1), was distributed in the biota, water, and sediment at Kesterson Reservoir. Ecotoxic levels were achieved in this environment by high Se mobility, recycling, reactivity, and efficiency of transfer of Se among biota, water, and sediment.

A complete inventory of Se in water, sediment, and biota was not made, but might have enabled prediction of Se behavior through detailed mass balance models using various factors for load attenuation and ecotoxicity. The low level of Se in the terminal pond further demonstrates that waterborne Se alone may not be a good indicator of its level of toxicity; low levels of Se can occur in the water column even though food chain exposure of fish and wildlife may be substantial (Skorupa et al., 1996). According to Skorupa et al., low waterborne Se concentrations can indicate low mass loading (low risk) or high biotic uptake (high risk).

Since its burial, Kesterson Reservoir is no longer subjected to drainage or wetland flows. However, winter rains in this otherwise dry habitat create ephemeral pools whose waters contain up to 1600 μg/L Se (USBR, 1996), a concentration more than sufficient to classify it as as a hazardous waste (USEPA, 1980; USBR, 1986; Table 1). The concentrations of Se in samples of aquatic invertebrates from these ponds (geometric means of 8.5–12.5 μg/g Se, dry weight, from 1988 to 1995) exceeded toxicity thresholds for adverse hatchability and teratogenic effects to birds feeding on these biota (Skorupa and Ohlendorf, 1991; Heinz, 1996; Table 1). The Se concentrations in invertebrates sampled in 1996 indicated some of the highest values of Se bioaccumulated in aquatic organisms (up to 60 μg/g Se, dry weight) since the original sampling at Kesterson Reservoir (CH2MHill, 1996). Geometric mean Se concentrations in samples of vegetation have equaled or exceeded concern levels (2-6 μg/g, dry weight) since monitoring began in 1988. Since 1990, when a maximum mean of 5.2 μg/g, dry weight, was reached, mean Se levels in plants have not changed significantly. Maximum Se concentrations increased though, to 90 μg/g, dry weight, in 1990. Organic detritus from three habitats (filled, open, or grassland) sampled in 1996 all showed extremely high maxima of Se (230–340 μg/g, dry weight). Although these food chain pathways are thought to represent relative degrees of risk, there has been no evidence of recent selenotoxic effects to higher species in the terrestrial ecosystem.

The appearance of these elevated concentrations of Se raise questions about the persistence of Se in the environment and the future remediation of wetlands contamination by Se. For example, how is the cumulative depuration or loss of Se from contaminated ecosystems to be monitored and what is the operational definition of "inert" (i.e., unavailable) form(s) of Se? Recent experiments (Zawislanski and Zavarin, 1996; Zawislanski et al., 1996) have shown that (1) up to 50% of "refractory" Se was actually oxidized to soluble Se(VI) and (2) rates of volatilization from present-day sediments at Kesterson Reservoir are low (1–5%).

B. Tulare Subarea

Tulare drainage management subarea (Fig. 1) is a hydrologically closed basin where intensively farmed lands are located next to managed wetlands on the Pacific Flyway that remain as part of the relict Tulare Lake (Presser et al., 1995). Subsurface drains are widely used to manage groundwater salinity and water levels, with disposal in privately owned evaporation basins. In 1992, 2700 ha of evaporation ponds, divided into 21 separate basins, existed as part of the management alternative for disposal of subsurface drainage in the larger Tulare Basin. Most pond systems consisted of a series of connected evaporation ponds, each representing a closed system (CCVRWQCB, 1990).

Dry climatic conditions and runoff into this subarea, from both the Coast Ranges on the west and the Sierra Nevada on the east, complicate and intensify effects in the Tulare Basin associated with soil salinization over those seen at Westlands subarea and consequently seen at Kesterson Reservoir. Elemental concentration patterns in the waters from different geographic zones of the basin (alluvial fan, trough, and lake bed) are discernible (CCVRWQCB, 1990; Fujii and Swain, 1995). In the alluvial fan zone, the geometric mean Se concentration in ponds is 320 μg/L and in inlet flow it is 250 μg/L (CCVRWQCB, 1990), comparable to the average inflow seen at Kesterson Reservoir of 330 μg/L. The geometric means for pond inflows for the lake bed and trough zones are low (11 and 2 μg/L Se, respectively) as are concentrations in ponds of these zones. Inlet concentrations for ponds in these two zones reached a maximum of 62 μg/L Se. Other trace elements, mainly oxyanions, also show elevated concentrations in certain zones. Concentration maxima (μg/L) in ponds of the alluvial fan, trough, and lake bed zones are Se 6300, U 8000, As 420, Mo 12,000, V 112, and B 700,000 (CCVRWQCB, 1990). Samples of shallow groundwater reach the following maxima (μg/L): Se 1000, U 5400, As 2600, Mo 15,000, and B 73,000, showing the close linkages of the surface water and groundwater systems (Fujii and Swain, 1995; Presser et al., 1995).

Intensive management of the constructed ponds in the Tulare Basin, popularly labeled as a series of "mini-Kestersans," was initiated to minimize bird use and, therefore, lessen potential adverse effects. Unfortunately, the Kesterson

analogy turned out to be all too prophetic and management efforts inadequate. From 1987 to 1990, greater than 50% of bird eggs in 11 of 17 basins studied were documented to have Se means in species-specific reproductive effect ranges (Skorupa et al., 1996; Skorupa, this volume, Chapter 18). Selenium levels in at least 13 of the basins were elevated enough to lead to the prediction that waterbird populations breeding at these ponds would experience either reduced hatchling success or increased teratogenic levels (CH2MHill et al., 1993). In Chapter 18 Skorupa documents a 10–50% rate of embryo teratogenesis in one or more species of waterbirds at four sites in the Tulare Basin ponds, comparable in both type and rate of deformity to Kesterson Reservoir birds (Presser and Ohlendorf, 1987). Because avian toxicity, in fact, occurred at ponds containing relatively low Se concentration (7–18 μg/L), (Bay Institute, 1993; Skorupa et al., 1996; Skorupa, this volume, Chapter 18), the adequacy and applicability of traditionally defined Se toxicity to the ponds (i.e., 1000 μg/L as a hazardous Se waste, based on an allowable concentration that is two orders of magnitude above that defined for the drinking water standard—USEPA, 1980), as opposed to functional toxicity, was questioned by the U.S. Fish and Wildlife Service (USFWS) and environmentalists before the SWRCB during 1995 (CSWRCB, 1996). In view of those studies and of data presented at the evidentiary hearing process, pond acreage was decreased and alternative and compensating aquatic habitats were created to mitigate and remediate "unavoidable losses" of aquatic birds.

At two recently constructed experimental pond sites, accelerated evaporation of concentrated drainage water is employed to reduce aquatic bird use and thereby bird loss. At these sites, the rate of evaporation is increased by spraying brine into the air at a rate that prevents ponding. For future management, construction of numerous 0.80 ha sites containing this type of "pond" has been suggested as part of an overall drainage reduction strategy. The management objective is to maintain bird-free ponds. However, shorebirds (i.e., stilts, avocets, killdeer) nested after a winter storm in 1996 when ponding of water occurred at these sites and adjacent experimental areas, where extremely salt-tolerant plants (halophytes, including trees) are grown . At the Red Rock Ranch site, Se concentrations in the inlet water (average 1400 μg/L Se) were greater than 1000 μg/L (a hazardous Se waste); moreover, pond Se concentrations measured up to 18,000 μg/L, and inviability of eggs was 67% (J. P. Skorupa, personal communications April 11, July 1, 1996; Chapter 18, this volume). The level of teratogenicity (56.7%) surpasses the level found at Kesterson Reservoir. Although these pools containing high Se concentrations were deemed a management problem that could be corrected, the question remains as to how biomagnification that led to this extent of deformity could have occurred in the food chain over a relatively short period of time.

One of the Tulare Basin series of ponds is experiencing an apparent loss, or load attenuation, of Se between inlet water and the terminal evaporation pond.

This series of ponds contained an approximate total of 3.9 kst in solution in the summer of 1995 (Tulare Lake Drainage District, 1995). Dissolved Se concentrations showed a continuous decrease from cell 1 to cell 7, whereas salt concentrations (represented by electrical conductivity) increased. Fan et al. (1996) attributed depletion from water to possible Se volatilization as well as precipitation in evaporation ponds and recommended such pond systems for "in situ Se removal." Because the trend was based on Se concentrations for the water column alone, rather than a loss from the entire system, the conjectured loss of Se via volatilization cannot be quantified until a complete inventory of major Se reservoirs is made. A mass balance monitoring approach that includes, in addition to the amount of Se volatilized, Se in water, suspended matter, precipitated material, bottom sediment, and biota would document the partitioning of Se between its different reservoirs, thus permitting an evaluation of the relative importance of removal mechanisms. Use of pond systems and of plants (phytoremediation) for depleting Se from the water, although promising, may still present risks, since Se in certain phases of the ecosystem concurrently increases and subsequent exposures to wildlife occur. As at Kesterson Reservoir, elevated concentrations of Se in the precipitated salts, sediment, and vegetation accumulating from these ponds may persist for years, or require exorbitant sums for cleanup.

