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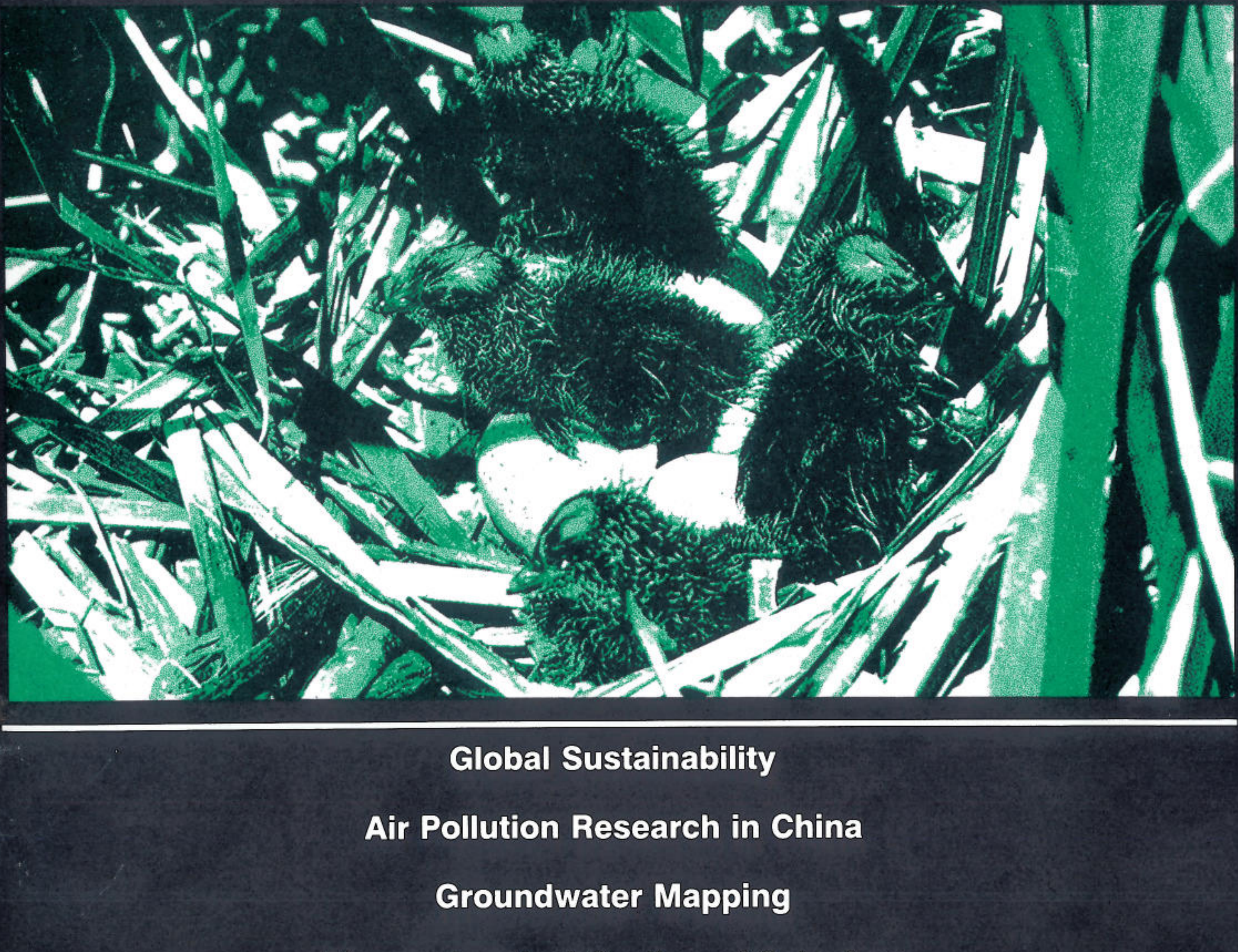

Global Sustainability

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RESEARCH

Cover: Newly hatched American coot (*Fulica americana*) chicks in a nest at Kesterson Reservoir, Merced County, California, USA, in 1983. Three of the chcks are normal but the one in the foreground has no eyes. Other eggs in this nest failed to hatch, and the one that was analyzed contained 44 ppm (dry weight) selenium—about 20 times the normal level. High incidence of embryo mortality and developmental abnormality in several species of aquatic birds at Kesterson Reservoir has been related to high levels of selenium in food organisms, birds, and eggs. The selenium was transported to Kesterson Reservoir in subsurface agricultural drain water that had mobilized natural deposits in sediments of the San Joaquin Valley and Coast Ranges, the selenium then becoming available for cycling and bioaccumulation. Photo: H. M. Ohlendorf, US Fish and Wildlife Service.

Biogeochemical Cycling of Selenium in the San Joaquin Valley, California, USA

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ABSTRACT / Subsurface agricultural drainage waters from western San Joaquin Valley, California, were found to contain elevated concentrations of the element selenium in the form of selenate. In 1978, these drainage waters began to replace previous input to Kesterson Reservoir, a pond system within Kesterson National Wildlife Refuge; this substitution was completed by 1982. In the 1983 nesting season, unusual rates of deformity and death in embryos and hatchlings of wild aquatic birds (up to 64% of eared grebe and American coot nests) occurred at the refuge and were attributed to selenium toxicosis. Features necessary for contamination to have taken place included geologic setting, climate, soil type, availability of imported irrigation water, type of irrigation, and the unique chemical properties of selenium. The mechanisms of biogeochemical cycling raise questions about other ecosystems and human exposure.

California is the leading agricultural state in the United States today mainly as a result of the productivity of its Central Valley (Figure 1), which relies on a program of extensive government-supported irrigation. However, the geologic setting and climate of the southwestern Central Valley have created soil salinization problems that are accentuated by that irrigation. Engineering solutions to save threatened agricultural lands from salinization have themselves created problems that affect the quality of irrigation return waters. These waters have been used in wildlife habitats where serious biological effects from elevated levels of selenium have been documented. The contamination of the ecosystems has developed from naturally occurring selenium, in a form that is highly mobile in the environment. In this article, we summarize the history of the geology and of agricultural water development in the Central Valley, outline geochemical pathways of selenium, and discuss the occurrence, causes, and impacts of water quality problems resulting from agricultural wastewater disposal. Our goal is to describe a case of conflict between maintaining agricultural production in a marginally supportive environment and retaining an ecosystem capable of supporting major environmental resources—two legitimate, but in this case opposing, interests. The problems attendant to the dispersal of such a chemically and biologically complex element as selenium have the potential for the generation of further aberrations, which will be discussed.

KEY WORDS: Aquatic birds; Biogeochemical cycling; Selenium

Geohydrology of the Central Valley

Present-Day Geohydrology

The Central Valley of California is a heterogeneous system because of climatic and geologic variations from the northern Sacramento to the southern San Joaquin River Basins and from the western Coast Ranges to the eastern Sierra Nevada (Figure 1). A treatise by Mendenhall and others, as early as 1916, described the essential processes that account for the present valley surface, and predicted much of the agricultural outcome that is realized today. The essence of their description is that the valley structure is a direct result of stream action and deposition of materials brought down from the surrounding mountains. The compositions of the soils or alluvium of the valley reflect closely the type of rock outcropping in the drainage basin from which they are derived.

The large and perennial streams of the Sierra Nevada build the flat, extensive alluvial fans of the eastside slopes. Precipitation in the Sierra ranges from a mean annual amount of 203 cm (80 inches) in the north to 89 cm (35 inches) in the south (USBR 1976). These mountains are composed of granitic and metamorphic rocks whose potassium, sodium, and calcium compounds are in the form of relatively insoluble silicates. Therefore, the streams transport very little salt, and coarse-grained alluvium is produced.

