

CHEMICAL QUALITY OF WATER IN RELATION TO
WATER USE AND BASIN CHARACTERISTICS,
TUCSON BASIN, ARIZONA

by

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A Thesis Submitted to the Faculty of the
GRADUATE COMMITTEE ON HYDROLOGY
In Partial Fulfillment of the Requirements
For the Degree of
MASTER OF SCIENCE
In the Graduate College
THE UNIVERSITY OF ARIZONA

1966

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ACKNOWLEDGMENTS

The writer wishes to thank Dr. E. S. Simpson, who suggested the thesis topic, sought financial assistance for it, and directed the study in its early stages. To Dr. J. W. Harshbarger, who directed the thesis during Dr. Simpson's absence, I am especially grateful. I also wish to thank Dr. G. R. Dutt, Department of Agricultural Chemistry, and Mr. J. G. Ferris, U.S. Geological Survey, for their very helpful criticisms and suggestions.

I am very much indebted to Mr. H. C. Schwalen of the Agricultural Engineering Department for so generously providing the data, maps, and guidance.

This study was conducted pursuant to a Graduate Research Assistanceship awarded for the spring semester, 1965.

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ABSTRACT

The areal distribution of the chemical quality of the Tucson basin ground water has been mapped. The basin was divided into five study sections, according to the relative concentrations of the chemical ions studied. The five chemical quality sections are as follows:

1. Canada del Oro; Catalina, Tanque Verde, and Rincon Mountain foothills and extension into the northeast half of the basin—low concentrations except for Tanque Verde anomaly.
2. Tucson-Benson Highway area extending from east of Vail northwest to the Santa Cruz River—moderately high concentrations.
3. Foothills of the Santa Rita and Sierrita Mountains extending to the Santa Cruz bottom land—moderate concentrations.
4. The Santa Cruz bottom land from Arivaca to Rillito—moderately high to high concentrations.

5. The Tucson Mountain foothills extending to the Santa Cruz bottom land—low-moderate to moderately high concentrations.

The water quality of these sections is correlated to the geology of the basin, according to the principles set forth in the section on the "Geochemistry of Ground Water."

The effects of man's lowering of the water table are not as yet evidenced in the chemistry of the ground water.

In conclusion, the part of the Rillito Creek drainage basin in the northeast Tucson basin fill is found to have both the best water quality and the highest specific capacities of the entire basin. Sub-surface storage and impermeable boundary limitations may restrict further development of this area, however. Artificial recharge into this aquifer, from Rillito Creek, could alleviate the quantity problems.

INTRODUCTION

Statement of Problem

Data on the chemistry of ground water in the Tucson basin have been accumulating for more than 70 years (Collingwood, 1891). Although various studies have been made to systematize and interpret the data (Schwalen and Shaw, 1957; Smith and others, 1963, 1964), the relation of spatial and temporal changes in ground-water chemistry to basin geology and water use is still not fully understood.

The purpose of this thesis is to study the ground water of the basin in the light of its chemical properties. A relation between the ground-water chemistry and the geology of the basin and to water use within the basin will then be developed.

Location and Extent of the Study Area

The study area for this thesis is that part of the upper Santa Cruz River basin lying between the towns of Rillito and Arivaca Junction. The political boundaries of the study area are shown on figure 6. The size and location of the study area in the State of Arizona are shown on figure 1. The study area primarily covers the lowlands of

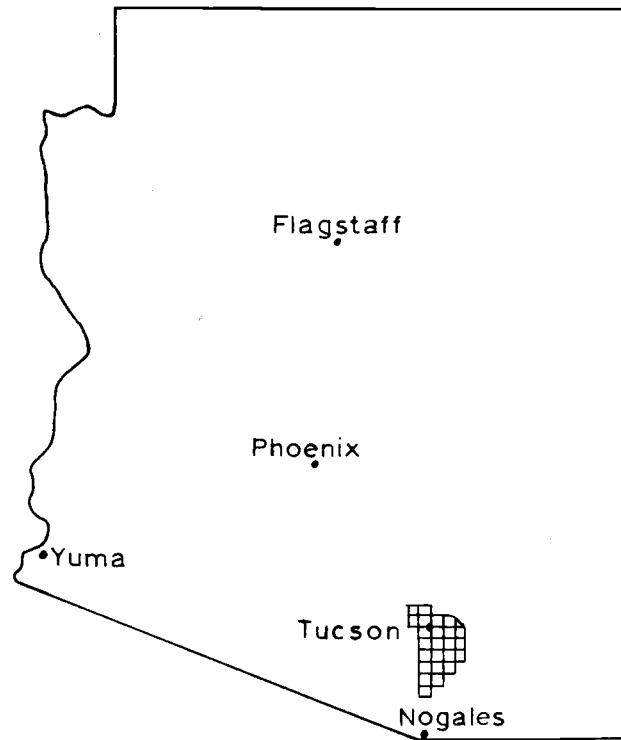


Fig. 1, -- Map Showing Location of the Study Area

the basin. Some of the mountainous regions are included in the peripheral townships.

Methods of Study

The investigation of the problem has been carried out in three basic steps: (1) a literature survey; (2) a presentation of data; and (3) an interpretation of the data.

The literature survey was conducted to study the use of geochemical methods in studying ground-water reservoirs. Of the methods studied, maps of chemical isograms, Collin's comparative table, the Piper trilinear diagram, and frequency diagrams were found to be the most useful in presenting and interpreting the data.

After a critical review of the data and the application of the chemical methods mentioned, it was evident that the quality of the ground water is controlled by geological features of the basin. For this reason, it will not be possible to study the water chemistry brought about by the progressive chemical changes of a water within a single aquifer.

In view of the importance of the geological controls, the mapping of chemical isograms is found to be the most significant method of interpretation. Therefore, this study has been almost entirely concerned with the areal mapping of the most significant chemical parameters.

All wells used in this study penetrate only the upper unconfined aquifer. The well casings are perforated for the full saturated thickness of the aquifer. The more permeable strata provide most of the water pumped. Thus, the chemistry of the water sample is indicative of these permeable zones. The areal distribution of the water quality is then a composite representation of the water quality for the several water-bearing zones penetrated by the wells.

The graphical and tabular methods dealt primarily with the progressive changes of ground-water chemistry within a single aquifer. Because of the complexity of the lithology of the unconfined aquifer, there is little opportunity for the ground water to change progressively without these effects being masked by the geological influences.

Of the graphical and tabular methods of analysis that have been reviewed, the Piper trilinear diagram was the most enlightening. The Piper diagram shows both a good overall picture of the quality of water in the basin and provides a means for classifying ground water of different chemical composition.

GEOLOGY

A brief description of the basin geology has been taken from publications by Schwalen and Shaw (1957), The Rillito Creek Hydrologic Research Committee (1959), and G. E. P. Smith (1938).

The upper Santa Cruz basin is a part of the Desert Region of the Basin and Range physiographic province of the southwestern United States. It is typified by north-south-trending mountain ranges and valleys.

Major Rock Units

The Tortolita, Catalina, Tanque Verde, and Rincon Mountains border the northern and eastern sides of the basin. Geologically, they are a crystalline complex of banded granitic gneiss, granite, and smaller bodies of sedimentary rocks.

The Tucson Mountains border the western side of the study area. These rocks are of a volcanic nature and consist of rhyolites, andesites, and basalts. Some sedimentary rocks cover these volcanics. The southwestern and southeastern parts of the study area are bordered by the Sierrita and Santa Rita Mountains, respectively. They are

primarily composed of volcanics; however, many parts are covered with sedimentary rocks.

At approximately the same time the block faulting was taking place and forming the basin, volcanic extrusions of basalt also occurred to a minor extent. Some typical examples of this activity are "A" Mountain, Tumamoc Hill, Sahuarita Butte, and the Black Hills.

After and during this period of mountain building, a long period of erosion resulted. The basin was filled with vast quantities of alluvium from the surrounding mountains. Probably the earliest of these basin deposits were the Pantano beds. They consist of several thousand feet of tightly cemented conglomerate, sandstone, siltstone, and claystone. The Pantano beds crop out along the Catalina Mountains north of Rillito Creek, in the eastern part of Tanque Verde Creek, and in the Cienega Gap area south of the Rincon Mountains. Also, probable outcrops are found in the southern part of the Tucson Mountains and on the eastern slopes of the Sierrita Mountains.

Overlying the older Pantano deposits is about 500 to more than 1,000 feet of gravel, sand, silt, and clay. This material extends to the surface and is known as the basin fill. At the time of maximum filling, the basin was typified by comparatively smooth slopes extending from the base of the mountains into the valley trough. The majority of the basin fill was contributed by the higher more massive mountain ranges to the north and east of the basin and by through-flowing streams from

the south and east. Flood-plain deposition was the most effective filling mechanism; however, some fine-grained material was probably deposited in localized ephemeral lakes. The greater mass of detrital outwash from the east caused the Santa Cruz River to move west of the axis of the valley.

The alluvial deposits constitute the major storage medium for ground water in the basin. For the most part, the wells are in the upper 500 feet of basin fill. The permeability, porosity, and lithology of this material is quite variable both vertically and horizontally. Only recently (since 1961) have some exploratory wells been drilled to any great depth. These wells were constructed by the Tucson Gas and Electric Co. and are located in secs. 2 and 3, T. 15 S., R. 14 E.

The deep wells intersected the underlying Pantano formation at depths of about 2,000 to 2,500 feet (Ganus, 1965). The artesian water yielded by the older confined formations was very high in total soluble salts and in fluoride content. The quality of the water from these deep wells will be discussed only in the light of how it might affect the quality of the water in the basin fill. There are not sufficient data to undertake a study of the deep Pantano aquifers at this time. Therefore, this thesis can only investigate the geochemistry of the ground water in the upper 500 feet of alluvium.

Another component of the basin lithology is the alluvial-fan deposits along the mountain fronts and at the mouths of the canyons.

Although a minor part of the basin lithology, these deposits are thought to be important channels of mountain runoff to the ground-water reservoir. Some canyons important in this respect are those of Rincon Creek, Tanque Verde Creek, Sabino Creek, and Canada del Oro. The alluvial-fan material is not directly connected with the basin fill; however, the fans at the mouths of the canyons probably do serve to channel water into the flood-plain deposits, which in turn make a direct connection with the basin fill.

The flood-plain deposits are the most recent, in fact current, part of the basin geology. They are defined as the material underlying the channels and flood plains of today's existing stream channels. The sands, silts, and gravels that make up the deposits have neither been cemented nor compacted to any appreciable degree. They range in depth from tens to as much as 100 or 200 feet below the surface.

The wells in these flood-plain deposits are much more productive than those in the extensive basin fill. They rely upon direct recharge from the streams, and correspondingly the water level fluctuates with the amount of precipitation and runoff.

Structure

The mountain ranges and valleys in this area are the result of the block faulting typical of the Basin and Range province. The Santa Cruz River basin represents a depressed block between the surrounding

mountains, which were uplifted. The boundary faults of the basin trend in north-south and east-west directions.

These boundary faults are particularly noticeable along the southern face of the Catalina Mountains. Here there is a distinct fault between the Pantano beds of the basin and the mountainous crystalline complex. The angulate pattern of the boundary faults and the tilted, fractured, and faulted Pantano beds indicate that the block mountain topography could extend into the basin. Such topography on the valley floor would be on a much smaller scale than the surrounding mountains and would probably have been modified by erosion.

HYDROLOGY

Surface Water

Drainage Network

The Santa Cruz River is the master stream of the Tucson basin. Its source is in the San Raphael Valley 22 miles east of Nogales, Ariz. The river flows south into Mexico, turns west, and loops back into Arizona crossing the border just east of Nogales. From Nogales the Santa Cruz River flows north and enters the study area at Arivaca Junction in the southwest corner of T. 19 S., R. 13 E. It continues to flow north along the western edge of the Tucson basin and then flows out of the study area at Rillito in the northwest corner of T. 12 S., R. 12 E.

Rillito Creek is the major tributary to the Santa Cruz River in the study area. Rillito Creek and its tributaries drain the southern slopes of the Catalina Mountains, the western slopes of the Tanque Verde Mountains, the western and southern slopes of the Rincon Mountains, and the Cienega Creek valley to the east of the study area.

Precipitation

The floor of the basin receives about 10 inches of rain in the low north to 14 inches in the high south. The surrounding mountains receive much more rain with annual averages greater than 30 inches near the Catalina peaks. As is to be expected in a semiarid climate, the rainfall is extremely variable from one year to the next.

The study area receives about 50 percent of its total annual precipitation during the summer months of July, August, and September. This rainfall is brought about by convective mechanisms that cool the moist subtropical air carried north by anticyclonic circulation. The resultant rainfall comes in heavy thundershowers that are very localized.

The remaining half of the rainfall comes with the less intense and widespread winter storms. These storms occur randomly throughout the rest of the year except during the dry spring months. The winter rainfall is brought about by the westward movement of cyclonic storms from the Pacific Ocean (Schwalen and Shaw, 1957).

Runoff

All streams in this semiarid climate are intermittent. Most of the surface flow occurs during the winter and summer rainy seasons. The average annual discharge for the Santa Cruz River gaged on W.

Congress St., Tucson, was 15,560 acre-feet for the years 1906 to 1954. For Rillito Creek, 4-3/4 miles above its confluence with the Santa Cruz River, the average annual discharge was 12,950 acre-feet for the years 1909 to 1954 (Schwalen and Shaw, 1957).

The majority of the precipitation on the floor of the basin is probably lost to evaporation. In the mountain areas, the heavier rains, steep slopes, etc. produce substantial amounts of runoff. This runoff eventually flows to the sandy stream channels of the bottom land where it is recharged to the water table. The evaporation losses from the mountain runoff are much less than from the runoff on the floor of the basin.