Location of evaporation ponds that represent oxygen-depleted depositional environments juxtaposed to trace-element-enriched geologic formations and farmlands that represent alkaline-oxidized sources, leads to the repetitive cycling of trace elements in arid hydrologically closed basins like the Tulare Basin. With this type of land use and disposal system, the concentration of trace elements in pond sediment, surface waters, and groundwaters seems inevitable. The economic analysis of whether "evaporation pond farming" is sustainable in view of the need to provide compensating and alternative habitat for wildlife was not definitive (CSWRCB, 1996). Connecting the Tulare subarea to the existing 137 km SLD is viewed by state planners (CCVRWQCB, 1994a, 1995) as the answer to water quality problems in the Tulare Basin. This export drain could potentially remove salt- and Se-laden agricultural waste as well as industrial and municipal waste from the basin. No recipient of the drainage has yet been selected.

C. Grassland Subarea

Agricultural drainage from the Grassland subarea has historically been disposed of in the SJR (Fig. 2). Subsurface drains, originally called "deep drains," were installed in the 1950s. The route of the drainage water to the SJR changed following the demise of Kesterson Reservoir. Prior to 1985, drainage water was mixed with freshwater in wildlife habitats, including duck clubs and wetland channels of the Grassland Resource Conservation District, which is tributary to the SJR. From 1985 to 1996, drainage water was alternated with freshwater in

fewer wetland channels to reduce exposure of the entire habitat, with the drainage water eventually traveling through Mud and Salt Sloughs to the SJR. In September 1996, the drainage water was routed into the northernmost 45 km section of the SLD and 10.6 km of Mud Slough and then into the SJR, largely bypassing the wetland habitat (USBR, 1995). Unless otherwise noted the data presented in the discussion below of the loads discharged along the pathway the drainage takes, from agricultural drainage collector sump through earthen canals or drains and wetlands to the SJR, are referenced in state documents CCVRWQCB (1996a, 1996b, 1996c).

Average annual Se concentrations in the water from source agricultural drainage canals in the Grassland subarea (Figs. 1 and 2) were as high as 82 μg/L for water year (WY) 1986 to WY 1995, lower than that in water delivered to Kesterson Reservoir by the SLD (330 μg/L). Water from individual farm field collector sumps contained Se concentrations as high as 4200 μg/L Se, three times greater than the maximum collector sump for the SLD of 1400 μg/L (Presser and Barnes, 1985) (Table 1). A recent limited assessment of the mean Se concentration for drainage sumps showed 211 μg/L, with a median concentration of 134 μg/L (CCVRWQCB, 1996c). Annual loads originating in the subarea at the beginning of management in 1986 and 1987 were 0.56 and 0.62 kst, respectively. Annual loads did vary with drought and flood conditions in subsequent years, but in WY 1995, which was 10 years after institution of the state drainage control program and 5 years after completion of the federal–state drainage management plan, the annual Se source load was the highest ever recorded, 0.65 kst.

Except for WY 1990, Se loads discharged from source sumps and drains have been higher than loads measured downstream of Grassland Resource Conservation District wetland area (i.e., at Mud and Salt Sloughs; Fig. 2). The 1986 Se load in Mud and Salt Sloughs decreased by 0.18 kst between the source load and the load discharged after traveling through the wetland channels. This pattern of load attenuation has been repeated in successive years. For WYs 1986–1994, the cumulative difference between the input drains and Mud and-Salt Slough outputs was 0.95 kst (CCVRWQCB,1996a, 1996b, 1996c). The USBR (1995) data also showed Se input loads higher than exported loads with a comparable difference of 0.89 kst and an annual maximum attenuation of 50%. This loss of Se approximately equals the mass loading of Se that created the ecotoxicity at Kesterson Reservoir (1 kst). Failure to account for this Se loss in the Grasslands (0.89–0.95 kst) could be due to several factor, but in the absence of comprehensive monitoring data, we can only speculate on the reasons. Possible factors include errors in flow and concentration measurements owing to temporal and spatial extrapolations used to define calculated load, and failure to document accurately the partitioning and bioaccumlation of Se among water, sediment, and biota.

Elevated levels of Se in fish and invertebrates taken from Mud and Salt Sloughs during 1992 and 1993 indicate that bioaccumulation accounts for some of the loss of Se. Approximately 77 % of whole-body fish samples in Mud Slough and 85% in Salt Slough were in the concern range (Henderson et al., 1995, Table 1). Selenium concentrations in invertebrates were also in the concern range (Table 1), with 15% of Mud Slough samples exceeding the toxicity threshold of 7 μg/g Se. The most recent Se levels in water birds in the Grassland wetlands (Fig. 2) were measured from 1984 to 1988 (Ohlendorf and Hothem, 1987; Paveglio et al., 1992). In the southern wetlands, species averages of Se decreased overall for livers of both coots (from 23 μg/g to 10 μg/g) and ducks (from 24 μg/g to 14 μg/g). These Se levels are elevated when compared to mean background levels in coots (5.4 μg/g) and ducks (8.4 μg/g) but below levels associated with adverse effects on reproduction in coots (82 μg/g) and ducks (20 μg/g) at Kesterson Reservoir (Paveglio et al., 1992). Eggs collected in WY 1995 by the USFWS from Grassland birds, as background data for the reuse of the SLD project, have not been analyzed. USFWS's overall objectives for reuse of the SLD are to maintain Se concentrations below toxicity threshold levels in biota in the area of Mud Slough (where drainage has been increased) and to lower Se concentrations in biota in the area of Salt Slough (where drainage has been removed) to background levels (Henderson et al., 1995).

VI. POTENTIAL FOR LOAD ATTENUATION IN GRASSLAND BYPASS CHANNEL PROJECT

Because the 5 μg/L Se objectives in the lower SJR have been violated a majority of the time since Se concentrations have been monitored in the river, the cumulative Se load discharged from the Grassland subarea to the SJR from WY 1986 through WY 1994 (4.3 kst) is greater than the allowable loads calculated using a conservative element, standard steady state TMDL model for the SJR (1.35–0.60 kst). Annual load targets for the SLD reuse project are 0.38 kst (Table 1) for each of the first two years, with a 5% load reduction for each succeeding year of a 3-year period (USBR, 1995). The cumulative load for the 5-year project, if load targets are met, is 1.80 kst. However, the impact to the SJR will likely increase because drainage collected in the SLD and Mud Slough will discharge directly into the SJR without traveling through wetland channels containing freshwater dilution flows. If the same logic of in-transit loss of Se through uptake in biota and sediment of evaporation ponds and distribution channels observed at the Kesterson, Tulare, and Grassland wetland areas is applied to the pathway now taken by the drainage, a significant potential for load attenuation exists for the SLD, Mud Slough, and the SJR. The cumulative load of Se discharged to the SJR system from WY 1986 to WY 1995, including the in-transit loss of Se, was

5.85 kst. Despite this large load compared to that at Kesterson Reservoir, few samples of sediment and biota have been taken to document the Se inventory in the SJR system, although plankton and clam samples show levels of contamination (up to 5 μg/g, dry weight) (CSWRCB, 1991) that could adversely impact fish and birds (Table 1).

Except for WY 1989, Se loads measured for the SJR at Crows Landing (Fig. 1), a state compliance site for Se further downstream in the SJR below the Merced River (CCVRWQCB, 1994a), were higher than those discharged from Mud and Salt Sloughs. The cumulative difference between annual loads for Mud and Salt Sloughs and annual loads measured at Crows Landing from WY 1986 to WY 1994 is 0.58 kst, with an annual maximum difference of 0.25 kst in 1986. The 1995 load measured at Patterson (Fig. 1), yet further downstream than the Crows Landing site and the only SJR load data available that year, was 0.90 kst, a historical maximum. This value compares to 0.65 kst for the drains and 0.61 kst from Mud and Salt Sloughs.

The relation among the agricultural drainage area source loads, the Mud and Salt Slough loads, and the SJR loads "remains unexplained" (CCVRWQCB, 1996b), although Mud and Salt Sloughs have been identified as contributing most of the total Se load drained into the SJR (e.g., 81% in WY 1988 and 86% in WYs 1993 and 1994). In addition to load attenuation of Se in the wetlands, these data suggest a significant second source of Se (0.58 kst) added to the SJR that may be perceived as worsening yet further the SJR condition. From a mass balance perspective, these data show that 5.85 kst has been loaded into the SJR system between 1986 and 1995, and the current annual rate may be as great as 1 kst (Table 1). This comes 12 years after the Kesterson disaster and 10 years after identification and implementation of management and treatment strategies intended to control subsurface agricultural drainage. Because no causal connection is seen between pollution load reduction and improvements in water quality in the SJR, there would seem to be a rational and even urgent need to identify monitoring requirements, including accurate flow measurements, that adequately determine a mass balance for Se and the processes controlling it. Despite variable system inputs (rainfall and applied water) and outputs (drainage), these large loads would seem to be driven, in part, by increased agricultural production levels. In the Grassland subarea, production is now at a maximum for the region (38,000 ha) as a result of availability of full allotments of irrigation water.

VII. SELENIUM ENRICHMENT IN SAN LUIS DRAIN SEDIMENT

During its initial operation, from 1978 to 1986, the SLD conveyed subsurface agricultural drainage to Kesterson Reservoir. During its closure from 1987 to

1996, the SLD acted as an evaporator and seepage collector, although it briefly acted as a conduit for flood and drainage water during SJV flooding in WY 1995. Therefore, analyses of bed sediment of the SLD may provide a continuing history of Se partitioning and flux occurring in the sediment during static, controlled flow, and flooding regimes between 1978 and 1996.

