FEASIBILITY OF USING ISOTOPES AS TRACERS OF THE SOURCES OF DISSOLVED SOLIDS IN THE UPPER GILA RIVER, ARIZONA

by
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INTRODUCTION

Water quality issues are becoming increasingly important in the upper Gila River drainage area as competition among municipal and industrial water use, agriculture, environmental concerns, and conflicts over water rights set greater demands for use against those of conservation and water quality protection. Water users downstream from the Safford area are affected by the natural processes and human activities that may increase the total dissolved solids (TDS) in river water.

Water quality has been measured extensively in the Gila watershed. It is well established that the concentration of total dissolved solids (TDS) in Gila River water increases with distance downstream from where it enters Arizona, and with decreasing flow during dry periods (Hem, 1950; 1992). During low-flow periods, water quality is sometimes degraded by high salinity by the time the river reaches the NW end of the Safford basin.

Although the increase in salinity downstream, especially during dry seasons, is well established, the ultimate sources of the various TDS constituents have not been determined. The usual list of suspects includes agriculture, mining, grazing, and wastewater. It is commonly assumed that in agricultural areas, irrigation runoff is the main reason for increased salinity. However, in the Safford and Duncan basins a significant portion of the TDS contribution to the Gila River may be from natural sources. The largest natural contributions may be from hot springs and artesian leakage of groundwater with extremely high TDS as a result of leaching natural evaporite minerals in the basin-fill sediments. Another unrecognized source may be improperly abandoned oil exploration wells drilled in the 1920s, and other non-agricultural artesian wells producing saline water. Given the probability of other sources of TDS, attempts to mitigate water quality problems in the Gila River that focus only on agriculture may be misdirected.

The purpose of this pilot study is to assess the viability of using a combination of stable isotopes and chemical ratios to characterize dissolved solids from suspected natural and human-caused sources. Routine chemical analyses reveal how much chloride, sulfate, or nitrate are in the water, but those numbers alone rarely indicate the source those constituents. Applying the isotope tracer method in detail may yield results that can be used to constrain the identity of sources and their magnitude. Most studies of isotopes as groundwater tracers in Arizona have focused on wastewater effluent or agricultural runoff as primary contributors to water quality problems. In the upper Gila River watershed, there is the important added factor that the primary source of dissolved solids in the river may be natural soluble minerals found throughout the region. Knowledge of the sources of dissolved solids is essential for making decisions about mitigation of water quality problems affecting the Gila River and its tributaries.

Isotopic and chemical ratios can be used to characterize different potential sources of river contaminants, and similar analyses of river water can then be used to determine the relative contributions of solutes to river water from the different identified sources. This report presents the isotopic composition and selected chemical ratios of various basin-fill sediments, groundwater, surface water, and wastewater in the upper Gila River watershed.

GEOLOGY AND HYDROLOGY OF THE STUDY AREA

Geology

The study area encompasses a large portion of the Gila River watershed between the Arizona-New Mexico border on the east and the San Carlos Indian Reservation on the west (Figure 1). The upper Gila watershed includes the San Francisco River and San Simon Wash.

Two basins are traversed by the Gila River in Arizona, the Duncan, and Safford-San Simon basins. Bounding the Safford-San Simon basin on the southwest are the Chiricahua, Dos Cabezas, and Pinaleño Mountains. Rocks in these mountains include Precambrian granite and schist, Paleozoic and Mesozoic sedimentary rocks, and Tertiary igneous rocks. On the northeast side of the basin are the Gila and Peloncillo Mountains, composed of Late Cretaceous to mid-Tertiary igneous rocks (Drewes, 1980; Reynolds, 1988).

The Duncan basin is bounded on the west by the Peloncillo Mountains and on the east by the Black, Summit, and Big Lue Mountains. The Arizona portion of these ranges are composed of mid- to late Tertiary volcanic rocks (Morrison, 1965; Richter and others, 1983; Reynolds, 1988).

Both the Duncan and Safford basins are deep, sediment-filled structural troughs containing abundant lacustrine (lake) and playa sediments, reflecting long periods of closed-basin conditions. Conditions during much of the history of the Safford basin were likely those of an alkaline, highly saline lake that periodically dried up, as evidenced by the abundant evaporite minerals, and deposits of zeolites (Eyde, 1982; Sheppard and others, 1978). Gravity models indicate that the Safford basin is up to 12,000 feet deep, and the Duncan basin may exceed 2000 feet in depth (Oppenheimer and Sumner, 1980; 1981). Soluble minerals such as halite (salt), carbonates, gypsum, and anhydrite are common in the basin-fill sediments (Marlowe, 1961; Harbour, 1966; Harris, 1997). These minerals commonly form by evaporation of water and deposits formed in this way are called evaporites. For example, in the Tenney #3 oil exploration well, half-way between Safford and Bowie, drillers encountered 2270 feet of anhydrite and gypsum containing numerous beds of pure salt. Evaporites in the Safford area have been studied and described in *Pay Dirt* (1984), and by Peirce (1969; 1981; 1984), Koester (1971), and Eaton and others (1972).

Typical Basin-and-Range basins were formed in the late Tertiary (12-6 Ma), when high-angle normal faulting dropped central blocks between uplifted bounding blocks, forming a more or less symmetrical, deep structural basin. The Safford basin, however, was formed earlier than Basin and Range time by low-angle faulting resulting from crustal extension. Detachment faulting during the mid-Tertiary (30-20 Ma) extension formed the metamorphic core complex of the Pinaleño Mountains and the tilted structural basin of the Safford Valley (Spencer and Reynolds, 1989; Kruger and others, 1995). Later Basin and Range faulting did not affect the Safford region to the extent that it did other areas of the southwest.

Seismic reflection profiling (Kruger, 1991; Kruger and Johnson, 1994; Kruger and others, 1995) has revealed the Safford basin to be a tilted half-graben, with the southwest side of the basin down-faulted along a high-angle fault that is younger than the main basin-forming detachment. As detachment faulting progressed, the basin grew deeper and wider and filled with sediment as the rocks above the fault were displaced away from what is now Mt. Graham. Sediments were tilted as extension continued, with older sediments tilted more than younger deposits. This style of faulting has produced an asymmetrical structural trough which is filled with sedimentary deposits that are wedge shaped in cross section.

Early models of the Safford basin, such as those by Schwennesen (1919), Knechtel (1936), and Harbour (1966) treated it as a standard, symmetrical Basin and Range type basin, with

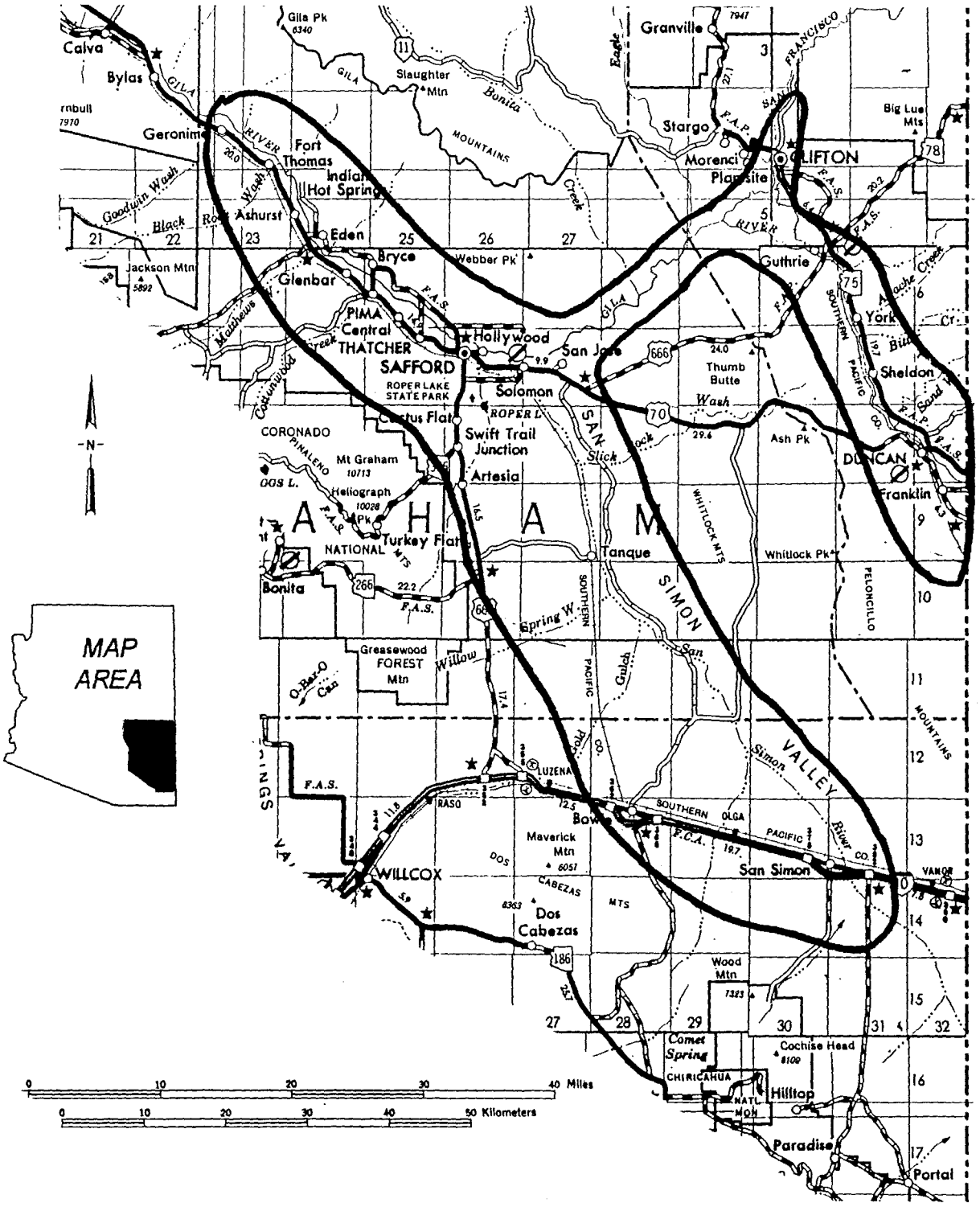


Figure 1. Location of study area

essentially flat stratigraphy. Attempts at correlation of units generally assumed that equivalent layers, or facies, should be at approximately the same elevation throughout the valley. More recent work has revealed a more complex stratigraphy in the Safford-San Simon basin. With a half-graben structure, equivalent layers are deeper and thicker to the southwest, and the difference in elevation between the southwest and northeast parts of equivalent layers is greater with increasing age because the southwestern part of the basin has subsided more since the sediments were deposited. The lateral and vertical changes in the basin-fill sediments reflect a combination of factors, including long- and short-term climate changes, different subsidence rates in different parts of the basins, changing sediment sources as erosion exposed older rocks, and sporadic inflow of water and sediment from outside the immediate basins.

Sediments in the Safford Valley were divided into an upper basin fill and lower basin fill by Harbour (1966). The boundary between the lower and upper basin fill was considered by Harbour to reflect a major climate change at the Pliocene-Pleistocene boundary.

The main Safford-San Simon basin is divided into four depositional sub-basins by Houser, (1990). From north to south are the San Carlos, Bylas, 111 Ranch, and San Simon sub-basins. Four basin-fill units have been recognized in the 111 Ranch sub-basin of the Safford-San Simon basin (Richter and others, 1983; Houser and others, 1985; Houser, 1990). The oldest unit, the Miocene-Pliocene Midnight Canyon conglomerate, is a proximal fan deposit containing only clasts of volcanic rock. The Midnight Canyon unit is inferred to extend across the Safford basin (Houser, 1990) and is equivalent to the basal conglomerate facies of the lower basin fill unit of Harbour (1966). Conformably overlying the Midnight Canyon conglomerate is the Pliocene Sanchez unit, consisting of silt and conglomerate. The Sanchez beds cover the same area and have the same clast composition as the Midnight Canyon unit, but are finer grained and less indurated. In the center of the Safford basin, the Sanchez beds are 250 m thick and consist of clay, gypsum (or anhydrite), and salt (Houser, 1990). The beds thin and pinch out toward the northeast side of the basin. Above the Sanchez beds are the Pliocene 111 Ranch beds, which include lacustrine and fluvial facies. The fine-grained lacustrine facies of the unit consists of silt, clay, limestone, marl, and diatomite. The type section of lacustrine sediments at 111 Ranch, 15 miles southeast of Safford, has been studied extensively (Van Horn, 1957; Clay, 1960; Seff, 1962; Galusha and others, 1984). The fine- to coarse-grained fluvial facies, representing a fan delta from Bonita Creek, interfingers with the lacustrine facies. The 111 Ranch beds attain a thickness of about 520 m near the center of the basin and thin toward the Gila Mountains (Houser and others, 1985; Houser, 1990). The Bear Springs Wash beds interfinger with the 111 Ranch and Sanchez beds in the southwest part of the Safford basin (Houser and others, 1985). This unit consists of fine-grained lacustrine sediments similar to the 111 Ranch beds interbedded with coarse-grained alluvial fan deposits.

Above the Sanchez, 111 Ranch, and Bear Springs Wash beds is Pliocene-Pleistocene alluvium of the ancestral Gila River. Thickness ranges from 85 feet at Safford to 30 feet at Geronimo (Black, 1991). The alluvium is similar to modern Gila River sediments, with clasts of volcanic rocks, quartzite, granite, and chalcedony (Houser and others, 1985). Capping the section is a layer of Quaternary alluvium. Along the Gila River are modern alluvial sediments of the flood plain.

Hydrology

At the time of deposition of the basin-fill sediments and evaporites in the Safford-San Simon and Duncan basins, an integrated drainage did not yet exist, at least in southeastern Arizona. Drainage in most of the deep basins of Arizona, and in most of the Basin and Range Province, was internal during much of their history, except for periods when the regional climate

was much wetter and some of the usually internally-drained basins may have overflowed into adjacent basins.

Integration of the drainages of southeastern Arizona into a large regional system - the Gila River- is geologically recent. Drainage in the lower San Pedro basin was apparently still largely, if not completely, internal at the time of deposition of the Quiburis Formation, dated at 5.35 to 6.43 million years (Ma) (Scarborough, 1975). The beginning of through-flowing drainage in the Safford basin may be constrained by the 3.6 Ma age of Flatiron Mesa basalt flows deposited on the highest terraces and pediments in the area around the San Carlos River (Houser, 1990). However, swampy to playa conditions were still present at the time of deposition of the 111 Ranch beds near Safford, which contain ash layers dated by Dickson and Izett (1981) at 2.17 to 2.67 Ma. Integration of the regional drainage had probably reached the 111 Ranch area and the Duncan Basin by 0.6 Ma, based on ash layers in Gila River gravel deposits (Houser, 1990). The Willcox and Animas Valley playas demonstrate that drainage in the upper Gila region is still not completely integrated.

Originating in New Mexico, the Gila River drains the region of the study area. The river enters Arizona near the town of Duncan and flows northwest to the north end of the Duncan basin, where the San Francisco River joins. The Gila then cuts across the Gila Mountains, entering the Safford-San Simon basin near San Jose. The San Simon River (or Wash), which drains the southern half of the Safford-San Simon valley, enters the Gila several miles east of Safford. The Gila flows northwest through the Safford Valley, leaving the basin near its northern extent, cutting southwest across the Mescal Mountains about 20 miles southeast of Globe.

River gages of the U.S. Geological Survey applicable to the study area are located on the Gila River near Blue Creek, 15 miles upstream from the Arizona-New Mexico border; at the north end of the Duncan Valley; at the head of the Safford Valley; and at Calva. A river gage on the San Francisco River is located at Clifton. Descriptions and detailed locations of the gages are given in Appendix A. Average flow of the San Francisco River is 244 cfs at Clifton, while that of the Gila at the north end of the Duncan basin just upstream from the San Francisco confluence is 197 cfs (Smith and others, 1997). Discharge of the Gila as it enters the Safford Valley averages 512 cfs. Determination of flow rates through the Safford Valley is hampered by lack of USGS gage stations and numerous diversions for irrigation.

Flow in the Gila River is seasonally variable, and salinity increases rapidly with decreasing flow. Hem (1950) found that salinity in the river varied in an inverse, nearly linear fashion versus flow rate. By the time the Gila River reaches site 29, just downstream from Pima, most of the river has been diverted for irrigation. At the time of the July sampling, the remaining river was diverted at site 29. The 'river' below site 29 (including site 30) consisted of water from seeps, springs, flowing artesian wells (e.g. sites 11 and 31) and possibly underground return of irrigation water. Thus the chemistry of the river was dominated for several miles by these additions.

Harbour (1966) described the groundwater hydrology of the Safford basin in terms of a single upper aquifer and a single lower aquifer, defined and separated by a "blue clay" layer separating his 'upper' and 'lower' basin fill units,. This simplistic model is not borne out by an examination of logs and cuttings for wells in the valley. Logs and cuttings commonly reveal several "blue" (gray) clay layers interbedded with brown, red, yellow or green clay, and sand and gravel in many wells.

Detailed mapping of the basin fill (Richter and others, 1983; Houser and others, 1985; Houser, 1990) and examination of well cuttings (Harris, 1997) has revealed that the basin fill is interfingered on large and small scales. This produces a situation in which innumerable water-bearing layers (aquifers) consisting of relatively coarse material, such as sand and gravel, are separated by equally numerous fine-grained layers (aquitards) of silt, clay, and evaporites.

Water is commonly reported from multiple intervals by drilling crews and deep wells of various depths produce waters of differing chemistry, temperature, and artesian head, not indicative of a simple, single aquifer. Differences in artesian head in adjacent wells have been noted in several Arizona basins (Anderson, 1995; Anderson and others, 1992). In the Safford basin, during drilling of the 1837-foot deep Whitlock Oil Co. #1 State oil exploration hole (D-10-28-36aa), salty water was encountered in six intervals between 640 and 1352 feet, while at 1363 feet, fresh artesian water was noted (AZGS, Oil and Gas Conservation Commission files). Similarly, the Gila Oil Syndicate well (site 31 of this study) produced strong artesian flow at six different intervals from 430 to 2405 feet (Knechtel, 1938). Logs for the Underwriters Syndicate "Mary Mack" oil well show numerous beds of sand and gravel, but most produced no water; only four water-bearing beds are indicated (AZGS, OGCC files; Knechtel, 1938).

ISOTOPES MEASURED IN THIS STUDY

Isotopes are species of an element, having the same number of protons, but different numbers of neutrons. Chemically, all isotopes of a specific element behave nearly identically, and cannot be distinguished by simple, standard chemical analyses such as those used to measure water quality. Some isotopes are radioactive; those that are not are called stable isotopes. Most elements have more than one stable isotope in nature. Each isotope of an element has a different atomic weight (a physical, not chemical property), and this difference in mass allows isotopes to be physically separated with a mass spectrometer. A mass spectrometer uses strong electric and magnetic fields to deflect beams of ionized atoms. The amount of deflection depends on the mass and charge of the ions, and the isotopes are separated in much the same way that a prism separates a beam of light into its component colors based on wavelength.

Various chemical, physical, and biological processes in nature separate light from heavy stable isotopes, a process called fractionation. As a result, different natural and human sources of dissolved solids commonly have distinctive isotopic compositions for certain elements. Knowledge of the distinct isotopic composition of specific materials can be used to determine sources and pathways of dissolved constituents in water.

Sulfur isotopes

Sulfate (SO_4^{-2}) is a major constituent in groundwater and surface water in the upper Gila River watershed. Levels of sulfate generally increase downstream in the Gila River. Possible reasons for increased sulfate in Gila River water include concentration by evapotranspiration, introduction by springs, use of well water for irrigation and municipal supply, natural weathering of mineralized areas, and natural leakage of groundwater in contact with deep basin-fill evaporites into the shallow aquifer and then into the river.

Sulfate in the form of naturally-occurring gypsum and anhydrite is ubiquitous in the basin-fill sediments of the Safford and Duncan basins (Harris, 1997). Many of the drill cuttings in the AZGS repository from wells in the Safford and Duncan basins contain abundant gypsum or anhydrite. Gypsum is common in surface exposures throughout the valleys. Sulfate is also a natural product of the weathering of sulfide minerals in mineralized areas.

Differences in isotopes ratios are quite small and are reported in part per thousand (per mil, or ‰). Sulfur isotopic compositions are reported in the standard delta (δ) notation which measures the relative deviation from the ratio of two isotopes in a standard:

$$\delta^{34}S\ (‰) = \frac{(^{34}S/\ ^{32}S)_{sample} - (^{34}S/\ ^{32}S)_{standard}}{(^{34}S/\ ^{32}S)_{standard}} \times 1000,$$

Sulfur isotopes were measured by Dr. Christopher Eastoe, at the University of Arizona Laboratory of Isotope Geochemistry, part of the Department of Geosciences. Two calibration standards were used, seawater sulfate and a barite that have been cross-calibrated at several labs. Analytical procedures follow those detailed in Coleman and Moore (1978). Precision for $\delta^{34}S$ is ±0.13‰ (1σ).

Chlorine isotopes

Chlorine isotopic ratios have increasingly been used to determine the origin of salinity in groundwater by measuring the small but characteristic variations in the isotopic composition of chlorine from different sources. Chlorine isotopes are of great use as a tracer because chloride is the most conservative constituent in groundwater, that is, it is not significantly affected by chemical reactions or biological activity. Degradation of water quality in the Gila River by high levels of sodium and chloride is a major concern. Given the documented widespread occurrence of evaporites in the Safford basin fill (Harris, 1997), and the degree of artesian leakage of groundwater from the deep aquifers into the shallow alluvial aquifer of the Gila flood plain (Turner and others, 1946; Halpenny and others, 1947; Hanson and Brown, 1972; Brown, 1989), much of the salt in the Gila River may be leached from basin fill sediments by natural processes.

Chlorine isotopic compositions are reported in the standard delta (δ) notation:

$$\delta^{37}Cl\ (‰) = \frac{(^{37}Cl/\ ^{35}Cl)_{sample} - (^{37}Cl/\ ^{35}Cl)_{standard}}{(^{37}Cl/\ ^{35}Cl)_{standard}} \times 1000$$

Chlorine isotopes were measured by Dr. Christopher Eastoe, at the University of Arizona Laboratory of Isotope Geochemistry, part of the Department of Geosciences. Methods of high-precision chlorine isotope analysis used by the lab are detailed in Long and others (1993). Isotopes are measured on a modified VG602C gas-source mass spectrometer, using seawater cross-calibrated with other universities, as a standard. Analytical precision for $\delta^{37}Cl$ is ±0.075‰ (1σ).

Boron isotopes

The ratio of two boron isotopes ($^{11}B/^{10}B$) have been used to identify the sources of contaminants, particularly nitrate, in several studies in Arizona (Gellenbeck, 1992, 1994; Leenhouts, 1994; Leenhouts and others, 1998). Boron is a common co-contaminant with nitrate, and boron isotopes can be more useful than direct nitrogen isotope measurements because boron is not subject to the chemical reactions that cause isotope fractionation of nitrogen in recharging waters.

Boron in silicic rocks occurs mostly in micas, and to a lesser extent, other phyllosilicates (Leeman and Sisson, 1996). Illite clay has more boron than chlorite, kaolinite, and montmorillonite (Leeman and Sisson, 1996). Tourmaline is the most common silicate containing significant boron; other common rock-forming silicates generally have little or no boron. Likewise, carbonates, sulfates, and oxides typically have low to nil boron contents. On the other hand, evaporites commonly have high levels of boron. The Safford basin contains extensive evaporites and lacustrine deposits that should have boron isotopic ratios readily distinguishable from common sources of boron, such as nitrate fertilizer and wastewater.

Boron isotopes are reported in the standard δ notation:

$$\delta^{11}B\ (‰) = \frac{(^{11}B/\ ^{10}B)_{sample} - (^{11}B/\ ^{10}B)_{standard}}{(^{11}B/\ ^{10}B)_{standard}} \times 1000.$$

Boron isotope analyses were performed at the University of Arizona Department of Hydrology and Water Resources under the supervision of Dr. R.L. Bassett. Precision of the B isotope results using a VG 336 thermal ionization mass spectrometer is on the order of 0.5‰. Isotopic ratios were corrected to the NBS951 standard.

Strontium isotopes

Ratios of strontium isotopes ($^{87}Sr/^{86}Sr$) are useful as a proxy for the source of calcium in carbonates and gypsum. The Safford and Duncan basins contain extensive lacustrine limestone, and evaporite gypsum and anhydrite; weathered rocks of the region contain abundant secondary calcite; soils in desert regions contain caliche. Spencer and others (1996) found Sr isotopes definitive in establishing the origin of lacustrine limestone and gypsum in western Arizona. The isotopic composition of limestone of the Bouse Formation was found to be the same as that of Colorado River water, while gypsum deep in the lower Gila basin near Gila Bend is substantially different, indicating that the origin of the gypsum in the lower Gila basin was not from the same water as the Bouse limestone. Van der Hoven (1994) used Sr isotopes to establish the source of calcium in soil caliche. Significantly, Van der Hoven's and other studies have shown that natural, wind-blown dust is a major source of exchangeable cations in soil and dissolved cations in stream water. Dolegowski (1988) successfully used Sr in a study of groundwater in western Arizona. Gellenbeck (1992) used Sr isotopes to demonstrate that some of the salinity in groundwater west of Phoenix is naturally derived from the large Luke Salt body. Strontium isotopes would be similarly useful for determining the relative contribution to Gila River water quality from natural dust and evaporites.

Strontium is reported as just the ratio of ^{87}Sr to ^{86}Sr in the sample, rather than in the δ notation common to most other isotopes. Natural variations in $^{87}Sr/^{86}Sr$ ratios are quite small, but high-precision instruments make possible measurements to six decimal places.

Sr isotopes were measured in the laboratory of Dr. P.J. Patchett, University of Arizona Department of Geosciences using a Micromass Sector 54 mass spectrometer. Analytical precisions depended on the amount of Sr in each sample, and were ±0.000012 to 0.000027. Strontium carbonate (NBS-987) dissolved in weak HCl was used as the analytical standard. Methods of Sr extraction and measurement are detailed in Patchett and Ruiz (1987).

Nitrogen

Nitrogen isotope studies in groundwater systems are useful for fingerprinting sources of nitrate contamination and for identifying redox reactions involving nitrogen compounds. Nitrogen isotopes are most commonly employed for tracking the effects on water quality from agricultural fertilizer and municipal wastewater. Hess (1992) measured N isotopes, along with Cl/Br ratios, and was able to identify agricultural irrigation infiltration, and rule out wastewater, as a contributor to high nitrate levels in groundwater in part of Avra Valley. Gonzalez (1990) showed that the major source of nitrate in the aquifer underneath Quartzsite was from wastewater.

Some of the nitrates in Quartzsite water were thought to possibly be from playa deposits, a situation similar to that in the Safford basin. The extensive evaporite and lacustrine deposits in the

Safford and Duncan basins are expected to contain natural nitrates that may be discernible from nitrate derived from fertilizers and wastewater by their different N isotope compositions.

Nitrogen isotopes are reported in the δ notation:

$$\delta^{15}N\ (‰) = \frac{(^{15}N/\ ^{14}N)_{sample} - (^{15}N/\ ^{14}N)_{standard}}{(^{15}N/\ ^{14}N)_{standard}} \times 1000.$$

Nitrogen isotopes, along with NO_3-N and NH_4-N concentrations, were measured by Dr. R.L. Mulvaney at the University of Illinois at Urbana-Champaign, Department of Natural Resources and Environmental Sciences. Extraction and analytical methods are detailed in Mulvaney and others (1997) and Kahn and others (1997).

Oxygen and hydrogen isotopes

Isotopes of oxygen and hydrogen are fractionated by evaporation and precipitation in the hydrologic cycle, by chemical reactions with rocks, and through biological processes. The large variations in isotopic ratios resulting from these processes provide a powerful and well-understood tracer for determining the sources and movement of water.

Stable isotope ratios of oxygen and hydrogen in water are expressed with reference to SMOW (Vienna standard mean ocean water). The relative differences are expressed in the delta notation:

$$\delta^{18}O \text{ or } \delta D(‰) = \frac{(R)_{sample} - (R)_{standard}}{(R)_{standard}} \times 1000,$$

where R is the ratio of O^{18}/O^{16} or $^{2}H/^{1}H$. The stable isotope ^{2}H is usually called deuterium, or D.

For this study, the uses of oxygen and deuterium are to 1) determine the degree of evaporation of irrigation water and 2) distinguish mixing of deep groundwater or hydrothermal waters with river water. Natural artesian flow of deep groundwater into the Gila River is suspected to be of a large magnitude (Hanson and Brown, 1972; Brown, 1989). This underflow is suspected as being a major source for dissolved solids in the river. Oxygen and hydrogen isotopes may be useful tracers for determining the amount of artesian leakage of saline groundwater into the Gila River.

Oxygen and hydrogen isotopes were measured by Dr. Christopher Eastoe, at the University of Arizona Laboratory of Isotope Geochemistry, part of the Department of Geosciences. Analyses were made with a Finnigan DELTA-S mass spectrometer. Analytical precision (1σ) is ±0.08‰ for $\delta^{18}O$ and ±0.08‰ for δD.

Chloride/Bromide ratio

In addition to the isotopic analyses, chloride/bromide ratios were measured in most of the samples in this project. Advantages of including Cl/Br ratios as a tracer are the simplicity and the very low cost per sample. Chloride is already part of the standard suite of constituents in water quality analyses, and bromide is included in many analyses. Results are reported as the simple ratio of the concentrations of Cl and Br.

Chloride/bromide ratios have been used successfully to identify groundwater recharge sources, particularly wastewater effluent and agricultural drainage, that have different Cl/Br ratios from ambient groundwater (Koglin, 1984; Goldwitz, 1989; Stevens, 1990; Knuth and others,

1990; Hess, 1992). Salt is one of the major factors in the water quality of Gila River and Cl/Br ratios are expected to be markedly different for halite in evaporites in the Safford Valley versus those of ambient Gila River water, municipal wastewater, and agricultural runoff. Changes in Cl/Br ratios could point to natural leakage of salty deep water into the shallow aquifer.

Chloride was measured at the University of Arizona Department of Soil, Water, and Environmental Science, by ion chromatography. Bromide was measured by Actlabs-Skyline Laboratory, using the ICP-MS method. Cl and Br were extracted from the solid samples using a simple cold-water leach. Analytical precisions were highly variable because of the different dilution factors necessary to overcome interference in the samples with high salinity.

SAMPLING RATIONALE AND METHODS

Basin-fill samples

Samples of lacustrine sediments and evaporite minerals contained in them were collected from well cuttings in the AZGS repository and from outcrop exposures in the Safford Valley. Sampling sites of well cuttings and outcrops of lacustrine sediments and evaporites were chosen based on availability of appropriate samples in the well cuttings repository, applicability to characterizing the lacustrine and evaporite deposits in the Safford basin, and exposures of the same lacustrine deposits at the surface that are found at depth. Wells with cuttings in the AZGS repository are listed in Table 1, and availability of files with information about those wells is indicated. All of these cuttings were examined for suitability; some were examined three or four times before a choice was made. Sample locations are plotted on Sheet 1. Detailed descriptions of the sites are presented in Appendix A. Available lithologic logs of sampled wells are presented in Appendix B.

