DISSOLVED CONSTITUENTS INCLUDING SELENIUM IN WATERS IN THE VICINITY OF KESTERSON NATIONAL WILDLIFE REFUGE AND THE WEST GRASSLAND, FRESNO AND MERCED COUNTIES, CALIFORNIA

By T. S. Presser and Ivan Barnes

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CONVERSION FACTORS

For use of readers who prefer to use metric units, conversion factors are listed below.

Multiply	By	To obtain
acre	4047	square meters (m^2)
foot (ft)	0.3048	meter (m)
mile (mi)	1.609	kilometer (km)
acre-foot (acre-ft)	1233	cubic meters (m^3)
micromhos per centimeter (μmhos/cm) at 25°C	1.000	microsiemens per centimeter (μS/cm) at 25°C

By weight:

micrograms per gram (μg/g) is equivalent to parts per million (ppm)
1 microgram (μg) = 10^{-6} gram (g)

For concentrations of dissolved solids less than approximately 7000 mg/L:

milligrams per liter (mg/L) is equivalent to parts per million (ppm)
micrograms per liter (μg/L) is equivalent to parts per billion (ppb)
1000 micrograms per liter (μg/L) = 1 milligram per liter (mg/L)

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ABSTRACT

Analyses were made for dissolved constituents including selenium (Se) in waters associated with subsurface agricultural drainage from the western San Joaquin Valley of California. In the vicinity of Kesterson National Wildlife Refuge and the Grassland wetlands area Se was found to be mobilized in water. As a consequence of this mobility and bioaccumulation in the aquatic food chain, Se occurred in waterfowl at levels toxic enough to cause deformities and deaths.

Se concentrations in sumps that collect subsurface agricultural drainage water and inflows to drains sampled, ultimately leading into Kesterson National Wildlife Refuge and the Grassland, ranged from 84 to 4,200 micrograms per liter (μg/L) Se. Levels of Se were reduced in the San Luis Drain flowing into Kesterson National Wildlife Refuge to approximately 300 μg/L Se and in three of the drains sampled flowing into the Grassland to approximately 50 μg/L Se. Serious effects on waterfowl habitat were caused by both these levels.

Se contents of algal mats and salt crusts from evaporation ponds or the San Luis Drain contained up to 20 parts per million Se. Total ecosystem assessment of Se may be necessary for the evaluation of the toxicity of Se to the environment. No other trace element reported exceeded the various criteria for water at the level of magnitude of Se.

Other dissolved constituents and the isotopic ratios of oxygen ($^{18}O/^{16}O$) and hydrogen (D/H) were analyzed to elucidate water types, reaction states of the aqueous solution with respect to minerals, and the origin of mixed waters. These data will be used later to evaluate the geologic source of Se. Methods used for collection and analysis are described and documented. Hydrologic effects were found to be complex. Preliminary indications from wells are also given. A historical sequence is adhered to and other data from the study area which serve as a guide to the toxicity of Se are included.

INTRODUCTION AND RECENT HISTORY OF SELENIUM TOXICITY

In May 1984, high levels of selenium (Se) were reported in waters tributary to and in the vicinity of the Kesterson National Wildlife Refuge (KNWR) located in the northwestern San Joaquin Valley of California (Presser and Barnes, 1984). The KNWR is the terminus for the San Luis Drain (SLD), an 85-mile concrete-lined canal carrying subsurface irrigation return flow from approximately 8,000 acres of farmland (Figure 1). It was built by the U.S. Bureau of Reclamation (USBR) in the period from 1968 to 1975. Beginning in 1981, the estimated volume of drainage water entering the 12 interconnected evaporation ponds (1,280 acres) at KNWR (5,900 acres) was approximately 7,000 acre-feet annually (USBR, 1984a and b). Water from the north end of the SLD at or near its discharge into Kesterson pond 2 contained 330 micrograms/liter (μg/L) Se in August, 1983, and 280 μg/L in December, 1983. Source subsurface agricultural drain water entering the SLD contained from 140 to 1,400 μg/L Se in samples taken in December 1983. Wastewater at KNWR was classified as a hazardous waste under two California state acts or codes in February, 1985 (SWRCB, 1985). Concentrations of Se in irrigation supply waters sampled in the vicnity of KNWR, but not receiving subsurface drainage water in October, 1983 (e.g. Delta-Mendota Canal and the Main Canal), contained <2 μg/L Se (Presser and Barnes, 1984).

Se concentrations in Kesterson pond 11, (Figure 2) the last pond to receive water and where flow normally terminates in the evaporation scheme, contained 15 μg/L Se in August, 1983. However, concentrations of sodium (Na) and sulfate (SO_4) increased from pond 2 to pond 11. An algal mat from pond 11 contained 13 parts per million (ppm) Se (dry weight). A thenardite (Na_2SO_4) salt crust from pond 11 contained 1.8 ppm Se (dry weight). Further, in the December, 1983 sampling, pond 11 contained 60 μg/L Se even though it was apparent from the isotopic and Na data that the sample had been diluted with rainwater. Although this sampling was not extensive, it does show that Se lost from solution in the ponds can enter the food chain through uptake by algae and that organic processes are probably more effective in removing Se than inorganic processes in surface water (Presser and Barnes, 1984).

It has since been shown from a monitoring study by the USBR (1984e) that as much as 60% of the water that enters the Kesterson ponds is lost by downward seepage rather than evaporation. Thus, the evaporation ponds are also recharge ponds which move water to saturate underlying permeable alluvial

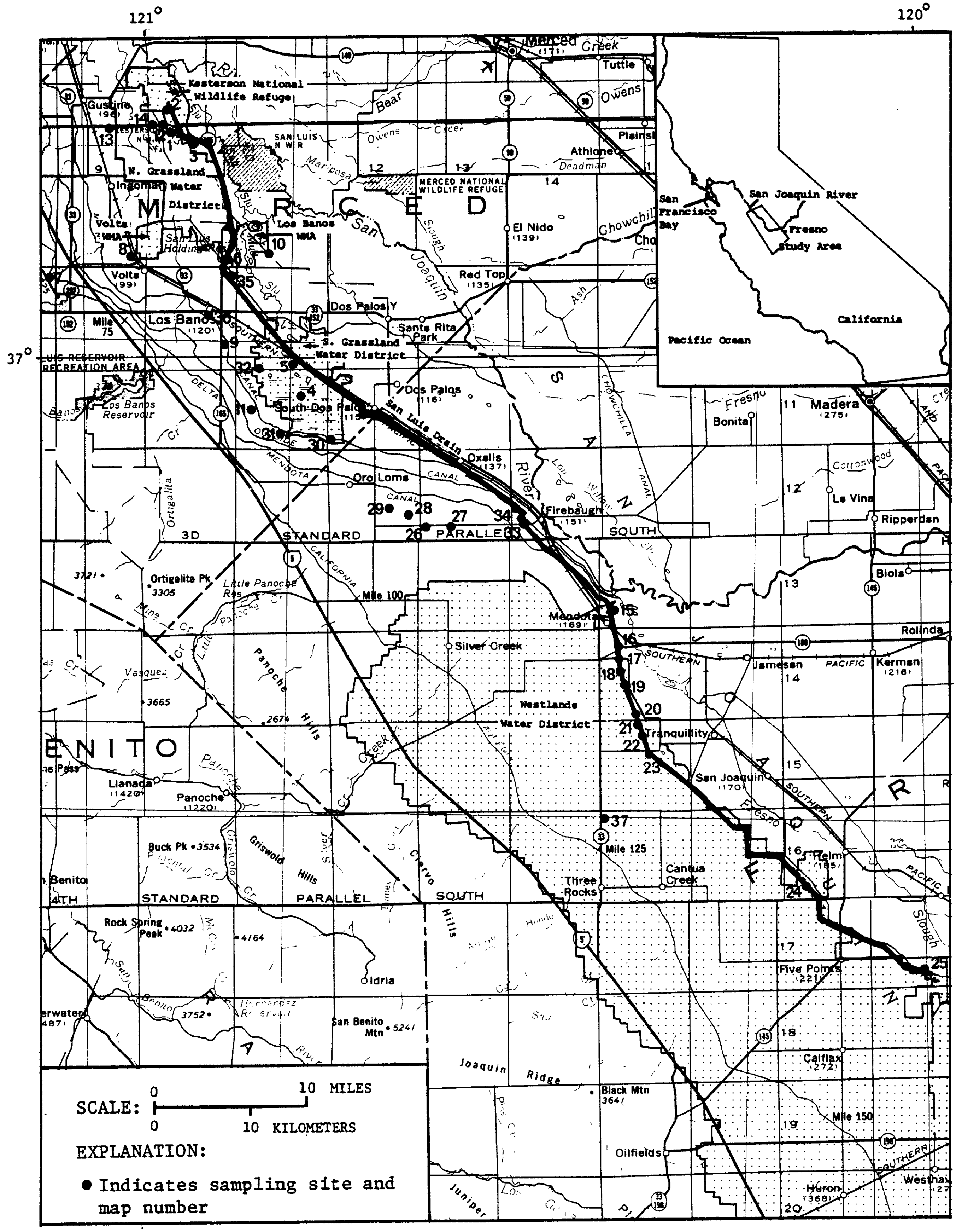

Figure 1.--Study area and sampling site locations in the San Joaquin Valley, California.

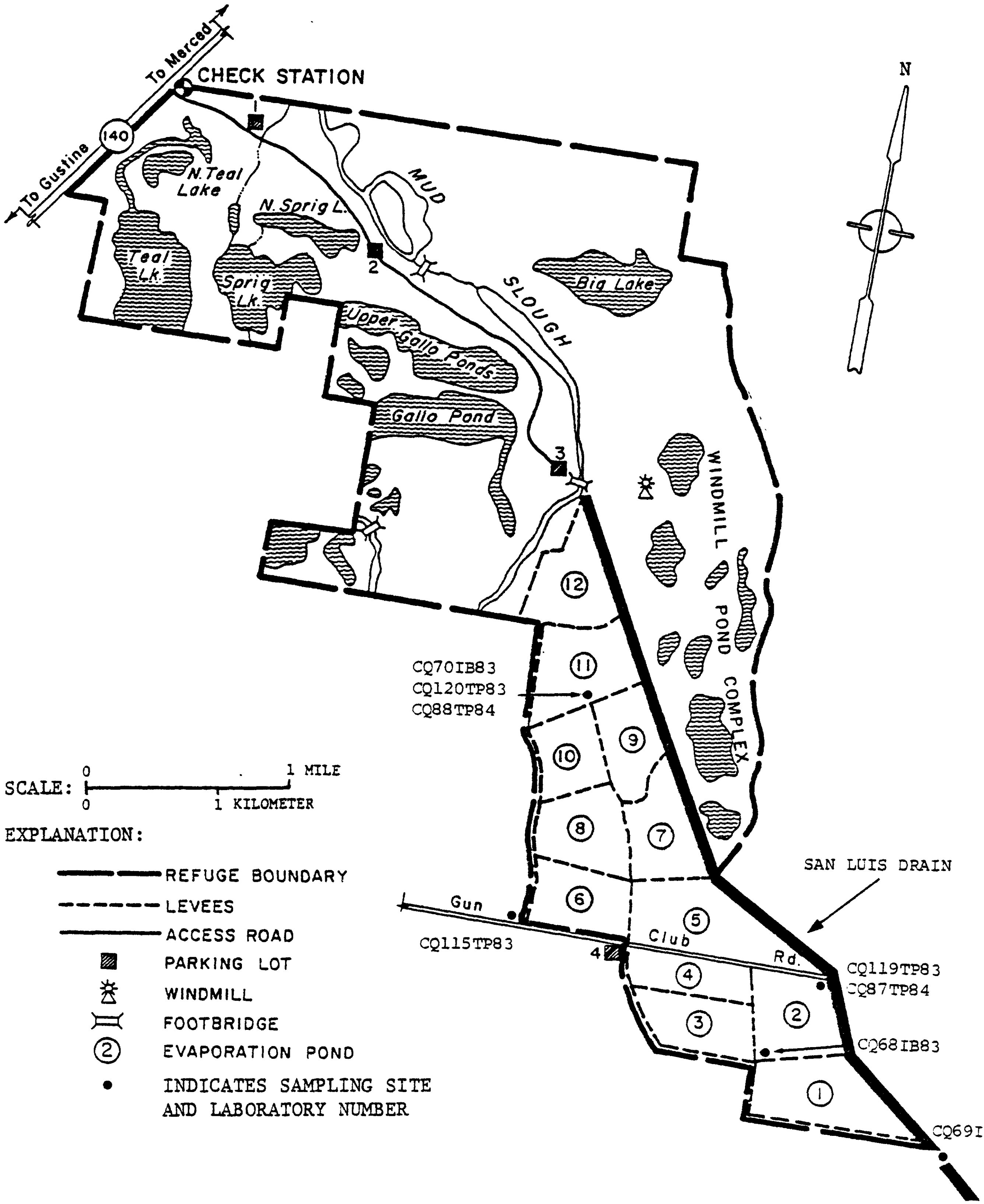

Figure 2.--Sampling site locations in Kesterson National Wildlife Refuge. (Map modified from State of California, Department of Fish and Game.)

sediments (Thomas, 1984a and b). Ground water monitoring data has not clearly shown the path of seepage, but the USBR (1984e) has concluded that it follows the historical shallow ground water gradient to the northeast. Flows would then contribute to Mud Slough in the north and the San Joaquin River in the east.

Two other reports addressing the problem of high levels of dissolved salts and minerals, including Se, in waters of the western San Joaquin Valley which includes the area of the KNWR have since been published: Izbicki (1984) and Deverel and others (1984). Data presented for Se by Izbicki for Kesterson ponds were similar to the data of Presser and Barnes, 1984. Both Izbicki and Deverel included data for waters from collector drains for the SLD system. These samples were collected during January, 1984 to June, 1984; values ranged from 140 to 1,400 μg/L Se. Sampling by Deverel also included shallow ground water taken at 130 sites during May 5-21, 1984 in the San Luis Drain Service Area. Twenty-one chemical constituents were determined including eight of the priority pollutants (arsenic, cadmium, chromium, copper, lead, mercury, selenium and zinc) designated by the U.S. Environmental Protection Agency (USEPA, 1979). The dominant ions in most samples were sodium and sulfate. The median and maximum Se concentrations found in the three different physiographic zones of the western San Joaquin Valley are: (1) the alluvial fan zone along the eastern edge of the Coast Ranges of California, 11 μg/L and 3,000 μg/L Se; (2) the basin rim zone, 10 μg/L and 3,800 μg/L Se; and (3) the basin trough zone adjacent to the San Joaquin River, <1 μg/L and 90 μg/L Se.

These studies were in response to observations by the U.S. Fish and Wildlife Service (USF&WS) of unusually high rates of deformity and death occurring in hatchlings of wild waterfowl (up to 40% for coots) in KNWR in the 1983 nesting season (Felix Smith, USF&WS, oral commun., July 7, 1983; Ohlendorf, 1984a; USBR, 1984b). KNWR is jointly managed by the USF&WS and the USBR (USBR, 1984e). Since that time, data have been collected by the USF&WS on aquatic food chain materials from KNWR which show the presence of high levels of Se when compared to material collected from the Volta Wildlife Management Area (VWMA), Figure 1, which receives little subsurface drainage. In Kesterson the geometric mean concentration of Se on a dry weight basis for samples collected in August, 1983 (M. Sakai, USF&WS, preliminary unpub. data, Dec., 1984) are: in algae from pond 2 (periphyton), 246 parts per million (ppm), and from pond 11 (filamentous algae), 24 ppm; in macrophytes (widgeon grass) from pond 2, 216 ppm, and from pond 11, 61 ppm; in aquatic insects (dragon fly nymphs) from pond 2, 171 ppm and from pond 11, 53 ppm; and in detritus from pond 2, 36 ppm, and from pond 11, 68 ppm. Plankton (net) collected in May, 1983 from pond 2 contained 83 ppm Se and from pond 11, 68 ppm Se. For comparison the values for VWMA on a dry weight basis are: in filamentous algae <1 ppm; in macrophytes ≤1.2 ppm; in aquatic insects ≤3 ppm; in plankton, ≤2.9 ppm; and in detritus ≤2.1. Concentrations of Se in mosquito fish, the only species of fish remaining in KNWR after 1981, were as much as 100 times higher than those of fish from VWMA in 1982 (USBR, 1984b and d). Se concentrations on a dry weight basis in mosquito fish taken in August, 1983 are: from KNWR pond 2, 247 ppm; from KNWR pond 11, 104 ppm; and from VWMA ≤1.4 ppm.

Suspected pathology from observation of deformed embryos and hatchlings and dead birds were substantiated by data from tissue analysis of a large sampling of both migratory and resident birds in both the 1983 and 1984 nesting seasons (Ohlendorf, 1984b). In 1983, Se concentrations (dry weight) in livers of adult and juvenile coots averaged 67.8 ppm from KNWR whereas those from VWMA averaged <5 ppm. In 1984, the Se concentrations in livers from dead or moribund coots ranged from 54 to 140 ppm (mean 83.7); from live coots, Se concentrations averaged 86 ppm. Both these values are considered significantly higher than the 1983 values. No nests of adult coots were found in 1984 in areas where 100 nests were found in 1983. The incidence of these abnormalities and deaths have been attributed by the USF&WS to Se poisoning (toxicosis) (USBR, 1984d and R. K. Shroud, USF&WS, written commun., 1984).

Concentrations of Se in ponds of Kesterson reported by the USBR (1984e) representing an average concentration of monthly samples collected during March-June, 1984, range from a high of 390 μg/L Se at the weir between ponds 5 and 7 to a low of 61 μg/L in pond 12. For the entry point from the SLD to pond 2, the average concentration during March-June, 1984, was 430 μg/L Se. In January, 1985, the USBR reported 270 μg/L Se for the inflow to pond 2. Further data collected by the USBR show levels of Se in the SLD water and the collector drains which discharge into the SLD continue to remain at concentrations similar to those originally reported.

To characterize the mechanism of the mobilization of Se in the subsurface irrigation waters that lead into KNWR, major element chemistry and isotopic compositions of the waters collected for Se analysis by Presser and Barnes in

August through December, 1983 and April, 1984 were determined and are reported. To rule out other types of contamination that might be involved in waterfowl toxicity, trace elements other than Se and pesticides were determined on waters from the Kesterson ponds and the SLD.

