PROCESSES AFFECTING THE DISTRIBUTION OF SELENIUM IN SHALLOW GROUND WATER OF AGRICULTURAL AREAS, WESTERN SAN JOAQUIN VALLEY, CALIFORNIA

U.S. DEPARTMENT OF THE INTERIOR
March 3, 1849

U.S. GEOLOGICAL SURVEY
Open-File Report 87-220

REGIONAL AQUIFER SYSTEM ANALYSIS

Prepared in cooperation with the SAN JOAQUIN VALLEY DRAINAGE PROGRAM

This report was prepared by the U.S. Geological Survey in cooperation with the San Joaquin Valley Drainage Program and as part of the Regional Aquifer System Analysis Program of the U.S. Geological Survey.

The San Joaquin Valley Drainage Program was established in mid-1984 and is a cooperative effort of the U.S. Bureau of Reclamation, U.S. Fish and Wildlife Service, U.S. Geological Survey, California Department of Fish and Game, and California Department of Water Resources. The purposes of the Program are to investigate the problems associated with the drainage of agricultural lands in the San Joaquin Valley and to develop solutions to those problems. Consistent with these purposes, program objectives address the following key areas: (1) Public health, (2) surface- and ground-water resources, (3) agricultural productivity, and (4) fish and wildlife resources.

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Sacramento, California 95825-1898

The Regional Aquifer System Analysis (RASA) Program of the U.S. Geological Survey was started in 1978 following a congressional mandate to develop quantitative appraisals of the major ground-water systems of the United States. The RASA Program represents a systematic effort to study a number of the Nation's most important aquifer systems, which in aggregate underlie much of the country and which represent an important component of the Nation's total water supply. In general, the boundaries of these studies are identified by the hydrologic extent of each system, and accordingly transcend the political subdivisions to which investigations have often arbitrarily been limited in the past. The broad objective for each study is to assemble geologic, hydrologic, and geochemical information, to analyze and develop an understanding of the system, and to develop predictive capabilities that will contribute to an effective management of the system. The Central Valley RASA study, which focused on studying the hydrology and geochemistry of ground water in the Central Valley of California, began in 1979. Phase II of the Central Valley RASA began in 1984 and is in progress. The focus during this second phase is on more detailed study of the hydrology and geochemistry of ground water in the San Joaquin Valley, which is the southern half of the Central Valley.

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DEPARTMENT OF THE INTERIOR

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CONVERSION FACTORS

Metric (SI) units are used in this report. For readers who prefer inch/pound units, the conversion factors for the terms used in this report are listed below.

Multiply	By	To obtain
centimeter (cm)	0.3937	inch
hectare (ha)	2.471	acre
kilometer (km)	0.6214	mile
meter (m)	3.281	foot

Selenium concentrations are given in micrograms per liter (μg/L). One thousand micrograms per liter is equivalent to 1 milligram per liter. Micrograms per liter is equivalent of "parts per billion."

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ABSTRACT

A study was undertaken to evaluate the processes affecting the chemistry of shallow ground water associated with agricultural drainage systems in the western San Joaquin Valley, California. The study was prompted by a need for an understanding of selenium mobility in areas having high selenium concentrations in shallow ground water. Ground-water samples were collected along transects in three artificially drained fields where the age of the drainage system varied (15, 6, and 1.5 years). Selenium concentrations in the drainage water also varied (430, 58, and 3700 micrograms per liter, respectively). Isotopic enrichment and chemical composition of the ground-water samples indicate that saline- and selenium-enriched water has evolved as a result of evaporation of ground water. This evaporated, isotopically enriched water is being displaced by more recent, less saline irrigation water percolating through the root zone. This displacement seems to be a process whereby sodium chloride and sodium sulfate water is being replaced by more dilute calcium sulfate and calcium bicarbonate water.

INTRODUCTION AND BACKGROUND

High concentrations of selenium in subsurface agricultural drainage water in the western San Joaquin Valley, California, have caused high mortality rates in waterfowl at Kesterson National Wildlife Refuge near Gustine, California (fig. 1) [Ohlendorf et al., 1986]. Agricultural drainage systems are installed throughout low-lying areas of the western San Joaquin Valley. These systems are designed to maintain the water table below about 1.5 m and to maintain a soil root-zone salt concentration that will not affect crop production. Evaporation of shallow ground water from a water table within 1.5 m of land surface can lead to accumulation of salts in the unsaturated zone and an increase in the salinity of the ground water. Shallow ground water affects about 100,000 ha of agricultural land in the western San Joaquin Valley [U.S. Bureau of Reclamation, 1984].

Saline soil is naturally prevalent in much of this arid region [Harradine, 1950]. Evaporation and evapotranspiration of shallow ground water has led to the accumulation of salts in ground water in the lowest elevations of the San Joaquin Valley, parts of which were natural discharge areas for regional aquifers [Mendenhall et al., 1916; Davis and Poland, 1957]. In recent decades, evapotranspiration by crops from a shallow water table has probably increased the salinity of the ground water in areas where the water table is naturally shallow or has risen because of irrigation.

Saline soils and the removal of associated saline drainage water in these areas where poorly drained soils and a high water table predominate have caused water-management problems for agriculture in the region for decades. However, the trace-element chemistry of the shallow ground water associated with saline soil and agricultural drainage systems only recently has been examined. Selenium, in particular, was not recognized as a problem or studied until toxicity effects on waterfowl became apparent in 1981. A recent regional study of shallow ground water in artificially drained areas of the western valley indicated that selenium concentrations are highest in saline ground water [Deverel et al., 1984]. The highly mobile selenate ($SeO_4^{=}$) seems to be the predominant selenium species in the regional shallow ground water [Deverel and Millard, 1986].