Quality

Surface water is generally low in total dissolved solids and relatively soft. There are few detailed chemical analyses for surface water. One interesting quality section where surface flow has been analyzed is the Cienega Creek near Vail. Here the flow of Cienega Creek into Pantano Wash is quite high in total soluble salts and in hardness. This is effluent ground water from limestone and gypsum terrain and will be discussed later in this text.

The amount of suspended sediment in the runoff is an important factor governing its rate of recharge to the ground-water reservoir. The suspended sediment will clog the infiltration pores in the

soil. Thus, the comparatively silt-free spring runoff from snowmelt is most susceptible to infiltration and eventual percolation to the water table. The intense summer storms erode the channel beds, sides, and surrounding terrain and carry large quantities of suspended sediment. Water from these storms is not as effective a recharge mechanism as the winter runoff.

Ground Water

The inhabitants of the Tucson basin depend wholly upon underground water supplies. The future development of such a semiarid region will depend on the availability of this resource. Therefore, it is essential that as many characteristics of the ground-water reservoir be known as possible. This will enable better planning for maximum practical use of this water supply. It is hoped that the chemical study herein investigated will aid in developing a master plan for the maximum utilization of this precious resource.

A review of some of the important characteristics of the basin's ground water that have been previously studied are given as follows.

Occurrence

The alluvial fill is the principal aquifer of the basin. The flood-plain deposits along the present stream channels provide the most

permeable aquifers. This aquifer is of limited extent, however, and has been almost completely dewatered in most parts of the basin.

Neither the crystalline nor the Pantano formations provide an aquifer of any substantial yield.

Recharge and Movement

Recharge of the ground-water reservoir is brought about in several different ways. Schwalen and Shaw (1957) outlined them to be the following: (1) direct infiltration from rainfall; (2) seepage from stream channels; (3) seepage from irrigated fields; and (4) sewage effluent.

The seepage from stream channels is by far the most important recharge mechanism. It is possible that some significant recharge is taking place in the alluvial fans along the mountain fronts and at the mouths of the larger canyons. Direct recharge to the water table from precipitation on the valley floor is not very important.

The contribution of irrigation waters and sewage effluent to the water table is substantial. However, this is merely a recirculation of water that has been previously pumped from the ground. It is thought that about 25 percent of the irrigation water percolates back to the water table (Schwalen and Shaw, 1957). This process, although not a real part of the recharge, is important to the chemistry of the surface and ground waters.

The major flow of ground water into the study area is in the Santa Cruz River bottom lands south of Arivaca Junction. In the study area, the movement of ground water in these bottom lands is generally parallel to the river channel. Another major flow of ground water in the study area is in the bottom lands of Rillito Creek. This flow is also parallel to the stream channel. Ground-water movement in the central part of the basin to the east of the Santa Cruz River and south of Rillito Creek is generally from the southeast to the northwest.

All the ground water leaving the basin flows through the relatively narrow valley between the Tucson and Catalina Mountains. At the northern tip of the Tucson Mountains near the town of Rillito, the ground-water flow turns and flows due west.

Water-Table Elevations and Changes

The water table in the Tucson basin ranges from about 10 feet to 600 feet below the land surface. Since pumping started in the 1900's, the water table has been dropping generally throughout the basin. Ganus (1965) has shown the displacement of water-table contour lines over a period of 17 years from 1947 to 1964. It is evident that this trend will continue unless major changes in the well field pumping are made.

Specific Capacities of Wells

The specific capacities of wells pumping in the Tucson basin are highest—200 gpm (gallons per minute) per foot of drawdown—in northeast Tucson near Speedway Blvd. and Craycroft Road and along the Santa Cruz bottom land west of Tucson. It is also these highly productive areas that are experiencing the greatest amount of dewatering. During the period 1947 to 1964, the water table has dropped more than 60 feet in the area just south of the intersection of 22nd St. and Wilmont Road, 50 feet at Speedway Blvd. and Wilmont Road, and 40 to 50 feet along the Santa Cruz bottom land west of Tucson. "The 1947-1964 dewatering has been found to be the composite result of four factors: the location of pumping well density, the capacity of each pumping well or well field, the lithology of the sediments yielding water, and any permeable or impermeable boundaries that exist in the basin" (Ganus, 1965).

GEOCHEMISTRY OF GROUND WATER

The geochemistry of ground water has probably been the least studied facet of the geochemical cycle. The effect of circulation controls on the concentration and distribution of chemical constituents within a ground-water reservoir are very important, particularly in arid regions. A knowledge of the laws of ground-water geochemistry provides a means by which a better understanding of the occurrence and movement of the water can be gained.

The most intensive study of ground-water chemistry has probably been done by Schoeller, professor of hydrogeology and geology in the Bordeaux faculty of science. Most of the material on ground-water chemistry in this thesis has been taken from the English translation of his UNESCO publication (1959). This publication contains an excellent bibliography of work done in ground-water geochemistry. Another important source of information is a U.S. Government publication by Hem (1959). This too contains an excellent bibliography.

Mechanisms of the Chemical Buildup of Ground Water

In order to define the sources of the chemical constituents of ground water a knowledge of how ground water acquires its chemical

composition and what changes may come about in it is necessary.

Water starts to undergo chemical changes from the minute it occurs as raindrops in the atmosphere. The raindrops combine with gases and dust in the atmosphere. By the time they reach the earth, they contain a variety of impurities. These impurities consist mainly of oxygen, nitrogen, carbon dioxide, and mineral matter. These atmospheric contributions are not as important as the chemical constituents provided by the soil of the land surface.

There is no doubt that the main part of the chemical constituents of the ground water are obtained from the top soil. As stated by Schoeller (1959): "...the phenomena of mineralization are complex, for in the zone of evapotranspiration downward water movement towards the aquifer is the result of infiltration and evapotranspiration and it is the resultant of these respective associated chemical phenomena—dissolution and precipitation—which determines the composition of the water of infiltration finally reaching the aquifer." The evapotranspiration and associated precipitation processes are especially prevalent in the upper layers of soil in arid regions.

The dissolution of the soluble products of rock weathering and decomposition in the top soil supply almost all the chemical constituents. There is generally little chance of many changes taking place between the soil water zone and the zone of saturation. The lack of chemical change is due to the scarcity of soluble products of rock weathering in

this zone. Chemical changes could take place, however, if soluble rock, such as gypsum, is encountered or if ion exchange mechanisms prevail.

The water's next chemical change will probably be undergone in the ground-water reservoir. Here the movement is usually slow, and the water can attack the aquifer.

Upon first entering the soil, the water picks up nitrogen, helium, hydrogen, carbon dioxide, ammonia, and hydrogen sulfide gases. CO_2 and H_2S are the most soluble of the gases in the soil air. The solution of these gases in the infiltrating water forms acids, which are the most effective agents of dissolution. Chemical actions in the form of hydration, hydrolysis, oxidation, and chemical attack are the most important mechanisms of dissolution in the soil and the zone of decomposition.

Hydration is that process by which anions and cations in solution attract the positive and negative ends of adjacent water molecules, respectively. The number of the water molecules binding the ions is dependent on the size of the ions. Hydration of calcium and magnesium sulfates would be a typical reaction in the Tucson basin.

Hydrolysis refers to the general chemical reactions in which a molecule or ion is converted into two or more molecules or ions by reaction with the water. Reactions of this nature with silicates (feldspars) are important in ground water.

Oxidation is the chemical process in which molecules lose electrons. Sulfide oxidation to sulfate is important here. The oxidation is a maximum in the upper top soil near the atmosphere where the oxygen is derived. If the water table should come to the surface, however, then a reducing environment may be established.

The principal agent of chemical attack on minerals is carbonic acid. Almost all the CO_2 in ground water is gas evolved from biological and chemical combustion of organic matter in the soil, respiration of plant roots, and from the many living organisms in the top soil. Solution of the CO_2 gas in the atmosphere by raindrops is of minor importance. The partial pressure of CO_2 in the atmosphere is 0.0003 atmospheres, while in the top soil pressures range from 0.001 to 0.01 atmospheres (Schoeller, 1959).

The principal reactions governing the dissolution of limestones by carbonic acid are as follows:



Where K_1 and K_2 are the first and second dissociation constants of carbonic acid and K_c is the solubility product of limestone, CaCO_3 .

Combining these three expressions, a general expression for the commonly analyzed ions is obtained. This equation along with Henry's law for the solubility of a gas in a liquid are shown below.

$$[\text{H}_2\text{CO}_3] = \frac{K_2}{K_1 K_c} [\text{HCO}_3^-]^2 [\text{Ca}^{++}]$$

$$\delta = \frac{22.4}{\alpha} [\text{H}_2\text{CO}_3]$$

Where δ is the partial pressure of CO_2 , α is the coefficient of dissolution of free CO_2 in water, and $[\text{H}_2\text{CO}_3]$ is the concentration in mols of free CO_2 dissolved in the water in equilibrium with the solution of HCO_3^- and Ca^{++} .

It is obvious from the latter equation that the concentration of carbonic acid varies directly with the partial pressure of free CO_2 . Likewise, the ability of the water to dissolve carbonates and other rocks is directly proportional to the strength of the carbonic acid. If the CO_2 pressure is lowered because of a decrease in hydrostatic pressure, exposure to the atmosphere, or an increase in temperature, then CaCO_3 will precipitate out.

Silicates are also attacked by the action of carbonic acid. At first there is a true dissolution of silicates, but the main factor determining the rate of chemical attack is the acidity or alkalinity of the water. As we have already seen, the acidity of the water is largely

controlled by solution of CO_2 . Generally, when the solution is acidic, kaolinite is formed, and when the solution is basic, montmorillonite or illites are formed. Silicates release potassium, sodium, and calcium ions and molecular silica and very little chloride.

Other acids are developed in the soil by the oxidation of sulfides—sulfuric acid—and by nitrification processes—nitric acid. The soil also yields some organic acids.

Water from the Principal Types of Rocks

The nature and amount of the chemical constituents present in a ground water are directly related to the type of rocks the water has traveled through. In this section eight major rock types and their corresponding chemistry reached by solution with distilled water will be discussed. They are: calcareous; gypsum and saliferous; marls and clays; impure sand and sandstones; pure siliceous sands and sandstones; organic matter; granite and gneiss; and basalts.

Calcareous Formations

The calcium carbonate saturation point is reached rather quickly in limestone terrain. Corresponding to the relatively slight changes in the CO_2 pressure in the soil, the concentration of Ca^{++} and HCO_3^- varies within narrow limits also.

The surface area exposed to chemical attack in limestone is small since the main part of the flow is through solution cavities. Because most of the soluble salts (chloride and sulfate) are locked in the limestones, the lack of interstitial circulation prevents their dissolution. In porous limestones, the soluble salts are naturally free to dissolve, but only after the surrounding CaCO_3 is dissolved. Thus, the water is still of the same general chemical composition as in the solution fissures.

Most often the water from calcareous terrain will be high in carbonates and low in Cl^- , SO_4^{--} , and dry residue. Dolomites experience the same general phenomenon as the limestones.

Gypsum and Saliferous Formations

Water flowing through gypsum quickly dissolves the Ca and Mg sulfates, often to the point of almost immediate saturation. The speedy dissolution is due to its solubility and not to prolonged contact with the rock. There is also a high content of other very soluble salts that dissolve in a similar manner.

Usually the calcium sulfate saturation point is reached first. Thereafter dissolution of magnesium sulfate will continue, but the calcium sulfate will stop.

The solubility of the calcium sulfate rises with the concentration of chloride in the water. Thus, water that is high in sodium

chloride will tend to have higher concentrations of calcium sulfate than purely gypsiferous water. The ratio of $\text{Mg}^{++}/\text{Ca}^{++}$, in equivalents, has a tendency to increase upon continued circulation.

Generally the water is quite high in SO_4^{--} , Cl^- , Ca^{++} , Mg^{++} , and Na^+ . It will yield dry residues that may rise to more than 200 grams per liter. The concentration of combined carbonate usually remains near normal or even slightly below. This is because of the influence of the added Ca upon the CaCO_3 solubility product.

Marls and Clays

Marls and clays contain large quantities of salts. This is due to the colloidal nature of part of their constituent elements and the fineness of their pores being able to adsorb salts either during deposition in the stream or in connate sea water. The high porosity and low permeability of marls and clays further enhances their ability to retain large quantities of salts.

Normal CO_3^{--} content, high SO_4^{--} and Cl^- concentrations usually exceeding the HCO_3^- content, and high dry residue are characteristic of water from marls and clays. Gypsiferous and saliferous rock is the only other type that has such high SO_4^{--} and Cl^- content.

Base exchange mechanisms are very prominent in clays and marls. This will be discussed in the section on "Modifying Phenomena."

Impure Sands and Sandstones

Water in impure sands and sandstones is in contact with almost all grains composing the rock. This enables it to gain its chemical composition quickly. This water is usually more heavily charged with salts, such as $\text{SO}_4^{=}$, Cl^- , Mg^{++} , and Ca^{++} than limestone is. These constituents are derived from the soluble impurities in the sands and sandstone.

The $\text{CO}_3^{=}$ content remains fairly constant for the whole climatic region.

Pure Siliceous Sands and Sandstones

These rocks consist almost entirely of quartz. There are very few elements the water can dissolve, even in arid regions. This water is characterized by its purity and low pH, which comes from dissolved CO_2 in excess of the low solubility product which is caused by the low concentrations of Ca and Mg. The sodium may exceed the calcium content.