Subsurface waters in the SLD Service Area but not draining into the KNWR (USBR, 1984c; 1984d) were also studied for the present report. These samples were collected in June and July, 1984 and analyzed for the same major and minor elements. The sampling sites included collector sumps, agricultural drains and ponds. Trace elements were again determined on pond samples. These waters originate as do the inflows to the SLD, in collector sumps for drainage from irrigated agricultural fields affected by salt buildup in the west-central San Joaquin Valley (USBR, 1984a). Some of these waters also terminate in waterfowl ponds in an area collectively referred to as the Grassland Resource Conservation District. This area consists of 75,000 to 64,000 acres in the western flood plains of the San Joaquin River. KNWR is at the north end of this general wetland area. These grasslands are marsh and pasture lands which again provide important wintering habitat for waterfowl on the Pacific Flyway (USBR, 1984d). Over 200 duck hunting clubs are contained in this area and if the 45,000 acres to the east of the San Joaquin River are considered along with it, it is the largest tract of natural grassland remaining in the San Joaquin Valley. The largest water district in the area is the Grassland Water District (Grassland) which contains 52,000 acres of privately owned and managed wetland. Figure 1 shows the borders of the Grassland. The northern area contains approximately 31,000 acres and borders the KNWR and VWMA. The southern area contains 21,000 acres and includes Los Banos Wildlife Management Area (LBWMA). Data presented to the State Water Resources Control Board (SWRCB, 1985) stated that in 1981 the USBR (unpub. data) estimated that 53,000 acre-feet of tile drainage was discharged into this general wetland area west of the San Joaquin River. Of this amount, 7,160 acre-feet were distributed to Kesterson Reservoir, 28,700 acre-feet to the Grassland, and the remainder (17,140 feet) to the San Joaquin River. More recent estimates are that from 28,000 to 40,000 acre-feet of tile drain water are currently being discharged into the Grassland which receives drainage from approximately 18 entities (SWRCB, 1985).

Unlike Kesterson however, Grassland receives mixed agricultural drainage including surface waters (tailwater and freshwater), in addition to subsurface drainage (USBR, 1984d). Further, the USBR provides 50,000 to 53,000 acre-feet of Class I water to the Grassland annually for flooding of waterfowl habitat during September and November (SWRCB, 1985). Also unlike Kesterson (a closed marsh), Grassland is operated theoretically as an open system where water forms temporary ponds in winter, is flushed or drained into the San Joaquin River in spring and is irrigated in summer to generate forage (USBR, 1984c; SWRCB, 1985). Although substantial subsurface drainage to KNWR started in 1978, tile drains have been installed for subsurface drainage in the San Joaquin Valley since 1960 (U.S. Department of the Interior, 1985). F. E. Smith, USF&WS, (personal commun., Feb., 1985) concludes that it is reasonable to believe that tile drainage water of unknown composition has been entering the Grassland area for the past 15 to 20 years. More evidence on this issue is given by Greenberg and Kopec (1985) who point out that more lands with soils containing high levels of salts and trace elements were put into production with the availability of increased supply of irrigation water from the Delta-Mendota Canal which was installed in the early 1950's. Drainage from these lands has been transported into the San Joaquin River via the Grassland for the last 30 years.

Water samples from three wells in the sampling area were also collected in the present study. The analysis of the deepest well is a clarification of the data given in Deverel and others, 1984. Deverel and others (1984) reported Se analyses of waters from four wells tapping the regional aquifer. They found that the three municipal wells sampled, whose depth ranged from 205 to 335 feet, yielded water containing <1 μg/L Se and the deeper irrigation well (1,089 feet deep) yielded water containing 118 μg/L Se. However, Deverel reported adverse conditions which prevented sufficient pumping time for the deep well sample to assure a representative sampling of the penetrated aquifer. These samples are preliminary to a comprehensive study which has been started by the USGS in 1985 of Se and other inorganic chemical constituents in both the upper and lower water-bearing units of the regional aquifer. Davis and Poland (1957) among others have described these zones separated by the Corcoran Clay Member of the Tulare Formation and their complex hydrologic relationships.

Based on the various uses of water, several maximum-concentration criteria and standards have been established for Se. The USEPA (1977b) has set a maximum limit for public drinking water supplies at 10 μg/L Se. The agency also specifies 1,000 μg/L Se as the concentration of Se in waste that will qualify it as hazardous (USEPA, 1980) provided the source is not exempt. The USEPA 1980 water quality criterion for protection of freshwater aquatic life is <35 μg/L Se (24 hour average) as inorganic selenite. Bioconcentration factors range from 100 to 2,600 for algae and from 200 to 6,000 for fish (Brooks, 1984). The USEPA (1979) found the factors to range from 400 to 800 in freshwater and marine plants, invertebrates and fish. Food was found to be the most important source of Se for fish. Ohlendorf (1984b) found algae and aquatic plants as the most common food in coots that were shot. Seeds become an important source of protein for waterfowl during the breeding season. High incidence of embryo mortality and abnormality in birds occur when diets contain 7-10 ppm Se (Ohlendorf, 1984b). Levels of 9-12 μg/L Se in water have been associated with declines of lake fish densities in Belews Lake and Hyco Reservoir in North Carolina (Baumann and May, 1984).

Microorganisms have been shown to be effective agents in concentrating metals from solution. Studies involving uranium, selenium and molybdenum by Brierly (1981) showed enrichments are likely to occur at the sediment-water interface, where reducing conditions occur in contrast with water, in which oxidizing conditions prevail. Insoluble, soluble recycling of Se is also postulated by Shrift (1964) in reactions similar to those involving sulfur. It is known that microorganisms convert or detoxify soluble Se salts by use of the enzyme selenoreductase (NAS, 1976; Brierly, 1981). Red elemental Se (Se^{o}) is seen to form in these cells. Thiobaccilus ferrooxidans is known to convert copper selenide to Cu^{++} and Se^{o} (Torma, 1972). These studies elucidate the problem of what phase to assess in setting limits for the protection of an ecosystem. The concentration of soluble Se versus incorporated or particulate Se may be of importance, since, as Brierly states, the concentrated elements could be released back into the system as soluble ions or remain as accumulated elements in dead organisms at the bottom of ponds. These accumulated elements would then be available for eventual recycling. Greenberg and Kopec (1985) give evidence that Se concentrations in water cannot fully explain the Se levels found in fish samples in the San Francisco Bay/Delta/San Joaquin River estuary. They suggest that Se mass loading of the estuary rather than Se concentrations may be the determining factor in producing adverse effects in aquatic organisms, fish and wildlife, including a decline in fisheries. Se contamination (exposure and uptake) they continue, must be based on an ecosystem approach including food chain accumulation rather than relying only on determinations of Se in water.

Information concerning the nutritional requirements and toxic effects of Se in humans is given by Greenberg, 1985. He cites the 1977 and 1980 levels for Se ingestion in normal adults given by the National Research Council: adequate and safe levels, 20 to 200 μg/day; average U.S. dietary intake, 170 μg/day; and estimated toxic level, 500 μg/day. Not only is there a small margin of safety, he states, between the average intake and the level at which toxicity becomes evident, but continued recycling, bioconcentration, and rapid tissue saturation, causes unique concern. To this date, no adequate studies of Se levels in food crops grown in the San Joaquin Valley have been done. Data on uptake and availability of Se in plants (and animals) shows that it depends greatly on the chemical form of Se (NAS, 1976).

The biochemistry of Se in cells and in cellular metabolism is complex. Absorption of selenate and selenite and reduction to the -2 oxidation state, allows incorporation of Se into soluble amino acids and/or protein-bound amino compounds (USEPA, 1979). When available in the proper amounts, Se is incorporated in a highly specific way into certain functional proteins (enzymes) of the cell (Stadtman, 1974). These Se dependent reactions are all oxidation-reduction reactions. Stadtman postulates that if the organism receives larger amounts of Se, those enzyme systems which cannot distinguish Se from sulfur (S) begin substituting Se indiscriminately for S in many cellular constituents. These Se analogs cause metabolic problems and may lead to toxicity.

Two other priority pollutant elements, chromium (Cr) and mercury (Hg) may have exceeded levels specified to protect aquatic life in the waters of the SLD Service Area when sampled in 1984 (Deverel and others, 1984). Boron exceeded the criteria set for irrigation water but is generally toxic to plants, not animals. Considerable molybdenum (Mo) was found by both Izbicki and Deverel and others (1984), up to 5,000 μg/L, but no standards or criteria for Mo in water have been set. A 1948 study indicated that a peculiar abnormality shown by cattle when grazing in certain areas of the San Joaquin Valley of California was caused by excessive Mo in certain species of plants (Barshad, 1948). This is similar to the well documented relationship of Se accumulator plants with alkali disease (Anderson, 1961).

FIELD AND HYDROLOGIC RELATIONS

Laboratory numbers, location descriptions and sampling dates are given in Tables 1 through 5. Maps of the study area are given in Figures 1 through 3. The sampling sites are identified in Figure 1 by the map numbers given in the tables. Sampling sites in Figures 2 and 3 are designated by laboratory number.

Surface hydrologic features are of great complexity and diversity in the San Joaquin Valley (e.g. Figure 3). Underground drainage systems and temporal switching and pumping mechanisms add other dimensions to the already complex issues of direction of flow and routing of water. Drainage from a grid of buried permeable tile or perforated plastic pipe installed in irrigated fields may be collected in a drain sump (pictured in Deverel and others, 1984). Several drain sumps may flow or be pumped into a collector drain. The SLD is an example of the catchment of concentrated subsurface flow from collector drains. Concentrated irrigation return water may also be diluted and routed by siphons, gates and pumps across, under and into channels (canals) that may be drains or supplies to users. Words such as sump and drain are used somewhat simplictically in this report to describe our somewhat limited observations. Our inital effort was to identify areas of greatest contamination and drainage systems rather than quantify the loading factor through use of flow measurements; flows in drains and canals are subject to continual change. Detailed studies still need to be done of present day total amounts of trace elements, which are subject to inorganic and organic uptake, and salts entering the KNWR (8,000 acres), the Grassland (50,000 to 75,000 acres) and the San Joaquin River basin, per year.

Approximately 85 miles of the SLD are now completed, from Five Points, 27 miles southwest of Fresno in the south, to KNWR in the north (USBR, 1984a; Deverel and others, 1984). In 1979 the preferred terminus of the originally planned 207 mile SLD was Suisun Bay in the San Francisco Bay-Delta Estuary (USBR, 1984a). Subsurface irrigation return flow from farmlands in the Westlands Water District (Figure 1) is drained into KNWR via the SLD. Westlands comprises about 90% of the SLD Service Area and includes about 600,000 acres extending from near Mendota on the north to near Kettleman City on the south (Westlands, written commun., 1985). Subsurface drains from only 8,000 acres of this farmland are connected to the SLD. However, in data presented to the SWRCB in 1985, Westlands states that "closing Kesterson would

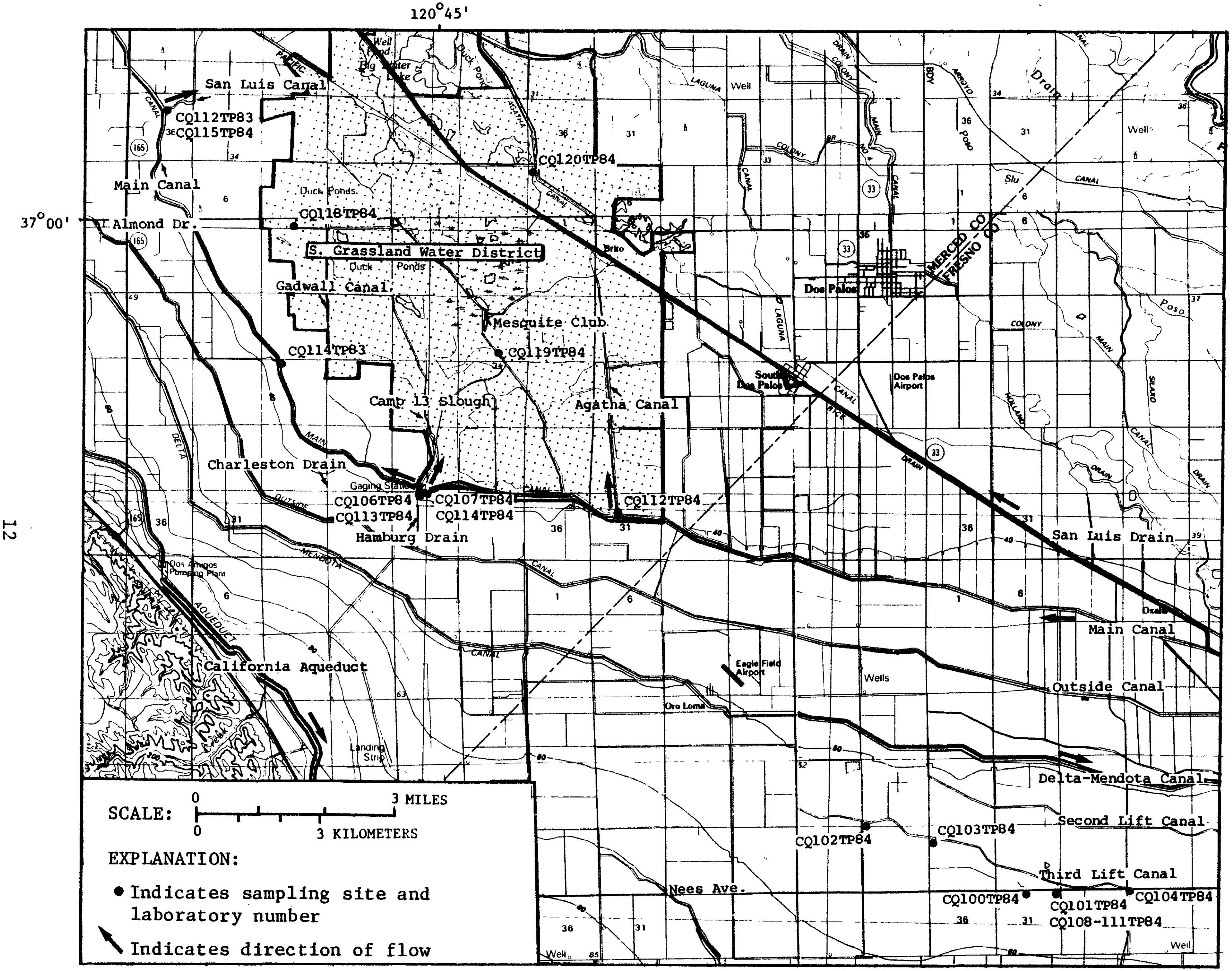

Figure 3.--Sampling site locations and hydrologic features in the Grassland area, 1984.

make it necessary to terminate irrigation on at least a 42,000 acre area of Westlands Water District where the drainage water discharged into Kesterson is collected . . .". Collector drain sumps for the SLD are recently installed thick concrete cisterns equipped with pumps. The waters entering the SLD from the collector drains can do so by gravity or by pumping if water starts to collect in the farmed fields. Details of Westlands drainage collector system is given in Westlands, 1984. Leakage from these collector devices was not investigated.

Figure 2 is a map of KNWR distributed by the State of California, Department of Fish and Game. Sampling site locations are denoted by laboratory number. The evaporation ponds are numbered 1 through 12. The SLD borders the ponds on the east. The only visible entries from the SLD into the Kesterson ponds are into ponds 1, 2 and 12. The water evaporates as it flows from pond 1 to pond 11 in a northerly direction. Pond 12 receives flow intermittantly when there is a surplus of water in the SLD.

Samples were collected in August, 1983 to show conditions characteristic of KNWR at the end of the dry summer. Water samples were obtained from Kesterson ponds 2 and 11 and the SLD (Figure 2 and Table 1). This sampling included collection of water samples for pesticide analysis. A salt crust and an underlying algal mat were also sampled at pond 11. Samples were collected in October, 1983 of irrigation supply waters and irrigation return waters in the area surrounding, but not draining into, KNWR and the SLD. These include the Delta-Mendota Canal, the Volta Drain, the San Luis Canal (Main Canal water), the Devon Drain (including the Boundary Drain), Fremont and Mud Sloughs, and the Santa Fe Canal (Table 2).

In late November and early December, samples of the ten actively inflowing waters to the SLD and waters at the south end of the SLD were collected (Table 3). Water samples from Kesterson pond 11 and the inflow into pond 2 were also obtained (Table 1). Collection of samples for pesticide analysis was included in the sampling scheme for the inflow into pond 2. In a further study in early 1985, a sample of salt efflorescence was collected from the inflow point to the SLD at American Avenue. The analysis of this sample is included in this report.

In April 1984, water samples from Kesterson pond 11 and the SLD inflow to Kesterson pond 2 were again collected (Table 1).

In June 1984, samples were taken of water in collector sumps from western

Nees Avenue (Figure 3). This water is pumped into agricultural drains (canals) which flow northwest to entry points to the Grassland (Table 4). Three of these major agricultural drains entering Grassland at Camp 13 Slough and Agatha Canal were also sampled. Also included was a resampling of the Main Canal during active irrigation at the same location as in October, 1983 (Table 2). Waters from some of these sampling points were recollected two weeks later in an effort to clarify sources of drainage into the Grassland during the irrigation season and the effect of water from a sump with an exceptionally high concentration of Se (4,200 μg/L). The area drained along western Nees Avenue contains some of the lands more recently reclaimed, between the California Aqueduct and the Delta-Mendota Canal, near the foothills of the California Coast Ranges. On June 14, 1984, a sample of gypsum was collected from a quarry in the California Coast Ranges, approximately 9 miles south of Los Banos. This gypsum is used locally for agricultural purposes as a soil amendment.

In July, 1984, three ponds in the Grassland were sampled (Table 1). The first pond sampled (CQ119TP84) was an example of a closed basin, that is, a pond which evaporated to dryness or near dryness just before flooding in September. This pond receives drainage from Camp 13 Slough. An algal mat and salt crust from the Mesquite Duck Club near the location of this water sample was provided by Donald Blake of the State of California, Department of Fish and Game (DFG), Los Banos Wildlife Management Area (LBWMA) in August, 1984. Food chain materials for waterfowl including bullrush tubers and seeds, cattail tubers and swamp timothy seeds, were also provided to us by DFG in August 1984. The second pond sampled (CQ120TP84) was located in an agricultural field which was subjected to summer irrigation by Agatha Canal water. The third pond sampled (CQ121TP84) was located in the LBWMA which received drainage from south Mud Slough, among other sources.

