

**SELENIUM CONCENTRATIONS IN WATERS TRIBUTARY TO AND
IN THE VICINITY OF THE KESTERSON NATIONAL WILDLIFE REFUGE,
FRESNO AND MERCED COUNTIES, CALIFORNIA**

By T. S. Presser and Ivan Barnes

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ABSTRACT

Analyses were made for selenium in waters and other materials of the Kesterson National Wildlife Refuge. Analyses were also made of source agricultural drainage waters from the San Luis Drain discharged into the refuge, and surrounding irrigation supply and return waters.

Selenium concentrations range from 140 to 1,400 micrograms per liter ($\mu\text{g/L}$) in irrigation drain waters supplied to the San Luis Drain. The selenium supplied to the Kesterson National Wildlife Refuge is to a small extent precipitated in sodium sulfate (thenardite) but a higher concentration was found in an algal mat.

Most other waters of the area contain less than detectable ($<2 \mu\text{g/L}$) concentrations of selenium.

Oxidation of organic matter and reduction of selenate (SeO_4^{-2}) to selenite (SeO_3^{-2}) were found to be necessary for a quantitative analysis of total selenium.

INTRODUCTION

The United States Fish and Wildlife Service (U.S.F. & W.S.) reported to the U.S. Geological Survey (U.S.G.S.) that unusually high rates of mutation occurred in hatchlings of wild waterfowl (up to 40% for coots) in the Kesterson National Wildlife Refuge (Felix Smith, oral commun., July, 7 1983). The U.S.F. & W.S. further stated that analyses of hatchling tissue showed high selenium (Se) concentrations. Information on Se concentrations in fish from the Kesterson Reservoir and San Luis Drain was released later in a report by the U.S. Bureau of Reclamation (February, 1984). Concentrations of Se were as much as 100 times higher than those of fish from the Volta Wildlife Refuge comparison test area.

A map of California (No. 214-308-5165), Central Valley Project, San Luis Unit, West San Joaquin Division by the Bureau of Reclamation in September, 1975 gives a description of the San Luis Drain Federal Facility:

"(San Luis Drain) will be a concrete-lined canal extending 188 miles from the vicinity of Kettleman City to the lower San Joaquin-Sacramento Delta. The Drain will convey and dispose of subsurface irrigation return flows from the San Luis Service area. A feature of the Drain is the Kesterson Reservoir area where water is stored and regulated. The reservoir is designated as a National Wildlife Refuge for the conservation and management of wildlife and recreation."

Predictions about the mobility of Se are given by Lakin in a chapter in "Selenium in Agriculture" (1961). He stated that in regions of low rainfall and alkaline soils, part of the Se would occur as selenate (SeO_4^{-2}). As SeO_4^{-2} , it would be available to vegetation and readily transported in ground water. In contrast, are regions of acid environment where Se would tend to occur in ferric hydroxide precipitates as basic ferric selenite

($\text{Fe}_2(\text{OH})_4\text{SeO}_3$). This form is more stationary and presumably of low availability to plants. The areas supplying water to the San Luis Drain have low rainfall, approximately 10 inches annually, (National Oceanic and Atmospheric Administration, 1981).

Because of the potential hazards of mutagens in water, the U.S.G.S. Initiated a study of the waters in and tributary to the Kesterson National Wildlife Refuge. Other water supplies in the area were studied to provide a basis for comparison with the Kesterson water supply. The study included but was not limited to analyses for Se.

The chemistry of Se is complex, especially in natural systems where a range of oxidation states may be expected and a variety of biochemical effects may be anticipated. Further complications were expected in analytical procedures because large variations in concentrations of solutes lead to complex matrix effects. A broad analytical experience with wide ranges of inorganic solutes in water facilitated this study (Presser and Barnes, 1974).

FIELD AND HYDROLOGIC RELATIONS

Maps of the study area are shown in Figures 1 and 2. Approximately 80 miles of the San Luis Drain are now completed, from Burrel, 20 miles southwest of Fresno in the south to Kesterson in the north. Figure 1 shows sample locations in the vicinity of the Kesterson National Wildlife Refuge. Figure 2 shows sample locations of inflows into the San Luis Drain. The two areas are not contiguous. Figure 3 is a map of Kesterson National Wildlife Refuge distributed by the State of California, Department of Fish and Game. The evaporation ponds are numbered 1 through 12. The San Luis Drain borders the ponds on the east. The only visible entries from the San Luis Drain into the Kesterson ponds are into ponds 2 and 12. The water evaporates as it flows from pond to pond in a northerly direction from pond 2 to pond 11 where flow