Organic Matter

The organic matter supplies the energy for reduction modification in the water chemistry. Particular reactions here are lowering of the SO_4 content, production of H_2S , and a rise in the amount of combined

CO₃. The latter action is due to the large amounts of CO₂ in these rocks.

Granite and Gneiss

Decomposition of the rocks' mineral components (quartz, orthoclase, plagioclase, biotite, and muscovite) provides the water with SiO₂, K, Na, and Fe. Sodium is usually more predominant than potassium because of the latter's adsorption to the residue of decomposition. Because of the slow decomposition processes, the water is usually low in all salts and has a low pH. There is generally a high silicon content. There may be an inherent chloride-alkali imbalance because of the very small amount of chlorides released by silicates.

Basalts

Water from basalts is usually rich in silica, as is the water from granites and gneisses. With basalts, however, large quantities of Ca and Mg are released. These are normally about 3 epm (equivalents per million) of Ca⁺⁺ and 2 epm of Mg⁺⁺. Sodium is low— < 2 epm. SO₄⁼, Cl⁻, and HCO₃⁻ are also low, and the pH is neutral. The dry residue is also low.

Modifying Phenomena

The chemistry of underground water changes constantly as it travels through subsurface strata. Many chemical reactions occur when the water comes in contact with different lithologic facies and with the mixing of different ground waters. The most important of these modifying phenomena are reductions, base exchanges, concentration, and chemical precipitation.

Reductions

The elements affected by reducing processes are the sulfates and to some minor extent the nitrates. The reduction of sulfur is principally a biochemical process. The processes change the fully oxidized S^{+6} state in the form of sulfate ions to the S^{-2} of sulfide state. During the reduction process, the sediment may turn black due to the formation of sulfides and emit a strong hydrogen sulfide odor (Hem, 1959). The data used in this study have shown no evidence of this unmistakable odor. Therefore, this type of reaction does not appear to be important in the Tucson basin.

Soil bacteria also reduce the nitrate ion, NO_3^- , to the ammonium ion, NH_4^+ . There is not sufficient data to investigate this type of reaction in the Tucson basin.

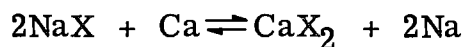
Base Exchanges

Ground water is apt to contact a variety of subsurface media that have the ability to exchange some of their own ions with those ions in the water. The geologic strata in which this process occurs most frequently are the fine-grained sediments, such as clays. The montmorillonite clay is probably the most important because of its high capacity for this reaction and its wide distribution in soils and sediments.

The degree of ion fixation on the rock is determined by the nature of the cations and the degree of hydration. The fixation of divalent ions is stronger than that of monovalent ions. For the ions studied in this thesis, the power of fixation, f , is usually as follows:

$$f \text{ Ca} > f \text{ Mg} > f \text{ K} > f \text{ Na}$$

The equation for a typical base exchange reaction is:



where "X" represents a unit of exchange capacity in the solid phase material.

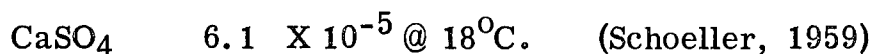
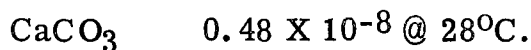
The equilibrium of this equation may be displaced to either the right or left, depending upon the predominant ion in the water. Base exchanges depositing sodium and taking Ca and Mg from the soil may

be harmful to the soil. A soil high in exchangeable sodium is deflocculated, tends to have a hard crust, and may be nearly impermeable to water (Hem, 1959). This condition may be reversed by waters containing a high proportion of Ca and Mg. The sodium hazard of a water can be evaluated by inspecting the $\text{Na}^+ / (\text{Ca}^{++} + \text{Mg}^{++})$ ratio. Waters with a ratio greater than one can be harmful to the soil.

Concentration

The principal mechanisms of mineral concentration are evaporation and dissolution. Infiltrating water with its load of dissolved chemical constituents may be evaporated before reaching the water table. When evaporated, a residue is deposited in the soil. This action may happen several times before sufficient infiltration and percolation can leach the concentrated soluble residue from the soil and carry it down to the water table.

The role of dissolution beneath the water table is the same as that in the upper soil layers. The solubility products play a more important part, though, because the different minerals are closer to saturation limitations. The solubility products govern the rate and type of dissolution taking place. The rate of dissolution is directly proportional to the saturation deficit. Two of the most frequently encountered solubility products are:



The units of the solubility product are moles²/liter² because it involves the product of two concentrations.

Chemical Precipitation

Natural water chemistry may be modified by precipitation of insoluble constituents. The precipitation may occur above or below the water table and be caused by ions in solution from adjacent rock or from the mixing of different ground-water systems.

The precipitation due to mixing of different ground waters would have a channeling effect by forming an impermeable barrier between the two waters. Thus, mixing of the waters is very limited in this case. Mixing may occur in ground waters that do not form precipitates. This is discussed later in reference to the Tucson basin.

Chemical Composition of Ground Water

Several rules can be deduced from examining the chemical characteristics of ground waters. Four of these have been set forth by Schoeller (1959).

First, "water from rocks of the same petrographic nature, whatever the nature of the storage in them may exhibit common

characteristics." Some of these main petrographic units were pointed out in the section on "Water from the Principal Types of Rocks." These waters can still vary chemically by differences in the quality of recharge water, velocity of the ground water, and the climate.

Secondly, "water from formations of the same petrographic age and in the same region usually has common characteristics, and is much more closely akin than water coming from formations of the same petrographic nature but of different ages belonging to different ground water systems."

Thirdly, "nevertheless, the water from two separate bodies in the same geologic horizon may differ in chemical composition even if they lie side by side. The greater the distance between ground water bodies, the greater the likelihood of their presenting chemical differences." Some causes of quality differences may be the quality of recharge water, facies may change from point to point, and trajectories in the different systems may vary in length.

Fourthly, "on the other hand, waters from the same system in the same geological formation have relatively constant chemical characteristics which are much more so than those of the water from two separate systems even coming from the same horizon from petrographically identical rocks in it of the same age and even with the same substratum." "Horizon," as used by Schoeller in the third and fourth laws, refers to "formation."

Progressive Changes in Chemical Composition Within a
Single Ground-Water Body

As previously noted, there are many changes taking place in the chemical composition of a ground water that are controlled by the geology of the subsurface strata. On the large scale, however, there is a general progressive chemical change caused by the many local geological influences.

In general, the total mineral concentration increases downstream through the further dissolution of the ever-present salts in the aquifer. The increase in salts is directly proportional to the time and surface area of the water contact with the aquifers.

To get an accurate picture of the progressive chemical changes in a ground water, it is very helpful to plot chemical isograms. Some significant parameters are Cl^- , $\text{SO}_4^{--}/\text{Cl}^-$, and $\text{Mg}^{++}/\text{Ca}^{++}$.

The values of chloride concentration will increase downstream with the increasing salt concentration.

The $\text{SO}_4^{--}/\text{Cl}^-$ ratio will decrease downstream since chlorides are dissolved faster than the alkaline earth sulfates. The ratio may increase initially due to excess CaSO_4 and (or) MgSO_4 , but as soon as these ions are saturated, the chloride will take over, and the ratio will decrease. The ratio will also decrease with the reduction of sulfates.

The $\text{Mg}^{++}/\text{Ca}^{++}$ ratio usually tends to increase downstream.

Calcium carbonate reaches saturation very quickly. Also, the gypsum dissolves less rapidly than MgSO_4 and MgCl_2 .

METHODS OF ANALYZING GROUND-WATER CHEMISTRY DATA

From the foregoing discussion of the ground-water geochemistry, it is apparent that certain parameters may be more significant than others. The chemical parameters can be shown and interpreted by isograms, graphs, and tables that best denote their composition, distribution, and changes.

Chemical Isograms

If an area can be treated as one aquifer system and the variations in quality with depth are known to be minor, then chemical isograms (maps showing lines of equal chemical concentrations) are a very important means of interpreting the data. This type of map extrapolates the data between sampling points. It shows the areal distribution of the water chemistry more clearly than any other procedure.

The isograms may be mapped directly by drawing lines of equal concentration or shading, or coloring in, areas of concentrations within specified ranges. The accuracy of these maps is dependent upon the homogeneity of quality in a vertical section and the completeness and accuracy of the sampling. Hem (1959) states:

An isogram is particularly helpful in the study of ground-water bodies in wide-spread uniform aquifers. In alluvial fill in the Basin and Range physiographic province of the Western United States, the water-bearing zones usually are of a lenticular nature but are usually closely enough interconnected to constitute simple hydrologic systems over large areas. Isogram maps have been used successfully in several areas of this kind.

Some of the most significant values to be mapped are the absolute values and products and relative values.

Absolute Values and Products

The most important absolute value for consideration is the bicarbonate radical, HCO_3^- . We have already discussed the importance of the CO_2 gas in dissolution mechanisms. It is essential to take into account the calcium carbonate solubility product when studying this value. The addition of calcium from other sources (base exchange and dissolution of gypsum) may lower the HCO_3^- concentration if the solubility product is reached.

The absolute value of the sulfate radical, $\text{SO}_4^{=}$, also deserves consideration. Again, the solubility product, CaSO_4 , must be considered to evaluate the importance of the sulfate concentration. For example, a low value of $\text{SO}_4^{=}$ might indicate sulfate reduction, but it could also be due to large quantities of calcium being taken into solution upsetting the equilibrium.

Finally, the absolute value of the chloride ion, Cl^- , is to be considered. The concentration of this ion may denote the degree of stagnation of a ground-water body, the time in contact with the rocks, the length of trajectory, and the degree of evapotranspiration.

The absolute values of Ca, Mg, and Na are dependent upon the action of the anions and the base exchange mechanisms.

Relative Values

Ratios will often provide meaningful methods for analyzing the data. Important ratios are $\text{SO}_4^{=}/\text{Cl}^-$, $\text{Mg}^{++}/\text{Ca}^{++}$, and $\text{Na}^+ / (\text{Ca}^{++} + \text{Mg}^{++})$. The significance of these ratios has been discussed previously. Particular attention should be given these ratios when either or both the numerator and denominator are very low, less than 0.5 epm. For such low values, there is a large variation in the ratios for small changes in the concentrations.

Graphical Techniques

A wide variety of graphical methods have been used to investigate ground-water chemical analyses. The methods used in this study will now be outlined.

Ionic-Concentration Diagrams

One of the most widely used systems of this type is the Collin's comparative table (Collins, 1923). With this method each chemical analysis is represented by a divided vertical bar graph, whose total heights are proportional to the concentration of anions and cations expressed in ep_m. Comparing the heights of the two columns will at once show the chloride-alkali imbalance.

Percentage Composition Diagrams

These graphical methods emphasize or show only the relative proportions of the principal cations and anions. They are usually expressed in terms of percent of total anion and cation equivalents.

One of the most useful methods used in percentage plotting is the Piper trilinear diagram (Piper, 1944). This original version has been modified by Mr. Piper, and the present method was published in 1953.

The methods of plotting this diagram are illustrated in the plotting key shown in figure 2. It is first necessary to calculate the concentrations in ep_m, and from these values compute the percentage of each anion and cation of the total anions and cations, respectively.

In addition to this point on the diamond field, a circle proportional to total soluble salts may be constructed around each point. This

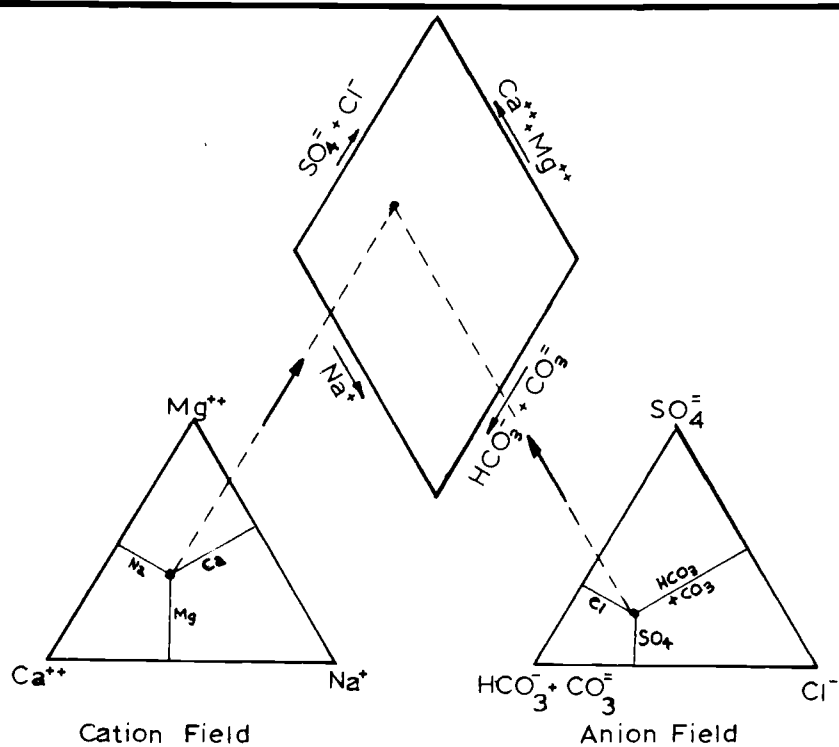
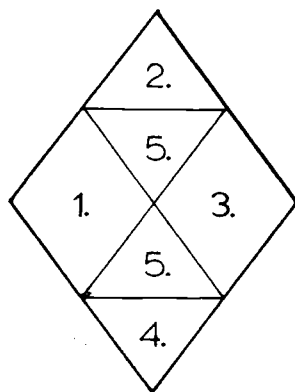


Fig.2.-- Plotting Key for the Piper Diagram



1. Carbonate Hardness -- Secondary Alkalinity
2. Noncarbonate Hardness -- Secondary Salinity
3. Noncarbonate Alkali -- Primary Salinity
4. Carbonate Alkali -- Primary Alkalinity
5. No One Cation-Anion Pair Exceeds 50%

Fig.3.-- Diamond Field Water Quality Classes

will serve to separate magnitudes, which the percentage composition neglects.