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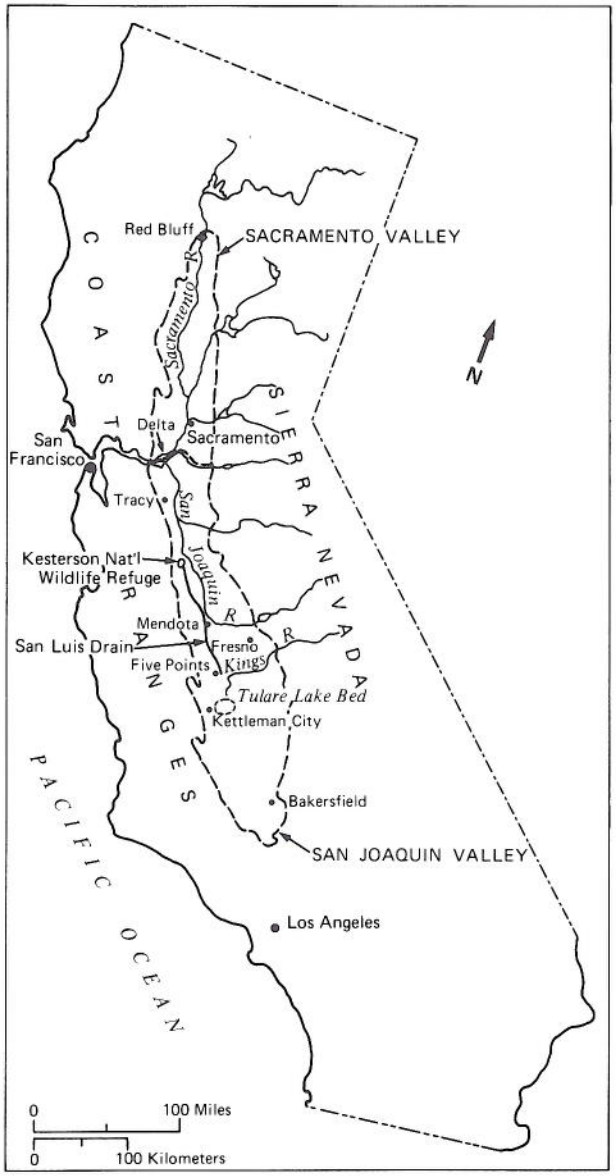

Figure 1. Geographic and hydrologic features of California's Central Valley including the Sacramento and San Joaquin Valleys (*dashed lines*).

The west-side alluvial fans associated with the Coast Ranges, particularly those in the middle of the valley and near its southern end, are steep, complex, coalescing forms that are characteristic of areas of low, erratic rainfall. The Coast Ranges receive much less precipitation than the Sierra Nevada, with large variations from year to year, the maximum rainfall being seven times the minimum (USBR 1976). The sedimentary sandstones and shales of the Coast Ranges, which are rich in gypsum and other readily soluble minerals, produce fine-grained, highly saline alluvium.

Red Bluff, on the valley floor at the relatively humid northern end of the Sacramento Valley (Figure 1), receives approximately 66 cm (26 inches) of rainfall annually. Bakersfield, in the arid, Mediterranean climate of the southern end of the San Joaquin Valley (Figure 1), receives approximately 20 cm (8 inches) of precipitation annually; evaporation measured at three sites along the southwestern San Joaquin Valley is approximately 229 cm (90 inches) per year (NOAA 1982). A study of an irrigation system in this arid part of the valley (Presser and Barnes 1985) using the isotopes of oxygen ($^{18}O/^{16}O$) and hydrogen ($^{2}D/^{1}H$) in water showed an evaporative pattern comparable to desert basins, for example, the Sahara Desert (Craig 1961, Fontes and Gonfiantini 1967).

The transportation of salts from the Coast Ranges and their concentration by the arid climate of the southwestern Central Valley are the major sources of the present agricultural and water quality problems in this unique quadrant of the Central Valley. Although salinity is the foremost problem in this study area, accessory trace elements associated with the salts, and their consequences, are also of concern.

Geologic History of the Source of Salinity

The origin of the Central Valley began in the Mesozoic Era during the Late Jurassic or Early Cretaceous Periods, between about 120 and 150 million years ago (mya) (Miller 1957, Hackel 1966). During this time, a trough developed down the middle of the area now known as California between a volcanic arc on the east, at the site of the present Sierra Nevada, and a marine trench and subduction complex on the west. Prior to this orogenic event, seawater had covered much of the area. The trough is estimated to have been 1280 km (800 miles) long and 160 km (100 miles) wide. Erosional products of the volcanic arc were deposited in this salt-water-filled subsidence basin, thus producing the Cretaceous marine formations at the western margin of the present Central Valley. The greatest accumulation took place in the Sacramento Valley, resulting in strata interpreted to be 15.2-km (50,000-feet) thick. The greatest invasion of the sea was during the Late Cretaceous (between about 75 and 65 mya) when the Panoche Formation, followed by the Moreno Formation, were deposited in the study area in the western San Joaquin Valley.

During the Cenozoic Era, which includes the Tertiary and Quaternary Periods, the Coast Ranges were raised and the Sierra Nevada was uplifted. During the Tertiary Period (63 to 2 mya), marine strata were again deposited over large parts of the Central Valley. The sea withdrew from the northern part of the valley at about middle Tertiary time and was restricted to the southern San Joaquin Valley through the remainder of the Tertiary. Apparently, at no one time during the Tertiary was all of the western California region above sea level, providing access, although limited, to the Pacific Ocean. The greatest accumulation of these sediments in the Tertiary was in the southwestern San Joaquin Basin, >7.6 km (>25,000 feet) thick, with all epochs of the period well represented. Within the study area, two formations of particular interest were deposited: the Domingene, a widespread, fossiliferous, marine sandstone; and the Kreyenhagen, a diatomaceous marine shale. Toward the end of the Tertiary Period, the marine waters withdrew entirely. During the Quaternary Period (a period of relatively short age, beginning 1.5–2 million years ago and continuing to the present), significant folding, faulting, and uplift affected the distribution of 6.1–9.8 km (20,000–30,000 feet) of strata.

From this deformation and uplift of the Quaternary Period came the Coast Ranges and Central Valley as they exist today. Terrestrial conditions have shaped the present-day erosional features and developed the soils of the valley from this alluvium over periods of approximately 100,000 years. Two important features of the resultant soil column in the western San Joaquin Valley are impermeable clay layers within the column (Davis and Poland 1957) and accumulation of alkali toward the top of the column (USBR 1984a).

Man-Induced Hydrology

Irrigation of the arid west side of the San Joaquin Valley, and subsequent agricultural development and land reclamation, began in the 1870s with the diversion of water from the San Joaquin River. Large-scale irrigation with groundwater was initiated in 1915 (Davis and Poland 1957). In about 1945, the use of groundwater exceeded recharge, causing declining water levels. Importation of surface water to make up the deficiency in supply became operational in the early 1950s. Named the Central Valley Project, it included 17 dams and 10 major canals to move surface water generally from the north and east to the south (USBR 1976).

Much of the 485,640 ha (1.2 million acres) of farmland on the west side of the San Joaquin Valley is underlain by clay layers at depths of 3–12 m (10–40 feet) that seriously impede the vertical movement of water (USBR 1984a). These natural barriers, coupled with extensive irrigation, have caused formation and enlargement of shallow groundwater bodies that inhibit the transport of salts out of the root zone of crops. Because evaporation occurs at a rapid rate and salts occur naturally in both the soil and the irrigation water, alkali deposits build up throughout the crop root zone and ultimately form on the soil surface. Agricultural production is consequently reduced, eliminated, or limited to salt-tolerant crops. At present, 102,389 ha (253,000 acres) of irrigated farmland on the west side of the San Joaquin Valley are affected.

Tile subsurface drains, which remove the concentrated saline waters from the root zone, were first suggested by Mendenhall and others in 1916 as a remedy for alkali buildup in soils in California. Since 1960, subsurface drainage systems have been installed in approximately 34,400 ha (85,000 acres) of irrigated farmland in the western San Joaquin Valley (USBR 1984a).

