

Sources of High-Chloride Water to Wells, Eastern San Joaquin Ground-Water Subbasin, California

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Introduction

As a result of pumping and subsequent declines in water levels, chloride concentrations have increased in water from wells in the Eastern San Joaquin Ground-Water Subbasin, about 80 miles east of San Francisco (Montgomery Watson, Inc., 2000). Water from a number of public-supply, agricultural, and domestic wells in the western part of the subbasin adjacent to the San Joaquin Delta exceeds the U.S. Environmental Protection Agency Secondary Maximum Contaminant Level (SMCL) for chloride of 250 milligrams per liter (mg/L) (fig. 1) (link to animation showing chloride concentrations in water from wells, 1984 to 2004). Some of these wells have been removed from service. High-chloride water from delta surface water, delta sediments, saline aquifers that underlie freshwater aquifers, and irrigation return are possible sources of high-chloride water to wells (fig. 2). It is possible that different sources contribute high-chloride water to wells in different parts of the subbasin or even to different depths within the same well.

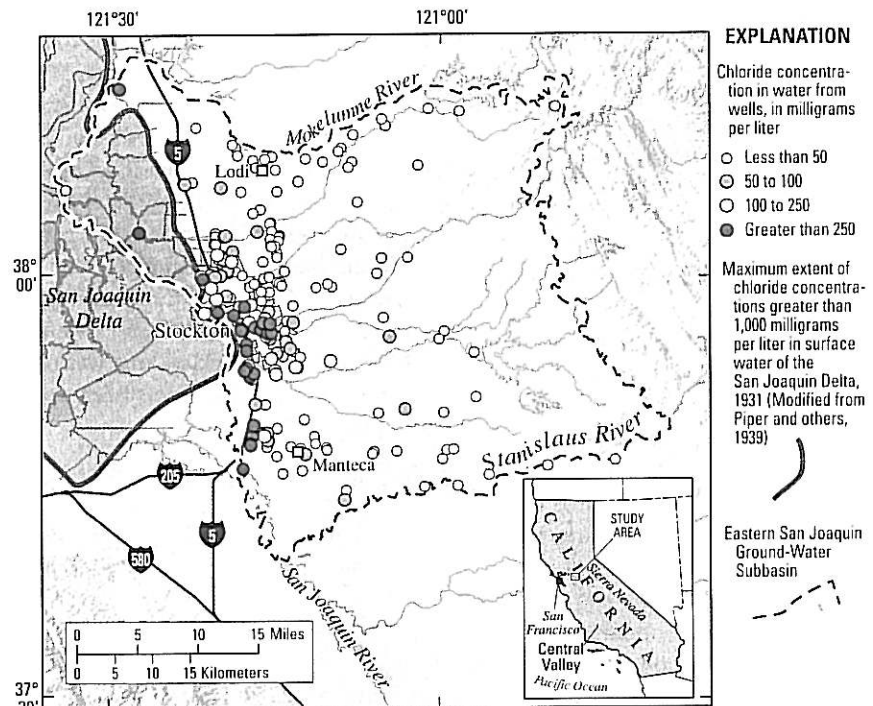


Figure 1. Chloride concentrations in water from wells in the Eastern San Joaquin Ground-Water Subbasin, California, 1984–2004.

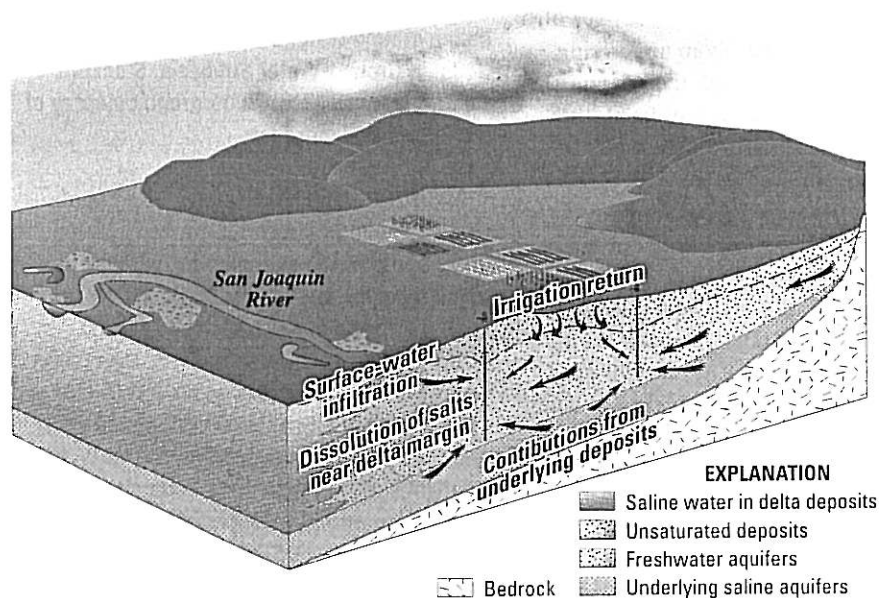


Figure 2. Sources of high-chloride water to wells, Eastern San Joaquin Ground-Water Subbasin, California.