The diamond-shaped field gives the most interesting representation of the data. Mixtures of waters and progressive changes of water within a ground-water reservoir will plot as straight lines on this diamond. Another application of the diamond field is to use it to classify waters according to their chemical constituents. The classifications recommended by Piper are shown in figure 3.

Frequency Diagrams

When studying large numbers of analyses, the frequency of occurrence of certain values or relationships may be helpful. The data treated in such a manner should have some definite relationship for this method to be of value.

For the purposes of this study, frequency diagrams were used to investigate the possible vertical variation in water quality and to select concentration intervals for isogram mapping.

COLLECTION AND ANALYSIS OF CHEMICAL SAMPLES OF THE TUCSON BASIN GROUND WATER

The Department of Agricultural Engineering provided almost all the chemical data used in this thesis. These analyses were made by the Department of Agricultural Chemistry at the University of Arizona. A limited number of analyses were taken from the files of the U. S. Geological Survey, Quality of Water Branch, in Tucson.

All the data selected for use in this study, along with the legal description of well locations, are on file in the Hydrology Department.

Chemical Analyses of Well Water

Principal Ions

The chemical analyses reported concentrations in parts per million (ppm) for eight ions and a value for the total soluble salts (TSS) also in ppm. The ions analyzed were: calcium, Ca^{++} ; magnesium, Mg^{++} ; sodium, Na^+ ; chloride, Cl^- ; sulfate, SO_4^{--} ; carbonate, CO_3^{--} ; bicarbonate, HCO_3^- ; and fluoride, F^- . All the samples selected for use in this study gave concentrations for the first seven ions, but not all samples reported fluoride.

Some of the analyses contained nitrate concentrations, but there were not enough such data to make a study feasible.

Limitations of the Analyses

The accuracy to which the chemical analyses were made was learned through personal communication with Mr. G. Draper and Dr. G. Dutt of the Agricultural Chemistry Department.

Calcium and magnesium contents were determined by the soap titration method prior to June of 1955. After this time the versenate method was used. The accuracy of the soap titration is very poor, and such an analysis can only be used to indicate the sum of the two ions at best. Since about 50 percent of the data was determined by this early method, it will only be possible to study the sum of the two concentrations. The versenate method is accurate to ± 5 percent.

The sodium content is determined by calculation from concentrations of the other ions analyzed. Thus, it will include the algebraic sum of all the errors in the other ions. Therefore, it is the least accurate and not reliable enough to warrant close study at this time.

The chloride content is determined by titration with silver nitrate. It is the most accurate of all ions analyzed. Less than 5 percent error can be expected.

The turbidimetric method was used to determine the sulfate content. This method is good to about 10 percent error.

Carbonate and bicarbonate are both titrated with sulfuric acid. Problems encountered in alkalinity measurements will be discussed after the fluoride ion.

The fluoride ion concentrations, when reported, are usually accurate to ± 10 percent.

Several important chemical changes occur in the water sample between sampling and analysis. Primarily, the changes are due to changes in the partial pressure of CO_2 . The content of Ca^{++} , Mg^{++} , HCO_3^- , and CO_3^{--} is all directly proportional to the CO_2 pressure. Thus, if the water is not analyzed immediately in the field, the concentration of these ions will decrease after exposure to atmospheric conditions. The pressure of CO_2 will also change with temperature, type of sampling bottle, and amount of light on the sample. All these factors are responsible for the many negligible carbonate concentrations reported in the data.

Since the samples were usually analyzed in the laboratory several hours or days after sampling, the reported concentrations can hardly be expected to be representative of actual field conditions. The error in the analyses is consistent, however, as shown in the chemical isograms.

Another important limitation of the analyses is that neither the pH nor the temperature of the sample has been determined. Again these measurements have to be made in the field. Without knowing the

temperature and pH of the water it is impossible to examine the solubility product of calcium carbonate. The saturation and (or) unsaturation of such a product is essential in evaluating the occurrence of its constituents. Thus, this study cannot fully interpret the significance of the Ca^{++} , Mg^{++} , CO_3^{--} , and HCO_3^- ions.

Distribution of Data

Figure 6 shows the distribution of the wells used in this study with chemical analyses of the ground water. A total of 837 wells was used. Their average depth was 303 feet.

The wells were selected on the basis of the completeness of the chemical analysis and upon the depth of the well. Wells penetrating the deep consolidated sediments, Pantano beds, were discarded because this water is of a different aquifer system. It is not possible to study this deep aquifer at this time because of the scarcity of data. The Pantano water is studied where its effects are apparent in the wells penetrating the upper aquifer.

The quality of the water in the inner valley fill (upper unconfined aquifer) was found to be independent of depth. Since the quality is independent of depth, the chemical isogram can be used to interpret the distribution and changes in the chemistry of the ground water.

Isograms

The chemical isogram has been found to give the best interpretation of the water quality in the Tucson basin. Several absolute values, products, and relative values have been investigated for mapping in the study area. The following parameters have been studied in detail by chemical isogram mapping in this thesis: total soluble salts, (Ca + Mg), Cl, SO₄, HCO₃, and F. These isograms are shown figures 7 through 12, respectively.

For reasons of insufficient data and inaccurate data mentioned earlier, solubility products and relative values involving Ca, Mg, and Na were not mapped. The data for the fluoride ion concentrations were not as widespread as the other constituents. Consequently, its isogram will not be as accurate. The relative value SO₄/Cl could have been mapped; however, since the concentration distribution of both ions is similar, a map of this sort would be very much like either of the individual value distributions.

The method used to plot the isograms was that of shading and coloring in areas within specified concentration limits. This was found to be very satisfactory.

Graphical Analysis

Collin's Comparative Table

It would be impractical to show all analyses used on the Collin's table. Therefore, only a few analyses representative of different quality areas will be reported in this manner. The Collin's bar graphs for the different quality areas are shown in figure 5.

Piper Trilinear Diagram

The distribution of all chemical analyses used in this study is shown on the diamond-shaped field of the Piper diagram in figure 4. The analyses have been divided into the five quality classes. The areal distribution of these water types is shown in figure 13. It should again be noted that this diagram and map show only percentage composition. The actual concentrations in epm or ppm should also be used to obtain a meaningful interpretation of the chemistry.

Frequency Diagrams

Some frequency diagrams have been used in this study during the preliminary steps of analysis. It is felt that they need not be shown in the thesis since the isograms so aptly show their results.

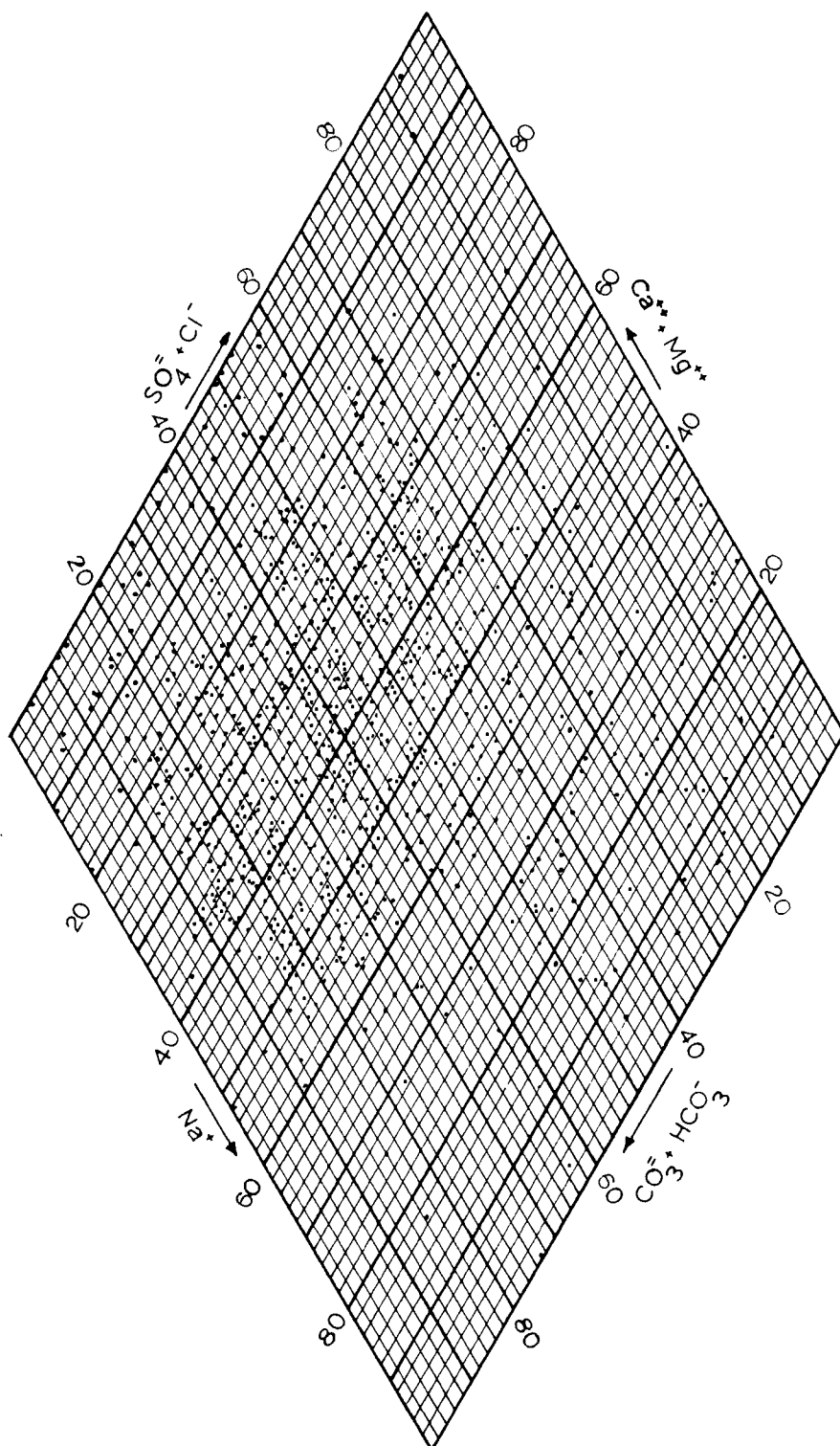


Fig. 4.-- Data on Piper Diagram

INTERPRETATION OF THE GROUND-WATER CHEMISTRY WITH RESPECT TO BASIN GEOLOGY AND WATER USE

Some general relations of the geochemistry of ground water to geology and water use have been set forth. Now specific relationships will be investigated in the Tucson basin using the maps and diagrams prepared for this purpose.

Regional Variations in Water Quality

A comparison of the isochemical maps readily shows a distinct similarity in the relative concentration distribution of all ions, total soluble salts, and the Piper water classes. The fact that all magnitudes vary similarly indicates that changes in the ground-water chemistry are controlled by regional factors affecting all constituents. Mechanisms changing concentrations of individual ions without affecting other ions are of little significance.

The only area where all ions do not vary similarly in magnitude is in the Tanque Verde Creek area. Here, the $\text{Ca}^{++} + \text{Mg}^{++}$ sum is comparatively low, while all other ions remain high.

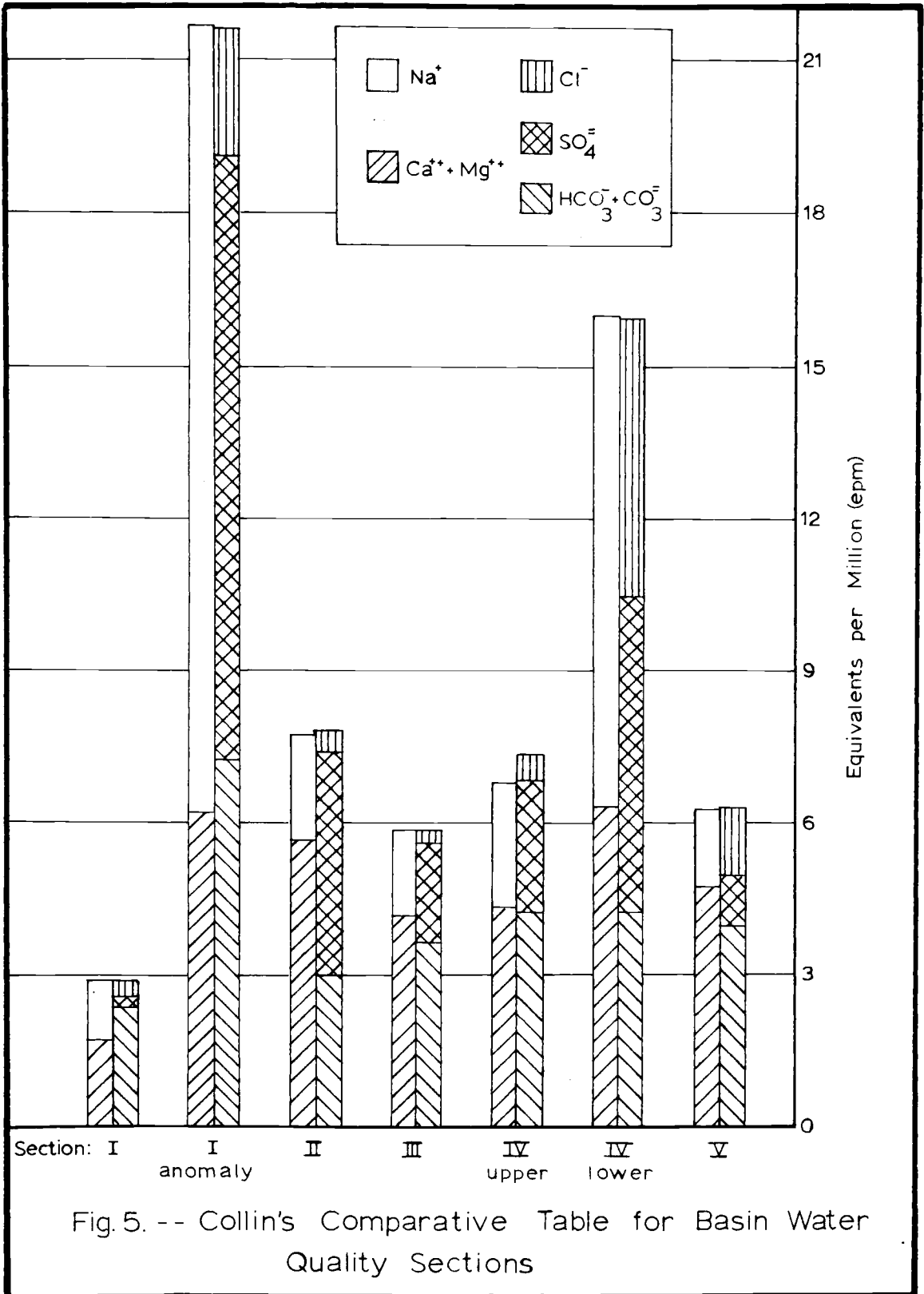
In general, the Tucson basin can be divided into five sections of differing water quality. This was done in accordance with the rules

set forth in the section on the "Geochemistry of Ground Water." Because the ion concentrations vary similarly in magnitude, the quality distinctions will be made according to low, medium, and high relative concentrations. Representative analyses of these quality sections are shown in figure 5.

