

HYDROCHEMICAL FACIES STUDY  
OF  
GROUND WATER IN THE TUCSON BASIN

by  
Peter Bernard Smoor

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THE UNIVERSITY OF ARIZONA

GRADUATE COLLEGE

I hereby recommend that this dissertation prepared under my direction by Peter Bernard Smoor entitled HYDROCHEMICAL FACIES STUDY OF GROUND WATER IN THE TUCSON BASIN be accepted as fulfilling the dissertation requirement of the degree of DOCTOR OF PHILOSOPHY

Eugene S. Simpson 21 April '67  
Dissertation Director Date

After inspection of the dissertation, the following members of the Final Examination Committee concur in its approval and recommend its acceptance:\*

<u>Eugene S. Simpson</u>	<u>21 April '67</u>
<u>[Signature]</u>	<u>4-21-67</u>
<u>[Signature]</u>	<u>4-21-67</u>
<u>[Signature]</u>	<u>4-21-67</u>
<u>John B. Ferris</u>	<u>4-21-67</u>

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SIGNED: Peter B. Moore

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## ABSTRACT

The concept of hydrochemical facies is used to study the distribution and, indirectly, to identify the origin of the chemical character of ground water in the basin-fill aquifer of the Tucson Basin in relationship to the hydrogeologic framework. Hydrochemical facies of ground water is defined operationally in terms of the lateral (horizontal) variation of chemical quality. The following chemical constituents are included in this study: total dissolved solids, calcium, magnesium, sodium, potassium, chloride, sulfate, bicarbonate, pH, nitrate, fluoride, strontium and zinc.

A conceptual process-response model relates the regional distribution of dissolved constituents to the following hydrogeologic controls: (a) the chemical composition of the rock and soil in the drainage area before recharge to the ground-water basin and conditions at the recharge sites, (b) the lithology of the basin-fill aquifer, and (c) the direction of ground-water flow within the aquifer itself.

Trend surface analysis suggests that the regional distribution patterns of total dissolved solids, calcium,

sodium, sulfate and strontium show a tendency to parallel the direction of ground-water flow. The distribution pattern of chloride ions based on old analyses shows a trend opposite to the distribution pattern of chloride ions based on new analyses from the same area. Nitrate content of ground water and specific capacity of wells seem to be related. Q-factor analysis of data from the basin-fill aquifer demonstrates that the overall chemical character of the ground water does not change substantially as it moves through the basin.

It is concluded that the chemical character of ground water in the basin-fill aquifer of the Tucson Basin was acquired mainly during contact with various rock types in the drainage basin before recharge. The lithology of the aquifer, presumably, only plays a secondary role in determining the overall chemical composition of the ground water. After recharge to the basin-fill aquifer the distribution of dissolved constituents is controlled primarily by the flow pattern.

A chemical equilibrium model of calcite and water is used to approach the problem of determining whether precipitation or dissolution of calcite takes place in the aquifer. Measured calcium ion concentrations and pH values are compared to calcium ion

concentrations and pH values computed for the equilibrium model. Assuming that the equilibrium model represents actual conditions in the aquifer, departures from the equilibrium model may be used to predict the chemical behaviour of calcite in the basin-fill aquifer.

## I. INTRODUCTION

The City of Tucson and its surrounding area completely depend on ground water as its single source of water supply. Large scale development of ground water has resulted in substantial declines of the water table. For future development and management of the restricted ground-water supplies available in the Tucson Basin accurate information on the quality and quantity of ground water is indispensable.

One of the more difficult problems in evaluating the water supplies of a ground-water basin in the arid Southwest is the question of natural recharge. Study of ground-water quality may help identify past and present sources and recharge areas for ground water in the basin. In other words, we would like to know from where and how has the ground-water reservoir of the Tucson Basin been recharged in the past and up to the present time. Additional water supplies for Tucson may be secured by capturing and storing water at or near the present recharge sites.

## Statement of the Problem

Until recent years little work has been done to explore the relationships which are known to exist between hydrogeology and chemical characteristics of ground water in a specific environment. Data on the chemical quality of ground water has been collected from many locations in the Tucson Basin but no adequate interpretation of the hydrogeologic relationships underlying the regional distribution of the chemical constituents is available.

Previous students of water quality in the Tucson Basin (Professor Schwalen, personal communication) had noticed that in some instances the chemistry of the ground water varies significantly within a small local area. Other wells, however, several miles apart show remarkable similarity in chemical composition.

Provisional mapping of the regional distribution of ground-water quality in the Tucson Basin has indicated that the isogram contours of some of the chemical constituents, notably total dissolved solids, sulfate, calcium and chloride show a remarkable tendency of parallelism to the direction of ground-water flow. These

results are contradictory to the observations and theories of several workers who have studied the occurrence of ground-water quality in desert areas (Chebotarev, 1955, Schoeller, 1962). However, a geo-hydrologic reconnaissance study of the Dateland area along the Gila River, Arizona, by Weist (1965) indicates possible banding of total dissolved solids and fluorides parallel to the general direction of ground-water movement.

In particular, the work by Schoeller (1962) suggests that the chemical composition of ground water in a basin does not, in general, remain constant in time and space. As water moves from its recharge area through the aquifer its concentration tends to increase because ground water gains mineral constituents as it moves through the basin. Schoeller pointed out that this tendency is particularly evident in desert areas. Not only is this due to the interaction of ground water and the rock matrix of the aquifer but also because of the increased role of evapotranspiration.

Seaber (1965), who studied the variations in chemical character of ground water from the Englishtown formation underlying the Atlantic Coastal Plain in New Jersey, also shows that the chemical character of the

ground water of the same aquifer progressively changes as the water moves away from its recharge area. Similar results were obtained by Back (1960, 1966) but his study included several water-bearing formations of the Atlantic Coastal Plain.

An aquifer study by Maderak (1964) in Minnesota indicates that the areas of low concentration of total dissolved solids coincide with recharge areas. The direction of ground-water flow is towards areas of high dissolved solids concentration. Based on a study of the geochemistry and movement of ground water in another part of Minnesota, Maclay and Winter (1967) also came to the conclusion that ion concentration changes as water moves from recharge to discharge areas.

The observations of these authors therefore seems to suggest that there is a trend of progressively changing chemistry along the flow lines. Contour lines of equal concentrations may be anticipated to show a general tendency perpendicular to the direction of ground-water movement.

In the alluvial basins of the Southwest the quality of ground water has been found to be greatly affected by the lithologic character of the sediments

constituting the aquifer (Kister and Hardt, 1961, Davis and DeWiest, 1966). Differences in chemical quality of ground water, therefore, are related to the mineralogy and texture of the sediments and in general, reflect the regional variation in geologic character of the aquifer.