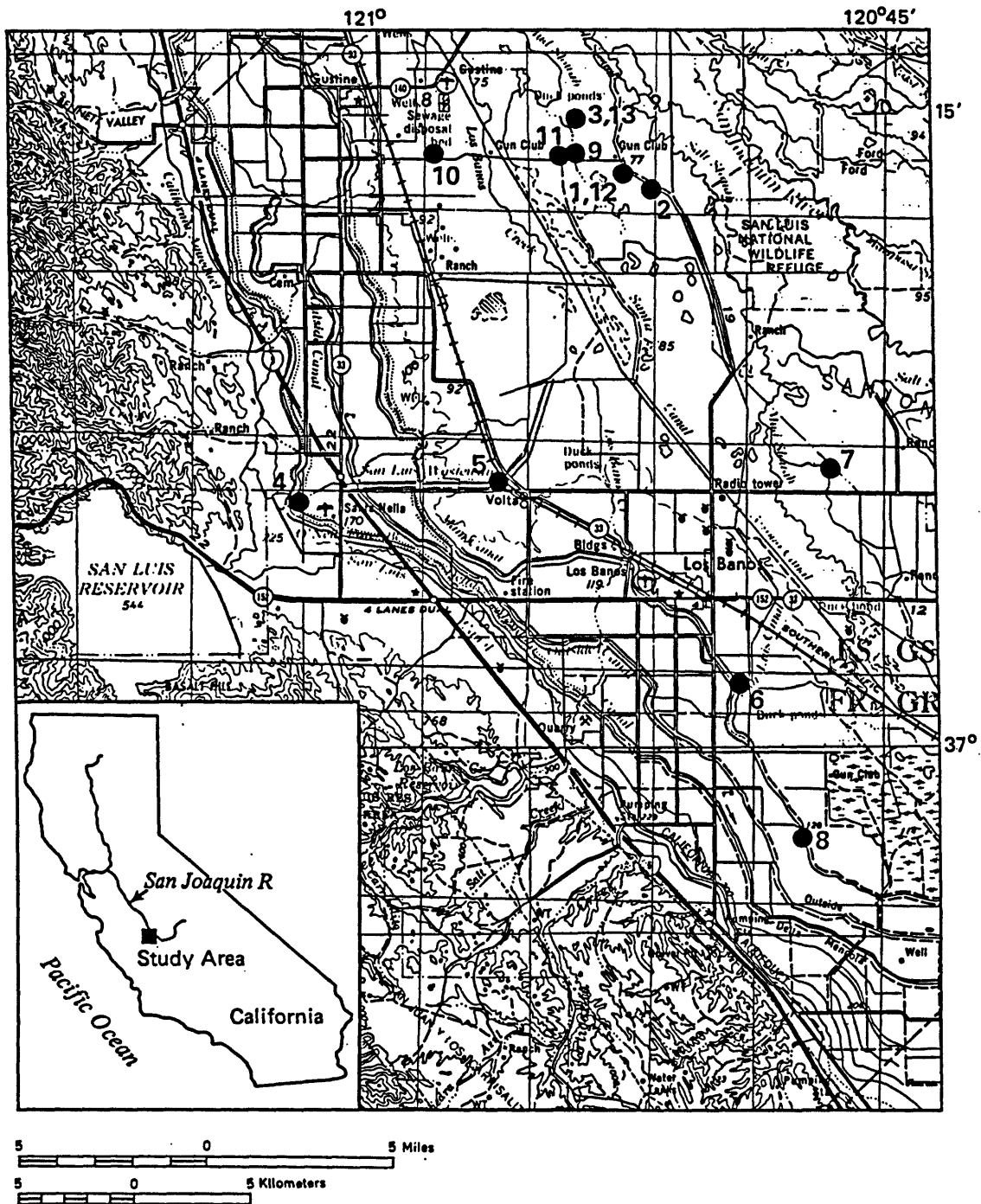


Figure 1.--Sampling site locations in the vicinity of Kesterson National Wildlife Refuge.

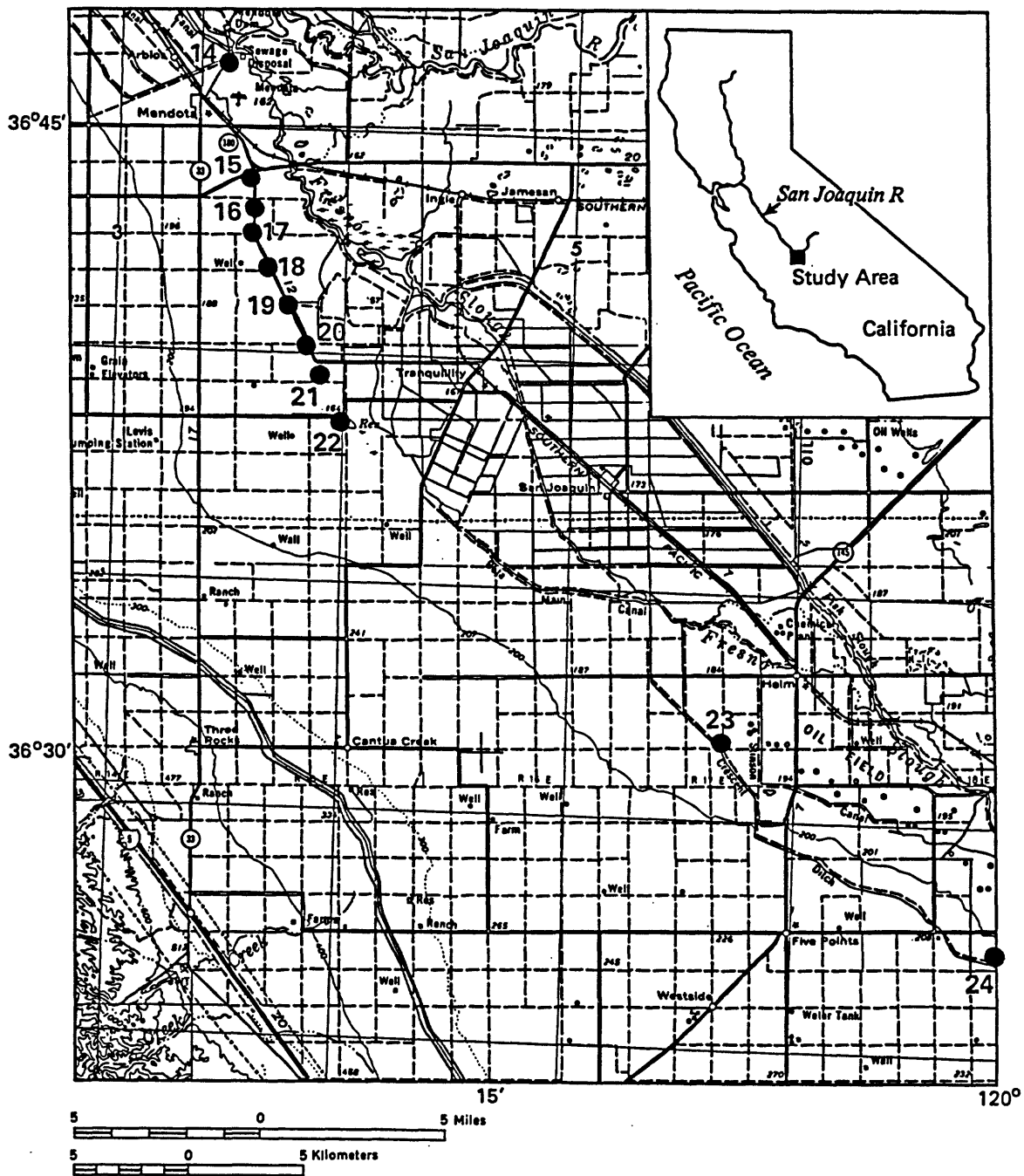


Figure 2.--Sampling site locations of inflows into the San Luis Drain.