First, a large section of water low in total soluble salts is found along the north and northeast boundaries of the basin. It extends into much of the north and east portions of the city of Tucson. It has low to low-medium concentrations everywhere except for the Tanque Verde anomaly, where very high concentrations exist.

Secondly, there is a band of moderately high to high ion concentrations coming from just southeast of Vail in the Cienega Gap region and going northwest along the Benson-Tucson Highway to where that road meets the Santa Cruz River bottom land.

It is this band of poor-quality water that separates the low concentrations in section I from the low-moderate to moderate concentrations of the slopes of the Santa Rita and Sierrita Mountains (section III). These slopes cover most of the southern part of the study area. They extend as far north as Black Mountain on the west side of the Santa Cruz River bottom land and as far as 4 to 5 miles north of Sahuarita Butte on the east side. Here, it is pinched out by section II on the east and the Santa Cruz bottom land water on the west.



The fourth section of distinctive quality is the Santa Cruz River bottom land. This section extends the full length of the study area from Arivaca Junction north to Rillito. The water quality generally averages from moderately high to high ion concentrations. There are spotty highs south of Sahuarita Butte. The stretch from San Xavier Mission north to Cortaro is the largest area of very poor quality water in the basin. The Jaynes area is of particularly poor quality.

The poor-quality water appears to flow north into the finger-like projection of the Tucson Mountains. From here it flows parallel to the barrier and then out of the basin at Rillito between the Tucson Mountains and the good-quality water from the Canada del Oro (section I).

The fifth quality section covers the east slopes of the Tucson Mountains above the Santa Cruz River bottom land. The quality along these slopes ranges from moderate high to high in the southernmost part to low medium in the area southwest of Cortaro. The Santa Cruz River bottom-land water is predominant north of there, and Tucson Mountain slope water has negligible influence.

Chemical Isograms Relation to Rock Types of the Basin Periphery and to the Alluvium of the Basin

As we have seen from the "Geochemistry of Ground Water" section, there is a direct relationship between the chemical quality of

a ground water and the path the water has taken since falling as precipitation. A general correlation of the ground water in the five different quality sections will now be made with the geology of these areas.

Because the water samples were obtained by pumping, they will reflect the chemistry of all water-producing strata. Thus, the correlation will have to be done in a composite or general geologic way also.

Section I—Low Concentrations

This section is typically represented by the following water quality:

TSS	0-500 ppm
Ca ⁺⁺ + Mg ⁺⁺	3.00 epm
Cl ⁻	0-1.00 epm
SO ₄ ⁼	0-1.00 epm
HCO ₃ ⁻	3.00 epm
F ⁻	0-0.2 ppm
Piper class: Carbonate hardness	

The relatively low ion concentrations in this area indicate that the aquifer should be composed of clean sandy gravel sediments. The carbonate hardness on the Piper isogram and the individual isograms show that calcareous material is predominant over gypsiferous and saliferous material.

The Cl^- concentrations along the southwest slopes of the Catalina Mountains appear to be relatively higher than other ions in that area. The F^- is also high in some areas on these slopes.

An inspection of the geology in the low-concentration areas shows that the predictions from the water chemistry are partially correct. As indicated by Ganus (1965), there is a large area of clean sands and gravels in the central part of quality area one. The area to the northeast of this sand and gravel is a mixture of sands, gravels, and clays. To the southeast of the central clean sand and gravel area lies a region almost entirely made up of clays. This poses the very interesting question of how the water quality can remain constant over both clayey and sand-gravel areas. Apparently the thesis that the water quality is a direct result of the composition of the aquifer is wrong. However, if we look at the probable source of the basin fill for this area, we see that it is primarily crystalline rock (Tortolita, Catalina, Tanque Verde, and Rincon Mountains).

Crystalline rock decomposes slowly because of the low solubility of its constituents. Thus, it will yield low concentrations of dissolved ions. It is characteristically high in silica, but no analyses have been made for this ion. The carbonate hardness of these waters is best explained by the few outcrops of limestone present in the mountains. Surely this limestone was present at the time of basin filling and was deposited along with the sediments from the crystalline complex.

This discussion indicates that the basin fill, although composed of mixtures of sand, gravel, and clay, yields water characteristic of the rock formation supplying the alluvial material. Of course there will be local variations where base exchanges, etc., support quality changes in the same material.

Because there is such a distinct variation in quality between the different areas of the basin, one could hardly believe that the basin fill could have been predominantly deposited by a single source. It is not likely that regional deposition of basin fill from say a lake covering the entire basin could have taken place. If there were such a lake, then it appears to have had a negligible effect on providing constant quality ground water throughout the basin.

The Tortolita Mountains and the upper reaches of the Canada del Oro are granites as opposed to the gneisses of the Catalina, Tanque Verde, and Rincon Mountains. Both granite and gneiss produce water of the same chemical characteristics, as noted in "Water from the Principal Types of Rock."

The moderate concentrations of Cl found in the foothills of the Catalina Mountains probably come from the Pantano(?) conglomerates, sandstones, siltstone, and claystone that crop out in this area. The higher values of fluoride also found in this area, which are characteristic of the Pantano formation, would help to verify the presence of these formations. The gneissic material in this area, from the Catalina

Mountains, would be expected to have low concentrations of chloride.

Thus, the older red beds probably contribute most of the chloride.

Because none of the other ions exhibit relatively high concentrations, it is doubtful that these beds are the same as the other Pantano beds that have high concentrations of all ions. There are very few chemical analyses for this area, and no definite correlations can be made.

Section I—Tanque Verde, High Anomaly

The water quality in this small area of section I is:

TSS	500-1,000 ppm with some places > 1,000 ppm
$\text{Ca}^{++} + \text{Mg}^{++}$	8.00 epm in the west 3.00 epm in the east
Cl^{-}	1.20-3.00 epm with some places > 3.00 epm
$\text{SO}_4^{\bar{2}}$	2.00-5.00 epm with some places > 5.00 epm
HCO_3^{-}	0-3.00 epm in west 4.00-5.00 and > 5.00 in east
F^{-}	> 1.5 ppm
Piper class: Noncarbonate alkali	

The Tanque Verde area of high concentrations lies in the southwest portion of T. 13 S., R. 16 E. The high concentrations of all ions would indicate the presence of older fine-grained sediments, such as clays.

Geologically, this area is primarily made up of Pantano formations (personal communication, E. F. Pashley). The Pantano beds are known to produce very poor quality water, particularly high in fluorides. This fact was established from water-quality information from the deep wells penetrating the Pantano beds in southeast Tucson. Both the Pantano beds and the lower artesian aquifer produced this poor-quality water.

Some extremely high concentrations of Na^+ , Cl^- , and SO_4^{--} have probably been caused by thermal water reported in this area (personal communication, H. C. Schwalen). This thermal water could very well be associated with the hot waters of the lower artesian aquifer.

Section II

The band of moderately high ionic concentrations along the Tucson-Benson Highway is characterized by:

TSS	500-1,000 ppm
$\text{Ca}^{++} + \text{Mg}^{++}$	5.00-8.00 epm
Cl^-	0.40-1.20 epm

$\text{SO}_4^{=}$	2.00-5.00 and 5.00 epm to the southeast
HCO_3^-	3.00-4.00 epm
F^-	0.3-0.5 ppm, 0.8 ppm to the southeast

Piper class: No one cation-anion pair exceeds 50 percent

The isochemical maps show the predominance of Ca + Mg and SO_4 over the other ions. This definitely indicates the presence of gypsum somewhere along the path of this ground water. The other ions do not appear to be abnormally high when compared to the surrounding areas. Thus, the gypsum water must come from an area outside the immediate Tucson basin.

This water was traced by Schwalen and Shaw (1957) to the Cienega Gap area where the ground water is forced to the surface by an impermeable barrier. The Cienega Gap area has many Pantano beds (Brennan, 1957). As mentioned previously, the Pantano formations are known to produce very poor quality water. However, the fluoride concentrations in the Vail area are not exceptionally high. The Pantano beds are not very permeable, and, thus, their small quantity of water is soon diluted in a short distance. Therefore, these beds cannot be wholly responsible for the section II water quality.

Upon further investigation the valley of Cienega Creek is found to have many gypsum deposits as well as limestones (personal communication, R. J. Shaw). This will definitely account for the high concentrations of Ca^{++} , Mg^{++} , and SO_4^{--} .

It should also be noted that the HCO_3^- concentrations in epm are generally half the $\text{Ca}^{++} + \text{Mg}^{++}$ concentrations. The sulfate concentrations are also considerably higher than the HCO_3^- . This could indicate that the CaCO_3 solubility product has been reached, and the addition of more Ca from gypsum has upset the equilibrium and caused the low HCO_3^- content. A detailed study of the CaCO_3 saturation in this area would be necessary to verify this.

Section III

The water quality in the Santa Rita and Sierrita foothills above the Santa Cruz River bottom lands is:

TSS	300-500 ppm
$\text{Ca}^{++} + \text{Mg}^{++}$	2.00-5.00 epm
Cl^-	0.40-1.20 epm
SO_4^{--}	1.00-2.00 epm
HCO_3^-	3.00-4.00 epm
F^-	0.3-0.5 ppm
Piper class: Carbonate hardness	

The higher concentrations in this area as opposed to section I can be explained by the predominance of sedimentary rocks in the Santa Rita and Sierrita Mountains, as compared to the crystalline rocks of the Catalina Mountains, etc. Sedimentary rocks decompose much more easily than crystalline rocks, and thus provide the ground water with more chemical constituents. The carbonate hardness is undoubtedly caused by the presence of many limestones in the sedimentary rocks. The sedimentary rock distribution is plainly shown on a geologic map of the area.

Section IV

The water of the Santa Cruz bottom land has the following quality:

TSS	500-1,000 ppm in south, > 1,000 in north
$\text{Ca}^{++} + \text{Mg}^{++}$	5.00-8.00 epm in south, > 8.00 epm near Tucson
Cl^{-}	0.40 in south to > 3.00 epm near Tucson
$\text{SO}_4^=$	2.00-5.00 in south to > 5.00 near Tucson
HCO_3^{-}	4.00-5.00 epm in south to > 5.00 epm near Tucson

F^- 0.3-0.5 ppm in
south to > 1.5
near Tucson

Piper class: South, no cation-anion pair
exceeds 50 percent
North, noncarbonate alkali

The high concentrations of most all ions would be expected in the bottom land where fine-grained sediments are found. Young ground water from recharge quickly picks up many salts from the fine-grained material in the flood-plain deposits and by dissolution of soluble precipitates from infiltrating water that was previously evaporated. Deep water in the bottom land may have traveled long distances from where it originally infiltrated. This would permit the dissolution mechanisms much time to build up large quantities of dissolved salts. The chemistry of the Santa Cruz bottom-land ground water is characteristic of that from impure sands and sandstones.

The high Ca^{++} , Mg^{++} , HCO_3^- , and SO_4^{--} concentrations must be due to the presence of both calcareous and gypseous sediments. The water coming from surrounding areas has traveled through many such sediments giving the dissolution, etc., mechanisms ample time to build up chemical content.

Ganus (1965) and Kidwai (1957) have shown large areas of fine-grained sediments to exist in the bottom land. These sediments consist of material from all parts of the Santa Cruz basin, which has been

transported by the river into the study area. The bottom-land sediments are characterized by volcanic material throughout.

The fact that the Santa Cruz River is an intermittent stream would indicate that its ground water should have higher ionic concentrations. As discussed in the dissolution mechanisms section, the rainfall-dissolution-evaporation process is very effective in concentrating the chemical constituents.