Approximately 31,162 ha (77,000 acres) of this subsurface-drained land lie between Mendota and the San Francisco Bay Delta Estuary (Delta) (Figure 1). This subsurface drainage is eventually discharged into the San Joaquin River, the only natural outlet from the valley to the Delta (USBR 1984a). On its way to the river, however, the great complexity of hydrologic features (including natural wetland habitats) and diversity of mechanisms for irrigation/drainage (including temporal switching mechanisms) provide dilution and routing into canals that may be supplies or drains for other users. Once into the Delta system, these mixed waters are included in the source of drinking water for southern California (through the California Aqueduct) and for the south San Francisco Bay area (through the South Bay Aqueduct). The Delta system then further connects to the immense, already stressed, ecosystem of the San Francisco Bay (Greenberg and Kopec 1986, Nichols and others 1986).

No natural outlet exists for removal of subsurface drainage between Mendota and Kettleman City (USBR 1984a) (Figure 1). The area includes the 242,820 ha (600,000 acres) of the Westlands Water District (WWD 1984). It is estimated that approximately 121,410 ha (300,000 acres) in the WWD eventually will need subsurface drainage. In a joint project between the WWD and the US Bureau of Reclamation (USBR), the WWD has constructed collector subsurface drains for 16,997 ha (42,000 acres) of this area.

The San Luis Drain was authorized by the US Congress in 1960 to be constructed by the USBR exclusively for the purpose of transport of subsurface drainage (USBR 1984a). Approximately 137 km (85 miles) of this concrete-lined canal, extending north from Five Points (Figure 1), were built by the USBR between 1968 and 1975. When evaluated in 1979, the preferred terminus of the planned 333-km (207-mile) San Luis Drain was to have been Suisun Bay in the San Francisco Bay Delta Estuary. Due to project appropriation restrictions, however, construction of the drain was stopped at Kesterson Reservoir, a pond system within Kesterson National Wildlife Refuge (KNWR) originally designed to regulate flows from the San Luis Drain to the Delta.

Wildlife Areas of the San Joaquin Valley and the Pacific Flyway

KNWR includes a 518-ha (1280-acre) reservoir consisting of 12 interconnected evaporation ponds and 1870 ha (4620 acres) of native grassland and seasonal wetland (USBR 1984a). KNWR is currently managed jointly by the US Fish and Wildlife Service (USF&WS) and the USBR.

The KNWR is at the north end of a general wetland area in the floodplains of the San Joaquin River. Approximately 28,329 ha (70,000 acres) to the west of the San Joaquin River and 18,212 ha (45,000 acres) to the east constitute the largest tract of natural grassland remaining in the San Joaquin Valley (USBR 1984a). These marsh and pasture lands provide important wintering habitat for waterfowl on the Pacific Flyway, supporting a peak migratory waterfowl population of approximately 1.7 million (USF&WS 1978).

Within the entire Central Valley, 5–6 million ducks and geese overwinter each year, representing approximately 60% of the Pacific Flyway population and 18% of the entire continental population (USF&WS 1978, Gilmer and others 1982, Gilmer 1984). Because of the historic loss of nearly 95% of the wetland habitat in California, birds have been concentrated into the remaining limited refuge areas, causing increased vulnerability to disease and environmental toxicants. Migratory ducks and geese are highly mobile and probably experience shorter exposures than do breeding birds (for example, coots), which are more sedentary and experience longer exposures.

Preliminary Investigations of the Use of Subsurface Agricultural Drainage Water

Until 1978, the water discharged to Kesterson Reservoir contained only surface water from local sources, with quality similar to applied irrigation water (USBR 1984a). Beginning in 1978, flow was increased from subsurface collector drains as they were installed and connected to the San Luis Drain. By 1982, the flow into the reservoir was primarily subsurface agricultural drainage water. Since 1981, approximately 8.63×10^6 m^3 (7000 acre-feet) representing drainage from 3238 ha (8000 acres) of WWD farmland have entered the evaporation ponds at KNWR annually.

The USBR and USF&WS had recently considered the possible use of agricultural wastewater in refuge management and in the creation of new wetlands (Gilmer and others 1982, USBR 1982, Gilmer 1984). Use of KNWR for the assessment of potential effects was feasible, as it was an established productive wetland habitat (Ohlendorf 1984).

In preliminary studies, samples of mosquitofish (*Gambusia affinis*) collected from KNWR in 1982 by the USF&WS showed low or nondetectable levels of pesticides and normal levels of heavy metals, but contained abnormally high concentrations of selenium (Se), approximately 30 parts per million (ppm), wet weight (Ohlendorf 1984). This was approximately 100 times the level found in the Volta Wildlife Management Area (VWMA), a nearby control area (approximately 10 km southwest of KNWR) that does not receive subsurface drainage water (Presser and Barnes 1985, Saiki 1986). All other species of fish in KNWR had died since 1981, when increasing amounts of drainage water were added to the reservoir (USBR 1984a). Because Se is toxic to livestock, poultry, and fish under certain environmental conditions (Fishbein 1977, Wilber 1980, Sorensen and others 1984, Lemly 1985a, Finley 1985, Gillespie and Baumann 1986), studies were initiated in the 1983 nesting season to determine whether Se or other contaminants were present in the evaporation ponds at KNWR at concentrations harmful to aquatic birds, and to determine the extent of the Se contamination on the west side of the San Joaquin Valley.

A search of the literature showed few data on the concentration of Se in Coast Range streams, or in other waters, biota, or geologic material and soils from this area. Most of the Se found in the environment, and consequently in water, results from the weathering of seleniferous rocks (USEPA 1979), which usually contain <1 ppm Se, with shales having the highest concentration at approximately 1 ppm Se (Lakin 1961).

Symptoms of "alkali disease" in animals (Trelease and Beath 1949, Anderson and others 1961, Rosenfeld and Beath 1964) were reported as early as 1275 by Marco Polo in China. Investigations in 1933 of this disease in livestock of South Dakota, Nebraska, and Wyoming showed that the toxic factor was Se, and that it was related to plants grown on soils that had developed from the Pierre Shale. These seleniferous accumulator plants are of the genus *Astragalus* and contain concentrations of Se up to 10,000 ppm. The Pierre Shale is of Cretaceous age and was formed in an inland sea that accumulated sediments for 55 million years. These sediments later became the chalks, shales, and sandstones that are the parent materials of many of the soils of the region. The Pierre Shale has great areal extent with outcrops occurring in North Dakota, South Dakota, Nebraska, Montana, Wyoming, Colorado, and New Mexico.

A study of the marine sedimentary rocks and soils of Cretaceous formations, in addition to vegetation, was conducted from 1935 to 1941 by the US Department of Agriculture and included ten western states and parts of the east coast (Byers 1935 and 1936, Byers and others 1938, Williams and others 1940 and 1941). Concentrations of Se in sedimentary rocks of the Pierre Shale ranged up to 103 ppm. It was concluded that, in addition to the Pierre Shale, numerous other geologic formations were sufficiently seleniferous to form soils that were potentially hazardous to ranch animals.

Data from California are particularly scarce (Lakin and Byers 1941). A reconnaissance in 1941, including 56 samples of shales and soils from 16 counties, showed an average value of 1.4 ppm Se. A shale obtained near Hospital Creek in San Joaquin County (Figure 1, 19 km south of Tracy) yielded the highest value of 28 ppm Se. This area in the Coast Ranges is in the Moreno Formation of Late Cretaceous age.

In his summary of Se in agriculture in 1961, Lakin stated that rainfall in excess of 64 cm (25 inches) appeared to be sufficient to leach out the readily soluble and available Se at a low contant rate, therefore causing less reason for concern. Integrating the rainfall (Rantz 1969) and geologic (Jennings 1977) maps of California shows that an isohyetal line of 30 cm or less (<12 inches) of precipitation approximately defines the study area in the southwestern San Joaquin Valley where leaching has been limited and alkali has been deposited; this same area geologically includes, as described before, extensive exposures of Cretaceous and Tertiary marine deposits.