In an early ground-water study of Sulphur Springs Valley, Arizona, Meinzer (Meinzer and Kelton, 1913) observed a distinct relationship of the chemical quality of ground water in the valley and the geologic nature of the rocks in the drainage area before recharge. In this report he also notes that "a general increase in mineralization toward the south no doubt results partly from difference in derivative rocks, but it may be in a measure due to the gradual acquisition of soluble matter as the water moves south-ward." The limited amount of data available from that study does not permit a clear cut decision whether mineral concentration is primarily due to progressive acquisition down gradient or perhaps more a reflection of the chemical nature of the derivative rock.

Summarizing, the differences in chemical quality from place to place is the result of several interdependent factors. Probably the more important factors

are the physical and chemical properties of the material through which the water moves, source and amount of recharge, geology of the derivative rocks in the drainage basin before recharge and the direction of ground-water movement. Regional patterns of chemical quality in ground water exist but in some cases the quality of water from wells is influenced more by local conditions.

In most studies of ground-water quality little quantitative information is available to define any of the possible relationships between ground-water quality and the hydrogeology. The main difficulty, perhaps, lies in the fact that although numerous chemical analyses of ground water are available, rarely these chemical analyses are from wells located and drilled with the specific purpose of conducting a study of ground-water quality. In the case of the Tucson Basin chemical analyses of wells were made to comply with public health regulations or as a standard procedure rather than with the objective to study the regional distribution of ground-water quality. In addition, therefore, the problem is one of how to deduce or test assumed relationships from an essentially incomplete set of chemical analyses not adequately representing all the hydrologic and geologic factors involved.

## Purpose and Scope

The general purpose of a hydrochemical facies study is to relate the chemical character of ground water to the geologic and hydrologic environment. The more specific objectives of this study are twofold:

1. Can the distribution of chemical constituents in a ground-water basin be simulated by a quantitative model, and can this model be used for the purpose of testing the occurrence of chemical quality of ground water predicted on the basis of some conceptual model?
2. Can quantitative models also be used to clarify the relationships between the distribution pattern of dissolved minerals in ground water and the direction of ground-water flow, the geologic and hydraulic properties of the aquifer, the nature of the derivative rocks in the drainage area before recharge and the conditions at the recharge site?

This study also explores the application of statistical models employing digital computers to the

regional study of ground-water quality in a basin. In addition to the advantages of using computers to store and retrieve data effectively, computers may also be useful in the evaluation of various hypotheses that may be set up to explain the relationships of hydrogeologic factors to the quality of ground water. An understanding of the dominant controls on the ground-water quality system in terms of a cause and effect relationship is prerequisite to a more exact formulation and eventually correct representation of ground-water quality models.

The chemical relationships involving ground water and dissolved constituents are complex and the study of chemical processes in ground water is usually restricted to relatively simple chemical systems. By relating field data to chemical models formulated on the basis of experimental and theoretical work and by applying the principles of chemical thermodynamics valuable insight may be gained into the chemical behavior of ground water.

#### Method of Treatment

It is assumed that the natural distribution of chemical quality of ground water in the Tucson Basin

is organized in a very specific manner related to a few dominant controls. One of the more important controls of the distribution of dissolved constituents seems to be the chemical composition of the rock and soil in the drainage area and at the recharge site before the water is recharged to the ground-water reservoir. Within the basin itself the dominant controls are the direction of ground-water flow and the characteristics of the material through which the water moves. Ground water now present in the basin was either recharged through alluvial fans in the periphery of the basin or through stream channels in the basin itself. In the case of some chemical constituents, little change seems to take place as water follows the hydraulic gradient to the exit of the basin, once the content had been established in the recharge area. Other constituents are more affected by facies changes in the geology and acquire concentration levels in accord with the mineralogy and texture of the aquifer.

The hypothesis that the chemical composition of the rock and soil in the drainage basin plays an important role in determining the quality of ground water in the basin-fill aquifer offers a more likely explanation than a theory proposed by H. Schoeller (1962,

1959), and supported by other students of arid zone hydrology (Chebotarev, 1955, M. Schoeller, 1964). The theory suggested by Schoeller to explain the distribution of dissolved constituents in an aquifer is largely based on the observation that the chemical quality of ground water changes progressively in the direction of ground-water movement. According to P. Cohen of the U.S.G.S. (personal communication) who has investigated ground-water quality in many basin-fill aquifers of the Basin and Range Province the latter situation is not uncommon in the western United States.

To investigate various hypotheses concerning the distribution of ground-water quality, it is useful to conceive a physical model of the basin at the time that water, which is presently being pumped from the basin-fill aquifer, was being recharged somewhere else in the basin. This physical model assumes the following to be the major controls of ground-water quality in the basin-fill aquifer of the Tucson Basin. These are in order of importance: (a) the chemical composition of the rock and soil of the drainage area before recharge and at the recharge site itself, (b) the direction of ground-water movement within the ground-water reservoir itself and (c) the lithology of the aquifer. Consequently,

the chemical quality pattern that may be anticipated should parallel in general the direction of groundwater flow. Superimposed on this trend are patterns related to the lithology of the aquifer. These modifications of the trend will be different for each of the chemical constituents.

The physical model may be evaluated by fitting polynomial trend surfaces to the regional distribution of each of the chemical characteristics to test the assumption that the chemical quality pattern has a tendency to parallel the general direction of groundwater movement. Trend surface analysis also will be useful in identifying those chemical constituents in ground water that are most affected by the lithology as water travels through the aquifer.

Factor analysis can be used in two modes. One application is to explore relationships among the different chemical constituents based on the chemical analysis of a number of water samples (R-mode analysis). Here each chemical constituent is considered a variable. The second way is to apply factor analysis with the objective to study relationships among water samples based on the different chemical composition of each water sample (Q-mode analysis). In the second case each water sample is considered a variable.

Q-mode factor analysis is applied to generate a model of water-quality distribution by grouping natural associations of water samples, each of the water samples representing a different locality. A grouping or association of water wells constitute a set of wells which resemble one another closely, taking into account all available information on chemical quality. By grouping the water wells which belong together, at least chemically speaking, the relationship between water-quality distribution and the dominant controls on water quality may become apparent.

R-mode analysis may be used to interpret the geochemical significance and the relationship of the chemical constituents analyzed from the Tucson Basin. Both trend surface and factor analysis can be helpful in predicting the nature of ground-water quality in a basin using only a limited amount of information.