The upper Santa Cruz River down to Sahuarita Butte is classed as carbonate hardness. This is to be expected because the surrounding tributary areas are also of this type. Again, this is because of the calcareous sediments in the mountains as well as in the bottom land.

Quality changes begin in the Sahuarita area but do not become distinctive until just north of this. Here, the presence of noncarbonate alkali (primary salinity) is observed in the ground water. All the chemical isograms show particularly high concentrations between the south end of the Tucson Mountains and Black Mountain. The Piper isogram shows this water is particularly high in sodium, sulfate, and chloride.

This predominantly saline water can be traced along the Santa Cruz bottom land. A large area of this water is again found between "A" Mountain and Jaynes. The isograms indicate that the high concentrations of TSS here are accentuated by the confluence of the section II stream of water with the Santa Cruz bottom-land ground water. This

combination of waters is shown very well on the TSS isogram in the vicinity of Stone Avenue and Broadway in the city of Tucson.

The Santa Cruz bottom-land ground water north of Sahuarita Butte has the same chemical characteristics as the poor-quality water of the Pantano sediments of section I. The high ion content could be due to simple concentration mechanisms; however, the fluoride content correlates particularly well with the Pantano water. Thus, one would expect this bottom-land area to be underlain by Pantano-type formations. There is one outcrop of possible Pantano beds at the south end of the Tucson Mountains. Schwalen and Shaw (1957) have noted the presence of tough clays and clays and conglomerate in the area between Sahuarita Butte and "A" Mountain. They note that these sediments have the appearance of being a much older formation than those encountered within the basin fill. They have also noted the presence of what they believe to be buried volcanic peaks in this area. Such volcanic activity could have forced up the Pantano beds in this region and (or) created sufficient fractures to allow the poor-quality confined artesian water to rise into the basin fill.

E. F. Pashley (personal communication) of the U. S. Geological Survey in Tucson has also studied this area. He notes that the basin fill in this area is very shallow. It lies on top of deformed material of volcanic origin rather than the gneissic gravels, etc., in section I. The deformed gravels, etc., underlie the Santa Cruz bottom land and

extend to the basalt formations of the Tucson Mountains. These gravels are older than the basin fill, but Pashley does not believe that they are associated with the Pantano beds.

From the Jaynes area north to Rillito, the bottom-land ground water is forced toward the Tucson Mountains by the flow of good-quality water from section I. This is evidenced both on the chemical isograms and the ground-water contours.

Because of the large quantities of bottom-land water used for irrigation and the influence of the fresh section I water, the Santa Cruz bottom-land water finally leaves the Tucson basin at Rillito in a small ground-water channel. This channel is less than half a mile wide. The chemical isograms indicate that a major portion of the Santa Cruz water might be flowing underneath the fingerlike barrier of the northern Tucson Mountains. This is not substantiated by the ground-water contours, which are perpendicular to the barrier and show the flow to be parallel to it.

Section V

The quality of the Tucson Mountains slope water is:

TSS	500-1, 000 ppm in the south, 300-500 ppm in the north
-----------	---

$\text{Ca}^{++} + \text{Mg}^{++}$	2.00-5.00 epm in north and central 5.00-8.00 epm in the far south
Cl^{-}	0.60-1.20 epm, slightly higher in north
SO_4^{-}	0.25-1.00 epm, somewhat higher in south part
HCO_3^{-}	3.00-4.00 epm in the north, > 5.00 epm in the south
F^{-}	0-0.8 ppm with higher parts in the north

Piper class: Carbonate hardness

This is a relatively small area just to the west of the Santa Cruz bottom land in the northwest portion of the study area. The generally moderate ionic concentrations and carbonate hardness are typical of the mountainous areas discussed in quality section III. As in the Santa Rita and Sierrita Mountains, the Tucson Mountains are mainly igneous rock covered in places by sedimentary rocks (Coulson, 1950). There are several limestone sediments that would account for the carbonate hardness in the water.

As noted in the discussion of water from basalt and other crystalline rocks, their total soluble salt content is low, silica concentrations are high, and the pH is low.

The water from this area is obviously of small quantity due to the size of the watershed. The chemistry of the water in the foothills does not appear to influence the adjacent bottom-land ground water.

Probably the most significant effect of the Tucson Mountains on the water chemistry of the basin is the possibility that it uplifted and fractured the lower confining strata. This would have allowed the poor-quality deep water to contaminate the fresher water in the upper aquifer.

Changing Chemistry Through the Basin

In the previous discussion of the chemical isograms, a direct relation of the water chemistry to the geology was found. The very presence of the five distinct water-quality areas indicates geologic control of the water quality rather than the basin-wide evolution of a single ground-water body.

The Santa Cruz River bottom lands represent the longest water course in the study area. Its chemistry is largely controlled by the local geology. No widespread evolutionary trends have been found. The Tucson basin is not geologically uniform or long enough to permit evolutionary changes to have any significant effect.

Mixing of Different Ground-Water Bodies

There is very little mixing of the different ground waters in the Tucson basin. This is evidenced by the quite distinct differences

in the qualities of the ground water. Of course, there is dilution between different quality areas, but even where the quality varies greatly from one area to another, this is very small. This is particularly evident on the chemical isograms in the division of the Santa Cruz River and the Rillito Creek ground water in the Jaynes area. Here, concentration magnitudes in epm change from 10 to 100 times within half a mile.

Correlation with Flow Net

The quality of ground water may indicate the path of the flow. Source areas of distinctive chemical constituents may act as the injection of a tracer into the ground-water reservoir. The influence of this source may be traced downstream.

Where the geology controls the water chemistry, as we have in the Tucson basin, the source being traced should follow the flow lines. The differing water quality should be traceable downstream until it is diluted to the concentration of the surrounding water.

In the case of progressive changes in the ground-water chemistry in a single aquifer, lines of equal concentration will be perpendicular to the flow lines. The ionic concentration will increase downstream as the dissolution mechanisms continue to dissolve soluble material.

There are two point sources of geological influence that can be traced in the Tucson basin. The first is the high-concentration anomaly in quality section I, and the second is quality section II.

The Pantano formation in section I supplies noncarbonate alkali water high in all ion concentrations to an area of predominantly carbonate hard water that is low in all ion concentrations. Generally, all the chemical isograms show the influence of this poor-quality water downstream. The Piper class isogram clearly shows the concentration band from the high in the east near Houghton Road extending west between Grant Road and Speedway Blvd. and then paralleling Grant Road to Alvernon Way. Here, it is completely diluted by the carbonate hard water. The chemistry indicates that the major flow of water from the Tanque Verde area is around the north end of the impermeable barrier (dike?) in the northwest corner of T. 14 S., R. 15 E. noted by Ganus (1965). This flow pattern is generally substantiated by the flow pattern indicated by the ground-water contours.

In the second area where flow-line tracing is possible, distinct concentrations of Ca^{++} , Mg^{++} , and SO_4^{--} ions are found in quality section II. The chemistry here is quite different than in the sediments to the north from the Catalinas and to the south from the Santa Ritas. As discussed earlier, the chemistry of the water has been associated with the sediments in the Cienega Creek area. This band of quality is

parallel to the ground-water flow lines from the Cienega Gap northwest into the center of the Tucson basin.

Today the Cienega Creek flows into the Pantano Wash and northwest to meet Rillito Creek. The ground-water chemistry, however, shows that at some time in the past there was probably a much larger flow of surface water that followed an ancient stream course now buried beneath the sediments along the Tucson-Benson Highway. This ancient stream would have carried and deposited sediments in its channel that would yield water chemistry characteristic of its headwaters in gypsum and limestone terrain.

It seems natural that such a stream could have existed here where the old alluvial fans from the Catalina and Rincon and Santa Rita and Empire Mountains might have met to form a trough. The outwash from the Catalina and Rincon Mountains would have been to the southwest and that from the Santa Rita and Empire Mountains would have been to the northwest. The runoff from the Cienega Valley could have then easily flowed along this trough and eventually into the Santa Cruz River.

The Cienega Valley is bordered on the east, south, and west by mountains from 6,000 to more than 9,000 feet high. The height of these mountains would cause much orographic precipitation to fall in the valley and mountains. Consequently, large amounts of runoff would

have been available to flow out of the valley and along the ancient stream course in the Tucson basin.

The present ground-water contours are generally perpendicular to the Tucson-Benson Highway. This indicates that there is still a flow of ground water in the approximate direction of the ancient stream course.

Changing Water Quality with the Lowering of the Water Table

There have been no distinct changes in water quality directly associated with the lowering of the water table in the Tucson basin. Heavy withdrawals from some areas have altered the flow pattern so that poorer quality water may move laterally into previously good-quality areas. The breaks in the quality areas, however, would indicate that little of this occurred. The ground-water contours also show the water to be flowing consistently in the same general direction.

A very important question has been raised as to whether there is any upflow from the lower artesian aquifers due to the lower confining pressures. Two parts of the basin have experienced considerable drops in the water table—the Santa Cruz bottom lands adjacent to the city of Tucson and the east-central part of Tucson.

The Santa Cruz bottom land has very poor quality water similar to that of the Pantano beds in the Tanque Verde area. The high ionic

concentrations could indicate upward flow of poor-quality water from a deep aquifer, as discussed earlier. In an attempt to solve this problem, water analyses taken before much lowering occurred in the early 1940's were compared with recent analyses for the same area. There was no really consistent information to substantiate such upward flow. In fact, some wells even have better quality now than in the 1940's. Schwalen and Shaw (personal communication) think that the water quality is changing for the better in parts of this bottom land.

There is no evidence of upward flow of poor-quality water in east-central Tucson. This area is of consistently good quality. Ganus (1965) made a study of possible changing chemical concentrations in his study area but did not publish it in his thesis. He was particularly interested in high-fluoride concentrations, which are characteristic of the Pantano beds. Ganus' study did not show any such upward flow (personal communication, W. J. Ganus).

This subject is worthy of further study, particularly in the Santa Cruz River bottom land. Depth versus quality data and statistical comparisons of quality before and after water-table lowering would be very helpful.

CONCLUSIONS

General Statement

The chemistry of the Tucson basin ground water can definitely be related to the geology of the immediate basin and tributary areas.

The very good chemical quality areas are associated with the gneissic material from the mountains to the northeast. The poorest quality water generally comes from the Pantano beds, which are much older than the basin fill. Other poor-quality water comes from the Santa Cruz bottom land west of central Tucson. This area reportedly consists of older sediments, but no Pantano beds have been definitely located.

Man's lowering of the water table has not affected the water quality of the basin significantly at this time.

Recommendations for Future Development of the Tucson Basin Water Supply

Presently, the areas of best ground-water yield (high specific capacity) and the best water quality lie near Rillito Creek in the north-east portion of Tucson. Unfortunately, however, this area is experiencing much dewatering due to production well density and

capacity and to impermeable boundaries that exist in this area. Thus, this must be considered a limited supply unless substantial recharge can be effected in the Rillito Creek drainage basin. Artificial recharge of Rillito Creek water may be practical.

Another area of good production is the Santa Cruz bottom land between Sahuarita Butte and "A" Mountain. There is some good-quality water here; however, continued extensive pumping could cause surrounding poor-quality water to intrude the area. The Santa Cruz River bottom land is generally a good producer. The poor quality, however, makes this water more suitable for irrigation than for domestic purposes unless the water is purified to comply with drinking-water standards.

Good-quality water is found in the Canada del Oro area, but the production rates are low. Faulted areas where the crystalline rocks grade into the basin fill would probably be good producers for domestic use. Such faulted areas in the gneisses of the Catalina Mountains would also be good producers; however, caution should be taken to avoid contact with the Pantano beds in the foothills.

The paucity of information on both production and quality makes it impossible to study the mountain foothills in detail at this time.

Recommendations for Future Studies

Some of the projects that remain to be studied with respect to the Tucson basin water quality are:

1. Application of detailed statistical analysis and isogram mapping by computer methods.
2. Poor-quality water from the Pantano beds.
3. Poor-quality water from the Cienega Creek area extending into the Tucson basin.
4. Sources of poor-quality water in the Santa Cruz bottom land west of Tucson.
5. Field determinations of carbonates, including pH and temperature, for saturation studies.
6. Chemistry of artificial-recharge possibilities in the Rillito Creek area.

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Figure 12. --Isogram of F⁻ concentrations.