Hydrogeology

The study area is the Eastern San Joaquin Ground-Water Subbasin near Stockton, California. The ground-water subbasin is about 1,100 square miles (California Department of Water Resources, 2006) and is part of the larger San Joaquin Ground-Water Basin that forms the southern half of the Central Valley of California. The climate of the area is characterized by hot, dry summers and cool, moist winters. Average annual precipitation ranges from about 10 to 18 inches (Soil Conservation Service, 1992). Precipitation is greater in the Sierra Nevada to the east of the study area. Runoff from those mountains, primarily as snowmelt, sustains flows in rivers and streams that cross the study area. The largest of these, the Mokelumne and Stanislaus Rivers, bound the study area to the north and south, respectively. The San Joaquin River, which drains the San Joaquin Valley to the south, bounds the study area to the west, and the foothills of the Sierra Nevada bound the study area to the east (fig. 1).

The study area is underlain by several thousand feet of consolidated, partly-consolidated, and unconsolidated sedimentary deposits (California Department of Water Resources, 1967). Volcanic deposits about 1,000 feet (ft) below land surface in the Stockton area, and at shallower depths to the east, separate overlying deposits from underlying marine deposits. Although they contain freshwater near the mountain front, the marine deposits contain saline water in most parts of the study area. The marine deposits have been explored for oil and gas and for the potential storage of waste. The overlying deposits can be divided into alluvial-fan deposits eroded from the Sierra Nevada, and delta deposits along the San Joaquin River. The alluvial-fan deposits are pumped extensively for water supply.

Under predevelopment conditions prior to the onset of ground-water pumping, ground-water movement in the alluvial-fan deposits was from the front of the Sierra Nevada to ground-water discharge areas near the San Joaquin Delta. Ground-water discharge to springs and seeps

in this area was fresh and low in dissolved solids (Mendenhall, 1908). Surface water also infiltrated from the upstream reaches of rivers and streams into underlying alluvial deposits and ground water discharged along the downstream reaches of these streams (Piper and others, 1939). Regional ground-water movement in the San Joaquin Valley under predevelopment conditions was from south to north along the axis of the valley, with regional ground-water discharge to the delta. In a large part of the study area, ground water in deep wells completed below the volcanic deposits flowed to land surface under artesian conditions. Water from most of these deep artesian wells was saline (Mendenhall, 1908) and not used for agricultural or public supply. Saline water extracted from deep wells, especially those used for natural gas production, was "allowed to waste" (Mendenhall, 1908), or in the Stockton area was used for recreational swimming pools because of its warm temperature (fig. 3).



Figure 3. Recreational pools developed from saline ground water discharge in the San Joaquin Ground-Water Subbasin, Stockton, California, circa 1910. (Photograph courtesy of the Stockton Record.)

In 2000, the study area had a population of about 580,000 (CDM, Inc., 2001), and population is expected to increase to more than 1.2 million by 2040 (CDM Inc., 2001). Ground-water recharge is about 900,000 acre-feet per year (acre-ft/yr), and pumping exceeds recharge by 150,000 acre-ft/yr. Water levels in parts of the subbasin declined to below sea level in the early 1950's (California Department of Water Resources, 1967). The pumping depression expanded and shifted eastward in recent years (*link to animation showing changes in water-level contours, 1974 to 1999*), and water levels in parts of the basin were declining at rates as high as 2 feet per year (Northeastern San

Joaquin County Groundwater Banking Authority, 2004). Within the pumping depression, ground water flowed from recharge areas near the mountain front, from major streams and rivers, and from the San Joaquin Delta toward pumping wells.

Purpose and Scope

The purpose of this report is to illustrate the types of data collected, and to present preliminary (2006) results from an ongoing study of the source of high-chloride water to wells in the Eastern San Joaquin Ground-Water Subbasin. The scope of the study includes test-drilling, geophysical logging, and identification of the source of high-chloride water to wells using geochemical techniques. The study couples a basin-wide areal assessment of water quality with more detailed geologic, geophysical, and geochemical data collection along geologic sections in the area affected by declining water levels and increasing chloride concentrations (fig. 4). Although beyond the scope of this preliminary report, extrapolation of data along the cross-sections is intended to extend detailed data collected from multiple-well monitoring sites and from large-capacity wells to other wells along the geologic sections. This approach will aid in the development and a more complete understanding of how the spatial and vertical distribution of subsurface geology, hydrology, and geochemistry combine to influence the movement of high-chloride water to wells.