Chemical equilibrium between ground water and calcite, using simplifying assumptions, can be studied as an initial attempt to investigate the complex chemical processes involving ground water and the rock matrix.

Information which is becoming available on the trace element content in ground water of the Tucson Basin, hopefully will contribute towards a more complete

understanding of the geochemical behaviour of ground water in the basin.

### Sources of Data

Part of the chemical analyses used in this study are taken directly from the files and publications of the Agricultural Experiment Station of the University of Arizona. Most of these analyses were made over a period of several years by the Soil and Water Testing Laboratory of the University of Arizona. The author also collected water samples from wells of the same area for trace element analysis. Although most of the wells had been sampled before for standard chemical analysis, new analyses were made with the objective to compare old and new data. At the time of sampling, temperature and pH of water from these wells were measured in the field. All laboratory analyses on the samples collected by the author were made by the Soil and Water Testing Laboratory of the University. These data are also on file with the University of Arizona Agricultural Experiment Station and available on request.

Specific capacity data of municipal wells were furnished by the City of Tucson Water Department. These

specific capacity data are based on pump tests conducted by City personnel in the course of several years.

## II. HYDROGEOLOGIC ENVIRONMENT OF THE TUCSON BASIN

Discussion of the geology and hydrology of the Tucson Basin will be restricted to basic features only, with emphasis given to aspects pertaining to the quality of ground water in the basin-fill aquifer. For more complete and detailed information concerning the general hydrology and many of the geologic features reference is made to Schwalen and Shaw (1957), The Rillito Creek Hydrologic Research Committee Report (1959) and several bulletins published by the Agricultural Experiment Station of the University of Arizona (Reports 217 and 223). Other pertinent information on more specialized aspects is incorporated in several recent theses submitted to the Graduate College of the University of Arizona (Ganus, 1965, Feldman, 1966, Pashley, 1966, AbuaJamieh, 1966).

### Geology

#### Surrounding Mountain Ranges

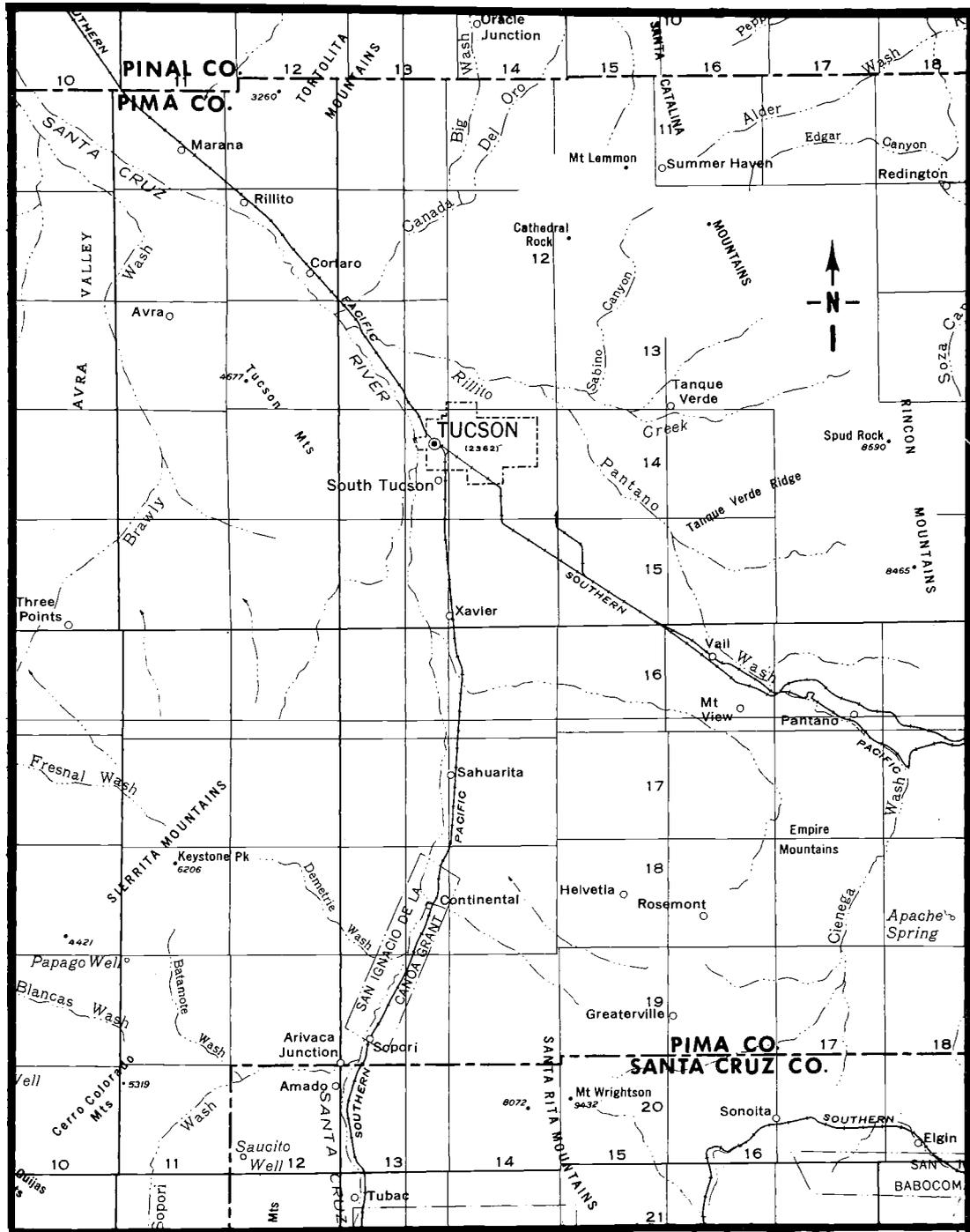
The Tucson Basin is a structural depression typical of the Basin and Range Province of the

southwestern United States. It is bordered on the north and the east by the Santa Catalina, Tanque Verde and Rincon Mountains (Figures 1 and 2). These mountain ranges are largely composed of granite and gneiss. To the southeast the area is bordered by a variety of igneous, metamorphic and sedimentary rock types. The Cienaga Gap area and the adjacent part of the Empire Mountains area characterized by the dominant occurrence of sedimentary rock, including carbonates and evaporites. The northern part of the Santa Rita Mountains at the southern and southeastern edge of the basin is composed of volcanic and volcanic intrusive igneous rocks, Paleozoic and Mesozoic sedimentary rocks. The Tucson Mountains at the west side are made up of predominantly post-Paleozoic sediments covered and dissected by younger volcanics and intrusives (Bikerman and Damon, 1966).