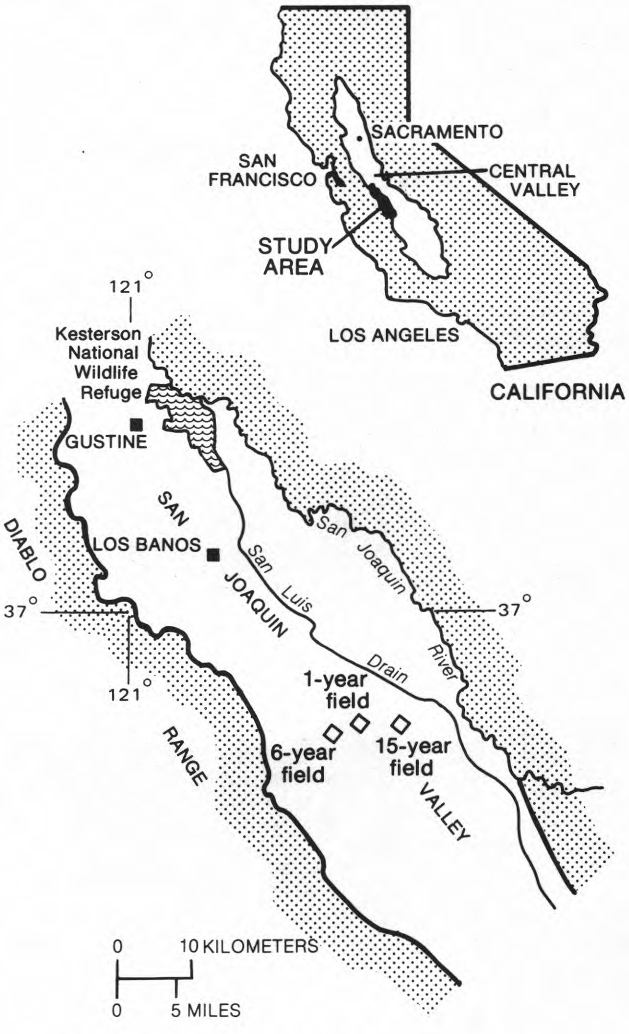

FIGURE 1.-- Location of three agricultural fields.

On a smaller scale, movement of nonreactive solutes in ground water in artificially drained agricultural fields in the western San Joaquin Valley has been examined by Pillsbury et al. [1965] and Jury [1975a, b]. These authors generally agreed that amounts of time on the order of several decades would be required for saline ground water to travel to drain laterals from midway between laterals, which are typically 50 to 100 m.

The specific objectives of this study were to assess (1) the effects of agricultural drainage on the chemistry of the shallow ground water, and (2) the distribution and mobility of selenium in ground water associated with agricultural drainage systems. This study is a part of a comprehensive investigation of the hydrology and geochemistry of the San Joaquin Valley conducted as part of the Regional Aquifer System Analysis Program of the U.S. Geological Survey and in cooperation with the San Joaquin Valley Drainage Program. The staff of the U.S. Department of Agriculture, Water Management Laboratory in Fresno, California, under the direction of Glenn Hoffman, provided invaluable field assistance for this study.

STUDY DESIGN AND DESCRIPTION OF AGRICULTURAL FIELDS

Three agricultural fields were selected based on (1) different ages of drainage systems, and (2) a substantial variation of selenium concentrations in the drainage water. The fields are all within 16 km of each other and are located on soils of the Panoche clay loam series (Typic Torriorthent) [Harradine, 1950]. At the time of sampling in May 1985, one field had been drained for 15 years, one for 6 years, and one for 1.5 years. These are hereafter referred to as the 15-year, 6-year, and 1-year fields.

The drainage water from the three fields was analyzed for selenium prior to the initiation of the study. The concentrations of selenium were 430 μg/L in the 15-year field, 58 μg/L in the 6-year field, and 3700 μg/L in the 1-year field. Because the 1-year field has been drained for the shortest amount of time, the selenium concentration of the drainage water would be expected to be decreasing at the fastest rate. Results of monthly sampling of drainage water for the 1-year field indicate that the temporal variability of selenium concentrations is small; the coefficient of variation for 1 year was 22 percent. Similar data for other drainage systems in the area indicate similarly low temporal variability [Deverel et al., 1984].

In each system, buried drain laterals lead into main collector lines at the lower end of the field (see fig. 2). The depth of the laterals varied among the fields. All drain laterals in the 6-year field were about 1.8 m below land surface and all laterals in the 1-year field were 2.7 m below land surface. In the field drained for 15 years, three drain laterals were buried at variable depths: lateral 1 was buried at 1.8 m, lateral 2

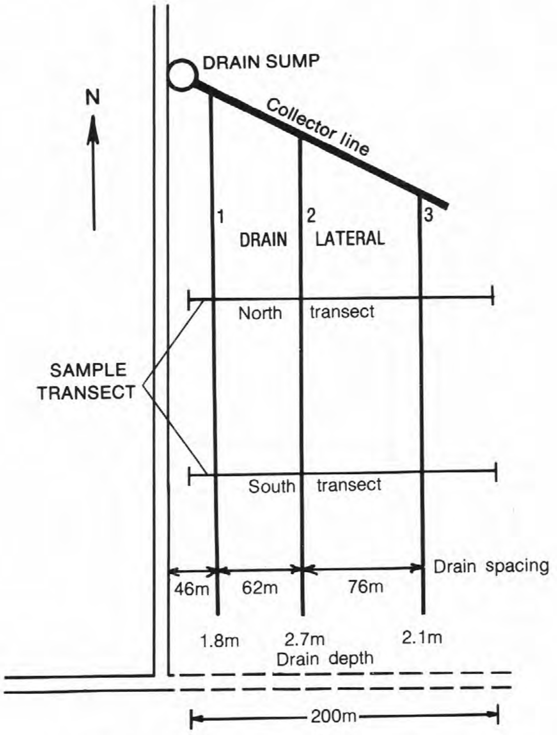

FIGURE 2. -- Drainage system for the 15-year field.

at 2.7 m, and lateral 3 at 2.1 m (fig. 2). The greatest hydraulic gradient (0.025) was associated with drain lateral 2 when the observation wells were installed in the 15-year field. The lateral drain spacings are 100 m in the 6-year field, 130 m in the 1-year field, and 46 to 76 m in the 15-year field. The sampling transect in the 6-year field traversed three drain laterals, the transect in the 1-year field traversed five laterals, and the transect in the 15-year field traversed three laterals.

METHODS

Field

Observation wells were installed along transects perpendicular to the direction of the buried permeable drain laterals in each field. Water samples were obtained from about the top 1 m of the shallow aquifer along the transects and thus in line with the expected direction of lateral flow within the fields. Boreholes were hand augered to 3 m below land surface, and polyvinyl chloride well casings were installed. The wells were screened over the bottom 1.2 m of the pipe. Ground-water samples were collected within 12 hours of well installation. Samples were collected through Teflon[1] tubing placed down in the well and attached to peristaltic pumps. The well was pumped prior to sampling until several well casing volumes had been extracted and the electrical conductivity (specific conductance) of consecutive well volumes did not vary more than ±10 percent. The samples were collected in polypropylene bottles that were rinsed 3 times with well water prior to sampling. Samples to be analyzed for aluminum, calcium, iron, magnesium, manganese, selenium, sodium, and potassium were pressure filtered through filters having a nominal pore size of 0.45 μm. These samples were collected in acid washed bottles and preserved with sufficient HNO_3 to obtain a pH less than 2. Samples to be analyzed for chloride, silica, and sulfate also were filtered on site but were not acidified. All sampling and filtering apparatus were thoroughly rinsed with well water prior to sample collection.