Test Drilling and Well Installation

Test drilling and well installation was done to obtain samples of geologic materials, lithologic and geophysical logs, and to install wells for use as measuring points for water-level and water-quality data collection. Between May and October 2005, three multiple-well sites—each containing three to

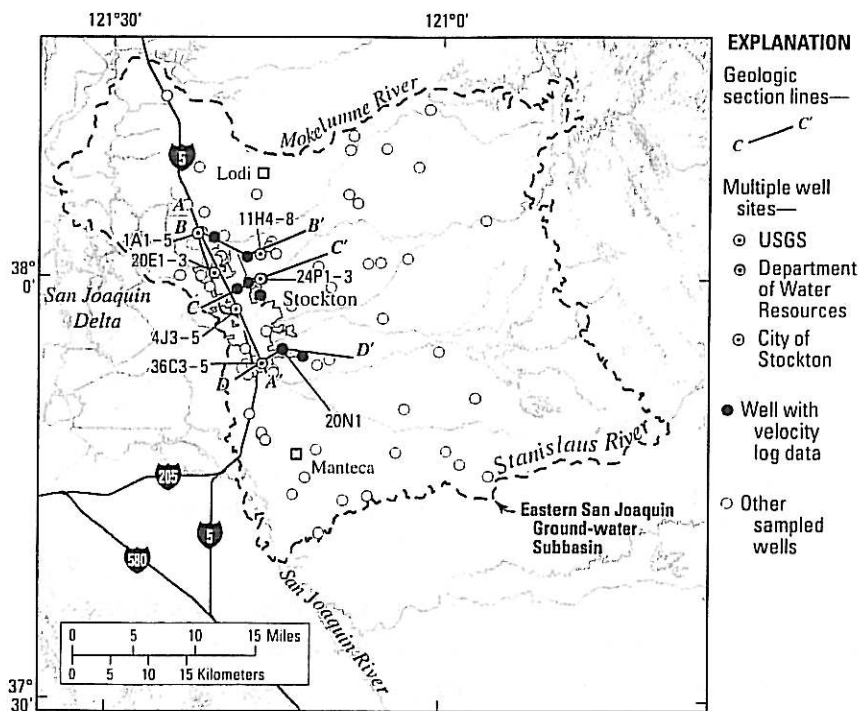


Figure 4. Location of selected wells and geologic sections, Eastern San Joaquin Ground-water Subbasin, California.

five 2-inch diameter monitoring wells with PVC casings installed at different depths, were completed. Data from these sites were supplemented with data from multiple-well sites installed previously at two locations by the California Department of Water Resources (2003), and at an additional location by the City of Stockton (fig. 4).

Geophysical logs and well-construction data for multiple-well site 2N/5E-1A1-5, installed near the eastern edge of the San Joaquin Delta, are shown in figure 5. This site was selected because two wells less than one-half mile east of this site were removed from service as a result of high-chloride concentrations. Water levels at this multiple-well site ranged from about 13 to 27 ft below land surface in May 2005, and depth to water increased with well depth. The site is located in what would have been a ground-water discharge area under predevelopment conditions, and the increase in depth to water with well depth is probably the result of regional ground-water pumping. In May 2005, chloride concentrations at this site ranged from 550 to 1,800 milligrams per liter (mg/L). At that time, the shallowest and deepest wells had chloride concentrations of 1,800 and 1,700 mg/L.

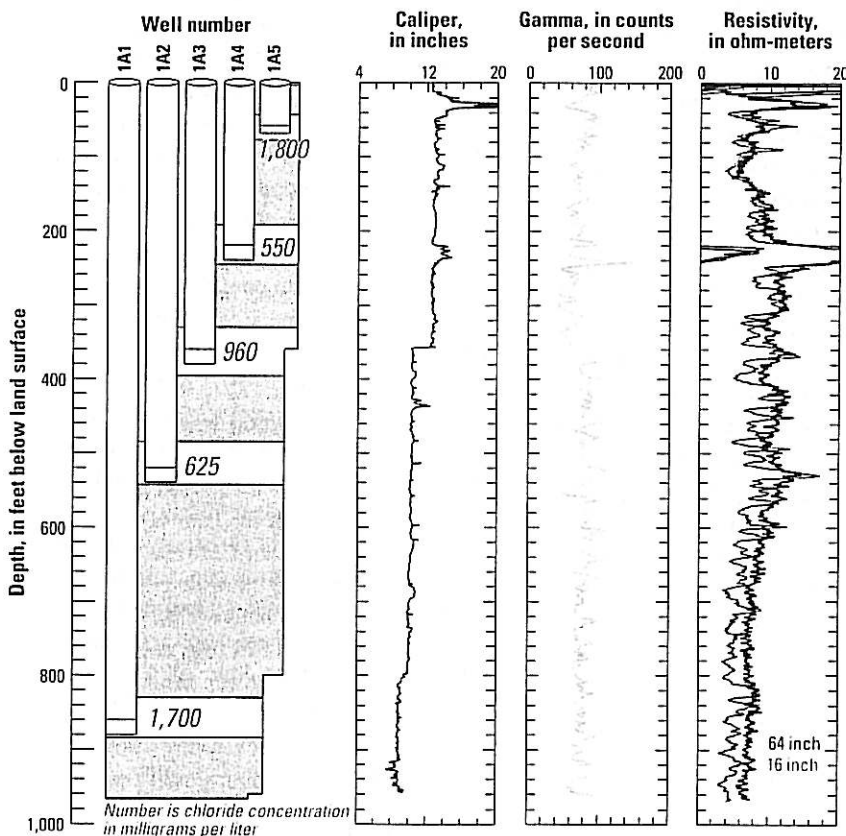


Figure 5. Selected geophysical logs and well-construction data for multiple-well site, 2N/5E-1A1-5, Eastern San Joaquin Ground-water Subbasin near Stockton, California, May 2005.

respectively (fig. 5). Data from the wells at this site and from monitoring wells at other multiple-well sites will be used to evaluate the chemical and isotopic composition of potential sources of high-chloride water to these wells.