A few samples for isotopic analyses were taken from outcrops of lacustrine deposits rather than from well cuttings. The reasons include, in addition to those above:

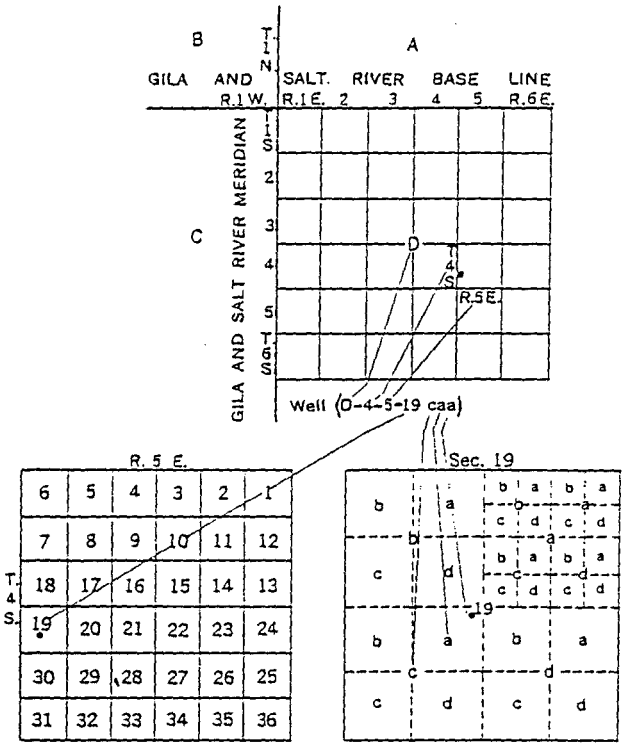
- Sample size is limited from well cuttings, but is not a problem with surface exposures.
- Many of what would be choice wells for sampling of evaporitic salt and sulfate do not have cuttings. Numerous localities around the Safford basin have surface exposures containing salt, gypsum, and lacustrine clay.
- Because of the necessarily small size of the samples, extracting a useable amount of some trace constituents such as boron or nitrate for isotopic analyses from small well-cutting samples might not be achievable.
- Some well cuttings in the AZGS repository may not contain soluble minerals, as a result of dissolution during drilling. In some wells, possible salty layers are indicated in electrical or lithologic logs, but the cuttings show no obvious salt. During drilling, a fluid (mostly water and clay) is often used to lubricate the bit and to aid in the removal of cuttings from the hole. Water is also encountered at some point during the drilling of wells, which would dissolve salt. On the other hand, relatively unweathered surface exposures should still contain most of their original content of soluble evaporite minerals.
- Lacustrine sediments and evaporites are the same in both subsurface cuttings and in outcrops. They are the result of the same period of deposition and formed under the same conditions. The only difference is that outcrops have been exposed by the 1000 feet of erosion that has taken place in the Safford basin over the last few hundred thousand years. These surface exposures were formerly deeply buried.

Table1. Well cuttings in AZGS repository examined in this study

LOCATION	ID	NAME	DATE	# SAMP	INTERVAL	CABINET	FILE	O&G #
D(3-21)9d	211	POOL AT CALVA			70-240	B-10	no	
D(3-22)31c	210	SOTO		62	230-870	B-10	no	
D(5-23)15a	3362	SUPERIOR OIL #1 FEDERAL		22	928-1294	L-44	yes	5-16
D(5-24)30ac	643	ASHURST #1	1927-28	none			yes	5-2
D(5-24)30ac	644	GILA OIL SYNDICATE #1	1927-31	none			yes	5-3
D(6-24)13ab	646	UNDERWRITERS SYNDICATE - MARY MACK	1928	none			yes	5-5
D(6-25)36cbb	495	SMITHVILLE CANAL CO.	1957	79	235-2160	C-78	yes	
D(6-27)36	181	ADIEL SANCHEZ		4	200-294	B-8	no	
D(6-28)31aa	169	M.P. EARVIN - FEDWELL #3A		9	460-540	B-8	no	
D(6-28)5ac	837	CITY OF SAFFORD #6		3	60-80	C-82	no	
D(6-28)5bcd	694	SAFFORD CITY WELL #2		16	85-173	C-47	no	
D(6-28)5bd	1509	CITY OF SAFFORD		8	70-165	D-39	no	
D(7-25)27dcc	425	CITY OF SAFFORD		33	0-335	C-72	no	
D(7-26)17	647	SOUTHERN PACIFIC CO. WATER WELL		none			no	
D(7-26)26aaa	1580	NO NAME (aka ALF CLARIDGE)		79	250-2240	D-47, 48	yes	
D(7-25)27dad	2298	CITY OF SAFFORD		88	130-1396	F-12	no	
D(7-26)4cad	2300	W.A. MCBRIDE		19	0-200	F-12	no	
D(7-26)19aa	2936	EL PASO NATURAL GAS		20	20-400	I-46	no	
D(7-25)6cca	4298	WHITMORE #1 STATE		73	10-760	P-14, 15	yes	684
D(8-26)6cbc	496	ANN CHLARSEN	9/13/57	58	10-651	C-78	no	
D(8-26)19dcc	996	DEPT OF JUSTICE	1/5/59	24	0-240	C-82	no	
D(8-26)7acb	1064	NO NAME	5/4/60	29	0-668	D-49	no	
D(8-26)8adc	1500	CACTUS FLAT - RR-3	11/20/62	18	0-271	D-19, 20	no	
D(8-26)8adcd	1501	CACTUS FLAT - RR-4	11/20/62	51	0-753	D-29	no	
D(8-26)8acc	1502	CACTUS FLAT - RR-2	11/20/62	54	0-829	D-20	no	
D(8-26)7dda	1701	RR #6	6/26/64	80	19-1382	E-19	no	
D(8-26)8bdd	1708	RR-#5	6/26/64	46	0-1399	E-18	no	
D(8-26)33cdcd	2306	R.G. LAYTON	1/31/66	38	0-1200	F-11	no	
D(8-26)30baa	2911	SAFFORD FEDERAL PRISON	5/1/70	34	50-390	J-19	no	
D(8-28)29dbd	2930	BLM	12/1/68	61	5-600	I-46	no	
D(9-26)5b	2940	EL PASO NATURAL GAS		20	20-400	I-43	no	
D(9-27)36cd	2945	TENNEY #3 STATE [?]		268	280-3480??	I-45, 46	yes	
D(9-27)36cd	3060	TENNEY #3 STATE	3/1/72	216	1210-3480	J-3, 4	yes	541
D(9-26)16ab	4207	PHILLIPS PETROLEUM #1 SAFFORD STATE	1/1/81	618	45-8500'	N-28-30	yes	798
D(10-28)25dd	653	BEAR SPRINGS OIL - #1 ALLEN (PINAL OIL #1)		none			yes	5-7
D(10-28)36aa	654	WHITLOCK OIL CO. #1 STATE		none			yes	5-9

Table 1. Well cuttings in AZGS repository examined in this study, continued

LOCATION	ID	NAME	DATE	# SAMP	INTERVAL	CABINET	FILE	O&G #
D(10-29)21acc	655	WHITLOCK OIL CO. #1 PENROD FEDERAL		none			yes	5-10
D(10-28)7bdd	1543	ELLSWORTH	3/4/63	14	0-122	D-43	no	
D(11-28)28ac	658	BEAR SPRINGS OIL - #1 FINN-REED		none			yes	5-13
D(13-28)16bdd	25	BOWIE OIL SYNDICATE #1	8/7/50	3	3700-3800	A-4	yes	2-4
D(13-28)15dcc	194	TAYLOR	6/5/52	35	80-470	B-9	no	
D(13-28)15dcc	1823	JONES ENTERPRISES	6/26/64	43	180-805	E-15	no	
D(13-28)14cbd	1875	NO NAME	6/26/64	18	815-1000	E-22	no	
D(13-29)29abd	2764	H.C. GRUENWALD	1/1/70	15	0-150	I-11	no	
D(13-30)27ad	26	FUNK BENEVOLENT #1	8/7/50	39	3700-6651	A-4	yes	2-5
D(13-31)31dca	27	FITZWATER - THAYER #1	8/7/50	264	1733-4100	A-5	yes	2-6
D(13-31)30c	3972	SAN SIMON SCHOOL	3/1/83	23	400-625	N-24	no	
D(14-30)36add	337	ARIZONA OIL & GAS #1 STATE		249	0-7580	A-23	yes	21
D(14-30)16cab	470	EL PASO NATURAL GAS - SAN SIMON #3	4/29/57	60	10-460	C-75	yes	
D(14-30)34bd	669	RYAN ET AL - #1 RYAN		76	0-630	C-49	yes	2-13
D(14-31)16dc	671	STATE DEEP ARTESIAN TEST WELL	1923	none			yes	2-14
D(14-31)34acc	1029	D.W. CONWAY	6/15/59	50	490-1000	D-48	no	
D(14-31)16bdc	1541	EL PASO NATURAL GAS - SAN SIMON #4		49	0-480	D-55	no	
D(14-32)19daa	1722	BARNES	6/26/64	61	0-755	E-20	no	
D(14-32)9ccd	2933	ARIZONA STATE HIGHWAY DEPT	3/1/70	10	289-470	I-46	no	
D(15-32)27dcc	2603	BLM	9/1/68	20	0-200	H-20	no	
D(16-31)19aca	255	PORTAL DRILLING CO - 9 STATE - C		none			yes	2-18
D(16-31)10aaa	814	L.A. THOMSON - #1 STATE	10/27/58	383	1800-5435	A-37,38	yes	48
D(16-31)10aaa	1269	L.A. THOMSON - #1 STATE	8/31/61	161	3500-5300	D-14	no	



The well numbers used by the Geological Survey in Arizona are in accordance with the Bureau of Land Management's system of land subdivision. The land survey in Arizona is based on the Gila and Salt River meridian and base line, which divide the State into four quadrants. These quadrants are designated counterclockwise by the capital letters A, B, C, and D. All land north and east of the point of origin is in A quadrant, that north and west in B quadrant, that south and west in C quadrant, and that south and east in D quadrant. The first digit of a well number indicates the township, the second the range, and the third the section in which the well is situated. The lowercase letters a, b, c, and d after the section number indicate the well location within the section. The first letter denotes a particular 160-acre tract, the second the 40-acre tract, and the third the 10-acre tract. These letters also are assigned in a counterclockwise direction, beginning in the northeast quarter. If the location is known within the 10-acre tract, three lowercase letters are shown in the well number. In the example shown, well number (D-4-5-19caa) designates the well as being in the NE¼NE¼SW¼ sec. 19, T. 4 S., R. 5 E. Where there is more than one well within a 10-acre tract, consecutive numbers beginning with 1 are added as suffixes.

Figure 2. Well location system used in this study

Well cuttings were collected after repeated examination and comparison with available well logs revealed which wells had appropriate material. Well cuttings chosen for analyses were sampled by forming a composite of various sample intervals from a given well, collected in 5-dram pill-bottles. Sample intervals for the wells are included in the sample site descriptions in Appendix A.

Outcrops samples for nitrogen were collected in one-gallon plastic zipper bags. The samples were frozen on dry ice and shipped overnight to the University of Illinois for nitrogen isotope analyses.

Water samples

Samples for major cation and anion analyses were filtered through a 6-micron filter placed in a Nalgene™ model 300-4100 filter holder. Water was drawn through the filter with a Nalgene™ model 6130-0010 hand-operated vacuum pump. Nitrogen and boron water samples were filtered at all sites except the wastewater treatment plant, where filtering was impossible because the filter was plugged immediately with organic material such as algae. Strontium samples were filtered if the water was very turbid with clay. Water samples for sulfur, chlorine, oxygen, and hydrogen did not need to be filtered.

Electrical conductivity was measured with a Markson™ model 103 digital conductivity meter, with a range of 0-20,000 μS/cm. A one-point calibration of the instrument using a standard solution was performed at each site. Sample pH was measured with a Sentron® model 1001 pH meter. A two-point calibration of the instrument using standard solutions was performed at each site. Conductivity, pH, and temperature were measured in water collected in a plastic bucket that was rinsed with sample water prior to sample collection.

Five well-water samples were collected. Four of these wells were flowing or being pumped at the time of collection. The San Simon Fire Department well was turned on and allowed to run for about five minutes before sample collection. Oxygen/deuterium samples were placed in clean 50 ml glass bottles. The other samples were collected in clean plastic bottles of 50 to 1000 ml.

Chemical analyses

Cl, SO_4, F, NO_3, and PO_4 were measured by ion chromatography, and Na, Ca, Mg, and K by ICP at the University of Arizona Department of Soil, Water, and Environmental Science. Br, Sr, Li were analyzes by Actlabs/Skyline labs using ICP. Cl and Br were extracted from the solid samples using a simple cold-water leach. NO_3-N and NH_4-N concentrations were measured by Dr. R.L. Mulvaney at the University of Illinois at Urbana-Champaign, Department of Natural Resources and Environmental Sciences. NO_3-N from both UA and UI-UC are reported here, but the results from UI-UC are favored because they were analyzed within 48 hours of collection, whereas the UA samples collected in July and October were not analyzed until late December through early February. Storage of samples for long periods of time may affect NO_3 and NH_4 concentrations (Mulvaney and Kahn, *in press*). Boron concentrations were determined by Turner Laboratories as part of the B isotope analysis.

RESULTS

CHEMISTRY

Chemical analyses of basin fill, river water, springs, well, and wastewater were performed as part of this study. Results of two rounds of sampling are presented in Table 2; the second round of samples have the same site number plus the designation 'b', or in the case of Clifton Hot Springs, 'c'. Values are in mg/l (equivalent to ppm), except pH in standard units, and conductivity in µS/cm (equivalent to micromhos/cm). Primarily intended to provide Cl and Br concentrations to be used to determine Cl/Br ratios, the analyses are also required for mass balance calculations.

Results were not obtained for some components in some samples because of the need to dilute high-TDS samples to reduce interference from Na. In some samples, for example, PO_4 was reported with values of '<50 mg/l', reflecting a greatly elevated detection limit from the dilution factor. As PO_4 is not commonly found in concentrations over 1 mg/l, the high detection meant that many analyses were not meaningful. Results which were reported as below a greatly-elevated detection limit due to severe dilution effects are shown in Table 2 as an asterisk.

Trends of solutes in the Gila River are shown in Figure 3a-k. Distances are measured in stream miles from the initial sampling point, site #3, near the Fuller Ranch, New Mexico T19S, R19W, section 18. Mileage, based on that of Hem (1950), is approximate. Dotted lines connect sequential sampling sites; these lines are mainly for distinguishing the first and second-round samples. The straight lines do not imply that the change between any two points is linear (i.e., constant rate).

Through the Duncan Basin, constituents increase slightly downstream, while pH decreases. No samples of groundwater or basin fill were analyzed in this study, so the sources of any additional constituents are not known.

Changes over the interval between sites 4 and 5 are dominated by the confluence with the San Francisco River, which carries more water on average than the Gila. The chemistry of the San Francisco is in turn dominated by discharges averaging about 1104 gpm from nearly four miles of hot springs (Lindgren, 1905a, 1905b; Witcher, 1979; 1981; Witcher and Stone, 1980) contributing more than 50 tons of TDS per day (Hem, 1950, Mann, 1980). Concentrations of some constituents, such as Na, Cl, and Sr, are higher in the San Francisco than in the Gila, while B, SO_4, and F are lower. Gillard Hot Springs also contributes measurable salinity to the Gila between sites 4 and 5 (Hem, 1950; Stone and Withcher, 1982), but not as much as Clifton Hot Springs. The Gillard springs (Tellier, 1963, 1964) were not measured in this study. Other additions to the Gila River between sample sites 4 and 5 include Eagle Creek and Bonita Creek, neither of which were sampled in this study.

In the Safford Valley, conductivity, Na, Ca, K, SO_4, Sr, and Li increase markedly in Gila River samples from the head of the valley (site 5) to near Fort Thomas (site 30), but then decrease sharply by Geronimo a short distance downstream. Chloride continues to increase over the last interval, and fluoride does not change appreciably. Boron was not determined in site 30, so it is uncertain whether the concentration decreases from there to site 12 at Geronimo as the other elements do. The trend of pH is generally opposite from the other solutes, showing a decrease, then an increase between Eden and Geronimo

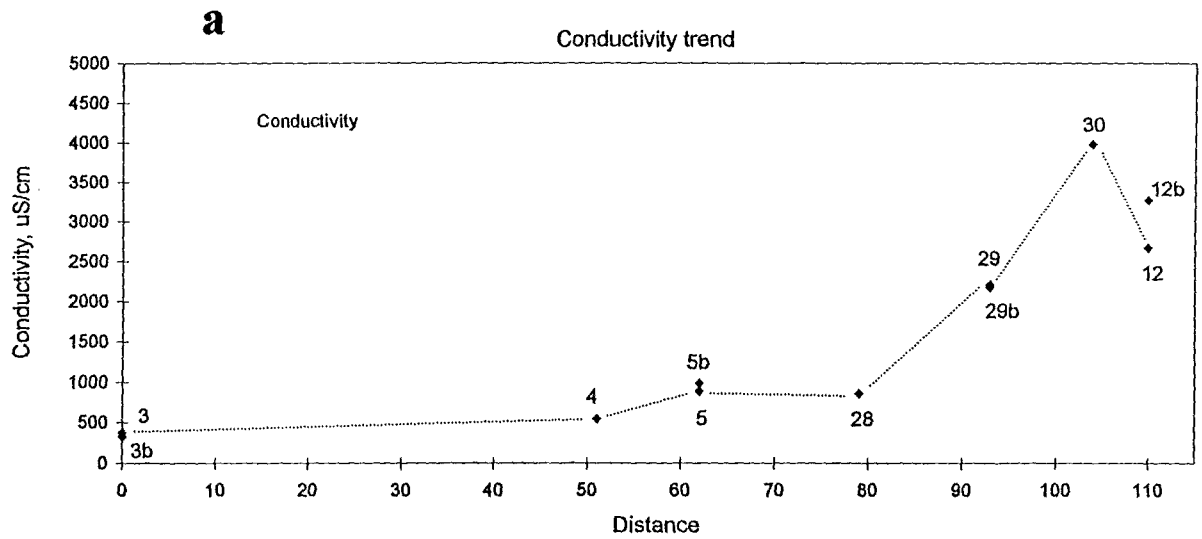
What is more interesting than the general increase in TDS downstream is the reversal of the trend to lower TDS between Fort Thomas and Geronimo. If the increase in salinity is caused by farming, the cause of the decrease certainly cannot be attributed to the same factor, and vice versa. Originally, the project called for a sample at the head of the Safford Valley and one at

Table 2. Results of chemical analyses

Site	Location	Type	Cond.	pH	Ca	Mg	Na	K	SO4	Cl	F	Br	UA NO3-N	UI-UC NO3-N	UI-UC NH4-N	PO4	B	Sr	Li
	July, 1998 samples																		
1	D(3-30)32	river	450	8.1	35.6	9.51	45.5	3.74	18.5	66.6	0.39	<0.3	<0.07	nil	nil	<0.50	0.315	0.247	<0.1
2	D(4-30)18	spring	18020	6.7	829	16.8	2960	161	77.6	6380	*	1.27	*	nil	nil	*	1.36	24.3	5.65
3	NM-19S,19W	river	380	8.3	35.2	7.58	26.6	2.13	35.3	11.3	*	<0.3	*	nil	nil	*	0.575	0.183	<0.1
4	D(5-29)25d	river	550	8.1	39.8	9.41	70.2	4.0	82.9	30.7	1.41	<0.3	0.78	nil	nil	<0.5	0.746	0.291	<0.1
5	D(6-28)29	river	890	8.2	48.2	11.5	87.8	5.03	61.8	150	0.94	<0.3	0.69	nil	nil	<0.5	0.591	0.559	0.124
6	D(7-26)22b	well	2090	7.2	68.1	14.3	415	2.5	220	435	1.7	<0.3	8.74	11.2	1.1	*	0.881	0.647	0.281
7	D(7-26)13da	well	920	7.3	61.7	16.2	91.9	3.87	68	175	1.3	<0.3	2.51	7.4	nil	<0.5		0.593	0.141
8	D(7-26)22b	irrigation	2330	7.8	66.8	12.7	492	3.42	225	443	2.09	<0.3	12.42	14.2	nil	*			0.308
9	D(13-31)31bba	well	3090	7.4	279	40.2	437	5.9	1110	396	2.1	1.62	16.19	6.3	nil	*	1.04	3.21	0.243
10	D(7-25)22	sewage	1110	7.2	43.2	16.3	107	9.22	75.6	184	0.73	<0.3	2.98	6	4.7	9.48	1.37	0.337	<0.1
11	D(6-25)23b	well	5290	7.7	25.5	3.99	415	8.6	489	1170	4.43	0.442	*	nil	nil	*	1.76	0.623	1.47
12	D(4-23)18	river	2670	8.4	59.7	21.2	625	6.87	336	1660	1.3	0.399	3.09	nil	nil	*	1.19	0.928	0.332
14	D(7-26)26aaa	basin fill								5599		<0.3		9.1	12.3		0.343	5.06	0.114
15	D(6-25)36cbb	basin fill								83.4		<0.3		3.3	17.9			5.29	<0.1
16	D(7-27)7bc	basin fill								5643		4.07		8.5	5.6			2.03	0.231
17	D(7-25)21ca	basin fill								758		1.02		15.6	5			0.307	1.62
18	D(9-27)36cd	basin fill								4906		<0.3		8.6	14.8		0.248	6.75	0.174
19	D(7-26)26aaa	basin fill								8319		<0.3		8.3	15.2		0.392	7.68	<0.1
20	D(7-25)6cca	basin fill								5771		<0.3		8.6	18.5		0.493	0.198	0.407
21	D(4-23)17	basin fill								110809		2.89		66.3	8.2			25.2	5.01
22	D(6-25)22ad	basin fill								16322		0.688		199.9	5.2		0.4	0.218	0.337
23	D(14-31)34acc	basin fill															1.2		
24	D(5-23)15a	basin fill																	
25	D(7-26)26aaa	basin fill																	
26	D(3-22)31c	basin fill																	
27	D(8-28)33bc	basin fill								616		<0.3		49.9	8.2			0.08	0.276
28	D(6-26)5d	river	860	8.2	52.2	12.3	109	5.56	66.7	161	1.02	<0.3	1.12			<0.5		0.548	0.116
29	D(6-24)4	river	2210	8.1	73.4	20	426	5.11	243	432	1.3	0.369	6.52			*	0.943	0.967	0.236
30	D(4-23)35	river	3980	7.9	73.2	29.9	855	7.81	477	1190	1.29	0.519	3.18			*		1.26	0.409
31	D(5-24)30	well	31000	7.4	73.8	78.7	7150	11.4	1960	9770	*	1.78	*			*	4.17	4.61	2.48
	October, 1998 samples																		
1b	D(3-30)32	river	450	8.4															
2b	D(4-30)18	spring	20036	6.6															
3b	NM-19S, 20W	river	330	8.4	45.7	8.85	35.5	4.6	38	13.3	4.1					*	nil		
5b	D(6-28)29	river	990	8.4															
6b	D(7-26)22b	well	2020	7.1	90.5	16	405	4.2	219	330	4.4					*	0.424		
12b	D(4-23)18	river	3270	8.2	91	32.7	730	11.9	409	613	3.98					*	0.91		
29b	D(6-24)4	river	2180	8.1	95	30.4	365	13.8	237	360	3.68			1.63			0.472		

Figure 3. Chemical trends in the Gila River

Site #	Location	Miles	Description
3	NM-19S,19W	0	Upstream of AZ-NM border
4	D(5-29)25d	51	North end of Duncan Valley
5	D(6-28)29	62	Head of Safford Valley
28	D(6-26)5d	79	Safford
29	D(6-24)4	93	near Eden
30	D(4-23)35	104	near Fort Thomas
12	D(4-23)18	110	Geronimo



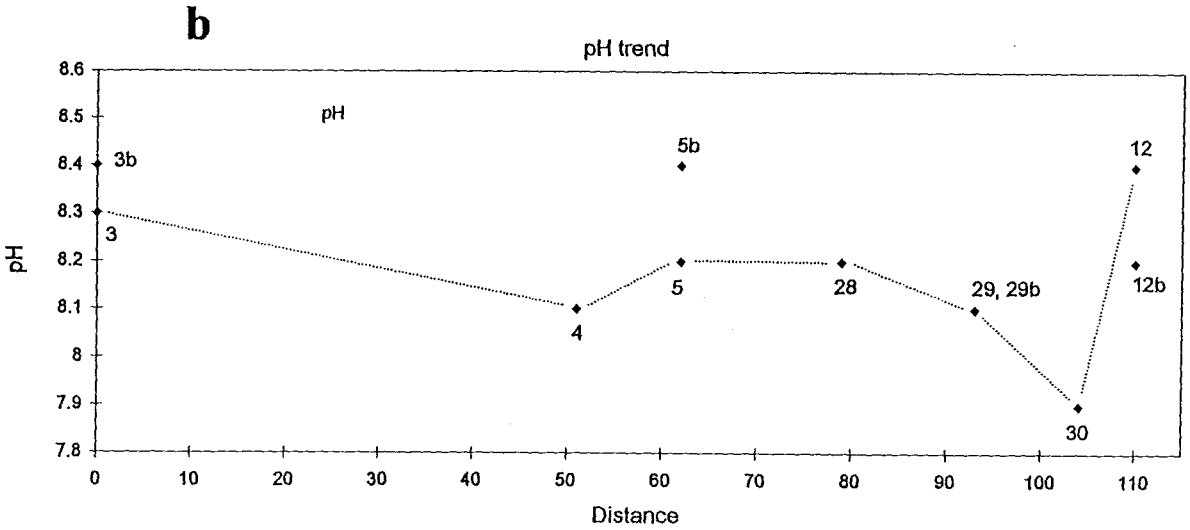
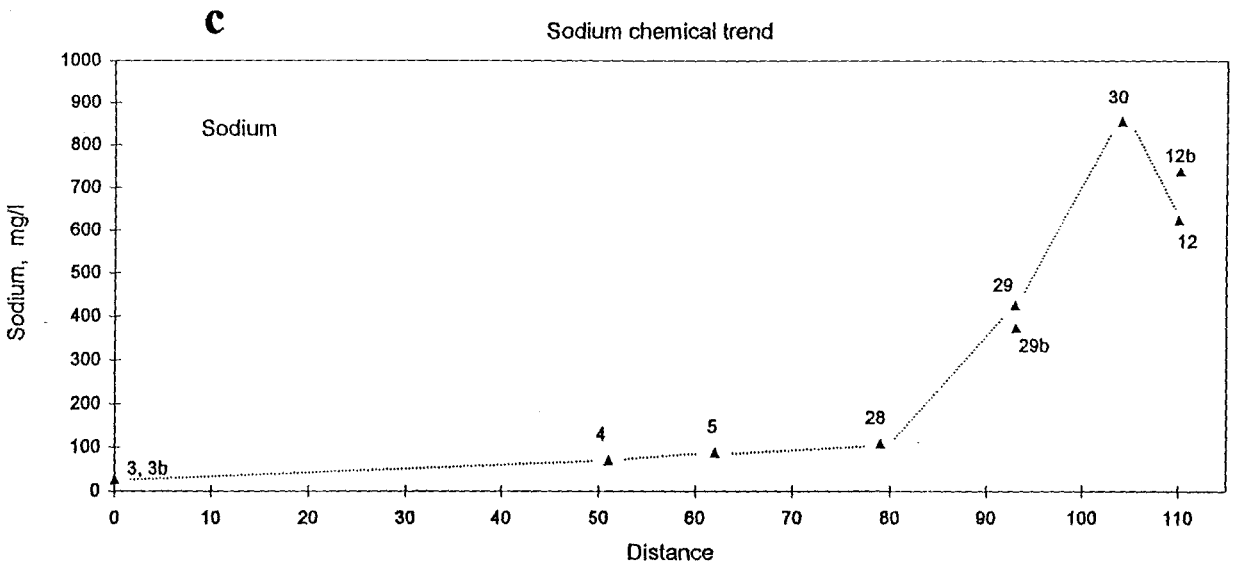
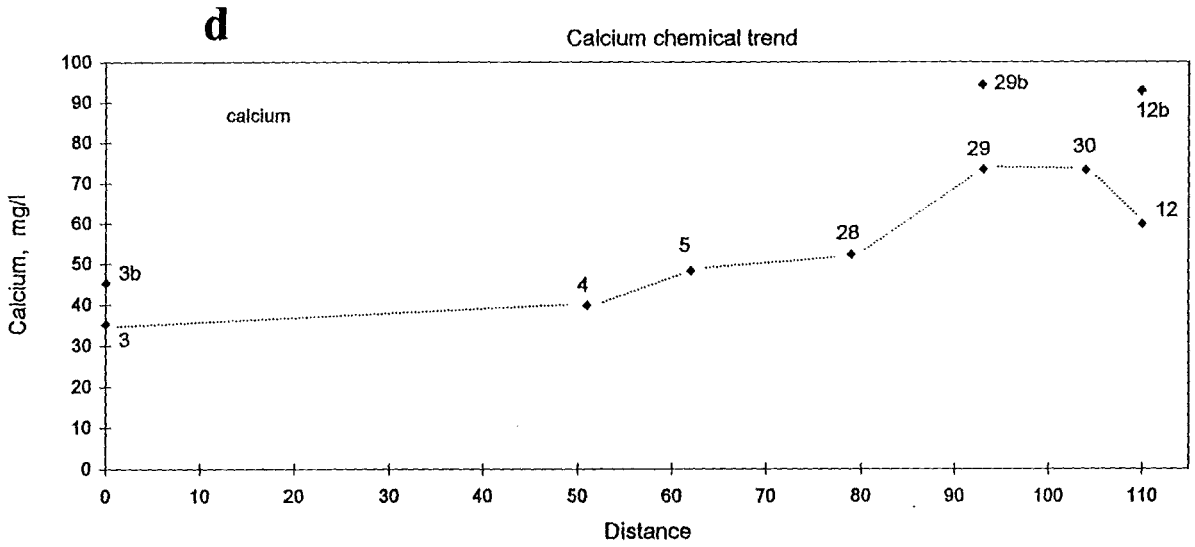