Unfiltered samples for analysis of the oxygen- and hydrogen-stable isotope composition were collected in glass bottles with polyethylene lids so that there was no air space. Unfiltered samples were analyzed by incremental titration with dilute sulfuric acid for bicarbonate concentrations within 1 hour of collection. Portable pH meters and electrodes were calibrated at each well and for each bicarbonate titration using pH buffers maintained at the temperature of the sample water within ±2 °C. Electrical conductivity meters were standardized using potassium chloride standards within 2000 μS/cm of the well water. Electrical conductivity and pH were measured several times at each well prior to collection of samples.

In December 1986, 10 additional observation wells were installed to measure the ground-water levels at deeper depths (up to 13 m) in the 15-year field. The 5-cm diameter, polyvinyl-chloride wells were placed in 20-cm boreholes. The wells have 60-cm screens which are surrounded by sand. The annular spacing was filled with bentonite grout above the sand to land surface.

Laboratory

All constituents except selenium (calcium, magnesium, sodium, potassium, sulfate, chloride, aluminum, iron and silica) were determined by methods described in Skougstad et al. [1979]. Calcium, magnesium, sodium, potassium, aluminum, and iron were determined by

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

atomic-absorption spectrometric methods. Chloride was determined by the ferric thiocyanate colorimetric method. Sulfate was determined by the turbidimetric procedure.

Selenium was determined by hydride generation and atomic absorption spectrometry [Fishman and Bradford, 1982]. The method used for selenium in this study is designed to determine the total concentration of all forms of selenium present in the water sample. A sample is first subjected to an oxidative digestion to release any selenium from the organic fraction. The selenium released by this digestion, together with the inorganic selenium originally present, is then reduced to the selenite form using a stannous chloride and potassium iodide mixture. The selenium hydride is generated by reducing the selenite form using sodium borohydride. The hydride gas is stripped from the solution by a stream of nitrogen gas and its concentration is determined by atomic-absorption spectrometry.

Environmental isotope data have been used to provide information on the history of the shallow ground water associated with agricultural drainage systems. Gat [1971] and Zak and Gat [1975], as well as others, have distinguished among the possible ways ground water becomes saline using isotopic and geochemical data. The oxygen-isotopic compositions of the water samples were determined using a modification of the carbon dioxide equilibration method of Epstein and Mayeda [1953]. The results are reported relative to Vienna Standard Mean Ocean Water (V-SMOW):

$$\delta^{18}O = \frac{(^{18}O/^{16}O)_{sample} - (^{18}O/^{16}O)_{V\text{-}SMOW}}{(^{18}O/^{16}O)_{V\text{-}SMOW}} \times 1000$$

The hydrogen-isotopic compositions were determined by analyzing hydrogen quantitatively extracted from water [Kendall and Coplen, 1985]. Hydrogen results are reported relative to V-SMOW in the per mil notation. The standard deviations of the oxygen- and hydrogen-isotopic compositions are 0.10 percent and 1.00 per mil, respectively. The hydrogen- and oxygen-isotopic compositions were determined in the Isotope Fractionation Project Laboratory of the U.S. Geological Survey, Water Resources Division, Reston, Virginia.

RESULTS AND DISCUSSION

General Relations

Water-chemistry data for the three agricultural fields shows the general relations between selenium, salinity, and the evaporative concentration process. Ground-water salinity, as measured by specific conductance, explains most of the variance ($r^2=0.88$) in measured selenium concentrations among all three fields (fig. 3). This is consistent with results of the regional study by Deverel

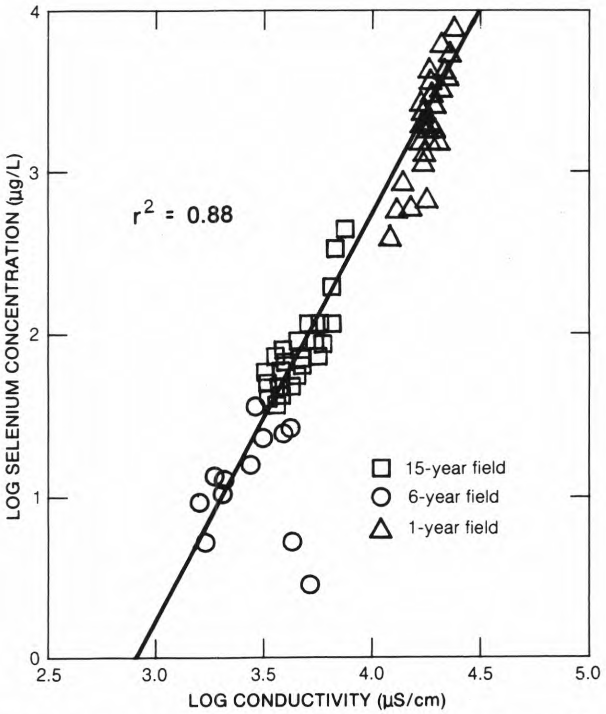

FIGURE 3. -- Correlation of log selenium concentrations and log specific conductance for samples from the three agricultural fields.

et al. [1984] and with the finding that the dominant form of selenium is selenate, which behaves as a conservative solute in alkaline and oxidized ground water.

Hydrogen- and oxygen-isotope data shows that ground-water salinity and associated selenium concentrations are mainly the result of evaporation or evapotranspiration of the shallow ground water. The comparison of delta deuterium (D) and delta oxygen-18 shown in figure 4 illustrates the evaporation that has taken place in the shallow ground water. The line of $\delta D=4.28\times\delta^{18}O-20$ representing the data is similar to other drainage water in the same area [Presser and Barnes, 1985]. Evaporation trend lines for isotope data from other arid regions have been reported with slopes similar to that found in this study. Gat and Issar [1974] reported an evaporation trend line with a slope of 5.5 for ground water of the Sinai Desert. Fontes and Gonfiantini [1967] reported an evaporation line with a slope of 4.6 for ground water of the Sahara Desert.

Selenium concentrations ($r^2=0.65$) and specific conductance ($r^2=0.89$) are correlated with oxygen-18 enrichment. This is evidence that evaporation of shallow ground water is a key factor that has affected the present distribution and levels of selenium and other dissolved constituents in shallow ground water of the three fields. The patterns in ground-water chemistry and isotopic enrichment along sampling transects in each individual field provide further evidence about the processes that result in high selenium concentrations in agricultural drainage water.