KESTERSON NATIONAL WILDLIFE REFUGE MERCED COUNTY

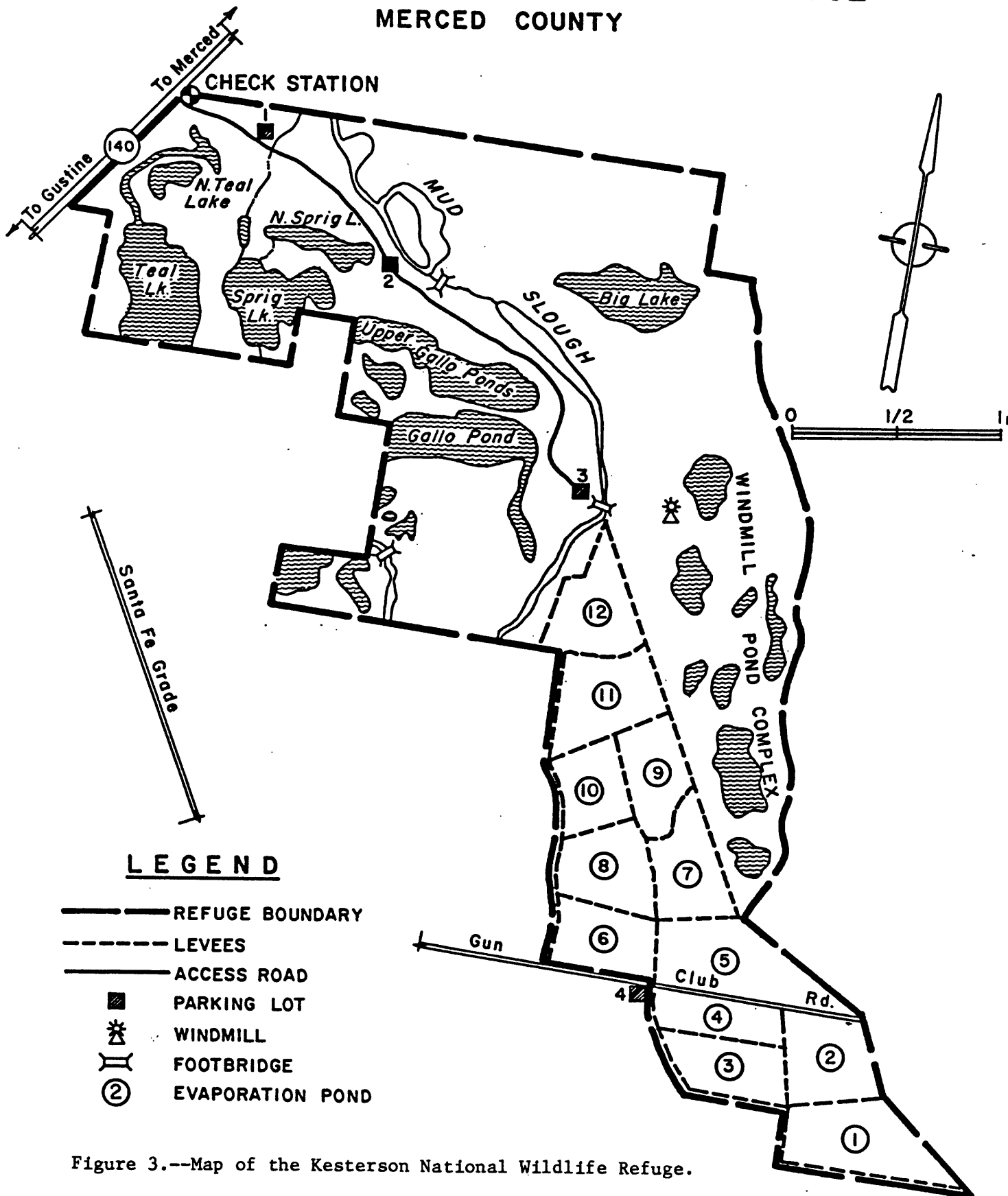


Figure 3.--Map of the Kesterson National Wildlife Refuge.

normally terminates. Pond 12 receives flow intermittently when there is a surplus of water in the San Luis Drain.

Samples were collected in August, 1983 to show conditions characteristic of the study area at the end of the dry summer. Water samples were obtained from the Kesterson Ponds 2 and 11. 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 surrounding area. These included the Delta-Mendota Canal, the Volta Drain, and the San Luis Canal (Main Canal water).

In late November and early December, samples of the ten actively inflowing waters to the San Luis Drain were collected. Stagnant water in entries to the drain were not collected. The waters of the south end of the San Luis Drain, Kesterson Pond 11 and the inflow into pond 2 were also obtained.

Sample numbers, locations, descriptions and dates are given in Table 1.

FIELD METHODS

Water samples for subsequent selenium and other determinations were collected in stainless steel pressure vessels. The vessels were rinsed three times with distilled water after each use and were rinsed three times with the next water to be sampled before the sample was collected.

Samples were pressure filtered in the field through membrane filter discs 142 mm in diameter. The large diameter allowed faster filtration of samples that were turbid with algae and sediment. The effective pore size of the filters is 0.1 micrometers. Pressure was supplied by compressed nitrogen. After use the stainless steel filter holder was rinsed three times with distilled water. The first filtrate of the next sample was discarded and subsequent filtrate was used to rinse sample bottles and caps three times

Table 1.—Locations of sampling sites.