Figure 3. Chemical trends in the Gila River, continued





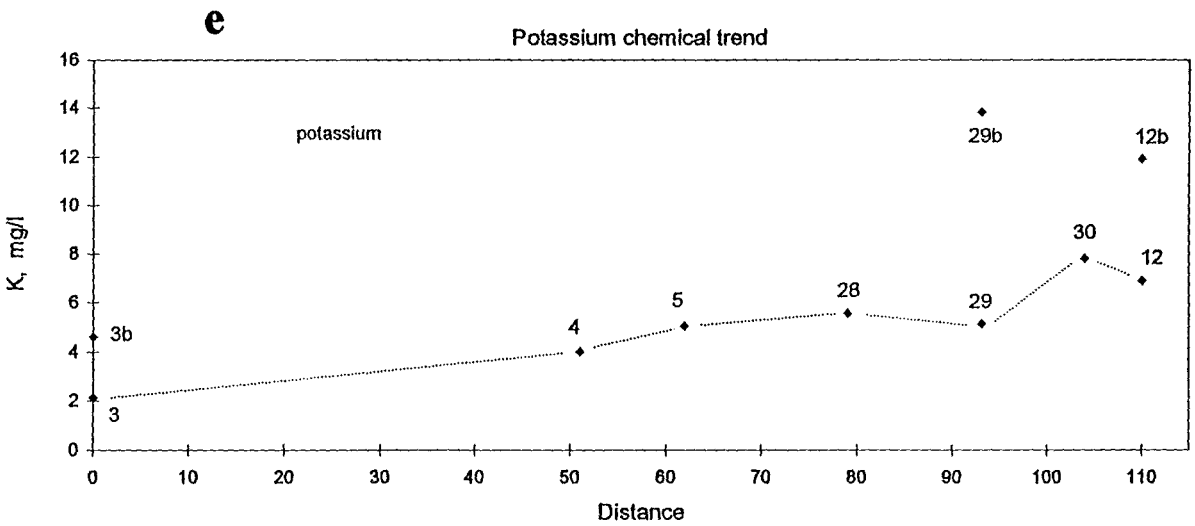


Figure 3. Chemical trends in the Gila River, continued

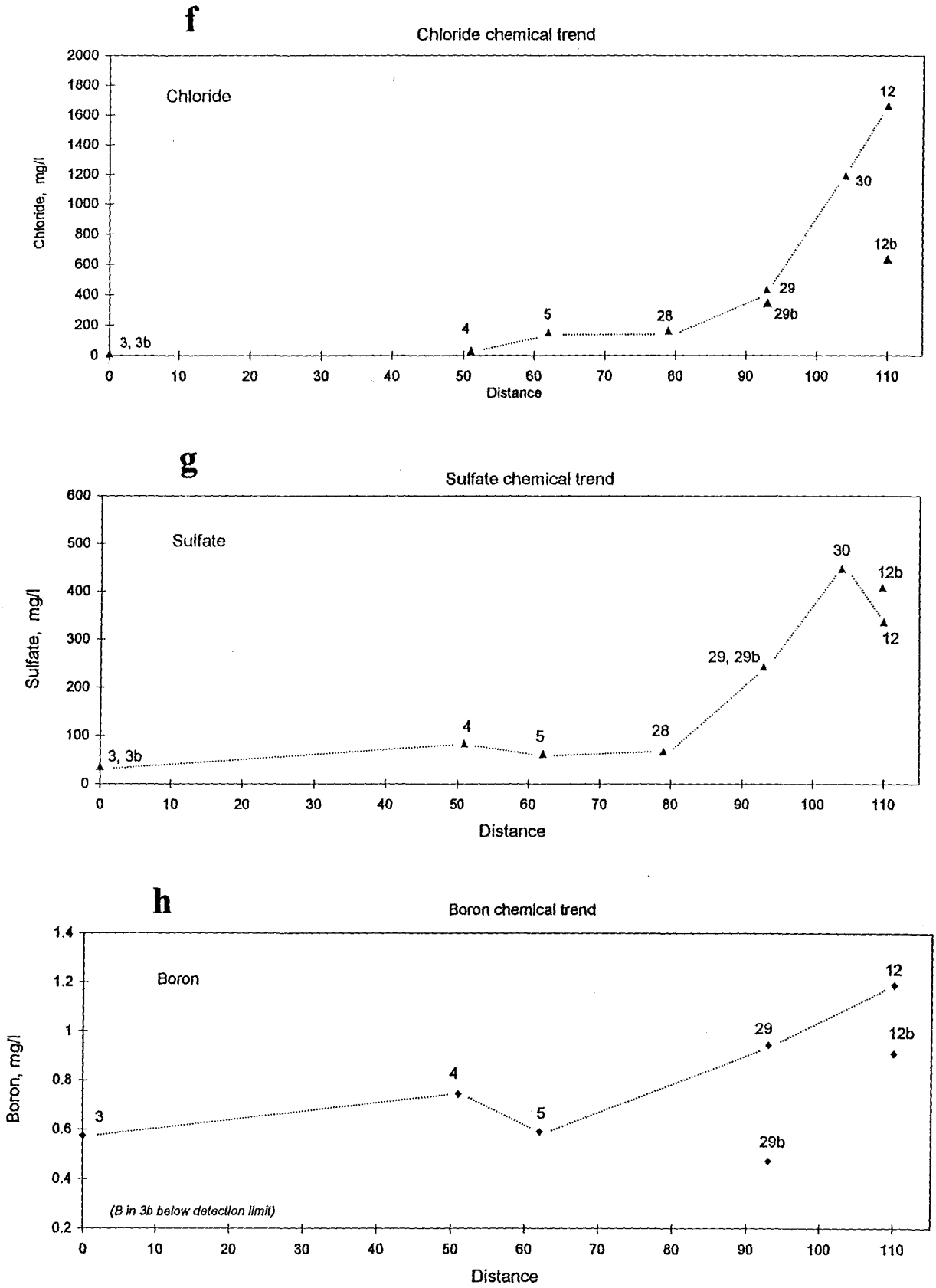
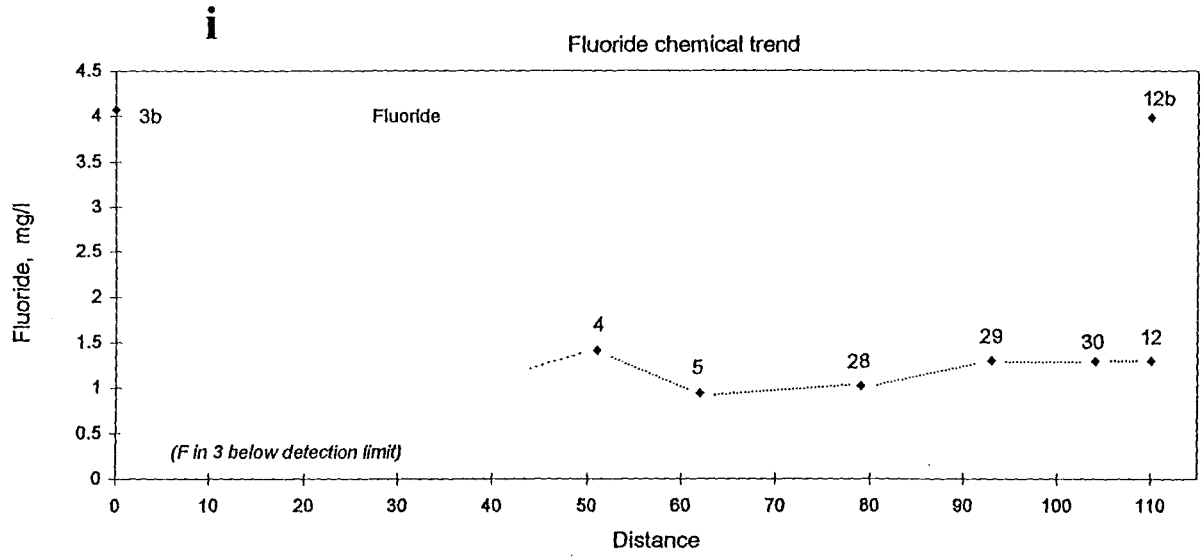
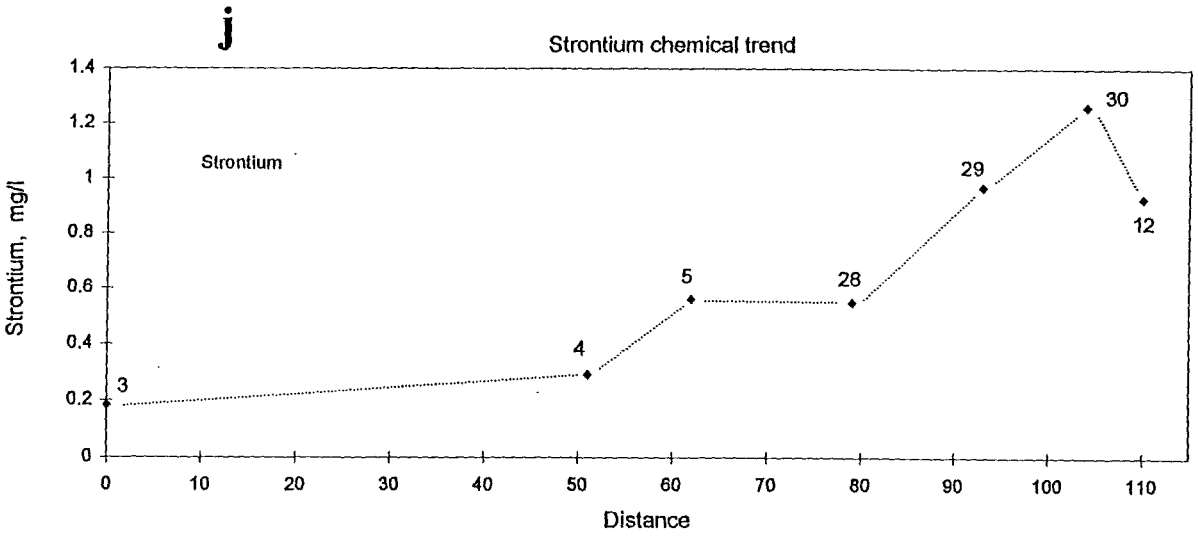
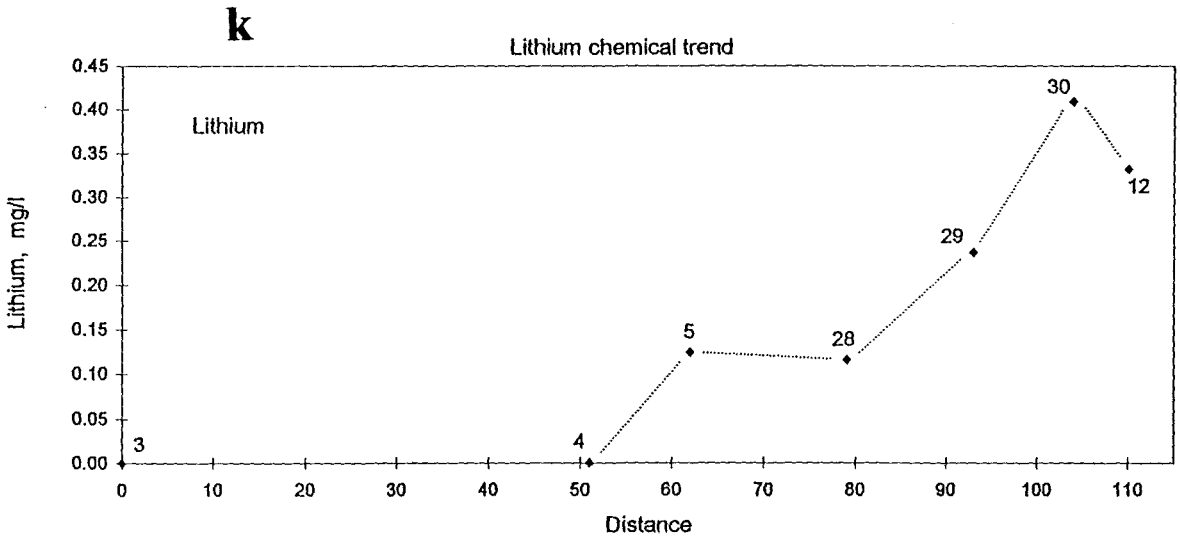


Figure 3. Chemical trends in the Gila River, continued







Geronimo. Additional funding allowed more samples to be taken. Without the additional sampling, the trend reversals below Safford would not have been discovered.

One explanation is that the chemical analyses from site 29 and 30 do not reflect an intact river. By the time the Gila River reaches site 29, just downstream from Pima, most of the river has been diverted upstream for irrigation. At the time of the July sampling, the remaining river was diverted at site 29. The 'river' below site 29 (including site 30) consisted of water from seeps, springs, flowing artesian wells (e.g. sites 11 and 31) and possibly underground return of irrigation water. Thus the chemistry of the river was dominated for several miles by these additions. The amount being contributed from each source was not determined.

A cursory examination of the river bed revealed that some of the seeps were quite salty, but were on the opposite side of the river from irrigated land, while other seeps, on the agricultural side of the channel, were lower in conductivity (1600 μS/cm) than unadulterated river water (2200 μS/cm). Hem (1950) sampled dozens if not hundreds of these seeps and found them to be of highly variable salinity. Hem's conclusion was that much of the salinity in the river was from natural artesian leakage that entered the river in the form of these seeps.

Chemistry (and isotopes) at and below site 29 therefore reflected a much smaller amount of water, which varied from no more than a trickle at Eden to an increased but still much diminished stream at site 30. By Geronimo, the flow had increased greatly, possibly from a combination of direct reversion of excess irrigation water, subflow of infiltrated irrigation water, and contributions from major tributaries such as Black Rock Wash and Goodwin Wash (along with additional seeps, springs and artesian leakage).

The increase in salinity in the lower part of the Safford basin is due to a combination of factors, including natural leaching of salty sediments, natural artesian leakage of deep basin water, natural discharge from salty springs, discharge from non-agricultural flowing artesian wells, evapotranspiration by riparian vegetation, and evaporation of irrigation water. Given the documented occurrence of a multitude of sources of saline water in the region, it is scientifically indefensible to attribute all of the increase to agricultural practices.

Of the wells in the study, only the SAC well was sampled twice. Both the chemistry and isotopes were different in the two samples. Hem (1950) found that river water and groundwater chemistry varies significantly over short periods of time. Adjacent wells were commonly found to have quite different salinity levels. Unpublished water quality data from the Safford Agricultural Center, as well as other studies (Smith and others, 1963; Smith and others, 1964) demonstrate the wide range of TDS and other parameters over short distances and from one sampling to the next.

Given the documented variability of water chemistry in the upper Gila region, the results of this TDS pilot study should not be taken as proving an average, typical, or characteristic value for any of the water samples from the river or wells. *The chemical compositions reported here are valid only for the conditions that were present at the time of sampling.* Sampling under different conditions could yield significantly different results. The reader is cautioned against over-interpreting the scant data presented here.

ISOTOPES

Isotopic analyses of basin fill, river water, springs, well, and wastewater were performed as part of this study. Results of the first round of sampling, in July 1998, are presented in Table 3. A limited second round of isotope sampling was carried out in October; the results from that sampling, plus miscellaneous samples are given in Table 4. Trends of each isotope in the Gila River are shown graphically in Figure 5a-g. Reasons for the behavior of the trends are discussed in a following section.

Table 3. Results of isotopic analyses, first sampling

Site	Location	Type	S	Cl	87Sr/86Sr	B	N	Cl/Br	D	O	Site description
1	D(3-30)32	river	6.0	-0.1	0.712586	7.5	IN	IN	-68.5	-9.2	San Francisco River above Clifton
2	D(4-30)18	spring	7.6	-0.7	0.724969	8.4	IN	5024	-82.0	-10.8	Clifton Hot Springs
3	NM-19S,19W	river	4.8	0.6	0.710862	8.1	IN	IN	-62.5	-8.5	Gila River upstream from AZ-NM border
4	D(5-29)25d	river	4.7	-0.2	0.711080	13.6	IN	IN			Gila River at N end of Duncan Basin
5	D(6-28)29	river	4.3	-0.4	0.717487	10.2	IN	IN	-65.5	-8.5	Gila River at entrance to Safford basin
6	D(7-26)22b	well	5.8	0.1	0.715016	1.0	3	IN	-70.0	-9.4	Safford Ag. Center well
7	D(7-26)13da	well	5.0				IN	IN	-65.0	-8.5	Safford City well
8	D(7-26)22b	irrigation					3.3	IN			Irrigation water - Safford Ag.Center
9	D(13-31)31bba	well	8.3	0.7	0.711707	20.4	IN	244	-65.0	-8.9	San Simon Fire Dept. well
10	D(7-25)22	sewage	5.5	-0.1	0.713472	3.5	20.0	IN			Safford municipal wastewater
11	D(6-25)23b	well	9.4	-0.7	0.716308	-9.0	IN	2647	-85.9	-11.3	Watson Wash well
12	D(4-23)18	river	7.0	-0.1	0.714270	8.5	IN	4160	-66.0	-8.4	Gila River at Geronimo
13	D(9-27)36cd	basin fill			0.715763						Gypsum - Tenney #3 well cuttings
14	D(7-26)26aaa	basin fill	16.8		0.715585	-9.2	IN	IN			Gypsum facies - No Name well cuttings
15	D(6-25)36cbb	basin fill	9.4		0.718815		16.4	IN			Gypsum facies - Smithville Canal well cuttings
16	D(7-27)7bc	basin fill	8.2		0.712147		IN	1386			Gypsum/clay - Tidwell Wash outcrops
17	D(7-25)21ca	basin fill	-21.3		0.714494		IN	743			Gypsum/clay - Spring Canyon outcrops
18	D(9-27)36cd	basin fill	8.1	-0.3		-21.6	IN	IN			Salt facies - Tenney #3 well cuttings
19	D(7-26)26aaa	basin fill	9.5	0.1		-8.9	IN	IN			Salt facies - No Name well cuttings
20	D(7-25)6cca	basin fill		0.3		-6.5	17.8	IN			Salty clay - Whitmore #1 State well cuttings
21	D(4-23)17	basin fill		0.3			1.1	38342			Salty lacustrine clay - Ft. Thomas outcrops
22	D(6-25)22ad	basin fill	12.5	2.9		-7.8	1.7	23742			Salty lacustrine clay - Watson Wash outcrops
23	D(14-31)34acc	basin fill			0.711866	16.1					Marly clay - Conway well cuttings
24	D(5-23)15a	basin fill			0.719403						Limestone/marl - Superior Federal well cuttings
25	D(7-26)26aaa	basin fill			0.715726						Marly clay - No Name well cuttings
26	D(3-22)31c	basin fill			0.720566						Lacustrine limestone - Soto well cuttings
27	D(8-28)33bc	basin fill			0.713424		2.8	IN			Lacustrine limestone/marl - 111 Ranch outcrops
28	D(6-26)5d	river	4.7	0.2				IN	-61.5	-8.1	Gila River at Safford
29	D(6-24)4	river	5.2	0.1		6.3		1171	-60.0	-7.6	Gila River near Eden
30	D(4-23)35	river	7.8	-0.3				2293	-60.5	-7.9	Gila River near Ft. Thomas
31	D(5-24)30	well	11.3	0.6		-4.9		5489	-80.0	-11.2	Gila Oil Syndicate well

Table 4. Results of isotopic analyses, second round and miscellaneous samples

Site	Location	Type	S	B	D	O	Site description
1b	D(3-30)32	river			-67.5	-9.2	San Francisco River above Clifton
2c	D(4-30)18	spring			-84.0	-11.2	Clifton Hot Springs
3b	NM-19S,19W	river	5.3	9.9	-65.5	-7.8	Gila River upstream from AZ-NM border
5b	D(6-28)29	river			-64.5	-8.5	Gila River at entrance to Safford basin
6b	D(7-26)22b	well	4.0	1.9			Safford Ag. Center well
12b	D(4-23)18	river	6.5	9.1	-61.5	-8.4	Gila River at Geronimo
29b	D(6-24)4	river	4.2	7.3			Gila River near Eden
	Misc. samples; January, 1997						
32	D(7-27)1	river	2.6				Gila River near Sanchez
33	D(9-27)36cd	basin fill	13.6				Tenney #3 well

Sulfur isotopes

Sulfur isotopes were analyzed on a variety of samples in this study. Trends in S isotopic composition of the Gila River are plotted in Figure 5a. For comparison, representative isotopic compositions of various sources of sulfur are compiled in Table 5. This table, and others compiled for the other isotopes include some examples from other areas of the world to give an idea of the range in isotopic compositions in similar geologic settings or ages where analyses are lacking or meager for Arizona.

Sulfur isotopes in the Safford basin sediments are typical of those found in nonmarine (i.e., continental or lacustrine) evaporites, with high positive values of +8.1 to +16.8‰ in all the sites except one. One exception to the high $\delta^{34}S$ values was the lacustrine outcrops in Spring Canyon (site 17) that have a $\delta^{34}S$ of -21 to -23‰. These extremely low values correspond to a history of bacterial reduction of sulfate producing biogenic pyrite (strongly negative, typically -20 to -60‰), followed by re-oxidation to sulfate, retaining the negative $\delta^{34}S$ value. The site is an outcrop of green clay, resulting from reduced conditions, with numerous fine layers of yellow to orange ochre indicating the oxidation of sedimentary sulfide at various times in the history of the basin.

Sulfides formed in basins where bacterial reduction of sulfate occurs have $\delta^{34}S$ values 40 to 60‰ lower than the original sulfates (Ohmoto and Rye,1979). Metabolic processes in sulfur-reducing bacteria are efficient at selecting lighter isotopes of sulfur and oxygen (Krouse, 1987), and the remaining sulfate-sulfur in the system is thus enriched in ^{34}S. Biological reduction of sulfate to sulfide, such as pyrite, lowers the $\delta^{34}S$ by 30‰ (Holser and Kaplan, 1966). The reducing bacteria generate hydrogen sulfide or bisulfide gas. H_2S can be lost to the atmosphere if there is not enough iron to combine with the sulfide to form pyrite.

A similar outcrop of greenish to grayish clay(Tidwell Wash, site 16) had a 'normal' sulfur isotopic value of +8.2‰. The other outcrop and well cutting samples were red to brown clay, typical of the basin. The relative abundance of strongly negative-$\delta^{34}S$ sediments versus the highly positive-$\delta^{34}S$ sediments is not known, owing to the small number of basin-fill samples analyzed for sulfur. Whether the negative $\delta^{34}S$-sulfur is only associated with the ochre-bearing layers has not been determined. (That would require detailed, layer-by-layer sampling, which was beyond the scope of this project).

The two deep wells in the Safford Valley samples in this study have $\delta^{34}S$ values that seem to be controlled by the isotopic composition of basin fill sulfate. The 2645 foot-deep Gila Oil Syndicate well, and the Watson Wash hot well, depth unknown, have water with sulfur isotopic compositions in the range of the basin fill sediments, 11.3‰ and 9.4‰, respectively, clearly different from the Gila River above Safford.

The sulfur isotopic composition in the City of Safford Kempton #2 well, near the Solomon bridge, resembles that of river water (5.0‰), while in the deeper Safford Agricultural Center (SAC) well, farther from the river, the $\delta^{34}S$ is slightly higher (5.8‰). Water in the 800-foot deep San Simon Fire Department well (8.3‰) reflects the composition of the basin fill in that area.

The Gila River has sulfur isotopes that vary little from upstream of the Duncan basin to Safford (4 sites: 4.8, 4.7, 4.3, and 4.7‰ going downstream; trend shown in Figure 5a). Below Safford, $\delta^{34}S$ increases to 5.2‰ near Eden and 7.8‰ near Ft. Thomas, then decreases to 7.0‰ at Geronimo. The increase in $\delta^{34}S$ at the lower end of the Safford Valley indicates that the river is picking up enough evaporite sulfate to shift the sulfur isotopic composition by 2 to 3‰, a significant change. Simple evaporation of water or recycling of river-derived sulfate will not produce such a shift in the sulfur isotopic composition.

Table 5. Sulfur isotope composition ($\delta^{34}S$) of various sources.

Source	Mean ‰	Range ‰	Reference
Sea water	+20.1		Thode and Monster, 1965
	+20.99		Rees and others, 1978
Precipitation/Dry fallout			
Maine		+3.4 to +9.4	Stam and others, 1992
US		+3 to +15	Holser and Kaplan, 1966
Freshwater sulfate			
(rock weathering)	+10		Thode and Monster, 1965
runoff		+1.15 to +7.6	Stam and others, 1992
Marine evaporites (gypsum, anhydrite)			
Europe (Permian)		+9.7 to +12.0	Thode and Monster, 1965
Texas (Permian)		+9.6 to +11.5	" "
Windsor, Canada (Miss.)		+13.7 to +16.5	" "
Illinois (Miss.)		+14.3 to +17.0	" "
Nova Scotia (Miss.)		+13.9 to +19.4	" "
New York (Precambrian)		+14.5 to +28.6	" "
East US (Silurian)		+24.2 to +28.8	" "
Sicily (Miocene)		+21.0 to +23.9	Holser and Kaplan, 1966
Baja (Recent)		+18.7 to +21.8	" "
Playa/Lacustrine evaporites			
Searles Lake, CA (Recent)		+11.8 to +15.0	Holser and Kaplan, 1966
Connate brines		+10 to +30	
ARIZONA			
San Pedro Valley			
Artesian aquifer	+7.76	+6.08 to +9.93	Rice, 1991
Channel aquifer	+6.75	+1.88 to +14.1	' '
Sulfide deposits	~ 0	-7 to +1	Jensen, 1971

The trend of $\delta^{34}S$ increasing from Safford to Fort Thomas, then decreasing to Geronimo mirrors the trend seen in the chemistry results discussed above. This same reversal is seen in most of the other isotopes as well. The reason for the trend reversal after Fort Thomas is the same explanation as with the chemistry (also discussed in the next section). Isotope compositions in the interval from site 29 to 30 are dominated by additions of generally high-TDS water from deep, saline wells, seeps, springs, and artesian leakage to a greatly diminished river. Compositions below Fort Thomas probably reflect the importance of low-TDS additions from Goodwin and Black Rock Washes and reversion of unused irrigation water, plus lesser additions of high-TDS sources.

Sulfur isotopes appear to be ideal for use as a tracer for TDS sources in the Gila River. Sulfur is abundant, is found in nearly every suspected source, has a wide range in $\delta^{34}S$ values, and has characteristic values in the different sources tested here. A wide range of values are seen in some sources, such as the basin fill and deep wells. Further sampling is required to establish the true range and determine the average value for each type of source.

Strontium Isotopes

Strontium ratios ranges from 0.711866 to 0.720566 in the basin sediment. Basin-fill Sr isotopes seem to reflect a mixture of the various rock types present in the source areas for the material that fills the Safford basin. That mix has not changed appreciably over the past several million years, and so the isotopes of the basin fill are about the same as isotopes in surface runoff today. All of the different rock types have abundant calcium, which Sr follows, so all rock types contribute Ca and Sr. Typical Sr isotopic compositions in various materials are compiled in Table 6 and representative concentrations are shown in Table 7.

Sr isotopes do not fractionate in physical or chemical processes, and variations are largely a function of the age and original rubidium concentration of the source rock. This effect seems to be present in the hot spring near Clifton (0.724969), where the deep-circulating hydrothermal system is in contact with Precambrian rocks. Well cuttings from the Soto well near Calva have high Sr values, at 0.720566. The source of some of the carbonate for the lacustrine limestone in the Soto well is probably from Precambrian and early Paleozoic limestone near Globe. The age of the rocks which were the likely sources of Sr in the hot spring and Soto well means that they will yield higher Sr ratios than sediment derived from younger rocks.

Strontium isotopes in the Gila River reflect the sum of all the sources in the region, including:

- Dust (known to be a major source of Sr in caliche and soils);
- Laramide igneous rocks (55-65 Ma);
- Mid-Tertiary volcanic rocks (18-22 Ma);
- Precambrian metamorphic, igneous, and sedimentary rocks (1700Ma, 1400 Ma, and ~1200Ma, respectively); and
- Paleozoic and Mesozoic sedimentary rocks 600-110 Ma).

The Gila River Sr varies from 0.710862 to 0.717487 from New Mexico to Safford, and changes little by Geronimo (0.714270). The increase in the Sr ratio from site 4 to site 5 is due to the influence of hot springs near Clifton, which have very high Sr ratios, reflecting Precambrian basement rock in the region.

The deep well at San Simon has a Sr isotope composition close to that of the basin fill in that area. Water in the deep Watson Wash well has a Sr value higher than most of the clay-rich sediments, but slightly lower than gypsum deposits in the nearby Smithville well.

Table 6. Strontium isotopic compositions ($^{87}Sr/^{86}Sr$) of various sources.

Source	Range	Reference
Present seawater	0.709	Elderfield and Greaves, 1981
Late Neogene seawater (0-7Ma.)	0.70895 to 0.70920	Farrell and others, 1995
Cretaceous seawater	0.7072 to 0.7075	Bralower and others, 1997
Cambrian-Ordovician seawater	0.70907 (average)	Burke and others, 1982
Late Proterozoic seawater (600 Ma.)	0.7076 to 0.7089	Veizer and others, 1983
Continental shield waters	0.7086 to 0.7251	Brass, 1976
Precambrian granites, US	0.76 to 0.80	Moorbath and others, 1967
PreC (1.32Ga) granites, Canada	0.73207 to 0.74066	Emslie and Loveridge, 1992
Oracle Granite (1.4 Ga.)	0.71374 to 0.77991	Welty, 1988
Laramide intrusives	0.706 to 0.708	Moorbath and others, 1967
Sierrita granodiorite (58-62 Ma.)	0.7084 to 0.7097	Anthony and Titley, 1988
San Manuel porphyry (67 Ma.)	0.7058 to 0.7096	Welty, 1988
Late Cenozoic basalts, S. Basin-Range	0.7027 to 0.7045	Leeman, 1970; 1982
Mogollon-Datil volcanic field	0.7056 to 0.709	Leeman, 1979; 1982
Thirteenmile volcinics (3.0-7.5 Ma)	0.7028 to 0.7054	Scott, 1974
Hickey basalts (10-11 Ma)	0.7025 to 0.7050	Scott, 1974
Lacustrine limestone, Bouse Formation	0.7102 to 0.7114	Spencer and Patchett, 1997
Pinacate soil carbonate	0709±0.001	Slate, 1985
Soil carbonate, NW New Mexico	0.70825 to 0.716	Van der Hoven, 1994
NW New Mexico dust	0.708 to 0.709	Van der Hoven, 1994

Table 7. Strontium contents of various sources.

Source	Range (ppm)	Reference
Seawater	7.56	Elderfield and Greaves, 1981
Colorado River water	1.16	Spencer and Patchett, 1997
Smithville Canal well D(6-25)36	0.59 to 1.9	USGS database
Permian anhydrite, AZ	mean 1358	Dean and Tung, 1974
Permian salt, AZ	mean <100	Dean and Tung, 1974
Late Cenozoic basalts, B&R	330 - 978	Leeman, 1970
Sierrita granodiorite (58-62 Ma)	420 - 528	Anthony and Titley, 1988
Sierrita andesite (67 Ma)	458 - 926	Anthony and Titley, 1988
Santa Rita Mts granitic rocks (57-70Ma)	93 to 758	Trapp, 1987
PreC Oracle granite, unaltered	154	Welty, 1988

Only two samples of the Gila River were taken in the Safford Valley, at the head of the valley and at Geronimo. Other isotopes showed marked variations, especially between Eden and Geronimo, but with no samples in that stretch of river the fine-scale trend of Sr is unknown. However, more detailed sampling could yield information about the sources of TDS in the lower end of the valley.

Chlorine Isotopes

The fractionation of Cl isotopes much more restricted than other isotopes such as sulfur, boron, or nitrogen. Use of Cl isotopes as a tracer is relatively new, so there are few studies similar to this one that have looked at high-precision Cl isotopic ratios of lacustrine/playa deposits. Examples of chlorine isotopes from various sources measured in other studies are listed in Table 8.

Five basin fill samples, all salty clay, were analyzed for chlorine isotopes and these have $\delta^{37}Cl$ values of -0.3, 0.1, 0.3, 0.3, and 2.8‰ (Table 3). The first four values seem consistent with likely Cl sources and with the amount of fractionation associated with evaporative crystallization of halite. The +2.8‰ value was replicated and is surprisingly high. It is not easily explained by source, evaporative, or diffusive effects. With so few samples, there is no clear geographic or stratigraphic distribution of the different values.