#### Basin Fill Material

Much of the margin of the Tucson Basin along the edge of the Santa Catalina and Tanque Verde Mountains is underlain by tilted and faulted conglomerate, sandstone, mudstone and gypsum deposits, called Rillito Beds (Pashley, 1966). The Rillito Beds, of

Figure 1. Index Map of Tucson Basin and surrounding area. Numbering system refers to subdivision in Townships and Ranges with respect to the Gila and Salt River meridian and baseline.



Scale 1:500 000

1 inch equals approximately 8 miles

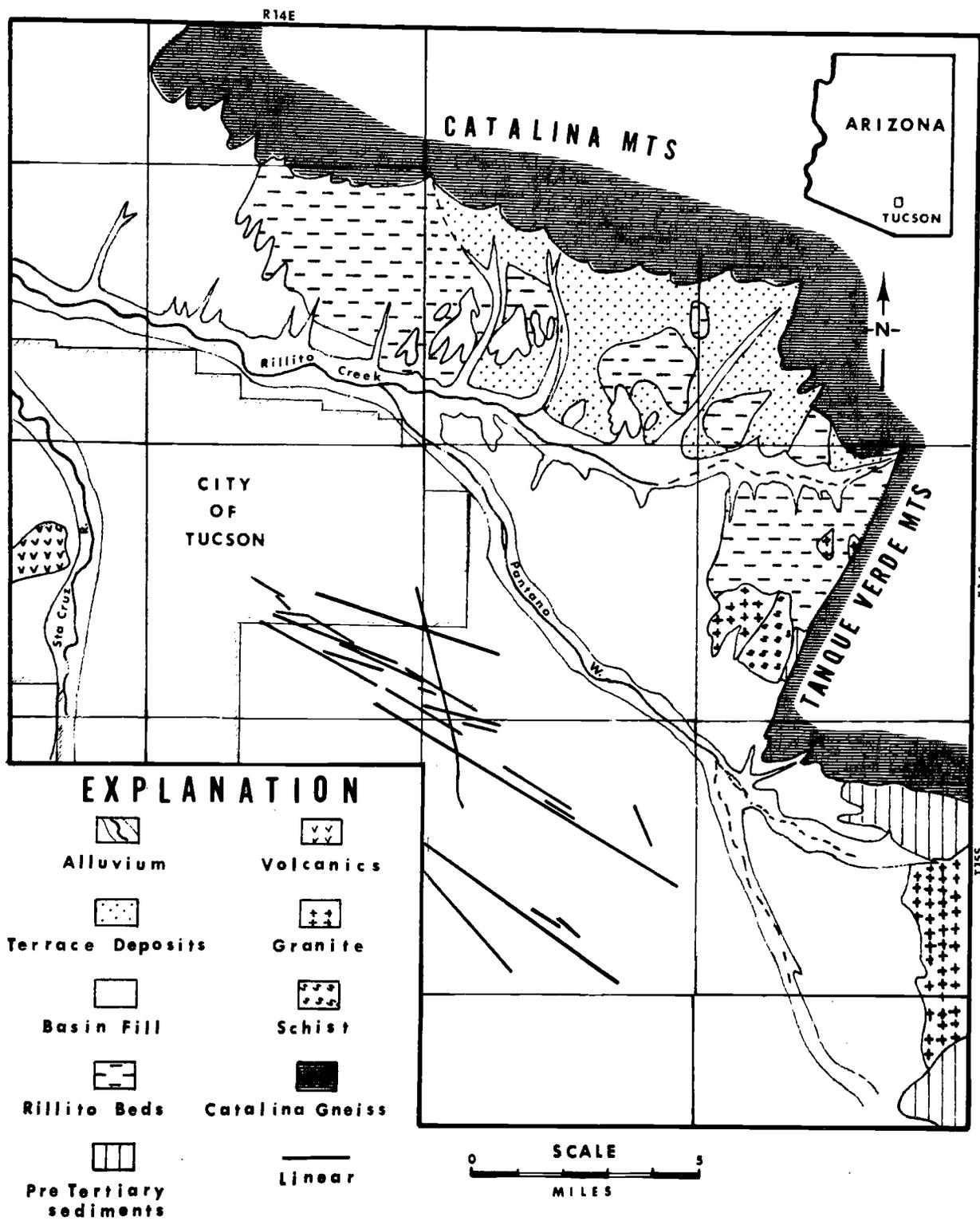
Miles



INDEX MAP OF TUCSON BASIN AND SURROUNDING AREA

FIGURE 1

Figure 2. Generalized geologic map of the Tucson Basin. Geology largely after Pashley (1966). Linear features from Sherman and Hatheway (1964).