Concentrations of and Criteria for Selenium in Water

Descriptions and analyses of waters sampled in the study area are presented in Table 1. Our field collection and preservation techniques for unstable elements and methods of elemental analysis have been adapted and tested for use in geochemical environments; complete methods reference is given in Presser and Barnes (1985). The reported concentrations represent those originally in solution. Se methodology is discussed separately in the following section. In general, cations were analyzed by atomic absorption spectrophotometry and anions by colorimetry or ion chromatography. The agricultural return waters and the Kesterson pond waters were indeed found to be highly saline, with specific conductances as high as 31,000 microseimens per centimeter (μS/cm) at 25°C. These waters were all of the sodium–sulfate type. The highest concentration of sodium in these waters was 10,500 mg/liter and, of sulfate, 22,500 mg/liter.

Water from the north end of the San Luis Drain at or near its discharge into Kesterson pond 2 contained 300 μg/liter Se in August 1983 and 280 μg/liter in December 1983 (Presser and Barnes 1984 and 1985). Subsurface agricultural drainage water entering the San Luis Drain contained from 140 to 1400 μg/liter Se in samples taken in December 1983. Concentrations of Se in irrigation supply waters sampled in the vicinity of KNWR, but not receiving subsurface drainage water in October 1983 (for example, Delta–Mendota Canal and Main Canal), contained <2 μg/liter Se.

Based on the various uses of water, several maximum-concentration criteria and standards have been established for Se. The US Environmental Protection Agency (USEPA 1977) has set a maximum limit for public drinking water supplies at 10 μg/liter Se. The USEPA 1980 water quality criterion for protection of freshwater aquatic life is 35 μg/liter Se (24-h average) as inorganic selenite (USEPA 1980a). It has been suggested that levels for protection of aquatic ecosystems be revised downward to 2–5 μg/liter total Se (Cardwell and others 1979, Lemly 1985b, North Carolina DNR&CD 1986).

Contamination of groundwater through the leaching of contaminants from land-disposed wastes is a prevalent pathway for the migration of some toxic substances into the environment. The USEPA (1980b) has addressed this problem by "developing a test procedure called the Extraction Procedure (EP) designed to identify wastes likely to leach hazardous concentrations of particular toxic constituents into the ground water under conditions of improper management." If the extract contains a contaminant concentration 100 times greater than that specified in the National Interim Primary Drinking Water Standards, the waste is to be considered dangerous. Drainage waters from agricultural lands could ostensibly be classified as leachates; however, irrigation return flows and solid wastes generated from the growing and harvesting of agricultural crops are excluded from solid wastes to which the Extraction Procedure is deemed to legally apply. Recyclability or reuse of agricultural drainage waters further complicates classification. In the case of Se, 1000 μg/liter is specified as the maximum allowable concentration in such an extract (USEPA 1980b), a concentration that has been exceeded in subsurface inflow waters of the San Luis Drain (1400 μg/liter). The absence of criteria for allowable levels of contami-

Table 1. Locations and chemical compositions of water tributary to and in the vicinity of KNWR (sites included KNWR ponds 2 and 11, the San Luis Drain, subsurface inflow waters for the San Luis Drain, and irrigation supply waters).[a]

	Se	Na	SO_4	K	Mg	Ca	HCO_3[b]	Cl	SiO_2	B	pH	Sp. cond.[c]
	(µg/liter)	(mg/liter)										(µS/cm)
KNWR												
Pond 2												
3 Aug 83	350	2750	5550	6.4	360	620	214	1950	1.2	18	7.87	12,000
Pond 11												
3 Aug 83	15	6259	11,500	19	705	765	397	4500	33	37	8.24	23,000
30 Nov 83	60	3150	6000	15	390	510	241	2400	7	19	8.75	13,000
San Luis Drain												
South end												
2 Dec 83	<2	30	48	3.6	9.4	29	140	11	9	<1	7.5	350
North end (near KNWR)												
3 Aug 83	330	2250	4700	6.2	320	565	158	1650	11	15	8.47	11,000
Inflow to pond 2												
30 Nov 83	280	2000	4100	5.7	260	460	204	1300	27	13	8.48	—
5 Apr 84	340	2150	4450	5.4	280	560	—	1500	2.2	15	8.70	10,000
Inflows to SLD[d]												
Ranges for 9 sites												
1–2 Dec 83	140–1400	935–10,500	2050–22,500	4.2–8.0	150–700	330–610	145–300	660–2750	26–48	5.4–79	7.8–8.5	5200–31,000
Irrigation Canals												
Delta–Mendota												
12 Oct 83	<2	40	44	1.7	11	22	62	57	11	<1	7.95	350
Main												
13 Oct 83	<2	49	90	1.3	12	20	59	36	11	<1	7.75	330

[a] Fluoride concentrations were <1.0 mg/liter and predominantly <0.5 mg/liter.

[b] Total alkalinity as bicarbonate (HCO_3).

[c] Specific conductance in microsiemens per centimeter (µS/cm) at 25°C.

[d] Complete data for the ranges of the San Luis Drain inflows are given in Presser and Barnes (1985).

nants in agricultural drainage waters as a specific class to be regulated is noteworthy.

Methodology and Speciation of Selenium in Water

Initial efforts to isolate the suspected toxicant Se were hampered by complex analytical methodology for aqueous samples. Chemical complexities involved both the high salinities present in the water samples and the existence of the different species or oxidation states that are known to exist for Se. These are: $SeO_4^{=}$, selenate (Se +6); $SeO_3^{=}$, selenite (Se +4); elemental selenium (Se 0); and H_2Se and organic forms, selenide (Se −2). The method of choice for the analysis of Se in water proved to be hydride generation with heated quartz tube atomization and detection by atomic absorption spectrophotometry (Pierce and Brown 1977, Gunn 1981, Nakahara 1983). Inherent in the hydride technique is the removal of the gaseous selenide from its interfering background, as the gas is physically purged from the liquid sample. Great care must be taken in sample pretreatment, in a method to determine total dissolved Se, to include steps that both digest organic Se and convert all forms to selenite, as only the +4 oxidation state is detected in the hydride method. After digestion of the sample, it proved imperative that conversion conditions used in the laboratory be optimized since too mild a reduction could lead to incomplete reduction of selenate and too rigorous a reduction to plating out of elemental Se (Cutter 1978, Presser and Barnes 1984).

Recovery of Se added to pond samples averaged 98%; results of Se analysis compared favorably with those from two independent laboratories (USF&WS and USGS Central Laboratory, Denver) and within specified limits of a standard reference water sample (Presser and Barnes 1984).

Since different sensitivities are exhibited for selenite and selenate in the hydride generation technique, this supposed disadvantage has potential for use in the selective determination of the different oxidation states of Se. Se in the alkaline agricultural drainage waters under study was found to be predominately in the form of selenate. It was estimated that failure to include the reduction step in the hydride generation technique could have accounted for up to 98% of the total Se not being measured initially in the agricultural drainage waters (Presser and Barnes 1984).

The theoretical basis for the prediction of large amounts of selenate in water appears to be absent in aqueous chemical equilibrium models. These models predict the presence of selenite rather than selenate, due to lack of sufficiently high oxidation potentials. The selenite oxyanions are strongly adsorbed onto ferric oxides, producing immobilization of Se (Hem 1970, Howard 1977). Soil–solution equilibrium models agree with this assessment in regions of acid soils, but predict the oxidation of selenite to selenate in moist, aerated alkaline soils. As selenate, Se is soluble, easily transported by water, and potentially highly toxic (Lakin 1961, Geering and others 1968, NAS 1976).