| Map # | Number | Name | Location | Date |
|-------|-----------|--|------------------------------------|------------|
| 1 | CQ681B83 | Kesterson Pond #2, south side, 20 ft offshore | sec. 21 T. 8 S., R. 10 E. | 3 Aug. 83 |
| 2 | CQ691B83 | San Luis Drain at bridge, 0.6 mi NW of Lander Ave., at sec. 22 and 27 boundary | SW, sec. 22, T. 8 S., R. 10 E. | 3 Aug. 83 |
| 3 | CQ701B83 | Kesterson Pond #11, south side of intersection of roads rounding pond 11 and that between ponds 9 and 11 | SW, sec. 8, T. 8 S., R. 10 E. | 3 Aug. 83 |
| 4 | CQ110TP83 | Delta-Mendota Canal at gate to San Luis Wasteway | SE, sec. 1, T. 10 S., R. 8 E. | 12 Oct. 83 |
| 5 | CQ111TP83 | 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. | 12 Oct. 83 |
| 6 | CQ112TP83 | Main Canal at discharge into San Luis Canal | NE, sec. 36, T. 10 S., R. 10 E. | 13 Oct. 83 |
| 7 | CQ113TP83 | Devon drain at pumping station, 0.6 mi north of Henry Miller Ave. | NW, sec. 33, T. 9 S., R. 11 E. | 13 Oct. 83 |
| 8 | CQ114TP83 | Irrigation return water at discharge into ditch parallel to to and immediately west of Main Canal, south of farm access road | NW, sec. 20, T. 11 S., R. 11 E. | 14 Oct. 83 |
| 9 | CQ115TP83 | Fremont and Mud Sloughs at confluence, north side of Gun Club Road | SW, sec. 17, T. 8 S., R. 10 E. | 14 Oct. 83 |
| 10 | CQ116TP83 | 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. | 14 Oct. 83 |
| 11 | CQ118TP83 | Santa Fe Canal, north side of of Gun Club Road | SE, sec. 18, T. 8 S., R. 10 E. | 30 Nov. 83 |
| 12 | CQ119TP83 | San Luis Drain into Kesterson Pond #2, south side of Gun Club Road | N, sec. 21, T. 8 S., R. 10 E. | 30 Nov. 83 |
| 13 | CQ120TP83 | Kesterson Pond #11, south side, same location as CQ701B83 | SW, sec. 8, T. 8 S., R. 10 E. | 30 Nov. 83 |
| 14 | CQ121TP83 | Waste entry into San Luis Drain at Bass Avenue, Mendota | NE, sec. 30, T. 13 S., R. 15 E. | 1 Dec. 83 |
| 15 | CQ122TP83 | Waste entry into San Luis Drain at Panoche Road | NW, sec. 8, T. 14 S., R. 15 E. | 1 Dec. 83 |
| 16 | CQ123TP83 | Waste entry into San Luis Drain at California Road | NW, sec. 17, T. 14 S., R. 15 E. | 1 Dec. 83 |
| 17 | CQ124TP83 | Waste entry into San Luis Drain at Jensen Avenue | SW, sec. 17, T. 14 S., R. 15 E. | 2 Dec. 83 |
| 18 | CQ125TP83 | Waste entry into San Luis Drain at North Avenue | SE, sec. 20, T. 14 S., R. 15 E. | 2 Dec. 83 |
| 19 | CQ126TP83 | Waste entry into San Luis Drain, south of Mendota Wildlife Management Area Headquarters | NW, sec. 33, T. 14 S., R. 15 E. | 2 Dec. 83 |
| 20 | CQ127TP83 | Waste entry into San Luis Drain at American Road | NE, sec. 4, T. 15 S., R. 15 E. | 2 Dec. 83 |
| 21 | CQ128TP83 | Waste entry into San Luis Drain at Lincoln Avenue | SW, sec. 3, T. 15 S., R. 15 E. | 2 Dec. 83 |
| 22 | CQ129TP83 | Waste entry into San Luis Drain at Adams Avenue | NE, sec. 15, T. 15 S., R. 15 E. | 2 Dec. 83 |
| 23 | CQ130TP83 | 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 Dec. 83 |
| 24 | CQ131TP83 | Standing water in south end of San Luis Drain | SE, sec. 27, T. 17 S., R. 18 E. | 2 Dec. 83 |

before filling with aliquots for the determinations.

Glass bottles with polyethylene inserts in the caps were used as containers for water samples for isotope analyses.

Conventional polyethylene bottles were used as containers for filtered samples for Se determination. One aliquot was acidified with nitric acid (Fa-HNO₃) and one with hydrochloric acid (Fa-HCl), both to a pH less than 2.5 as measured with pH paper. Amounts of acids added to each sample were recorded.

Shendrikar and West (1975) reported a loss of 2% when 1 milligram per liter (mg/L) Se was preserved with 0.5% nitric acid (HNO₃) in polyethylene bottles for a test period of 15 days. The second set of samples was preserved with hydrochloric acid (HCl) because there are conflicting reports in the literature of different acids acting as an interferent in the hydride formation technique used for analyzing Se (Pierce and Brown, 1977). HCl was chosen because it is the acid used later in the hydride formation. Further information about the stability of Se in aqueous solutions is given in Cheam and Agemian (1980). Agreement in the literature exists that adjustment to a pH <2 is adequate. Information on the preservation of the natural distribution of Se between its different oxidation states will be discussed later.

LABORATORY METHODS

Waters

Sodium was determined by atomic absorption spectrophotometry using a filtered, acidified (Fa-HCl) sample. Deuterium and hydrogen (D/H) were released from water samples for isotope analysis by reaction with uranium. The oxygen isotope ratio ¹⁸O/¹⁶O, on water was measured on carbon dioxide in equilibrium with the water. Determinations were made of the D/H and ¹⁸O/¹⁶O

ratios using a Finnigan Mat 251¹ gas source mass spectrometer. Sulfate was determined by ion chromatography on a filtered, unacidified sample. Estimates of organic carbon were made by determining total carbon and inorganic carbon and computing the difference and also by analyzing a sample which had been freed of inorganic carbon for total carbon. Samples were run on a Beckman Total Organic Carbon Analyzer Model 915-B.

Because prior knowledge of Se speciation was not available, precautions were taken to determine the total of whatever forms of Se were preserved in the sample aliquots, selenate (SeO_4^{-2}), selenite (SeO_3^{-2}) and/or elemental selenium (Se^0). Further differentiation had to be made as to whether the Se was combined with organic compounds since rather high organic carbon concentrations were suspected and found in the drain and ponds (20 to 60 mg/L C). Organic selenides (Se^{-2}) are volatile (Chan, 1975; Cutter, 1978 and 1982) and in general selenides were not preserved or looked for in these oxic waters. The analysis scheme is detailed in Figure 4.

In order to break down organo metal compounds the traditional oxidative digestion was applied to the waters as a first step in the determination of total Se. A digest applied specifically to Se using acid and potassium persulfate ($\text{K}_2\text{S}_2\text{O}_8$) is described by Goulden and Brooksbank (1974) as a manual step before introduction of the sample into an automated procedure. $\text{K}_2\text{S}_2\text{O}_8$ was also added as a further step in digestion for the analysis of mercury in organic mercurials, improving the recovery in waste waters to 100% (U.S. Environmental Protection Agency, 1971).