Wells are variable in their Cl isotopic composition with the Safford Agricultural Center well at 0.1‰ and the San Simon well is -0.7‰. The two deep wells sampled in the Safford Valley have conflicting ratios of -0.7‰ in the Watson Wash well versus an average of +0.55‰ in two sample runs for the Gila Oil Syndicate well. The results from the evaporites and deep wells seem to indicate that individual layer of lacustrine sediments may have distinct Cl isotopic compositions, and that particular deep aquifers may be distinguished by their unique isotopic compositions. It is also possible in a basin with widely varying salinity that diffusive effects may be important.

The hot spring near Clifton has a $\delta^{37}Cl$ of -0.7‰. This value overlaps with several potential types of sources, such as Precambrian rocks and connate brines in sedimentary rocks. Both types of rocks are found in the Clifton area. The ultimate source of the tremendous amount of NaCl discharged from the springs, unfortunately, was not unequivocally identified by the Cl isotopes.

The high NaCl content of the Clifton area hot springs has no obvious explanation. Most igneous rocks contain chlorine in the mineral structure of certain minerals, as well as in fluid inclusions. For example, chloride leached from the Stripa Granite, Sweden, ranged from 11.1 to 21.5 mg Cl per kilogram of rock, which represents 7 to 36% of the total Cl in the rock (Wirt, 1988). Minerals such as micas, amphiboles, and apatite can have significant amounts of chlorine in their chemical formulas, typically with high $\delta^{37}Cl$ values up to +4.0‰ (Eastoe and Guilbert, 1992; Frape and others, 1996), although these minerals make up only a small fraction of the mass of the rock. In crystalline bedrock of the continental interiors, high chloride concentrations have been found in some locations (Frape and others, 1996). Occurring in fractures and voids, the brines from both shallow and deep levels have characteristic $\delta^{37}Cl$ values.

Water in the Gila River has $\delta^{37}Cl$ values ranging from 0.55‰ to -0.4 (Figure 5c). The $\delta^{37}Cl$ values in the river do shift, but do not mirror those of the other isotopes. With only five basin-fill samples analyzed in this study, it is not really possible to say whether or not the river or groundwater reflects the isotopic composition of the sediments. The sediments themselves have some variability, and only more extensive sampling will show what the 'average' Cl isotopic composition of the sediments is. With further refinement of the range of isotopic composition of the basin-fill, groundwater, and river water, Cl isotopes should be useful as a tracer for the sources of NaCl.

Table 8. Chlorine isotope compositions ($\delta^{37}Cl$) of various sources.

Source	Mean ‰	Range ‰	Reference
Seawater	0		by definition
Gulf Coast connate brines		-1.0 to +0.8	Eastoe and Guilbert, 1992
Oil field brines		0.0 to -0.36	Kaufman, 1984
Santa Catalina Mtns. springs		-0.1 to -0.3	Eastoe, 1998
Tucson basin groundwater		-0.3 to +0.2 ???	Eastoe, 1998
Tucson rainfall		-0.5 to +0.4	Kayaci, 1997
Canadian Shield groundwater	<0	-0.51 to +0.17	Frape and others, 1996
Fennoscandian shield water	>0	0.0 to +1.05	Frape and others, 1996
Stripa groundwater		-0.29 to +0.26	Wirt, 1988
Stripa Granite rock leachate		-0.28 to +0.31	Wirt, 1988
Tucson sewage effluent (2 samples)		+0.2, +0.4	Eastoe, 1998
Tucson sediments (2 samples)		-0.9	Eastoe, 1998
Luke salt body, AZ		+1 to +3	Eastoe, 1998
Louisiana salt domes		+0.12 to +0.33	Kaufman, 1984
Porphyry copper deposits		-0.5 to +0.4	Eastoe and Guilbert, 1992
Hydrous silicate minerals		+0.2 to +7.5	Ransom and others, 1995

Boron Isotopes

As with sulfur, boron isotopes appear to be ideally suited for use as a tracer. In the Gila River region, various sources have widely different, characteristic B isotopic compositions. For comparison, representative boron isotopic compositions of various materials are listed in Table 9 and ranges of B concentrations are shown in Table 10.

Basin-fill sediments in the Safford area have negative $\delta^{11}B$ isotopic values of -6.5 to -21.6‰, which are typical of continental evaporite deposits. The two very deep Safford area wells have low B values of -4.9 and -9.0‰, indicative of the influence of the basin-fill evaporites on the composition of deep groundwater.

Boron in the Gila River starts at 8.1‰, increasing to 13.0‰ going through the Duncan Valley. No sampling was done of basin fill or groundwater in the Duncan Valley, so the source of the $\delta^{11}B$ shift is not known. The $\delta^{11}B$ value decreases to 10‰ by the head of the Safford basin, attributed to the addition of San Francisco River water with $\delta^{11}B$ of 7.5‰. River water has a final composition of 8.5‰ at Geronimo, representing a negative shift. This shift in the river toward a lower $\delta^{11}B$ value between Safford and Geronimo indicates that water in the Gila River is picking up significant boron from a source or sources with strongly negative $\delta^{11}B$, which appears to be from the basin-fill sediments.

The deep Watson Wash and Gila Oil Syndicate wells have boron with isotopic values (-9.0 and -4.9‰, respectively) essentially that of the basin-fill, reflecting the influence of evaporites on the chemistry of groundwater in the basin. The Safford Agricultural Center well, with a $\delta^{11}B$ of 1.0‰, significantly lower than the river, apparently controlled by groundwater in contact with natural evaporites. Although the SAC well is on the lower river terrace, where it is assumed that wells are under the influence of Gila River water, the water does not resemble river water in its isotopic composition.

To the south, the San Simon Fire Department well has a B composition of 20.4‰. This is much more positive than the other water samples in the study area, and reflects the strongly-positive B isotopic composition of basin fill in the area, 16.4‰ in the Conway well cuttings. Basin fill in the San Simon area does not contain evaporites as in the Safford area and the B composition is probably controlled by the composition of nearby bedrock, which includes much more Paleozoic and Mesozoic sediments than near Safford. Groundwater and sediments from the two areas are distinguishable on the basis of B.

^{10}B is preferentially adsorbed onto the clay minerals (Vengosh and others, 1992), raising the ratio of ^{11}B in the residual brines. Adsorption onto clay is probably the most important control of the boron isotopic composition of seawater (Swihart and others, 1986), and by analogy is likely to partly control the isotopic composition of saline-alkaline lacustrine deposition. Owing to the sequestering by clays, marine sedimentary rocks have boron contents 20 to 40 times that of seawater (Leeman and Sisson, 1996). Boron adsorption onto clays is quite rapid, on the order of hours (Spivack and others, 1987). Adsorption is a surface phenomenon, and does not involve incorporation into the crystal structure on the host mineral. Adsorbed boron may be leached under proper conditions. On the other hand, B incorporated into the crystal structure is only released via mineralogical change (recrystallization or reaction) or upon dissolution of the mineral. In the case of marine clay, typical total B concentrations range from 64 to 157 ppm, while the desorbable fraction (that which is easily leached) accounts for 10 to 29 ppm and averages 10% (Spivack and others, 1987). The higher B content in well water from San Simon versus in the shallow wells at Safford may be due to leaching of adsorbed high-$\delta^{11}B$ in clays.

Table 9. Boron isotopic compositions ($\delta^{11}B$, ‰) of various sources.

Source	Range	Reference
Seawater	+39.5	Spivack and Edmond, 1987
	+38.7 to +47.6	Bassett, 1990
Continental waters	-3 to +5	Vengosh and others, 1992
Marine evaporites (world)	+18.2 to +31.7	Bassett, 1990
Marine clay adsorbed B	+14.2 (average)	Palmer and others, 1987
Boron minerals, USA	-9.8 to +10.2	Oi and others, 1989
Lacustrine evaporites	-21.9 to +49	Bassett, 1990
Nonmarine evaporites	-7 to +10 (-6 average)	Swihart and others, 1986
Tucson wastewater	~ +3	Leenhouts and others, 1998
	+1.8 to +4.7	Craddock and others, 1998
Marana groundwater	+9.0 to +29.7	Leenhouts and others, 1998
Japanese hot springs	+9.5 to +12.0	Bassett, 1990
Yellowstone hot springs	-9.7 to +4.4	Leeman and Sisson, 1996
The Geysers, CA	+3 to +10	Leeman and Sisson, 1996
Granite (USGS G-1)	5.3 ±3.8	Bassett, 1990
Granite	+1.6	Spivack and others, 1987
Island arc volcanics	-5.3 to 6.4	Spivack and others, 1987

Table 10. Boron concentrations in various sources.

Source	Range (mg/l or ppm)	Reference
Duncan Valley wells	0.18 to 1.15	Smith, 1949
Safford, irrigation canal	0.08	"
Artesia area, flowing well	0.63	"
Eden Community supply	0.26	"
Ft. Thomas city water	0.00	"
Smithville well D(6-25)36	0.89 to 1.6	USGS database
Safford Ag. Center well	0.54	unpublished SAC data
Gillard Hot Springs	0.49	Tellier, 1973
Indian Hot Springs	0.75	Tellier, 1973
Clifton Hot Springs	0.64 to 1.4	Mariner and others, 1977
Seawater	4.7	Vengosh and others, 1992
Seawater (Pacific)	5.1	Shima, 1963
Igneous rocks, average	10	Spivack and others, 1987
Shales, average	100	Spivack and others, 1987
Great Salt Lake	30	Whitehead and Feth, 1961

Nitrogen Isotopes

Nitrogen, in the form of nitrate (NO_3), nitrite NO_2), and ammonia (NH_4) are common constituents in water. The presence and isotopic composition of nitrogen in various end members were measured primarily to determine the possible contribution to the Gila River of nitrate from evaporite deposits versus wastewater and fertilizer. Nitrate deposits are known to have formed in evaporites and other settings (Gale, 1912; Mansfield and Boardman, 1932). Results of the chemical analyses are shown in Table 2 and the isotope results are presented in Table 3. Representative isotopic compositions of various materials are compiled in Table 11.

Nitrogen was interesting for the reason that none of the five river samples contained N above the detection limit (Table 2). Therefore, nitrogen isotopes could not be measured for any of the river samples. The low levels of N in the river were probably due to a monsoon runoff pulse, which diluted whatever N, if any, is normally present in the river. Significantly, even with all of the diversions of river water, and all of the agriculture in the Safford Valley, NO_3-N and NH_4-N were reported as 'nil' in the nitrogen isotope samples at the lower end of the basin at Geronimo.

Despite assurances by the lab that a liter of sample was adequate, this was not enough to obtain isotopic measurements from most of the water samples. That most of the samples had so little N that it was not possible to determine the isotope ratios is actually useful information. In mass-balance terms, the low levels of N means that some sources, represented by the 'insufficient'-N samples, are not contributing significant N to the Gila River (at least at the time of sampling).

Of the well and spring samples, only the Safford Agricultural Center (SAC) well contained enough N to yield reportable N-isotopes. The well had 11.2 mg/l of nitrate-N and 1.6 mg/l NH_4-N. Irrigation water in a field at SAC contained less NH_4-N and NO_3-N (nil; 8.9 mg/l) than the well supplying the water, and the $\delta^{15}N$ shifted (probably insignificantly) from 3.04 to 3.32‰.

All of the basin-fill samples had measurable amounts of both ammonium-N and nitrate-N, with a minimum of 5.0 mg/l NH_4 and 3.3 mg/l NO_3. The Watson Wash sample , #22, had a large amount of nitrate, 199.9 mg/l NO_3 in dry sample equivalent.

Igneous rocks contain a fairly consistent average of 12 ppm nitrogen (Scalen, 1959, in Stevenson, 1962). The amount of N in igneous rocks increases during weathering because NH_4 in rain is fixed in clay weathering products. Most of the nitrogen in igneous rocks is held in the lattice structure of silicate minerals, particularly biotite mica (Stevenson, 1962) and is therefore not water-soluble.

Other sources of N include rainfall and decay of organic material in the basin fill (Summons, 1993). Organic matter in sediments is commonly oxidized by bacteria using, in order of preference, dissolved oxygen, nitrate, or Mn- and Fe-oxides as oxidizers (Emery and Robinson, 1993). Nitrate used in this process is reduced to N_2 gas. Nitrogen in soil gas is converted to nitrate by symbiotic root-nodule bacteria in legumes such as mesquite, acacia, and palo verde.

Of the ten basin-fill samples, five had sufficient N for an isotopic measurement. Three of these were outcrop samples, from Ft. Thomas, Watson Wash, and 111 Ranch, had $\delta^{15}N$ values of 1.06, 1.65, and 2.75‰, respectively. The two other samples were well cuttings, and had $\delta^{15}N$ of 16.37 and 17.18‰. Why the outcrop samples and well cuttings have such markedly different $\delta^{15}N$ values is not known. The cuttings have values typical of wastewater or animal waste, but this cannot be the source of the N in samples from clay 400-700 feet deep (site 20), nor from gypsum in an evaporite sequence 975-2000 feet deep (site 15). The outcrop samples fall within the range of fertilizer and fertilized soil, but all are a distance from (and higher than) agricultural areas.

Preliminary indications are that N isotopes are not useful when the river flow is as high as it was during the July sampling when a monsoon storm pulse was going through. (The original

Table 11. Nitrate-nitrogen isotopic compositions ($\delta^{15}N$) of various sources.

Source	Mean ‰	Range ‰	Reference
Atmospheric nitrate	close to 0		Kendall and others, 1996
Rain		-0.9 to+5.61	Hoering, 1957
Forest runoff		-1 to +9	Kendall and others, 1996
Septic tanks	+10.9	+6 to +13	Behnke, 1990
		+10 to +20	Mariotta and others, 1988
Animal waste	+12.4	+10 to +18	Bhenke, 1990
		+9 to +19	Heaton and others, 1983
		+9 to +18	Gormly and Spalding, 1979
		+10 to +22	Krietler, 1979
		+10 to +24	Mariotti and others, 1988
Nitrogen fertilizer		0 to +3	Mariotti and others, 1988
Fertilized soil		-2.1 to +2.1	Gormly and Spalding, 1979
Fertilizer leachate	+6.3		Flipse and Bonner, 1985
Natural soils	+7.3	+3 to +8	Behnke, 1990
		+4 to +9	Gormly and Spalding, 1979
		+2 to +8	Krietler, 1975
Igenous rocks	+4.2		Sakai and others, 1984
Sedimentary rocks	+5.5		Sakai and others, 1984
Metamorphic rocks (German)			
Schist		+3.4 to +15	Haendel and others, 1986
Gneiss		+4.1 to +17	" "

sampling plan called for sampling before the beginning of the monsoon for just that reason). During low-flow periods, or in stretches of the river (if any) where nitrates are a periodic concern, N isotopes could still be useful for determining the source of nitrates.

Chloride-Bromide ratios

Bromide is a trace solute in surface and groundwater. Possible sources of Br (and Cl) in the area include dust, atmospheric dry deposition, leaching of evaporites, agricultural chemicals, hot springs, and weathering of rocks. Representative values for Cl/Br ratios are presented in Table 12 and typical Br concentrations are shown in Table 13.

Cl/Br ratios increase rapidly in the Gila River downstream from Safford (Figure 5e). Br concentrations are below the detection limit in the river until near Eden, where the salinity begins to climb. At site 29 and downstream, Cl/Br ratios in the river trend toward the high values in the deep, hot wells (Cl/Br of 2647 in 11-WWW, 5489 in 31-SYN) and the extreme ratios in the salty clay in outcrops in the Watson Wash and Fort Thomas areas (23742 and 38342, respectively). Unlike the isotopes, Cl/Br does not have a reversal of trend between Fort Thomas and Geronimo.

Br is below the detection limit in the Safford Agricultural Center well, so the Cl/Br ratio could not be calculated. In the San Simon Fire Department well Cl/Br is 244, higher than the average for Tucson groundwater (Stevens, 1990), but lower than typical irrigation return (Goldowitz, 1989).

Salty clay in the basin fill has extremely high Cl/Br ratios, which can be partially explained by the phenomenon of Br exclusion in halite crystallization. As evaporation increases the salinity in a body of water, halite will start precipitating before complete evaporation. Bromine is incorporated into early-formed halite in trace amounts, thus increasing the Br concentration in the residual water. Typical Br concentrations in halite are only about 12% of the Br concentration in the coexisting brine from which the salt is precipitating (Raup and others, 1970). High concentrations of bromide such as the 86 ppm in the Great Salt Lake (Whitehead and Feth, 1961) occur where halite precipitates without complete evaporation to dryness. Upon further evaporation, Br will be incorporated in the later-formed salts in increasing amounts. Eaton and others (1972) document this occurrence in the Luke salt body near Phoenix, where Br is found to be minimal at the base of individual salt beds and increases toward the top. Br contents range from <1 ppm to 6 ppm.

Extremely high Cl/Br ratios in the Fort Thomas area and Watson Wash samples might be explained by this mechanism of Br exclusion in early-formed halite. Selective concentration of Br by clay-membrane effects may affect movement of Br through fine-grained sediments (Hem, 1992) but what effect this has on controlling the Cl/Br ratios has not been investigated. Adsorption onto Fe-hydroxides and exchange with Cl takes place in sediments, but the effect decreases with increasing pH (Brooks and others, 1999) and is therefore probably not an important mechanism controlling Cl/Br ratios in the Safford basin.

Oxygen and hydrogen isotopes

Oxygen and hydrogen isotopes are useful for determining the source area of groundwater because the isotopic composition of precipitation varies with temperature (i.e. elevation). The Gila River flow at the time of the July sampling carried a significant amount of monsoon rain runoff from the high mountains of New Mexico. The lower temperature and higher elevation source of this rain would, for example, yield water of lower $\delta^{18}O$ and δD (more negative in both oxygen and deuterium) than rain falling on Safford.

Table 12. Chloride/Bromide ratios of various sources.

Source	Average	Range	Reference
Seawater	300		Hem, 1992
Colorado River	1250		Goldowitz, 1989
Verde River		25.6 to 36.0	Goldowitz, 1989
Lower Gila precipitation	100		Goldowitz, 1989
Tucson precipitation	100		Koglin, 1984
Tucson basin groundwater	130		Koglin, 1984
Tucson groundwater	111	61 to 233	Stevens, 1990
Runoff, Tucson		25 to 156	Koglin, 1984
Sewage, Tucson	334	276 to 392	Koglin, 1984
Sewage, Tucson	572	291 to 1857	Stevens, 1990
Sewage, Tucson	420		Behl and others, 1987
Irrigation return, Wellton		626 to 1350	Goldowitz, 1989
Igneous rocks	127		Hem, 1992

Table 13. Bromine concentration (mg/l, or ppm)of various sources

Source	Average	Range	Reference
Seawater	65		Hem, 1992
Seawater	67		Vengosh and others, 1992
Rainfall		0.005 to 0.15	Hem, 1992
Colorado River	0.07		Goldowitz, 1989
Verde river		0.36 to 0.66	Goldowitz, 1989
Geothermal waters		up to 20	Hem, 1992
Tucson groundwater	0.14	0.04 to 1.65	Stevens, 1990
Sewage, Tucson	0.2	0.35 to 0.07	Stevens, 1990
Irrigation return, Wellton		0.32 to 1.74	Goldowitz, 1989
Great Salt Lake		86	Whitehead and Feth, 1961

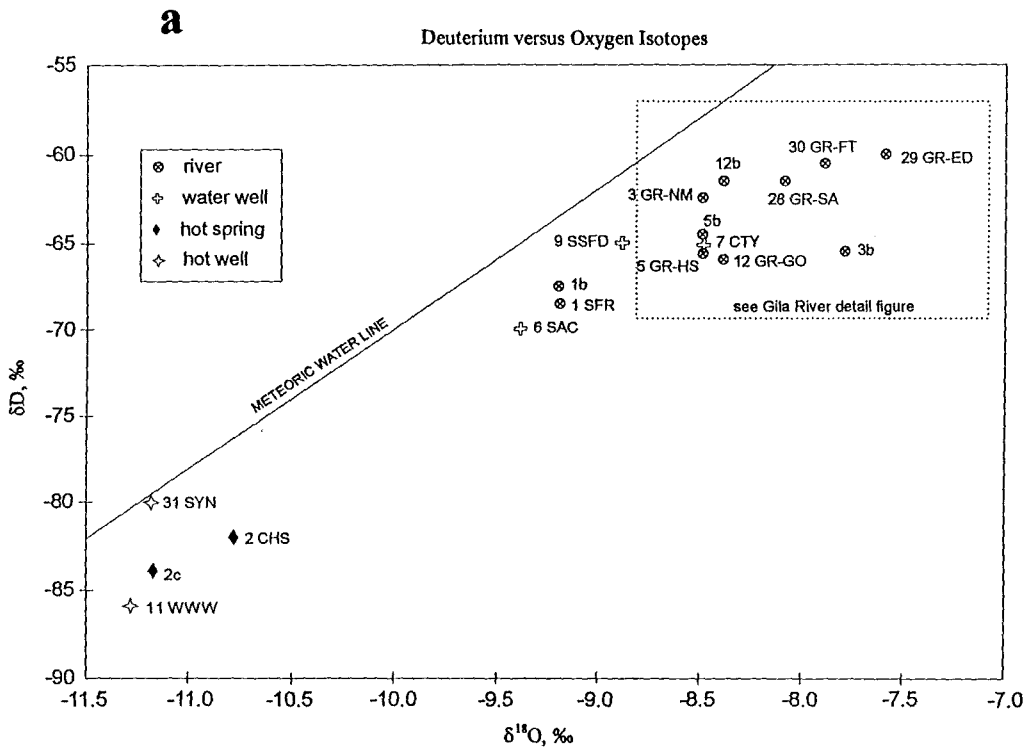
The Gila River samples had a narrow range in oxygen and deuterium ($\delta^{18}O$ -7.6 to -8.5‰; δD -62.5 to -66.0‰), but trends are discernible (Figures 5f and 5g). The river starts out in New Mexico at $\delta^{18}O$ of -8.5 and δD of -62.5‰ and by Geronimo, $\delta^{18}O$ increases, but not significantly, to -8.4‰ and δD decreases to -66.0‰, probably reflecting a net addition of isotopically lighter deep groundwater. Simple evaporation of water increases the δD and $\delta^{18}O$, as the lighter isotope preferentially evaporates, leaving the residual water slightly heavier, i.e., less negative. All of the water samples except 31 show some evaporation, as indicated by their positions to the right of the meteoric water line in Figure 4.

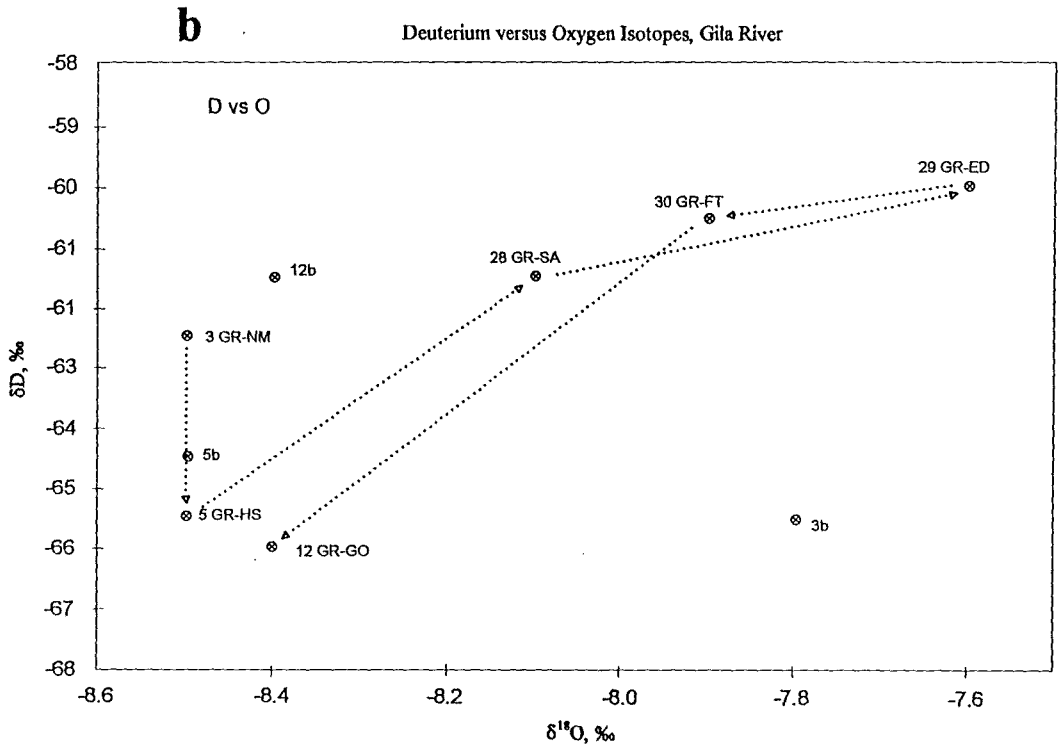
The insignificant net shift in $\delta^{18}O$ in Gila River water downstream, -8.5 at Safford to -8.4 at Geronimo, may be the result of a balance between evaporation, which would raise the $\delta^{18}O$, and the addition of deep, low-$\delta^{18}O$ water via artesian leakage. If this is the case, the magnitude of influence from deep basin water (or water derived from Mt. Graham) would equal the effect of agriculture, and by knowing one, the other could be determined.

Oxygen and deuterium isotopes in the hot spring near Clifton and in the deeper wells in the Safford Valley have values much more negative ($\delta^{18}O$ -10.8 to -11.4‰; δD -80 to -85.9‰) than the surface flow, reflecting a source for the water that originated at higher elevation/lower temperature (or even in the Pleistocene). The results of measurements show that deep wells in the Safford Valley are not connected to the Gila River. Oxygen and deuterium isotopes values in the deep wells indicate a high elevation/low temperature source. The Watson Wash and Gila Oil wells have $\delta^{18}O$ (-11.3, -11.2) significantly different from the Gila River.

The SAC well also shows a difference from the from the Gila River, indicating that at least some of the water in the well recharged from a source other than the river. One likely source is recharge originating on Mt. Graham. Groundwater in the area around the SAC well was found by Smalley (1983) to show evidence of a Mt. Graham connection based on O/D isotopes.

Figure 4. Deuterium versus oxygen isotopes





Isotope trends in the Gila River

Trends of isotopes in the Gila River are shown in Figure 5 a-g. Distances are measured in stream miles from the initial sampling point, site #3, near the Fuller Ranch, New Mexico T19S, R19W, section 18. Mileage, based on that of Hem (1950), is approximate. Dotted lines connect sequential sampling sites; these lines are mainly for distinguishing the first and second-round samples. The straight lines do not imply that the change between any two points is linear (i.e., constant rate). Originally, the project called for a sample at the head of the Safford Valley and one at Geronimo. Additional funding allowed more samples to be taken. Without the additional sampling, the trends below Safford would not have been discovered. (To illustrate the importance of sampling at these added sites, try connecting site 5 directly to site 12 with a straight line).

Through the Duncan Basin, some elements show a trend, but it must be remembered that the concentration of solutes in the river to site 4 is very low, and so shifts in isotopic compositions are not as significant as those in the Safford basin, where TDS is much higher. No samples of groundwater or basin fill from the Duncan basin were analyzed in this study, so the sources of any additional solutes that are causing shifts are not known. Halpenny and others (1946) report that "common salt and gypsum occur widely throughout the lake and playa beds in the older alluvial fill" in the Duncan Basin. The natural deposits are probably the source for some of the shift in isotopic compositions between sites 3 and 4.

Changes over the interval between sites 4 and 5 are dominated by the confluence with the San Francisco River, which carries more water on average than the Gila. The chemistry of the San Francisco is in turn dominated by discharges from nearly four miles of hot springs. Using the average of the computed daily salt load given in Hem (1950, table at bottom of page 34), an estimated 54 tons of TDS every day, or 19,710 tons of TDS per year is discharged from the springs into the San Francisco River. Other references give the salt discharge at 50 tons per day, or 18,000 tons per year (Feth, 1954; Feth and Hem, 1962, 1963; Mann, 1980). B and Sr isotope trends display the most obviously shifts resulting from the addition of San Francisco river water.

In the Safford Valley, isotopic compositions of most of the elements in Gila River samples shift in one direction from the head of the valley (site 5) to near Fort Thomas (site 30), but the trends reverse sharply by Geronimo, a short distance downstream (Figures 5a-h). Only Cl/Br continues a trend with no reversal over the last interval. Boron and Sr were not determined in site 30, so it is uncertain whether those trends have reversals between Eden and Geronimo as the other elements do. In every case, the most significant shifts are toward the isotopic compositions of the deep well water and the evaporites.

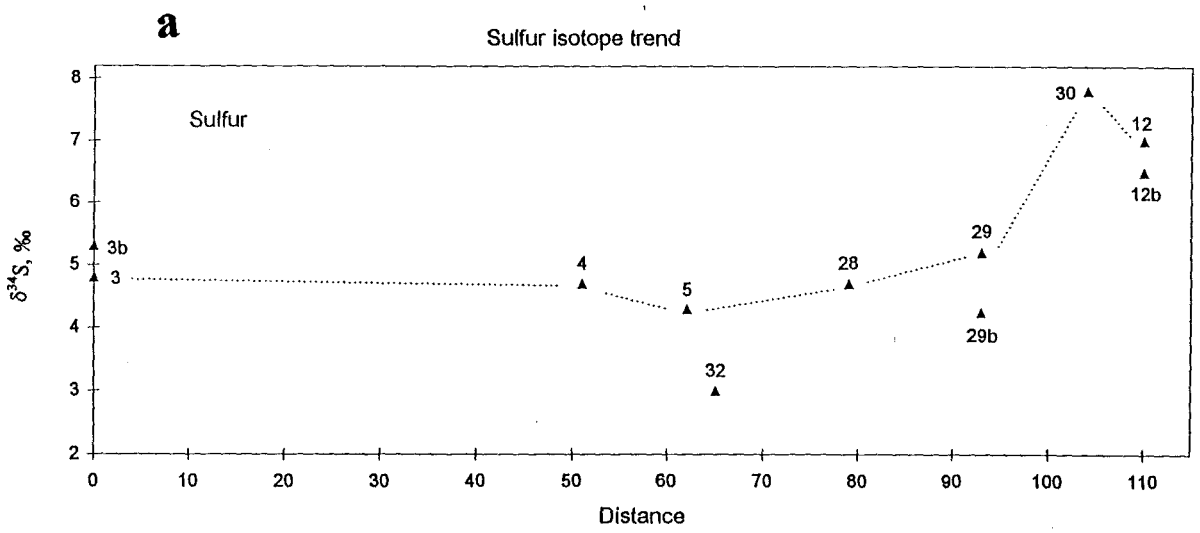
The changes in isotopic composition of the Gila River in the lower part of the Safford basin are due to a combination of factors, including natural leaching of salty sediments, natural artesian leakage of deep basin water, natural discharge from salty springs, discharge from non-agricultural flowing artesian wells, evapotranspiration by riparian vegetation, and evaporation and infiltration of irrigation water.