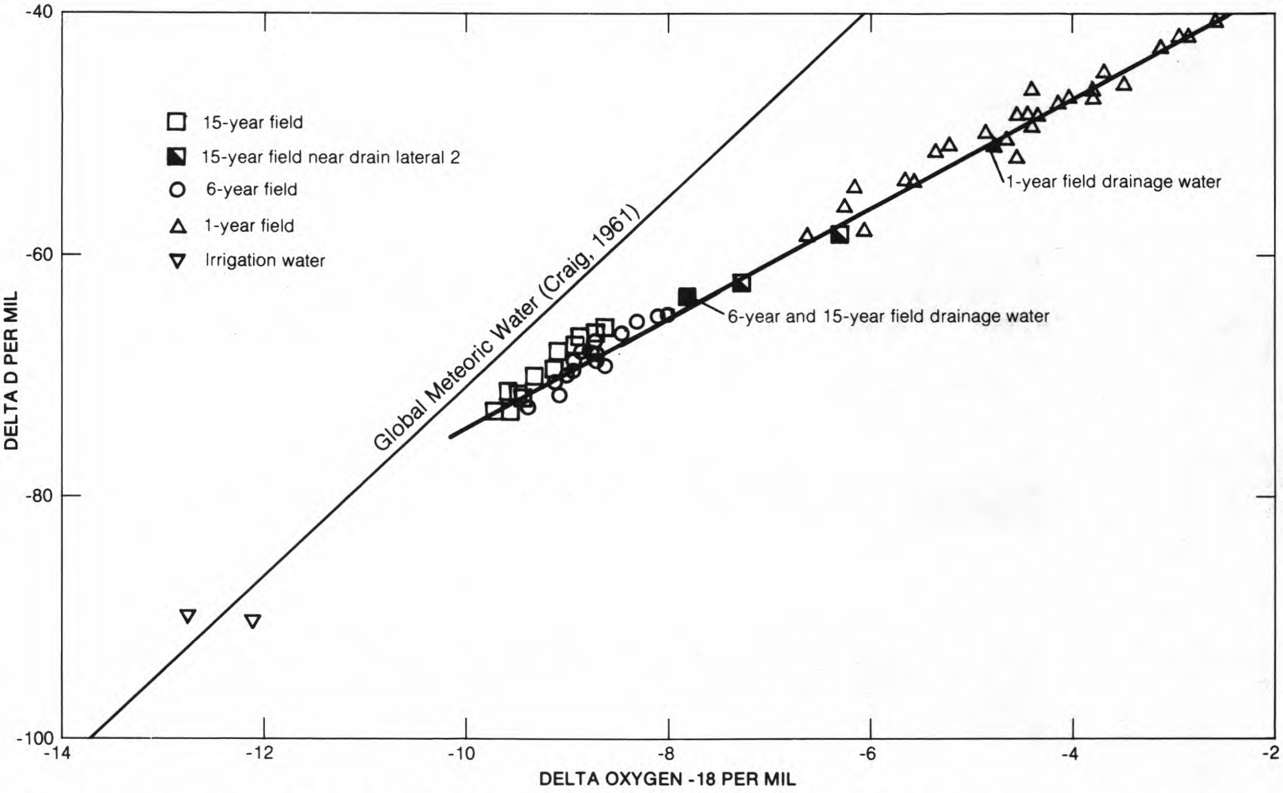

FIGURE 4. -- Comparison of delta D and delta oxygen-18 for ground-water, drainage-water, and irrigation-water samples from the three agricultural fields.

15-Year Field

Ground-water samples collected along both sampling transects in the 15-year field (fig. 5) show a similar pattern. Generally, selenium concentrations, salinity, as measured by specific conductance, and isotopic enrichment were greatest near the drain laterals, particularly near drain lateral 2 (figs. 5 and 6). The greater isotopic enrichment of water collected nearest drain lateral 2 indicates it has been subjected to more evaporation than other water collected along the transects (fig. 6).

This water that has been subjected to more evaporation probably was near land surface sometime in the past at a point near midway between the first and second drain laterals. This water seems to have been slowly displaced toward drain lateral 2 since the drainage-system installation. Water levels in 1952 were within 1.2 m of land surface in this field [U.S. Bureau of Reclamation, 1953], which could have resulted in evaporation and isotopic enrichment prior to drainage-system installation. The distribution of chemical constituents along the transect could be explained by movement along a concentric flow path, which travels deeper than the level of the drain laterals and was only intercepted by the observation wells installed nearest drain lateral 2. Jury [1975a, b] used a steady state, dimensionless solution for a stream function on typical farm-drainage systems in the western San Joaquin Valley to predict solute travel times of nonreactive solutes. Jury's [1975a, b] analysis predicts slow movement along long concentric flow paths to drain laterals under homogeneous, isotropic conditions.

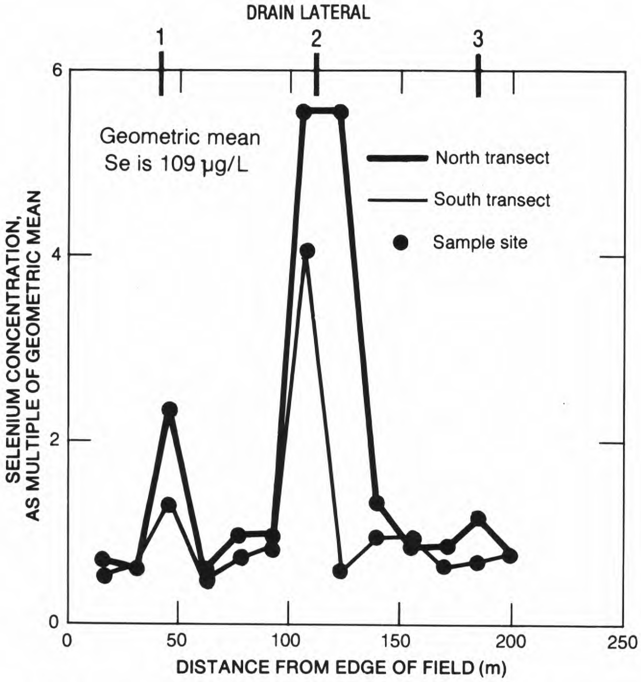

FIGURE 5. -- Relation of selenium concentration to distance along sampling transect for the 15-year field.