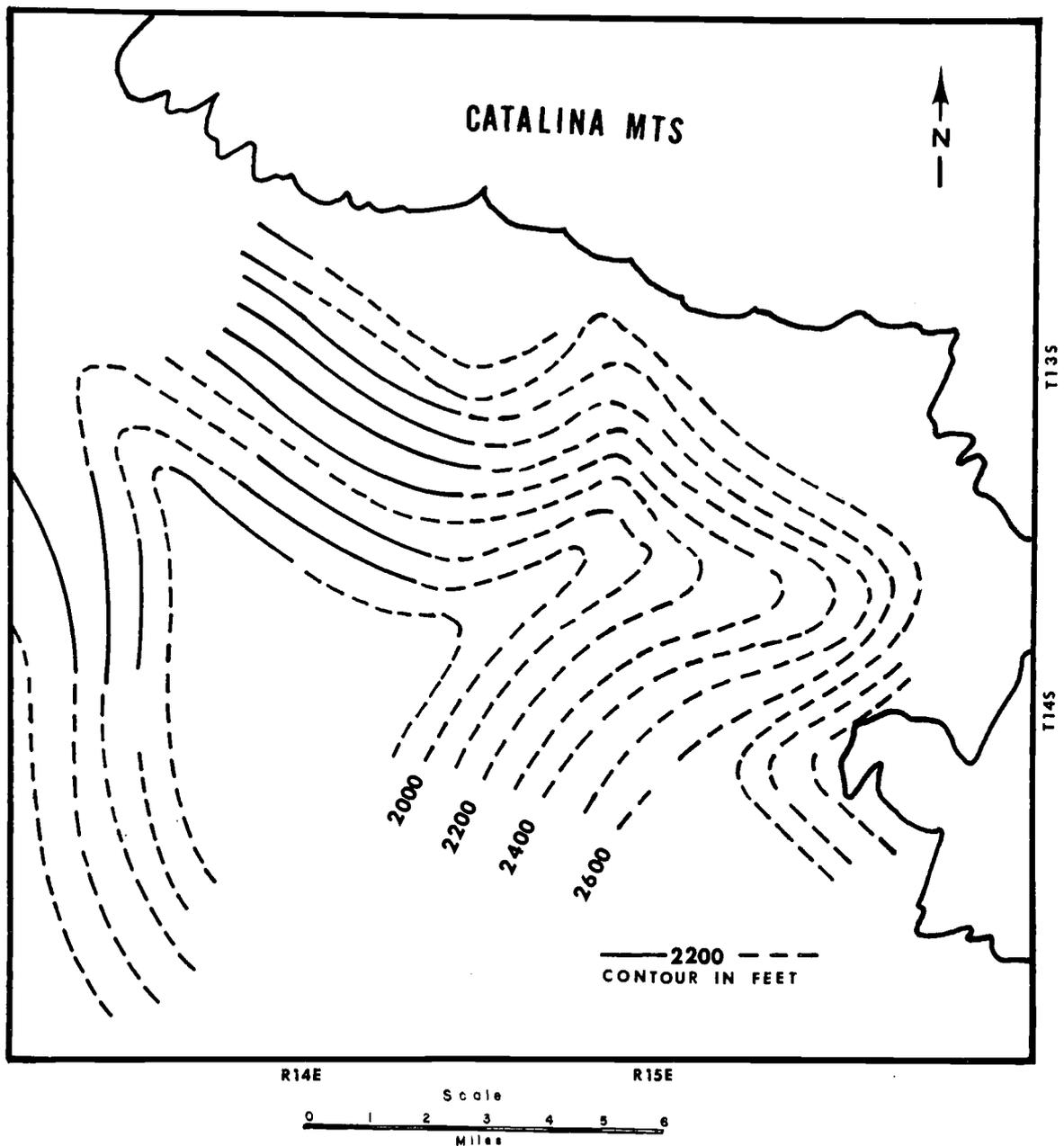


**GEOLOGIC MAP OF TUCSON BASIN**

**FIGURE 2**

Tertiary age, were buried over most of their present extent by younger undeformed deposits referred to as basin fill by Pashley (1966). The basin-fill deposits lie with angular unconformity over the generally poorly permeable Rillito Beds and all water analyses used in this study are from wells that penetrate this basin fill only. According to Pashley the basin-fill deposits were laid down as alluvial fans in late Tertiary and Quaternary time. The formation of the present drainage outlet in the northwest corner of the basin in middle-Quaternary time resulted in increased stream gradients and the beginning of basin erosion. This erosion has removed much of the basin fill from large areas adjacent to the mountain front, uncovering Rillito Beds and bedrock pediments. In the central part of the basin the average thickness of the basin fill is about 700 feet (Figure 3).

The basin-fill material consists of poorly consolidated gravel, sand and silt, most likely derived from the surrounding mountain ranges. The sand and gravel fraction of the basin fill deposits is largely composed of fragments of gneiss exposed only in the Santa Catalina, Tanque Verde and Rincon Mountains. This is a good indication that the basin fill material



### CONTOUR MAP OF BASE OF THE BASIN FILL SEDIMENTS

Figure 3. Contour map of base of the basin-fill sediments on top of the Rillito Beds (modified after Pashley, 1966). Contour lines are dashed where approximate.

Figure 4. Generalized lithology of basin-fill sediments in the saturated part of the aquifer at selected intervals above mean sea level (modified after Ganus, 1965). Perpendicular solid lines indicate Township T14S-R14E.

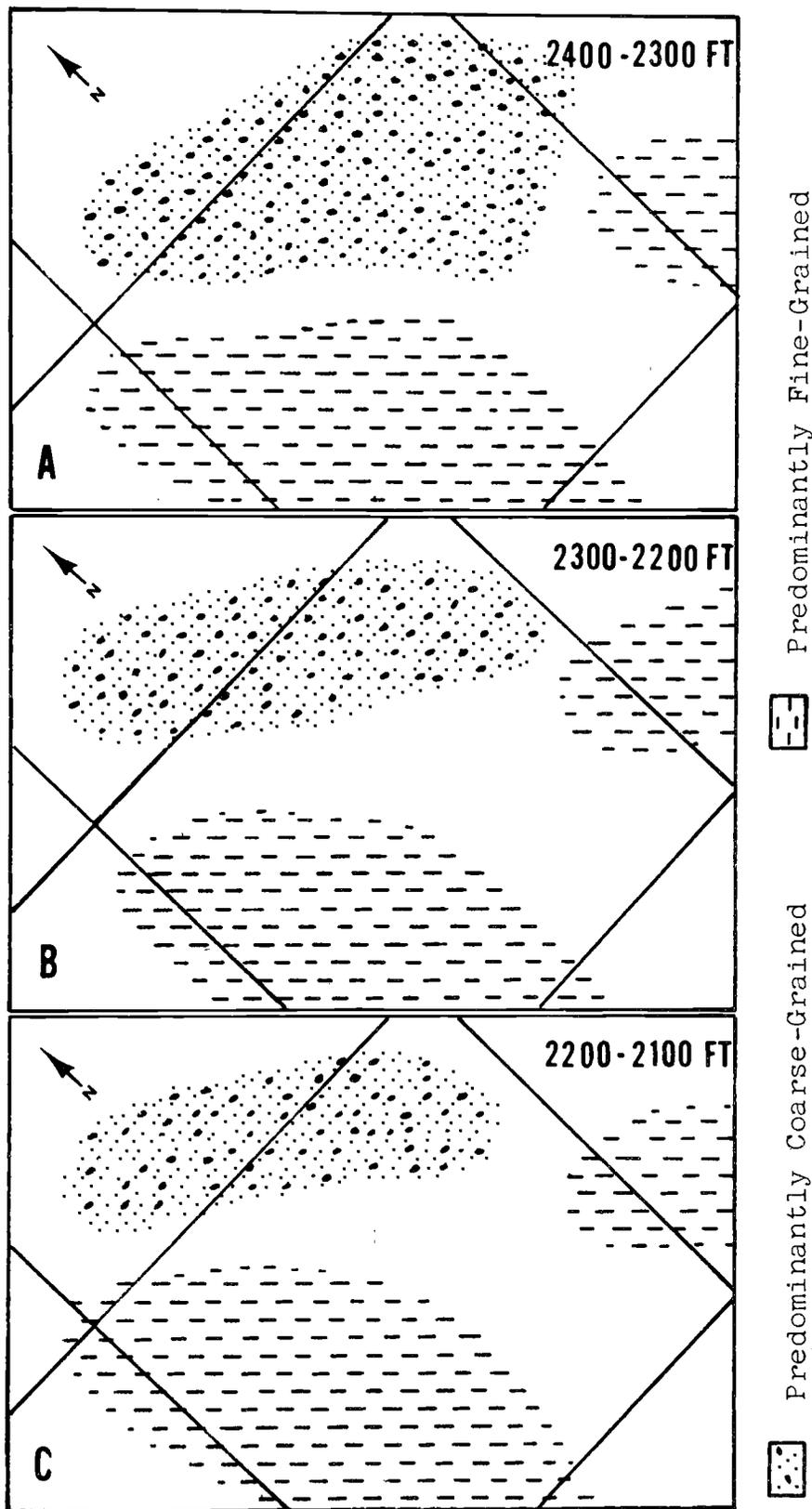


Figure 4. Generalized lithology of basin-fill sediments.

originated as alluvial fans of drainage basins within the mountain ranges. The orientation and imbrication of the pebbles in the basin-fill deposits also suggest deposition by streams from the mountain ranges toward the central part of the basin (Pashley, 1966).