An important aspect of the trends in the individual isotopes downstream is the reversal of some of the trends between Fort Thomas and Geronimo. (B and Sr were not measured at site 30, so it is not known if these display the reversal). If the isotope shifts in one direction are caused by any particular source, the trend reversal certainly cannot be attributed to the same source. For example, cycling of salts derived from Gila River water by evaporation of irrigation water followed by leaching and return to the river will not cause a shift in the isotopic composition of the solutes. Only the addition of salt from new sources will produce a change in trend.

The explanation for the isotope shifts is the same as for the chemical trends and their reversals: the isotopic analyses from site 29 and 30 do not reflect an intact river. By the time the Gila River reaches site 29, just downstream from Pima, most of the river has been diverted

Figure 5. Isotope trends in the Gila River

Site #	Location	Miles	Description
3	NM-19S,19W	0	Upstream of AZ-NM border
4	D(5-29)25d	51	North end of Duncan Valley
5	D(6-28)29	62	Head of Safford Valley
32	D(7-27)1	65	near Sanchez
28	D(6-26)5d	79	Safford
29	D(6-24)4	93	near Eden
30	D(4-23)35	104	near Fort Thomas
12	D(4-23)18	110	Geronimo



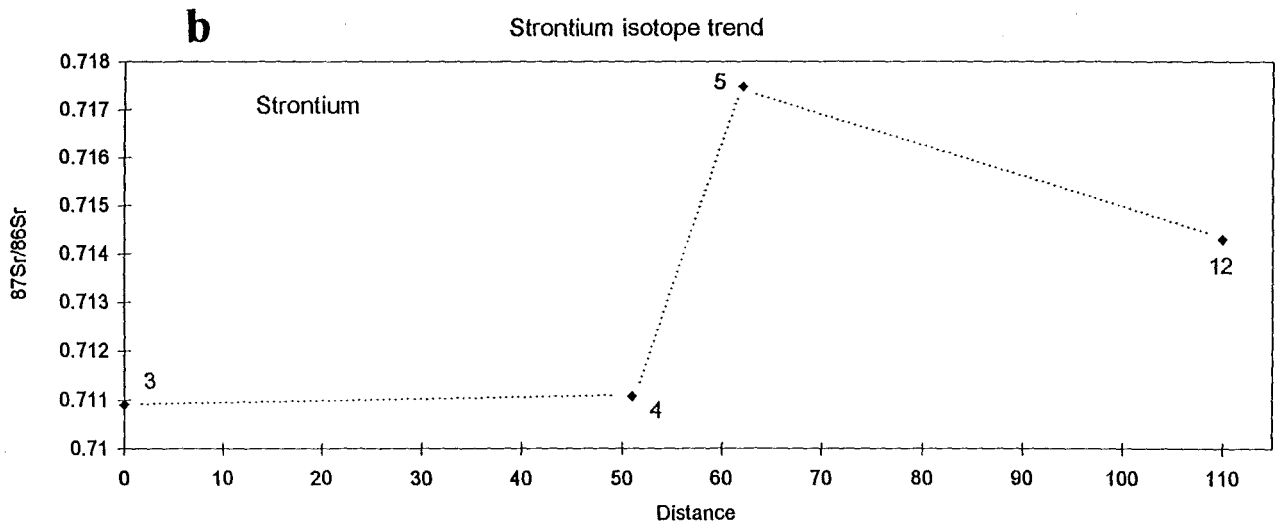


Figure 5. Isotope trends in the Gila River, continued

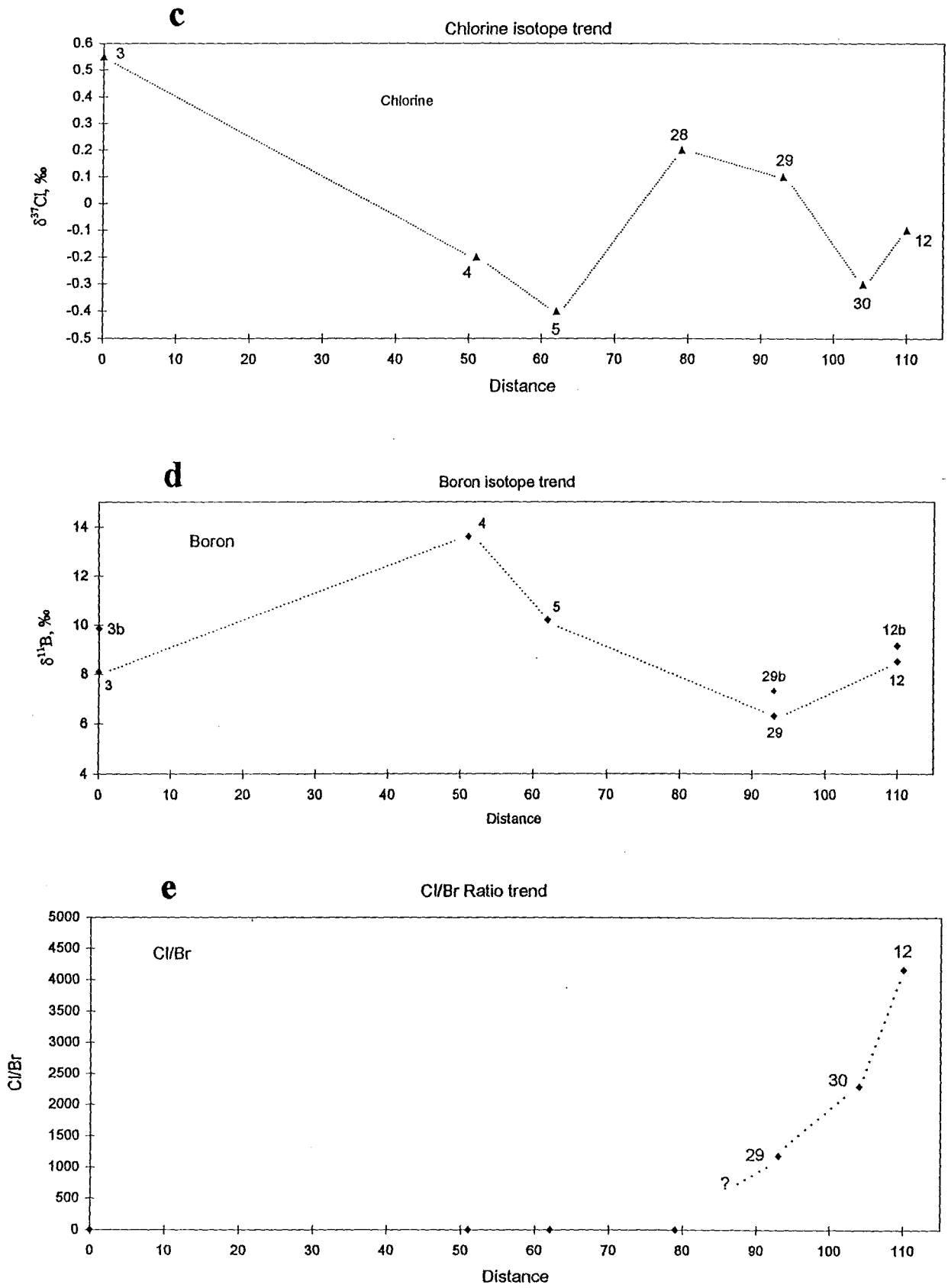
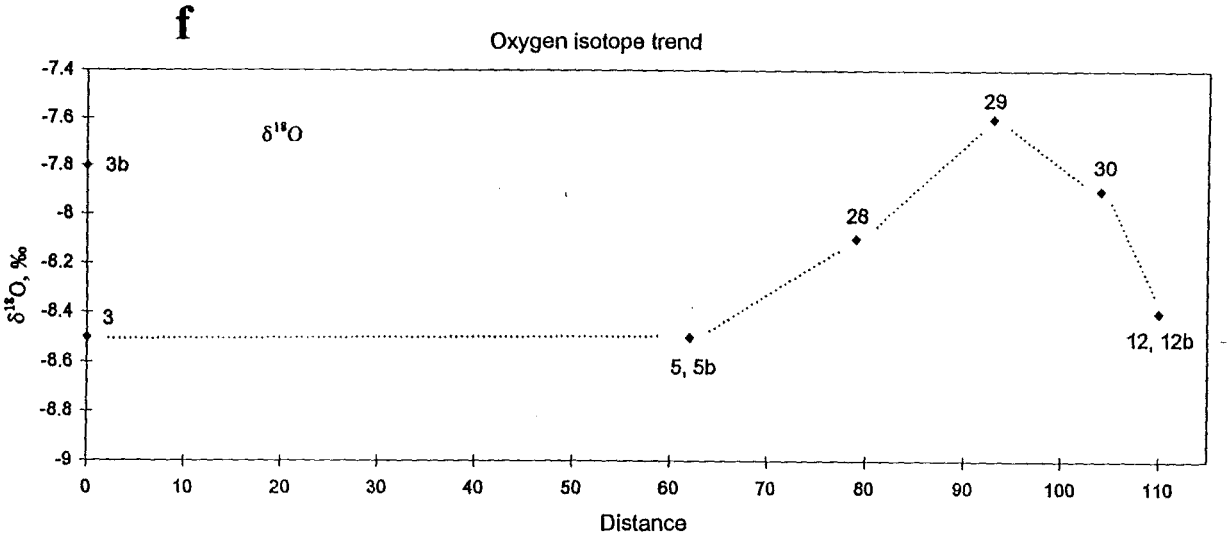


Figure 5. Isotope trends in the Gila River, continued



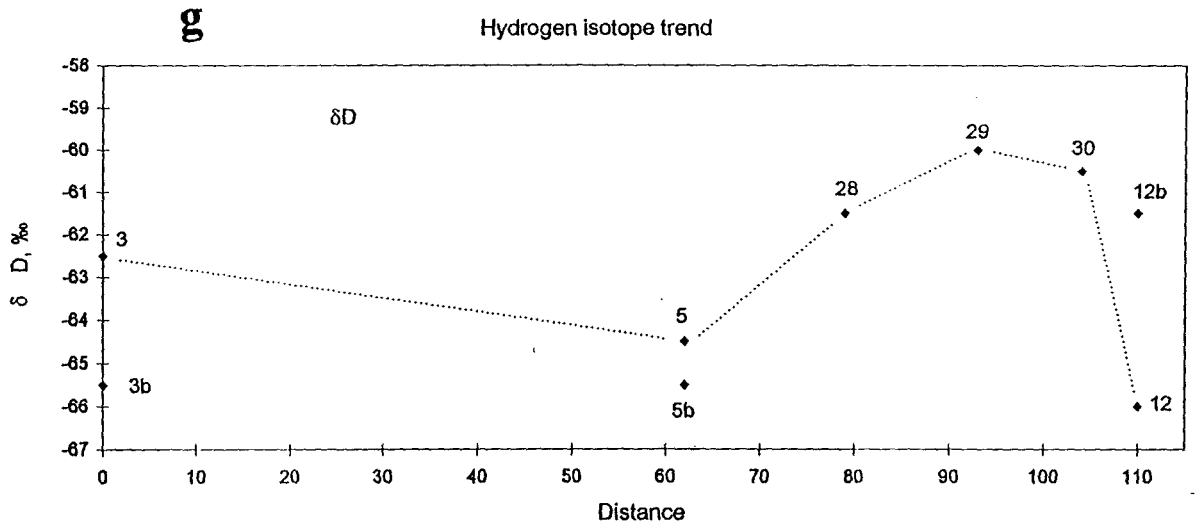


Figure 6. Isotope relations

1 SFR	San Francisco River		
2 CHS	Clifton Hot Springs	14 NON	No Name well
3 GR-NM	Gila River in New Mexico	15 SMV	Smithville Canal Co. well
4 GR-DB	Gila River, N end Duncan Basin	16 TID	Tidwell Wash outcrops
5 GR-HS	Gila River, head of Safford Valley	17 SPC	Spring Creek outcrops
6 SAC	Safford Ag. Center	18 TNY	Tenney #3 well
7 CTY	Safford City well	19 NON	No Name well
9 SSFD	San Simon Fire Dept well	20 WHT	Whitmore #1 well
10 STP	Safford sewage treatment plant	21 FTO	Fort Thomas outcrops
11 WWW	Watson Wash well	22 WAT	Watson Wash outcrops
12 GR-GO	Gila River at Geronimo	23 CON	Conway well

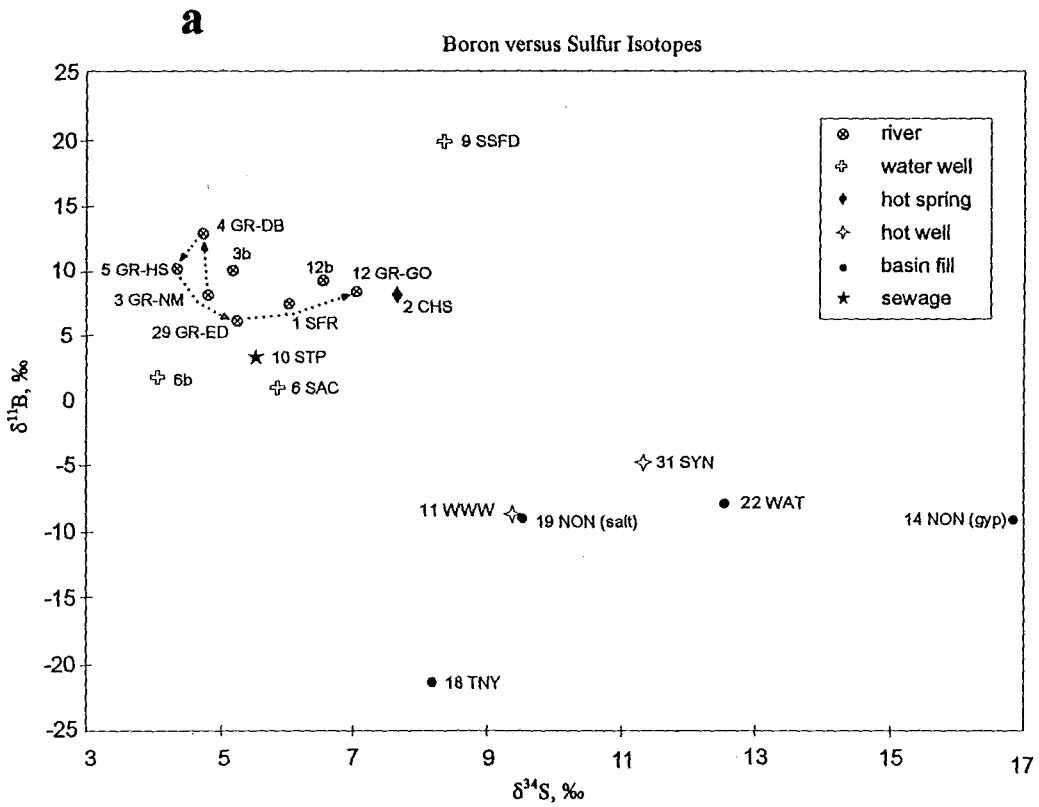
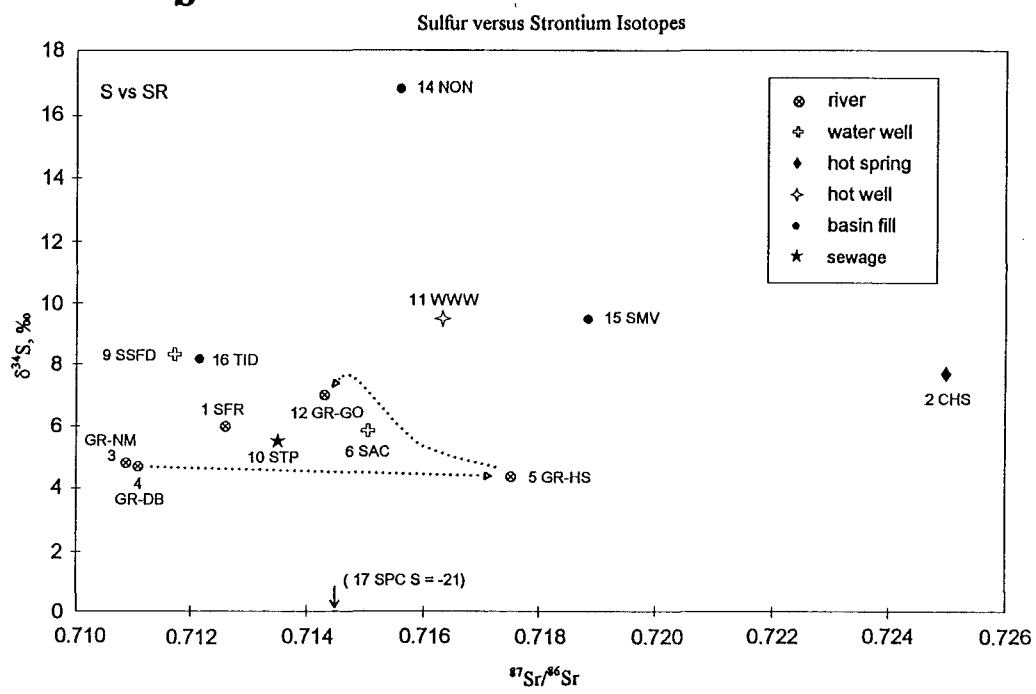


Figure 6. Isotope relations, continued

b



c

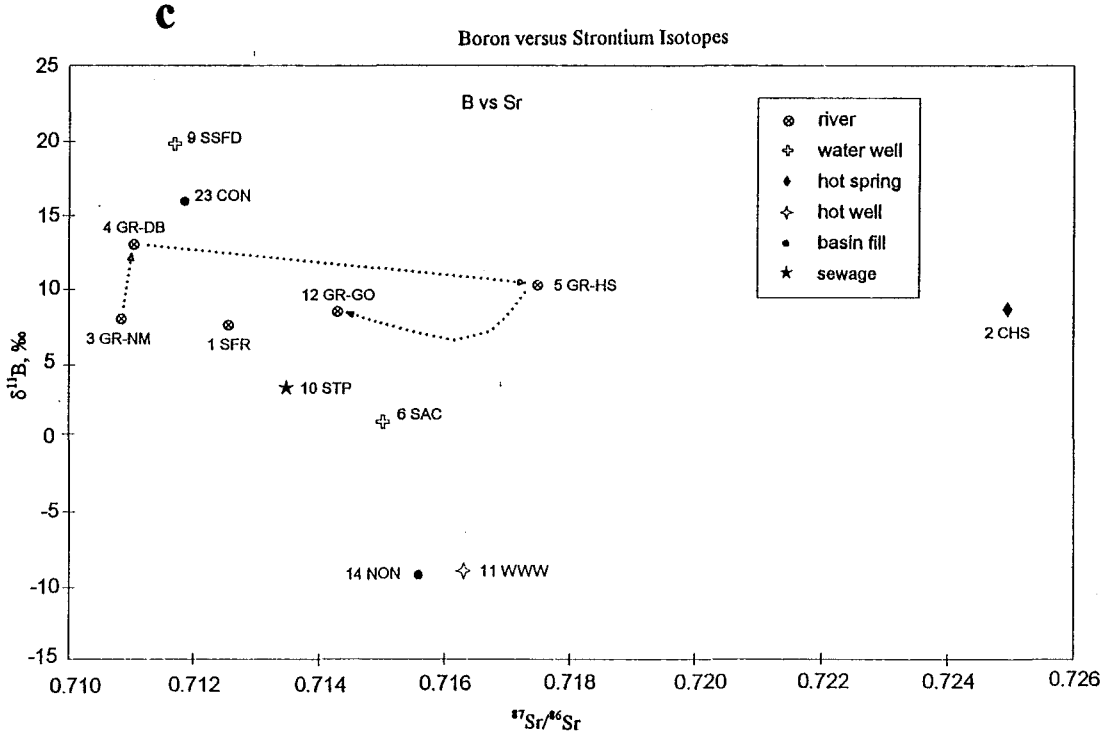
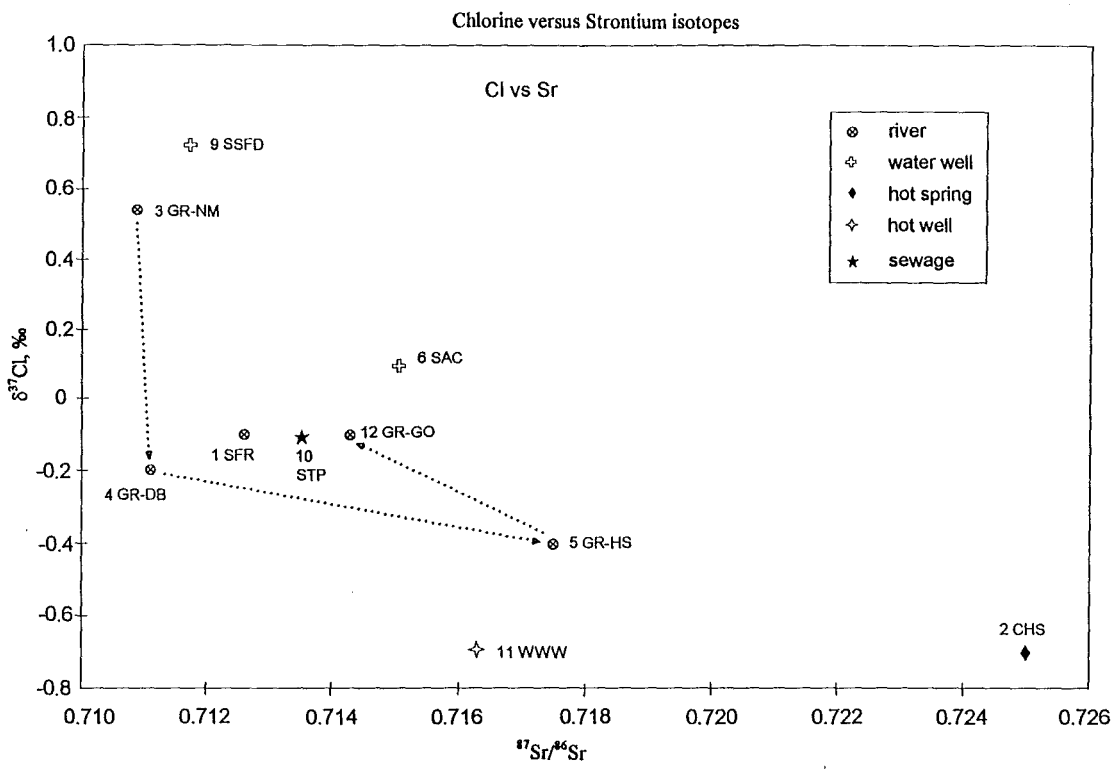


Figure 6. Isotope relations, continued

d



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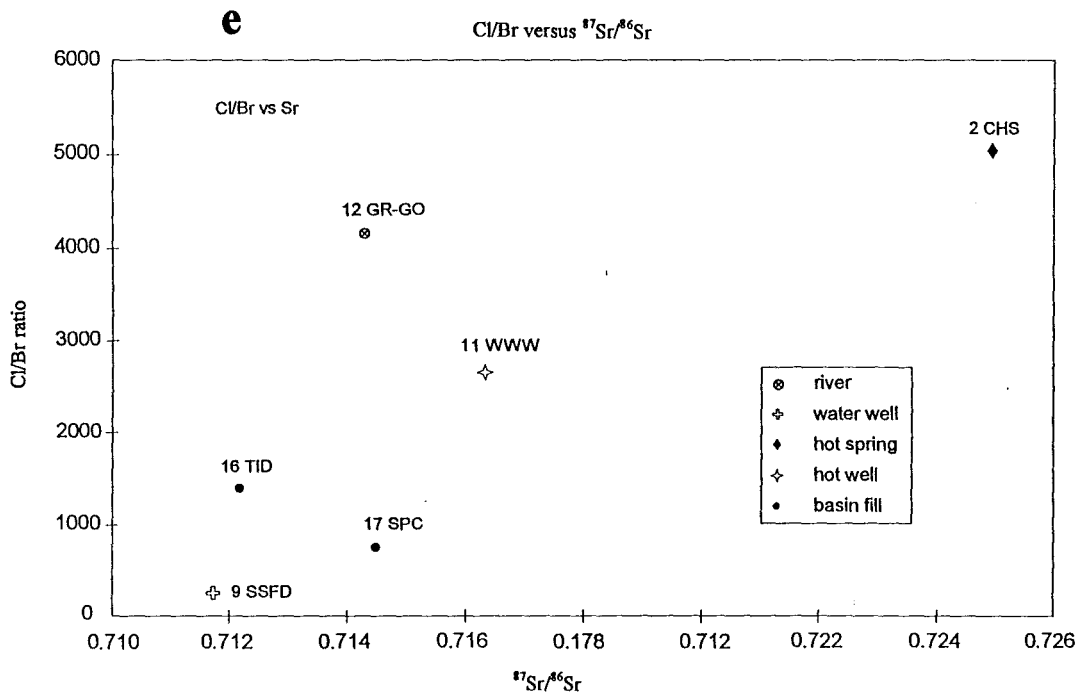
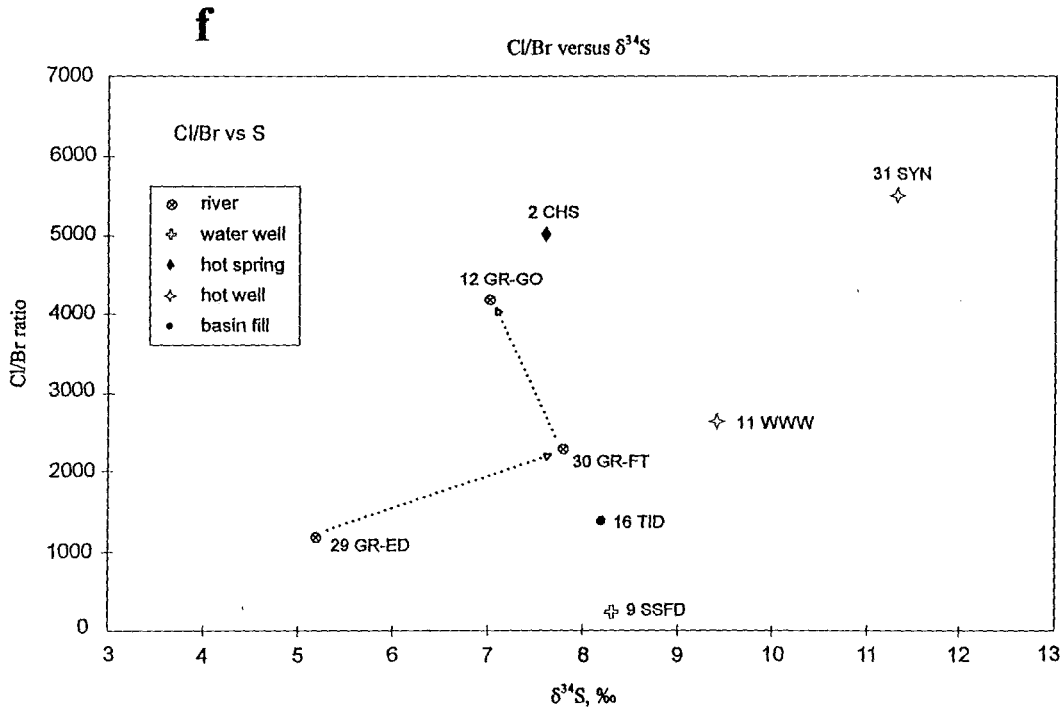


Figure 6. Isotope relations, continued



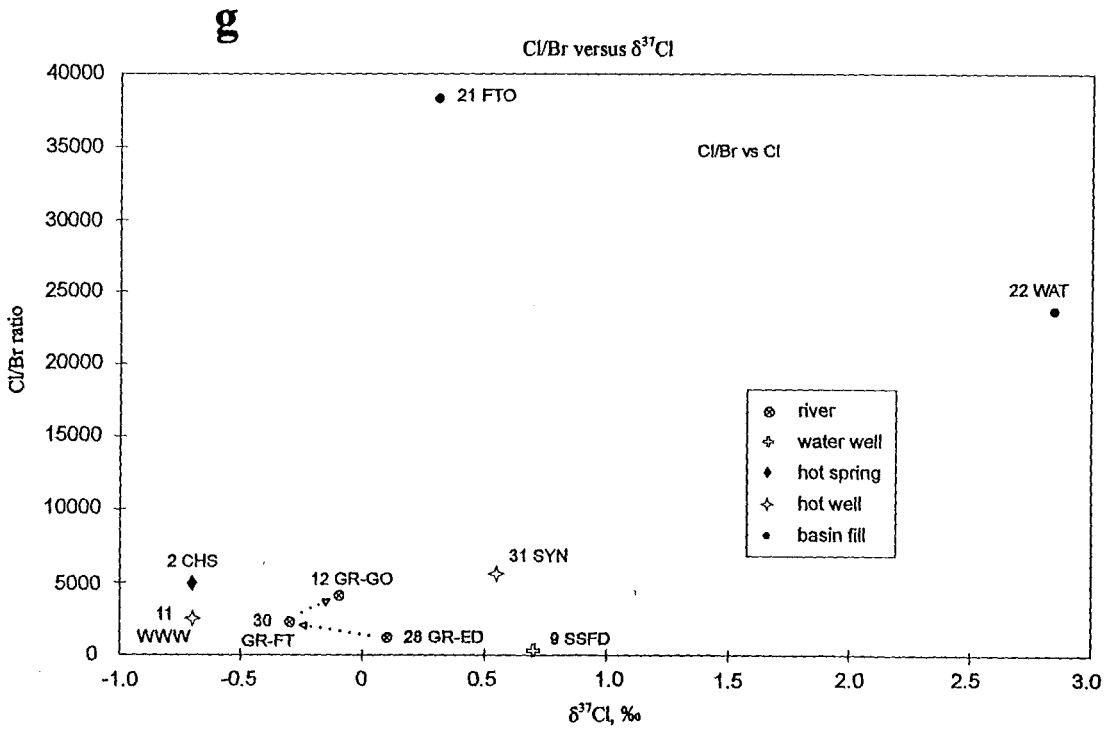


Figure 6. Isotope relations, continued

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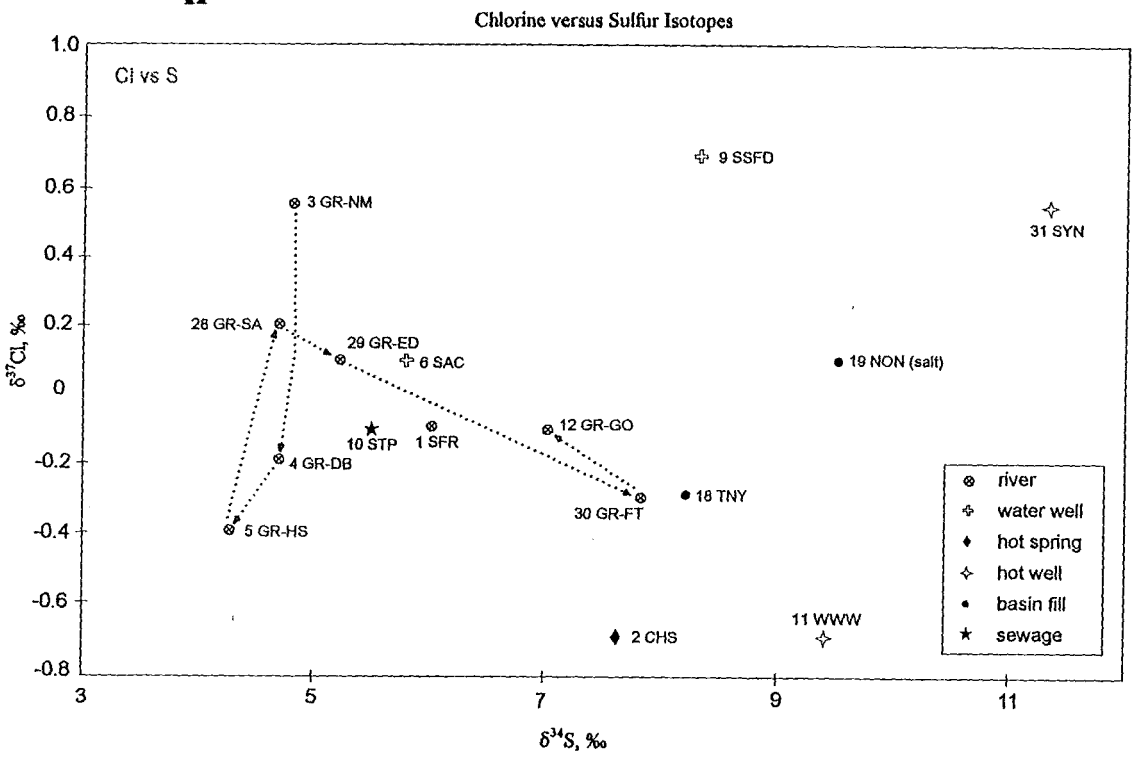