EXPLANATION

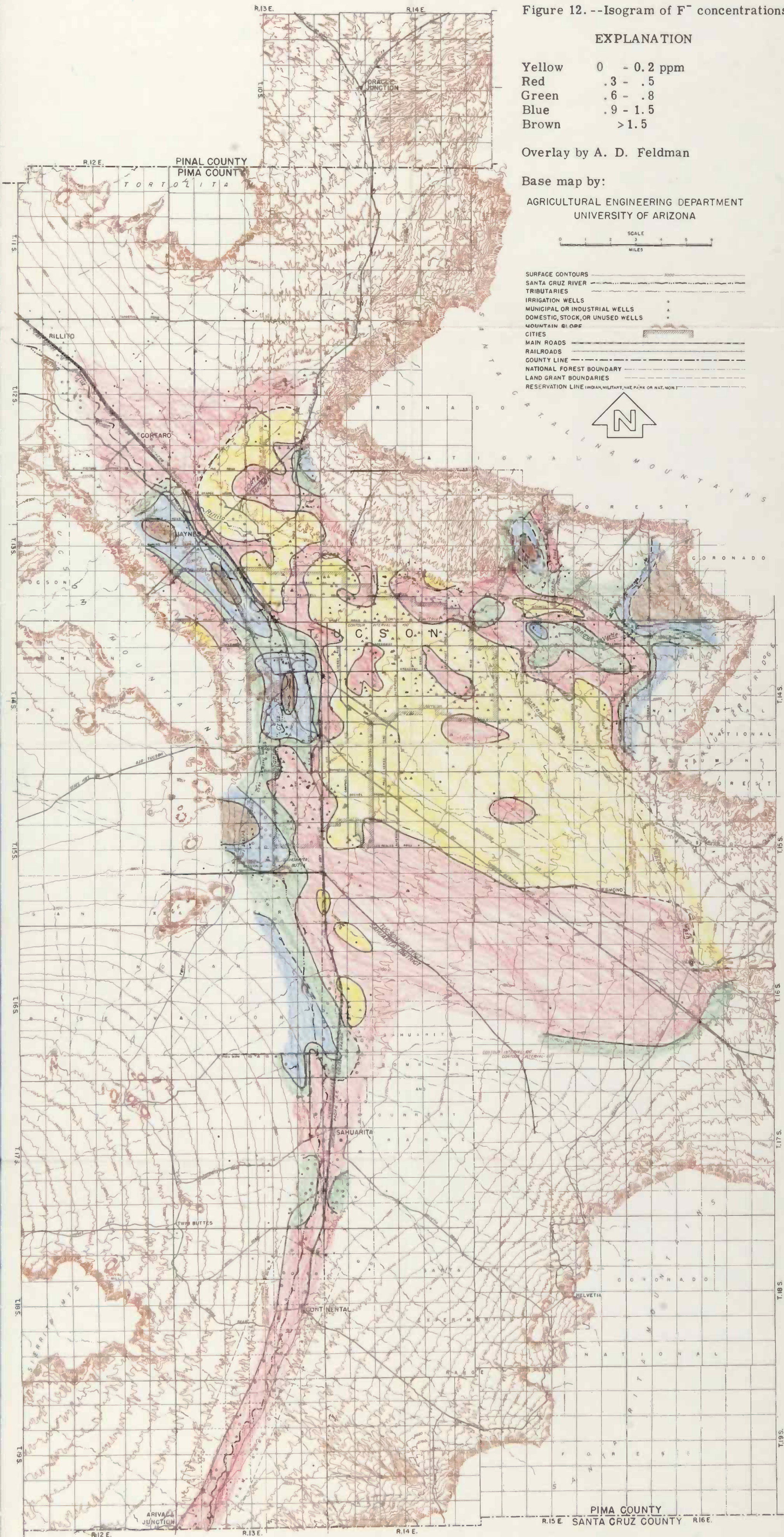
Yellow	0 - 0.2 ppm
Red	.3 - .5
Green	.6 - .8
Blue	.9 - 1.5
Brown	>1.5

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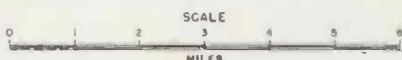
Figure 11. --Isogram of HCO_3^- concentrations.

EXPLANATION

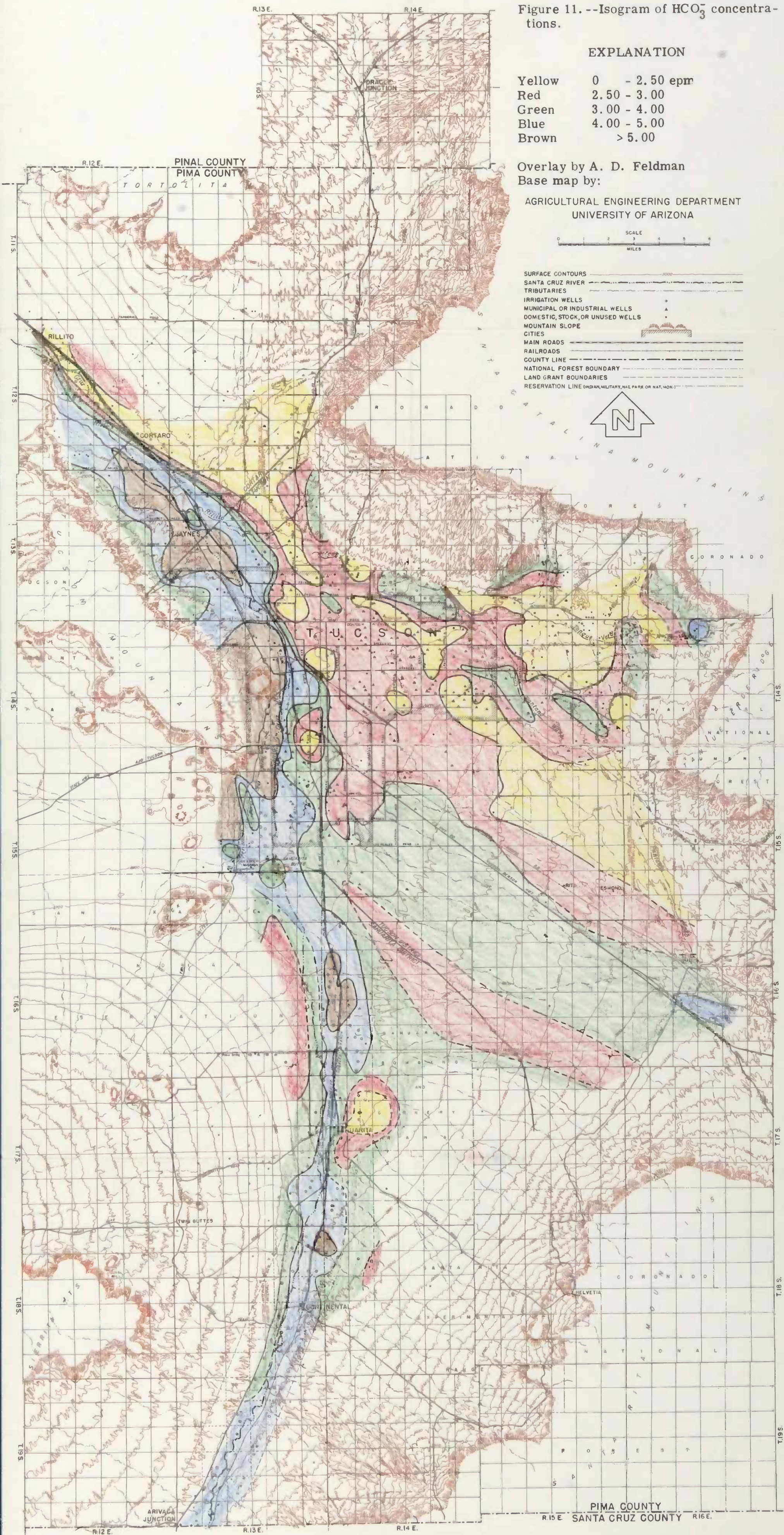
Yellow	0 - 2.50 epm
Red	2.50 - 3.00
Green	3.00 - 4.00
Blue	4.00 - 5.00
Brown	> 5.00

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Figure 10. --Isogram of SO₄ concentrations.

EXPLANATION

Yellow	0 - 0.25 epm
Red	.25 - 1.00
Green	1.00 - 2.00
Blue	2.00 - 5.00
Brown	> 5.00

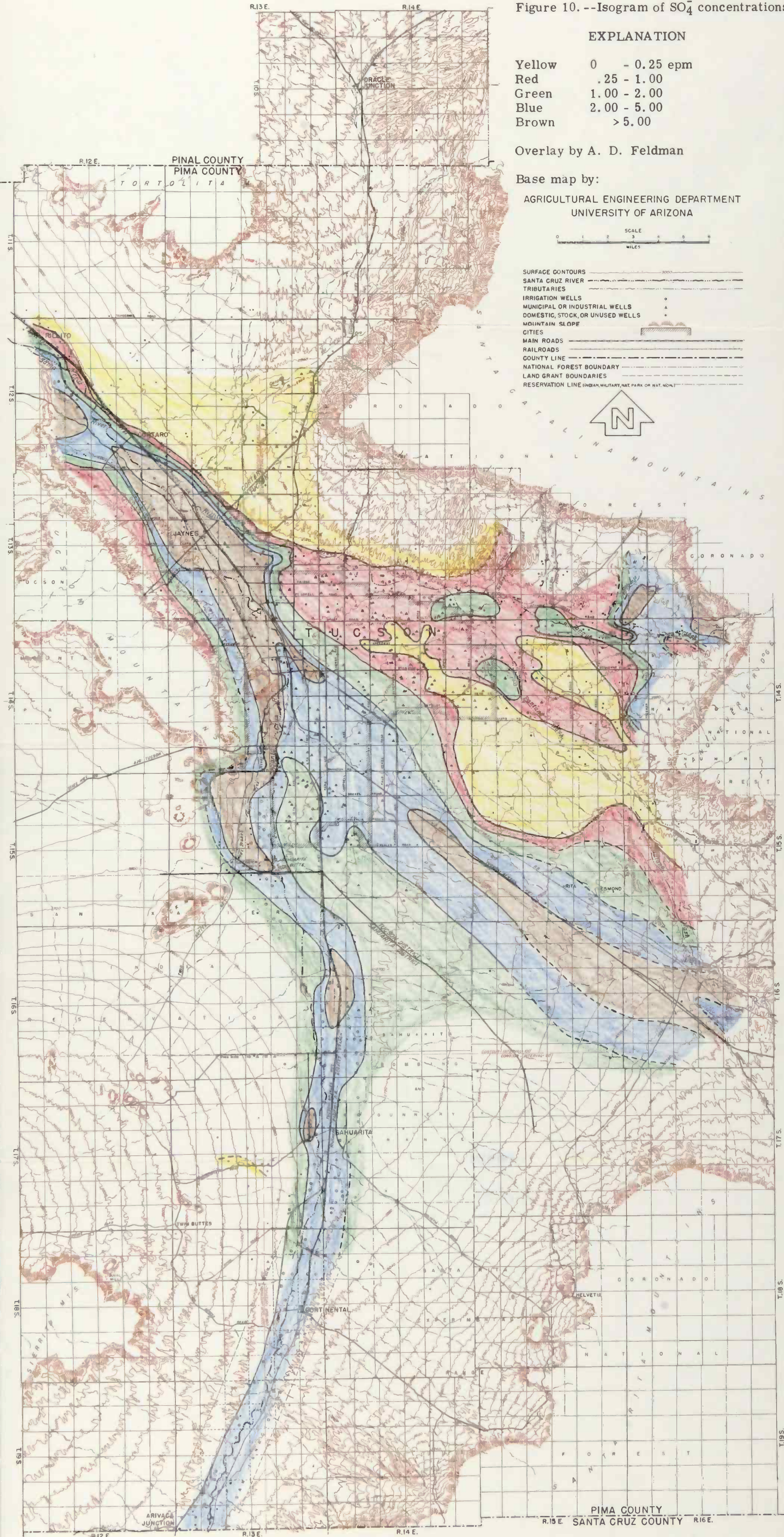
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Figure 9. --Isogram of Cl^- concentrations.

EXPLANATION

Yellow	0 - 0.40 epm
Red	.40 - .60
Green	.60 - 1.20
Blue	1.20 - 3.00
Brown	> 3.00

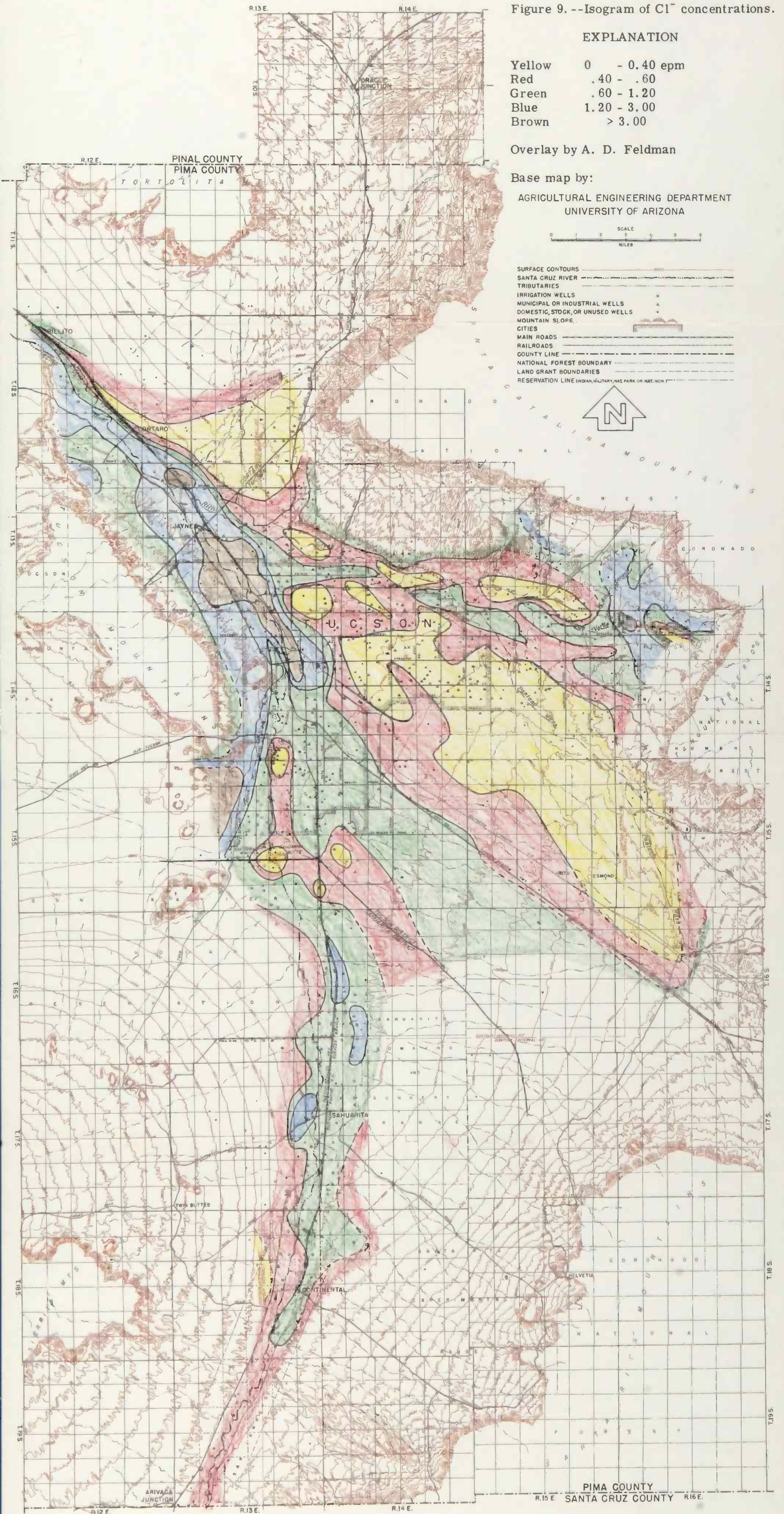
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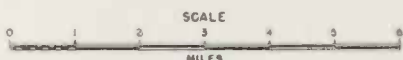
Figure 8. --Isogram of $\text{Ca}^{++} + \text{Mg}^{++}$ concentrations.