Ganus (1965) has interpreted the lithology of the basin-fill deposits on the basis of drillers' logs and specific capacity data from a large number of wells. The generalized lithology at three selected 100 foot intervals, corresponding to the saturated part of the basin-fill aquifer, is shown by Figures 4A, 4B, and 4C. These rectangular maps of the study area, located in the north-central part of the Tucson Basin, cover most of Township T14S-R14E (Figure 2) and some adjacent area. The size, shape and orientation of the map area were determined mainly by the desire to include as many evenly distributed well locations as possible.

#### Linear Features

Some interesting linear patterns can be clearly observed on areal photographs of the Tucson Basin and are shown as "linears" on the geologic map of the Basin (Figure 2). Sherman and Hatheway (1964) suggested the term "linear" for these straight

physiographic features. Field investigation by Sherman and Hatheway indicated some relationship between building fractures, vegetational alignment and erosional characteristics, and the occurrence of these linears. They suggested two possible modes of origin for the occurrence of linears in the Tucson Basin: (1) structural activity of the deep subsurface strata or basement rock transmitted to the surface, (2) differential compaction of the alluvial material.

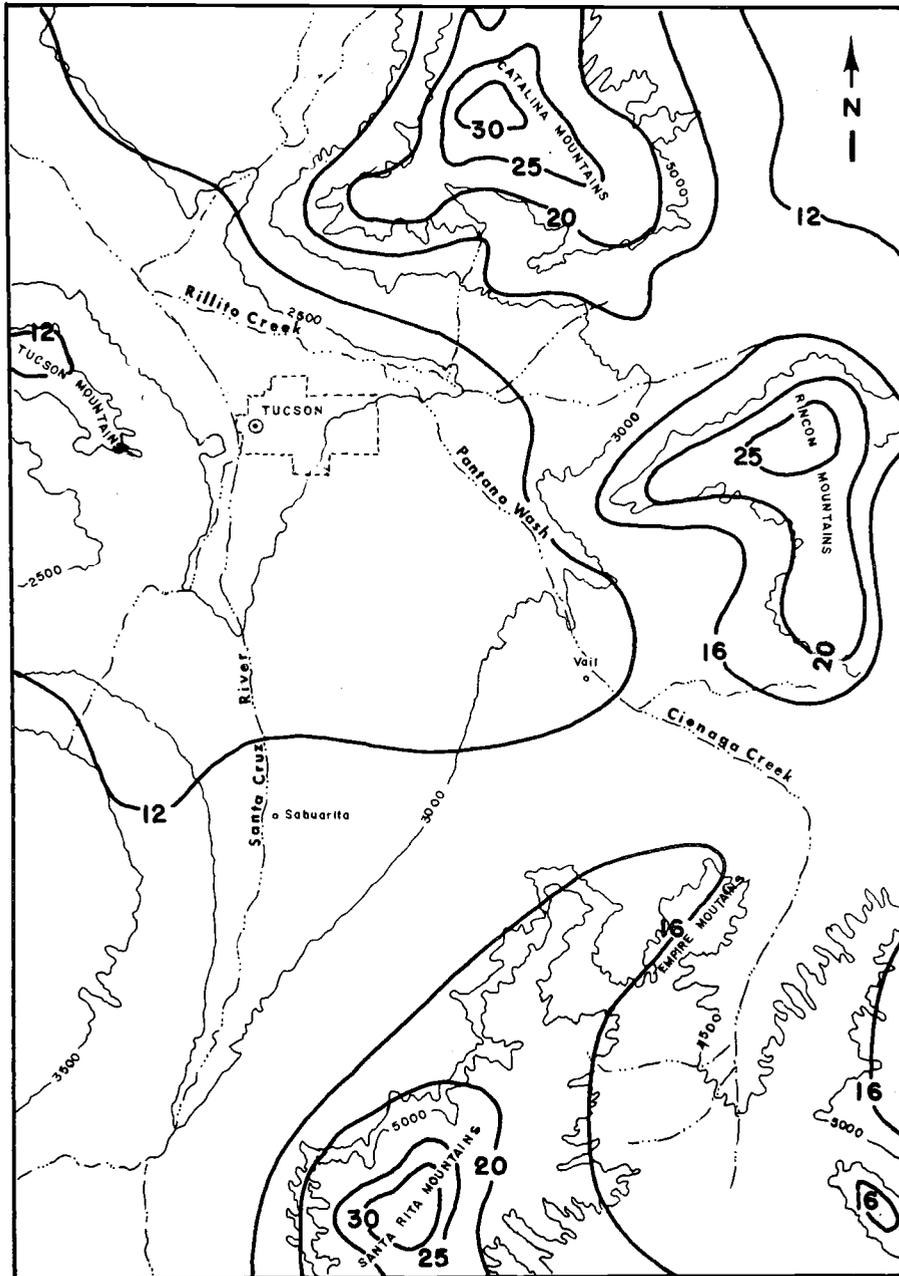
It may be noted in this context that cracks and fissures, usually not as straight as these linear features, have been reported from alluvial basins elsewhere in southern Arizona (Robinson and Peterson, 1962). These earth fissures seem to be due to compaction of sediments resulting from heavy withdrawal of ground water.

## Hydrology

### Precipitation

Precipitation is extremely variable with time and location as is common in an arid climate. High altitudes surrounding the Tucson Basin receive proportionally more precipitation (Figure 5). Thunderstorm activity during the summer months provides almost

Figure 5. Normal annual precipitation distribution, Santa Cruz Valley, Arizona (1931-1960). From map published by University of Arizona Hydrology Program based on U. S. Weather Bureau data.