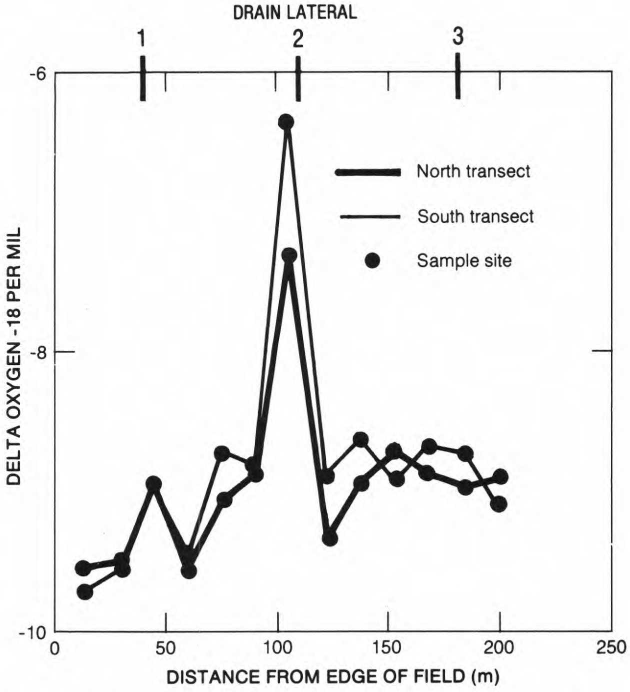

FIGURE 6. -- Relation of delta oxygen-18 to distance along transect for the 15-year field.

Figure 7 shows depth to ground water as measured in the observation wells installed for the 1985 sampling. Additional wells were installed in 1986 to measure hydraulic head distribution in and around drain lateral 2. Figure 8 shows that there is upward and lateral flow to the drain lateral. Although hydrogeologic conditions are not as assumed in the Jury analysis, deeper

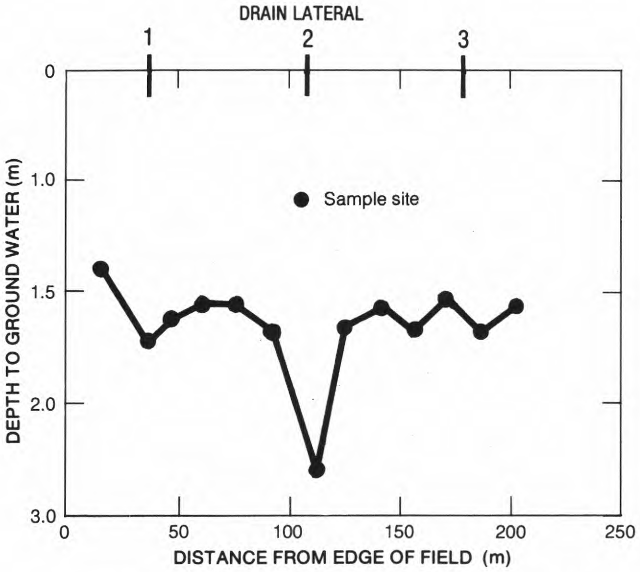

FIGURE 7. -- Depth to ground water in the 15-year field.

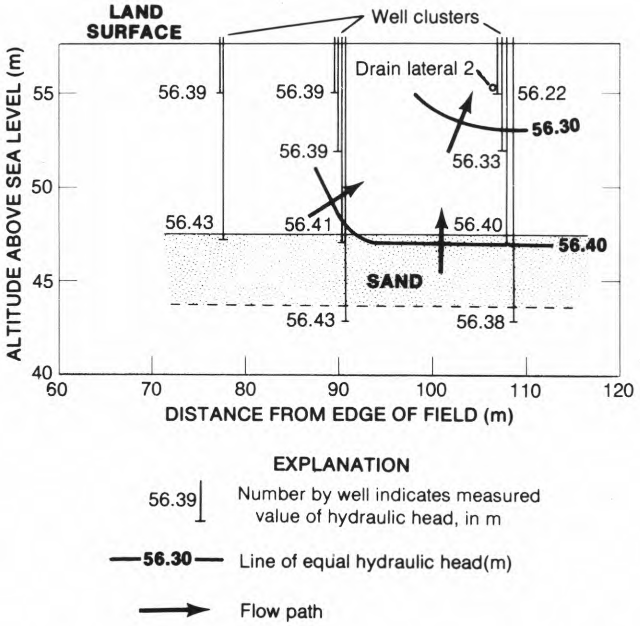

FIGURE 8.-- Hydraulic head distribution in and around drain lateral 2 in the 15-year field.

flow paths exist (fig. 8). Solute transport along concentric flow paths above the sand layer would certainly result in long periods of time [on the order of several decades] for complete displacement of saline ground water by less saline irrigation water. Hydraulic heads are higher in wells that are completed in the sand layer than in the predominantly fine textured materials above. Therefore, flow to the drain lateral is primarily from the area to the left of the lateral in figure 8. Ground water also flows upward toward the drain from the sand layer.

6-Year Field

Slow displacement of saline, isotopically enriched ground water by isotopically depleted irrigation water also seems to be taking place in the 6-year field. Ground water with the highest selenium concentrations and salinity levels were collected nearest the drain laterals (fig. 9). This coincided with the highest oxygen-18 enrichment. The generally lower salinity levels and selenium concentrations in ground water in this field compared to the other two are probably the result of evaporation from a recently developed shallow water table. The soils in this area are also less saline (Harradine, 1950). In 1985, water levels in this field were similar to those measured in the other two fields, however, this field is at a higher altitude and was not in an area of shallow ground water

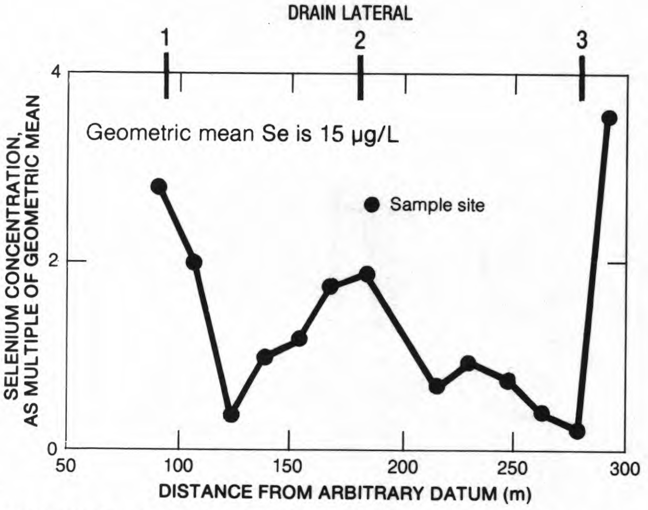

FIGURE 9. -- Relation of selenium concentration to distance along transect for the 6-year field.

in 1953 when the 15-year field was in an area of shallow ground water [U.S. Bureau of Reclamation, 1953]. The 6-year field developed a shallow water table within the last decade.