EXPLANATION

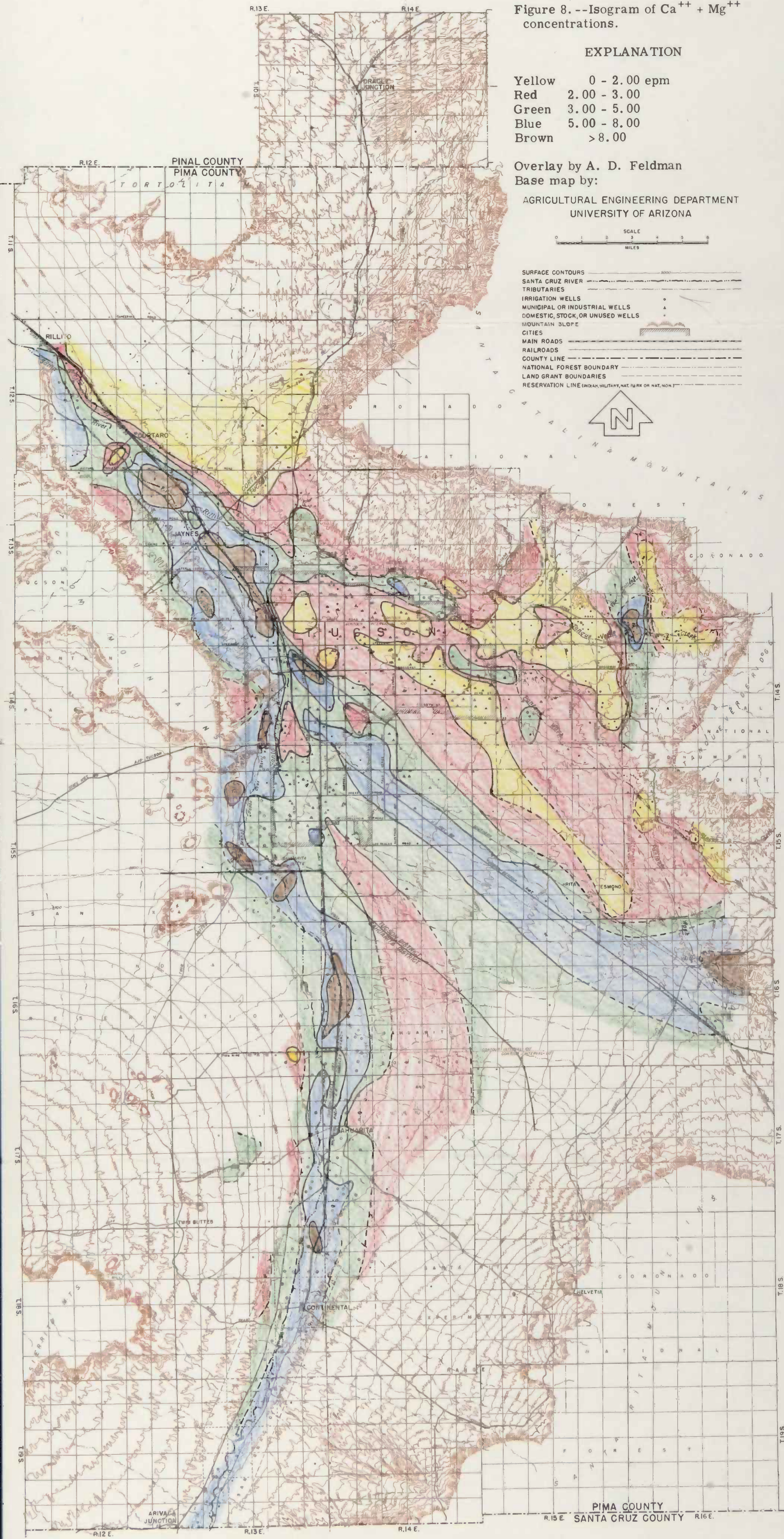
Yellow	0 - 2.00 epm
Red	2.00 - 3.00
Green	3.00 - 5.00
Blue	5.00 - 8.00
Brown	>8.00

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Figure 7. --Isogram of total soluble salts concentrations.

EXPLANATION

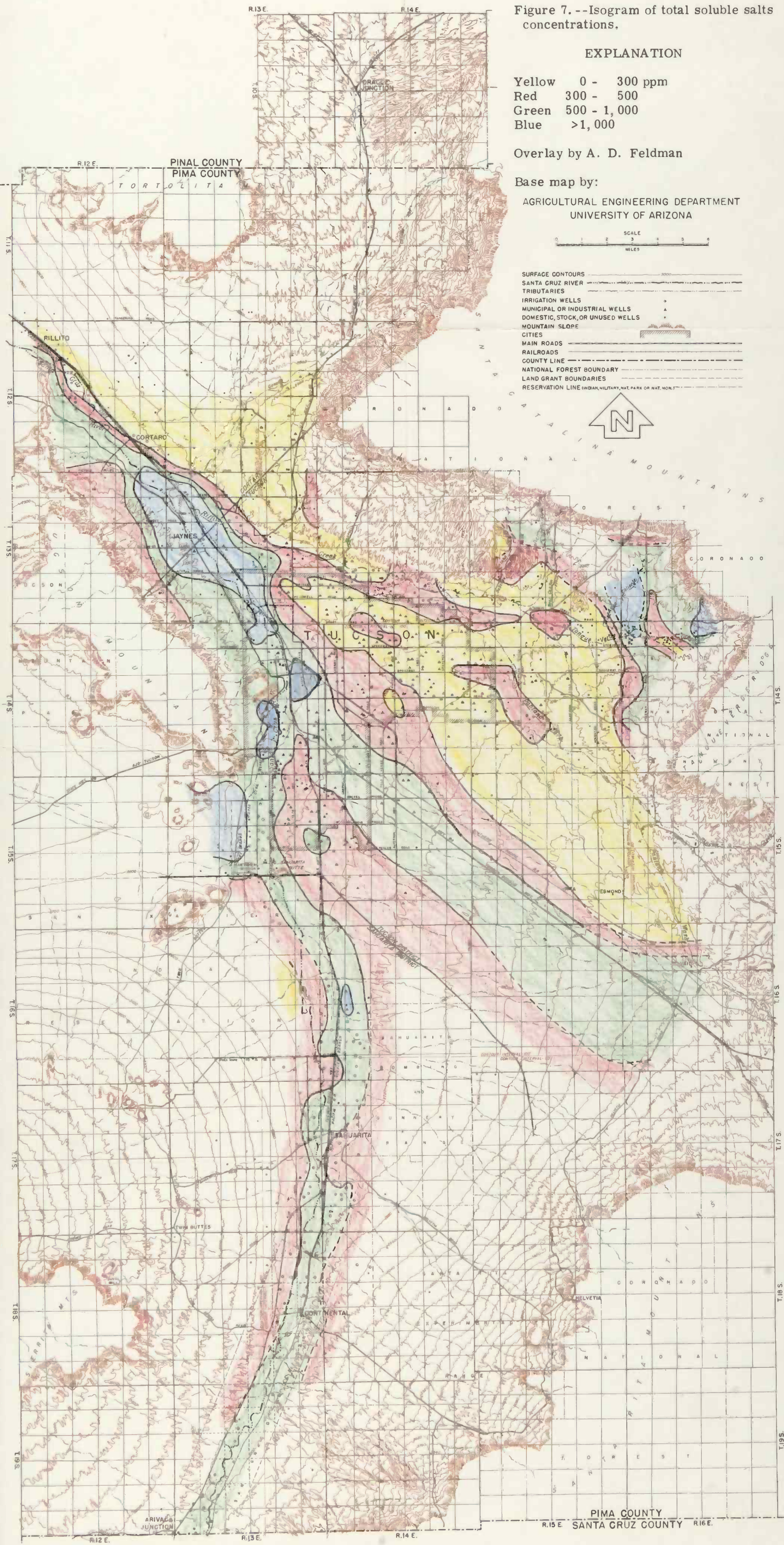
- Yellow 0 - 300 ppm
- Red 300 - 500
- Green 500 - 1,000
- Blue >1,000

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Figure 6. --Distribution of data and political boundaries of the study area.

EXPLANATION

• Well for which chemical analysis was used

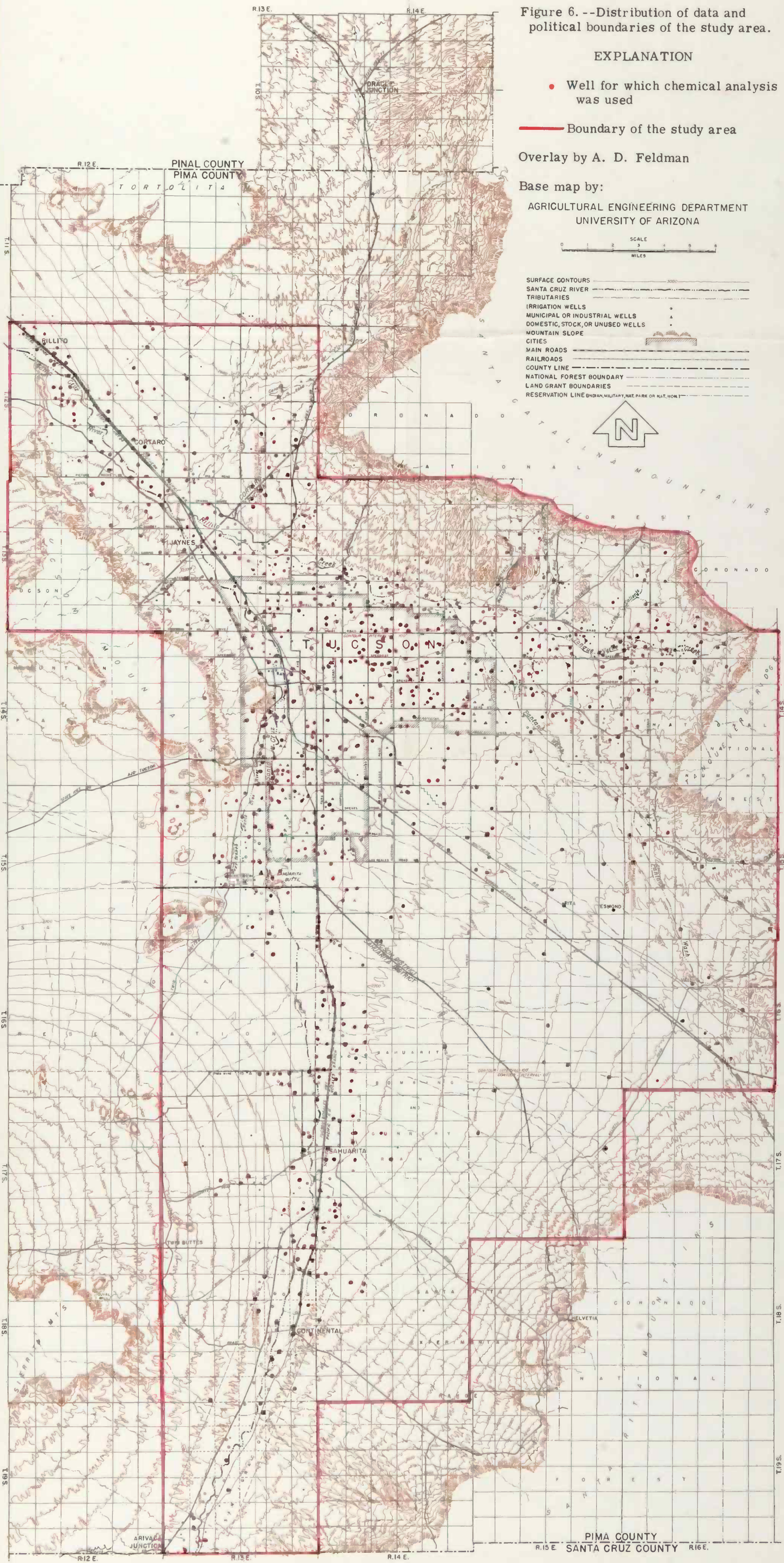
— Boundary of the study area

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W.A.

Figure 13. --Isogram of Piper water quality classes.

EXPLANATION

- Red Secondary alkalinity - carbonate hardness
- Green Primary salinity - non-carbonate alkali
- Blue No one cation-anion pair exceeds 50 percent

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