Data from a survey in 1994 (45 km segment) indicated that Se concentrations in bed sediment in the SLD averaged 44 μg/g dry weight, with a maximum of 146 μg/g (Presser et al., 1996). Earlier surveys (137 km segment), made when the SLD was in operation, found a maximum of 210 μg/g Se in sediment samples, with an average concentration of 84 μg/g (USBR, 1986). These data sets are difficult to compare because variation at single sampling sites is large and trends with depth are opposite for the 1985 and the 1994 surveys (Presser et al., 1996). However, the elevated Se levels cannot be explained by geologic source material. Seleniferous rocks in the California Coast Ranges average 8.9 μg/g Se (Presser et al., 1990; Table 1). Western SJV soils average 0.14 μg/g Se. Soils from the most contaminated alluvial fan, Panoche Fan, average 0.68 μg/g, with a maximum of 4.5 μg/g (Tidball et al., 1989; Table 1). It seems reasonable to assume that bioaccumulation is the mechanism whereby Se concentrations increased in the sediment under flowing conditions when the drain contained irrigation drainage water.

Because of the high levels of Se documented in the SLD in 1985, the sediment residing in the drain was classified for regulatory purposes (USBR, 1986). SWRCB Order No. WQ 85-1 found the soils and wastewater associated with Kesterson Reservoir to be a "designated waste" that posed a hazard to the environment, and, as such, should be handled, stored, or disposed of in a manner consistent with hazardous waste management provisions. This concern, prompted a recommendation for complete sediment removal from the portion of the SLD to be reopened as part of the Grassland Bypass Channel Project as the project was originally conceived by the San Joaquin Valley Drainage Program (1990). However, this recommendation was never carried out. Rather, management of the sediment in the drain is to take place (USBR, 1995; Presser et al., 1996) even though levels of concern and hazard have been exceeded (Table 1). California's criterion for a solid hazardous Se waste is defined as 100 μg/g wet weight (California Code of Regulation, 1979; USBR, 1986; Table 1).

The Kesterson Reservoir cleanup criterion called for filling and grading of pond sediments (and associated vegetation) if Se concentrations were greater than 4 μg/g. The sediment Se toxicity threshold for ecological risk developed by the USFWS for the reuse of the SLD is 4 μg/g, dry weight (Henderson et al., 1995). A concern level of 2 to 4 μg/g Se, dry weight, is recommended for bottom sediment as a performance guideline for remediation of contaminated irrigation drainage sites across the western United States studied under USDOI's National Irrigation Water Quality Drainage Program (Gober, 1994). Luoma et al. (1992)

further identified the surficial layer of bottom sediment and suspended material as important indicators of toxicity based on bivalve uptake, defining 1.0 to 1.5 μg/g Se, dry weight, for particulates as a limit for protection of aquatic life.

A mass balance estimation made during initial use of the SLD showed 0.30 kst of Se residing in the accumulated sediment in the drain (137 km segment) (USBR, 1986). Within the 45 km section of the SLD reopened in September 1996, an estimated 42,650 m^3 of sediment was present. In terms of mass loading, an average concentration of 44 μg/g Se represents 0.26 kst contained in the sediment (Table 1). A statistically significant inventory of Se in SLD sediment to establish a baseline would reveal the degree to which Se is being gained or lost from the water column and concentrated or removed from the sediment during future projects. Even without the data necessary to quantify this transfer, sediment has proven to support a substantial food chain (Moore, 1990) that further contributes to Se bioavailability.

In contrast to a Se accumulation mechanism in SLD sediment during its initial operation, mobilization or depuration of Se from sediment was hypothesized during an emergency discharge of water to the SLD during flooding in WY 1995. The SLD acted as a conduit for floodwater into the SJR that included runoff from the Coast Ranges, which was expected to contain elevated Se concentrations. Panoche Creek (Fig. 1), the source of the major loading of Se to the western SJV, was sampled where it issues from the Coast Ranges onto the alluvial fan of the SJV to represent drainage from the approximately 81,000 ha upper watershed. The creek waters contained low levels of dissolved Se (approximately 5 μg/L) during nonstorm periods and approximately 60 μg/L dissolved Se in first-flush runoff events during storms in 1988 as evaporated salts were mobilized and debris flows occurred (Presser et al., 1990). At the same location during the large-magnitude flood of March 1995 (estimated as a 50 to 100-year event), dissolved Se concentrations in composited runoff samples of water and sediment from Panoche Creek showed a maximum of 45 μg/L at a flow rate of 15.6 m^3/s and 19 μg/L at a flow rate of 283 m^3/s (USEPA, personal communication, 1996). The Se concentration in the sediment portion of the runoff was estimated as approximately 10 times that of the dissolved fraction.

A short-duration maximum concentration of 120 μg/L Se was seen in the SLD outfall during that event, with a downstream concentration of 33 μg/kg in Mud Slough. Altogether, approximately 0.1 kst was discharged to the SJR during the 15 days the SLD was open during this flood event, mainly from the SLD, Mud Slough, and Salt Slough. Agricultural drainage collector sumps were not shut off during this flood period, and flooded fields were pumped into the SLD. The amount of Se attributable to each potential source of Se (subsurface drainage, runoff, or that mobilized from sediment) discharged to the SJR during the WY 1995 flooding is still unknown, in part, because no conclusive data were collected to differentiate sediment load from dissolved load. The section of the SLD re-

opened during the flood event (approximately 105 km) was estimated to hold 133,800 m^3 of sediment (USBR, 1986). If the average Se concentration in the sediment was 44 $\mu g/g$, then Se in the sediment on the floor of the SLD contained roughly 0.85 kst. Mobilization or resuspension and subsequent transport of about 12% of this sediment could account for the discharge of the 0.1 kst measured at the check point on the SJR.

VIII. DISCUSSION

Wetlands and agriculture in the SJV are inexorably linked via irrigation drainage. As a consequence of this linkage, elevated Se concentrations occur, leading to avian reproductive toxicity as at Kesterson Reservoir, Tulare Basin, and Red Rock Ranch (see also Skorupa, this volume, Chapter 18). In a recent evaluation, a load reduction of 47–80% of the amount of agricultural drainage disposed of in the SJR is necessary to meet the state compliance schedule (CCVWQCB, 1996c). A model using dynamic drainage effluent limits based on the real-time assimilative capacity of the SJR was suggested recently as a future management tool (Karkoski, 1996). This "real-time" model would allow approximately 140% more Se to be disposed of in the SJR than the amounts calculated by previous quasi-static models (TMML model) and those adopted as load targets by the Grassland Bypass Channel Project (Table 1). Hence, the "real-time" model amount is substantially greater (293–603%) than that allowed if a standard steady state TMDL method with a 5 $\mu g/L$ Se objective is used for determining the load to the SJR. With "real-time" Se management, ponds for flow regulation would be necessary to maximize release of Se loads during different flow conditions in the river. Models such as this, and the site-specific TMDL and TMML models developed for the SJR, address, to some degree, the complexities of flow, but fail to consider the complexities of Se chemistry and biology. In these models, the behavior of an element is defined solely on the basis of dilution, thus treating Se as a conservative element. If real-time management is enacted, Se disposal would be maximized and the SJR kept continuously at a 5 $\mu g/L$ concentration based on flow conditions; it is unknown what overall effect this regime would have on the SJR. For example, this scheme would eliminate beneficial natural flushing of the system during high flow events and would create a concentration that could be thought of, to some degree, as "static."

The available data suggest that the definition of Se contamination must be formulated on an ecosystem level and a mass balance basis. For future management, the lessons learned at Kesterson Reservoir may be applicable to the Tulare evaporation ponds and those learned at Grassland wetlands, applicable to the SLD/Mud Slough/SJR system. A final repository for Se, if the SLD is extended, is the San Francisco Bay/Delta Estuary and/or the Pacific Ocean. Based on flow

rates and transport, residence time and exposure pathway for Se in the ecosystems associated with these repository water bodies may be important variables to measure to define Se uptake and retention and thus, ecotoxicity. The bay may represent a system intermediate between static (evaporation ponds) and flowing (SLD, Mud Slough, and SJR) systems.

Assimilative capacity for Se in a receiving water cannot be based on a dilution model. Allowable Se loads need to be determined using a mass balance approach that recognizes the cumulative loading of Se in water, sediment, and biota, including past loading (e.g., in bed sediment). Although not all the ramifications of Se cycling are known, a mass balance approach to understanding Se transport and fate would contribute to establishing limits of bioaccumulation of Se in relation to such important variables as flow and speciation. These data are essential for the design of management strategies that optimize Se concentrations and loads and also comply with regulatory and environmental commitments that adequately protect the environment.

The efficiency of Se transfer through an environment may center on the dominance of biological versus chemical processes that may be a function of flow. Oremland et al. (1989) have shown that for reactions involving Se, biological reactions are much the faster. High rates of exchange are expected among Se species (selenate, selenite, elemental Se, and organic and inorganic selenide) and between intercellular pools. Such exchange makes for an efficient transfer of Se among water, sediment, and biota. Selenium is known to bioaccumulate very efficiently in terminal (static) sink evaporation ponds (e.g., Kesterson Reservoir, Tulare evaporation ponds). Flushing flows, either natural or managed, in some wetland areas (e.g., Grassland) may mitigate the effects of Se mass loadings. To this end, a management strategy could be developed whereby flow is slow enough to prevent sediment movement but fast enough to minimize Se bioaccumulation. At present, the data necessary to evaluate this scheme, or to determine an optimum flow condition have not been collected. Bioconcentration of waterborne dissolved Se and bioaccumulation (possibly biomagnification) of food-borne particulate Se are required to quantify potential toxicity levels. These exposure pathways require monitoring strategies that include measurement of Se concentrations in water (dissolved) and in organic and inorganic suspended particulate matter, in addition to those in bed sediment and biota. Speciation considerations also lead to two types of Se assessment for which amounts and ranges of risk need to be quantified: (1) ecological hazard created by the high mobility of dissolved selenate species, and (2) bioassay toxicity created by the high toxicity of the dissolved organic selenide species (e.g., selenomethionine).