The two other multiple-well sites 1N/6E-4J3-5 and 2N/6E-11H4-8 (fig. 4) were drilled to depths of 600 and 643 ft below land surface, respectively. In January 2006, chloride concentrations in water from sites -4J3-5 near the San Joaquin Delta ranged from 120 to 510 mg/L, with the highest concentration in well -4J4 that was completed between 360 and 340 ft below land surface. In May 2005, chloride concentrations in water from sites -11H4-8, near ground-water recharge ponds east of the delta, were between 9.9 and 3.4 mg/L.

Borehole Geophysical Data

In addition to geophysical logs collected during test drilling, two types of borehole geophysical data were collected as part of this study. Electromagnetic (EM) logs were collected from selected multiple-well sites to evaluate changing water quality at depth. Fluid-velocity logs were collected under pumping conditions from selected public supply wells to determine the depth at which water enters those wells. Velocity logs were coupled with depth-dependent water-quality data, also collected under pumping conditions, to determine the quality of water entering the well at different depths.

Electromagnetic logs

Only a limited number of wells screened over selected intervals can be installed at multiple-well monitoring sites. As a consequence, changes in water quality are not measured directly through much of the aquifer thickness. To address this issue, the deepest well at multiple-well sites was used as access tubes for repeated measurement of electromagnetic resistivity through the entire aquifer thickness penetrated by the well. EM logs collected through the PVC casings of monitoring wells are sensitive to the lithology of the deposits and to the resistivity of the pore fluids within the deposits (McNeill and others, 1990). Because the lithology remains constant with time, repeated EM logs differ only if the fluid resistivity changes as a result of the movement of water of differing quality at depth (Williams and others, 1993). The radius of the material measured by the logging tool is between 10 and 50 inches, and as a result the tool is relatively insensitive to borehole fill material adjacent to the well (McNeill and others, 1990). These properties make EM resistivity a suitable tool for identifying changes in water quality, particularly changes in salinity, at locations from which ground-water samples cannot be collected directly.

EM resistivity values at corresponding depths from logs collected within well 2N/6E-20E1 in June 2004 and

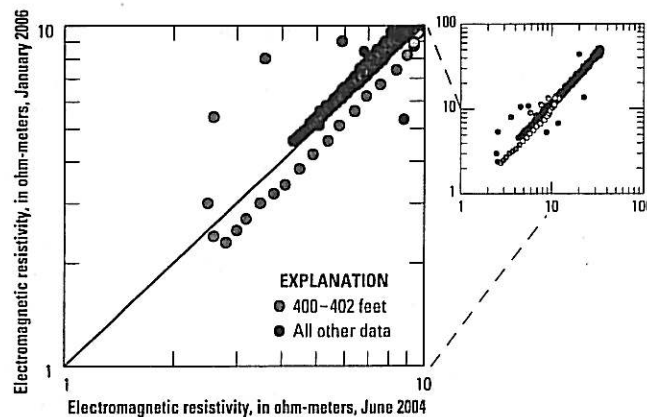


Figure 6. Comparison of electromagnetic resistivity values collected in well 2N/6E-20E1, Eastern San Joaquin Ground Water Subbasin near Stockton, California.

January 2006 are shown in figure 6. In the time between collection of the two logs, EM resistivity values decreased in a narrow interval between 400 and 402 ft below land surface (fig. 6). The January 2006 values, between 400 and 402 ft, were among the lowest collected from the well. Because the lithology has not changed, decreased EM resistivity at this depth may be the result of decreased fluid resistivity (increased fluid conductivity) resulting from increased salinity between the two logging dates. Horizontal movement of poor-quality water through thin, permeable zones that are either areally extensive, or well-connected hydraulically, commonly occurs in coastal California aquifers (Nishikawa, 1997). Given this scenario, the three monitoring wells at this site (screened from 472 to 507, 289 to 319, and 189 to 209 ft below land surface, respectively) would not have detected changes in water quality that caused changes in EM resistivity observed near 400 ft.

Decreases in EM resistivity consistent with increasing chloride concentrations also were observed between 40 and 45 ft below land surface in EM logs collected from well 1N/6E-36C3 between June 2004 and January 2006. Previous work (California Department of Water Resources, 1967) indicated the presence of poor-quality water near the water-table in this part of the study area and suggested that this shallow ground water may have been the source of high-chloride water in some production wells.

Additional EM logging at these sites would be required to determine if EM resistivity values will continue to decrease through time. Additional data collection, possibly including the installation of new wells, may be required to determine if changes in EM resistivity are the result of changes

in water quality or the result of some other cause.