Also in July, an irrigation supply well near the LBWMA and two sumps near Nees Avenue at Firebaugh were sampled. Records for the depth of the well were found to be unavailable, but may be from 125 to 300 feet. The well is situated in the immediate proximity of the Santa Fe Canal and near the San Luis Canal.

Two more well samples are included in the study (Table 5). The Los Banos City Well 1 was sampled in December, 1984. This city waterworks well was drilled to 710 feet, plugged at 300 feet and screened from 160 to 300 feet. A deeper well south of Mendota was sampled by USGS, Water Resources Division, California District staff in November, 1984. As reported by Deverel and others (1984), due to adverse sampling conditions in September, 1984, the well data was preliminary. This more recent sample is felt to represent a less contaminated or truer picture of the pumped aquifer. The sample location was selected because of high levels of Se in shallow ground waters (Deverel and others, 1984). The irrigation well was drilled to a depth of 1,089 feet and was screened from 464 to 1,089 feet.

The hydrology of the San Joaquin Valley and its relationship to these wells will be discussed in a later section on ground water where it is more pertinent to the results given.

FIELD COLLECTION AND METHODS

Water collected in a 4-liter (L) stainless-steel pressure vessel was immediately pressure-filtered through a 0.1 μm (micrometer) membrane filter (142 mm diameter) using a stainless-steel filter holder and compressed argon as the pressure source. Filtered water samples for chemical analysis were stored in conventional polyethylene (low density) bottles which were rinsed prior to use with distilled deionized water in the laboratory and with sample filtrate at the field site. Samples for trace element analyses were immediately acidified with concentrated nitric acid (identified as Fa-HNO_3) to pH <2.0 as measured with pH paper. Samples for major cation analyses and Group II metals were acidified with concentrated hydrochloric acid (identified as Fa-HCl) to pH <2.0. Amounts of acid added to each bottle were recorded. Se was determined on both the Fa-HNO_3 and the Fa-HCl samples as a check of total Se preservation (Presser and Barnes, 1984). An unacidified filtered sample (Fu) was taken for major anion analysis.

Water samples for isotopic analysis were stored in 15 milliliter (ml) glass bottles with polyethylene cone inserts in the caps. No air space was left in the filled container.

Filtered water samples for mercury (Hg) analysis from Kesterson ponds 2 and 11 were stored in glass bottles with polyseal caps. Hg was stabilized in the field by addition of 2:1 sulfuric acid:nitric acid mixture, 5% weight/volume (w/v) potassium permanganate, and 5% w/v potassium persulfate (USEPA, 1971).

Field determinations were made of water temperature, pH, total alkalinity, and in the case of pond samples and some background waters, ammonia (NH_3) and total sulfide. These constituents are considered to be unstable and must be measured in the field at the time of sampling if the concentrations are to accurately represent those originally present in the water (Presser and Barnes, 1974; Wood, 1976). The pH was measured and an alkalinity titration performed on-site using an Orion[1] portable pH meter and an Orion Ross pH electrode following the method of Barnes (1964). Sulfide was precipitated as zinc sulfide and titrated by the iodometric method (USGS, 1979). Ammonia was determined by adding sodium hydroxide to raise the pH of the sample to approximately 12, and measuring the dissolved ammonia with an Orion ammonia specific-ion electrode. This method is similar to one specified in ASTM, 1981, Method D1426-79D. Samples were not preserved for analysis of other nutrients.

No odor of hydrogen sulfide (detection limit 0.067 ppm, USEPA, 1977a) was noted in any of the other waters collected, therefore no chemical analyses of dissolved H_2S were made in the field. Laboratory determinations of pH and alkalinity, not field determinations, were made on samples of the inflows of the SLD because these samples were collected in an initial effort to isolate areas of contaminated waters. Specific conductance was measured either in the field or the laboratory; values obtained were used only as a guide in sample selection and/or further laboratory analysis.

Samples for pesticide analyses were preserved in specially prepared glass bottles. This preparation included rigorous cleaning and oven heating of the containers (Goerlitz, 1972). "Surrogate" compounds were added to some samples in the field. Samples were sent chilled to the USGS Central Laboratory in Denver, for immediate analysis (USGS, 1983).

The sample from well CQ161SD84 was collected in accordance with USGS, Water Resources Division district operations (Deverel and others, 1984).

Solids were collected in ziplock plastic bags or glass bottles.

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[1] Use of trade names in this report is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.

LABORATORY METHODS

Details of the method for Se analysis are given in Figure 4 and in Presser and Barnes (1984). The first step in the method consists of a hot acid oxidative digestion with potassium persulfate ($K_2S_2O_8$) to free Se from any organic compounds present. The second step is a preliminary reduction of the selenate ($SeO_4^=$) generated in the first step, to the selenite ($SeO_3^=$) form, which is accomplished by the addition of hydrochloric acid (HCl) and boiling of the solution. In this second step, reduction must be vigorous enough to reduce all the Se^{+6} to Se^{+4}; but, care must be taken not to reduce Se further to elemental Se (Se^0), in which case the Se^0 may be plated out or agglomerated. In the final reduction step Se is volatilized as hydrogen selenide (H_2Se) gas, with a change in the oxidation state from +4 to -2. It was found that all of the Se present in the sample must be in the +4 state before the final reduction, or recoveries could be as low as 2% in agricultural drainage waters (Presser and Barnes, 1984). If the oxidative digestion step was eliminated in a sample containing approximately 18 mg/L organic carbon as C, 14% of the total Se was not recovered. The reagents used for this final step are HCl and sodium borohydride ($NaBH_4$). The gas is swept by a stream of argon gas into a quartz tube heated by an air-acetylene flame. The H_2Se is atomized and subsequent absorbance measurements are made at a wavelength of 196 nanometers (nm). An Instrumentation Laboratories (IL) Model 751 Atomic Absorption Spectrophotometer (AAS) equipped with a deuterium arc background corrector and Atomic Vapor Accessory (AVA) was used. The working range of the method is 1-20 μg/L. The detection limit is listed as 2 μg/L because samples are diluted 1:2 during the digestion procedure. Recoveries of added Se averaged 98%. Values for Se on two samples were found to be in close agreement by two independent laboratories, USF&WS and USGS, Denver (Presser and Barnes, 1984). USGS, Denver, uses the method described in USGS, 1982. No interferences from the upper limits of matrix components were found in these waters. Se was usually determined on both the Fa-HCl and Fa-HNO_3 samples. Background samples containing <10 μg/L were analyzed only once. Algal mat and salt crust materials were also analyzed for Se by this method. The sample was first solubilized (or leached) in 1% HNO_3 for oxidative digestion. After digestion and reduction, the decanted solution was pipetted into the hydride generator. The value obtained by this method may be low when compared to values from methods which completely destroy the organic

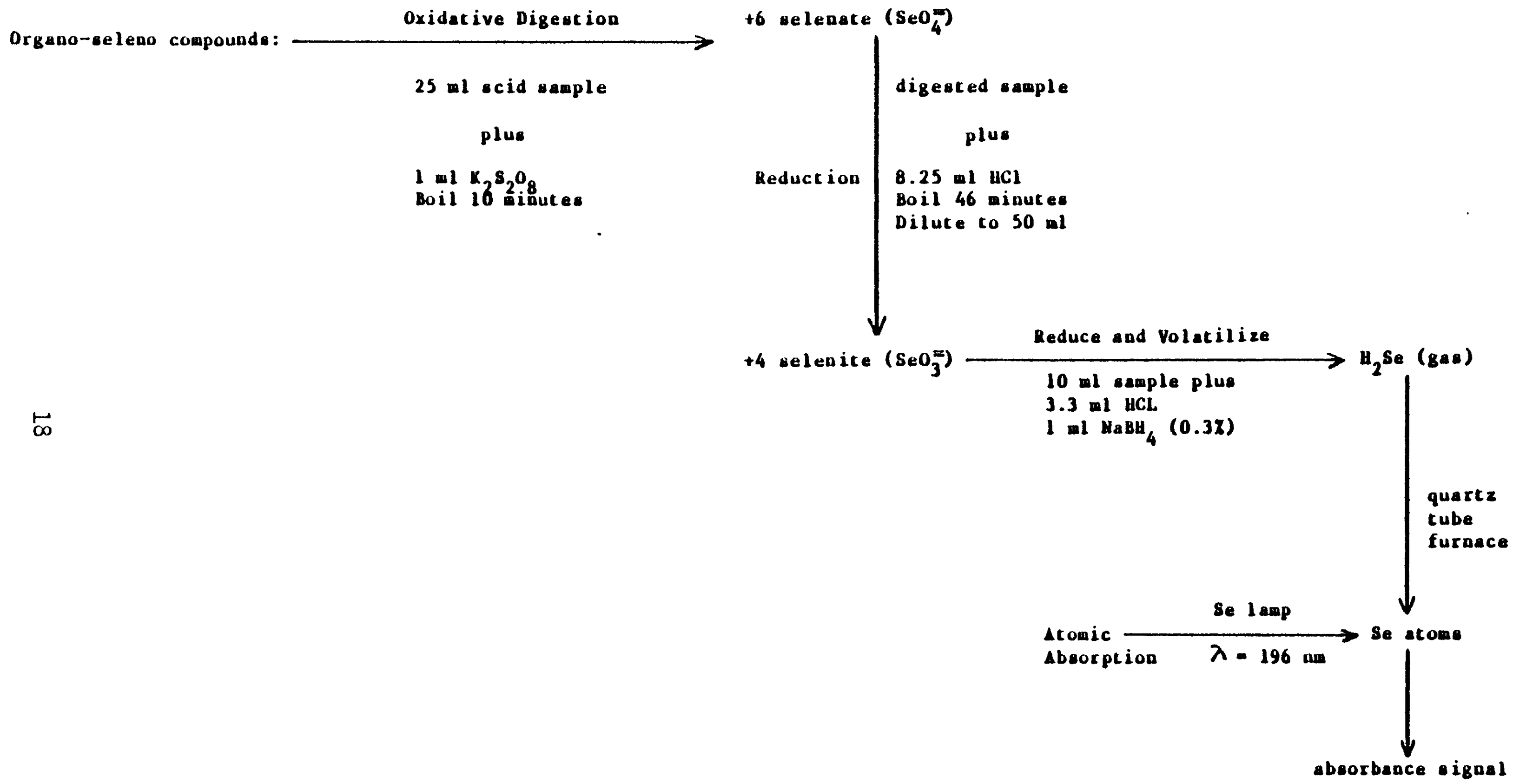

Figure 4.--Analytical scheme for selenium in water.

or sediment matrix of the sample. However, this value may be more representative of the amount of Se available biologically.

Pierce and Brown (1977) found that the hydride generation method using $NaBH_4$ and a heated quartz tube yielded the least interference when compared to graphite furnace atomization or hydride generation with flame atomization. Extensive reviews of hydride generation techniques are given by Gunn (1981) and Nakahara (1983).

Waterfowl food chain materials (tubers and seeds) were analyzed for Se by Thelma F. Harms, USGS, Branch of Exploration Geochemistry. Her method consists of digestion by nitric acid, hydrogen peroxide and perchloric acid; reduction by hydrochloric acid; complexation with 2,3-diaminonaphthalene; extraction into cyclohexane; and measurement of the fluorescence. This is an updated version of a method published by Harms and Ward in 1975.

Other cations were determined by AAS. Additions of ionic suppressors and releasing agents, background correction and/or matrix matching were used as appropriate for the absorbance measurement. The detection limits for the trace elements determined on water from the ponds are: iron (Fe) 20 μg/L; manganese (Mn) 20 μg/L; cadmium (Cd) 20 μg/L; cobalt (Co) 20 μg/L; copper (Cu) 20 μg/L; nickel (Ni) 50 μg/L; lead (Pb) 100 μg/L; and zinc (Zn) 40 μg/L. The detection limits were higher for Kesterson pond 11, because of the large background interferences. Mercury (Hg) was determined on the preserved samples by flameless cold vapor atomic absorption technique (USEPA, 1971). The detection limit is 0.1 μg/L Hg.

Major anions were determined by ion chromatogaphy (Dionex Model 10). With this system, the anions fluoride (F), chloride (Cl), phosphate (PO_4-P), bromide (Br), nitrate (NO_3-N) and sulfate (SO_4) can be sequentially eluted using a single sample injection of 0.5 ml or less. This method is similar to that described for determination of major anions in rain water and surface water by Fishman and Pyen (1979) and USEPA (1984). The more reduced species, nitrite (NO_2-N) and sulfite (SO_3) will appear on the elution profile if present. Nitrate (NO_3-N) was determined as an estimate only; the samples were not preserved for nitrogen, phosphorous or reduced sulfur species. When determined, ammonia (NH_3) and total sulfide (as H_2S) were analyzed in the field. No unaccounted for peaks appeared on the chromatograph at the dilutions of the sample used. Br and PO_4-P were not major contributors to ion totals in the more saline water samples, adding a maximum of 2 milliequivalents/liter (meq/L) in a total of >100 meq/L. This calculation depends on the dilution factor necessary to obtain calibrated concentration ranges on the ion chromatograph. In water samples containing low amount of dissolved constituents, Br and PO_4-P concentrations were <1 mg/L.

The F peak eluted in the anion profile was used as an estimate of the F concentration. More precise values were obtained uisng an Orion F specific-ion electrode. The interferences of this method are well documented [American Society of Testing and Materials (ASTM), 1981; USGS, 1979]. A sample dilution which is known to have an ionic strength <0.06 is diluted with an equal volume of a buffer which adjusts the pH, decomplexes F, and provides a constant background ionic strength.

Boron (B) was determined by the colorimetric carmine method with a range of 1 to 10 mg/L (USGS, 1979). The tubes containing the samples plus the carmine dye and sulfuric acid are immersed in an ultrasonic energy bath to ensure completeness of the reaction. Silicon as SiO_2 was determined by the spectrophotometric molybdate blue method with a range of 1 to 50 mg/L (USGS, 1979) with the following pretreatments and modifications. The formation of SiO_2 polymers, which are unreactive in this method, is not expected below 50 mg/L SiO_2. If concentrations >50 mg/L SiO_2 are expected, pretreatment of the sample is necessary. This can include dilution and/or acidification at the field site, or digestion of the polymers with sodium hydroxide in the laboratory before analysis. Iron hydroxide precipitates in water samples may also decrease the reactivity of SiO_2. If an acidified water sample is used for either of these reasons, the reaction time in the above method for the formation of the silicomolybate complex must be increased to 2 hours (Govett, 1961).

Estimates of dissolved organic carbon were obtained with a Beckman Total Organic Carbon Analyzer (Model 915-B). Carbonaceous matter is converted to carbon dioxide and detected by an infrared analyzer. The sample volume is 10 to 25 microliter (μl) and the range is 5 to 100 mg/L carbon (C). Estimates were made both by determining total carbon and inorganic carbon and computing the difference and also by analyzing a sample which had been freed of carbon dioxide by acidification for total carbon.

Deuterium and hydrogen (D/H) were released from water samples for isotopic analysis by reaction with uranium (Bigleisen and others, 1952). The oxygen isotope ratio ($^{18}O/^{16}O$) of water samples was measured on carbon dioxide in equilibrium with the water by the method of Cohn and Urey (1938). Determinations were made of the D/H and $^{18}O/^{16}O$ ratios using a Finnigan Mat 251 gas source mass spectrometer.

Minerals encountered in this study were identified by both index of refraction measurements and x-ray diffraction using copper K_α radiation.

Sample CQ161SD84 was analyzed in the USGS Denver Central Laboratory according to USGS methods (USGS, 1979 and 1982). Se and the isotopic compositions were analyzed both in Denver and by the methods described above.

Water and sediment samples were analyzed for pesticides and organics by USGS Denver Central Laboratories. Methods for organic determinations are given specifically in Tables 9, 10 and 11 and generally, including methods for pesticides, in USGS Techniques of Water-Resources Investigations, 1983.

RESULTS AND COMPARISON TO OTHER RECENT DATA

The results of the analyses of water samples are given in Tables 1 through 11. Tables 1 through 5 are arranged by kind of water sampled and location: Table 1, the SLD and ponds of KNWR and Grassland; Table 2, background irrigation supply and return waters in the areas surrounding KNWR and the SLD; Table 3, inflows to the SLD; Table 4, sumps and agricultural drains near the Grassland; and Table 5, wells in the study area. Results of analyses for $\delta^{18}O$ and δD are listed separately in Tables 6 and 7. Results of analyses for herbicides, insecticides, volatiles and extracted organic compounds for samples from KNWR and the SLD are given in Table 8 through 11. The time of the year at which the sample was taken is important due to irrigation practices, wetland habitat formation, and the arid, Mediterranean climate with approximately 10 inches of precipitation and 90 inches of evaporation per year (Los Banos Retention Dam and San Luis Dam, National Oceanic and Atmospheric Administration, 1982).

Pesticides and Organics in Kesterson National Wildlife Refuge and the San Luis Drain

Results of analyses for pesticides and herbicides in water from Kesterson pond 2 (CQ68IB83), the SLD (CQ69IB83), Kesterson pond 11 (CQ70IB83) and the inflow from the SLD to Kesterson pond 2 (CQ119TP83) are given in Table 8. All pesticide and herbicide determinations were below detection limits in water samples except sample CQ119TP83 which contained 0.06 µg/L 2,4-D (2,4-

dichlorophenoxyacetic acid). The detection limits for the organochlorine insecticides are above the available criteria given by USEPA (1980) for protection of aquatic life (24 hour average). No criteria were adopted in 1980 for the organophosphorous insecticides or for the chlorinated phenoxy acid herbicides. In 1977(b), USEPA listed the following organic chemicals and their maximum contaminant levels in drinking water in mg/L: 2,4-D, 0.1; silvex, 0.01; endrin, 0.0002; lindane, 0.004; methoxychlor, 0.1; and toxaphene, 0.005.

Volatiles found in these same water samples and recovery data for field-added "surrogate" compounds added to sample CQ119TP83 are listed in Table 9. Tribromomethane (bromoform), chloromethane, and trichlorofluormethane are listed as USEPA priority pollutants. Insufficient evidence exists to indicate that bioaccumulation or biotransformation is important in the environmental behavior of these compounds (USEPA, 1979). These compounds are known to be common in the environment and have been detected in finished drinking water and/or surface water (USEPA, 1979).

Results of analysis of water and sediment extracts from near the inflow to pond 2 (CQ119TP83) are given in Tables 10 and 11. Analysis was by capillary gas chromatography and subsequent mass spectrometry (GC/MS). No compounds were identified in water extracts. Tentative concentrations and reliability factors are listed for those compounds identified in the sediment extract. "Surrogate" recoveries are also listed.