Waters and wildlife of the San Francisco Bay/Delta Estuary are already at risk (Nichols et al., 1986). The bay, which is the largest estuary on the west coast of North America, has lost 80% of its historic marshes to urban encroachment (i.e., filling and diking). Preservation and restoration of the bay wetlands are long-term goals of a new cooperative effort (CALFED Bay–Delta Program, 1996)

among federal and state governments and the general public to ensure a healthy ecosystem and reliable, high quality water supplies. As stated previously, the levels of Se in the San Francisco Bay/Delta Estuary had been listed as "of concern" (CSFBRWQCB, 1992) mainly as a result of six petroleum refinery point sources of Se pollution, but the agricultural drainage component of the Se load has not been quantified. Samples collected in 1987–1989 from sites in the bay, principally Suisun Bay and San Pablo Bay, showed site-mean-Se levels in scoter and scaup (waterfowl) liver tissue of 40 to 209 and 14 to 83 μg/g, dry weight, respectively (CSFBRWQCB, 1992), surpassing levels in the waterfowl (46 to 82 μg/g, dry weight Se) at Kesterson Reservoir that showed deformities.

More significantly, deformed embryos have been recovered from a small marsh in the northern bay specifically designed for remediation of Se-enriched oil refinery effluent after 4 years of receiving effluent containing elevated Se concentrations (20 μg/L). Selenium levels in bird eggs similar to those found at Kesterson Reservoir have been detected, and 30% of mallard nests and 10% of coot nests contained deformed embryos (Skorupa et al., 1996; Skorupa, this volume, Chapter 18). An additional source of Se due to agricultural drainage into the bay via an extension of the SLD can only exacerbate these problems for this now multipurpose aquatic environment. To measure impacts in the future, comprehensive environmental monitoring on a mass balance basis is needed to relate effluent limits to Se bioaccumlative potential, rates of transfer, and effects in the ecosystem.

ACKNOWLEDGMENTS

We wish to acknowledge the technical and policy reviews by Marc A. Sylvester and E. C. Callender of the Water Resources Division of the U.S. Geological Survey and the support of the U.S. Fish and Wildlife Service, Division of Environmental Contaminants, Sacramento Field Office, especially senior biologists Joseph P. Skorupa and Steven E. Schwarzbach.

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Bioaccumulation of Selenium from Natural Geologic Sources in Western States and Its Potential Consequences

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ABSTRACT / Ecological impacts of water-quality problems have developed in the western United States resulting from the disposal of seleniferous agricultural wastewater in wetland areas. Overt effects of selenium toxicosis occurred at five areas where deformities of wild aquatic birds were similar to those first observed at Kesterson National Wildlife Refuge in the west-central San Joaquin Valley of California. These areas are: Tulare Lake Bed Area, California, Middle Green River Basin, Utah, Kendrick Reclamation Project Area, Wyoming, Sun River Basin, Montana, and Stillwater Wildlife Management Area, Nevada. Potential for ecological damage is indicated at six more sites in Oregon, Colorado, the Colorado/Kansas border, and South Dakota out of 16 areas in 11 states where biological tissue data were collected. This conclusion is based on the fact that selenium bioaccumulated in bird livers to median levels that had exceeded or were in the range associated with adverse reproductive effects. Selenium concentrations in samples of fish and bird eggs support these conclusions at a majority of these areas. Reason for concern is also given for the lower Colorado River Valley, although this is not exclusively a conclusion from these reconnaissance data. Biogeochemical conditions and the extent of selenium contamination of water, bottom sediment, and biota from which this assessment was made are given here. In a companion paper, the biogeochemical pathway postulated for selenium contamination to take place from natural geologic sources to aquatic wildlife is defined.

In the San Joaquin Valley of California, seleniferous irrigation drainage water has become a new source of environmental pollution (Presser and Ohlendorf 1987). Waterlogging of soils by intensive irrigation may be remediated by installation of subsurface drains 2.5–3.5 m (8–10 ft) below ground surface. These drains collect what is essentially a soil leachate that contains natural trace elements, including selenium (Se), that have been concentrated by physical weathering in the process of soil formation and evapotranspiration. The enrichment of Se, and some part of the extensive salinization of soil that takes place in the arid climate of the valley, are thought to have their origin in Cretaceous marine sedimentary rocks, which historically have been shown to be seleniferous in the western United States (Trelease and Beath 1949). Current practices of agricultural wastewater management allow the transfer and storage of subsurface drainage to wetland areas. This leads to extended exposure of the ecological community to Se. The wetlands receiving irrigation drainage water, in the course of being used as wildlife habitat, are then operated as evaporation systems to concentrate this agricultural wastewater further, to the form of salts, for eventual disposal. The future means of disposal of the end product is now an issue of concern and controversy in the San Joaquin Valley of California.

KEY WORDS: Selenium; Avian teratogenicity; Bioaccumulation; Environmental contamination; Western United States

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First discovered in 1983, high rates of embryonic deformity and death in wild aquatic birds occurred at Kesterson National Wildlife Refuge (NWR), the terminus of the subsurface drains, and was attributed to

Se toxicosis (Ohlendorf and others 1986). Selenium was found to be one of the elements that is mobile and able to bioaccumulate in the food chain. Its concentration in the diets of birds and consequently in their eggs, exceeded levels known to cause deformity (Presser and Ohlendorf 1987). In this same study, Se concentrations in livers of birds have been shown to be indicators of toxicity.

Approximately 200 wildlife refuges and management areas receive water from more than 400 US Department of the Interior (USDOI) water projects in the western United States [US Bureau of Reclamation (USBR 1981)]. The majority of these projects consist of agricultural irrigation–drainage facilities constructed by the USBR. In response to concern expressed by the US Congress over Kesterson NWR, the USDOI started a program in 1985 to identify the nature and extent of irrigation-induced water-quality problems that might exist in other parts of the western United States in settings similar to that surrounding Kesterson NWR, i.e., Cretaceous marine sedimentary basins (Sylvester and others 1988, Feltz and others 1990, Harris 1991). Outcrops of Cretaceous marine sedimentary rocks in the western United States comprise a total area of approximately 300,000 square miles from Texas north to Canada, east to Iowa, and west to Utah (Trelease and Beath 1949). However, this survey did not include the coastal states of Washington, Oregon, and California nor the state of Arizona. Twenty-eight areas in 17 states underwent or are to undergo reconnaissance investigations including, in some cases, a search for waterfowl deformities. In lieu of the more time-dependent and time-consuming, field-intensive search for eggs and deformities, concentrations of Se in water, bottom sediment, and biota were used to indicate potential adverse ecological effects and Se in bird livers was used as evidence of toxicity. Historically, only one of the 28 water project sites selected for study had been previously investigated for the presence of Se (Crist 1974). At the Kendrick Reclamation Project in Wyoming in 1974, it was shown that Se movement was accelerated by irrigation, and irrigation drainage water contained up to 1200 μg/liter Se.

In this paper, we identify areas of possible Se contamination in the western United States from reports of the USDOI on reconnaissance investigations of water, bottom sediment, and biota where wetland habitats are receiving agricultural drainage. Most of these areas have similar climatic, geologic, soil, and hydrologic conditions to that of the west-central San Joaquin Valley. These are the first data available on the extent of the Se problem. These data show that bioaccumulation of Se is occurring in most of the wetland areas studied. We also describe the complex chemistry associated with the biological cycle of Se, an element that is both an essential micronutrient in animals and a priority pollutant. Based on the extent of Se contamination found, we propose that there is a fundamental problem in the disposal of agricultural drainage water, particularly to wetland areas, where Se can bioaccumulate to toxic levels in wildlife. This presents a danger to aquatic birds on both the Pacific and Central Flyways. Under federal law, the resulting death of aquatic birds may violate the Migratory Bird Treaty Act, which in recent years has acted as an environmental safeguard (Margolin 1979). The geologic source area and the mobilization and transport mechanisms for the contamination at Kesterson NWR will be presented in detail in the following companion paper. The setting and conditions will be compared to those existing in the USDOI reconnaissance areas.

Entrance of Selenium into the Food Chain and the Chemistry of Uptake

Introduction of Se into the food chain was first demonstrated in Kesterson NWR in 1983 (Presser and Ohlendorf 1987). Selenium in the entrance pond, as soluble selenate, was at a concentration of 350 μg/liter in that year. Selenium in this form is the highest oxidation state, +6. The water was classified as a sodium-sulfate water with a sulfate concentration of 5550 mg/liter. Concentrations of these soluble constituents were expected to progressively increase with evaporative concentration as water flowed from one pond to another, in a series of 12 interconnected ponds. In the terminal evaporation pond at Kesterson NWR, the concentration of Se in water was low (14 μg/liter), even though the sulfate concentration was extremely high (11,500 mg/liter), indicating concentration of inorganic constituents. The Se was found to have been taken into an organic state in an algal mat that covered the almost dry pond. The concentration of Se in the algal mat approached a level of 13 μg/g dry weight, in May 1983 and 24 μg/g in August 1983, a level that is toxic to aquatic birds. Although this sampling was limited, it did demonstrate that selenium lost from solution in the ponds could enter the food chain through uptake by biota and that organic processes were probably more effective in removing Se than the inorganic processes in surface water.