Fluid-velocity logs and depth-dependent water-quality sample collection

Fluid-velocity logs from unpumped and pumped wells were collected using an EM flowmeter. The EM flowmeter measures uphole or downhole velocities according to Faraday's Law, where the voltage generated by the movement of charged ions in water flowing through an induced magnetic field is proportional to the velocity of water flowing through the field. The tool has a range from 0.3 to 260 feet per minute, and is suitable for both the low velocities in unpumped wells and the high velocities in pumped wells (Newhouse and others, 2005). Fluid resistivity and fluid temperature data collected during logging were used to constrain interpretations of fluid-velocity logs.

Fluid-velocity logs from pumped wells were coupled with water-quality samples collected under pumping conditions from selected depths within the well. Sample depths were selected on the basis of measured velocity logs, lithologic logs, geophysical logs, and well-construction data. The samples were collected using a commercially available, small-diameter gas-displacement pump (Izbicki, 2004). Water samples collected using this method are mixtures of water that entered the well from different depths. However, when coupled with velocity log data,

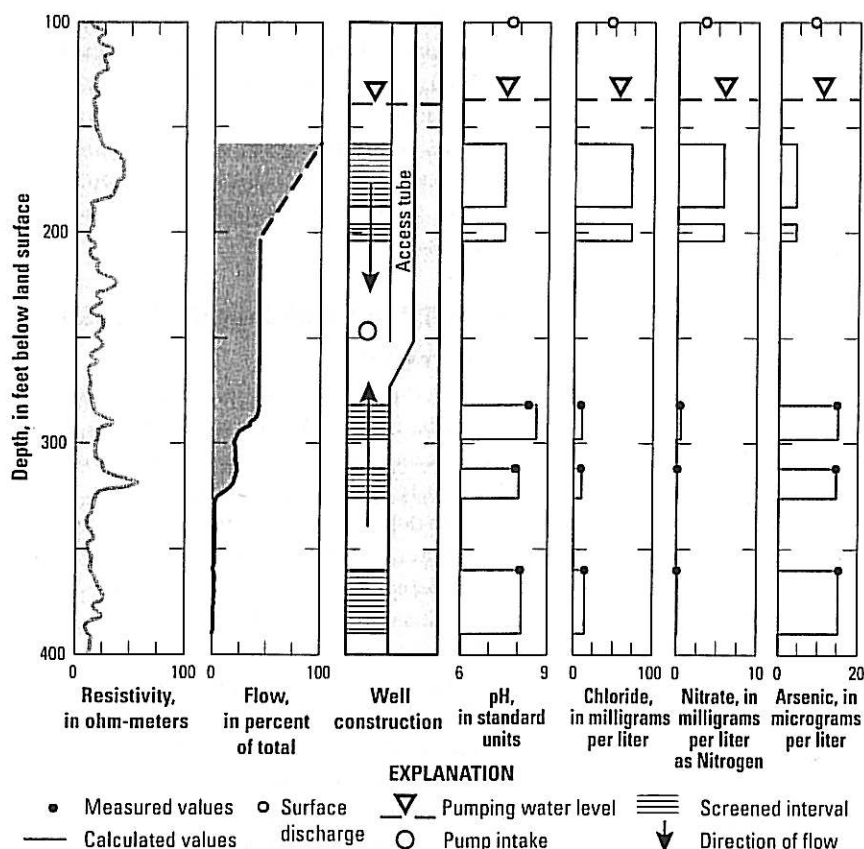


Figure 7. Fluid velocity and depth-dependent water-quality data from well 1N/7E-20N1, Eastern San Joaquin Ground-Water Subbasin, California, August 2004.

depth-dependent water-quality data can be used to estimate the quality of water entering a well from selected depths in an aquifer (Izbicki, 2004).

Fluid-velocity logs from well 1N/7E-20N1 show that slightly more than one-half of the water entered well -20N1 through the two upper screens located 158 to 204 ft below land surface (fig. 7). Most of the remaining water entered the well through screens at 282 to 298 and 312 to 326 ft below land surface. Only a small amount of water entered the well through the deepest screen 360 to 390 ft below land surface (fig. 7). In well -20N1, the higher yielding upper zones correspond to electrically resistive sand and gravel units indicated on the electric log (fig. 7). Where present in other wells, this high-resistivity zone also contributes large amounts of water to wells. The small amount of yield from the deepest screen was unexpected on the basis of lithologic and geophysical logs, and may reflect increased consolida-

tion and decreased hydraulic conductivity of alluvial deposits with depth.

Depth-dependent water-quality samples collected within well -20N1 under pumping conditions reflect the vertical distribution of water-quality within the aquifer (fig. 7). Chloride and nitrate concentrations are higher in water entering from the upper well screens than the deeper well screens. In contrast, pH and arsenic concentrations were higher in water entering from the deeper parts of the well. Arsenic concentrations in the deeper parts of well -20N1 were as high as 15 micrograms per liter ($\mu\text{g/L}$). Mixing of water having lower arsenic concentrations from shallower depths within the well caused water discharge at the surface to approach the Maximum Contaminant Level (MCL) for arsenic of 10 $\mu\text{g/L}$ (U.S. Environmental Protection Agency, 2006). Changes in well drilling and construction practices could exclude zones having high

concentrations of constituents such as chloride, nitrate, or arsenic from newly installed wells, and modifications in well design could exclude zones contributing poor-quality water to existing wells—thereby improving the quality of water from those wells.