In the 1982 preliminary study of organochlorine pesticides and trace metals in mosquito fish from KNWR, Ohlendorf and Sakai concluded that levels of all organochlorine pesticides were practically identical in KNWR, the SLD and VWMA and did not approach dangerous levels. Further information on 1984 pesticide monitoring is given in USBR (1984e). A further report on pesticide occurrence in waters of the western San Joaquin Valley is being prepared by J. Setmire, USGS, Water Resources Division, San Diego, California.

Se in Kesterson National Wildlife Refuge and San Luis Drain areas

Results of Se analyses for the August through December 1983 sampling of KNWR pond and the SLD waters, other waters in the vicinity of the KNWR and the inflow waters to the SLD are listed in Tables 1, 2 and 3 respectively. These results were discussed by Presser and Barnes (1984) and in the introduction of this paper. Se in these waters was found to be predominantly in the form of selenate ($SeO_4^=$) where Se is in the +6 oxidation state, its highest oxidative state. This is in accordance with theory [Lakin, 1961 and National Academy of Science (NAS), 1976] which states that as selenate, Se is soluble, can be transported by water, and is highly toxic. This occurs in areas of alkaline soil rather than acid soil. Preliminary data on Kesterson ponds 2 and 11, show 20 to 30% of the total Se is in the selenite form. Biological processes appear to be involved in the reduction of Se (NAS, 1976) and its consequent entrance into the food chain. Shrift (1964) has proposed a Se cycle similar to biological cycles for sulfur, carbon and nitrogen.

The amount of subsurface drainage is not known in some of the background waters (Table 2). For example, the difference in the value for Se in the Main Canal, (CQ112TP83 and CQ115TP84) from October, 1983 (<2 μg/L Se) to June, 1984 (10 μg/L Se) may reflect subsurface drainage which may be returned to the canal in larger amounts during crop irrigation in June. The Delta-Mendota Canal, also an irrigation supply canal, sampled at the San Luis Wasteway (CQ110TP83) contained <2 μg/L Se. The Volta drain (CQ111TP83) which enters the San Luis Wasteway downstream of the Delta-Mendota Spillway contained <2 μg/L Se. The San Luis Wasteway is the major supply source for the VWMA which has been a comparison test area for Se content of fish and wildlife because it receives little agricultural drainage water (USBR, 1984b). Most other background samples (CQ113TP83 through CQ118TP83) contained <2 μg/L Se when collected in October and November, 1983. Exceptions were a farm drain near the Main and Gadwall Canals (CQ114TP83) which contained 5 μg/L Se and the Santa Fe Canal (CQ118TP83) which contained 10 μg/L. These other background waters are not discharged into the SLD, but rather are mixed with other irrigation supplies and return water and flow in general into Salt Slough to the east of KNWR and into Mud Slough to the west of KNWR and eventually into the San Joaquin River. CQ114TP83 may be diverted first into the Grassland and CQ113TP83 into the LBWMA.

Se in the Grassland area

Sampling site locations in the Grassland area are detailed in Figure 3 by laboratory number. Larger arrows denote general direction of flow in canals, drains or sloughs. Levels of Se found in three major agricultural drains bordering the Grassland (Table 4) near the Main Canal in June, 1984 (during crop irrigation) were 65, 50 and 45 μg/L Se (CQ112TP84, CQ113TP84 and

CQ114TP84). Samples taken by the USBR on the same day (June 27, 1984) at the same locations yielded 76, 60 and 54 μg/L Se (USBR, written commun., July, 1984). Two of these locations had been sampled earlier (CQ106TP84 and CQ107TP84) and found to contain 46 and 47 μg/L Se. USBR data for the June 27th sampling date also included the Charleston Drain at the Main Canal which contained 102 μg/L Se. Entrance points of these drains into the Grassland include but may not be limited to the Agatha Canal, Camp 13 Slough, and the Gadwall Canal. Another inflow to the Gadwall Canal via the Almond Drive Ditch, sampled in July, 1984 contained 17 μg/L Se (CQ118TP84).

Drainage sumps pumped into these and possibly other drains which flow into the Grassland are shown in Figure 3 in the vicinity of Nees Avenue (CQ100TP84 through CQ104TP84 and CQ108TP84 through CQ111TP84). Flow from these sumps is not shown in detail in Figure 3 since it is complex and transitory. In general, flow is from this area northwestward toward the southern Grassland in drains including the Panoche and Main Drains (USBR, written commun., 1984). The sump water sampled at site CQ101TP84 contained 4,200 μg/L Se, an amount much greater than found in inflows to the SLD in December, 1983. This sump was rechecked two weeks later and values of 3,800 to 4,000 μg/L Se were found (CQ108TP84 through CQ111TP84). This sump was reported by the USGS as a toxic waste hazard to the SWRCB and other agencies on July 5, 1984. From USBR data (1984e) it was noted that this sump had remained at this high level (4,000 to 3,400 μg/L Se) during a period of sampling from March through June 19, 1984. Other sumps in the same vicinity, (CQ100, 102, 103 and 104TP84), contained 1,600, 360, 84, and 540 μg/L Se, respectively. A sump further east on Nees Avenue near Firebaugh contained 76 μg/L Se (CQ124TP84). An inflow to the Outside Canal at Firebaugh (CQ123TP84) which included drainage water from CQ124TP84 and several other sumps and drains, contained 8 μg/L Se. The Outside Canal is an irrigation supply canal, similar to the Main Canal.

Tailwater (or excess irrigation water that runs off the surface of a field) used to dilute this subsurface drainage was not sampled. The subsurface drainage may also be diluted with imported water or pumped ground water. Tailwater is easily distinguished in the field from subsurface water by its turbid appearance and large volume of flow.

Mixing of irrigation waters is complex at any time in the Grassland area, but may be even more so at peak crop irrigation times. In the toxic waste statement referred to above, it was stated that an agricultural drain containing the sump discharge from the west end of Nees Avenue, including the 4,200 µg/L Se discharge, and identified as CQ106TP84, flowed directly into the Main Canal, an irrigation supply source, at Camp 13. The USBR reply to this statement (USBR, written commun., received July 16, 1984) pointed out correctly that the water in question flowed into the Grassland at the Agatha Canal site, and not into the Main Canal at Camp 13. However, field observations show that agricultural drainage water (CQ106TP84 and CQ113TP84) containing approximately 50 µg/L Se was entering the Main Canal at Camp 13 Slough in June, 1984, from some supply source. Water at the site of samples CQ106TP84 and CQ113TP84 can easily be diverted either into the Main Canal or Camp 13 Slough. The Main Canal was sampled at the same point downstream from the entry of the agricultural drain in October, 1983 (CQ112TP83) and in June, 1984 (CQ115TP84). The October, 1983 sample contained <2 µg/L Se and was similar in composition to water from the Delta-Mendota Canal (CQ110TP83). The June, 1984 sample, however, had a conductivity about 3 times as high as the October, 1983 sample and contained 10 µg/L Se. Entry of relatively saline drainage water was indicated qualitatively by conductivity measurements made across the Main Canal in June, 1984, at Camp 13. Conductivity ranged from 700 to 1,400 micromhos/centimeter (µmhos/cm) where water in the canal was mixing with an entering drain water of 2,800 µmhos/cm. The Main Canal is also a drinking water source for Dos Palos (Merced Sun Star, July 11, 1984). Dos Palos is east of the southern Grassland.

The three ponds sampled in the Grassland area (CQ119TP84, CQ120TP84 and CQ121TP84) in July, 1984 and receiving water from the drains just described, among other sources, contained low levels of Se: 10, 2 and 9 µg/L, respectively, Table 1. This is similar to the low level of Se found in Kesterson pond 11 (15 µg/L) at the end of the dry season (August, 1983). However, the Grassland pond waters were much lower in total solute concentration (64 meq cations/L average) than Kesterson pond 11 (368 meq/L).

Organic and inorganic uptake of Se in Kesterson National Wildlife Refuge, the San Luis Drain and the Grassland

Se was found bioaccumulated in algae from Kesterson pond 11, at a concentration of 13 ppm (dry weight). Se was also found in the salt thenardite (Na_2SO_4), which had formed as a crust on pond 11, at a concentration of 1.8 ppm (dry weight). Samples were taken in August, 1983.

Details are given in Presser and Barnes, 1984.

An algal mat plus salt crust was obtained near the end of August, 1984, at the Mesquite Club in the Grassland, near the location of water sample CQ119TP84, when evaporation was nearly complete. The water supply for this pond was Camp 13 Slough (Donald Blake, written commun., August, 1984). The evaporative mat was analyzed as a composite because it was not easily separated into component parts. The solid samples contained a salt crust consisting of calcite ($CaCO_3$) and gypsum ($CaSO_4 \cdot 2\ H_2O$), green matted material probably consisting of blue-green algae, a variety of aquatic organisms and woody debris and sediment. Composite sample A of the mat excluded the white salt crust as much as possible and more sediment was possibly included. In composite sample B, the white salt crust was included and more algae may have been included. Sample A contained an average of 20 ppm Se (dry weight) and Sample B, 15 ppm. The algal mat from the Mesquite Club differed in type from that collected from Kesterson pond 11. Pond 11 crust was easily separable into a sample of blue-green algae containing 13 ppm Se (dry weight) and a sample of thenardite containing 1.8 ppm Se (dry weight). Very little sediment, if any, was contained in the algal mat from pond 11. However, the concentration of Se in composite samples from the Mesquite Club was higher than that found in the algal sample from Kesterson pond 11.

The salt crust collected from the SLD at American Avenue in February, 1985 was identified as thenardite. A total digestate of the crust contained 17 ppm Se (dry weight). The form of this compound is highly dependent on environmental conditions. Thenardite is known to hydrate in wet and/or colder climates to form the mineral mirabilite ($Na_2SO_4 \cdot 10\ H_2O$) (Driessen, 1973). Transport and subsequent laboratory analysis of hydrated Na and Mg sulfate salts in their natural state is difficult (Whittig, 1982) due to the changing amounts of water in the crystal lattice. Both of these minerals along with mixed Na and Mg sulfate salts have been identified at certain times in the Coast Ranges bordering the western San Joaquin Valley (Murata, 1977 and Presser and Barnes, unpub. data).

The sample of gypsum ($CaSO_4 \cdot 2\ H_2O$) which was obtained from a quarry located above and to the south of Los Banos in the Coast Ranges contained <0.5 ppm Se (dry weight). This gypsum is used locally as a soil amendment. Inorganic uptake of Se in sulfate salts is a topic of continuing research on the source of Se in the San Joaquin Valley.

Bottom sediment samples taken on August 30, 1984 by the USBR from the SLD in a preliminary reconnaissance, were analyzed by the USGS, Geologic Division Laboratory at Denver, (E. J. McClelland, written commun., Dec., 1984). Analyses showed that the highest level of Se occured near where collector drains were actively discharging into the SLD. Concentrations of Se in the bottom sediments covered by water ranged from 3.1 to 210 ppm; concentrations in dredge spoils ranged from 28 to 100 ppm. Samples from a dewatered section of the drain not receiving water from collector drains averaged 1.2 ppm. E. J. McClelland stated that it is not known which part of the sample the Se is bound to or concentrated in because these sediments are described as organic-rich muck. And further, the contributions of anaerobic conditions, windblown soil and subsurface soil washed into the drain are not known.

At the same time the algal mat was collected near site CQ119TP84, representative samples of food materials grown in the Grassland wetlands for waterfowl were collected by D. Blake. These included bullrush seeds and tubers, swamp timothy and cattail tubers. Again the source water was the Camp 13 Slough. The results of the analysis by T. Harms, (USGS, Denver) in ppm Se (dry weight) are: bullrush tuber, 2.4 ppm; bullrush seeds, 0.45 ppm; cattail tubers, 2.2 ppm; and swamp timothy seeds, 1.0 ppm. Sakai reported Se in alkali bullrush seeds collected in June, 1983 as follows: from Kesterson pond 2, 4.9 ppm; from Kesterson pond 11, 1.1 ppm; and from Volta 0.1 ppm (M. Sakai, written commun., 1984). Bullrush roots and cattail roots taken from the Department of Water Resources (DWR) Desalination Facility ponds near Los Banos in September, 1984, which uses SLD water as source water contained from 100 to 119 ppm Se (at 50°C moisture level). These samples were collected and analyses performed by U.S. Department of Agriculture (G. Hoffman, written commun., Dec. 19, 1984).

Waterfowl were collected by the USF&WS in the 1984 nesting season from the Grassland area (May 23 to July 3) and their livers analyzed for Se (Ohlendorf and Hothem, 1985). The sampling was considered small but the effort was predominantly focused on the south Grassland where subsurface drainage enters the area (e.g. Agatha Canal and Camp 13 Slough). The results of this study reported to the SWRCB in January, 1985 are stated as follows: "Selenium occurred at elevated levels in some birds from all areas in the Grassland. . . . Selenium concentration in avocets from the south Grassland

(67.3 ppm, dry weight) was similar to that in the stilts from Kesterson." Mean Se concentrations in livers from stilts from Kesterson in 1983, averaged 62.8 ppm (dry weight). Fish from Camp 13 Slough, Mud Slough and Helm Canal also showed elevated levels in samples taken September, 1984 (M. Sakai, 1985). From preliminary data, it was found that some samples exceeded 5 µg/g (wet weight). Studies conducted by Columbia National Fisheries Research Laboratory seem to indicate that Se residues in whole body fish >2 µg/g (wet weight) are associated with reproductive problems (Baumann and May 1984). Baumann and May suggest that the Se concentration not to be exceeded for protection of aquatic life be revised downward, as toxicity to fish as been shown at 9 to 12 µg/L Se in water.

Other trace elements in Kesterson National Wildlife Refuge, the San Luis Drain and the Grassland

Levels of the trace metals Fe, Mn, Cd, Co, Cu, Ni, Pb, Zn, and Hg in the waters of the ponds at Kesterson are in most cases at or below the detection levels reported (Tables 1A and 1B). The same is true for the Grassland ponds except that Hg was not determined. Detection limits are below USEPA water quality criteria for protection of human health (1976) for Fe, Mn, Cu, Zn and Hg. Detection limits for Cd and Pb are two times the drinking water standard (USEPA, 1977b). No criteria are given for Co. The only criterion given for Ni is that for protection of freshwater aquatic life (160 µg/L 24 hour average, 200 mg/L hardness) (USEPA, 1980b). In general, available water quality criteria for protection of freshwater life (24 hour average) are lower than criteria for protection of human health (USEPA, 1980b). Sample CQ119TP84, from a Grassland pond, contained the highest concentrations of Fe (200 µg/L) and Mn (2,725 µg/L). Mn concentration was found to be variable in our sampling even within the same pond. For example, Kesterson pond 2 contained <20 and 450 µg/L Mn at different sampling times. The concentration of Mn in Kesterson pond 11 in April, 1984 (120 µg/L) was double that found in November, 1983 (60 µg/L). Izbicki (1984) found 420 µg/L Mn in the inflow to Kesterson pond 2 and values similar to those reported in Table 1B for the other trace metals. In trying to trace the high concentrations of Mn in the Grassland pond it was found in preliminary analyses that the sumps on Nees Avenue contained <20 µg/L Mn and the drains to the Grassland contained approximately 60 to 90 µg/L Mn at the various sampling times. The agricultural inflow to the Gadwall Canal contained approximately 300 μg/L Mn. The Main Canal contained <20 μg/L Mn at the sampling in October, 1983 and 90 μg/L in June, 1984. Mn was also found to be at a higher level (340 μg/L) in the confluence of Mud and Fremont Sloughs (CQ115TP83).

Trace metal data for two agricultural drain waters at Camp 13 are given by the USBR for samples taken in May and June, 1984. Average concentrations for trace metals other than analyzed for this report are, in μg/L: arsenic, 3; chromium, 42; mercury, 0.1; and molybdenum, 12 (USBR, 1984e). Data for these elements in KNWR are given by Izbicki 1984 and for the shallow ground water in Deverel and others (1984).

Organic C, H_2S and NH_3 in Kesterson National Wildlife Refuge, the San Luis Drain and the Grassland

Organic carbon estimates for pond samples ranged from a high of 64 to a low of 17 mg/L C (Table 1B). The highest value of organic carbon in each area (KNWR vs. Grassland) was associated with the lowest Se concentration. However this observation does not hold true between areas. A Grassland pond (CQ119TP84) and Kesterson pond 2 (CQ68IB83) contain equal amounts of organic carbon and extremely different amounts of Se (10 and 350 μg/L, respectively).

Hydrogen sulfide concentrations were <0.5 mg/L H_2S in all pond and background water samples analyzed in the field.

Ammonia determinations on pond samples are listed in Table 1B. All values were <1 mg/L NH_3-N (ammonia nitrogen as N) except sample CQ119TP84 which contained 1.2 mg/L. The only other ammonia concentrations determined were on background waters (Table 2). These are not listed in Table 2 but the values obtained were all <0.1 NH_3-N, except for samples CQ111TP83 (0.14 mg/L) and CQ116TP83 (1.6 mg/L).

B and NO_3 in Kesterson National Wildlife Refuge, the San Luis Drain and the Grassland areas

Boron concentrations (Tables 1 through 5) exceeded that recommended for long term irrigation on sensitive crops, 750 μg/L B (USEPA, 1976), for all water samples except water from the south end of the SLD (CQ131TP83) and some background waters near KNWR which were <1000 μg/L. The highest B concentration of 79,000 μg/L was found in a sample of an inflow to the SLD (CQ127TP83).

Nitrate estimates were as high as 50 mg/L NO_3-N (nitrate nitrogen as N) in Kesterson pond 2 and the SLD waters, 220 mg/L in water from the inflows to the SLD and 280 mg/L in waters from the inflows to the Grassland.