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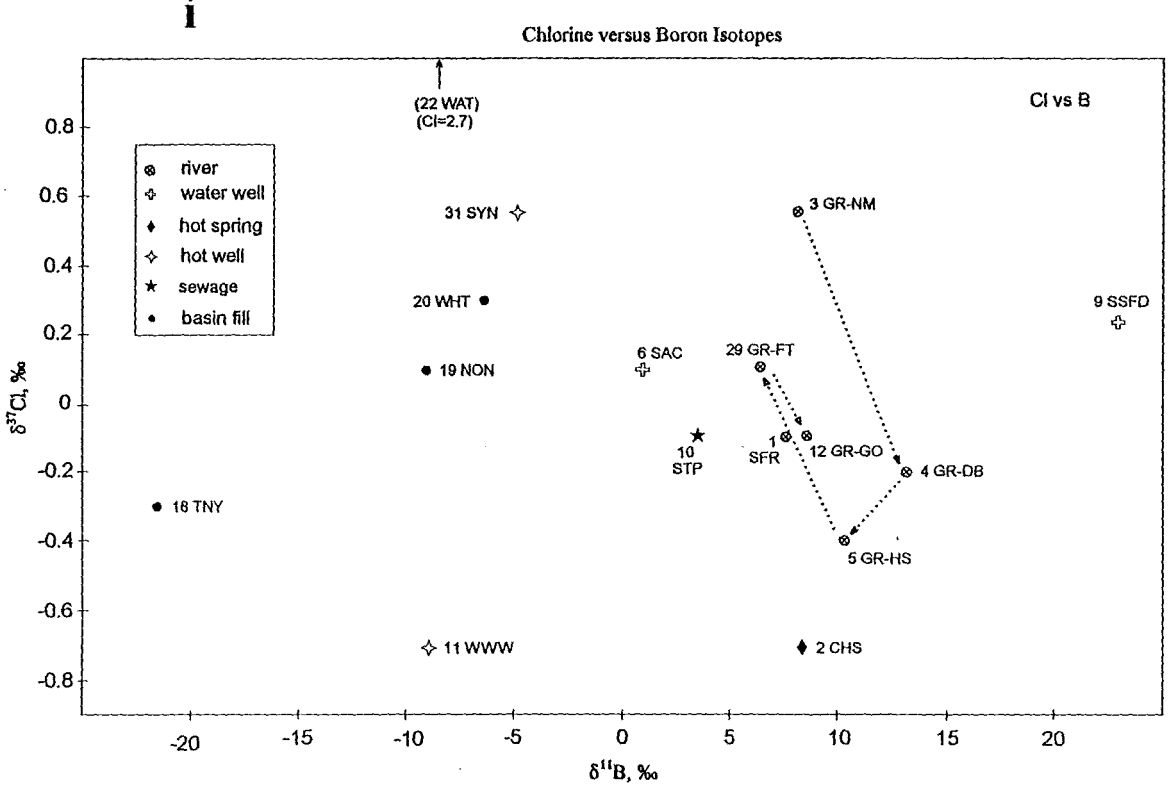

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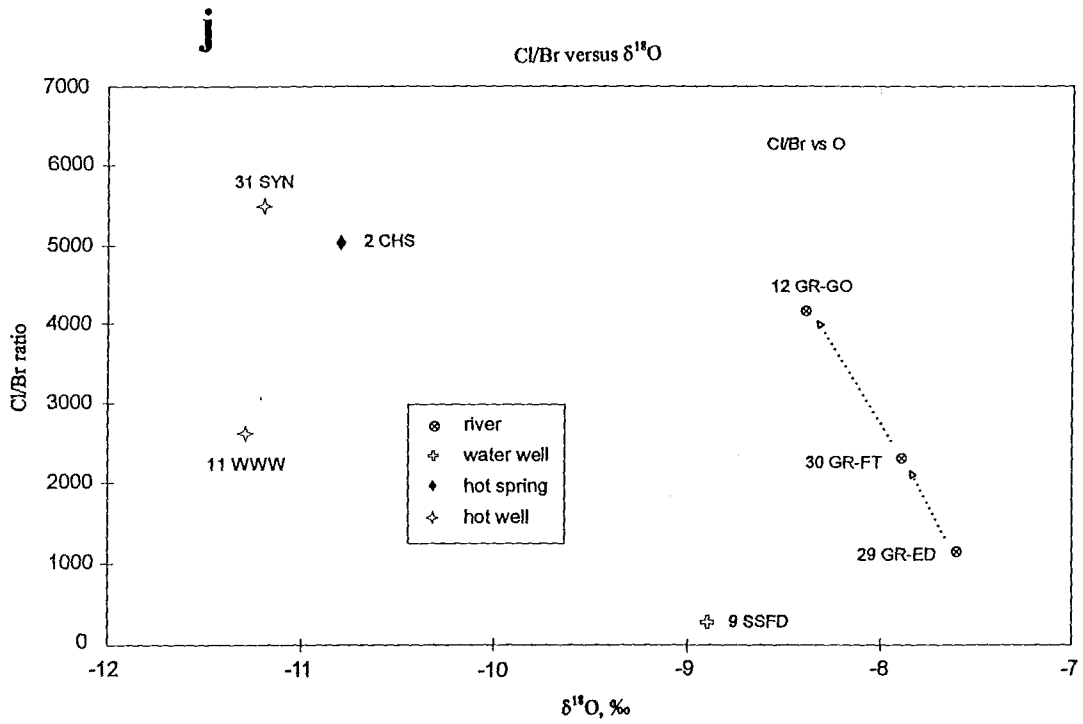

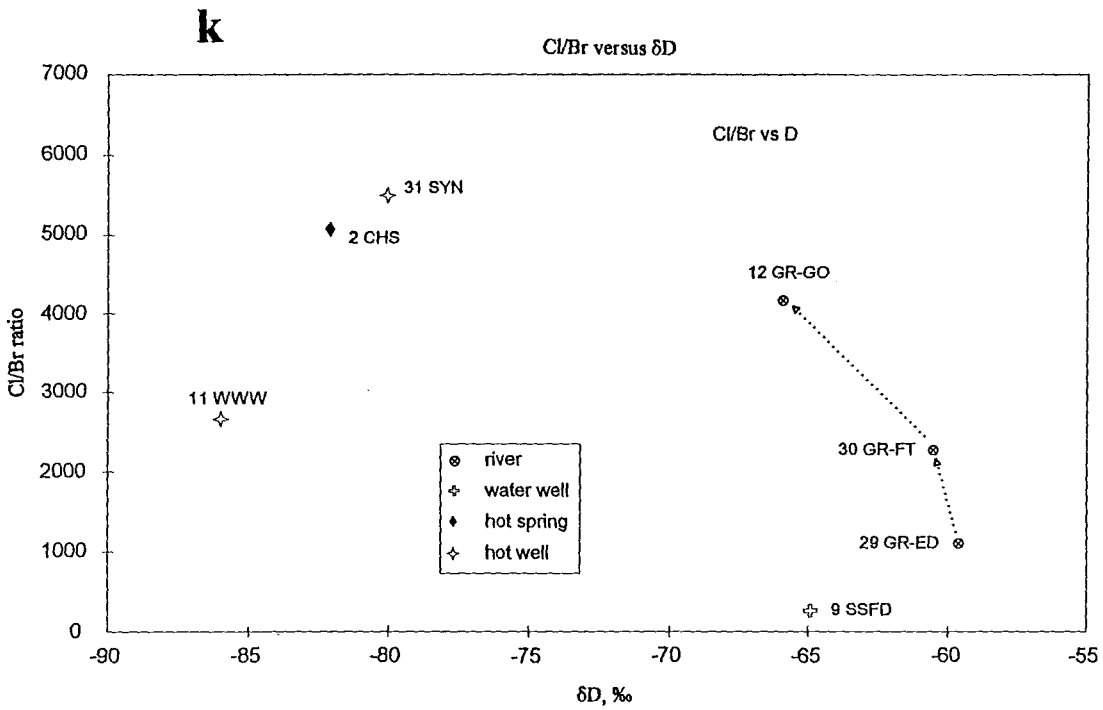

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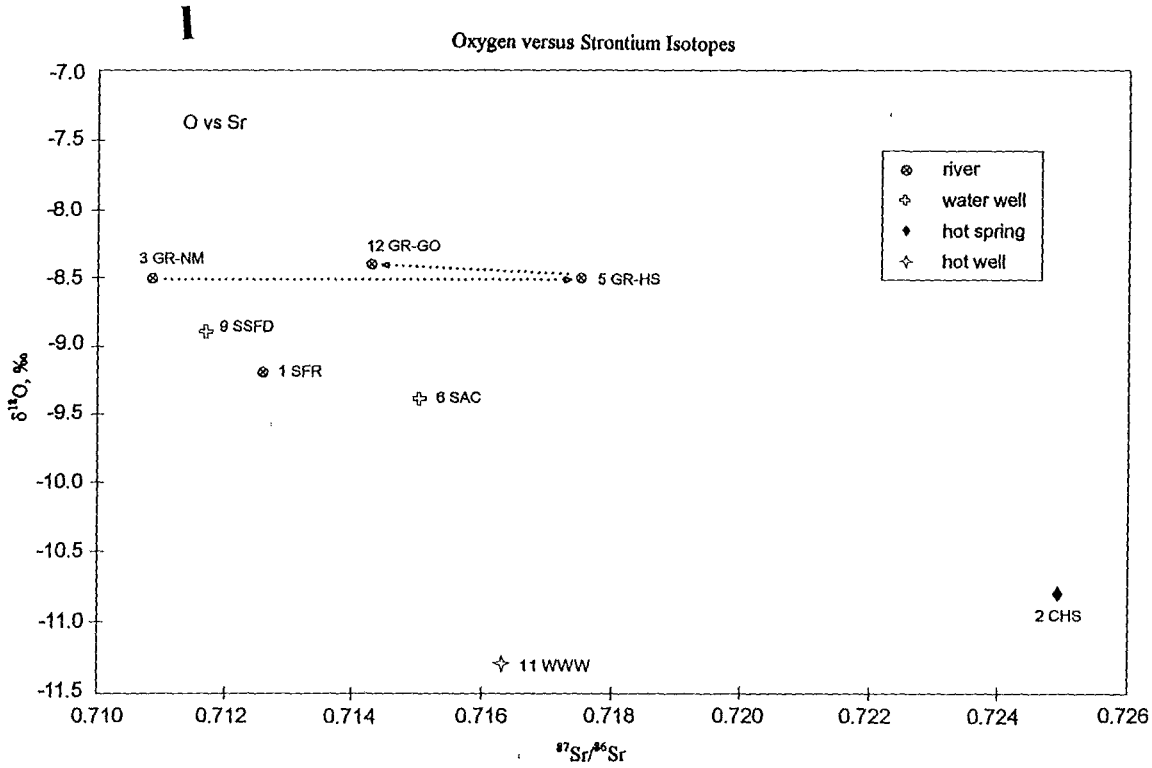


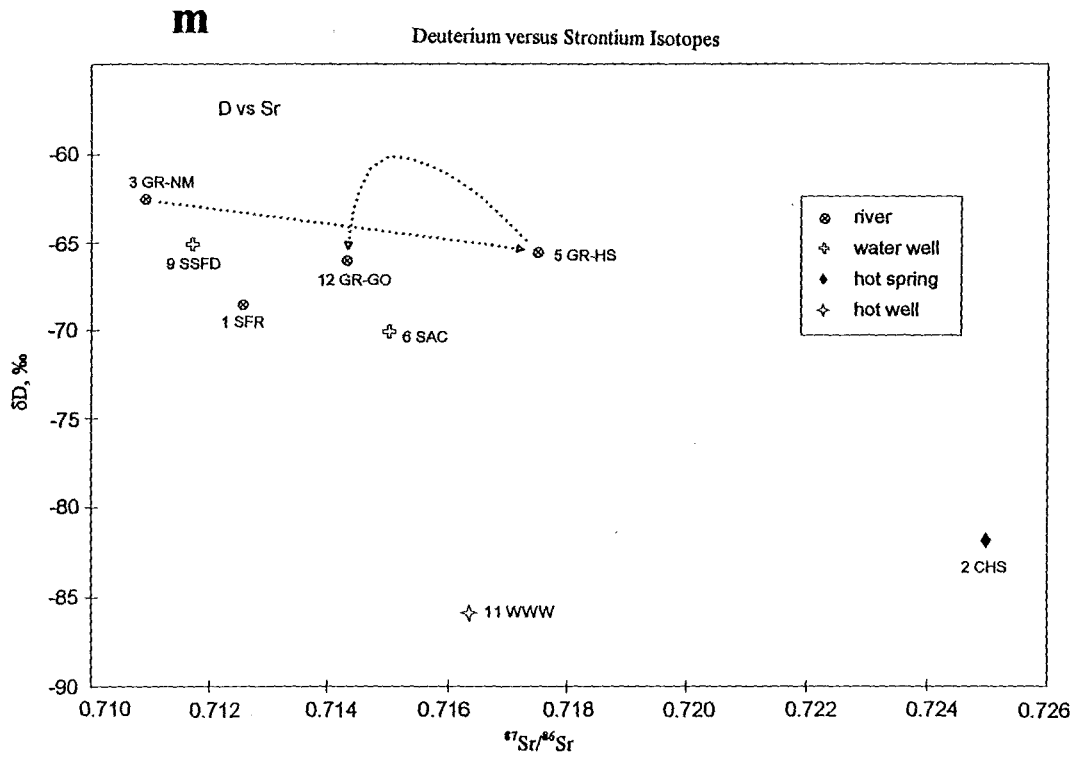
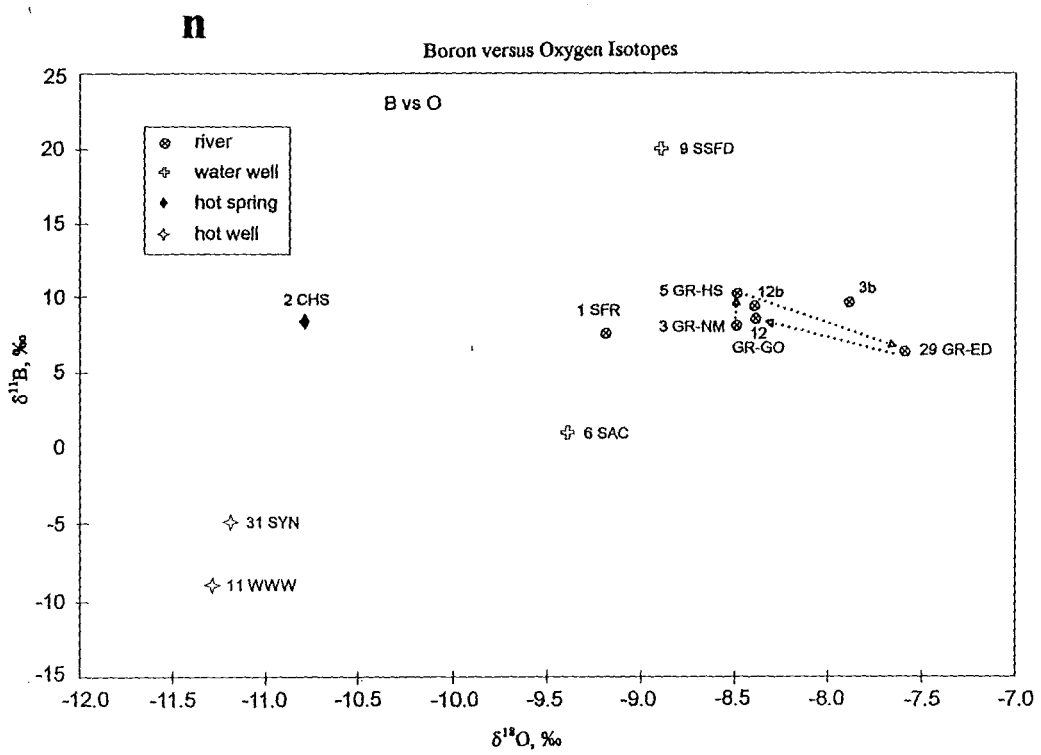
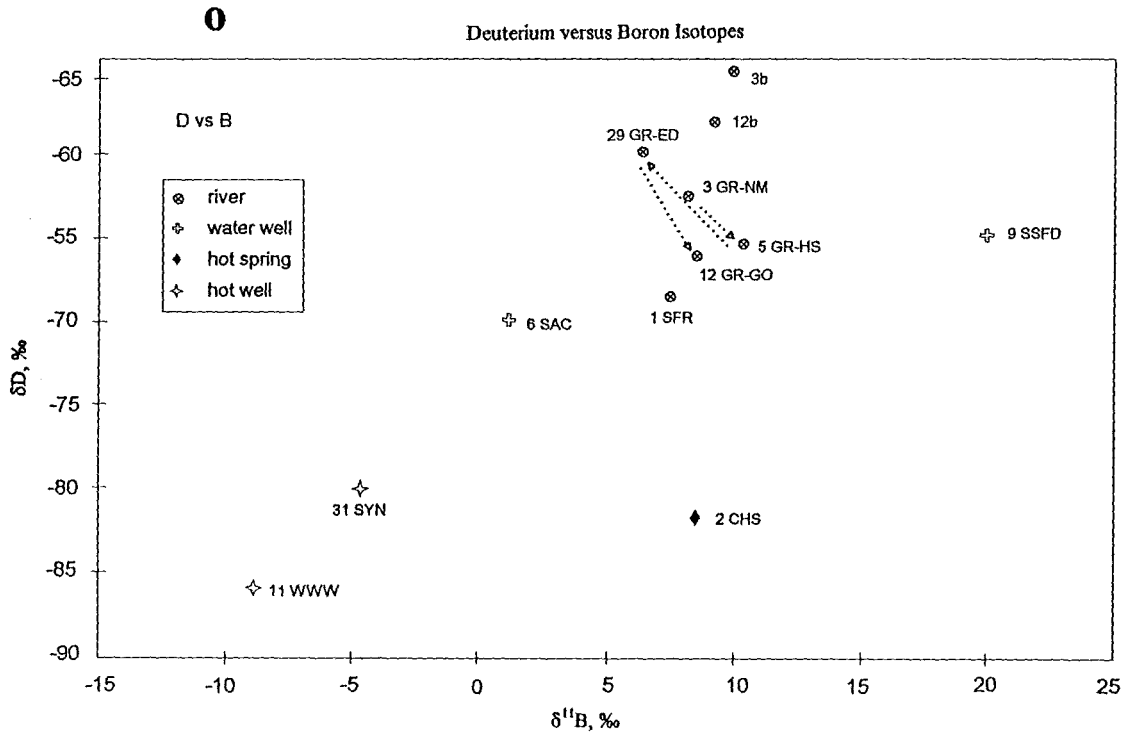


Figure 6. Isotope relations, continued





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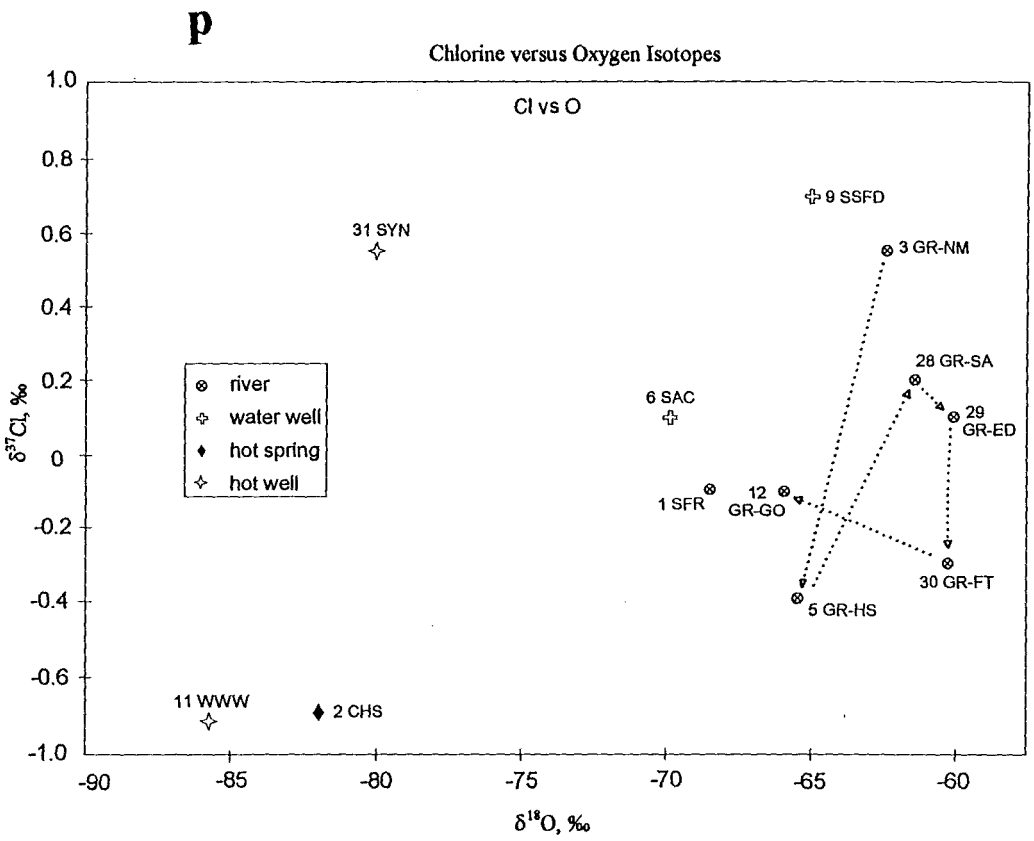

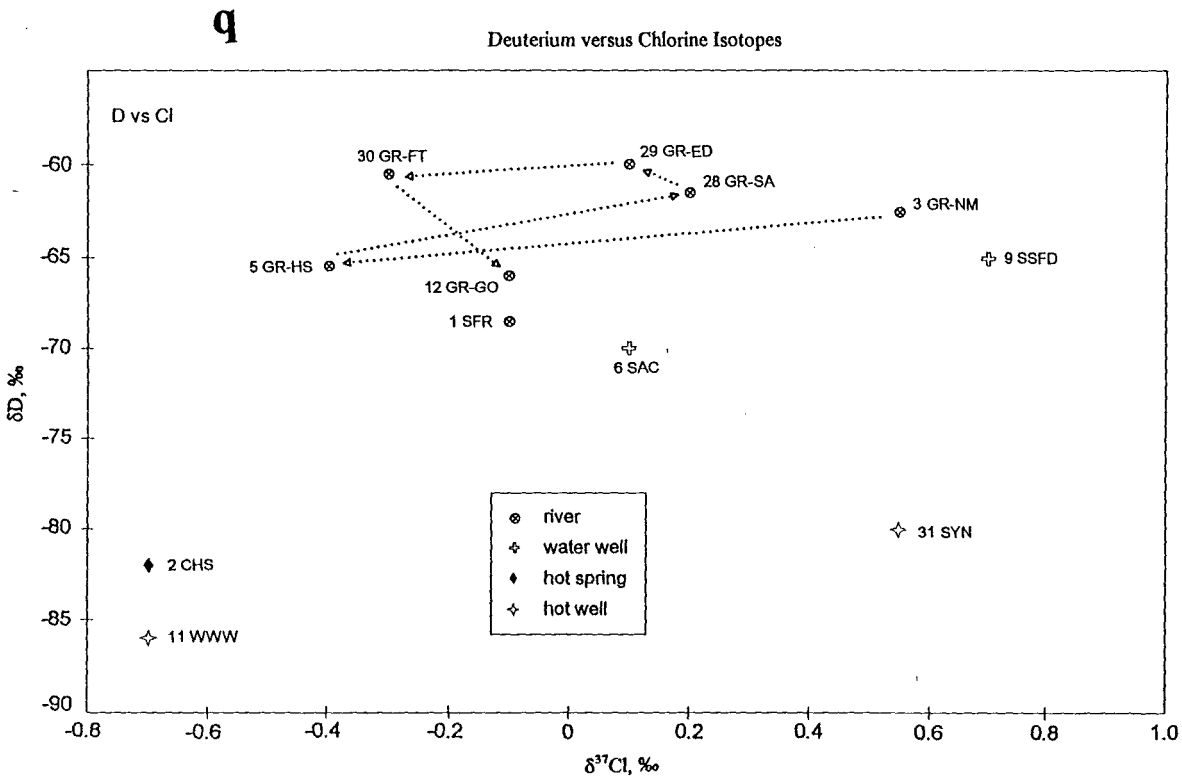

Figure 6. Isotope relations, continued

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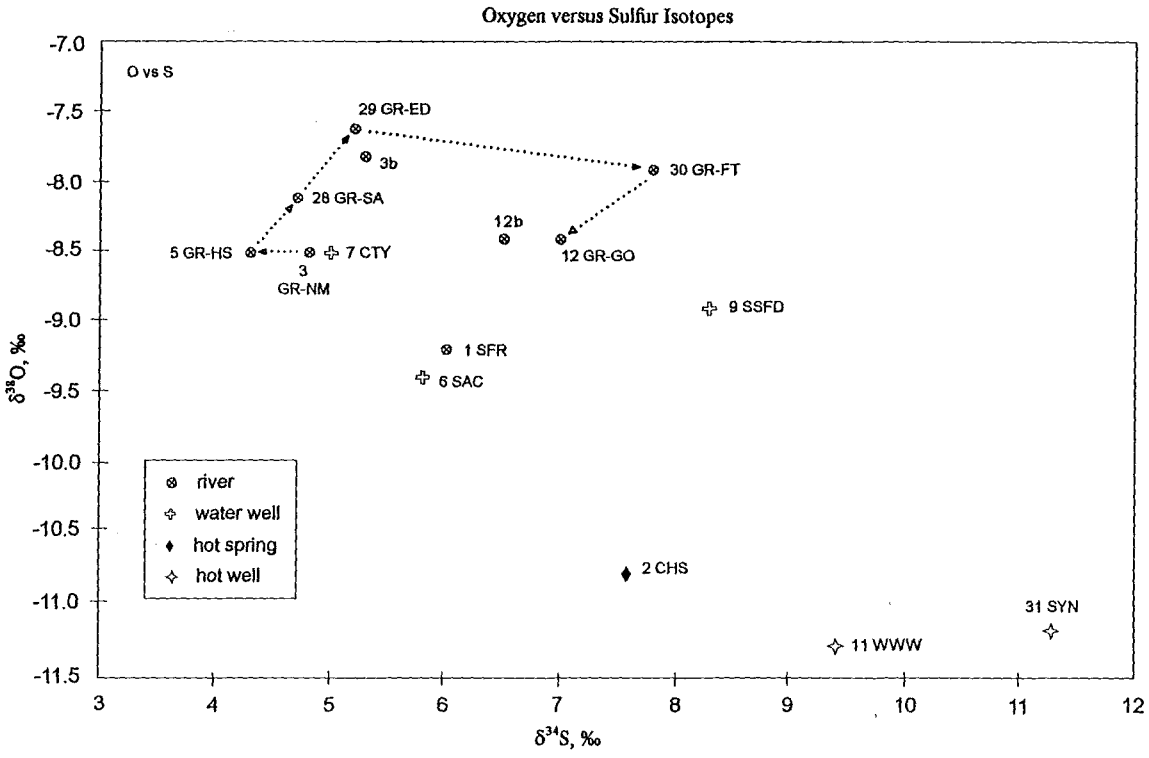

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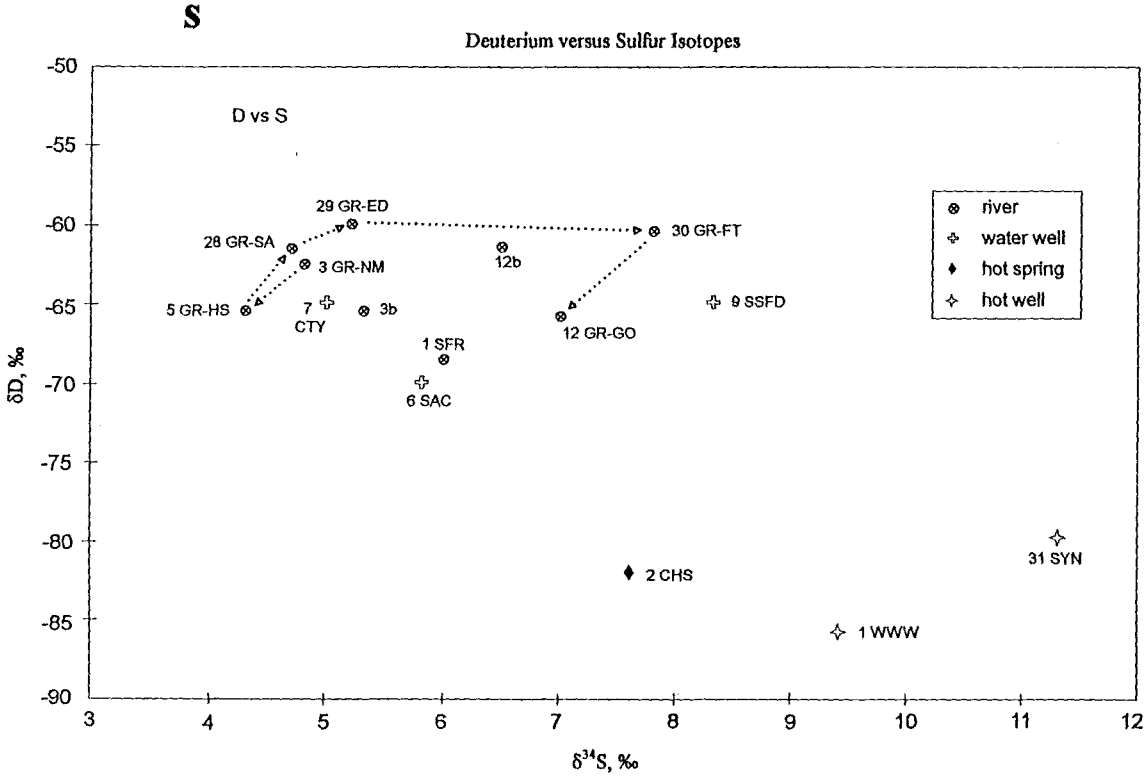

upstream for irrigation. At the time of the July sampling, the remaining river was diverted at site 29. The 'river' below site 29 (including site 30) consisted of water from seeps, springs, flowing artesian wells (e.g. sites 11 and 31) and possibly underground return of irrigation water. Thus the chemistry of the river was dominated for several miles by these additions. The amount being contributed from each source was not determined.