Bioaccumulation of Selenium

Se concentrations in Kesterson pond 11, the terminal pond receiving water in the evaporation scheme, were 15 μg/liter Se in August 1983 as compared with 350 μg/liter in pond 2 (Table 1). However, concentrations of sodium and sulfate increased from pond 2 to pond 11. An algal mat from pond 11 contained 13 ppm Se dry weight; a thenardite (Na_2SO_4) salt crust from the same location contained 1.8 ppm Se (dry weight) (Presser and Barnes 1984). Further, in the November 1983 sampling, pond 11 contained 60 μg/liter Se even though it was apparent from major ion data (Table 1) that the water in pond 11 had been diluted, probably by rainfall. Amounts of selenite in pond waters were estimated, by the differential hydride generation technique, to be 20%–30% of the total Se present, versus 2% in drainage water (Presser and Barnes 1984 and 1985). Although these samplings were not extensive, they did demonstrate that Se 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 were inorganic processes in surface water. Also, it appeared that biological processes were involved in the reduction of Se and its consequent entrance into the food chain.

Extensive collection of organisms eaten by aquatic birds at KNWR reflected biomagnification of Se in the food chain (Ohlendorf and others 1986a). The mean concentrations in filamentous algae, rooted plants, and net plankton at KNWR were 35–85 ppm Se (dry weight) in samples collected in May 1983. Mean concentrations in insects and fish from KNWR were 22–175 ppm Se. These means were approximately 12–130 times those found at VWMA where Se concentrations were <3 ppm. Highest mean Se concentrations occurred in midge larvae (Chironomidae, 139 ppm), dragonfly nymphs (Anisoptera, 122 ppm), damselfly nymphs (Zygoptera, 175 ppm), and mosquitofish (170 ppm). In the San Luis Drain itself, organic-rich sediments lining the canal showed concentrations of Se (dry weight) from 3.1 ppm to an exceptionally high 210 ppm (McClelland 1984); the highest levels occurred near discharging collector drains.

Observed Deformities and Tissue Analyses of Aquatic Birds

The adverse biological effects of elevated Se were most clearly manifested in birds. Species studied in the 1983 nesting season (April through June) in the ponds of KNWR included American coot (*Fulica americana*), mallard (*Anas platyrhynchos*), cinnamon teal (*A. cyanoptera*), gadwall (*A. strepera*), American avocet (*Recurvirostra americana*), black-necked stilt (*Himantopus mexicanus*), pied-billed grebe (*Podilymbus podiceps*), and eared grebe (*Podiceps nigricollis*). Of 347 nests followed through late incubation or hatching, 41% contained one or more dead embryos and 20% contained at last one embryo or chick with obvious abnormalities (Ohlendorf and others 1986a). Of 1681 eggs studied, 14.6% contained dead embryos and 6.3% contained abnormal embryos. Coots were the most severely affected, with 60% of the nests containing eggs with dead embryos, and more than 40% of the nests containing one or more abnormal embryos or chicks. The deformities included malformations of eyes, beaks, legs, wings, and brains (Figure 2). For comparison, three epidemics of teratogenicity in natural bird populations have been reported in recent years (Hoffman 1984, Hoffman and others 1987); dioxin was the suspected agent in two of the cases, and polychlorinated biphenyls (PCBs) and mercury in the third. The rate of abnormality in these cases was just over 1%; the rate was as high as 40% at KNWR.

The probability of embryo death or deformity (embryotoxicity) was found to be statistically related to Se concentrations in the egg, and both these factors are known to be influenced by dietary Se levels (Ohlendorf and others 1986b). Mean Se concentrations in eggs (dry weight) from KNWR were significantly ($p < 0.05$) higher than at VWMA for all species. For KNWR, eared grebe eggs averaged 69.7 ppm Se and coot eggs 30.9 ppm. These two species contained the highest frequency of embryotoxicity with 63%–64% of nests affected. Ducks and stilts had lower frequencies (23%–24% of nests) of embryotoxicity at KNWR; mean Se in eggs from these species ranged from 6.85 to 28.2 ppm. By comparison, mean concen-

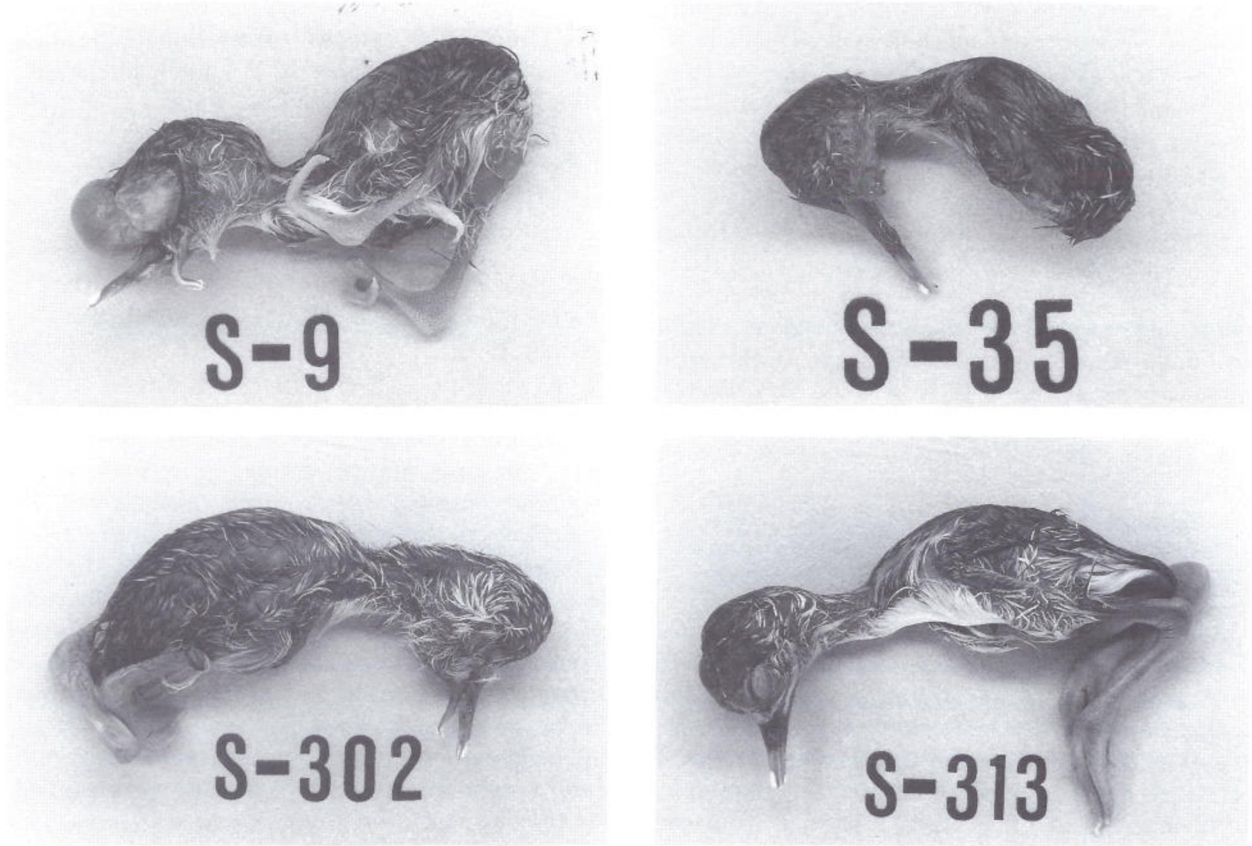

Figure 2. Black-necked stilt embryos from nests at Kesterson Reservoir: **(S-9)** Eyes missing, severe exencephaly through orbits, lower beak curled, upper parts of legs shortened and twisted, and only one toe on each foot. **(S-35)** Eyes missing, encephalocele, upper beak elongated and eroded at nostrils, lower beak missing, legs missing, and only one (small) wing. **(S-302)** Eyes missing, upper beak curved, lower beak shortened and tip of lower beak "hooked," hydrocephaly, edema in throat, legs twisted, and feet shortened with only one toe on each foot. **(S-313)** Normal.

trations in eggs from VWMA were generally below 2 ppm, and no abnormal embryos were found.