CHEMICAL RELATIONS

Dissolved constituent data were analyzed with the computer program SOLMNEQ (Kharaka and Barnes, 1973). This program computes the equilibrium distribution of 162 chemical species in aqueous solutions over the temperature range of 0° to $350^\circ C$. States of reaction of the aqueous solutions with respect to 158 solid phases (minerals) are also computed. Positive values of ΔG_R ($\Delta G_R > 0$) indicate that the solution is supersaturated with respect to the solid phase; $\Delta G_R = 0$ indicates equilibrium; and $\Delta G_R < 0$ indicates undersaturation. ΔG_R is the difference in the Gibbs free energy (in kilocalories) between the actual state and the equilibrium state. States of reaction data must be used with caution. Near equilibrium conditions and supersaturations are an indication of what reactions could be of interest and have the potential to take place. Reaction products may be difficult to observe or in small quantity (McCulloh, 1981). Open system conditions and field observations must be taken into account besides these theoretical data. For example, calcite requires supersaturation of 1.5 kilocalories (kcal) or greater to precipitate (Barnes, 1965). Dolomite, magnesite and huntite require supersaturation and HCO_3 concentration of >500 mg/L (Barnes, 1973). None of the sampled waters had sufficient HCO_3 concentration to promote formation of these minerals. From field relations, large supersaturations and pH values of 11.0 or greater are necessary to form talc and chrysotile (Barnes, 1969 and 1972) which were found supersaturated in some waters sampled. Evaporative effects and periodic dilution must also be taken into account. For example, in Kesterson pond 11, thenardite was found forming around the periphery of the pond although the water in the pond was unsaturated with thenardite or mirabilite.

A descriptive term for the general chemical character of the water was used to assess the water type. For example a sodium-sulfate (Na-SO_4) water is one in which $\geq 50\%$ of the cations or anions on a milliequivalents/liter (meq/L) basis, is comprised of Na or SO_4, respectively, (Hem, 1970).

In general in the study area, values of pH for samples ranged from 6.82 (CQ159IB84) to 9.25 (CQ121TP84), with the majority of measurements >7.5.

Values for total alkalinity, reported as mg/L bicarbonate, ranged from 59 to 452 mg/L HCO_3 in the waters studied. Most samples contained <300 mg/L HCO_3 which is common in surface and ground waters.

Kesterson National Wildlife Refuge and the San Luis Drain areas

Waters from Kesterson ponds, the SLD and the active inflows to the SLD from the west (i.e., excluding the waters at the south end of the drain, CQ130TP83 and CQ131TP83) are all Na-SO_4 waters. Percent Na ranges from 55 to 92% and SO_4 from 54 to 85%. The highest concentration of SO_4 in these waters was 22,500 mg/L. Only in the samples from the three northernmost entries to the SLD is Cl >30% of the total anions. The correlation coefficient of linear regression between Na and SO_4 is 0.99 for the nine actively inflowing waters to the SLD (CQ121TP83 through CQ127TP83), pond 2 (CQ68IB83) and the SLD water (CQ69IB83). The correlation coefficient between Se and SO_4 for these same waters is 0.93.

All of these KNWR and SLD waters, including the resampling of pond 2, are supersaturated with respect to calcite, aragonite, dolomite, magnesite and most are supersaturated with respect to huntite, the Ca, Mg carbonates. They also all are nearly in equilibrium with gypsum ($CaSO_4 \cdot 2\ H_2O$), with undersaturations averaging -0.13 kcal. The sample of Kesterson pond 11 (CQ70IB83) was supersaturated by 0.23 kcal for gypsum, the highest value found. In both acidified filtered samples of pond 11 collected in August, 1983, gypsum was found precipitated as an artifact upon return to the laboratory. The lowest values of undersaturation for mirabilite ($Na_2SO_4 \cdot 10\ H_2O$) were seen for samples of Kesterson pond 11 and two inflows to the SLD (CQ127TP83 and CQ129TP83). Thenardite (Na_2SO_4) was identified and analyzed from two of these locations (see Section, Organic and inorganic uptake of Se). The values calculated for ΔG_R averaged -2.6 kcal.

All inflow waters to the SLD and the SLD water are supersaturated with respect to quartz. In at least one sampling, waters from Kesterson ponds 11 and 2 were supersaturated with respect to quartz. These silicate states were calculated without aluminum data and consequently alumino-silicate saturation status cannot be calculated. Quartz is not likely to be precipitated from these waters possibly due to changing temperature gradients.

Silica concentrations in waters entering the SLD were as high as 48 mg/L SiO_2 (CQ128TP83). The concentration of SiO_2 in water entering the KNWR in

November, 1983 was 27 mg/L (CQ119TP83). It is reasonable to infer that silica concentrations of some 30 to 50 mg/L are the result of leaching (weathering) of silicate minerals of the soils in a ground water regime. During spring and summer conditions silica concentrations decreased markedly. In April, 1984, the silica concentration was only 2.2 mg/L (CQ87TP84) at the same sampling point at which 27 mg/L had been found in November. The lowest concentration of silica was in August in Kesterson pond 2 (CQ68IB83). The silica concentration of 1.2 mg/L is much lower than the solubility of quartz, the least soluble silica mineral. Presumably in the spring and summer, diatoms effectively control silica concentrations because no known mineral reaction can yield such low concentrations.

The waters in the south end of the SLD (CQ130TP83 and CQ131TP83) are dilute Ca-Na-HCO_3 waters, with almost equal amounts of Ca and Na ($\sim$40%). CQ130TP83 was the only active entry to the SLD from the east side. CQ131TP83 was from standing water at the south terminus of the drain. The specific conductance values measured at these sites were 270 and 350 μmhos/cm, respectively. At both these sites facilities are provided to pump water, presumably irrigation supply water, into the SLD. Between 1972 and 1978, water from local sources was discharged into the SLD to maintain hydrostatic balance on the concrete lining due to locally high ground water conditions (USBR, 1984e).

Grassland area

In the three Grassland pond samples (Table 1), Na comprises 60 to 65% of the total cations. SO_4 percentages are from 51 to 60%; Cl ranges from 37 to 42%. The agricultural sumps and drains entering this area (Table 4) are again composed mostly of Na-SO_4 waters (48 to 81% Na; 49 to 76% SO_4). Cl comprises approximately the remaining half of the total anions (45 to 47%) in the two sumps sampled from Nees Avenue containing the highest concentrations of Se (CQ100TP84 and CQ101TP84). These higher Cl components and those noted (>30%) for the three northernmost entries to the SLD (CQ121TP83 through CQ123TP83), may be related to the higher Cl content of Little Panoche Creek (Davis, 1961 and Presser and Barnes, unpub. data) as opposed to the higher SO_4 content of other creeks in the area. Cl concentrations in the other drain and sump samples were less (17 to 36%). Ca comprises a major portion of the remaining cations (36%) in samples CQ107TP84 (drain into Camp 13 Slough) and CQ123TP84 (inflow to Outside Canal).

For the samples given in Table 4, the correlation coefficient of linear regression calculated between Se and specific conductance is 0.76. This comparison of Se and specific conductance from the Grassland area shows that conductance is not a reliable guide to Se concentrations. Further support for this statement is given by the fact that the conductance of sample CQ129TP83 (Table 3), an inflow to the SLD containing the highest concentrations of Se of all the inflows sampled (1,400 µg/L Se), measured 25,000 µmhos, whereas the conductance of the sample containing 4,200 µg/L Se, near the Grassland area (CQ101TP84), measured 23,000 µmhos. Of all the samples considered from the Grassland area given in Table 4, CQ118TP84 contained the highest amount of SO_4 (9050 mg/L). If inflows to the SLD are also considered, this sample contained the third highest amount of SO_4. The Se to SO_4 ratio calculated for this sample is the lowest observed except for Kesterson pond 11 samples. A low correlation (0.46) between Se and SO_4 is seen in Grassland area samples.

The Grassland pond waters follow the same supersaturations for the Ca, Mg carbonates as seen in the KNWR and SLD. However, the Grassland pond waters are not as close to equilibrium with gypsum as the waters of the Kesterson and SLD areas. Undersaturations range from -0.62 to -0.79 kcal. Therefore, the Grassland ponds were seen to differ from Kesteron ponds in this respect. Only the pond fed by Agatha Canal water is supersaturated with respect to quartz and chalcedony.

Waters sampled near the Grassland (Table 4) are not always supersaturated with respect to huntite and magnesite, but are supersaturated with respect to the other Ca, Mg carbonates. These waters are also supersaturated with respect to quartz and nearly always chalcedony. Gypsum is near equilibrium saturation in the waters from sumps (-0.14 kcal average), but not in the three agricultural drain waters (CQ106TP83, CQ107TP83 and CQ112TP83) or the inflow to the Outside Canal (CQ123TP84). Mixed waters in canals or ditches have the possibility of more complex relationships than may be shown by SOLMNEQ.

Background areas

The background waters collected in the initial reconnaissance in October and November, 1983 (Table 2) are more varied in water type. Specific conductance for most of these waters was below 100 µmhos/cm. The Delta-Mendota Canal (CQ111TP83) and the Devon Drain (CQ113TP83) are predominantly

Na(50%)-Cl(47%) waters. The Devon Drain contains appreciable SO_4 (36%). The samples from the Main Canal (CQ112TP83 and CQ115TP84), the Santa Fe Canal (CQ111TP83), the confluence of Fremont and Mud Sloughs (CQ115TP83) and the irrigation return ditches (CQ114TP83 and CQ116TP83) contain large percentages of Na (48 to 68%) and SO_4 (47 to 50%). CQ114TP83 and CQ115TP83 contain appreciable Cl (36%) and CQ116TP83 appreciable HCO_3 (35%). A water source for the VWMA, the Volta Drain (CQ111TP83), contains 60% Na and nearly equal percentages of Cl (39%) and HCO_3 (38%). None of the background waters are supersaturated with respect to gypsum; all are supersaturated with respect to quartz. The waters from the Delta-Mendota Canal, the Main Canal and the Devon Drain are not supersaturted with respect to calcite or aragonite. The remainder of the background waters are in equilibrium or supersaturated with respect to calcite.

For comparison, a San Joaquin River sample taken in September, 1984, near Mendota, contained 46% Na, 28% Ca, 25% Mg, 42% HCO_3 and 34% Cl (Deverel, written commun., Feb., 1984). The San Joaquin River and consequently the Delta-Mendota Canal contain runoff from the Sierra Nevada.

ISOTOPIC RELATIONS

The purpose of the isotope study is to show the possible history and source of the waters sampled. Craig (1961) has shown that meteoric waters, water derived from snowmelt and rain water, lie on a line given by the equation $\delta D = 8\ \delta^{18}O + 10$. This meteoric water line is plotted for reference in Figures 5-7 which show the relationship of δD and $\delta^{18}O$ for samples from the study area. The study area has an annual evaporation potential about ten times the precipitation rate. As a consquence, isotopic compositions of waters may shift not along the meteoric water line, whose slope is determined by equilibrium processes, but along trends with different slopes determined additionally by the kinetics of evaporation (Craig, 1961; Siegenthaler, 1979). Thus, extensively used irrigation water and Kesterson pond water that has had more of a chance to evaporate would be enriched in the heavier isotopes (D and ^{18}O) relative to water from, for example, the San Joaquin River. Craig has found a slope of 5 for the heavy isotope enrichment ratio $D/^{18}O$ for free evaporation. Evaporation trend lines for arid climates have been reported. Gat and Issar (1974) reported an evaporation trend line with a slope of 5.5 for the Sinai desert. Gat and Tzur (1967) report slopes of from

2.0 to 8.0 for evaporation trend lines for other parts of Israel. Fontes and Gonfiantini (1967) in a study of evaporation in two basins in the Sahara showed the evaportation trend line to have a slope of 4.6.

Results of isotopic analyses in water are given in Tables 6 and 7. Values for $\delta^{18}O$ are within ± 0.05 to 0.1 per mil of the reported values; values for δD are within ± 0.5 per mil.

Kesterson National Wildlife Refuge and the San Luis Drain areas

The results for the KNWR and SLD areas show (Table 6 and Figure 5) that there is indeed an evaporation effect with the trend from the D and ^{18}O depleted waters of the Delta-Mendota Canal (Map #7) and the Main Canal (Map #9, Oct., 1983) to the extreme enrichment of water in Kesterson pond 11 (Map #2). The sample of pond 11 taken in November, 1983 with less enrichment in $\delta^{18}O$, was taken during a rain storm. The distinct clustering of the isotopic compositions of the waters entering the SLD from the southwest (Map #15 to 23) indicates that the waters have similar histories. Samples taken from the Kesterson ponds and inflows to the SLD in 1983 have isotopic compositions that lie on a line given by the equation $\delta D = 4.8\ \delta^{18}O - 25.9$. The correlation coefficient for these waters (Map #1 through 3, August, 1983; and 15 through 25, December, 1983) is 0.98. Note that the isotopic values for both samples of the inflow to pond 2 (Map #1) regardless of sampling date (August or November), lie on the calculated line. The intersection of the evaporative trend line and the meteoric water line, give a starting composition point of $\delta D = -82.5$ per mil and $\delta^{18}O = -11.6$ per mil. This composition is less depleted than the irrigation supply water from the Delta-Mendota Canal (Map #7), with values of $\delta D = -90$ per mil and $\delta^{18}O = -12.7$ per mil. It is also less depleted than the Main Canal irrigation supply water collected in October, 1983 with values of $\delta D = -98$ per mil and $\delta^{18}O = -13.7$ per mil. The condition of waters at the south end of the SLD (Map #24 and 25) are reflected in the isotopes. A sample of standing water at the south end of the drain (Map #25) identified previously as irrigation supply water is seen to be enriched in the heavy isotopes by evaporation. A sample of the only active entry to the SLD from the east side (Map #24) also identified previously as irrigation supply water, is as depleted in ^{18}O as other background waters (Map #7 through 14) and shows little evaporation effect.

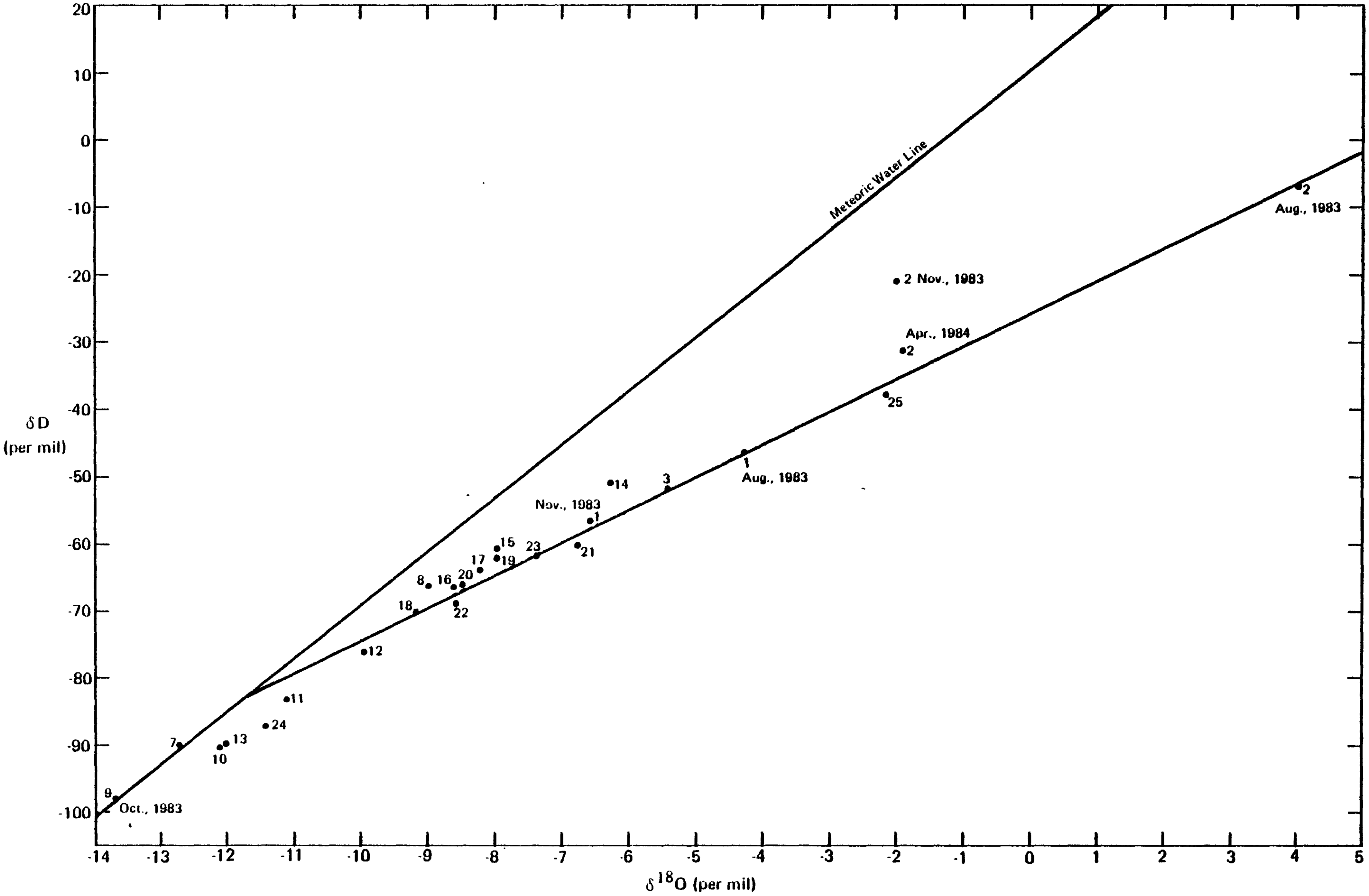

Figure 5.--Variations in δD and $\delta^{18}O$ for waters from the KNWR and SLD areas denoted by map number.

Grassland area

A similar trend is seen in the Grassland area (Table 7 and Figure 6) between source and pond waters. Sampling dates in the Grassland were in an even shorter interval (June and July, 1984) and therefore less scatter about the trend line is seen. The least squares regression analysis gives an equation of $\delta D = 4.5\ \delta^{18}O - 28.8$. The correlation coefficient for Grassland pond waters (Map #4, 5 and 6) and sump and agricultural drain waters near the Grassland (Map #26 through 34) is 0.99. If the intersection point is calculated for this evaporation line and the meteoric water line, the starting composition point is $\delta D = -79.5$ and $\delta^{18}O = -11.5$. Since this theoretical source water would be more depleted than the irrigation supply water of the Main Canal sampled in the same time period (Map #9: $\delta D = -70.8$ and $\delta^{18}O = -9.21$), a possible explanation would be greater reuse of the irrigation water, leading to enrichment in δD and $\delta^{18}O$ in water added to the distribution system. Another explanation would be that the Main Canal water sampled was not representative of the usual condition. The enrichment of δD and $\delta^{18}O$ in the Main Canal water puts the composition off the meteoric water line, and puts it on an evaporation trend line.

The slope of the regression line for the isotopic compositions of the Grassland waters (4.54) is similar to that of the waters of the Kesterson system (4.85). These values are comparable to those found in desert basins.