By January 2006, fluid velocity logs coupled with depth-dependent water-quality data had been collected from eight wells that are distributed along the sections shown in figure 4. Data from these wells will be used with geochemical data collected from the surface discharge of wells throughout the study area to determine the sources of high-chloride water to wells.

Sources of High-Chloride Water to Wells

Prior to the construction of reservoirs on rivers tributary to the San Joaquin Delta, water having chloride concentrations as high as 1,000 mg/L intruded the delta during low-flow periods (Piper and others, 1939) (fig. 1). Under present-day (2006) conditions, surface flows are managed to protect freshwater resources in the delta and to prevent the inland movement of seawater. However, high-chloride water may originate from water trapped in delta sediments during their deposition—constituents dissolved within this water may retain a chemical composition consistent with a seawater origin. High-chloride water also may originate from soluble salts emplaced in sediments from ground-water discharge along the delta margin—constituents dissolved within this water would have a chemical composition different from seawater. It is likely that water from deeper aquifers that underlie freshwater aquifers pumped for supply also has markedly different chemical composition and may contribute high-chloride water to wells in different parts of the subbasin. In addition, irrigation return may increase chloride concentrations near the water table. To further complicate the issue, multiple sources of high-chloride water may occur at different depths within the same well. Water from wells was sampled and analyzed for major-ions, selected minor ions, and its isotopic (oxygen-18

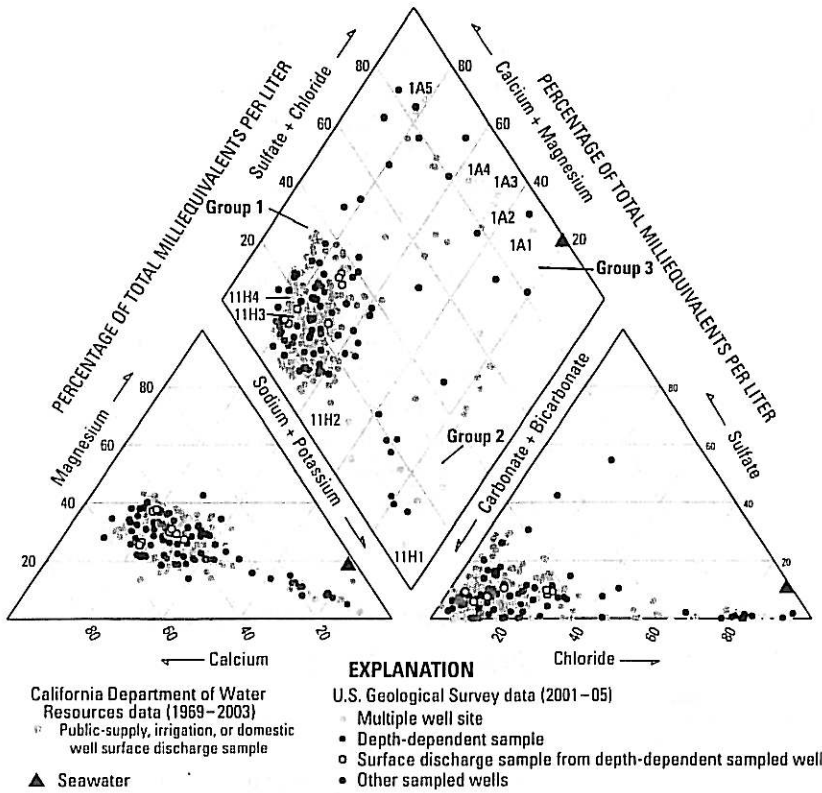


Figure 8. Major-ion chemistry of water from selected wells in the Eastern San Joaquin Ground-Water Subbasin, California, 2004–2005.

and deuterium) composition, to determine the composition of fresh and high-chloride waters in the study area and the sources of high-chloride water to wells.

Major-Ion Composition of Water from Wells

The major-ion composition of 100 water samples from 76 public-supply, irrigation, domestic, and observation wells collected as part of this study between May 2004 and January 2006, and 245 historical samples from 42 wells were evaluated using a trilinear diagram (fig. 8). A trilinear diagram shows the proportions of the major cations (calcium, magnesium, and sodium plus potassium) and the major anions (carbonate plus bicarbonate, sulfate, and chloride) on a charge-equivalent basis (Hem, 1985). Cations are plotted on the lower left triangle, anions on the lower right triangle, and the central diamond integrates the data.