To twenty-five milliliters (ml) of the acidified sample, 1 ml of 5% wt/v

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

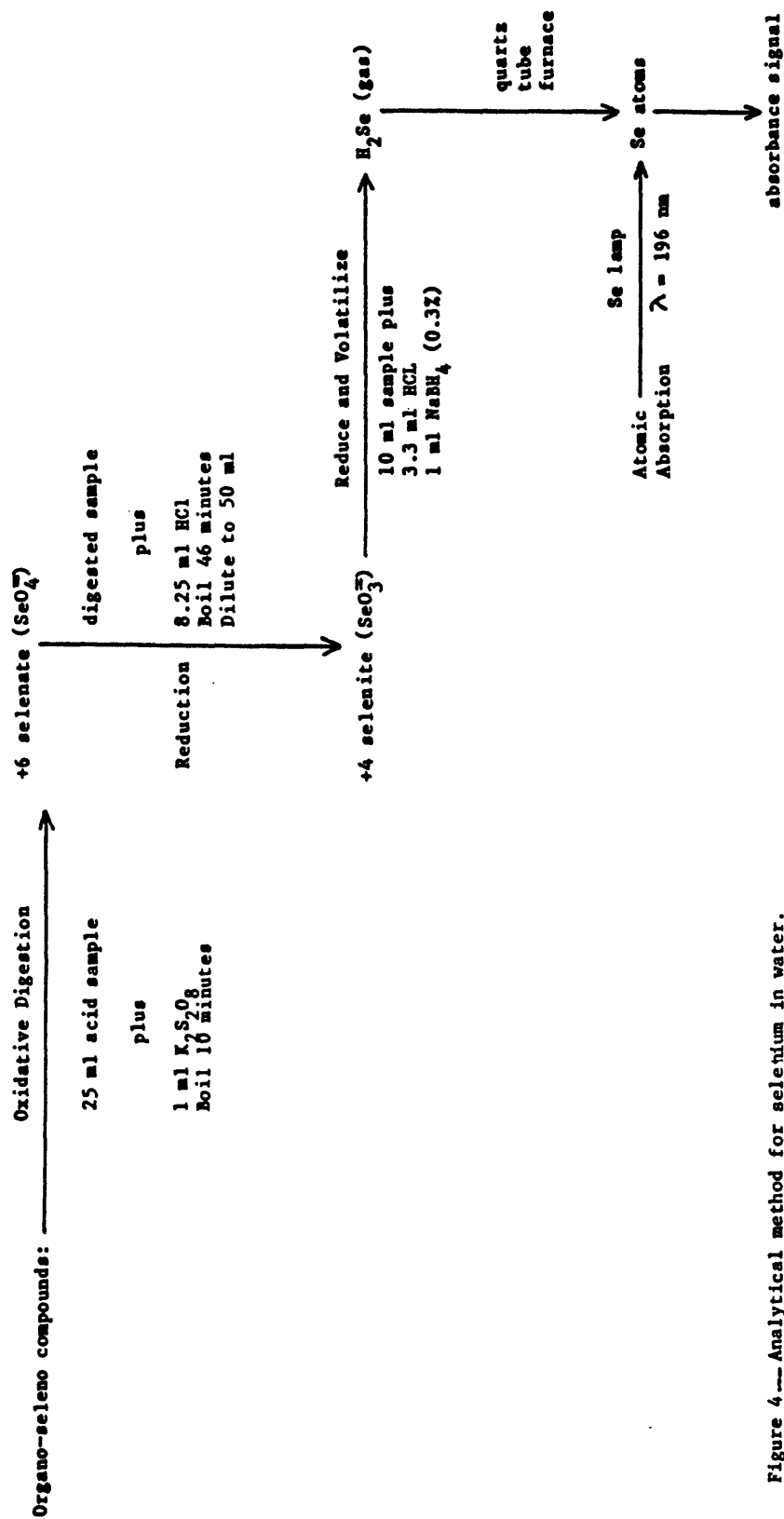


Figure 4—Analytical method for selenium in water.

$K_2S_2O_8$ is added, the solution slowly heated to boiling and then boiled for 10 minutes. This acid step also, if solid material is present, either from precipitation after the sample was collected and filtered, e.g. iron selenite, or in the case of the algal mat digests, desorbs or solubilizes the metal (U.S.G.S., 1979; Goulden and Brooksbank, 1974). Incomplete oxidation and volatilization both lead to erroneously low Se concentrations. Boiling longer than 10 minutes yields no increase in analyzed Se because of the decomposition of $K_2S_2O_8$ within that time. No increase in Se recovery resulted from the addition of two times the amount of $K_2S_2O_8$ or two times the amount of acid to the algal mat digests and pond 11 samples, those samples containing the most organics.

Analysis of a selenite standard by hydride generation after this first step showed no Se present indicating it was all oxidized to SeO_4^{-2} . Selenite was chosen as a standard to check on any loss of selenite originally present in the samples and to check the completeness of SeO_3^{-2} to SeO_4^{-2} oxidation.

The inorganic selenium thus yielded by oxidation of organo selenium compounds, and the inorganic selenium originally present, now both as selenate (+6), are reduced to selenite (+4) before further reduction and analysis as selenium hydride (Cutter, 1978). As Cutter states in "Species Determination of Selenium in Natural Waters", the inorganic forms of Se (+4 and +6) can be selectively reduced to hydride and analyzed spectrometrically. First, by his method for a total inorganic selenium concentration the sample was made 4M in HCl and boiled vigorously for 4-5 minutes to reduce SeO_4^{-2} to SeO_3^{-2} . The resultant solution was analyzed for Se by hydride generation. In a later publication (Cutter, 1983), boiling time was increased to between 12 and 30 minutes. A selenite value is found by taking a second aliquot of sample, stripping the volatile selenides from the solution with helium gas, and again

analyzing the solution for Se by hydride generation. The amount of SeO_4^{-2} is then calculated by difference: i.e. selenate = total Se - selenite. From the work of Cutter (1978) in which he presents a response curve of selenite and selenate to boiling in 4M HCl, an insight is given into the problem of not going far enough on the boiling curve to reduce all the selenate to selenite or of going too far and losing the selenite through plating out or agglomerating of elemental selenium. As with the oxidation step, optimum reducing conditions were found to yield maximum quantities of selenium. Incomplete reduction to SeO_3^{-2} or reduction to elemental selenium (Se^0) both yield erroneously low amounts of selenium (Cutter, 1978 and Walker, 1976). Because the matrixes of these samples are not identical to those found by other workers, the optimization of reduction was conducted on actual samples from this study. In response to the many conditions imposed by Se chemistry, acid concentrations and length of time between and after the two pretreatment steps were always kept at a minimum.

The optimum reduction to SeO_3^{-2} was found to occur with the addition of 8.25 ml of concentrated HCl and boiling for 46 minutes. From digested aliquots of the same sample (Table 3, CQ681B83) the yield of selenium by analysis was: 155 $\mu\text{g/L}$ Se (5 minutes boiling); 190 $\mu\text{g/L}$ Se (17 minutes boiling); and 350 $\mu\text{g/L}$ Se (46 minutes boiling). Boiling for 60 minutes yielded no further increase in Se by analysis, nor did increasing the acid concentration to 6 normal (N). Determinations of Se in this water sample from Kesterson Pond 2 with no digestion and no reduction yielded 67 $\mu\text{g/L}$ Se. A reduction of this water sample without the preliminary oxidation step showed a Se concentration of 300 $\mu\text{g/L}$. With both steps included, the value was 350 $\mu\text{g/L}$ Se. Therefore, with no digestion and no reduction, 19% of the Se was recovered; with reduction only, 86% of the Se was recovered.