The samples most enriched in $\delta^{18}O$ (Map #26), if pond waters are not considered (Map #4, 5 and 6), contain the highest concentrations of Se in the Grassland. This general trend is also observed in the KNWR area if pond waters (Map #1 and 2) and in this case standing waters in the SLD (Map #3 and 25) are again not considered. The two inflows (Map #21 and 23) to the SLD containing the highest concentration of Se (1400 μg/L) are the most enriched in ^{18}O except for the Santa Fe Canal water (Map #14).

GROUND WATER RELATIONS IN THE STUDY AREA

Hydrology of the San Joaquin Valley

The relationship between water compositions and depths of ground waters in the San Joaquin Valley has been discussed in the literature from at least as early as 1916 (Mendenhall, 1916) to the present. Mendenhall regarded waters as deep if they were yielded by wells of depths of more than 1,000 feet. He

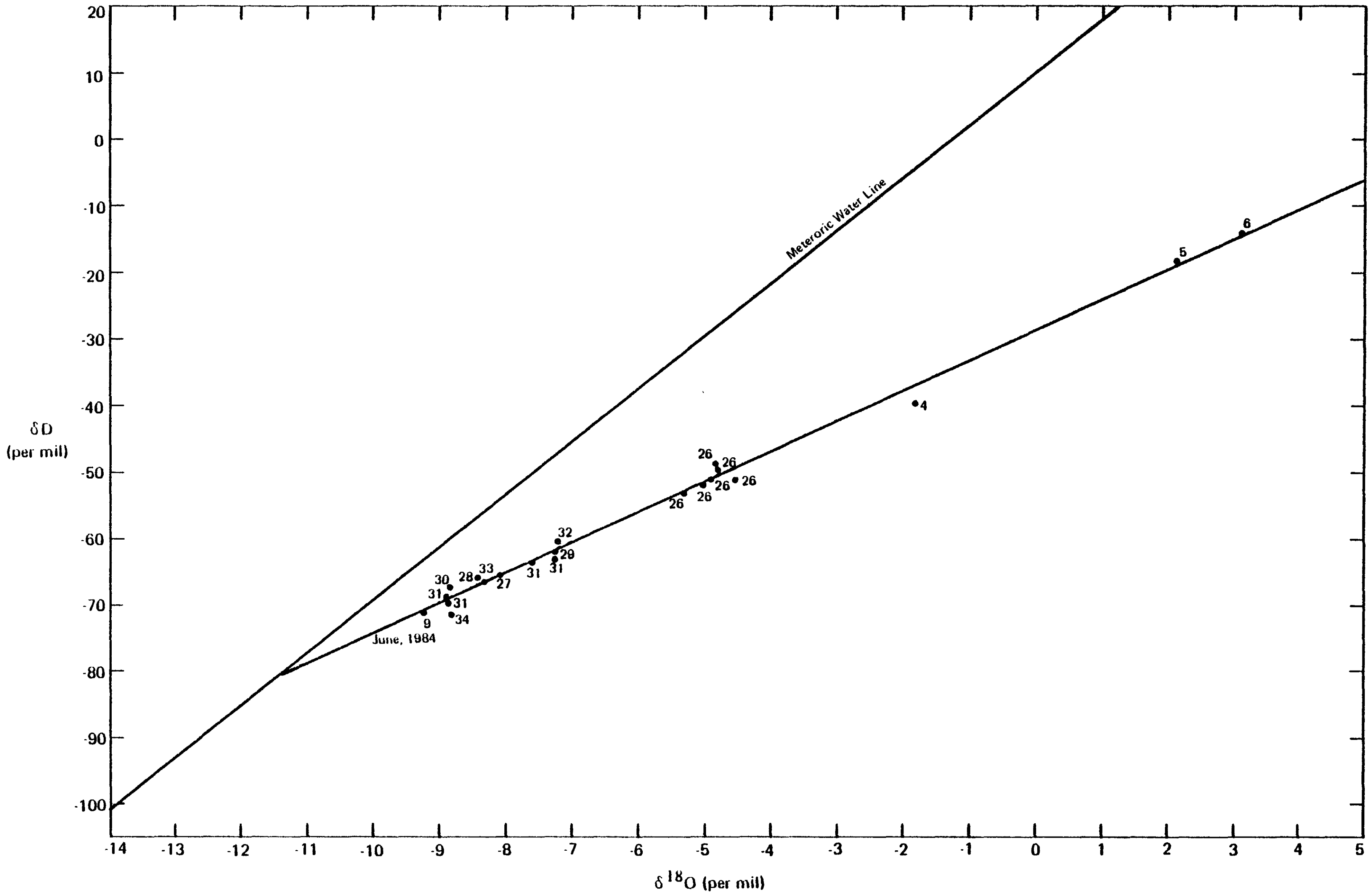

Figure 6.--Variations in δD and $\delta^{18}O$ for waters from the Grassland area denoted by map number.

referred to waters from wells at depths from 400 feet to 1,000 feet as shallow This usage has since been outdated and will not be followed in this report.

Davis and Poland (1957) distinguished between ground water in an upper and lower water-bearing zone. The boundary they used was the diatomaceous clay commonly referred to as the Pleistocene Corcoran Clay Member of the Tulare Formation. Croft (1972) included the Corcoran Clay Member in his E clay. The E clay of Croft lies at depths from 250 feet to more than 800 feet to the south. At Los Banos, the top of the Corcoran (E) Clay Member is at 300 feet (R. W. Page, written commun., 1985). The Corcoran Clay Member of the Tulare Formation will hereafter be referred to as the Corcoran Clay for the sake of brevity.

Deverel and others (1984) identified waters as shallow or perched at depths of near land surface to about 40 feet. These waters are probably in or on the A clay of Croft (1972) and in the study area include infiltrated irrigation water. Deverel and others stated that in some places, unsaturated zones lie beneath this shallow water-bearing zone. The upper and lower water-bearing zones previously identified by Davis and Poland, are grouped together in their report and referred to as the regional aquifer at depths >100 feet below land surface in most places.

The general trend of lateral ground water movement today, in all three zones (shallow, upper and lower), is thought to be northeastward toward the San Joaquin River (USBR, 1984e). Historically this trend has also been identified. Before large scale development in 1915, ground water, both in the unconfined (upper) and confined (lower) aquifers, moved from recharge areas along the sides of the valley, towards topographically low areas in the central part of the valley, then north towards the Sacramento-San Joaquin Delta (Mendenhall, 1916). During the extensive study of the Mendota-Huron area in the 1950's after a second stage of irrigation development, Davis and Poland (1957) found that primary recharge was from the erratically discharging streams on the west side of the valley. They found that secondary recharge induced by heavy pumping which had expanded since 1945, occurred from the northeast from runoff from the Sierra Nevada to some extent in the upper zone, and more appreciably in the lower zone. Eastside stream water had only local influence on the upper zone on the eastern border of the study area, in the immediate vicinity of the San Joaquin River, Fresno Slough and the Kings River. More recently, application of imported surface water has recharged the formerly overdrawn ground water bodies and has changed Mud Slough and parts of the San Joaquin River into ground water discharge areas. During such transition periods it is difficult to accurately identify gaining (ground water discharge) and losing (ground water recharge) reaches of streams. Imported surface water is partially made up of eastside stream waters, e.g. San Joaquin River.

Vertical movement within and between the zones depends on the vertical hydraulic gradient, the effectiveness of confinement, the extent of pumping and the type of sediment. Before large scale pumping in the San Joaquin Valley, water moved from the lower zone upward. Today the tendency is generally reversed, so that water from the upper zone is leaking slowly downward to the deep aquifer; in the shallow zone, water probably also moves downward (USBR, 1984e).

The USBR (1984e) reports that separation of the shallow ground water zone and the upper water-bearing zone is not readily apparent below the Kesterson ponds and generally the area is thought of as the shallow aquifer system. The USBR (1984e) estimates the depth of the upper zone below KNWR is approximately 230 feet. From data presented to the SWRCB (1985) it was concluded that seepage from Kesterson ponds has entered both the shallow and the upper zones. Their record references the San Joaquin Basin Plan of 1975 which indicates that the upper water-bearing zone is used as a drinking water supply. In general, pollutants could reach the lower water-bearing zone through wells perforating both and/or all zones and screened or gravel-packed from surface to bottom. The lower high quality aquifer is extensively used for drinking water supply (SWRCB, 1985). Davis and Poland estimated the number of irrigation wells to be about 1,000 in the Mendota-Huron area in 1951; Davis and others (1959) used well logs from 5,000 wells in making their estimate of storage capacity in the San Joaquin Valley.

Davis and Poland (1957) characterized the waters within the upper and lower zones from the canvass of wells in 1951 as follows. General water types were: the upper zone, Ca-Mg-SO_4; the lower zone, Na-SO_4; and at the bottom of the lower zone, Na-Cl brine. They found that the general character of the lower zone waters was fairly constant and the sum of the determined constituents was approximately 800 ppm. The Ca and Mg sulfate waters of the upper zone were higher in dissolved constituents averaging 3,000 ppm. In a cross-sectional area near Mendota, Davis and Poland found Na-SO_4-Cl and Na-

HCO_3 waters nearer the east side in the upper zone below 300 feet but above the Corcoran Clay. Two types of surface water affected the ground water: Ca-HCO_3 water from the eastside streams and Na-SO_4 from westside streams. In a more detailed description of westside streams from the eastern slopes of the Coast Ranges, Davis (1961) also noted two types of HCO_3-waters and a Na-Cl type water.

Chemical Results from Wells

Results of chemical analysis of the three wells sampled are given in Table 5. Depths and screened intervals are given under sampling site descriptions. Probable depth of the irrigation well at site CQ122TP84 is 125 to 300 feet. The following depths from land surface to the Corcoran Clay are interpreted from Page (unpub. data) for wells sampled: CQ122TP84, irrigation well northeast of Los Banos, 250 feet; CQ159IB84, Los Banos Municipal Well 1, 300-400 feet; and CQ161SD84 irrigation well south of Mendota, 600 feet. The Corcoran Clay layer itself is about 100 feet thick. Therefore the screened interval of CQ159IB84 is above the Corcoran Clay. From the well log, a blue clay was described at an interval from 360 to 425 feet. For CQ161SD84 the screened interval is above, in and below the Corcoran Clay. Probably for CQ122TP84, if the approximated screened interval is from 125 to 300 feet, the pumped interval is above and in the Corcoran Clay.

Se concentrations in waters from both wells near Los Banos (CQ122TP84 and CQ159IB84) were <2 μg/L. Waters from the well south of Mendota (CQ161SD84) contained 61 μg/L Se. The sample location of CQ161SD84 is in the alluvial fan physiographic zone as described by Deverel and others, 1984. The maximum concentration of Se found by Deverel in shallow water from that physiographic zone was 3,000 μg/L. The location of this site of maximum Se concentration is approximately 7 miles southeast of site CQ161SD84. Shallow water samples in the immediate vicinity (<2.2 miles) of CQ161SD84 contained 12 to 920 μg/L Se. Shallow water from the sample site nearest CQ161SD84 (approximately 1 mile) contained 59 μg/L Se. Site location CQ159IB84 is also in the alluvial fan zone. The nearest shallow water sampled by Deverel and others to this site (<1 mile) contained 19 μg/L Se. Site location CQ122TP84 is in the basin trough physiographic zone in an area of low Se contamination in shallow water (<1 to 4 μg/L Se).

Values for other trace elements determined for sample CQ161SD84 in μg/L were: chromium, copper and nickel, <1; aluminum, <10; mercury, 0.7; arsenic and silver, 1; lead, 4; vanadium, 5.6; zinc, 30; molybdenum, 75; and manganese, 320. The concentration for mercury was in the range found in shallow waters in the alluvial fan zone (maximum 1.6 μg/L) by Deverel and others. However, the median concentration was <0.1 μg/L Hg for this zone.

Boron concentrations in well samples ranged from <1 to 2.6 mg/L B. Nitrate in these same samples ranged from <1 to 13 mg/L N. The sample from well CQ161SD84 exceeded the drinking water standard for nitrate of 10 mg/L N (EPA, 1977b).

The well northeast of Los Banos near the Santa Fe Canal (CQ122TP84) contains 45% Na, equal amounts of Ca and Mg, 48% SO_4 and 34% Cl. The well water is supersaturated with respect to the Ca, Mg carbonates, quartz and chalcedony, but not with respect to gypsum. The Los Banos municipal well water (CQ159IB84) contains approximately equal amounts of Na, Ca and Mg and 50% HCO_3 and 31% Cl. The well water is supersaturated only with quartz, chalcedony and cristobalite. The irrigation well south of Mendota (CQ161SD84) contains 46% Ca, 29% Na, 24% Mg and 78% SO_4. The well water is supersaturated with respect to quartz and chalcedony. Due to probable degassing of CO_2 from this sample at the surface, the sample was found to have a slightly negative ΔG_R of -0.29 for calcite; gypsum was also undersaturated.

Therefore, water types for the wells are as follows: CQ122TP84, Na-Ca-Mg-SO_4-Cl; CQ159IB84, Na-Ca-Mg-HCO_3; and CQ161SD84, Ca-Na-Mg-SO_4. In view of the foregoing discussion of water types indicative of water-bearing zones in 1957, no clear relationships are seen. CQ122TP84 is more indicative of westside surface waters and water from the lower zone; CQ161SD84 is more indicative of the upper zone; CQ159IB84 is more indicative of imported surface water. Mixing of waters is clearly a possibility.

Isotopic Results and Indications from Wells

Values of δD and $\delta^{18}O$ for the three wells (Maps #35, 36 and 37) are given in Table 7 and are plotted in Figure 7.

Coplen and Davis (1984) isotopically distinguished confined ground waters, those below the Corcoran Clay, from the shallow ground water above the Corcoran Clay. They report average $\delta^{18}O$ values of modern water (1951) in shallow wells recharged from the Sierra Nevada in the flood plains of the San Joaquin and Kings Rivers to be -11 and -12.3 per mil, respectively. These

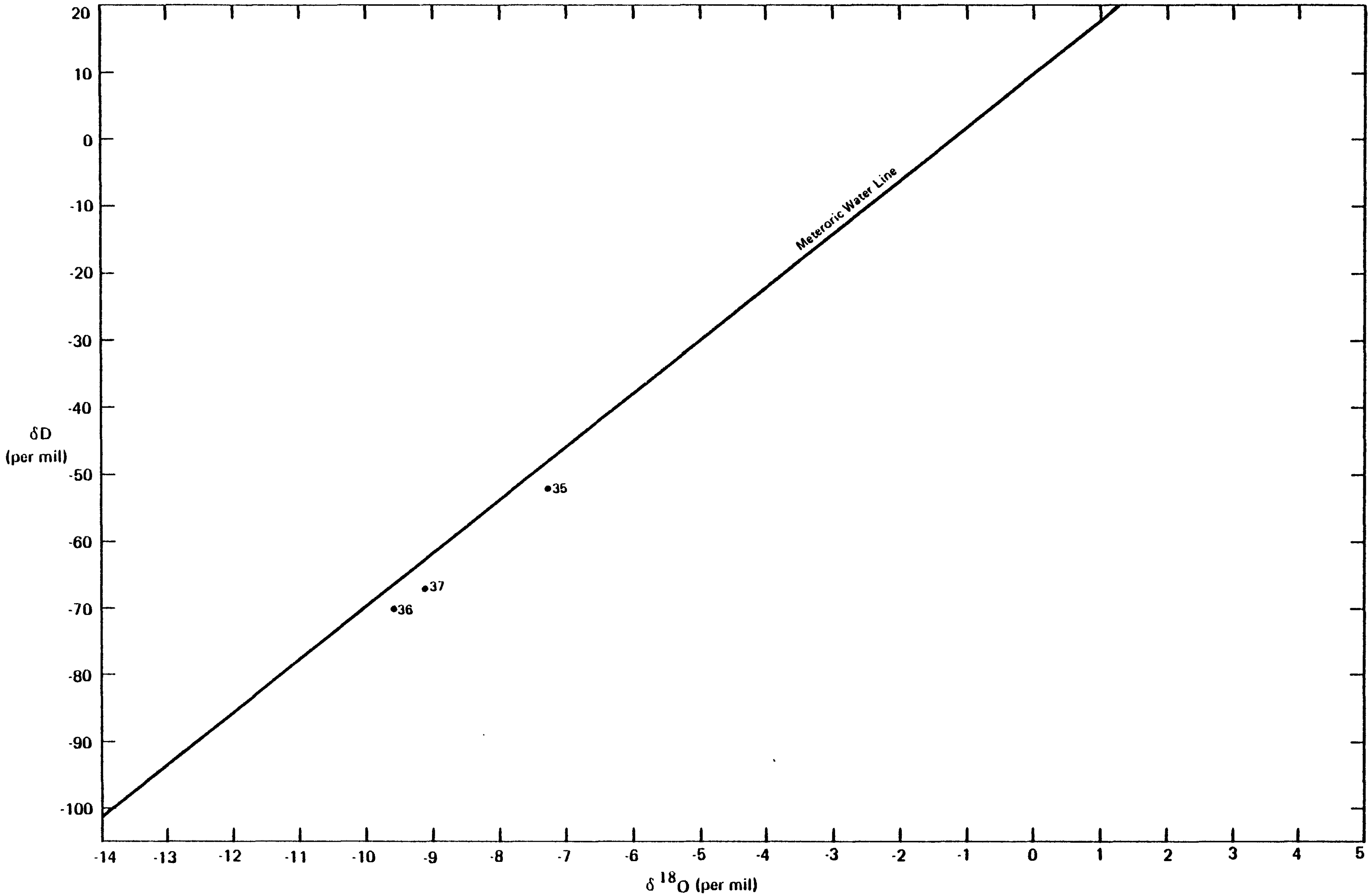

Figure 7.--Variations in δD and $\delta^{18}O$ for waters from wells in the study area denoted by map number.

shallow waters are more depleted in ^{18}O than water from wells in the same area recharged in the middle-Pleistocene. Waters in the colder Pleistocene time should be more depleted in ^{18}O than modern waters and are normally readily distinguishable (Gat, 1974). Coplen and Davis report $\delta^{18}O$ values of -9 per mil for deep (confined) ground water from beneath the Corcoran Clay. They theorize that modern precipitation in both the Central Coast Ranges and the Sierra Nevada is more depleted in ^{18}O than in Pleistocene time because the Coast Ranges have risen from 300 to 1,400 meter (m) and intercepted a higher cloud base. This uplift took place after the close of deposition of the Corcoran Clay, 615,000 years B.P. In general, increased depletion of the heavier isotopes in precipitation is seen with increasing altitude and/or with decreasing temperature (Siegenthaler, 1979). The overall depletion effect in precipitation in both the Sierra Nevada and the Coast Ranges described by Coplen and Davis is in addition to those effects occurring as storms move eastward from the Pacific. The eastward moving storms are intercepted first by the Coast Ranges and then by the Sierra Nevada. This results in an inter-mountain depletion of heavier isotopes in the precipitation of the Sierra Nevada as compared to the precipitation of the Coast Ranges. A further depletion effect is seen on the leeside of each mountain range as compared to the windward, an intra-mountain effect, for the same reason.