On the basis of their distribution within the trilinear diagram, data were separated into three groups having different chemical compositions. Group

1 represents the majority of sampled wells. Group 2 consists of depth-dependent samples from deeper depths within sampled public-supply wells, and samples from deeper observation wells at multiple-well sites. The composition of water from deeper aquifers represented by these samples is not apparent in historical data collected from the surface discharge of wells; because ground water from deeper depths mixes within the wells with ground water from shallow depths during pumping, thereby masking the composition of the deeper ground water. As a result of mixing within the well during pumping, samples from the surface discharge public-supply wells plot within Group 1 even though deeper samples from the same well plot within Group 2. All samples within Groups 1 and 2 had chloride concentrations of less than 100 mg/L. In contrast, all but two samples within Group 3 were from wells that had chloride concentrations greater than 100 mg/L. This group included several public-supply wells that are no longer in use due to chloride

concentrations that were greater than the Secondary Maximum Contaminant Level (SMCL) of 250 mg/L (U.S. Environmental Protection Agency, 2006). The major-ion composition of water from wells did not trend consistently toward the composition of seawater as chloride concentrations increased.

Minor-Ion Composition of Water from Wells

Certain minor ions in water, such as bromide, iodide, barium, and boron are present naturally in high-chloride water from different sources, and have been used to determine the origin of high-chloride water to wells (Piper and Garrett, 1953; Izbicki and others, 2005). Analysis of this combination of minor ions is especially effective because their differing abundances, chemical properties, and biological reactivity can produce a wide range of compositions, relative to chloride concentrations; these compositions reflect different geology, source-water composition, and aquifer chemistry. Of the four minor ions analyzed in this study, iodide commonly has the largest range in environmental compositions, relative to chloride and is commonly very useful in determining the source of high-chloride water to wells.

Iodide is depleted in seawater through uptake by marine organisms (Izbicki and others, 2005). As these organisms die, are buried, and decay, water within marine deposits may become enriched in iodide. In the plot of chloride-to-iodide ratio as a function of chloride (fig. 9), data are bimodally distributed and reflect contributions of high-chloride water from at least two sources. The chloride-to-iodide ratio from some wells follows a seawater mixing line with increasing chloride concentrations, and reflects high-chloride seawater minimally altered by contact with aquifer material. Water from most observation wells and from depth-dependent samples collected within the deeper parts of public-supply wells plotted to the right of the seawater mixing line. The iodide-enriched composition of water from these wells is similar to that of water from marine rocks and oil-field brine sampled elsewhere in

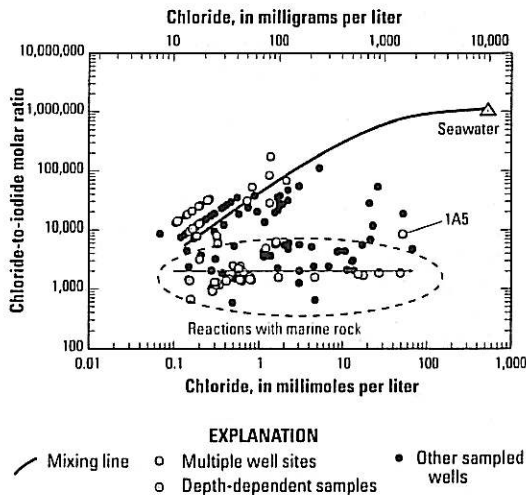


Figure 9. Chloride-to-bromide and chloride-to-iodide ratios as a function of chloride concentration in water from selected wells in the Eastern San Joaquin Ground-Water Subbasin, California, 2004–2005.

California (Piper and Garrett, 1953; Izbicki and others, 2005). Several wells having high-chloride water, including the shallow observation well -1A5 at the Oak Grove Park multiple-well site, have chloride-to-iodide ratios intermediate between compositions expected from seawater mixing and from deep brines. Water from these wells may be complex mixtures of high-chloride water from multiple sources, or the water may have reacted with aquifer materials to remove iodide from the solution.

Oxygen-18 and Deuterium Composition of Water from Wells

Oxygen-18 and deuterium are naturally occurring stable isotopes of oxygen and hydrogen, respectively. Oxygen-18 ($\delta^{18}\text{O}$) and deuterium (δD) abundances are expressed as ratios, in delta notation as per mil (parts per thousand) differences, relative to the standard known as Vienna Standard Mean Ocean Water (VSMOW). By convention, the value of VSMOW is 0 per mil. Negative per mil values have more of the lighter isotope than VSMOW (Craig, 1961), and highly negative per mil values have more of the lighter isotope than less negative values.

Most of the world's precipitation originates from the evaporation of seawater. As a result, the $\delta^{18}\text{O}$ and δD composition of precipitation throughout the world is

correlated linearly and distributed along a line known as the global meteoric water line (Craig, 1961). In many areas, water samples plot along a line slightly below the global meteoric water line that is known as the local meteoric water line. The $\delta^{18}\text{O}$ and δD composition of a water sample, relative to the composition of water from other areas, provides a record of the source and evaporative history of the water, and can be used as a tracer of the movement of the water. Differences in the $\delta^{18}\text{O}$ and δD composition of water from the global meteoric water line may result from differences in the temperature of condensation of precipitation that recharged the ground water. These differences may result from condensation at different altitudes, from seasonal or short-term climatic changes, or from long-term climatic changes such as those that occurred at the end of the Pleistocene Epoch. Partial evaporation of a water sample shifts the $\delta^{18}\text{O}$ and δD composition to the right of the global meteoric water line along an evaporative trend line (International Atomic Energy Agency, 1981).