Mean Se concentrations in bird livers (dry weight) from KNWR were also significantly ($p < 0.001$) higher than in the same or comparable species at VWMA (Table 2). The means for the different species collected at KNWR ranged from 19.9 to 127 ppm and those at VWMA ranged from 4.4 to 8.8 ppm.

Necropsy of 13 coots and two grebes found dead or moribund at KNWR showed no evidence of infectious disease. The pathology observed was, both grossly and microscopically, suggestive of a toxic process and was diagnosed as Se toxicosis (Ohlendorf and others in press b).

The birds studied had consumed diets higher in Se than those concentrations (7–25 ppm) known to cause reproductive malfunctions in poultry. The teratogenic effects observed at KNWR were similar to those found in poultry and mallards in experimental studies (Poley and others 1937, Ort and Latshaw 1978, Heinz and others 1987).

Concentrations of Other Trace Elements, Nutrients, and Pesticides

Concentrations of most other trace elements in the pond and San Luis Drain waters were generally low except for manganese, which was variable (Table 3), and boron, which was consistently high (Table 1). Dissolved uranium measured 47 μg/liter and dissolved radium (Ra-226) 0.09 picocuries/liter for the inflow to Kesterson pond 2 in June 1985. Maximum levels of trace elements, other than those measured in the original study, for seven samples from the collector drains tributary to the San Luis Drain were (in μg/liter): arsenic, 2; beryllium, <10; chromium, 40; molybdenum, 190; and vanadium, 65 (Izbicki 1984). None of these trace elements reported exceeded the various criteria for water use at the level of magnitude of Se (USEPA 1977, 1978, and 1979). Concentrations of heavy metals in bird livers and in food organisms from KNWR were generally similar to those at the control area (Ohlendorf and others 1986a).

Table 2. Selenium concentrations in livers of adult aquatic birds at KNWR and VWMA, 1983 (concentrations are in ppm, dry weight; VWMA is the control site).

	VWMA			KNWR		
Species	n	Geometric mean	Range	n	Geometric mean	Range
Coots	16	4.41	1.7–9.1	17	43.1	7.2–100
Ducks[a]	13	8.41	2.8–20	14	19.9	3.1–62
Stilts	14	8.82	4.0–17	20	62.8	16–140
Grebes[b]	7	5.58	2.6–8.7	12	127	56–360

[a] Mallard, gadwall, and cinnamon teal.

[b] Pied-billed grebe at Volta; eared grebe at Kesterson.

Table 3. Other trace elements and nutrients in waters of the ponds of KNWR and the San Luis Drain.[a]

	Fe	Mn	Cd	Co	Cu	Ni	Pb	Zn	Hg	Organic carbon as C	NH_3-N
	(µg/liter)									(mg/liter)	
KNWR											
Pond 2											
3 Aug 83	40	<20	<20	<40	<20	<50	<100	<40	<0.1	18	<0.1
Pond 11											
30 Nov 83	60	60	<20	<40	20	56	<100	<40	<0.1	64	<0.1
5 Apr 84	<40	120	<40	<80	<40	<100	<200	<80	—	—	—
25 Jan 84[b]	79	14	<1	—	<1	7	2	30	<0.1	—	0.08
San Luis Drain											
North end (near KNWR)											
3 Aug 83	40	<20	<20	<40	<20	<50	<100	<40	<0.1	28	0.26
Inflow to Pond 2											
30 Nov 83	<20	450	<20	<40	<20	<50	<100	<40	<0.1	—	0.30
5 Apr 84	<20	<20	<20	<40	<20	<50	<100	<40	—	—	—
25 Jan 84[b]	60	420	<1	—	2	9	<1	20	<0.1	—	0.17

[a] H_2S concentrations were <0.5 mg/liter in all pond samples.

[b] From Izbicki (1984); Al concentrations for pond 11 and the inflow for pond 2 sampled on the same data were 20 and 40 µg/liter, respectively, which may include polymeric forms.

Boron (B) concentrations exceeded that recommended for long-term irrigation of sensitive crops, 750 µg/liter B (USEPA 1978), for 83% of the waters sampled (Table 1). The highest boron concentration of 79,000 µg/liter was found in a sample of an inflow to the San Luis Drain. Boron occurred at higher concentrations in plants, insects, and fish at KNWR than at VWMA, but little is known about the effect of boron ingestion on the reproduction of birds (Ohlendorf and others 1986a).

Results of organic carbon and ammonia (NH_3-N) analyses for pond and San Luis Drain waters are presented in Table 3. Nitrate estimates exceeded the criterion for health (10 mg/liter NO_3-N) (USEPA 1977), and were as high as 50 mg/liter NO_3-N in Kesterson pond 2 and the San Luis Drain waters, and 220 mg/liter in water from the inflows to the San Luis Drain (Presser and Barnes 1985).

Results of analyses for pond and San Luis Drain waters for herbicides and insecticides showed that all of the 28 compounds tested were below detection limits (Presser and Barnes 1985), except for the inflow from the San Luis Drain to Kesterson pond 2, which contained 0.06 µg/liter 2,4-dichlorophenoxy acetic acid (2,4-D) (Table 4). Organochlorine concentrations in mosquitofish from KNWR were below the limits of detection for tissue [10–50 parts per billion (ppb)] except for PCBs (60 ppb) and *p,p'*-DDE (22–44 ppb), which were present at low levels (Ohlendorf and others 1986a).

Further Studies in Kesterson National Wildlife Refuge and Adjacent Ecosystems

Kesterson National Wildlife Refuge

Monitoring studies by the USBR through 1984 (USBR 1985) confirmed the persistence of the high Se concentrations found in waters of the San Luis Drain and KNWR ponds. Based on the Se concentration, wastewater at KNWR was classified as a hazardous waste under two California state acts or codes in February 1985 (California SWRCB 1985). At the same time, the State Water Resources Control Board (SWRCB) issued an order to control conditions that cause any threat to wildlife or humans from operation of Kesterson Reservoir (California SWRCB 1985, USBR 1986). In April 1985, the US Department of the Interior reached an agreement with waste water dischargers to eliminate flows to KNWR by 30 June 1986 (USBR 1986). The State Board ordered the USBR to clean up the toxic wastes and/or upgrade Kesterson Reservoir to meet requirements for a hazardous waste surface impoundment at KNWR by February 1988 (California SWRCB 1985).

Adult coots were present at KNWR ponds throughout the 1984 and 1985 nesting seasons, but apparently failed to nest as no nests were found in the area in which 92 nests had been noted in 1983; coot populations were believed to be similar in 1983 through 1985 (Ohlendorf and others 1986b and in press b, Ohlendorf in press). The coots shot at KNWR in 1984, and those found dead, were severely emaciated; body weights averaged 25% below normal (Ohlendorf and others in press b). Other signs of toxicosis included lesions of and biochemical changes to the liver, excess fluid and fibrin in the peritoneal cavity, feather loss, and inability to fly. Mean Se concentrations in coot livers (81.5 ppm, dry weight) were significantly higher than in 1983. Due to these and other findings, the area was posted by the California Department of Health Services advising limitation of consumption of coots shot, with particular emphasis for children and pregnant women (Ohlendorf and others 1986a).

Table 4. Total herbicides and insecticides in waters of KNWR and the San Luis Drain (August 1983 and November 1983).