Davis and Coplen (1984) present a combined chemical-stable isotope model that suggests that ancient waters with $\delta^{18}O$ values of -10 per mil from the Sierra Nevada, mixed in intermittent lakes during extreme flood events with waters from the pre-emergent Coast Ranges with $\delta^{18}O$ values of about -6 per mil. This resulted in blends of about -9 per mil in $\delta^{18}O$ and 950-500 mg/L SO_4 in the principal confined aquifer system (lower water-bearing zone). Low structural relief during most of the Pleistocene time among other variables combined to preserve the confined paleowaters from being flushed. Shallower ground waters above the Corcoran Clay are seen as more variable by Davis and Coplen and represent recharge from streams similar to ones of today.

Present day westside streams range in $\delta^{18}O$ values from -5 to -8 per mil (Presser and Barnes, unpub. data). Irrigation canals sampled for this report which may reflect precipitation from the Sierra Nevada are the Delta-Mendota Canal with a $\delta^{18}O$ of -12.7, and the Main Canal collected in October, 1983, with a $\delta^{18}O$ of -13.7.

The $\delta^{18}O$ values (Table 7) of -9.5 and -9.1 per mil for CQ159IB84 and

CQ161SD84 respectively, indicate waters associated with the confined aquifer (Coplen and Davis, 1984). However, as can be seen by the isotopic data for an inflow to the SLD (CQ124TP83) and two drains in the Grassland area (CQ107TP84 and CQ112TP84), -9 is not a unique value for $\delta^{18}O$ but can be attained by evaporation from present day shallow waters. Thus, the stable isotopic compositions may not be used to uniquely test for water sources. Consequently, it is not known whether the Se reported for CQ161SD84 of 61 μg/L is from contamination from the shallow seleniferous water or occurs naturally.

The δ^{18} value of -7.2 per mil for CQ122TP84 is more enriched in ^{18}O than the $\delta^{18}O$ values of the other two well waters. This $\delta^{18}O$ value is comparable to that of westside streams recharging the area today. Aridity of the climate during recharge of ground waters may become a factor in the interpretation of isotopic data. Lettis (1982) postulates five series of wet to dry transitions in his outline of the paleohydrology of the streams of the Diablo Range (of the California Coast Range) during the late Quaternary. His model suggests that alluvial deposits accumulate primarily in response to fluctuations in climate rather than episodic tectonism. The more depleted values of $\delta^{18}O$ for CQ159IB84 and CQ161SD84 (-9.5 and -9.1) are more indicative of ground waters that may have been recharged in a less arid climate than present, with meteoric water that had undergone less evaporation.

CONCLUSIONS

Lakin addressed the evaluation of natural Se contamination in the environment in a number of papers beginning in 1941 and continuing through 1973. The problem of salt build-up in the soils of the alluvial fans of the San Joaquin Valley has occurred over geologic time. Installation of underdrains as a solution to the agricultural problem of salt accumulation and water logging of soils in California was mentioned as early as 1916 by Mendenhall. The problem of Se movement in water and into the food chain and its consequent bioaccumulation is a problem that has seemed to occur over a period of only several years. The current source of Se may be different than the source on a geologic time scale. Beginning in 1978, increasing amounts of drainage water were mixed with irrigation water as farmers installed subsurface drains which were connected as inflows to the SLD. Starting in 1981, the majority of the water in the SLD was subsurface drainage water. At present, 253,000 acres of irrigated farmland on the west side of the San

Joaquin Valley are affected by inadequate drainage of salts and water logging (USBR, 1984c). Drainage water from approximately 8,000 acres is discharged into the SLD. Se levels in inflows to the SLD ranged from 140 to 1,400 μg/L in the sampling in August, 1983. Levels in waters of the SLD and the ponds of KNWR have remained at these same high levels through at least June of 1984. The inflow to Kesterson pond 2 contained 270 μg/L Se in January 1985 as compared to 280 μg/L in November, 1983. Effects of greater inflows of mixed waters containing lesser concentrations of Se, (approximately 50 μg/L) drained into the larger Grassland area (50,000 acres), are being seen in the 1984 nesting season sampling of birds. Source concentrations of Se in these mixed waters, originating from tile drainage collector sumps were as high as 4,200 and 1,600 μg/L. Se contents of pond waters despite concentration by evaporation at the end of the summer, in both KNWR (pond 11) and the Grassland, were low (15 and 10 μg/L Se). Se contents of algal mat samples which may contain some sediments taken from these ponds were high (13 to 20 ppm Se, dry weight). Se contents of salt crusts, identified as thenardite, collected from Kesterson pond 11 and the SLD contained 1.8 and 17 ppm Se, respectively. Accumulated amounts in these materials and other parts of the ecosystem may be available for eventual recycling and should be assessed in the evaluation of the toxicity of Se to the environment. No other trace element reported in the waters sampled in the KNWR and Grassland areas or pesticide reported in KNWR, exceeded the various criteria for water at the level of magnitude of Se.

Reaction states in water for various minerals and D/H and $^{18}O/^{16}O$ isotopic ratios were determined in order to trace the origin and history of the waters. These will be used in further studies on the geologic source of Se. For the nine actively inflowing waters to the SLD from the west, Kesterson pond 2 and the SLD water, the correlation coefficient of linear regression between Na and SO_4 is 0.99 and between SO_4 and Se is 0.93. The inflows and ponds at Kesterson all contain Na-SO_4 waters and these waters are all supersaturated with respect to calcite and nearly in equilibrium with gypsum. Grassland pond waters and mixed drainage waters flowing into the Grassland ponds are supersaturted with respect to calcite but are not supersaturated with respect to gypsum. Subsurface waters in collector sumps on and near Nees Avenue are supersaturated with respect to calcite and are near equilibrium saturation with gypsum. Some sumps and the Grassland ponds contain appreciable Cl beside SO_4. No reliable relationship between Se and conductivity was seen in waters of the Grassland area. Canal and mixed background waters are not supersaturated with gypsum. Evaporation trend lines between probable source and pond waters are seen in both KNWR and the Grassland when δD is plotted versus $\delta^{18}O$. A predicted starting composition point for KNWR waters is less depleted in the heavier isotopes (D and ^{18}O) than the irrigation supply water from the Delta-Mendota Canal. The opposite is true in the Grassland, where the predicted source water is more depleted than water from the Main Canal. The more enriched values of $\delta^{18}O$ and δD recorded in water of the irrigation supply of the Grassland is what would be expected from greater reuse (evaporated water returned to the supply) of irrigation water.

Well data were included on a preliminary basis to help elucidate the history of the waters and the possible presence or leakage of Se into the regional aquifers. Irrigation subsurface drainage in the study area is a form of recharge or potential recharge whose effect on the main ground water bodies should be considered. The stable isotopic ratios of $^{18}O/^{16}O$ and D/H could not be used to uniquely test for water sources. A sample from a deeper irrigation well, near an area of known shallow Se contamination, screened from 464 to 1,089 feet, contained 61 μg/L Se. Samples from two shallower wells near Los Banos however, contained <2 μg/L Se. Distribution and movement of Se in the ground water needs and is receiving further study.

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Table 1A.--Locations and chemical compositions of the SLD water, and KNWR and Grassland pond waters.

Map Number	Laboratory Number	Date	Sampling Site Description	Sampling Site Location	County & State	Se µg/L		Temp. °C	pH
						Fe-HCl	Fe-HNO_3		
1	CQ681B83	3 Aug. 1983	Kesterson pond #2, south side, 20 ft offshore	CTR, sec. 21, T. 8 S., R. 10 E.	Merced Co., California	330	350	24.8	7.87
1	CQ119TP83	30 Nov. 1983	San Luis Drain inflow to Kesterson pond #2, south side of Gun Club Road	N, sec. 21, T. 8 S., R. 10 E.	Merced Co., California	280	280	11.0	8.48
1	CQ87TP84	5 Apr. 1984	San Luis Drain inflow to Kesterson pond #2, same location as CQ119TP83	N, sec. 21 T. 8 S., R. 10 E.	Merced Co., California	340	-	17.0	8.70
2	CQ70IB83	3 Aug. 1983	Kesterson pond #11, midpoint of south side	SW, sec. 8, T. 8 S., R. 10 E.	" "	14	15	30.0	8.24
2	CQ120TP83	30 Nov. 1983	Kesterson pond #11, same location as CQ70IB83	SW, sec. 8, T. 8 S., R. 10 E.	" "	62	60	11.0	8.55
2	CQ88TP84	5 Apr. 1984	Kesterson pond #11, same location as CQ70IB83	SW, sec. 8, T. 8 S., R. 10 E.	" "	75	-	20.5	8.75
3	CQ69IB83	3 Aug. 1983	San Luis Drain near entrance to KNWR, at bridge 0.6 miles NW of Lander Ave., at boundary of secs. 22 and 27	SW, sec. 22, T. 8 S., R. 10 E.	" "	320	330	29	8.47
4	CQ119TP84	9 July 1984	Grassland pond on road between Mesquite Duck Club and Chateau Duck Club, 0.7 miles from Swamp Road intersection	SE, sec. 14, T. 11 S., R. 11 E.	" "	-	10	22	7.91
5	CQ120TP84	9 July 1984	Grassland pond in agricultural field 0.1 mile east of Santa Fe Grade Road near Agatha Canal	NW, sec. 2, T. 11 S., R. 11 E.	" "	-	2	25	8.15
6	CQ121TP84	9 July 1984	Grassland pond west of San Luis Drain at edge of Los Banos State Wildlife Area, 0.9 miles north of Henry Miller Avenue	NE, sec. 36, T. 9 S., R. 10 E.	" "	-	9	33	9.25

Map Number	Laboratory Number	Specific Conductance [1]	meq cations/L	Na	K	Mg	Ca	HCO_3 [2]	SO_4	Cl	F	SiO_2	B	NO_3-N [3]	Fe
				mg/L											
1	CQ68IB83	12,000	180	2750	6.4	360	620	214	5550	1950	< 1.0	1.2	18	40	0.04
1	CQ119TP83	--	131	2000	5.7	260	460	204	4100	1300	< 0.5	27	13	38	< 0.02
1	CQ87TP84	10,000	145	2150	5.4	280	560	-	4450	1500	< 0.5	2.2	15	50	< 0.02
2	CQ70IB83	23,000	368	6250	19	705	765	397	11500	4500	< 1.0	33	37	< 20	< 0.1
2	CQ120TP83	--	195	3150	15	390	510	241	6000	2400	< 1.0	7	19	< 10	0.06
2	CQ88TP84	13,000	182	3050	7.9	330	450	-	5350	2150	< 1.0	4.0	17	< 20	< 0.04
3	CQ69IB83	11,000	152	2250	6.2	320	565	158	4700	1650	< 0.5	11	15	49	0.04
4	CQ119TP84	5600	59	890	8.4	101	240	204	1300	785	0.38	5.1	11	3.0	0.20
5	CQ120TP84	6000	70	970	18	160	290	154	1800	920	0.55	21	13	< 1	0.04
6	CQ121TP84	5400	64	915	7.7	130	270	102	1700	785	0.5	12	9.9	< 10	0.02

[1] Micromhos/centimeter at 25°C.

[2] Total alkalinity as HCO_3.

[3] Estimated value.

(page 59 follows)

Table 1B.--Results of additional chemical analyses for the SLD water, and KNWR and Grassland pond waters.

Map Number	Laboratory Number	Fe	Mn	Cd	Co	Cu	Ni	Pb	Zn	Hg (μg/L)	Organic carbon[1/] as carbon (mg/L)	NH_3-N (mg/L)
		μg/L										
1	CQ68IB83	40	<20	<20	<40	<20	<50	<100	<40	<0.1	18	<0.1
1	CQ119TP83	<20	450	<20	<40	<20	<50	<100	<40	<0.1	-	0.30
1	CQ87TP84	<20	<20	<20	<40	<20	<50	<100	<40	-	-	-
2	CQ70IB83[2/]	-	-	-	-	-	-	-	-	<0.1	64	<0.1
2	CQ120IB83	60	60	<20	<40	20	56	<100	<40	<0.1	-	0.24
2	CQ88TP84	<40	120	<40	<80	<40	<100	<200	<80	-	-	-
3	CQ69IB83	40	<20	<20	<40	<20	<50	<100	<40	<0.1	28	0.26
4	CQ119TP84	200	2725	<20	<40	<20	<50	<100	<40	-	18	1.2
5	CQ120TP84	40	135	<20	<40	<20	<50	<100	<40	-	26	0.7
6	CQ121TP84	20	<20	<20	<40	<20	<50	<100	<40	-	17	0.1

[1/] Estimated value.

[2/] Sample contaminated by algae.

Table 2.--Locations and chemical compositions of background irrigation supply and return waters in the areas surrounding KNWR and the SLD.

Map Number	Laboratory Number	Date	Sampling Site Description	Sampling Site Location	County & State	Se µg/L		Temp. ^{o}C	pH
						Fa-HCl	Fa-HNO_3		
7	CQ110TP83	12 Oct. 1983	Delta-Mendota Canal at gate to San Luis Wasteway	SE, sec. 1, T. 10 S., R. 8 E.	Merced Co., California	-	<2	20.0	7.59
8	CQ111TP83	12 Oct. 1983	Volta Drain at screwgate, SE side of and immediately upstream of discharge into San Luis Wasteway	SW, sec. 36, T. 9 S., R. 9 E.	Merced Co., California	-	<2	25.0	8.68
9	CQ112TP83	13 Oct. 1983	Main Canal at discharge into San Luis Canal	NE, sec. 36, T. 10 S., R. 10 E.	Merced Co., California	-	<2	18.0	7.75
9	CQ115TP84	27 June 1984	Main Canal, same location as CQ112TP83	NE, sec. 36, T. 10 S., R. 10 E.	" "	-	10	25	7.6 L
10	CQ113TP83	13 Oct. 1983	Devon Drain and Boundary Drain at pumping station 0.6 mile north of Henry Miller Ave.	NW, sec. 33, T. 9 S., R. 11 E.	" "	-	<2	22.0	7.55
11	CQ114TP83	14 Oct. 1983	Irrigation return water at discharge into ditch parallel to and immediately west of Main Canal, south of farm access road	NW, sec. 20, T. 11 S., R. 11 E.	" "	-	5	18.0	7.68
12	CQ115TP83	14 Oct. 1983	Fremont and Mud Sloughs at confluence, north side of Gun Club Road	SW, sec. 17, T. 8 S., R. 10 E.	" "	-	<2	22.5	7.97
13	CQ116TP83	14 Oct. 1983	Water pumped into north flowing ditch from south flowing ditch north side of Gun Club Road	S, sec. 15, T. 8 S., R. 9 E.	" "	-	<2	21.0	7.79
14	CQ118TP83	30 Nov. 1983	Santa Fe Canal, north side of Gun Club Road	SE, sec. 18, T. 8 S., R. 10 E.	" "	-	10	9.5	8.18

Map Number	Laboratory Number	Specific Conductance [1]	meq cations/L	Na	K	Mg	Ca	HCO_3 [2]	SO_4	Cl	F	SiO_2	B	NO_3-N [3]	Fe
										mg/L					
7	CQ110TP83	350	3.76	40	1.7	11	22	62	44	57	0.17	11	<1	<1	0.02
8	CQ111TP83	1400	16.6	230	14	43	54	381	175	225	0.35	27	1.4	<1	0.02
9	CQ112TP83	330	4.15	49	1.3	12	20	59	90	36	0.14	11	<1	<1	0.02
9	CQ115TP84	1100	11.6	145	7.3	27	59	135 L	250	120	0.17	13	1.3	3.0	0.08
10	CQ113TP83	520	9.63	130	2.3	24	39	96	170	170	0.18	13	<1	<1	0.02
11	CQ114TP83	730	38.0	420	2.7	130	180	297	880	475	0.30	24	2.4	2.5	0.02
12	CQ115TP83	570	23.3	365	4.5	45	72	228	505	270	0.27	24	2.1	1.6	0.02
13	CQ116TP83	360	8.38	86	7.4	25	48	173	165	66	0.27	15	<1	<1	<0.04
14	CQ118TP83	--	16.8	210	4.1	40	85	227	360	170	<1	22	1.7	2.4	<0.02

[1] Micromhos/centimeter at 25°C.

[2] Total alkalinity as HCO_3.

[3] Estimated value.

L denotes laboratory determination.

Table 3.--Locations and chemical compositions of waters from inflows to the SLD.