The isotopic enrichment of the samples collected in the 6-year and 15-year fields, except for the samples collected nearest drain lateral 2, which is the deepest in the 15-year field, is generally similar (fig. 10). The salinities of the ground-water samples are generally higher in the 15-year field. The comparison of the isotopic enrichment between the two fields indicates that there is a similar degree of evaporation of shallow ground water. The higher salinity levels and selenium concentrations in the 15-year field probably are due to leaching of salts from the unsaturated zone of the more saline soils of that field. Prolonged evaporation from a shallow water table prior to subsurface drainage in the 15-year field resulted in a more saline soil condition than the 6-year field. This effect would not be apparent in the isotopic composition of the ground water because water leaching the salts from the unsaturated zone would be of approximately the same composition as the water introduced at the surface. This prolonged evaporation is reflected in the salinity and isotopic enrichment of water that was formally near land surface near midpoint between the laterals and was collected nearest drain lateral 2. Ground-water salinities measured in this study generally reflect the differences in soil salinities. Analysis of soil samples from the two fields indicated that soil salinities were significantly ($\alpha=0.05$) higher in the 15-year field.

1-Year Field

The higher selenium concentrations, salinity levels, and greater isotopic enrichment of the ground-water samples from the 1-year field compared to the other fields show that the displacement process which has occurred in the other two fields has not progressed as far (figs. 3 and 4). The randomness of the selenium concentrations along the sampling transect (fig. 11) indicates that the distribution of selenium has not yet been substantially affected by drainage. Oxygen-18 enrichment is randomly distributed along the transect, similar to the distribution of selenium concentrations. Limited information on the history of this field supports the interpretation of the data. For many years prior to cultivation, this field was a terminous for a creek originating in the Coast Range. The landowner described this field as being saline and having water levels less than 1 m from land surface prior to installation of the drainage system. Therefore, evaporation and evapotranspiration resulted in the current saline condition.

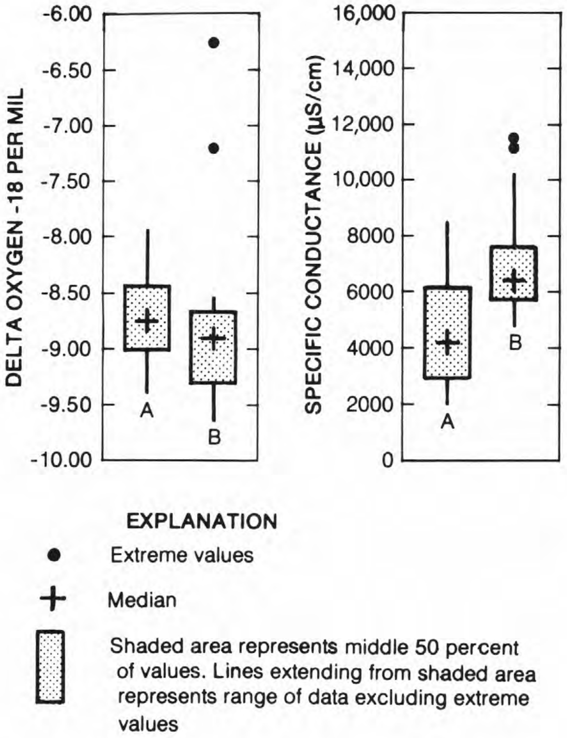

FIGURE 10. -- Ranges of values for delta oxygen -18 and specific conductance for the 6-year (A) and 15-year (B) fields.

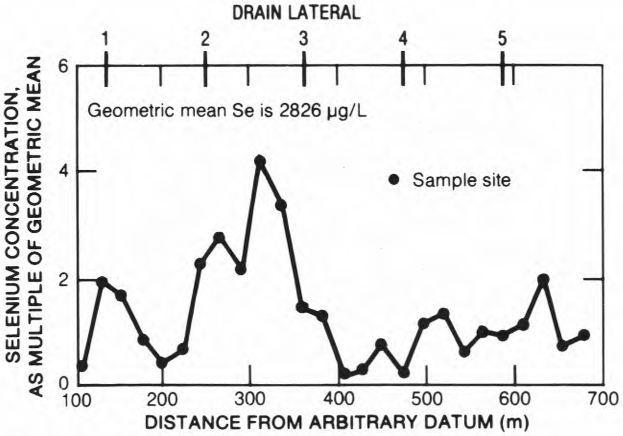

FIGURE 11. -- Relation of selenium concentration to distance along transect for the 1-year field.

Major-Ion Chemistry

Piper diagrams [Hem, 1985] further illustrate the mixing and displacement process (fig. 12). They also provide a useful means for comparing the water chemistry of the three fields. Water samples collected in the 1-year field are sodium dominated (fig. 12). The less saline water from the 15-year and 6-year fields are less dominated by sodium. The decreasing sodium dominance and increasing proportion of calcium with decreasing salinity seems to be due to increased mixing with water similar in composition to the irrigation water, which is calcium dominated. Mineral dissolution and ground-water mixing seem to affect the chemical patterns shown in the anionic Piper diagram (fig. 12). Sulfate is more dominant and chloride less dominant as the salinity decreases (comparing the 1-year and 15-year fields).

The three fields had different gypsum saturation indices as determined by the WATEQF simulation [Plummer et al., 1976]. Saturation indices for samples collected in the 1-year field were greater than for those samples collected in the 15-year field. All samples collected in these two fields were saturated or oversaturated with gypsum. The samples collected in the 6-year field were generally undersaturated with gypsum. This