Herbicides and insecticides	μg/liter
Chlorinated phenoxy acid herbicides	
Silvex	<0.01
2,4-D	<0.01[a]
2,4-DP	<0.01
2,4,5-T	<0.01
Organochlorine insecticides	
Aldrin	<0.01
Chlordane	<0.1
DDD	<0.01
DDE	<0.01
DDT	<0.01
Dieldrin	<0.01
Endosulfan I	<0.01
Endrin	<0.01
Heptachlor	<0.01
Hepachlor epoxide	<0.01
Lindane	<0.01
Methoxychlor	<0.01
Mirex	<0.01
Perthane	<0.1
Gross polychlorinated biphenyls	<0.1
Gross polychlorinated naphthalenes	<0.1
Toxaphene	<1
Organophosphorous insecticides	
Diazinon	<0.01
Ethion	<0.01
Malathion	<0.01
Methylparathion	<0.01
Parathion	<0.01
Trithion	<0.01

[a] Sample of the San Luis Drain inflow to KNWR pond 2 contained 0.06 μg/liter 2,4-D.

It is estimated that a minimum of 1000 migratory birds (adults, embryos, and chicks) probably died or were seriously malformed during 1983–1985 as a result of feeding on food-chain organisms with elevated Se concentrations. This number includes a conservative estimate of 100 adult birds, 500 embryos and young chicks, and 400 other chicks that failed to survive primarily as a result of the toxic effects of Se (Ohlendorf in press). From March 1985 through February 1986, 45 migratory birds of various species were found dead within the San Luis Drain or KNWR (G. R. Zahm, USF&WS, personal communication 1986).

The Grasslands

In 1984, field studies were expanded to the wetlands and inflow drains of the Grassland Water District (Pressor and Barnes 1985, Ohlendorf and others in press a). This area, approximately 32 km (20 miles) to the south and east of KNWR and also in the floodplains of the San Joaquin River, includes approximately 21,044 ha (52,000 acres) (California SWRCB 1985). Most of this acreage is permanent or seasonal marshland managed for waterfowl through the use of diluted subsurface drainage water. It includes national and state wildlife refuges and over 200 duck-hunting clubs (USBR 1984a). The Grasslands are ultimately connected to the San Joaquin River and consequently provide a pathway to the San Francisco Bay.

These studies have shown the potential for effects of subsurface drainage in the Grasslands similar to those found at KNWR. Source waters that originate from tile drainage collector sumps, in an area where lands have most recently been reclaimed, yielded Se concentrations as high as 4200 μg/liter. Se concentrations in waters entering the Grasslands were reduced to an average of 50 μg/liter by dilution with larger inflows of irrigation supply, return, and drain waters. Se concentrations of pond waters, despite concentration by evaporation at the end of summer, were low (approximately 10 μg/liter); Se content of algal mat samples, which may contain some sediment, taken from these ponds was high (20 ppm, dry weight). The Se concentrations of some of the source waters were higher than those found flowing into the San Luis Drain, which caused the wastewater at KNWR to be classified as a toxic waste.

Se concentrations were elevated in livers of birds and in whole fish from all the areas of the Grasslands (Ohlendorf and others in press a). Highest concentrations occurred at the south end of the Grasslands area where subsurface drainage waters entered the area. Mean Se concentrations in avocet livers from the South Grasslands (67.3 ppm, dry weight) were significantly higher than those from KNWR (28.4 ppm); and those in stilt livers from the South Grasslands (35.6 ppm) were not significantly different than those from KNWR (46.4 ppm) during the same year.

Two conclusions can be drawn from the above data: (a) If the correlation between Se concentrations in tissue and subsequent impairment of reproductive success follows that of KNWR, then Se-induced embryotoxicity in aquatic birds probably occurred in the Grasslands during 1984. A small number of nests was sampled, but the sampling was inadequate to assess reproductive success in these birds. However, as the result of our studies, irrigation supply water, not agricultural return water, was provided in September 1985 as a source of flooding for these ponds for bird habitation. (b) Our findings also demonstrate that elevated Se levels in biota and water from the Grasslands are an effect of subsurface agricultural drainage water, which originates in a different location within the valley with a different dilution history than the water in KNWR.

San Joaquin River and San Francisco Bay

The San Joaquin River, as the only natural outlet from the valley, receives discharge from approximately ten times the amount of subsurface drained acreage as the San Luis Drain (California SWRCB 1985). Cautions are raised not only for the river, but also for the ultimate fate of the Se-laden agricultural drainage water in the San Francisco Bay Delta Estuary (Figure 1). Sources and flow patterns are not as direct as those for KNWR and few data have been specifically collected for the element Se in the bay, although studies are now under way. In 1982, from the southern San Francisco Bay, two species of diving ducks that feed on shellfish, greater scaup (*Aythya marila*) and surf scoter (*Melanitta perspicillata*), had Se levels of 19.3 and 34.4 ppm, dry weight, respectively, in their livers. These levels of Se are similar to those in dabbling ducks (primarily herbivores and insectivores) from KNWR in 1983, and higher than the mean (10.8 ppm) for surf scoters collected from Humboldt Bay, a coastal "control" site, by the California Department of Fish and Game (Ohlendorf and others 1986c, California DFG and SWRCB 1986).

These studies from KNWR, the Grasslands, and, in a more general way, the San Francisco Bay emphasize that the basis of prevention of contamination must be formulated on the ecosystem level and include the concept of food-chain accumulation. These studies also point out that the indication of contamination cannot rely solely on the determination of Se in water.

Groundwater Recharge

In general, irrigation subsurface drainage in the study area is a form of recharge whose effects on the main groundwater bodies need to be considered. The San Joaquin Valley is underlain by an extensive regional aquifer (the upper and lower water-bearing zones divided by the Corcoran Clay member of the Tulare Formation) that is used as an irrigation and drinking-water supply (Davis and Poland 1957, California SWRCB 1985). Pollutants could reach the lower high-quality water-bearing zones through wells perforating shallower zones that are screened or gravel packed from surface to bottom. In the Mendota–Five Points area alone, 1000 irrigation wells were present in 1951 (Davis and Poland 1957).

It has also been shown from a monitoring study by the USBR (USBR 1984b and 1986, California SWRCB 1985) that as much as 60% of the water that enters the Kesterson ponds is lost by downward seepage rather than evaporation. The USBR has concluded that the path of seepage follows the historical shallow groundwater gradient to the northeast. Flows would then contribute to Mud Slough in the northwest and to Salt Slough in the east; both sloughs flow into the San Joaquin River. Although Se dissolved in the water could be reduced and remain in the sediments of the ponds, sand lenses under the Kesterson site could provide direct conduits to the sloughs and hence to the river. The time sequence of this contamination would then depend on rate of groundwater movement. Evidence for both processes has been reported (USBR 1984b and 1986).

Selenium Cycling

Steps chemically favored in the inorganic cycling of Se include weathering of elemental Se or metallic selenides (for instance, ferroselite, $FeSe_2$) in the parent rocks or sediments (mainly in the mineral pyrite, FeS_2) to selenite under acidic and reducing conditions, and selenate under alkaline and oxidizing conditions (Lakin 1961, NAS 1976, USEPA 1979). Selenite forms stable ferric oxide–selenite adsorption complexes (Geering and others 1968) and selenate forms compounds that are soluble and therefore mobile (Lakin 1961).

The reverse of these oxidative steps would be diagenesis, in which biological processes play a major or catalytic role (Berner 1984); these same processes appear to be involved in the reduction of Se and its consequent entrance into the aquatic food chain (NAS 1976). Lipman and Waksman in 1923 and Shrift in 1964 proposed a biological Se cycle similar to the cycles for sulfur, carbon, and nitrogen. The characteristics that these cyclable elements have in common are that the elements exist as a gas in at least one stage of transformation, and that the elements undergo a change in oxidation state (Konetzka 1977). Both of these conditions are met by Se in biological systems. Selenate or selenite in cellular metabolism, in sediments, or at the sediment–water interface is reduced to the -2 volatile oxidation state, which may include methylated selenides. Evidence for the reverse cycle of oxidation of selenides and elemental Se to selenate by microorganisms has been discovered more recently (Geering and others 1968, Torma and Habashi 1972, Ehrlich 1978). The process further includes a recycling of Se in soluble and insoluble phases similar to those involved in the recycling of sulfur by *Thiobaccilus ferrooxidans*. Involving areas such as KNWR or the Grasslands in the cycle adds the dimension of food-chain bioaccumulation.