Isotopic compositions at and below site 29 therefore reflected a much smaller amount of water, which varied from no more than a trickle at Eden to an increased but still much diminished stream at site 30. By Geronimo, the flow had increased greatly, probably from a combination of direct reversion of excess irrigation water, subflow of infiltrated irrigation water, and contributions from major tributaries such as Black Rock Wash and Goodwin Wash (along with additional seeps, springs and artesian leakage). None of these possible inflow sources downstream from Fort Thomas were sampled in this study, nor were the fluxes associated with each source determined.

Seasonal variations of isotopes in water samples

As called for in the project, a limited second round of sampling was performed to test for seasonal variations in isotopic composition of the Gila River and in the SAC well. The results show that there is a marked seasonal variation in chemistry, δD, $\delta^{34}S$, and $\delta^{11}B$, and to a lesser degree $\delta^{18}O$ in the sites re-sampled in October versus July.

In general, salinity was higher in the October samples than in July. Part of the reason is that in July, a monsoon storm pulse, originating from heavy rains upstream in New Mexico, was moving through the Gila and San Francisco Rivers. The original sampling plan called for sampling before the beginning of the monsoon to avoid this dilution effect, but bureaucratic delays pushed the river sampling back until after the start of the rainy season.

The second sampling, indicated by 3b, 5b, and 12b on the chemical figures, was marked by increases in most of the TDS components, except B and Cl. Chloride is inexplicably lower at site 12 in the second sample. None of the other constituents except B are lower at site 12 in the second round, and the reported decrease in Cl is inconsistent with the increase in conductivity and Na. TDS (the sum of the analyses) in sample 12 is higher than the field-measured conductivity value, another inexplicable situation. These inconsistent results demonstrate that one should not put absolute faith in any particular analysis or in any single number.

The ramifications of the seasonal variations are important in mass-balance calculations because they demonstrate that the results from a single sampling event do not fully characterize a typical or average chemical or isotopic composition of waters in a complex geohydrologic system such as the Safford basin. In order for isotopic studies such as these to be truly effective at defining "the" isotopic composition of an end member (at least for water samples), that end member must be sampled at many places enough times under different conditions to show what is the average isotopic composition, or must be sampled densely enough over a short period to get a reliable 'snapshot'.

Conditions that change seasonally in the Safford basin include:

- different flow regimes in the Gila River due to:
  - weather (dry vs. rainy periods) and
  - diversions for irrigation
- temperature and humidity (affects evaporation, ET rates)
- stage of crops (affects amount of irrigation, ET rates, fertilizer use)
- amount of groundwater used for irrigation (depends on flow and salinity of Gila River)

All of these conditions change tremendously over the course of a year, and vary from year to year, and such variations must be taken into account in order to fully characterize water in the Safford basin. Statistical methods of dealing with seasonal variability in water quality analyses are discussed in Montgomery and others (1987) and Harris and others (1987). In light of these factors, the results of this TDS pilot study should not be taken as proving an average, typical, or characteristic value for any of the water samples from the river or wells. *The isotopic compositions reported here are valid only for the conditions that were present at the time of sampling*. Sampling under different conditions could yield significantly different results. Sampling must be repeated many times before a true understanding can be achieved; a single sampling does not give an accurate picture. Attaching significance to any individual number presented here may constitute over-interpretation.

Variations of isotopic composition with depth in well cuttings

Cuttings from two wells were tested for variations in composition with depth. The 'No Name' well and Tenney #3 well were best suited for this test because both wells had repository sample sets large enough to put together composites from different intervals. Isotopic compositions varied in different intervals in both wells:

Table 14. Variations in isotopic compositions with depth.

Tenney #3 well, samples 18 and 33.

Depth (ft)	*Isotope*	*Result*
~1240	S	13.6
2450-3400	S	8.1

No Name well, samples 14, 19, and 25

Depth (ft)	*Isotope*	*Result*
1080-1600	Sr	0.715585
	S	16.8
	B	-9.2
1800-2240	Sr	0.715726
	S	9.5
	B	-8.9

In both wells, $\delta^{34}S$ was much lower in the bottom section than higher in the well. For the No Name well, $\delta^{11}B$ was slightly more negative and $^{87}Sr/^{86}Sr$ slightly lower in the higher part of the section.

These results show that the isotopic composition of the basin fill varied over time. Factors producing such shifts would include:

- Level of water, temperature, salinity and alkalinity in the lake, which would control biological activity that fractionates isotopes (important for S).
- Changing composition of source areas. For example, as Tertiary volcanic cover is eroded, older rocks are exposed, resulting in different source compositions.
- Amount and composition of clay, which (along with pH) would control B fractionation.

Such shifts in isotopic compositions over time complicate the determination of the 'average' or 'typical' values in the basin fill. With the limited number of samples in this study it is

impossible to determine a useful model for the variability of the data. In the case of strontium, for example, the expected shift would be toward higher isotopic ratios as older rocks are exposed in the drainage area, but the available data suggest the opposite. Whether the minor change in Sr over time in cuttings from one well is significant enough to worry about is questionable, but it still confirms that the composition of the basin fill is too variable (even in a single location) to be fully characterized by the small number of samples in this study.

For purposes of mass-balance calculations, many more analyses are required both in terms of geographic coverage and more detailed sampling of individual locations. For example, for a few wells in the AZGS repository, cuttings could be composited from several intervals rather than two broad sections. However, most wells do not have enough samples, or the repository samples are too small to do this kind of detailed analysis. Another limitation with cuttings is that there are so few deep wells represented in the repository. Compositions of the cuttings may be influenced by mixing with drilling mud.

Outcrops are good for detailed sampling because the sample size is unlimited, excellent exposures are found throughout the Safford and Duncan basins, and sampling can be done on any vertical scale, down to individual layers of an inch or less. One shortcoming with outcrop sampling is that only perhaps 200 feet of vertical section is exposed in any single location, limiting the applicability of the results to greater depths. Another possible concern is the effect of surface weathering.

MASS BALANCE CONSIDERATIONS

Mass balance calculations require knowing several quantities. The final isotopic composition of a water sample, δ_m, derived from different sources is given by

$$\delta_m = \Sigma_{i=1,n} (c_i \, \delta_i \, x_i)/C_m$$

where c is the solute concentration, δ is the isotopic composition, x is the fraction of each source *i* through *n*, and C_m is the concentration of the final sample.

In order to calculate the amount of TDS originating from different sources, one of the necessary numbers is the amount of water carrying the TDS from the sources. For the Gila River, flow rates are measured at USGS gage stations near sampling sites 1, 3, 4, and 5, but these are upstream of the area of interest for the mass balance calculations, that is, the main Safford Valley, where the salinity greatly increases. Sampling sites 28, 29, and 30, from Safford to Fort Thomas have no USGS gage stations nearby, so the precise flow in the river is unknown and those points cannot be used in mass-balance calculations.

At Geronimo, sampling site 12, the nearest gage station is at Calva, 6-8 miles downstream, an interval over which some change in flow rate occurs. Calculations done at Geronimo using Calva numbers are therefore not very precise.

Of major interest is the amount of irrigation water that eventually returns to the river. Several possible routes exist, including reversion of unused, excess water, direct surface runoff (which by the Globe Equity decree is zero), and subsurface flow. The amount of subsurface flow cannot be measured directly, so that part of the equation (x) is missing. Only one sample of irrigation water was sampled, at the Safford Agricultural Center. In this sample, only N and ClBr were analyzed. Because this is the only sample, it cannot be assumed to be representative (x, c, δ in the above equation) of the thousands of acres of agriculture in the valley, so any calculations based on that single sample would be more than just meaningless; they would be misleading.

Deep artesian wells and natural artesian leakage are suspected of being major contributors to the salinity of the Gila River. Only two out of dozens of artesian wells were sampled, and isotopic and chemical results were different for the two wells, making a determination of "the composition" (δ, c) of the deep aquifer water impossible without further sampling. Seeps in the Gila channel were not sampled in this study, so that important source of TDS remains completely uncharacterized (x, c, δ).

Another reason mass-balance calculations based on the first round of sampling would not be meaningful is that, owing to the small number of samples of each type of end member, the results do not necessarily reflect the average or typical isotopic composition (δ, c) of any of the sources. For example, the chlorine isotopes vary considerably, and there were too few samples to determine an average. Although sulfur isotopic compositions of the evaporite samples were generally positive, in Spring Canyon, they were highly negative. Whether the amount of negative-$\delta^{34}S$ sediment is a major fraction of the basin fill is not known, but knowing that is essential for using the right number for the basin-fill $\delta^{34}S$ in a calculation. For sources like springs, or irrigation water, only one sample of each was tested.

Seasonal variations add to the uncertainty of what numbers to use for the isotopic composition of some of the sources. With the exception of $\delta^{18}O$ at sites 5 and 12, all of the isotopes measured in the second round of sampling were different from the results in the first round. $\delta^{34}S$ was different in two samples of the Gila River near the head of the Safford Valley, with results of 2.6‰ in January, 1997, versus 4.3‰ in July, 1998, and was nearly as different between July and October, 1998 at site 29.

Loss of water due to evapotranspiration from phreatophytes was studied extensively by the U.S. Geological Survey from the 1950s (Gatewood and others, 1950) through the early 1970s (Laney, 1977; Hanson and Dawdy, 1976; Jones, 1977; McQueen and Miller, 1972; Turner, 1974; Weist, 1971; Hanson and Brown, 1972) . Floods washed out the experiment stations before the project was scheduled to end. Repeated flooding has rearranged the river channel and has changed the amount of phreatophyte cover. These changes mean that the preliminary assessments by the USGS may no longer be accurate today. Therefore, the amount of water loss from natural ET must be estimated for use in mass-balance calculations. Determination of ET rates and water losses are beyond the scope of this project.

Some of the missing numbers, such as the amount of ET, irrigation seepage, or artesian leakage could be estimated, and other workers have tried to estimate them in the past. But this study is not about estimating anything - it is about *measuring* real values. The purpose of this study is to show which isotopes are useful for determining the identity of the sources of TDS, so that with further detailed sampling, the sources and their character can be known rather than assumed, and hopefully the flux of each source can be determined with greater accuracy.

CONCLUSIONS

Isotopes are a useful method for determining the identity of solutes from different sources. The results of this study show that different suspected sources of TDS to the Gila River have isotopic compositions that differ from the background Gila River composition. Those differences allow the use of isotopic compositions as tracers for each source. In isotope-versus-isotope plots, end members are easily distinguished by their isotopic compositions.

Plots of isotope trends downstream in the Gila River, and of isotope versus isotope show that important shifts in the isotopic composition of the river water occur in the Safford basin, mostly below Pima. Qualitatively, the shifts at the time of sampling for this study appear to be the

result of leaching of natural salts or additions of deep artesian water. Cycling of salts derived from evaporation of Gila River water would not produce shifts of the magnitudes seen in the various isotopes.

Owing to the limited number of samples in the study, the basin fill sediments, groundwater, and river water have not been fully characterized, and others such as irrigation return and tributary inflows were not characterized at all. The results of this TDS pilot study should not be taken as proving an average, typical, or characteristic value for any of the basin fill samples or water samples from the river or wells. *The isotopic compositions reported here for water samples are valid only for the conditions that were present at the time of sampling.* Sampling under different conditions could yield significantly different results. Sampling must be repeated many times before a true understanding can be achieved. Given these caveats, it can still be said with assurance that isotopes are a useful method for tracing the sources of TDS in the upper Gila drainage.

RECOMMENDATIONS

- **More extensive sampling.**

An expanded investigation of the natural sources of TDS in the upper Gila River is warranted. This pilot study showed large variations in isotopic compositions of various potential sources of TDS. While this variability is a necessary prerequisite for distinguishing end members, further work is required to characterize sources well enough to constrain mass balances. Only much more extensive and repeated sampling will be adequate to reach any kind of understanding of the chemical and isotopic character of the upper Gila River.

- **Mapping of surface exposures of salty outcrops.**

Salty outcrops have been found by cursory reconnaissance to be more common than previously reported in the literature. Known outcrops of salty clay extend from a few miles south of Safford to the San Carlos Reservation. The extent of these exposures has not been mapped. Some clues are given in old soil surveys of the Duncan and Safford Valleys (Lapham and Neill, 1904; Carpenter and Bransford, 1924; Poulson and Youngs, 1938; Poulson and Stromberg, 1950; Gelderman and others, 1970; DeWall and others, 1981), where areas of saline soils (some outside of farmed areas) are mapped and alkali and salt deposits are discussed.

- **Test feasibility of other isotopes.**

Isotopes measured in this study are some of those that are commonly used as tracers in water quality investigations. A few other isotopes that could be applied to the Safford and Duncan Basins are isotopes of carbon and lithium. Carbon is useful as a measure of the residence time of groundwater in a system where the isotopic composition of the aquifer sediments differs from the initial water composition. Lithium, which behaves like sodium, is a potential tracer of the sources of salt. Neither of these isotopes have been measured in the Safford basin.

- **Survey saline wells in the Safford Basin**

Previous reports (e.g. Knechtel, 1938; Hem, 1950) document the widespread occurrence of highly-saline wells. Some are artesian, while others may be quite shallow wells in the flood plain alluvium. Several abandoned oil exploration wells are known that are discharging salty water directly into the river or into the shallow aquifer. The precise number of these wells is not known, nor is the total amount of salt contributed. (For illustration, a quick calculation of the salt load of the old Mary Mack oil well shows that in the 1970s, about 12,000 tons per year of TDS were

discharging through artesian flow (USGS data). About 2,100 tons per year TDS are discharged from Indian Hot Springs (Knechtel, 1938; Hem, 1950). Sources like these may contribute a major portion of the salt load in the Gila.

- **Dating of groundwater.**

One clue of where salinity is originating could be obtained by dating the groundwater carrying high salinity. If the water has a young character, it may be derived from recent recharge of surface water, but if the water is tritium-dead, or has a low percentage of modern ^{14}C, the water has probably resided in the deeper basin aquifer(s), where it picks up salts from the sediments.

- **Extend this type of geochemical study into the San Carlos Indian Reservation.**

This study covered only the portion of the upper Gila River upstream of the San Carlos Indian Reservation boundary. Lacustrine sediments and evaporites such as salt are known on the reservation (e.g. Marlowe, 1961) and likely represent a further possible source of TDS to the Gila River. Given the large amounts of salt in clay outside the Reservation in the Fort Thomas-Geronimo area, it is logical that these salty deposits continue onto the Indian land. Artesian leakage of deep groundwater into the shallow aquifer and the river has been calculated to be 106,000 cubic feet per day per mile of river in the Reservation (Hanson and Brown, 1972). Mass balances require a knowledge of all the major gains and losses of constituents. Without information from that part of the Gila on the Reservation, any study of water quality is incomplete. Including the Reservation would require the permission and cooperation of the San Carlos Apache Tribe.

- **Subsurface investigations.**

Under the heading of academic fantasy, our understanding of the Safford and Duncan basins would be immeasurably enhanced by the drilling of a few deep test holes through the evaporite deposits in the basin. A few deep holes, >6000 feet have been drilled for oil exploration in the valley, but not in the area of evaporites. Test holes for oil and borates have been drilled in the evaporite areas, generally to about 2000 to 3000 feet and for most of these, cuttings were not collected. The remaining >8000 feet of sediment and evaporites have not been explored. As a less expensive and therefore more practical substitute for actual drilling, geophysical surveys such as resistivity, gravity, and magnetic would be useful for refining hydrologic basin models.

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Appendix A

SAMPLE SITE DESCRIPTION

Site 1 - San Francisco River above Clifton (SFR)
D(3-30)32b; Lat 33°07'59" (33.1333°) Lon. 109°16'55" (109.282
East bank of San Francisco River, 8 miles above Clifton
Nearest USGS gage Station: 09444500 San Francisco River at Clift
109°17'43", in SW ¼, SE ¼ sec.30, T.4 S., R.30 E., on downst
Railroad Boulevard Bridge (U.S. Highway 191), at Clifton.)
Drainage area: ~2700 mi^2. Average discharge (72 years) 244 cfs, 1
6.1 cfs, 6/21/71 (Smith and others, 1997).
Discharge at time of 7/13 sampling, 1:55 pm: 71 cfs; stage, 10.19 f
Sample: river water
Analyses: S, Cl, B, Sr, N, O, D isotopes; Cl/Br ratio; cations, anion
Sample date:7/13/98 for all; again 10/13/98 for O, D.

Site 2 - Hot Spring near Clifton (CHS)
D(4-30)18c; Lat 33°04'46" (33.0795) Lon 109°18'5" (109.3015
Hot spring on east bank of San Francisco River, 2 miles above Clif
Sample: spring water
Analyses: S, Cl, B, Sr, N, O, D isotopes; Cl/Br ratio; cations, anio
Sample date: 7/13/98 (again 10/13/98 and 12/26/98 for O, D; 10

Site 3 - Gila River upstream from Duncan Basin (GR-NM)
NM, T19S, R19W, sec18); Lat 33°39'14" (33.6538°) Lon 108°5
Gila River near Fuller Ranch (now BLM), mouth of Nichols Cany
Near USGS gage station 09432000, "Gila River below Blue
32°38'53", long 108°50'43", in SE ¼, SW ¼ sec.18, T.19 S.,
Drainage area: 3,203 mi^2. Average discharge (69 years) 215 cfs,
cfs, 7/14/34 (Smith and others, 1997)
Discharge at time of July 13 sampling, 9:25 am: 109 cfs; stage 3.
Sample: Gila River water
Analyses: S, Cl, B, Sr, N, O, D isotopes; Cl/Br ratio; cations, an
Sample date: 7/13/98 for all; again 10/13/98 for O, D, S, B, Cl/

Site 4 - Gila River at north end of Duncan Basin (GR-DB)
D(5-29)25d; Lat 32°57'57" (32.965) Lon 109°18'36" (109.3

Site 5 - Gila River at entrance to Safford Basin (GR-HS)
D(6-28)29b; Lat 32°53'49" (32.897) Lon 109°30'24" (109.507)
Gila River, north bank, lower end of Gila Box, near San Jose
Nearest USGS gage station: 09448500, "Gila River at head of Safford
(Lat 32°52'06", long 109°30'38", in SE ¼, NE ¼ sec.31, T.6 S., R
downstream from intake of Brown Canal, 8 mi northeast of Solom
from San Francisco River.)
Drainage area: ~7800 mi^2. Average discharge (82 years) 512 cfs, 370,
cfs, 6/25/56 (Smith and others, 1997)
Discharge at time of July 14 sampling, 7:15 am: 161 cfs, stage 5.16 ft
Sample: River water
Analyses: S, Cl, B, Sr, N, O, D isotopes; Cl/Br ratio; cations, anions.
Sample date: 7/14/98; again 10/13/98 for O,D.

Site 6 - Safford Agricultural Center (SAC)
D(7-26)22b; Lat 32°48'46" (32.813) Lon 109°40'52" (109.681)
Irrigation well at Safford Agricultural Center (depth 106 feet)
Sample: Well water
Analyses: S, Cl, B, Sr, N, O, D isotopes; Cl/Br ratio; cations, anions.
Sample date: 7/14/98 for all; 10/14/98 for O, D, S, B, Cl/Br, cations,

Site 7 - Safford City Well (CTY)
D(7-26)13 da; Lat 32°49'29" (32.825) Lon 109°"37"57 (109.633)
Municipal water well: Kempton #2, City of Safford (depth 69 feet)
Sample: well water
Analyses: N, O, D isotopes; Cl/Br ratio; cations, anions.
Sample date: 7/14/98

Site 8 - Safford Agricultural Center (SAC)
D(7-26)22b; Lat 32°48'47" (32.813) Lon 109°40'51" (109.681)
Irrigation water, Safford Agricultural Center
Sample: Irrigation water at end of irrigated furrow
Analyses: N isotopes; Cl/Br ratio; cations, anions.
Sample date: 7/14/98

Site 9 - San Simon Fire Department well (SSFD)
D(13-31)31bba; Lat 32°15'49" (32.2637) Lon 109°13'26" (109.2
Well at San Simon Fire Department (depth approx. 800')

Site 11 - Watson Wash well (WWW)
D(6-25)26b; Lat 32°54'08" (32.9022) Lon 109°45'44" (109.7622)
Hot artesian well in Watson Wash (shown as spring on USGS maps)
Sample: Artesian well water
Analyses: S, Cl, B, Sr, N, O, D isotopes; Cl/Br ratio; cations, anions.
Sample date: 7/14/98

Site 12 - Gila River at Geronimo (GR-GO)
D(4-23)18; Lat 33°05'31" (33.092) Lon 110°01'49" (110.03)
Gila River at Gila Water Commissioner gage Station
Nearest USGS gage station: 09466500 Gila River at Calva, AZ . (Lat
110°:13'10", in SW ¼ sec.8, T.3 S., R.21 E. (unsurveyed), in San
on Southern Pacific Railroad bridge at head of San Carlos Reserv
Drainage area: ~11,400 mi^2. Average discharge at Calva, (53 years)
and Garret, 1984).
Discharge at time of July 14 sampling, 1:30 pm: 46 cfs, stage 1.07 ft
Sample: River water
Analyses: S, Cl, B, Sr, N, O, D isotopes; Cl/Br ratio; cations, anions.
Sample date: 7/14/98 for all; again 10/13/98 for O, D, S, B, cations,

Site 13 - Tenney #3 well (TNY)
D(9-27)36cd; Lat 32°36'10" (32.603) Lon 109°32'18" (109.538)
Well cuttings from Tenney #3 oil exploration well (ASGS cuttings re
Sample: Gypsum, sample interval 715-1240'
Analyses: Sr isotopes.
Sample date: April, 1998 (well drilled 1970)

Site 14 - "No Name" well (NON)
D(7-26)26aaa; Lat approx. 32°48'06" (32.802) Lon approx. 109°
Well cuttings from No Name well (AZGS cuttings repository)
Sample: Gypsiferous clay; Sample interval: 1080-1600'
Analyses: S, B, Sr, N isotopes; Cl/Br ratio.
Sample date: April, 1998 (well drilled prior to 1963 ?)

Site 15 - Smithville Canal Co. well (SMV)
D(6-25)36cbb; Lat 32°51'59" (32..866) Lon 109°44'57" (109.7
Well cuttings from Smithville well (AZGS cuttings repository)

Site 17 - Spring Canyon outcrop (SPG)
D(7-25)28bbb; Lat 32°48'26" (32.8073) Lon 109°47'39" (109.79
Lacustrine sediments exposed in east bank of Spring Canyon
Sample: gypsiferous lacustrine clay
Analyses: S, Sr, N isotopes; Cl/Br ratio.
Sample date: 7/7/98

Site 18 - Tenney #3 well (TNY)
D(9-27)36cd; Lat 32°36'10" (32.603) Lon 109°32'18" (109.538)
Well cuttings from Tenney #3 oil exploration well (AZGS cuttings re
Sample: Salt, salty clay; Intervals: Cl: 2450, 2560, 2640 (repository s
Cl/Br: 2450-2700 (#3060); B, N: 3200-3400 (#2945+3060); S: 335
Analyses: S, Cl, B, N isotopes; Cl/Br ratio.
Sample date: April, 1998 (Well drilled 1970)

Site 19 - "No Name" well (NON)
D(7-26)26aaa; Lat approx. 32°48'06" (32.802) Lon approx. 109°3
Well cuttings from No Name well (AZGS cuttings repository)
Sample: salty clay; Sample interval: 1800-2240'
Analyses: S, Cl, B, N isotopes; Cl/Br ratio.
Sample date: April, 1998

Site 20 - Whitmore #1 State well (WHT)
D(7-25)6cca; Lat approx. 32°51' (32.85) Lon approx. 109°50' (1
Well cuttings from Whitmore oil exploration well (AZGS cuttings r
Sample: Salty clay; Sample interval 400-740'
Analyses: Cl, B, N isotopes; Cl/Br ratio.
Sample date: April, 1998 (well drilled 1977)

Site 21 - Fort Thomas outcrops (FTO)
D(4-23)17ca; Lat 33°05'8" (32.086) Lon 110°00'32" (109.009)
Salty clay in lacustrine deposits exposed northwest of Fort Thomas
Sample: Salty clay
Analyses: Cl, N isotopes; Cl/Br ratio.
Sample date: 7/7/98

Site 22 - Watson Wash outcrops (WAT)
D(6-25)22ad; Lat 32°53'51" (32.8975) Lon 109°46'04" (109.7
Salty clay in lacustrine deposits exposed at mouth of Watson Was

Site 24 - Superior Federal well cuttings
D(5-23)15a; Lat approx. 32°00' (32.0) Lon approx. 109°58' (109
Well cuttings from Superior Federal oil exploration well (AZGS cut
Sample: Lacustrine limestone; Interval: 950-1051'
Analyses: Sr isotopes.
Sample date: April, 1998 (well drilled 1961, borate & brine test)

Site 25 - "No Name" well cuttings (NON)
D(7-26)26aaa; Lat approx. 32°48'06" (32.802) Lon approx. 109°
Well cuttings from "No Name" well (AZGS cuttings repository)
Sample: Marly clay; Sample interval: bottom
Analyses: Sr isotopes
Sample date: April, 1998

Site 26 - Soto well cuttings
D(3-22)31c; Lat approx. 33°07'30" (33.125) Lon approx. 109°07
Well cuttings from Soto well (AZGS cuttings repository)
Sample: Lacustrine limestone: Sample interval: 560-870'
Analyses: Sr isotopes.
Sample date: April, 1998

Site 27 - 111 Ranch outcrops (111)
D(8-28)33bc; Lat 32°41'42" (32.695) Lon 109°29'33" (109.493
Marly clay in lacustrine deposits exposed over 10 mi^2 near 111 Ran
Sample: Marly clay
Analyses: Sr, N isotopes; Cl/Br ratio
Sample date: 7/7/98

Site 28 - Gila River at Safford (GR-SA)
D(7-26)5d; Lat 32°50'53" (32.848) Lon 109°42'56" (109.7155
Gila River at Safford bridge
Sample: River water
Analyses: S, Cl, O, D isotopes; Cl/Br ratio; cations, anions.
Sample date: 7/13/98

Site 29 - Gila River near Eden (GR-ED)
D(6-24)4; Lat 32°56'38" (32.944) Lon 109°53'48" (109.897)
Gila River near Fort Thomas Canal diversion

Site 31 - Gila Oil Syndicate well (SYN)
D(5-24)30; Lat 32°58'22" (32.97278) Lon 109°55'03" (109.917
Artesian hot well (abandoned oil exploration well, drilled 1927-31)
Sample: Well water
Analyses: S, Cl, B, O, D isotopes; Cl/Br ratio; cations, anions.
Sample date: 7/15/98

Site 32 Gila River near Sanchez
D(7-28)6bb; Lat 32°51'33" (32.859) Lon 109°31'36" (109.527)
Gila River near Sanchez, north bank.
Sample: Gila River water
Analyses: S isotopes
Sample date: January, 1997
Analysis courtesy of University of Arizona

Site 33 Tenney #3 well cuttings
D(9-27)36cd; Lat 32°36'10" (32.603) Lon 109°32'18" (109.538)
Well cuttings from Tenney #3 oil exploration well (AZGS cuttings
Sample: gypsum/anhydrite from interval 1200-1300 feet
Analysis: S isotopes
Sample date: January, 1997
Analysis courtesy of University of Arizona

APPENDIX B

LOGS OF DRILL CUTTINGS IN AZGS R

Logged by RCH, 1996, 1998

The following are logs of drill cuttings in the Arizona Geological Surv
examined during this project. Not all wells sampled have logs. Althou
useful, these points need to be kept in mind:

- The cuttings generally reflect an average or composite sample over a
five to fifty feet. Any bedding or changes in lithology of a finer scale t
lost in the mix.
- The samples are commonly washed, or dipped from a container with
or all of the fines, and soluble minerals like salt, may have been remov
truly representative. Information on sampling methods are generally n
vary widely among drillers.
- Sloughing or caving of a layer can contaminate samples below that l
stem is raised above the layer or removed as in changing a bit. During
be dislodged by friction with the drill stem or by circulating fluids and
from the current depth.
- There is a physical limit on the size of particle that can make it into
some coarser material may not be represented.
- Commonly, samples are not taken over the entire depth of a hole, so
- Color of the cuttings is largely a judgment call and varies from pers
lighting conditions.
- Some cuttings were not logged if detailed logs were already availabl

Soto D-3-22-31c AZGS file #210; drawer B-10; 62 samples, 2

0 - 230	no samples
230 - 470	clay, silt; light brown; weakly consolidated; mod to s
480 - 510	1/2 light brown clay, silt; 1/2 white limestone
520 - 550	clay, silt; light red-brown; minor limestone; strong fi
560 - 870	white limestone, partly recrystalized to clear; minor

Appendix B

Whitmore #1 State D-7-25-6caa AZGS file # 4298; drawers P-14,

0 - 10	silt to fine sand; med-dark brown; strong fizz
20 - 40	med sand, mostly qtz; light brown
40 - 50	silt, minor sand; brown; strong fizz
50 - 60	fine sand, mostly qtz; light brown
60 - 70	silt; light gray; minor sand; very strong fizz
70 - 100	silt to fine sand; brown; very strong fizz
100 - 760	clay, silt; gray-brown, red-brown below 200'; strong fiz

No Name D-7-26-26aaa AZGS file # 1580; drawers D-47, 48; 79 s

0 - 250	no samples
250 - 260	sand to fine gravel (granitic/gneisses)
260 - 500	no samples
500 - 510	sand, fine to coarse (granitic/gneissic)
510 - 1035	no samples
1035 - 1080	sand, silt-clay; poor sample return
1080 - 1110	sand, clay-silt with clear and white gypsum; poor sample
1110 - 1570	gypsum (selenite common); minor clay, silt; minor sand
1570 - 2240	clay-silt; strong fizz; mod consolidated; brown-gray; gyp
	- salt crusts and disseminated salt crystals in clay 1895,
	- pure salt or clayey salt at 2075, 2090, 2105, 2120-215

Tenney #2 State (?) D-9-27-36dc AZGS file #2945; drawer I-45,46;

[Note: samples may be a composite from Tenney #1, #2, and #3

0 - 280	no samples
280 - 470	sand, fine gravel; gray
470 - 530	clay; gray
530 - 570	clay with abundant gypsum; gray

Appendix B

San Simon Fire Department D-13-31-31bba: Logs for this well are n
a substitute, the log for the San Simon School well, about a city block av
can be used to get an idea of the stratigraphy of the area. The samples fe
feet, whereas the Fire Department well is believed to be about 800 feet d
(San Simon School D-13-31-30c AZGS file #3972; drawer N-4; 2

0 - 400	no samples
400 - 500	sand, silt; brown
500 - 520	silt, fine sand; lt brown
520 - 540	sand, minor silt; lt brown
540 - 625	clay, silt, sand; brown

D.W. Conway D-14-31-34acc AZGS file #1029; Drawer D-48; 5

0 - 490	no samples
490 - 1000	tan silt-clay; minor sand; strong fizz

Well logs on the following pages are from Arizona Oil and Gas Conserva
AZGS.