Map Number	Laboratory Number	Date	Sampling Site Description	Sampling Site Location	County & State	Se µg/L		Temp. °C	pH
						Fa-HCl	Fa-HNO_3		
15	CQ121TP83	1 Dec. 1983	Waste entry into San Luis Drain at Bass Ave., Mendota	NE, sec. 30, T. 13 S., R. 15 E.	Fresno Co., California	195	200	-	7.9 L
16	CQ122TP83	1 Dec. 1983	Waste entry into San Luis Drain at Panoche Road	NW, sec. 8, T. 14 S., R. 15 E.	Fresno Co., California	155	140	-	7.9 L
17	CQ123TP83	1 Dec. 1983	Waste entry into San Luis Drain at California Road	NW, sec. 17, T. 14 S., R. 15 E.	Fresno Co., California	180	160	-	7.9 L
18	CQ124TP83	2 Dec. 1983	Waste entry into San Luis Drain at Jensen Avenue	SW, sec. 17, T. 14 S., R. 15 E.	" "	190	180	-	7.8 L
19	CQ125TP83	2 Dec. 1983	Waste entry into San Luis Drain at North Avenue	SE, sec. 20, T. 14 S., R. 15 E.	" "	355	385	-	7.8 L
20	CQ126TP83	2 Dec. 1983	Waste entry into San Luis Drain, south of Mendota Wildlife Management Area Headquarters	NW, sec. 33, T. 14 S., R. 15 E.	" "	375	400	-	8.0 L
21	CQ127TP83	2 Dec. 1983	Waste entry into San Luis Drain at American Avenue	NE, sec. 4, T. 15 S., R. 15 E.	" "	1350	1400	-	8.0 L
22	CQ128TP83	2 Dec. 1983	Waste entry into San Luis Drain at Lincoln Avenue	SW, sec. 3, T. 15 S., R. 15 E.	" "	500	490	-	8.5 L
23	CQ129TP83	2 Dec. 1983	Waste entry into San Luis Drain at Adams Avenue	NE, sec. 15, T. 15 S., R. 15 E.	" "	1250	1400	-	7.8 L
24	CQ130TP83	2 Dec. 1983	Water entry through pipe cast in east side of San Luis Drain at Clarkson Avenue	NE, sec. 32, T. 16 S., R. 17 E.	" "	-	<2	-	7.7 L
25	CQ131TP83	2 Dec. 1983	Standing water in south end of San Luis Drain	SE, sec. 27, T. 17 S., R. 18 E.	" "	-	<2	-	7.5 L

Map Number	Laboratory Number	Specific Conductance [1]	meq cations/L	Na	K	Mg	Ca	HCO_3 [2]	SO_4	Cl	F	SiO_2	B	NO_3-N [3]	Fe
				mg/L											
15	CQ121TP83	9200	128	1700	5.2	280	610	230 L	3050	1800	<0.5	39	9.9	50	<0.1
16	CQ122TP83	8300	115	1500	5.3	270	550	240 L	3100	1350	<0.5	41	8.3	38	<0.1
17	CQ123TP83	8000	115	1450	5.3	280	570	245 L	3200	1300	<0.5	43	8.7	46	<0.1
18	CQ124TP83	5200	64.7	935	4.2	150	330	145 L	2050	660	<0.5	29	5.4	50	<0.1
19	CQ125TP83	11,000	153	2300	4.2	340	490	230 L	4750	1550	<0.5	42	16	46	<0.1
20	CQ126TP83	8,300	118	1650	4.8	240	520	215 L	3900	950	<0.5	43	11	64	<0.1
21	CQ127TP83	31,000	531	10500	8.0	700	330	270 L	22500	2750	<2.0	26	79	70	<0.2
22	CQ128TP83	9400	133	2100	4.3	215	480	300 L	4350	1000	<0.5	48	15	50	<0.1
23	CQ129TP83	25,000	405	8550	7.4	180	370	285 L	16500	1750	<1.0	37	34	220	<0.2
24	CQ130TP83	270	3.03	32	2.1	2.3	28	85 L	28	24	0.14	10	1.9	<1	<0.02
25	CQ131TP83	350	3.62	30	3.6	9.4	29	140 L	48	11	0.23	9	<1	<1	<0.02

[1] Micromhos/centimeter at 25°C.

[2] Total alkalinity as HCO_3.

[3] Estimated value.

L denotes laboratory determination.

Table 4.--Locations and chemical compositions of waters from sumps and agricultural drains near the Grassland.

Map Number	Laboratory Number	Date	Sampling Site Description	Sampling Site Location	County & State	Se µg/L		Temp. °C	pH
						Fa-HCl	Fa-HNO_3		
26	CQ100TP84	13 June 1984	Sump (southern pipe) along Nees Avenue, 1/2 mile east of Brannon Avenue	N, sec. 31, T. 12 S., R. 13 E.	Fresno Co., California	1600	-	17	7.43
26	CQ101TP84	13 June 1984	Sump (southern pipe) along Nees Avenue, 1 mile east of Brannon Avenue	NE, sec. 31, T. 12 S., R. 13 E.	Fresno Co., California	4200	-	-	7.5 L
26	CQ110TP84	27 June 1984	Sump (southern pipe); same location as CQ101TP84	NE, sec. 31, T. 12 S., R. 13 E.	Fresno Co., California	-	3800	18	7.56
26	CQ108TP84	27 June 1984	Sump discharge, low flow; same location as CQ101TP84	NE, sec. 31, T. 12 S., R. 13 E.	" "	-	3800	18	7.48
26	CQ109TP84	27 June 1984	Sump discharge, high flow; same location as CQ101TP84	NE, sec. 31, T. 12 S., R. 13 E.	" "	-	4000	18	7.45
26	CQ111TP84	27 June 1984	Sump (southwestern pipe); same location as CQ101TP84	NE, sec. 31, T. 12 S., R. 13 E.	" "	-	3800	18	-
27	CQ104TP84	13 June 1984	Sump discharge, corner of Nees and Fairfax Avenues	NW, sec. 33, T. 12 S., R. 13 E.	" "	540	-	-	7.9 L
28	CQ103TP84	13 June 1984	Sump discharge, 1 mile west of Brannon Avenue	NW, sec. 25, T. 12 S., R. 12 E.	" "	84	-	-	7.6 L
29	CQ102TP84	13 June 1984	Pipe in sump 1 mile east of Russell Avenue	SW, sec. 23, T. 12 S., R. 12 E.	" "	360	-	-	7.5 L
30	CQ112TP84	27 June 1984	Agricultural drain at point of entry to Agatha Canal where drain flows under Main Canal	NW, sec. 31, T. 11 S., R. 12 E.	Merced Co., California	-	65	21	7.9
31	CQ106TP84	15 June 1984	Agricultural drain at point of entry to Main Canal at Camp 13 Slough	SW, sec. 27, T. 11 S., R. 11 E.	Merced Co., California	46	-	23	7.96
31	CQ113TP84	27 June 1984	Drain; same location as CQ106TP84	SW, sec. 27, T. 11 S., R. 11 E.	Merced Co., California	-	50	25	-
31	CQ107TP84	15 June 1984	Agricultural drain at point of entry to Camp 13 Slough where drain flows under Main Canal	SW, sec. 27, T. 11 S., R. 11 E.	" "	47	-	18	7.85
31	CQ114TP84	27 June 1984	Drain; same location as CQ107TP84	SW, sec. 27, T. 11 S., R. 11 E.	" "	-	45	25	-
32	CQ118TP84	9 July 1984	Ditch perpendicular to Almond Drive, 1/2 mile west of Gadwall Canal	SE, sec. 5, T. 11 S., R. 11 E.	" "	-	17	17	7.79
33	CQ123TP84	9 July 1984	Inflow to Outside Canal, Nees Ave. and Washoe Ave.	SW, sec. 29, T. 12 S., R. 14 E.	Fresno Co., California	-	8	33	7.99
34	CQ124TP84	9 July 1984	Sump discharge, 1.4 miles northwest of CQ123TP84	SW, sec. 19, T. 12 S., R. 14 E.	Fresno Co., California	-	76	21	7.8

Map	Laboratory	Specific [1]	meq	Na	K	Mg	Ca	HCO_3 [2]	SO_4	Cl	F	SiO_2	B	NO_3-N [3]	Fe
Number	Number	Conductance	cations/L							mg/L					
26	CQ100TP84	14,000	187	3000	5.2	270	680	278	4100	2750	<1.0	37	26	240	<0.1
26	CQ101TP84	23,000	306	5700	7.6	350	590	370 L	6900	4900	<1.0	40	52	280	<0.2
26	CQ110TP84	21,000	-	6000	-	-	-	-	-	-	-	41	53	-	-
26	CQ108TP84	19,000	-	5900	-	-	-	-	-	-	-	43	52	-	-
26	CQ109TP84	22,000	-	5750	-	-	-	-	-	-	-	42	53	-	-
26	CQ111TP84	22,000	-	5900	-	-	-	-	-	-	-	43	49	-	-
27	CQ104TP84	7900	106	1450	3.4	210	510	215 L	3250	920	<0.5	41	12	60	<0.1
28	CQ103TP84	7600	99.3	1400	4.6	180	470	295 L	2900	1000	<0.5	41	11	35	<0.1
29	CQ102TP84	9500	126	1800	3.3	240	570	275 L	3300	1500	<0.5	28	21	75	<0.1
30	CQ112TP84	3300	38.3	495	4.3	63	230	170 L	935	460	0.27	17	6.0	25	0.06
31	CQ106TP84	2500	28.7	400	6.6	50	140	179	730	245	0.33	13	3.2	10	-
31	CQ113TP84	2800	-	450	-	-	-	-	890	-	-	17	3.8	-	0.04
31	CQ107TP84	3700	44.2	500	4.5	78	320	154	1150	520	0.26	20	5.7	25	0.04
31	CQ114TP84	3300	-	440	-	-	-	-	1000	-	-	20	4.7	-	-
32	CQ118TP84	18,000	265	4050	2.7	790	480	452	9050	2350	<1.0	40	42	5.1	<0.2
33	CQ123TP84	1300	13.2	145	8.5	23	95	146	340	97	0.97	20	1.1	7.0	<0.02
34	CQ124TP84	7300	92.0	1300	2.3	200	380	375	3200	530	<0.5	51	18	14	0.02

[1] Micromhos/centimeter at 25°C.

[2] Total alkalinity as HCO_3.

[3] Estimated value.

L denotes laboratory determination.

Table 5.--Locations and chemical compositions of waters from wells in the study area.

Map Number	Laboratory Number	Date	Sampling Site Description	Sampling Site Location	County and State	Se µg/L		Temp. °C	pH
						Fa-HCl	Fa-HNO_3		
35	CQ122TP84	9 July 1984	Irrigation supply well; near Santa Fe Canal; 2-1/2 miles northeast of Los Banos Depth: unknown	SE, sec. 1, T. 10 S., R. 10 E.	Merced Co., California	--	<2	21	7.59
36	CQ159IB84	13 Dec. 1984	Municipal supply well #1; Los Banos City Water Works, 4th Street, Los Banos Depth: 710 ft, plugged at 300 ft; screened from 160 to 300 ft	NW, sec. 23, T. 10 S., R. 10 E.	Merced Co., California	<2	<2	19.5	6.82
37	CQ161SD84	19 Nov. 1984	Irrigation supply well, 12.5 miles south of Mendota Depth: 1,089 ft; screened from 464 to 1,089 ft	SE, SW, sec. 6, T. 16 S., R. 15 E.	Fresno Co., California	--	61 62 [4]	23	7.0

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[4] Analyzed by Denver Central Laboratory, USGS

Map	Laboratory	Specific [1]	meq	Na	K	Mg	Ca	HCO_3 [2]	SO_4	Cl	F	SiO_2	B	NO_3-N [3]	Fe
Number	Number	Conductance	cations/L	mg/L											
35	CQ122TP84	2700	30.3	310	3.6	100	170	314	690	360	0.2	38	2.6	<1	0.31
36	CQ159IB84	1200	12.2	100	2.6	44	83	349	105	126	<0.1	51	<1	5.9	<0.02
37	CQ161SD84 [4]	2700	30.2	200	5.6	90	280	193	1200	110	0.1	43	1.3	13	0.06

[1] Micromhos/centimeter at 25°C.

[2] Total alkalinity as HCO_3.

[3] Estimated value.

[4] Analyzed by Denver Central Laboratory, USGS.

L denotes laboratory determination.

Table 6.—Results of analyses for $\delta^{18}O$ and δD in waters from the KNWR and SLD areas.

Map Number	Laboratory Number	$\delta^{18}O-H_2O$ (per mil SMOW)	$\delta D-H_2O$ (per mil SMOW)
1	CQ68IB83	-4.24	-46.6
1	CQ119TP83	-6.55	-56.4
2	CQ70IB83	+4.03	-7.0
2	CQ120TP83	-2.01	-21.7
2	CQ88TP84	-1.87	-31.4
3	CQ69IB83	-5.42	-52.1
7	CQ110TP83	-12.74	-90.0
8	CQ111TP83	-8.96	-66.2
9	CQ112TP83	-13.67	-97.9
10	CQ113TP83	-12.10	-90.4
11	CQ114TP83	-11.06	-83.3
12	CQ115TP83	-9.92	-76.3
13	CQ116TP83	-12.03	-89.9
14	CQ118TP83	-6.22	-50.8
15	CQ121TP83	-7.92	-60.7
16	CQ122TP83	-8.59	-66.4
17	CQ123TP83	-8.23	-64.1
18	CQ124TP83	-9.19	-69.8
19	CQ125TP83	-7.96	-62.2
20	CQ126TP83	-8.49	-65.9
21	CQ127TP83	-6.69	-60.2
22	CQ128TP83	-8.57	-68.9
23	CQ129TP83	-7.40	-61.8
24	CQ130TP83	-11.40	-87.2
25	CQ131TP83	-2.15	-37.9

Table 7.— Results of analyses for $\delta^{18}O$ and δD in water from the Grassland area and study area wells.

Map Number	Laboratory Number	$\delta^{18}O-H_2O$	$\delta D-H_2O$
		(per mil SMOW)	
4	CQ119TP84	-1.77	-39.4
5	CQ120TP84	+2.17	-18.3
6	CQ121TP84	+3.18	-13.8
9	CQ115TP84	-9.21	-70.8
26	CQ100TP84	-5.32	-52.7
26	CQ101TP84	-4.49	-50.7
26	CQ110TP84	-4.78	-49.2
26	CQ108TP84	-4.87	-50.9
26	CQ109TP84	-4.81	-48.5
26	CQ111TP84	-4.97	-51.5
27	CQ104TP84	-8.06	-65.4
28	CQ103TP84	-8.42	-65.6
29	CQ102TP84	-7.22	-61.8
30	CQ112TP84	-8.83	-67.3
31	CQ106TP84	-7.22	-63.1
31	CQ113TP84	-7.58	-63.6
31	CQ107TP84	-8.89	-68.5
31	CQ114TP84	-8.85	-69.1
32	CQ118TP84	-7.18	-60.1
33	CQ123TP84	-8.31	-66.0
34	CQ124TP84	-8.78	-71.2
35	CQ122TP84	-7.24	-52.3
36	CQ159IB84	-9.54	-69.9
37	CQ161SD84	-9.11	-67.0
		-9.1	-67 1/

1/Anaylsis by Denver Central Laboratory, USGS.

Table 8.--Total herbicide and total insecticide analysis of water samples CQ68IB83, CQ69IB83, CQ70IB83 and CQ119TP83.

USGS, Denver Central Laboratory, analyst.

Results	µg/L
Chlorinated phenoxy acid herbicides	
Silvex	<0.01
2,4-D	<0.01 [1/]
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
Heptachlor epoxide	<0.01
Lindane	<0.01
Methoxychlor	<0.01
Mirex	<0.01
Perthane	<0.1
Gross polychlorinated biphenyls	<0.1
Gross polychlorinated napthalenes	<0.1
Toxaphene	<1
Organophosphorous insecticides	
Diazinon	<0.01
Ethion	<0.01
Malathion	<0.01
Methylparathion	<0.01
Methyltrithion	<0.01
Parathion	<0.01
Trithion	<0.01

[1/] Sample CQ119TP83 contained 0.06 µg/L 2,4-D

Table 9.—Volatiles analysis of water samples CQ68IB83, CQ69IB83, CQ70IB83 and CQ119TP83.

M. Brooks, analyst, USGS, Denver Central Laboratory.

Method

EPA Method 624: Purgeables by Gas Chromatography/Mass Spectrometry (GC/MS)

Compounds on EPA priority pollutant list plus EDB were identified and quantitated from standards analyzed under identical conditions. Other comparisons were from matches with National Bureau of Standards (NBS) MS library. Concentrations of these compounds (*) were estimated by assuming a response factor of 1.0 relative to the internal standard.

Results		µg/L
CQ68IB83	bromoform	9.8
	dibromomethane	0.8*
CQ69IB83	bromoform	0.6
	dimethylsulfide	0.7*
	trichlorfluoromethane	12
CQ70IB83	chloromethane	7.7
	dimethylsulfide	34*
CQ119TP83	dibromomethane	1.3*

Surrogate recoveries

bromochloromethane	92%
1-bromo-2-chloroethane	106%
1,4-dichlorobutane	98%

Table 10.—Capillary GC/MS analysis of extracts from water samples CQ68IB83, CQ69IB83, CQ70IB83 and CQ119TP83.

M. Schroeder and R. White, analysts, USGS,
Denver Central Laboratory.

Method

Three sets of methylene chloride extracts were performed in sequence using 1,000 ml sample: (1) neutral, no pH adjustment; (2) base, pH >11; (3) acid pH <2. Extracts were concentrated to 1.0 ml. Analysis was performed on a Hewlett-Packard 5985 GC/MS. Separation of sample components was done on a 25 m X 0.21 mm ID SE-54 fused silica capillary column held at 50°C for 5 minutes after a 1 µl sample injection, then programmed at 8°C per minute to 300°C. The capillary column was coupled directly to the mass spectrometer, which was set to analyze from 40-450 atomic mass unites with a scan time of 0.25 second. Spectrum matches were obtained from NBS computerized library. Best library matches were selected according to the reliability factor which indicates the quality of match between sample and library spectra. A value of 100 is most reliable. Compound concentrations relative to the concentration of the internal standard, perdeuteronapthalene. No recovery corrections from added surrogates were made.

Results

No compounds identified.

Table 11.—Capillary GC/MS analysis of extracts from sediment sample associated with water sample CQ119TP83.

M. Schroeder and R. White, analysts, USGS,
Denver Central Laboratory.

Method

25 grams (dry weight) of sample was continuously extracted with methylene chloride and methanol for 12 hours. Surrogate compounds were added prior to extraction. Extracts were concentrated to 1.0 ml. Analysis by GC/MS was under same conditions as given for water extracts.

Results

Compounds tentatively identified as actual sample components; concentrations are semiquantitative (order-of-magnitude).

	μg/kg	Reliability Factor
Dimethyltrisulfide	1265	83
Trans-4-chloro-cyclohexane	2086	11
Dibromomethane	209	25
1-methyl-1H-pyrrole	226	24
4-methyl-phenol	15,725	89
1,2,4-trithiolane	6678	63
1,3,dihydro-2H-indol-2-one	433	36
1,3-dihydro-1-methyl-2H-indol-2-one	390	36
1,2,3,5,6-pentathiepane	21,584	89
[1/] hydrocarbon	237	100
hexathiepane	721	27
Detection threshold	133	

Surrogate recoveries

D5-phenol	91%
1,4-dibromo-benzene	92%
2,4-dibromo-phenol	69%
2,2-difluorobiphenyl	84%
2,4,6-tribromophenol	18%
4,4-dibromobiphenyl	66%

[1/] unidentified