The nine actively inflowing waters to the San Luis Drain from the west, Kesterson pond 2, and the San Luis Drain water were all found to be sodium–sulfate waters (Table 1). Percent sodium ranges from 55% to 92% of the total cations, and sulfate from 54% to 85% of the total anions. The concentrations of sodium and sulfate ($r = 0.99$) and the concentrations of sulfate and Se ($r = 0.96$) in these waters were significantly ($p < 0.01$) correlated, showing that these elements are highly related. Through the use of a solution–mineral equilibrium model (Kharaka and Barnes 1973), the minerals mirabilite ($Na_2SO_4 \cdot 10H_2O$), thenardite (Na_2SO_4), and gypsum ($CaSO_4 \cdot 2H_2O$) were predicted to be associated with waters on the valley floor (Presser and Barnes 1985). These minerals were also identified in the Coast Ranges bordering the western San Joaquin Valley in 1977 (Murata), and more recently in our studies. During both studies in the Coast Ranges, magnesium sulfates and mixed sodium and magnesium sulfates were also found [for example, epsomite, $MgSO_4 \cdot 7H_2O$; and bloedite, $Na_2Mg(SO_4)_2 \cdot 4H_2O$]. Due to the similar chemical and physical properties of sulfur and Se, the inorganic uptake of Se as selenate in these sulfate evaporite or efflorescent minerals is now being evaluated as part of our continuing research on the source of Se in the San Joaquin Valley. In our preliminary results: on the valley floor, a sample of thenardite from the San Luis Drain contained 17 ppm Se; from the foothills, a sample of gypsum used locally as a soil amendment contained <0.5 ppm Se; and from higher elevations in the Coast Ranges, samples of sodium, magnesium, and mixed sodium and magnesium sulfates contained 2–14 ppm Se. Sodium–sulfate seep and stream waters from the Coast Ranges contained up to 2000 μg/liter Se. Samples of unweathered potential source material, pyrite, obtained from the cuttings from a 4877-m (16,000-foot) well, located on the valley floor near Mendota, contained up to 11 ppm Se. It may be concluded that recycling processes are at work both over geologic time in the Coast Ranges and their alluvial fans, and, on a smaller time scale but in a more complex way, in KNWR.

In a preliminary study by the US Department of the Interior on water quality in other areas of the western United States containing seleniferous source rocks, 18 of 23 sites using irrigation return flows, the majority of which are from USBR water projects, have been identified as needing further study (USDOI 1985). The existing information, however, suggests reason for concern for fish and wildlife, particularly in view of the studies conducted at KNWR and the Grasslands. The USBR has about 220 projects or units from which irrigation return flows discharge into refuge areas or into receiving water bodies used for drinking-water supply, irrigation, or recreation (USDOI 1985 and 1986).

Implications for Humans

The difference between essential and toxic dietary intake ranges of Se in humans is narrow. The National Academy of Science (NAS 1980) has defined the essential requirement in humans to be 50–200 μg Se/day, whereas 500 μg/day is defined as toxic to adults (Sakurai and Tsuchiya 1975, Lo and Sandi 1980, USEPA 1980c, Greenberg 1985). Safe and adequate ranges of daily Se intake vary by about 1 order of magnitude between infants and adults (10 μg/day vs 200 μg/day). The question of the chemical form of Se ingested has not been extensively addressed, but the form is known to affect toxicity (NAS 1976).

Se is an essential nutrient (Schwarz and Foltz 1957), and most reviews of Se biochemistry emphasize aspects of deficiency (Muth and others 1967, Allaway 1968, NAS 1976 and 1977, USEPA 1980c, Spallholz and others 1981, Shamberger 1983, Wilber 1983). Se toxicity can result in gross pathology analogous to that of Se deficiency as studied in animals, including impaired reproduction (Shamberger 1983, Wilber 1983). Stadtman (1974) has suggested that Se toxicity at the biochemical level results from incorporation of Se-containing amino acids into proteins in place of S-containing amino acids, thereby altering protein (enzyme) functions (Wittwer and others 1984, Zinoni and others 1986, Sliwkowski and Stadtman 1987).

Few reports of Se toxicity in humans have been published. In 1983, Yang and others described an endemic Se intoxication discovered in 1961 in Enshi County, Hubei Province, of the People's Republic of China; the average incidence was 50% in the inhabitants of the five most affected villages. Se from a stony coal entered the soil by weathering and was available from alkaline soils for uptake by crops. Daily dietary intake of Se averaged 4990 μg. The most serious effect of Se intoxication in adult humans was on the nervous system, to which one death was attributed. No data were reported for the effects on infants or newborns. Yang and others concluded, however, that young livestock in the area were the most sensitive indicators for the detection of selenosis; these effects included deformities of embryos. No reliable studies of Se concentrations in irrigation water versus Se concentration in food crops specifically from the western San Joaquin Valley are available to date.

According to the NAS (1976), inhibition of growth may be the best indicator of Se toxicity (USEPA 1980c). In studies involving the growth of cells, Se and Se-containing compounds have been reported to have a number of biological effects, including a mutagenic effect in the Ames' *Salmonella* assay (Noda and others 1979, Russell and others 1980), as well as in cultured animal cells (human fibroblasts) (Lo and others 1978), and activation of murine retroviruses in cultured AKR cells (mouse-embryo fibroblasts) (Rascati 1983). Addition of Se compounds to cultured animal cells has resulted in a concentration-dependent inhibition of proliferation (Rascati 1983), the mechanism of which is unknown. This inhibition of cell proliferation may underlie the reported suppression of the immune system in chicks (Marsh and others 1981), and could also account for the generation of multiple congenital anomalies and sterility if elevated Se concentrations were present in an organism at critical development stages where rapid cell proliferation and morphogenetic movement were occurring.

If these systems are particularly sensitive to Se status and if the effects take place at levels just above deficiency and below toxicity, the following statement by the NAS in an attempt to establish a "no effect" dose level for Se becomes particularly relevant (NAS 1976, USEPA 1980c):

> In consideration of the probable importance Se plays in the human diet, and the varied but definite exposure potential from food intake, drinking water, and other sources, the strategy for identifying a criterion level for ambient waters must be based on minimizing the likelihood of contributing a sufficient amount of Se that would increase an average total exposure above a selected toxic level.

Concluding Perspectives

The unique environment created in the San Joaquin Valley has provided all the conditions necessary for Se cycling. A geologic source is provided in the Cretaceous and Tertiary marine sediments of the Coast Ranges. Inclusion mechanisms of Se into sulfur minerals and salts are provided by diagenetic and weathering processes. Transport mechanisms are provided by the geomorphological processes of alluvial fan building, which include mass wasting and stream runoff. Concentrating mechanisms are provided by shallow clay barriers and evapotranspiration in the arid climate. Mobility of Se in water as selenate is provided by the alkaline and oxygenated conditions in sediments and soils. Irrigation leaches the salts, including Se, into the shallow groundwater that in some places is drained to surface canals by subsurface tile systems. Until 1986, the San Luis Drain collected subsurface drainage and transported it to KNWR, where it was available for uptake by organisms in the food chain.

Bioaccumulation mechanisms by plants and animals in the KNWR food chain include chemical reduction and methylation reactions of Se and replacement of sulfur by Se in sulfur-containing amino acids; uptake mechanisms by inorganic salts and sediments include substitution of selenate for sulfate and adsorption of selenite on ferric oxide surfaces. Elemental Se and gaseous selenide may also be generated, to either precipitate out as an insoluble form in sediments in the former case, or be released into the atmosphere in the latter. Oxidative reactions at any stage in these processes lead to recycling. Biomagnification of Se in organs of higher food-chain organisms through diet leads to impaired reproduction in birds and fish. Toxicity studies of cells of higher organisms show impaired reproduction, inhibition of growth, mutagenesis, and suppression of the immune system.

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