Extensive analyses of organisms consumed by aquatic birds at Kesterson NWR reflected biomagnification of Se in the food chain (Ohlendorf and others 1986, Presser and Ohlendorf 1987). The mean con-

centrations in filamentous algae, rooted plants, and plankton, all postulated to initiate entrance into the food chain, were 35–85 μg/g Se dry weight. Mean concentrations in higher food-chain organisms, insects and fish, were further enriched at 22–175 μg/g Se, dry weight. These means were approximately 12–130 times those found at Volta Wildlife Management Area (WMA), the control site in the San Joaquin Valley, where Se concentrations for biota were <3 μg/g dry weight. As the area continued to be impacted, 246 μg/g Se dry weight was eventually reached in the algae, 108 μg/g in plankton, 273 μg/g in macrophytes, 293 μg/g in aquatic insects, and 247 μg/g in mosquitofish, the only species of fish remaining in the ponds (Presser and Ohlendorf 1987, Saiki and Lowe 1987). In the wild aquatic birds, the geometric means for livers of adult birds ranged from 20 to 127 μg/g Se and in eggs from 7 to 70 μg/g Se dry weight, depending on species. For comparison, mean concentrations of bird livers (dry weight) from the Volta WMA ranged from 4.4 to 8.8 μg/g Se. Mean concentrations in eggs (dry weight) from Volta WMA were generally <2 μg/g, with no abnormalities found.

The guidelines given for the toxicity of Se do not specify its chemical form. The initial uptake of Se into the food chain involves a reductive incorporation (Cutter 1982), supposedly supported by the rate of development of anaerobic conditions. In the Kesterson NWR ponds, although Se was mainly in the selenate form (+6 Se), up to 30% of the total Se in the latter ponds was in the selenite form (+4 Se). In recent experiments with algae, it was found that organic Se, in the −2 state, with an amino fraction was produced even though the original dosing in the water was with selenite (Se+4) or selenate (Se+6) (USFWS 1990a, Maier and others 1993). This reduced form of Se is presumably as the selenoproteins, selenocysteine and selenomethionine, in which Se is directly substituted for sulfur. This demonstrates that, when introduced into algae, the metabolic fate of accumulated Se is independent of the initial Se species.

From marine studies in the North and South Pacific Oceans (Cutter and Bruland 1984), organic selenide in surface water (<300 m in depth) makes up 80% of the total dissolved Se and the downward flux of particulate Se, found primarily in the −2 oxidation state, decreases with depth. The reduced-state organic selenide maximum, supposedly consisting of selenoamino acids, coincides with the maxima of primary productivity, suggesting entrance into food-chain organisms. This relationship shows that bioaccumulation could be currently taking place in ocean water.

From the freshwater study of Besser and others (1993), selenomethionine at waterborne concentrations of <1 μg/liter have been shown to be bioconcentrated by a factor of 50,000 in algae and 350,000 in daphnids, greatly exceeding those measured with other Se compounds. Selenium concentrations in tissue residues for these food-chain organisms ranged from 5 to 12 μg/g Se dry weight, which is in the range of that which is toxic in the diet of fish and birds (Heinz and others 1987). Similar concentrations of Se were found in biogenic debris from the presentday Atlantic Ocean, which contained from 6.6 (zooplanton fecal pellets) to 8 (surface biogenic particulates) μg/g Se dry weight (Fowler and Knauer 1986).

Biological Cycling of Selenium

The bioaccumulative property of Se may be an essential function in the cellular metabolism of this element. Termed "bioreactive," it shows a nutrient-type distribution in marine environments (Bruland 1983). These bioreactive elements are termed as such, since they are proposed to be mainly involved in biological cycles of the sea (Broecker and Peng 1982). Lipman and Waksman (1923) and Shrift (1964) proposed a biological Se cycle similar to the cycle for sulfur, in which they determined the reductive half and left only a portion of the oxidizing half unsubstantiated. The characteristics that these cyclable elements have in common are that they exist as a gas in at least one stage of transformation and that they undergo a change in oxidation state (Konetzka 1977). Both these conditions are met by Se in biological systems.

Evidence for the reductive half of the cycle has been updated in recent research initiated to elucidate possible bacterial processes in bottom sediment from San Joaquin Valley evaporation ponds. Bacterial mineralization involving the use of inorganic elements as energy sources was found to take place anaerobically in cultures. Selenate (Se+6) was reduced to elemental Se (Se0) by using the selenate as an electron acceptor for bacterial respiration (Oremland and others 1989, Macy and others 1989). The laboratory cultures turned red with precipitation of elemental Se by bacteria thought to be ubiquitous in nature (Oremland and others 1991). The microbes easily reduced amounts of Se at nutrient levels (2860 mg/liter), greater than that occurring in any drainage water. An inorganic process however, has yet to be successfully proven for the reduction of selenate to elemental Se under field conditions. The organic reduction technique is a possible way of sequestering Se in sediments in the San Joaquin Valley. Fungi that aerobically re-

duce selenate to alkylselenide gas have also recently been cultured (Frankenberger and Karlson 1989), but the conversion rate has not been found to be cost effective as a means of removing Se.

Evidence for the reverse cycle of oxidation of metallic selenides (e.g., CuSe, Se−2) and elemental Se to selenate by microorganisms has also been researched since the experiments of Lipman and Waksman in 1923 (Geering and others 1968, Torma and Habashi 1972).

The oxidation–reduction processes further include a recycling of Se in soluble–insoluble phases similar to those involved in the recycling of sulfur by *Thiobacillus ferrooxidans*. A large population of sulfate-reducing bacteria has been found in ponds used for concentrating metals from solution by introducing microorganisms. There was removal of metals (U, Mo, Se) but no decrease of soluble sulfate in the water flowing through the system (Brierley and Brierley 1981). Reduced forms of sulfur may be oxidized by the aerobic thiobacilli in oxidizing regions, returning the sulfur to the soluble sulfate species. If the case is similar for Se cycles, equilibrium conditions may be attained in pond ecosystems with a rapid turnover time in the biomass, mainly involving the protein form of Se. Including areas such as wetlands in the cycle adds the dimension of higher food-chain bioaccumulation in fish and birds and increased risk of deformities and toxicity.

Reconnaissance Areas

With Kesterson NWR as a prototype, reconnaissance areas in the western United States were generally selected based on six factors, whose significance will be expanded on in the companion paper, being present: (1) a basin of saline marine sedimentary origin that includes soils derived from Cretaceous deposits; (2) oxidized, alkaline soils that promote the formation of selenate, the mobile form of Se; (3) an arid to semiarid climate with evaporation much greater than precipitation leading to salinization of soils; (4) irrigated agriculture served by USDOI-supported irrigation–drainage facilities to leach salts; (5) saline groundwater aquifers resulting mainly from alluvial clay layers that impede downward movement of irrigation water and that cause waterlogging of the crop root zone; and (6) drainage by natural gradient or through buried tile drain networks to USDOI managed migratory-bird refuges, wetland areas, or other areas in receipt of USDOI waters. Names and locations of areas of study by the USDOI are shown in Figure 1. Type (reconnaissance or detailed) and status (potential, underway, or completed) of the studies are also given. Because of early reports of bird deformities at Tulare Lake Bed Area and the expertise of the US Geological Survey in California hydrologic systems, the Tulare Lake Bed Area was studied by the US Geological Survey, not the USDOI. The study, however, conformed to the USDOI protocol and is included here. Data from 15 completed reports (Sorenson and Schwarzbach 1991, Roddy and others 1991, Peterson and others 1988, 1991, Ong and others 1991, Greene and others 1990, Low and Mullins 1990, Setmire and others 1990, Hoffman and others 1990, Stephens and others 1988, Schroeder and others 1988, Radtke and others 1988, Wells and others 1988, Lambing and others 1988, Knapton and others 1987) and data from five other reports that are not yet published (Butler and others 1993a,b, Dileanis and others 1993, Rinella and Schuler 1993, Mueller and others 1993), but where reconnaissance investigations are complete, are discussed in the following sections.

Although these 20 areas underwent reconnaissance as part of the USDOI program, not all biological media (i.e., food-chain items such as plankton and benthos) were sampled at all sites. The following discussion is based on all analytical results for Se in five basic categories in each area: water, bottom sediment, fish, bird livers, and bird eggs. For fish and birds, results for species were combined for each area to allow a comparison among areas.

Of the 20 areas, 13 contain a total of 20 national wildlife refuges (NWR) (Table 1), many of considerable size, up to 750 sq km (288 sq mi) in area. Ten areas are the home or breeding ground of designated endangered species of birds or fish. Before these studies were instigated, declines in or die-offs of birds or fish took place at six areas. Internal drainage basins present at eight sites are of particular concern because they compound the effect of evaporation in the arid to semiarid climate. For example, the Harney Basin is the largest closed basin in Oregon at 13,725 sq km (5300 sq mi). The basin drains to the Malheur NWR, one of the largest inland wetlands in the United States and the largest studied here. The extent of areas in the refuges devoted to evaporation ponds, where concentrating effects take place, is also a factor for consideration. The Tulare Lake Bed Area now contains 2700 ha (6680 acres) of evaporation ponds, whose acreage could be increased fivefold in a planned expansion in the next ten years.