A stronger reducing agent than HCl could have been used in the pre-reduction step. Substances that have been used include tin (Sn) (U.S.G.S., 1982) and aluminum (Al) (Goulden and Brooksbank, 1974). Problems occur with precipitation of elemental Sn or Al and the formation of SnH_2 when Se is further reduced to the hydride unless the solution is kept above 90°C . This is done as described by the above authors, using a block digester and continuous, automated systems.

The last steps in the analysis are generation and measurement of selenium hydride (H_2Se). A hydride generator coupled to an atomic absorption spectrophotometer was used. This method takes advantage of the property of Se to form a gas, H_2Se , in the -2 oxidation state. A review article of hydride generation techniques is given by Nakahara, (1983). An Instrumentation Laboratories Model 751 instrument equipped with a deuterium arc background corrector and an Atomic Vapor Accessory was used. The accessory is automated for one cycle per sample introduced. No secondary collection or stripping device was included.

Ten milliliters of the pre-digested and pre-reduced aqueous sample was pipetted into the generator and made 3M in HCl. The system was put on automatic operation and purged with argon. The reducing agent, 0.3% NaBH_4 , stabilized with 1% NaOH, is included in the closed system. It is pumped into the generator at a specified rate (#2) and the sample is stirred with a magnetic stirrer. This NaBH_4 -acid reduction system has replaced the older metal-acid (e.g. $\text{Zn-SnCl}_2\text{-KI}$) reduction system. Nakahara (1983) compares the two methods and lists among the advantages: applicability to other elements, yield increase, reaction time decrease, and blank-contamination reduction.

The selenide gas formed after a reaction time of 0.5 minute, (no argon flow) is swept into a quartz tube heated by an air-acetylene flame ($T > 800^\circ\text{C}$)

using the stream of argon gas. The spike of selenide is decomposed to gaseous metal atoms and subsequent absorbance measurements are made at a wavelength of 196 nm. Final molarity of HCl and NaBH₄ used in the generator were initially determined from guidelines published by Instrumentation Laboratories. Final optimization for this particular system includes such variables as size of generation flask, amount of sample, purge rate, size of quartz tube, temperature of flame and integration time of signal. Further additions of NaBH₄ yielded no further selenium. The working range for this method is 1 to 20 µg/L Se. Because of the type of water collected (agricultural drainage water) and the limit of 10 µg/L Se for drinking water (U.S. EPA, 1977), the sensitivity of this method was thought to be adequate.

Although one advantage of the gas generation method is removal of Se from ions present in aqueous solution, physical interferences may be present associated with the reduction or forming of the gas and the removal of the gas from the liquid (Cutter, 1978). These effects would vary with changes in acidity, salinity, oxidizing agents present (e.g. HNO₃), pre-reductants used and other hydrides formed. An interference study for the hydride generation method was made by Pierce and Brown (1977). No significant interferences were reported from the inorganic elements normally found in waters. In further studies by the authors specifically associated with the pond and drain waters which were high in SO₄ and Na, no interference was found from 10,000 mg/L SO₄, 10,000 mg/L Na, 10 µg/L As, 10% HCl, 10% HNO₃, and a digestion blank. Spectral interferences in the UV region were investigated by analyzing different dilutions of the pond and inflow waters. No aberrations were found: i.e. different dilutions yielded similar values.

Each sample was digested, reduced and analyzed on the same day. Differences in results of duplicate analyses of Fa-HCl and Fa-HNO₃ samples

ranged from 0% to 12% with an average of 6%. For samples with the highest concentrations of Se, the second analysis included a dilution of the sample which decreased the Se to be digested to less than 500 $\mu\text{g/L}$, the highest concentration of Se standard tested through the entire procedure. Recovery of Se added to pond samples averaged 98%. Background samples of the various canals and secondary drains were digested, reduced and analyzed only once. These are distinguished by levels of Se $<10 \mu\text{g/L}$.

Solids

Minerals encountered in this study (thenardite and gypsum) were identified by both index of refraction measurements and x-ray diffraction using copper $K\alpha$ radiation.

RESULTS

The results of the analyses of water samples for Se, Na, SO_4 , D/H and $^{18}\text{O}/^{16}\text{O}$ are given in Table 2. It is apparently of little significance whether aliquots are preserved with either HCl or HNO_3 . What is abundantly clear is that all the irrigation drainage water entering the San Luis Drain (Map Nos. 14 to 22) that was sampled, contained at least 140 $\mu\text{g/L}$ Se and as much as 1,400 $\mu\text{g/L}$. Fresh water entering the drain near its south terminus (Map No. 22) has less than 2 $\mu\text{g/L}$ Se and serves to dilute the Se rich drain water. Water from the north end of the San Luis Drain at or near the discharge into Kesterson Pond 2 (Map Nos. 12 and 2) showed similar concentrations of Se despite different sampling times. A value of 330 $\mu\text{g/L}$ Se was found in August during the dry season and 280 $\mu\text{g/L}$ Se in December during the rainy season. The water of Pond 2 (Map No. 1) in August contained 350 $\mu\text{g/L}$ Se. Note also, that the concentration of Se in pond 11 (Map Nos. 3 and 13) is much lower than that in pond 2 and that it increased from 14 $\mu\text{g/L}$ in August to 60 $\mu\text{g/L}$ in December.

The results of analyses for Se in other irrigation supply and return

Table 2.--Results of analyses for Se, Na, SO₄ and δD and δ¹⁸O
[n.d. indicates not determined.]