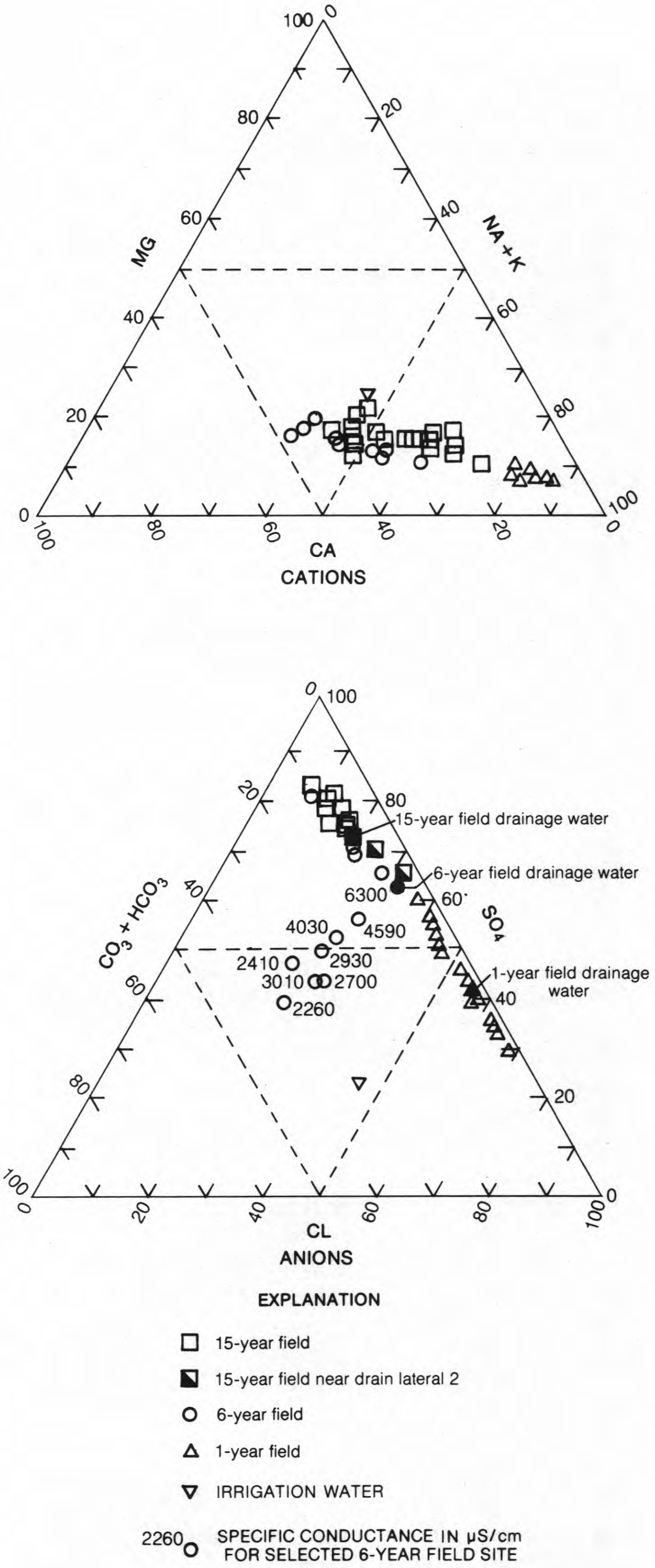

FIGURE 12. -- Chemical composition of ground water, irrigation water, and drainage water.

change in gypsum saturation is due to a decrease in sulfate activity with decreasing salinity. Calcium activity is relatively constant among all the water samples collected in the three fields. As ground water becomes more dilute, gypsum dissolution probably affects the ground-water chemistry to a greater degree as is illustrated by the tendency towards the greater calcium and sulfate percentages in the 15-year field. The water collected in the 6-year field seems to be less affected by gypsum dissolution and more affected by calcite dissolution. Calcite dissolution would tend to maintain the calcium activity constant as gypsum is dissolved.

Figure 12 shows that water collected in the 6-year field increased in bicarbonate percentage with decreasing salinity. The water-chemistry differences between the 6-year and 15-year fields generally are not accompanied by changes in the isotopic composition of the ground water (fig. 10). Therefore, the change in chemical composition that is associated with the lower salinity water collected in the 6-year field probably is associated with calcite dissolution. Water collected from all three fields was shown by the WATEQF simulation to be oversaturated with calcite. Suarez and Rhoades [1982] demonstrated that apparent calcite oversaturation in ground water and soil solutions may be the result of weathering of other minerals. This weathering would be expected to be relatively equal among the three fields and the increase in bicarbonate percentage with decreasing salinity is probably a manifestation of calcite dissolution not apparent in water having higher salinities. Furthermore, these soils are known to be calcareous and calcite was identified by X-ray diffraction in several soil samples from all three fields.

The down-gradient location of more evaporated chloride water in the 6-year and 15-year fields indicates that the water is being displaced by water with greater proportions of sulfate and bicarbonate (fig. 12). The drainage-sump samples from the 15-year and 6-year fields have higher percentages of chloride than most of the other samples collected in the field (the exceptions are the samples collected near drain lateral 2 in the 15-year field). In contrast, in the 1-year field where drainage has not caused as much displacement as the other two fields, the drainage-sump sample is similar to the median for all the samples collected in this field.

Isotopic Enrichment and Selenium in Drainage-Sump Water

The displacement process also is illustrated by the isotopic enrichment of ground water and drainage water collected within the three fields. The drainage water from the 15-year and 6-year fields are considerably more enriched in the heavy isotopes (fig. 4) as compared to most of the samples collected within the fields (the two samples collected nearest drain lateral 2 are more enriched than the sump water in the 15-year field). In contrast, the isotopic composition of the drainage-sump water in the 1-year field is similar to the median composition of all the water collected in that field.

The down-gradient location of the water with the highest selenium concentrations and the most isotopically enriched composition in the fields drained for longer periods of time provides further evidence for the displacement process that has taken place since installation of the drainage systems. The selenium concentrations in the drainage-sump water for the 15-year and 6-year fields are substantially higher than the geometric mean of concentrations between the drain laterals (430 compared to 109 µg/L for the 15-year field and 58 compared to 15 µg/L for the 6-year field). The selenium concentration in the drainage-sump water in the 1-year field is not as different from the geometric mean for samples collected from observation wells installed in the field (3700 µg/L in drainage-sump water compared to geometric mean of 2826 µg/L). In the 1-year field, very little displacement has taken place as indicated by the similarity in isotopic enrichments and selenium concentrations of water from the drainage sumps and observation wells.

The ratio of selenium to sulfate concentrations provide information about the processes controlling selenium levels in ground water and soil solutions (fig. 13). The ratio of selenium to sulfate concentrations is relatively low for the 6-year and 15-year fields except for the samples collected near drain lateral 2 in the 15-year field (fig. 13). The 15-year field samples have a slightly higher selenium-to-sulfate ratio than those collected in the 6-year field. This may be due to selenium being more available in the unsaturated zone in the 15-year field.

Selenium has increased relative to sulfate in the 1-year field because ground water is more evaporated. In the lower concentration range, selenium and sulfate concentrations are probably affected similarly by surface phenomena or mineral precipitation or dissolution. Gypsum seems to be the primary mineral controlling sulfate concentrations and may limit the increase in sulfate concentrations as ground water is evaporated. In contrast, selenium concentrations are apparently less affected by solid phase phenomena and increase more relative to sulfate.

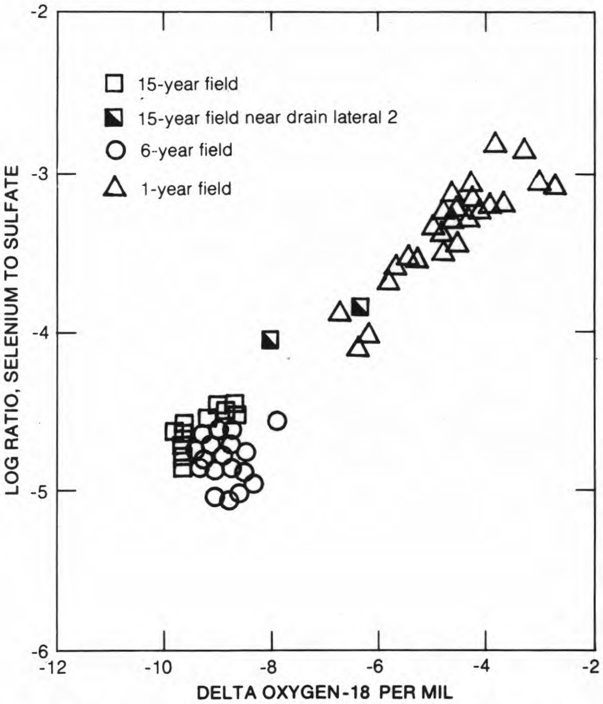

FIGURE 13. -- Relation between selenium-to-sulfate ratios and delta oxygen-18 for samples from the three agricultural fields.