The first factor was not always present at the 20 areas studied. Source rock designations given in Table 2 show that drainage from Cretaceous marine sediments is implicated explicitly in 12 and implicitly

Table 1. National wildlife refuges located in the 20 USDOI study areas

Montana
Benton Lake NWR
Texas
Laguna Atascosa NWR
New Mexico
Bosque del Apache NWR
Utah
Ouray NWR
Wyoming
Bowdoin NWR
Idaho
Lake Walcott and Minidoka NWR
Oregon
Malheur NWR
Nevada
Stillwater NWR
California/Arizona
Havasu NWR,
Cibola NWR
Imperial NWR
California
Lower Klamath NWR
Tule Lake NWR
Salton Sea NWR
Pixley NWR
Kern NWR
Sacramento NWR
Delevan NWR
Colusa NWR
Sutter NWR

(downstream areas) in four sites for a total of 16 of the 20 sites studied. Contributions of Se from ash or crystalline volcanic rocks at the other areas are unknown, due to lack of historical data. Other environmental risks considered in the selection of study areas were suspected elevated arsenic concentrations at Malheur NWR and Stillwater WMA and pesticide use in the vicinity of Bosque del Apache, Laguna Atascosa, and Lower Klamath NWRs and the Lower Colorado River Valley.

Methods

Selenium in water samples was analyzed in the National Water Quality Laboratory of the US Geological Survey, Water Resources Division, Arvada, Colorado, using the methods of Fishman and Friedman (1989). Selenium in bottom material was determined in the laboratory of the US Geological Survey, Geologic Division, Lakewood, Colorado, using the methods of Severson and others (1987). Selenium in biota was analyzed in US Fish and Wildlife Service Analytical Control Facility, Laurel, Maryland, or those laboratories under contract to it by the methods described in USFWS (1985). All of the analyses for Se utilized hydride generation atomic absorption spectrophotometry.

Table 2. Source rock designations

Cretaceous marine sedimentary rocks
Pierre shale
Belle Fourche Reclamation Project, South Dakota
Angostura Reclamation Project, South Dakota
Pierre shale and Carlile shale
Middle Arkansas River Basin, Colorado/Kansas
Niobrara, Carlile, Greenhorn, and Belle Fourche shales
Sun River River Basin, Montana
Cody shale
Kendrick Reclamation Project, Wyoming
Riverton Reclamation Project, Wyoming
Mancos shale or equivalent
Middle Green River Basin, Utah
Gunnison River Basin/Grande Valley Project, Colorado
Pine River Area, Colorado
Downstream areas from Colorado River
Salton Sea Area, California
Lower Colorado River Valley, California/Arizona
Downstream areas from Rio Grande River
Middle Rio Grande River Basin, New Mexico
Lower Rio Grande Valley, Texas
Bearpaw shale
Milk River Basin, Montana
Panoche formation and Moreno shale
Sacramento River Complex, California
Tulare Lake Bed Area, California
Permian marine sedimentary rocks
American Falls Reservoir, Idaho
Volcanic rocks
Salton Sea Area, California
Malheur National Wildlife Refuge, Oregon
Stillwater Wildlife Management Area, Nevada
Klamath Basin Refuge Complex, California/Oregon

Criteria for Selenium Toxicity

Selenium was the constituent of concern most commonly found at elevated concentrations in water, bottom sediment, and biota at the 20 reconnaissance areas (Figure 2). It has been designated as a priority pollutant by the EPA, and it has the greatest potential for toxicological effects in most of the study areas based on comparison to federal regulatory standards and thresholds for ecological damage. Statistical methods used in presentation of the data in Figure 2 are given in Tukey (1977). The data in Figure 2 are referenced to: the US Environmental Protection Agency (USEPA) drinking-water maximum contamination limit (MCL) of 10 μg/liter (USEPA 1988); the USEPA water-quality criteria for protection of freshwater aquatic life of 5 μg/liter (chronic, four-day aver-

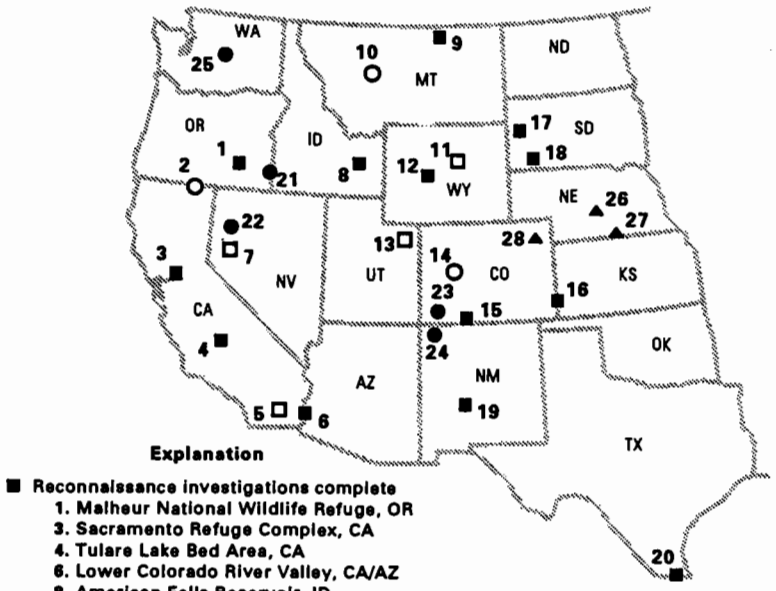

Figure 1. Locations and names of the US Department of the Interior study areas.

age) and 20 μg/liter (acute, 1-h average) (USEPA 1987); the US Geological Survey upper limit of the expected 95% baseline range for soils of the western United States of 1.4 μg/g dry weight (Shacklette and Boerngen 1984); the National Contaminant Biomonitoring Program of the US Fish and Wildlife Service (USFWS) 85th percentile baseline for fish of 2.8 μg/g dry weight (Lowe and others 1985) and the threshold concentration for adverse reproductive effects in fish of 8 μg/g dry weight (Baumann and May 1984); the USFWS concentration range (due to species difference) in livers of birds associated with adverse reproductive effects of 9–41 μg/g dry weight (Heinz and others 1987) and of 30 μg/g dry weight as a threshold for embryo deformity (USFWS 1990b); and the USFWS concentration range in eggs associated with deformities and reduced survival of hatchlings of 10–19 μg/g dry weight (Heinz and others 1987). More recent research has resulted in four further guidelines. A value of <2.3 μg/liter Se is the suggested limit for the protection of aquatic life in water (Skorupa and Ohlendorf 1991). A value of 0.5 μg/g Se for bottom sediments is flagged as an alert to possible contamination (SJVDP 1990), although no standardized sampling procedures or toxic waste standards have been set. The 10/30 guideline (Skorupa and others 1990) suggested for concentrations of Se in bird livers concludes that concentrations <10 μg/g are usually not associated with biological risk and those >30 μg/g usually result in deformity (100% teratogenesis was detected in assessed populations). The same rule is suggested for concentrations of Se in eggs and results in the corresponding 3/20 guideline.

Selenium in Water from the USDOI Reconnaissance Areas

Selenium concentrations varied from site to site in surface collective agricultural drains or streams used

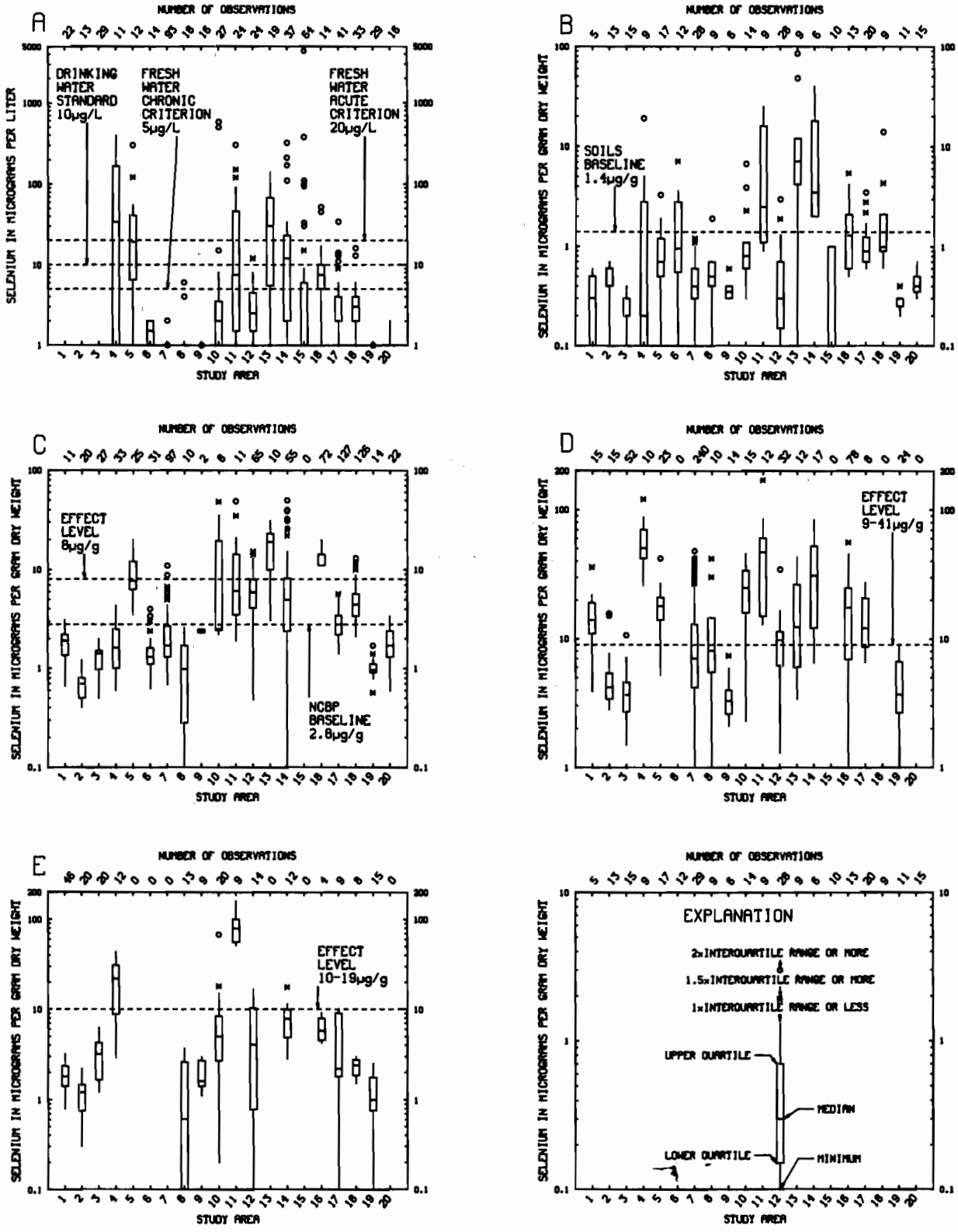

Figure 2. Comparison of selenium concentrations in: **(A)** water (box plots not shown when all observations are less than the reporting limit), **(B)** bottom material, **(C)** fish, **(D)** bird livers, and **(E)** bird eggs. Explanation of statistical representation is given in the lower right corner. Numbers on *x*-axis correspond to Figure 1 names of study areas.