| Map # | Number | μg/L Se (Fa-HCl) | μg/L Se (Fa-HNO ₃) | mg/L Na | mg/L SO ₄ | δ ¹⁸ O-H ₂ O (per mil SMOW) | δD-H ₂ O |
|-------|-----------|---------------------|-----------------------------------|---------|----------------------|--|---------------------|
| 1 | CQ681B83 | 330 | 350 | 2750 | 5550 | -4.24 | -46.6 |
| 2 | CQ691B83 | 320 | 330 | 2250 | 4700 | -5.42 | -52.1 |
| 3 | CQ701B83 | 14 | 15 | 6250 | 11500 | +4.03 | -7.0 |
| 4 | CQ110TP83 | n.d. | <2 | 40 | 44 | -12.74 | -90.0 |
| 5 | CQ111TP83 | n.d. | <2 | 230 | 175 | -8.96 | -66.2 |
| 6 | CQ112TP83 | n.d. | <2 | 49 | 90 | -13.67 | -97.9 |
| 7 | CQ113TP83 | n.d. | <2 | 130 | 170 | -12.10 | -90.4 |
| 8 | CQ114TP83 | n.d. | 5 | 420 | 880 | -11.06 | -83.3 |
| 9 | CQ115TP83 | n.d. | <2 | 365 | 505 | -9.92 | -76.3 |
| 10 | CQ116TP83 | n.d. | <2 | 86 | 165 | -12.03 | -89.9 |
| 11 | CQ118TP83 | n.d. | 10 | 210 | 360 | -6.22 | -50.8 |
| 12 | CQ119TP83 | 280 | 280 | 2000 | 4100 | -6.55 | -56.4 |
| 13 | CQ120TP83 | 62 | 60 | 3150 | 6000 | -2.01 | -13.4 |
| 14 | CQ121TP83 | 195 | 200 | 1700 | 3050 | -7.92 | -60.7 |
| 15 | CQ122TP83 | 155 | 140 | 1500 | 3100 | -8.59 | -66.4 |
| 16 | CQ123TP83 | 180 | 160 | 1450 | 3200 | -8.23 | -64.1 |
| 17 | CQ124TP83 | 190 | 180 | 935 | 2050 | -9.19 | -69.8 |
| 18 | CQ125TP83 | 355 | 385 | 2300 | 4750 | -7.96 | -62.2 |
| 19 | CQ126TP83 | 375 | 400 | 1650 | 3900 | -8.49 | -65.9 |
| 20 | CQ127TP83 | 1350 | 1400 | 10500 | 22500 | -6.69 | -60.2 |
| 21 | CQ128TP83 | 500 | 490 | 2100 | 4350 | -8.57 | -68.9 |
| 22 | CQ129TP83 | 1250 | 1400 | 8550 | 16500 | -7.40 | -61.8 |
| 23 | CQ130TP83 | n.d. | <2 | 32 | 28 | -11.40 | -87.2 |
| 24 | CQ131TP83 | n.d. | <2 | 30 | 48 | -2.15 | -37.9 |

waters of the surrounding area (Map Nos. 4 through 11) which included the Volta area, show much lower Se concentrations (<2 to 10 µg/L) than in the San Luis Drain and Kesterson Ponds 2 and 11.

A comparison of Se and sodium (Na) concentrations in water in Kesterson Ponds 11 and 2 in August show a loss of Se between the entry into pond 2 and the terminal pond 11 although the increase in Na shows the water is more concentrated in pond 11. The D/H and $^{18}\text{O}/^{16}\text{O}$ values (Table 2) show a normal evaporation trend. An analysis of the thenardite (Na_2SO_4) precipitated from pond 11 showed the salt contains 1.8 parts per million (ppm) Se, dry weight. That is a ratio of Se/Na of 3.75×10^{-6} . The water in the pond where thenardite was found contains 14 µg/L Se and 6,250 mg/L Na, a ratio of 2.2×10^{-6} . Obviously the Se is only partly lost to thenardite; the crystallization of thenardite results in an increase in the Se/Na in the remaining water and thus is inadequate to account for the Se decrease between pond 2 and 11. Microscopic examination revealed that the thenardite contained small amounts of algae.

The thenardite crust rested upon a mat of the filamentous algae *Microspora* with strands of the blue-green alga *Lyngbya(?) aesturii*. The mat also included larger woody debris. Acid oxidative digestion of the mat with a subsequent reduction and analysis of the decanted solution showed the algal mat contains an average of 13 ppm Se (dry weight). Clearly some algae take up Se. This amount of Se may be different from an amount of Se that could be leached from the mat by water (i.e. water-soluble Se), under the conditions obtained in the pond. Although this experiment is not definitive it does show that organic uptake of the Se is probably much more effective in removing Se than inorganic processes. The algae being primary producers, are one point of entry of Se into the food chain of higher organisms.

Crystals were found in both acidified, filtered samples of pond 11 collected in August after return to the laboratory. The precipitate, identified as gypsum clearly was grown from solution after sample collection. A nearly saturated leachate solution of that gypsum produced a Se value of <1 ppm (dry weight). Even though this gypsum is an artifact and may differ from natural deposits the results show that gypsum does not tolerate much SeO_4^{-2} substitution for the sulfate (SO_4^{-2}) in the crystal structure.

The question of cycling of Se through the ponds and/or through the food chain is complicated by the chemistry of Se itself with oxidation states of +6 to -2. Organic selenides (Se^{-2}) were not looked for. The form of Se in the water (Se^{+4} or Se^{+6}) or whether it is bound to organic material in the water, is not yet fully known. The preliminary data suggest a predominance of selenate.

The results of Se analyses in this study (T. S. Presser) compare closely with those obtained by the U.S. Geological Survey, the Water Resources Division Central Laboratory, Denver, Colorado, (J. Schoen, written commun., Feb. 1984) and results obtained by analysts in the U.S. Fish and Wildlife Service (U.S.F. & W.S.) Laboratory, Columbia, Missouri, (T. May, oral commun., Feb. 1984) whether using the same or different methods. For example, as shown in table 3 Kesterson Pond 2 was analyzed by both T. S. Presser (U.S.G.S.) and T. May (U.S.F. & W.S.) in August, 1983. The U.S.F. & W.S. samples were considered preliminary. If only the generation of H_2Se is performed without oxidizing organic matter or reducing the selenate the results are, respectively, 67 and 50 $\mu\text{g/L}$ Se. If the oxidation of the organic matter is omitted but SeO_4^{-2} is reduced to SeO_3^{-2} before reduction to H_2Se the results are much higher and