SUMMARY AND CONCLUSIONS

The results of this study can be summarized in the form of a conceptual model of mixing and displacement. Saline ground water that has been enriched in selenium due to evaporative concentration is being displaced toward drain laterals by less saline irrigation water. This is supported by the distribution of chemical constituents in shallow ground water associated with agricultural drainage systems which is affected by the movement of ground water to drain laterals. The main conclusions of this study are as follows.

- Variations in ground-water salinity explains most of the variance in measured selenium concentrations.
- The highest selenium concentrations and salinity levels in ground water are mainly the result of concentration by evaporation or evapotranspiration from a shallow water table.
- The field drained for the shortest period of time (1.5 years) showed little displacement of saline, isotopically enriched water.
- The distribution of ground-water salinity and isotopic enrichment in the 6-year and 15-year fields shows the effects of displacement that probably has taken place since the initiation of drainage of saline ground water by fresher irrigation water.
- The most saline and evaporated water is a sodium chloride type, whereas the less saline water is calcium sulfate and calcium bicarbonate water.
- Gypsum and then calcite dissolution seem to determine the chemical composition as ground water associated with these agricultural drainage systems becomes less saline.
- The results of this study qualitatively confirm earlier estimates by Jury [1975a, b] and Pillsbury et al. [1965], that this slow displacement process results in large time requirements (on the order of decades) for saline water to be displaced and removed from the shallow ground-water system in the types of hydrologic setting represented by fields in this study.

REFERENCES CITED

Craig, H., Isotopic variations in meteoric waters, Science 133, 1833, 1961.

Davis, G.H. and J.F. Poland, Ground-water conditions in the Mendota-Huron area, Fresno and Kings Counties, California, U.S. Geol. Survey Water-Supply Paper 1360-G, 1957.

Deverel, S.J. and S.P. Millard, Distribution and mobility of selenium and other trace elements in shallow ground water of the western San Joaquin Valley, California, U.S. Geol. Survey Open-File Report 86-538, 1986.

Deverel, S.J., R.J. Gilliom, Roger Fujii, J.A. Izbicki, and J.C. Fields, Areal distribution of selenium and other inorganic constituents in shallow ground water of the San Luis Drain Service Area, San Joaquin Valley, California, A preliminary study, U.S. Geol. Survey Water Res. Inv. Report 84-4319, 1984.

Epstein, S. and T. Mayeda, Variation of the O-18 content of waters from natural sources, Geochim. Cosmochim. Acta, 4, 213-224, 1953.

Fishman, M.J. and W.L. Bradford, A supplement to methods for the determination of inorganic substances and fluvial sediments, U.S. Geol. Survey Open-File Report 82-272, 1982.

Fontes, J.C. and R. Gonfiantini, Isotopic composition of evaporation waters of two Saharan Basins, Earth and Planetary Science Letters, v. 3, pp. 258-266, 1967.

Gat, J.R., Comments of the stable isotope method in regional ground-water investigations, Water Resour. Res. 7, 980, 1971.

Gat, J.R. and A. Isaar, Desert isotope hydrology, Water sources of Sinai Desert, Geochim. Cosmochim. Acta 38, 1117- 1131, 1974.

Harradine, F., Soil Survey of Western Fresno County, University of California Press, Berkeley, California, 1950.

Hem, J.D., Study and interpretation of thechemical characteristics of natural water, U.S. Geol. Survey Water-Supply Paper 2254, 1985.

Jury, W.A., Solute travel-time estimates for tile drained fields, I, Theory, Soil Sci. Soc. Am. Proc. 39, 1020-1024, 1975a.

Jury, W.A., Solute travel-time estimates for tile drained fields, II, Experimental, Soil Sci. Soc. Am. Proc. 39, 1024-1028, 1975b.

Kendall, C., and T.B. Coplen, Multisample conversion of water to hydrogen by zinc for stable isotope determination, Anal. Chem., 57, 1437-1440, 1985.

Mendenhall, W.C., R.B. Dole and H. Stabler, Ground water in the San Joaquin Valley, U.S. Geol. Survey Water-Supply Paper 398, 1916.

Ohlendorf, H.M., R.L. Hothem, C.M. Bunck, T.W. Aldrich, and J.F. Aldrich, Relationships between selenium concentrations and avian reproduction, 51st Annual Wildlife and Natural Resources Conference, Proceedings, Reno, Nevada, 1986.

Pillsbury, A.F., W.R. Johnston, F. Ittihadieh, and R.M. Daum, Salinity of tile drainage effluent, Water Resour. Res., 1, 531-535, 1965.

Plummer, L.N., B.F. Jones, and A.H. Truesdell, WATEQF - A Fortran IV version of WATEQ, a computer program for calculating chemical equilibria of natural waters, U.S. Geol. Survey Water Res. Inv. 76-13, 1976.

Presser, T.S. and I. Barnes, Dissolved constituents including selenium in waters in the vicinity of Kesterson National Wildlife Refuge and the West Grassland, Fresno and Merced Counties, California, U.S. Geol. Survey Water Res. Inv. Report 85-4220, 1985.

Skougstad, M.W., M.J. Fishman, M.J. Friedman, D.E. Erdman, S.S. Duncan, eds., Methods of determination of inorganic substances in water and fluvial sediments, U.S. Geol. Survey Techniques of Water Res. Inv., Book 5, Chapter A1, 1979.

Suarez, D.L., and J.D Rhoades, The apparent solubility of calcium carbonate in soils, Soil Sci. Soc. Am. J. 46, 716-722, 1982.

U.S. Bureau of Reclamation, Firebaugh Drainage Investigation, Delta-Mendota Canal, Central Valley Project, California, U.S. Bur. Reclamation, Div. Operation and Maintenance, Region 2, 1953.

U.S. Bureau of Reclamation, Kesterson Reservoir and Waterfowl, Information Bulletin 2, 1984.

Zat I., and Gat, J.R., Saline waters and residual brines in the Shiraz-Sarvistan Basin, Iran, Chem. Geol. 16, 179-188, 1975.

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