for drainage [e.g., Kendrick Reclamation Project Area (RPA), 27–300 μg/liter; Middle Green River Basin (RB), 4–140 μg/liter; Tulare Lake Bed Area, 36–390 μg/liter; Stillwater Wildlife Management Area (WMA), <1–1 μg/liter; and Salton Sea Area, 7–300 μg/liter]. The two highest Se concentrations observed for the reconnaissance areas studied are 4400 μg/liter in an abandoned well in the Pine RB and 580 μg/liter in a seep in the Sun RB.

Median selenium concentrations in waters, including irrigation supply, drainwater, and refuge-receiving sites such as ponds, to present an overall picture (Figure 2A), are generally low (<10 μg/liter). These levels, however, are not less than the suggested limit for the protection of aquatic life now under consideration by the USFWS (2.3 μg/liter). Two of the areas with high Se levels are the Tulare Lake Bed Area and the Middle Green RB, both of which have median Se concentrations that exceed 20 μg/liter. In addition, median concentrations in the Salton Sea Area and the Gunnison RB/Grand Valley Project exceed 10 μg/liter.

A rather more complicated case shows that time of sampling may be an important factor in assessment of contamination. Assessment may be affected by not only time of year in regards to irrigation but also by a particular year, depending on rainfall amounts or precedence of a drought. Two sites on Beaver Creek in the Milk River Basin contained high Se concentrations in 1985 (Everett Pitt, unpublished data, 1985, Northern Montana College, Havre, Montana). The value for the water at the site upstream of the associated Bowdoin National Wildlife Refuge was 100 μg/liter while the site downstream was 70 μg/liter Se. Although the hydrology of the area is complex, these high values were obtained after four years of drought (1980–1984). In the wetter than normal year that followed (i.e., 1986, two times normal), in which the study reported on here was done, low Se values for the area were obtained. From historical data (Miller and others 1980), water from wells and saline seeps in the Milk River basin, which may be indicative of deeper Cretaceous sources of Se with possible connections to the refuge, showed elevated concentrations of Se (up to 188 μg/liter). The source of this Se will be discussed in the following companion paper.

Selenium in Bottom Sediment from USDOI Reconnaissance Areas

Median concentrations of Se (3.5–7.1 μg/g) in bottom sediments are above the upper limit of the expected 95% baseline range for Se in soils of the western United States (Figure 2B) at three sites: Kendrick RPA, Middle Green RB, and Gunnison RB/Grand Valley Project. Greater than 25% of the values for these sites are above 10 μg/g, with a maximum of 85 μg/g at Gunnison RB/Grand Valley Project. Significant values also occur in other areas. At least 25% of the Se concentrations in bottom sediment exceed the upper baseline range at Tulare Lake Bed, lower Colorado River Valley, Middle Arkansas RB, and Angostura Reclamation Unit. Although the majority of medians for the 20 sites are less than the baseline level, it should be noted that these statistical representations may not have the detail to identify all potential processes of significance and a large variance in sampled material was reported. Limits for bottom sediments above which Se toxicity may be probable (0.5 μg/g) are now being considered and may be much lower, as mentioned before. The organic portion of the bottom sediment, which may include benthos and detritus as parts of the food chain expected to be elevated in Se, may well be the source of the elevated Se concentrations in sediment at the USDOI areas. The importance of this organic material and whether it was included in all samples collected here will be considered later in light of the values for Se obtained for the Kesterson NWR system.

Selenium in Biota from USDOI Reconnaissance Areas

Selenium concentrations in the majority of fish sampled exceed the 85th percentile baseline of the National Contaminant Biomonitoring Program (Figure 2C). At least 25% of the Se concentrations exceed the threshold for adverse reproductive effects in fish in seven of 19 sites where fish samples were collected. They are: Sun RB, Kendrick RPA, Gunnison RB/Grand Valley Project, Salton Sea Area, Riverton RPA, Middle Green RB, and Middle Arkansas RB. Maximum levels of 50 μg/g were seen at the first three of these areas.

Most concentrations of Se in bird livers collected in the study areas are within or greater than the levels associated with adverse reproductive effects in birds (Figure 2D). It is further noted that there are only four areas where nearly all Se concentrations in livers are below the level associated with biological risk. Medians were greater than or in the range of adverse effects at 10 of 16 areas, namely: Tulare Lake Bed Area, Kendrick RPA, Gunnison RB/Grand Valley Project, Sun RB, Malheur NWR, Salton Sea Area, Riverton RPA, Middle Green RB, Middle Arkansas RB, and Belle Fouche RPA. Selenium concentrations

in bird livers from the two areas of greatest contamination range from 26 to 120 μg/g dry weight with a median greater than 50 in the Tulare Lake Bed Area, and from 13 to 170 μg/g, with a median of 47 in the Kendrick RPA. The first three areas have median Se concentrations greater than the concentration (30 μg/g Se) at which 100% teratogenicity occurs. Deformed birds were actually observed at greater than background levels of teratogenicity at five sites—Tulare Lake Bed Area, Sun RB, Kendrick RPA, Middle Green RB, and Stillwater WMA. The types of deformities are consistent with Se toxicosis (Presser and Ohlendorf 1987). The evaporation ponds in the Tulare Basin are the ones most comprehensively studied. Deformed aquatic bird embryos from five different species were found at four of the five ponds; the maximum rate of embryonic deformities approached 38% (Skorupa and others 1993). Stillwater WMA, although not having a median concentration in bird livers in the range of adverse effects, has greater than 25% of those values in the effect range (Figure 2D). Deformities also were identified at Stillwater WMA, and "hot spots" were noted as evidenced by a skewed data set at values greater than 30 μg/g for this area. Thus, based on our assessment of bird liver and deformity data, 11 of 16 areas, including Stillwater WMA, are contaminated to a Se level that is associated with adverse reproductive effects. Seven of these areas match those where at least 25% of the Se concentrations in fish exceed the threshold for adverse reproductive effects.

At seven of 14 areas where bird eggs were collected (Figure 2E), medians for Se in eggs are above 3 μg/g, which is generally regarded as the no-risk background limit. These are: Tulare Lake Bed Area, Kendrick RPA, Sun RB, Riverton RPA, Gunnison RB/Grand Valley Project, Middle Arkansas RB, and Sacramento River Complex. Concentrations of Se in at least one egg equal or exceed the range of adverse effects at the first five of these areas, and deformities were observed in the first three of these areas. Concentrations of Se are greatest at the first two of these areas, Tulare Lake Bed Area (range 3–44; median 22 μg/g dry weight) and Kendrick RPA (range 51–160, median 79 μg/g dry weight), where deformities occurred. All of the seven areas, except for the Sacramento Refuge Complex, are in common with those identified as contaminated based on fish and bird liver data.

Complexities of the data from three areas warrant further discussion: (1) Although Stillwater WMA is located in the Carson Sink, recently exploited for containment of drainage and the site of previous extensive bird die-offs, contamination of the area by Se is difficult to understand. Selenium concentrations in water and bed sediment were low. Nearly all Se concentrations in fish were less than those associated with adverse reproductive effects. Yet, reproductive deformities in birds were observed in this area and Se concentrations in livers from many of the birds sampled (Figure 2D) were in the range associated with adverse reproductive effects. A better understanding of food-chain pathways and migratory patterns of birds sampled at Stillwater WMA may help explain this situation. (2) Although concentrations of Se were low at the Bowdoin NWR in the Milk RB in a year of twice-normal rainfall, the refuge overlies Cretaceous shale, and historical data on wells and saline seeps suggests penetration to a Se source that may affect the refuge at times of hydrologic stress. (3) Although not identified as an area of Se contamination in the USDOI reconnaissance studies or in our assessment of data from these studies, the lower Colorado River Valley might be an area of Se concern based on more recent biota and well-water data (Kepner and others 1993). Because of the relevance of data from this area in providing a regional perspective on factors involved in causing Se contamination, additional information from this area is included in the discussion that follows on the Colorado River as a source of Se.

Regional Sources of Selenium

Either Cretaceous marine sedimentary rocks or volcanic rocks are present in the 11 contaminated study areas. The impact of Cretaceous marine sedimentary rocks in the nine areas where this type of rock is a postulated direct or indirect source of Se is the main topic of the following companion paper. Additional comments are given here on their impact on the Colorado River.