Table 3.--Comparison of results of analyses for Se

| | | | |
|---|----------------------------------|---------------------|----------------------------------|
| Kesterson Pond #2 (August 3, 1983) | | | |
| CQ681B83 | no digestion, no reduction | | 67 $\mu\text{g/L Se}$ |
| | digestion, reduction (5 min) | | 155 $\mu\text{g/L Se}$ |
| | digestion, reduction (17 min) | | 190 $\mu\text{g/L Se}$ |
| | digestion, reduction (46 min) | Fa HCl | 330 $\mu\text{g/L Se}$ |
| | | Fa HNO ₃ | 350 $\mu\text{g/L Se}$ |
| | digestion, reduction (60 min) | | 350 $\mu\text{g/L Se}$ |
| | no digestion, reduction (46 min) | | 300 $\mu\text{g/L Se}$ |
| T. May (U.S.F. & W.S.) (August, 1983) | | | |
| | no digestion, no reduction | | 50 $\mu\text{g/L Se}$ |
| | no digestion, reduction | | 360 $\mu\text{g/L Se}$ |
| Inflow from San Luis Drain into Pond #2 | | | |
| CQ119TP83 | no digestion, no reduction | | 18 $\mu\text{g/L Se}$ |
| | digestion, reduction (46 min) | | 280 $\mu\text{g/L Se}$ |
| U.S.G.S. Denver Central Lab (January 24, 1984) | | | |
| | digestion, reduction | | 275 $\mu\text{g/L Se}$ |
| Inflow to San Luis Drain at American Road (December 2, 1983) | | | |
| CQ127TP83 | no digestion, no reduction | | 20 $\mu\text{g/L Se}$ |
| | digestion, reduction (46 min) | Fa-HCl | 1350 $\mu\text{g/L Se}$ |
| | | Fa-HNO ₃ | 1400 $\mu\text{g/L Se}$ |
| Standard Reference Water Sample Trace-85 | | | |
| SRS-T85 | no digestion, no reduction | | 1.4 $\mu\text{g/L Se}$ |
| | digestion, reduction (46 min) | | 3.4 $\mu\text{g/L Se}$ |
| | Reported Mean | | 2.9 \pm 0.5 $\mu\text{g/L Se}$ |

again the two laboratories agree. The results are:

| | $\mu\text{g/L Se}$ |
|---------------|--------------------|
| U.S.G.S. | 300 |
| U.S.F. & W.S. | 360 |

Two independent laboratories and two different methods are thus in close agreement. A sample of the inflow from the San Luis Drain into Kesterson Pond 2 was analyzed both by T. S. Presser, U.S.G.S., Menlo Park, and the U.S.G.S. Central Laboratory, Denver, Colorado. The Central Laboratory used a standard automated method (Fishman and Bradford, 1982). Both oxidation of organic matter and reduction of SeO_4^{-2} to SeO_3^{-2} were done but by different methods. The results are:

| | $\mu\text{g/L Se}$ |
|--------------------|--------------------|
| T. S. Presser | 280 |
| Central Laboratory | 275. |

The same sample with neither oxidation of organic matter nor reduction of selenate yielded $18 \mu\text{g/L Se}$. An extreme example of the possible effect of Se speciation on analytical results is sample CQ127TP83 of this study. Analysis with neither oxidation of organic matter nor reduction of SeO_4^{-2} to SeO_3^{-2} before H_2Se generation yields but $20 \mu\text{g/L Se}$ where analyses after both oxidation of organic matter and reduction of SeO_4^{-2} to SeO_3^{-2} gives Se values of $1350 \mu\text{g/L Se}$ (HCl aliquot) and $1400 \mu\text{g/L Se}$ (HNO_3 aliquot).

Sample SRS T85 was analyzed by T. S. Presser as a participant in the U.S.G.S Standard Reference Water Sample Program. This program provides standard samples for analytical data quality control in the participating laboratories. The undigested, unreduced value obtained on this sample was $1.4 \mu\text{g/L Se}$. The digested, reduced concentration was $3.4 \mu\text{g/L}$. The reported mean for 10 laboratories using the hydride procedure and 17 laboratories using a

flameless atomic absorption procedure was $2.9 \pm 0.5 \mu\text{g/L Se}$ at the 95% confidence interval.

SUMMARY AND CONCLUSIONS

Selenium determinations by three laboratories using three methods yield comparable results for water samples. Two laboratories also performed Se determinations without oxidizing organic matter and without reducing SeO_4^{-2} to SeO_3^{-2} before determining the Se. The results show that a preliminary oxidation of organic matter which converts all Se present to SeO_4^{-2} , followed by a reduction step to convert the SeO_4^{-2} to SeO_3^{-2} , is needed to yield consistently accurate results for total Se in water samples.

The results of analyses given in this report for Se in water show that all actively flowing agricultural drain waters entering the San Luis Drain that were sampled have at least $140 \mu\text{g/L Se}$ and as high as $1,400 \mu\text{g/L Se}$. The results also show that Se can enter the food chain by uptake by algae.

Based on the various uses of water, several maximum-concentration criteria and standards have been established for Se. Although these criteria and standards do not apply to waters of the San Luis Drain service area, they provide useful perspective about the hazard associated with above-normal concentrations of Se. Further perspective is provided by studies of dietary requirement, average intake, and levels at which toxicity is evidenced. The units used for dosage are parts per billion (ppb), micrograms (μg) and kilograms (kg). Se is an essential dietary requirement for many animals; the requirement is estimated to be $40\text{--}100 \mu\text{g Se/kg}$ of food ($40\text{--}100 \text{ ppb}$) (Schwarz, 1960; Nesheim and Scott, 1961; Oldfield, Schubert and Muth, 1963). No such requirement for humans has been established. The average daily dietary intake by the American population is $200 \mu\text{g Se/day}$ (Morris and Levander, 1970; U.S. Environmental Protection Agency, 1977). Smith and Westfall (1937) reported

symptoms of chronic toxicity at 10 to 100 $\mu\text{g Se/kg/day}$, which for a 70 kg man would amount to a daily intake of 700 to 7000 $\mu\text{g/day}$. The U.S. Environmental Protection Agency (1977) set the public drinking water maximum contaminant limit at 10 $\mu\text{g/L Se}$, based on the assumption that 2L of water per day would be consumed and that water should provide no more than a 10% increase in the average daily intake of Se. They further state that the basal 200 $\mu\text{g/day}$ intake plus the 20 $\mu\text{g/day}$ from water "results in a minimum safety factor of 3, considering the lower end of the range of selenium intakes that have been associated with minor toxic effects in man." The U.S. Environmental Protection Agency (1980) also specifies the concentration of Se in waste that will qualify the waste as "hazardous" under the Resource Conservation and Recovery Act of 1976, provided the source is not exempted. The Se concentration meeting the "characteristic" criteria for hazardous waste is 1000 $\mu\text{g/kg}$ if solid waste or 1000 $\mu\text{g/L}$ in the case of water having a density near 1.0. Based on the preceding considerations, it is apparent that some ground water entering the San Luis Drain contains Se in concentrations exceeding the maximum contaminant level for public water supplies by 140 times and exceeding the lower end of the range of Se intake associated with minor toxic effects in man by 2-4 times, without consideration of dietary intake.

Se can exist in multiple oxidation states in water. In the hydride generation technique for Se analysis, different sensitivities are exhibited in the two states Se^{+4} and Se^{+6} . This supposed disadvantage has potential for use in selective determinations. Determination of Se speciation leads in turn to information on oxidation potential, mobility and toxicity of Se in water.

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