Appendix B

Log of Gila Oil Syndicate's well in the SW¼NE¼ sec. 30, T
Ashurst

	Thickness	Depth	
	Feet	*Feet*	
Alluvium	50	50	Water.
Clay	380	430	
Sand	15	445	Flow of water.
White limestone	145	590	Salt water.
Limy shale	30	620	
Gray sand	80	700	Flow of water.
Limy shale	50	750	Salt water.
Blue shale	55	805	
Gravel	30	835	
Gray shale	200	1,035	
Brown shale	80	1,115	
Blue shale	20	1,135	
Brown shale	15	1,150	
Blue shale	15	1,165	
Brown shale	35	1,200	
Sandy shale	35	1,235	
Blue shale	20	1,255	
Brown shale	80	1,335	
Red shale	60	1,395	
Sandy shale	40	1,435	
Brown shale	80	1,515	
Brown sandstone	480	1,995	Flow of water.
Gravel	10	2,005	
Dark-brown shale	70	2,075	
Black sand	10	2,085	
Brown shale	125	2,210	
Dark-brown sandstone	70	2,280	
Gray shale	15	2,295	
Red shale	110	2,405	
Dark-brown sandstone	80	2,485	
Limestone	80	2,565	
Sandy limestone	30	2,595	
Blue shale	50	2,645	Bottom of well.

(Knechtel, 1938)

Appendix B (D-

Smithville Canal Co. well

Drilling Log of Water Well Drilled for the Smithvil
P. O. Box 266, Pima, Arizona. Located on Section 3
Range ~~23E~~ 22

Time - Stated August 3, 1957 Finished October

Hole Data - 15¼" hole from 0 to 1550
12¼" hole from 1550 to 2160

Casing Date - 12¼" I.D. x ¼" wall casing from 0 to
Cemented with 150 sax construction ce
by Haliburton Cement Co. 10¼" I.D. x
perforated liner from 1520 to 1905.
from 1905 to 2160.
Top of liner @ 1271' Bottom of lin

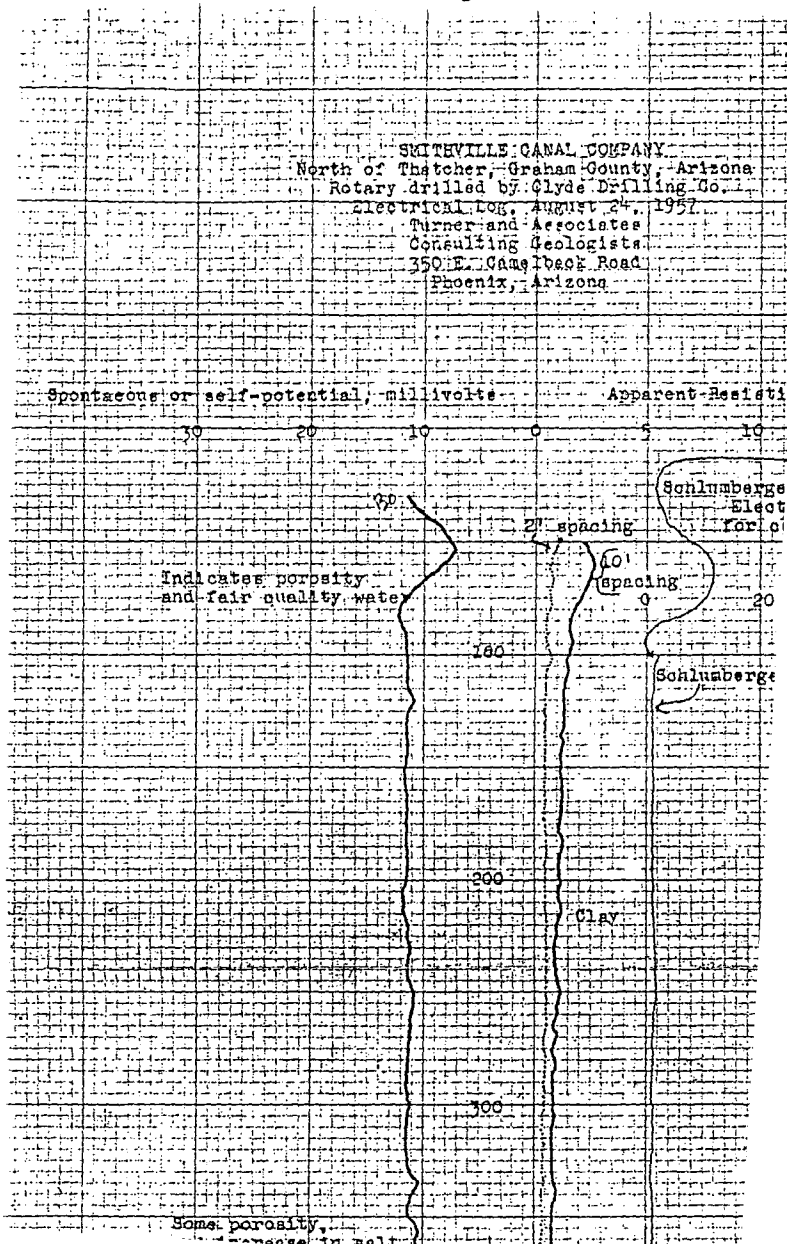
Perforation Data - Liner perforated with 4 rows of
torch cut perforations on 2' cen

***** DRILLING LOG *****

40	179		Silty clay
179	209		Soft clay
209	235		Hard clay
235	292		Sticky clay
292	440		Clay
440	507		Sticky clay
507	522		Hard clay
522	570		Sticky clay
570	715		Clay
715	754		Clay with streaks of shale
754	770		Soft sandyclay
770	881		Hard clay
881	897		Shale
897	911		Clay
911	1012		Clay with streaks of sand
1012	1044		Sandy shale
1044	1106		Shale with streaks of gravel
1106	1111		Hard cemented sand
1111	1198		Sandy shale
1198	1389		Sandy shale with streaks of ce
1398	1510		Cemented sandwith streaks of
1510	1561		Hard clay and shale
1561	1654		Sand and gravel with streaks
1654	1761		Course gravel with streaks of
1761	1812		Hard sandy shale with streaks
1812	1835		Hard sandy shale
1835	1918		Cemented sand
1918	1922		Soft bfeak
1922	1927	5'	Hard sandy shale
1927	1935	8	Soft break
1935	1938	3	Hard sand stone
1938	1945	7	Soft break "Lost some mud"
1945	1961	16	Hard sand stone
1961	1985	24	Sandy shale
1985	1996	11	Loose sand andggravel "Lost
1996	2001	5	Hard sand
2001	2025	24	Fine sand with streaks of s

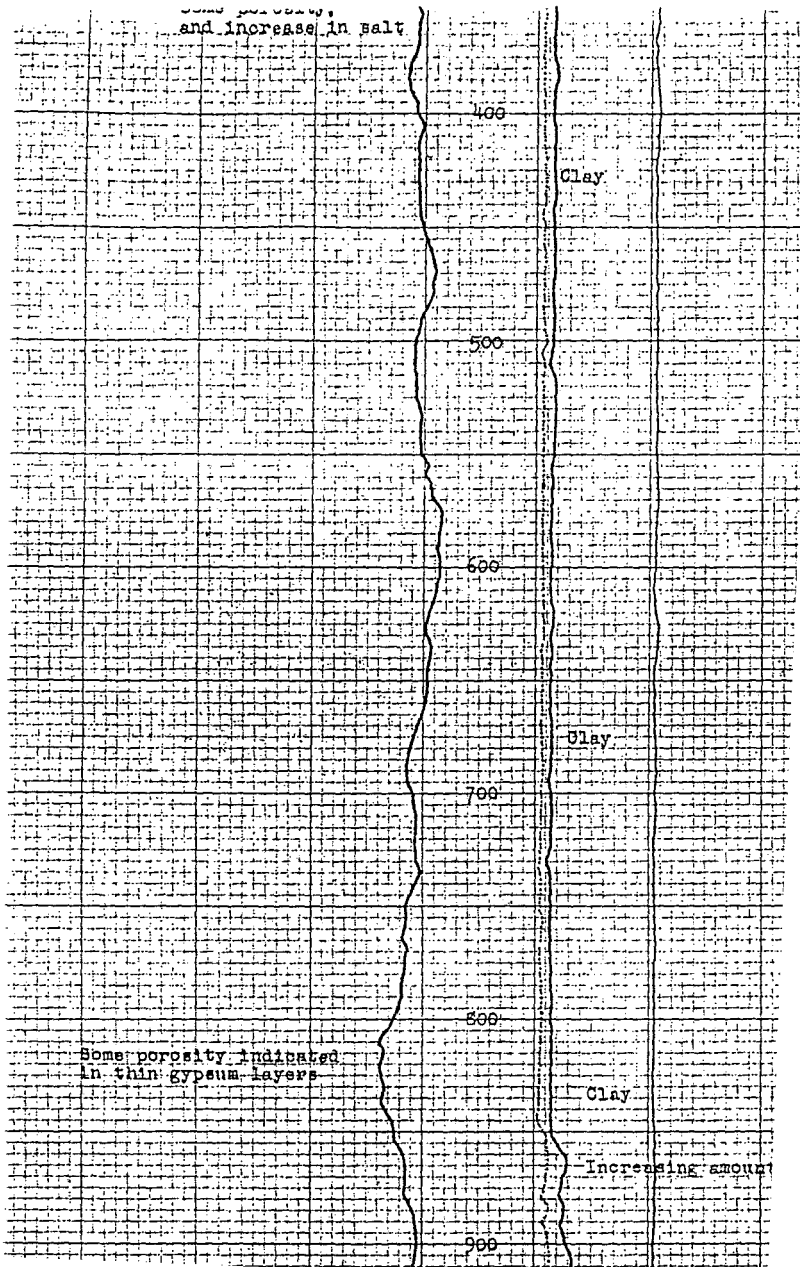
Appendix B

Electric Log, Smithville Canal Co. we



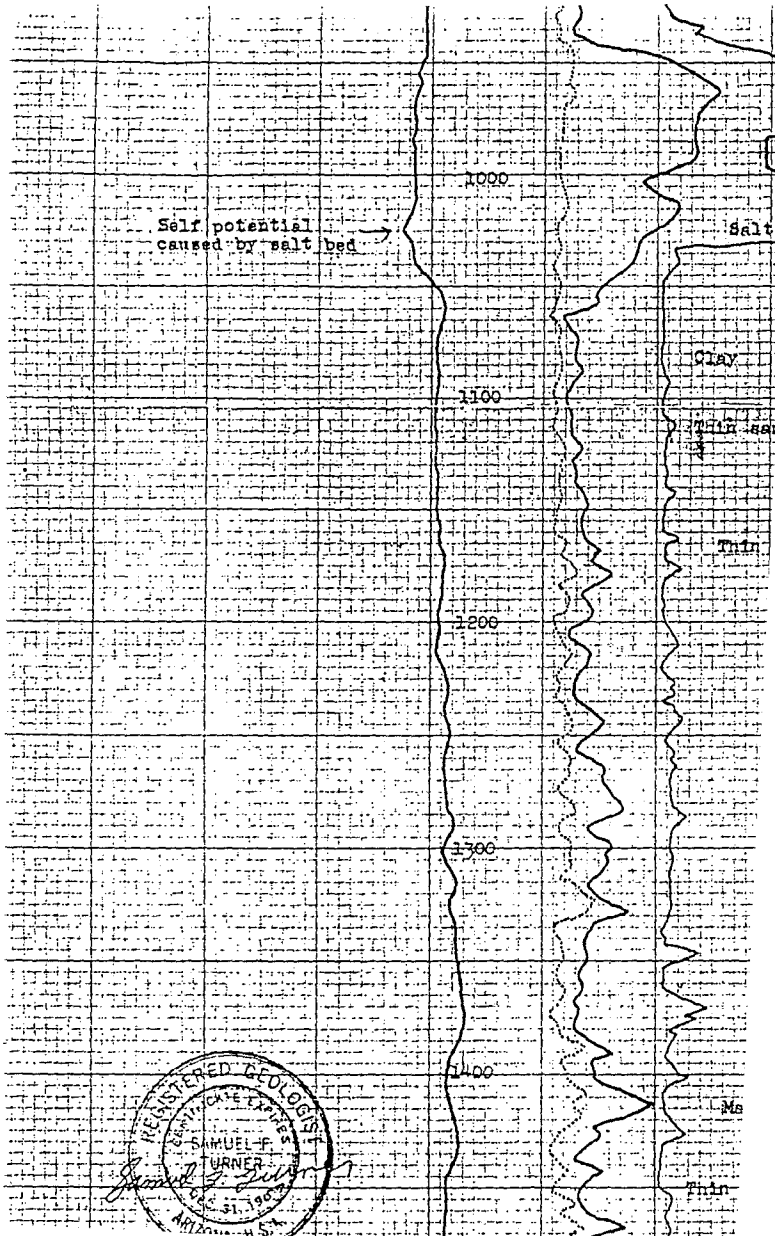
Appendix B

Electric Log, Smithville Canal Co. well, co



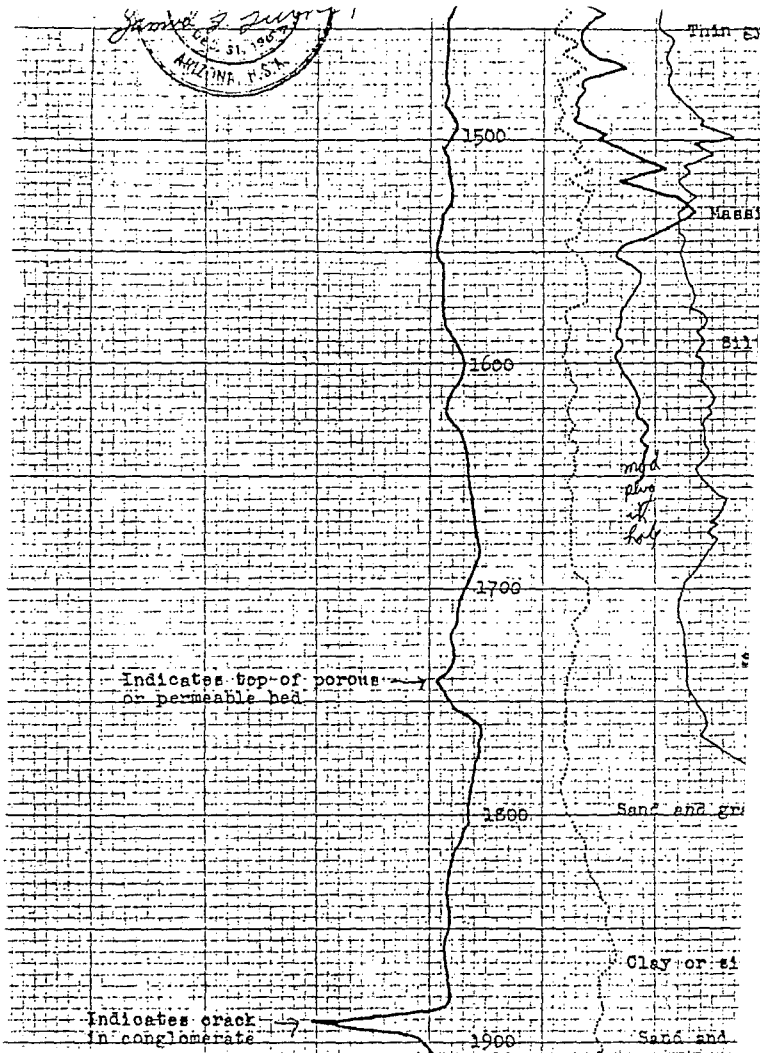
Appendix B

Electric Log, Smithville Canal Co. well, con



Appendix B

Electric Log, Smithville Canal Co. well,



Appendix B

Tenney # 3 well

AMERICAN STRATIGRAPHIC COMPANY

W

Log No D-4117 Net Footage 2290 ~~#~~ 541

State ARIZONA County GRAHAM

Well Name IVAN TENNEY NO.3 STATE

Spot SE SW Sec 36 T. 9S R 27E

Area (W)

Commenced April 29, 1970

Completed Jan. 29, 1971

Initial Production D & A

Elevation KB GR 3255

Producing Fm

Total Depth 3500

Producing Intervals -

Oldest Fm Tertiary Evaporites?

Casing 18" @ 623; 12 3/4" @ 1195; 8 5/8" @ 1450; 7" @ 2095

Mechanical Control Used to Adjust Lithology: No logs run

Sample Quality: Good, except where indicated

Remarks API No. No Mechanical Logs run

Studied by No. 9 6-74

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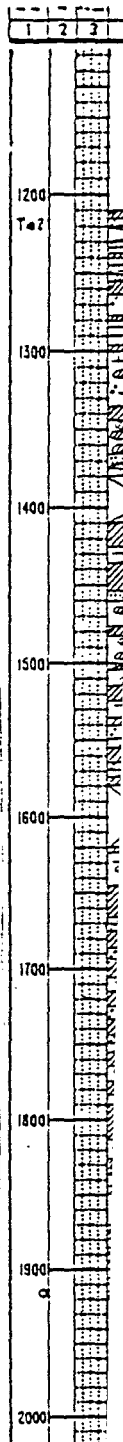
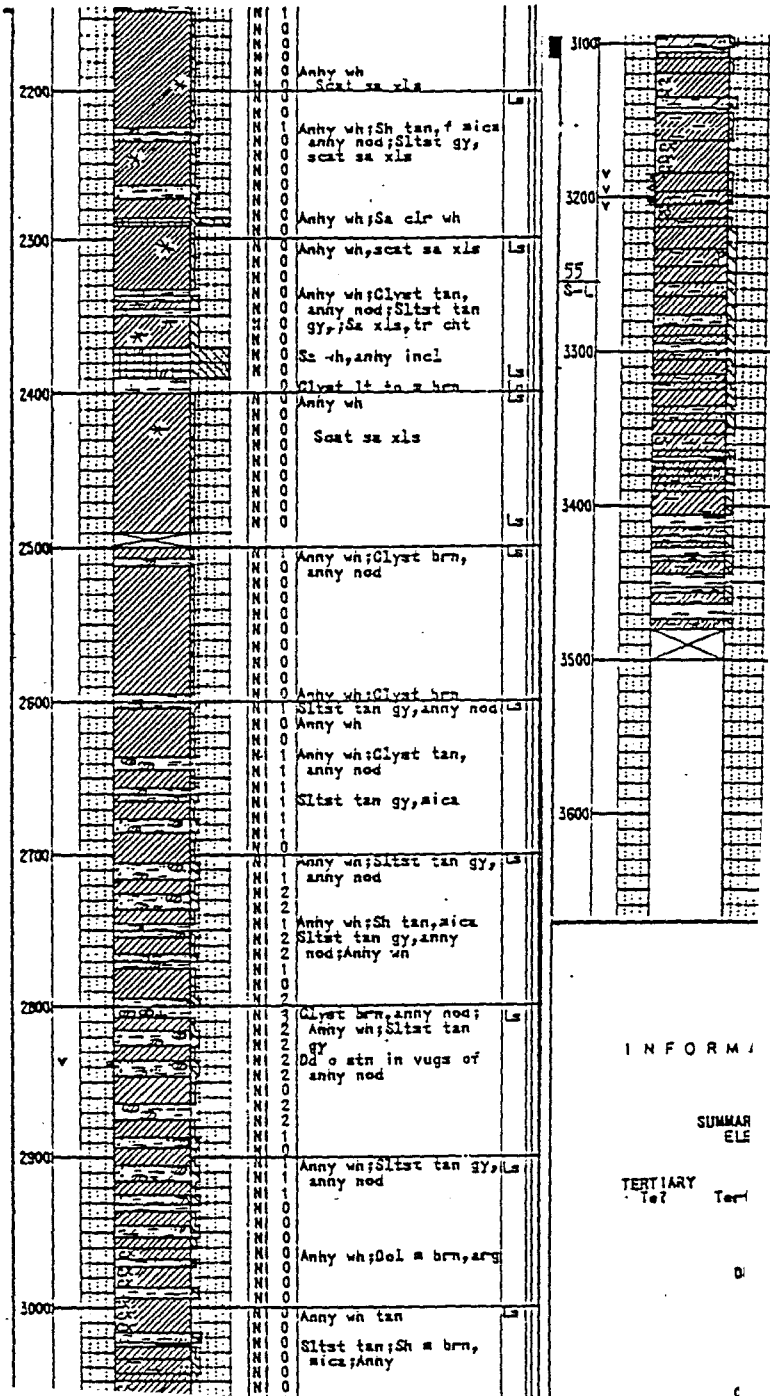
Spot SE SW Sec 36 T 9S R 27E Well Name IVAN TENNEY NO.3 STATE

Formation Tops Footage Thickness	Formation Tops Footage Depth	Lithology	Mineral Grain or Fossil Fragment Size	Cementing Agent Type	Percent of Fossil Work	Description	Suggested Environment
1	2	3	4	5	6	7	8



Appendix B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INFORM
SUMMAR
ELE
TERTIARY
Tet?

Appendix B

Whitmore #1 State (D-7-25-6cc

Professional Service

GOULDS Water Systems

JADCO
JIM ALLEN DRILLING CO.
P.O. Box 308 Safford, Arizona 85546 Phone:

DRILLING REPORT

Ralph Whitmore
206 College Ave.
Thatcher Az. 85552

WELL
Appro
On t

0 - 13	Sandy Fill	
13 - 16	Sand and Gravel	
16 - 25	Sand	
25 - 35	Brown Clay	
35 - 36	Red Clay	
36 - 44	Sand and Gravel	
44 - 55	Brown Clay	
55 - 80	Blueish Brown Clay	
80 - 82	Brown Clay	
82 - 96	Blueish Brown Clay	
96 - 105	Brown Clay	
105 - 111	Blueish Brown Clay	
111 - 1024	Red Clay	

There was also found layers of blue clay in the red
but they were so small that they were unable to be l

Appendix B

CORE LOG

Superior-Federal 63-15S
Sec. 15, T5S-R23E, Graham County, Arizona

Depth	Discription
0-5	Recent alluvium. (cutting spls.)
5-16	Clay, brown. (cutting spls.)
16-50	Clay & siltstone, brown, calcareous. (begi
50-52	Siltstone, light brown.
52-60	Clay & siltstone, chocolate brown, calcare
60-62	Sandstone, brown, medium grained, arkosic.
62-72	Siltstone & clay, choc. brown.
72-77	No recovery (prob. brown clay).
77-122	Clay, choc. brown.
122-122.2	Sandstone, tan, fine, arkosic.
122.2-141.7	Clay, slightly silty in part, choc. brown.
141.7-157	No recovery.
157-167	Clay, choc. brown (2ft. recovered).
167-172	No recovery (prob. brown clay).
172-202	Clay, choc. brown.
202-205	Sandstone, brown, fine, poorly consolidate
205-212	Clay, sandy to silty, brown.
212-214	Clay, choc. brown.
214-225	Clay, sl. sandy in part, choc. brown.
225-247	Clay, silty, brown.
247-259	Clay, brown, a few thin sandy stringers.
259-282	No recovery.
282-322	Clay, brown, a few thin sandy stringers.
322-334	Clay, choc. brown.
334-337.5	Clay, slightly sandy to silty, gray brown
337.5-338.4	Sandstone, fine, silty, gray-brown, iron
338.4-343	Clay, choc. brown, some slightly sandy.
343-353.5	Clay, choc. brown.
353.5-354	Siltstone, tan, crumbly.
354-356	Clay, choc. brown.
356-359	Mudstone, gray-brown to gray-green, sl. m
359-365	Clay, choc. brown.
365-375	Clay, silty, choc. brown.
375-376	Sandstone & clay, ss. is gray-brown, very
376-389.5	Clay, choc. brown.
389.5-419	Clay, silty to sandy, calcareous.
419-421	Silty sandstone, brown, fine, poorly cons

Appendix B

Ivan Tenney #3 State
(driller's log)

DETAIL OF FORMATIONS PENETRATED

Formation	Top	Bottom	Deso
Sandy soil	0	5	
Sand & clay	5	120	
Sand	120	240	surface water.
Gray-	240	260	
Brown clay & sand	260	400	
Blue clay-	400	1200	
Blue clay & anhy-	1200	1200	- small amount
Anhy & Blue clay	1200	1410	
Anhy	1410	1525	
Brown shale & anhy	1525	1675	
Anhy-	1675	1660	
Brown shale & anhy	1660	1825	
Brown sticky clay	1825	1895	
Gray shale & anhy	1895	2140	
Anhy & salt	2140	2475	
Anhy-	2475	2685	
Anhy & shale	2685	2750	
Lime	2750	2795	
Lime anhy & shale	2795	3150	
Anhy	3150	3200	
Anhy & Brown shale	3200	3500	T.D.

Appendix B

Depth	Discription
494.5-496.5	Clay, sandy to silty, calc.
496.5-499.5	Mudstone, brown, calc., slightly micaceo
499.5-519	Silty clay, brown, calc.; grades in minc
519-529	Shale, brown, calc.; a few thin silty & greater degree of concolidation than mat
529-531	Shale, light brown, calc., silty, micace
531-537	Clay, brown, calc.
537-539	Sandy clay, calc., micaceous.
539-541	Silty sandstone, brown, fine, micaceous,
541-544.5	Silty clay, brown calc.
544.5-546	Mudstone, green, calc.
546-548.5	Shale, brown, calc.
548.5-550.5	Sandstone, brown, very fine, silty, calc
550.5-552	Clay, brown, silty, calc.
552-584	Siltstone & shale, brown, calc.; grades sandstone; slight salt crust on core at
584-610	Shale & clay, brown, calc.; a few string fine sandstone.
610-617	Siltstone & fine sandstone, brown, calc.
617-620	Clay, brown.
620-622	Sandstone, fine, silty, soft.
622-630	Siltstone, grades to shale, calc.; sligt
630-631.2	Sandstone, very fine, silty, calc., soft
631.2-641	Clay & shale, brown, calc., some slightl
641-644	Siltstone & sandstone, soft, calc.
644-667	Shale & clay, sandy in part, brown, cal
667-669	Shale, red-brown, hard, calc.
669-678	Clay & shale, brown, calc.
678-688	Siltstone, brown, calc., soft (only 1 f
688-696.5	Clay, brown, calc.
696.5-700	Siltstone, gray-brown, calc., fairly ha
	(End of NX core; beginning of BX
700-700.3	Sandstone, very fine, brown.
700.3-712	Siltstone & silty shale, brown, calc.,
712-722	No recovery.
722-762	Shale & siltstone, brown, calc., slight of fine sandstone at 742.
762-769	Sandstone, brown, fine to silty, slight (3ft. recovered).
769-781	Shale & siltstone, brown, calc., micace

Appendix B

Depth	Discription
852-854.7	Shale, brown, calc.
854.7-862	Silty sandstone & siltstone, brown with bla inclusions; cross-bedded, calc., micaceous
862-872	No recovery.
872-927.5	Shale & minor silty shale, brown, calc., sl thin beds (up to 1 ft. thick) of fine brown containing carbonaceous material.
927.5-929.7	Shale, brown to gray, calc.
929.7-932.7	Shale, light gray-green, very calc., contai
932.7-936.2	Shale, brown, calc., fairly hard.
936.2-942	Shale & clay, brown, calc., brumbled.
942-946.5	Shale, brown, calc., fairly hard, sl. silty
946.5-951	Shale, brown, calc., inclusions of white li in abundance towards base.
951-952	Limestone, white, hard vugular
952-960	Limestone & shale; the ls. is vuggy and occ and inclusions in the brown shale.
960-962	Limestone, argillaceous, gray.
962-968	Shale, very calc., gray-brown to brown; con of $CaCO_3$.
968-971.5	Shale, gray, very calc., slightly silty in
971.5-985	Shale, brown, abundant small inclusions & t white limestone.
985-987	Sandstone, fine, porous, calc; interbedded
987-999.5	Limestone, argillaceous, white, very vugula bedded brown shale & clay.
X 999.5-1049	Limestone, white, honeycombed & vugular; vu crystal growth; minor stringers of brown to a little intermixed gypsum.
1049-1070	Limestone, white, vugular, intermixed gray (1/8" to 4") beds of gray, non-calcareous s
1070-1072	Argillaceous limestone & very calc. gray cl powdery $CaCO_3$.
1072-1072.5	Limestone, white, fine crystaline, hard, sl
1072.5-1075.5	Shale, gray to dark gray; a few thin white amounts of a green mineral.
1075.5-1078	Limestone, white, vuggular; large admixture
1078-1097	Limestone & shale; shale is gray to dark gr limestone occurs in numbrous thin stringers gypsum noted at 1078' and 1093.5'.
1097-1120	Shale, gray to brown, waxy in part; abundar $CaCO_3$ and some gypsum. Core suggests beds

Appendix B

Depth	Discription
1141-1142	Limestone, white, soft, powdery, possibly gyps admixture of dark brown clay.
1142-1144	Limestone, white, numerous irregular stringers
1144-1149	Shale, dark brown; numerous thin stringers of Beds have apparent dip of 5°± .
1149-1154	Shale & limestone, shale is waxy, brown to gra stone, hard to soft.
1154-1162	Shale with laminations of white limestone; sha gray, waxy in part; trace of green mineral at
1162-1172	Shale & white limestone; shale is green & gray shale at 1168.5'; green mineral in ls. at 1167
1172-1182	Shale, green to gray, hard, sl. silty in part; thin white calcareous stringers.
1182-1187	Shale, green, waxy, occasional thin white stri limestone & argillaceous limestone.
1187-1188	Clay, green, waxy.
1188-1189	Shale, green, brown & gray.
1189-1190	Limestone, white, sl. vuggy; minor gray shale.
1190-1198	Shale, brown, gray & gray-green, hard, sl. mic thin calcareous stringers.
1198-1199	Clay, brown, & white limestone.
1199-1205	Shale, dark green, gray, gray-brown; interbedd stringers.
1205-1206	Siltstone & silty shale, gray-green micaceous.
1206-1208	Shale & siltstone green to dark gray; a few ca
1208-1212	Shale & clay, green & very dark green; some ca
1212-1224	Shale & argillaceous limestone; shale is green
1224-1231.4	Shale, gray, very sl. calc., waxy in part, sl. part; occasional light gray calc. bands.
1231.4-1237	Shale, gray, green & brown; interbedded thin l
1237-1246	Shale, brown to olive green; interbedded limes
1246-1258	Shale, gray, occasional light gray to white ca 1 inch of vuggy white limestone at 1246'.
1258-1260	Limestone, white, intermixed with green shale;
1260-1270.5	Shale, gray-brown, gray, gray-green; a few ligh stringers; some gypsum stringers at 1270'.
1270.5-1271.5	Limestone, white, intermixed green shale.
1271.5-1274	Shale, gray, calc., crumbled core.
1274-1281	Shale, green to gray; a few thin calc. streaks
1281-1285	Shale, black & gray-green.
1285-1287	Shale, gray, slightly micaceous.