EXPLANATION

— 20 —

Isalines of Normal Annual Precipitation

SCALE

0 5 10  
Miles

# NORMAL ANNUAL PRECIPITATION (1931-1960) SANTA CRUZ VALLEY

FIGURE 5

one half of the annual precipitation. The remaining half of the rainfall is less intense but more widespread winter precipitation. In general it is assumed that in areas between stream channels recharge from precipitation through the soil zone to the groundwater basin is negligible.

### Surface Water

The main channels of runoff are the Santa Cruz and the Rillito with their tributary channels. The Santa Cruz river is the principal stream channel in the Tucson Basin but the Rillito Creek, which receives most of its runoff from the surrounding slopes of the Catalina, Tanque Verde and Rincon Mountains, is of greater interest to the study area.

Flood runoff along the Rillito Creek stream channel is generally of two types. In the spring, flow results from snow-melt at higher elevations, sometimes continuing for a period of several weeks until all the snow is gone. The flow pattern may be altered for either of two reasons: freezing temperatures which may decrease the flow at its source, or rain causing not only increased flow from precipitation but also by more rapid melting of snow. It is during this time

of extended runoff in the late winter and early spring that surface water with relatively low silt content gets a favourable chance to recharge the ground-water basin. During the summer time, but occasionally also during the winter months, thunderstorm rainfall may cause sudden flashfloods. The sediment load of these short duration floods is much higher than in runoff resulting primarily from snow-melt. Because of the short duration recharge from stream channels during flashfloods is probably less favourable than during runoff of longer duration in late winter and spring (Matlock, 1965).

#### Ground Water

Systematic ground-water studies of the Tucson Basin were initiated shortly after the turn of the century and the first water table map for part of the Tucson Basin was published in 1910 (Smith, 1910). Subsequent studies of ground water in the Tucson Basin were primarily concerned with the local and regional changes of the water table from year to year. We may assume that the regional water table before 1920 was virtually unaffected by pumping and that natural conditions were still reflected by the hydraulic

gradient. Unfortunately, the water level information of this early period in the modern development of Tucson covers a small area only.

Before large scale development by man, the regional hydraulic gradient was about twenty to twenty-five feet per mile in a generally northwest direction towards the basin outlet at Cortaro. Early reports on ground-water conditions of the Tucson Basin (Smith, 1910) indicate that the water table near major stream channels was encountered at less than twenty feet below the surface. The earliest interpretation of the regional water table is for conditions in 1947 (Figure 6A). The water table and flow net for that year is probably still a fair representation of the natural conditions. Accelerated development since then has resulted in declining water levels (Figure 6B) and modification of the natural hydraulic gradient. Ganus (1965) has attempted to interpret the changes in the water table that have resulted from heavy withdrawal of ground water in terms of the basin structure and the hydraulic and lithologic properties of the basin-fill sediments.

Figure 6. Generalized ground-water hydrology of basin-fill aquifer, Tucson Basin. Perpendicular solid lines indicate Township T14S-R14E.

- (A) Water-table map and flow net representative of Spring, 1947 conditions. Data supplied by the Agricultural Engineering Department, University of Arizona.
- (B) Water-table map representative of Spring, 1966 conditions. Data supplied by the Agricultural Engineering Department, University of Arizona.
- (C) Regional distribution of specific capacities of wells penetrating the basin-fill aquifer. Data supplied by the City of Tucson Water Department.

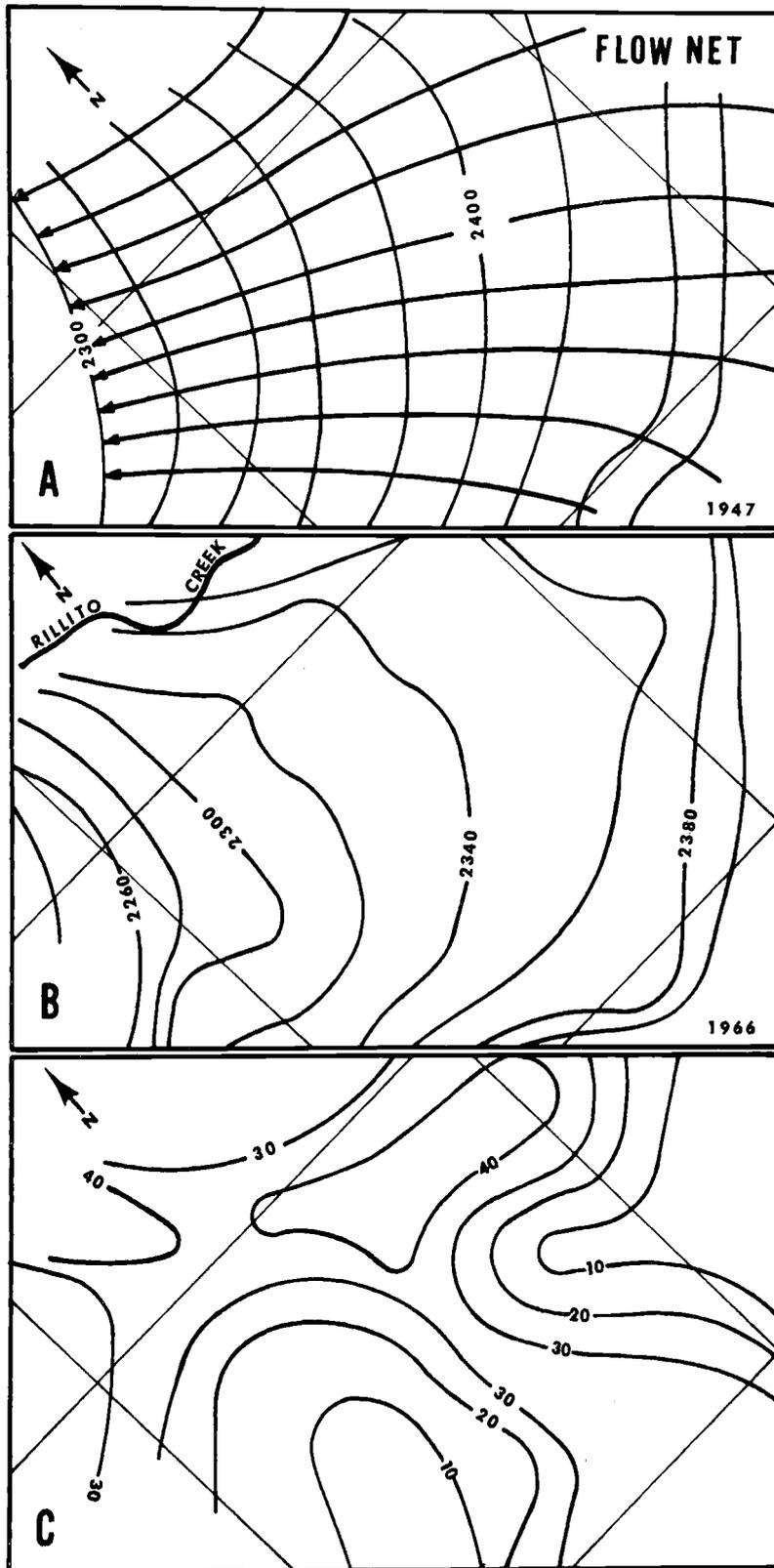


Figure 6. Generalized ground-water hydrology of basin-fill aquifer.