The $\delta^{18}\text{O}$ and δD composition of water from wells in the study area ranged from -6.3 to -11.2 per mil and -48 to -81 per mil with a median composition of -8.4 and -60 per mil, respectively (fig. 10). Most samples plot parallel to, but below, the global meteoric water line.

The more negative values are from shallow wells, typically about 100 ft deep, along the Mokelumne and Stanislaus Rivers (fig. 10). These rivers drain the higher altitudes of the Sierra Nevada to the east of the study area, and water from these wells probably originated as precipitation at cooler temperatures associated with higher altitudes instead of precipitation at warmer temperatures associated with lower altitudes. There was no consistent trend toward increasingly negative values from deeper wells at multiple-well sites installed as part of this study. However, δD values between -70 and -68 per mil were obtained from shallower wells at a multiple-well site 2N/6E-11H4-8 near ground-water

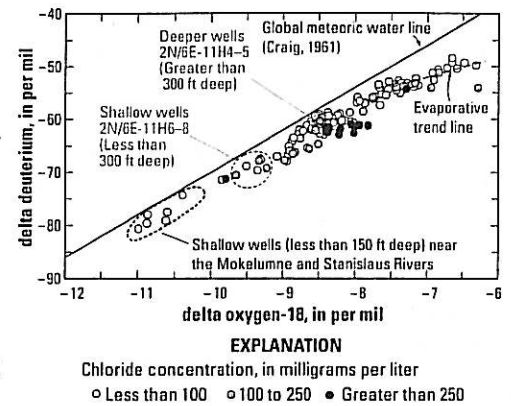


Figure 10. Oxygen-18 and delta deuterium composition of water from selected wells in the Eastern San Joaquin Ground-Water Subbasin, California, 2004–2005.

recharge ponds. These data are consistent with movement of recharge water from the ponds (that originated from reservoirs in the Sierra Nevada) to depths as great as 300 ft.

The less negative samples plot to the right of the local meteoric water line along an evaporative trend line (fig. 10). Although most high-chloride water plots to the right of the meteoric water line, chloride concentrations do not consistently increase with the evaporative shift in $\delta^{18}\text{O}$ and δD isotopic composition. These data suggest that the high-chloride concentrations are the result of processes other than evaporative concentration of ground water, and are consistent with high-chloride water mobilized from delta sediments or deeper deposits.

Summary

Water levels are declining and chloride concentrations are increasing in water from wells in the Eastern San Joaquin Ground-Water Subbasin near Stockton, California, as a result of pumping in excess of recharge. A study approach that utilizes a combination of data collection activities including (1) drilling and monitoring well installation, (2) borehole geophysical data collection from monitoring wells and large-capacity pumping wells, and (3) geochemical data collection was developed to evaluate the areal and vertical distribution of chloride within freshwater aquifers and

to determine the sources of high-chloride water to wells. The study couples a basin-wide areal assessment of water quality with detailed geologic, geophysical, and geochemical data collected along geologic sections in the area affected by declining water levels and increasing chloride concentrations.

Preliminary results show that water from multiple-well site 2N/5E-1A1-5 near the San Joaquin River Delta had chloride concentrations as high as 1,800 mg/L. High chloride concentrations were present at this site to almost 1,000 ft below land surface. EM logs collected from well 2N/6E-20E1 north of Stockton showed decreased EM resistivity. EM logs collected in well 1N/6E-36C3 south of Stockton, showed decreases in EM resistivity at shallower depths between 40 and 45 ft below land surface. High-chloride water from shallow depths has been observed in production wells in this part of the study area. Additional EM logging at these sites would be required to determine if EM resistivity values continue to decrease through time and if decreasing resistivity is the result of increasing salinity.

Water-quality in the study area changes with depth, and the major-ion composition of water from deeper aquifers is obscured by mixing within wells during pumping. As a consequence, the composition of water from deeper deposits penetrated by wells is not apparent in historical data collected primarily from the surface discharge of wells. Changes in the iodide composition of water from wells with elevated chloride concentrations are consistent with a marine origin of the chloride dissolved in water from wells. Entrainment of seawater in delta deposits may have occurred during deposition of delta sediments. Subsequent mobilization of this entrained water may have occurred as a result of ground-water pumping. High-chloride water in deeper parts of the aquifer is enriched in iodide, relative to seawater compositions and also contributes to increasing chloride concentrations in water from some wells. Such enrichment is common in deeper ground water from oil- and gas-producing regions in California (Piper and Garrett, 1953; Izbicki and others, 2005). Shifts in the $\delta^{18}\text{O}$ and δD composition of water from

some shallower wells are consistent with partial evaporation of water and irrigation return water. However, increases in chloride concentrations from evaporation of irrigation water are small compared to chloride inputs from the delta and underlying deposits.

Acknowledgements

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