If taken in a regional context, the Colorado River may be implicated as a system-wide source of Se contamination due to Cretaceous marine sedimentary rock exposures in its drainage. The river is of high salinity and is influenced by the Cretaceous Mancos Shale (Radtke and others 1988). Half of its salt load is added mainly from erosion of marine sediments and saline springs and approximately one third from irrigation-return flows, all being possible sources of Se. Shallow wells in the upstream reaches of the Colorado and Uncompahgre River Valleys, located in the extensive alluvium and residuum of the Cretaceous Mancos Shale, contained water with Se concentrations of up to 1300 μg/liter (W. G. Wright, written communication, USGS, Grand Junction, Colorado, 1992).

Two of the USDOI reconnaissance study areas associated with the Colorado River are the Salton Sea Area in the Imperial and Coachella Valleys of California and the lower Colorado River Valley located along a 200-mile stretch of river forming the borders of Nevada, Arizona, and California. The Salton Sea Area has been shown to be contaminated with Se based on results in this paper, and results from the lower Colorado River Valley USDOI study (Radtke and others 1988) led to a recommendation of continued monitoring for Se in this area.

The geology of the Salton Sea Area is characterized in Table 2 as complex in nature, receiving a combination of material derived both from Cretaceous marine and volcanic sources. The Imperial and Coachella Valleys and the depression that is the Salton Sea are made up in part by deposition of rocks of Cretaceous age (Norris and Webb 1990). Currently, both valleys are irrigated with Colorado River water, which ultimately drains to the below sea-level, hydrologically closed Salton Sea. During most years, annual evaporation losses approach or sometime exceed a balance with annual inflow, which can concentrate salts.

In the second area, the lower Colorado River Valley, biota data collected in 1988, but not yet published, show contamination associated with the Colorado River (Kepner and others 1993). The USDOI study data were inconclusive, showing whole body carp samples that were greater than baseline levels by approximately a factor of two (mean 6.0 μg/g Se, dry weight) and samples of whole body double-crested cormorants showing a mean of 5.0 μg/g Se dry weight. This latter mean may be significant but is difficult to compare to concentrations in wildfowl liver and egg samples on which toxicity levels are based. The most compelling evidence, however, is from levels of Se bioaccumulated in the Yuma clapper rail, a federally listed endangered species whose main habitat is along the lower Colorado River (Kepner and others 1993). Mean Se concentrations in rail livers (25.3 μg/g dry weight) and eggs (12.5 μg/g dry weight) are comparable to concentrations found in aquatic birds at Kesterson NWR and both exceed the threshold for embryo deformity. Crayfish (4.2 μg/g Se, mean concentration, dry weight), the main component in the diet of rails, are thought to be the source of Se.

The major geologic source of the Se in the lower Colorado River (Kepner and others 1993) appears to be the sediments eroded from Se-bearing Cretaceous formations upstream and deposited in connected backwaters and above dams of the river. Selenium concentrations are greatest in fine-grained bottom sediment containing a large portion of organic matter and not main channel sand deposits. Crayfish feed on this detritus and other benthic species that have already bioconcentrated the contaminants in the detritus. These results emphasize the possible long-term effects of Se cycling in Colorado river water and especially Se loading of sediments.

Importance of Defining Food-Chain Pathways

At specific areas known to be impacted by Se, e.g., Tulare Lake Bed evaporation ponds, concentrations in some food-chain organisms sampled were elevated to levels that exceeded those at Kesterson NWR (water boatman, up to 140 μg/g Se). Because of the reconnaissance nature of the studies, food-chain components were not always collected. Because of this unsystematic collection and the diverse nature of the food-chain materials that were collected, an analysis of these data is not possible here. In retrospect, even though this degree of detail was not required in a reconnaissance study, this was a limitation because these studies indicate that bioaccumulation is occurring, but do not define the food-chain pathways for this accumulation. Notably, the Stillwater WMA, Sun RB, and Riverton RPA have low concentrations of Se in water (generally <3 μg/liter) and bottom sediment (<1.4 μg/g dry weight) but large concentrations of Se in fish and/or bird livers (up to 48 μg/g dry weight). The importance of measuring bioaccumulation should be emphasized because water is not always a good indicator of Se contamination in a biologically active marsh, as seen at Kesterson NWR, where Se has already been taken up in food-chain organisms.

In the reconnaissance studies reported on here, the delivery of the seleniferous waters to the ponds and streams where bioaccumulation is taking place and the degree to which these ecosystems have built up decayed matter may differ. Drainage water began to replace previous input into Kesterson NWR ponds in 1978 and up to a 64% rate of deformity and death in embryos and hatchlings occurred in wild aquatic birds in the 1983 nesting season. The degree of development of organic-rich sediments (i.e., detrital layers), which is known to accelerate the entrance of Se biologically into the detrital food chain, and anaerobic and reducing conditions for geochemically sequestering it in bottom sediments, must be taken into account for determining the potential for Se bioaccumulation. This may well be illustrated by the differing amounts of Se found in the collective drain at Kesterson NWR and the Kesterson NWR ponds themselves. Data from ponds in 1983 showed sediment levels in the range of 5–10 μg/g Se but detritus (decomposing organic mat-

ter) in the range of 40–130 μg/g dry weight. Bottom material from the main collective drain at Kesterson NWR, which was described as rich in organics, was as high as 210 μg/g Se. In an attempt to separate out sediment and detritus in this drain in another sample, 92 and 308 μg/g Se, respectively, dry weight, were found. The drain water, although relatively fast flowing, contained a limited food chain and a relatively large amount of soil and debris blown in from the surrounding agricultural fields. Obviously, however, sediment loading of Se was taking place. These high concentrations in bottom material were found normally in the top 2 cm or, in the case of the drain, the 25-cm interval. In the dynamic wetland system of Kesterson NWR, where Se may have been constantly recycled, the food chain and organic debris were the dominant repositories and eventual outlet for Se. Reconnaissance sampling of sediment as an indicator of contamination did not differentiate soil, benthos, or detritus. Thus, significant media, both food-chain items and detritus, in which Se could have been present and was at Kesterson NWR were not fully assessed in the ecosystems studied.

Ecological damage by the same biogeochemical mechanism as reported here for wetlands receiving agricultural drainage may also occur in waterbodies receiving fly ash from the burning of sulfurous coal. A coal of approximately 5 μg/g Se can generate a Se concentration in fly ash (Kaakinen and others 1975) that is sufficient to cause deformities and/or death of fish in receiving reservoirs (Lemly 1985, Cumbie and Van Horn 1978). Bioaccumulation factors of up to 4000 have been observed in such reservoirs. In one reservoir studied, 16 of the original species of fish were eliminated. Studies by Lemly (1993) have shown sublethal effects of Se in fish including mouth, spine, and fin deformities that are analogous to beak, leg, and feet deformities caused by Se in birds. In the USDOI reconnaissance studies, deformities of fish were not looked for nor was the number or diversity monitored. These studies of Se contamination illustrate the importance of understanding the Se cycle from sources such as the weathering of exposed Cretaceous marine sedimentary rocks in the western United States and the burning of sulfurous coals in power plants to food-chain pathways that result in Se toxicity.

Summary

As we have shown, the definition of Se contamination must be formulated on an ecosystem level and these ecosystems have now been assessed for the USDOI reconnaissance areas. Contamination has proven to be prevalent in the western United States where wetland habitats are receiving agricultural drainage. Selenium was seen in detectable amounts in samples of water, sediment, or biota from all 20 reconnaissance areas investigated. Median levels of selenium bioaccumulated in bird livers exceeded or were in the range associated with adverse reproductive effects in ten of 16 reconnaissance study areas where bird liver samples were collected. These areas include seven for which 25% of the Se concentrations exceeded thresholds for adverse reproductive effects in fish and six areas for which medians of Se in eggs were greater than the no-effect level. From these data and the deformities found at five areas, 11 areas of 16 where fish and bird samples were collected have been assessed as being contaminated. With the areas where deformities were found listed first, these areas are: Tulare Lake Bed Area, California; Stillwater WMA, Nevada; Sun RB, Montana; Kendrick RPA, Wyoming; Middle Green RB, Utah; Malheur NWR, Oregon; Salton Sea Area, California; Riverton RPA, Wyoming; Gunnison RB/Grand Valley Project, Colorado; Middle Arkansas RB, Colorado/Kansas; and Belle Fourche RPA, South Dakota. In addition, the Colorado River Basin gives reason for concern in view of its regional contamination.

Concluding Perspectives

This study of USDOI water projects and wetland areas in the western United States is not exhaustive. However, possible predictions based on the many phases of this work may discover or prevent further damage in areas where maintaining high agricultural production and retaining major environmental resources are at issue. This study has documented that agricultural drainage is a source of Se in the western United States and that its introduction into wetlands is a danger to the life of the ecosystem. Selenium in these wetlands, which provide food and habitat to migratory birds, along with resident birds, poses a threat to the health of the populations of aquatic birds on the Pacific and Central Flyways. Death of aquatic birds by Se exposure from such wetlands could therefore lead to possible violations of the Migratory Bird Treaty Act.

In the companion paper, we describe the contamination pathway for the type locality, Kesterson NWR, as an example of the biogeochemical processes probably occurring in most other reconnaissance areas found to be affected. We summarize this "rock-to-duck" cycle and name it the Kesterson effect.

Acknowledgments

We wish to thank the members of the US Geological Survey, US Fish and Wildlife Service, and the US Bureau of Reclamation who participated in the US Department of Interior reconnaissance studies and prepared the reports.

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