## The Ground-Water Flow Net

Construction of the flow net of ground water in the Tucson Basin is based upon a ground-water contour map representing the conditions in the Spring of 1947 (Figure 6A). This is the earliest reliable regional interpretation of the potentiometric surface of ground water in the basin. Intensive development of ground water had just started and there is little evidence of large scale distortion of the regional gradient.

The flow lines are drawn on the assumption that the aquifer is isotropic but not necessarily uniform and the following procedure has been followed to construct the regional flow net. Stream lines are drawn such that the distance between any two adjacent stream lines where they cross the 2330 and 2340 equipotential lines is equal to the distance between those two equipotential lines. A series of squares called unit squares is then obtained with an index ratio of stream line to equipotential line interval of unity. Stream lines are then extended in both directions from the unit ratio areas perpendicular to each equipotential line it crosses. The index ratio of the distance between

stream lines and equipotential lines will not remain constant but vary depending on the relative uniformity of the aquifer. It is conceded that this might not be the best possible interpretation of ground-water flow in the Tucson Basin. However, there is little doubt that this flow net reflects the general direction of ground-water movement which is of primary concern in this study.

#### Natural Recharge

Estimates of natural recharge to the water table aquifer can be made from the balance of precipitation versus runoff, evapotranspiration and other consumptive uses of water. The difficulty in obtaining reliable estimates is caused by the lack of adequate information on the nature of the infrequent flood flows and the great variation from year to year. Matlock (1965) reports 28,000 acre-feet of annual recharge for the period March 1, 1959-March 1, 1960 when an unusually long period of spring runoff occurred. However, during the month of March, 1960, recharge was estimated to be approximately 14,000 acre-feet, or one-half of the previous annual total. The results of an electric analog study of the Tucson Basin by Matlock

(1966) suggest an average annual recharge of 14,000 to 20,000 acre-feet for the Rillito Creek area, depending on the assumed total annual recharge for the basin. For the system Pantano Wash, Rincon Creek, Rillito Creek and tributaries an average annual recharge of 32,000 to 45,000 acre-feet is estimated, again depending on the assumed total annual recharge to the basin. Estimated average annual recharge to the basin for the period 1961-1965 is between 56,000 and 79,000 acre-feet (Matlock, Schwalen and Shaw, 1965).

#### Hydraulic Properties

The transmissive properties of the water-bearing formations of the Tucson Basin can be estimated from specific capacity data. Specific capacity of a well is the ratio of the volume of water produced in a given time to the amount of drawdown due to pumping. Specific capacity is generally expressed as gallons per minute per foot of drawdown. High specific capacities generally indicate high coefficients of transmissivity and low specific capacities low coefficients of transmissivity. This relationship is less reliable for low specific capacity values because specific

capacity is affected by entrance losses, caused by poor well conditions, convergence losses due to partial penetration of the aquifer and by hydrologic boundaries. These factors have an adverse effect on specific capacity and actual transmissivity values, therefore are greater than the computed transmissivities based on specific capacity. Low specific capacities are proportionally more affected by these factors and therefore less representative of the true aquifer conditions than the high specific capacities. Because of the lack of adequate, more refined aquifer-performance tests in the Tucson Basin, specific capacity still serves a useful purpose as a rough estimate of aquifer transmissivity.

The distribution of specific capacity of wells in the basin-fill aquifer of the Tucson Basin is based on data supplied by the City of Tucson. Only the most reliable estimates based on several annual pump tests for each well were considered. An interpretation of the distribution of specific capacity in the north central part of the basin (Figure 6C) is generally in good agreement with an earlier map by Ganus (1965) and an unpublished map by the City of Tucson Water Department. Assuming a constant rate of well discharge,

a homogeneous isotropic non-leaky aquifer of infinite areal extent, full penetration of the well and negligible well losses, the coefficient of transmissivity may be approximated by the relationship,

$$T = 2000 C_s$$

where  $T$  = Coefficient of transmissivity in gallons per day per foot

$C_s$  = Specific capacity in gallons per minute per foot of drawdown.

Several pump tests of relatively short duration have yielded an approximate storage coefficient value of  $S = 0.02$ . It is generally assumed that water-table conditions are prevalent over most of the basin-fill aquifer suggesting that this low value is probably not realistic. Estimates of specific yields of the basin-fill aquifer based on change in aquifer storage due to pumping (Matlock, Schwalen and Shaw, 1965) and more recent aquifer-performance tests (Professor Ferris, personal communication) indicate that storage coefficient values of 10-20 percent are more likely.

Matlock (1966) achieved close simulation of the natural water table contours utilizing a passive element electric analog model of teledeltos paper.

This fact supports the concept that the basin-fill sediments may act as a large homogeneous aquifer.

#### Temperature of Ground Water

Temperature of ground water from wells was measured in the field during the collection of water samples for chemical analyses. Inspection of the results show a remarkable gradient perpendicular to the general direction of ground-water flow (Figure 7A). Comparison with the map showing linears in the Tucson Basin (Figure 7B) suggests a relationship between the presence of linears at the surface and the occurrence of higher temperatures in the central part of the basin. This area apparently acts as a heat source and this fact, perhaps, supports the idea of structural activity involving strata or bedrock at greater depth associated with the linears.

#### Age of Ground Water

Samples of ground water from wells penetrating the basin-fill aquifer of the Tucson Basin have been dated by Carbon-14 method (Bennett, 1965). The samples were not taken from a single depth interval but represent the entire length of penetration of

Figure 7. Hydrogeology of the Tucson Basin.  
Perpendicular solid lines indicate  
Township T14S-R14E.

- (A) Temperature distribution in ground water of the basin-fill aquifer in °C.
- (B) Pattern of linear features observable from areal photographs of the Tucson Basin (after Sherman and Hatheway, 1964).
- (C) Radiocarbon ages of ground water in the basin-fill aquifer at selected well sites (modified after Bennett, 1965).

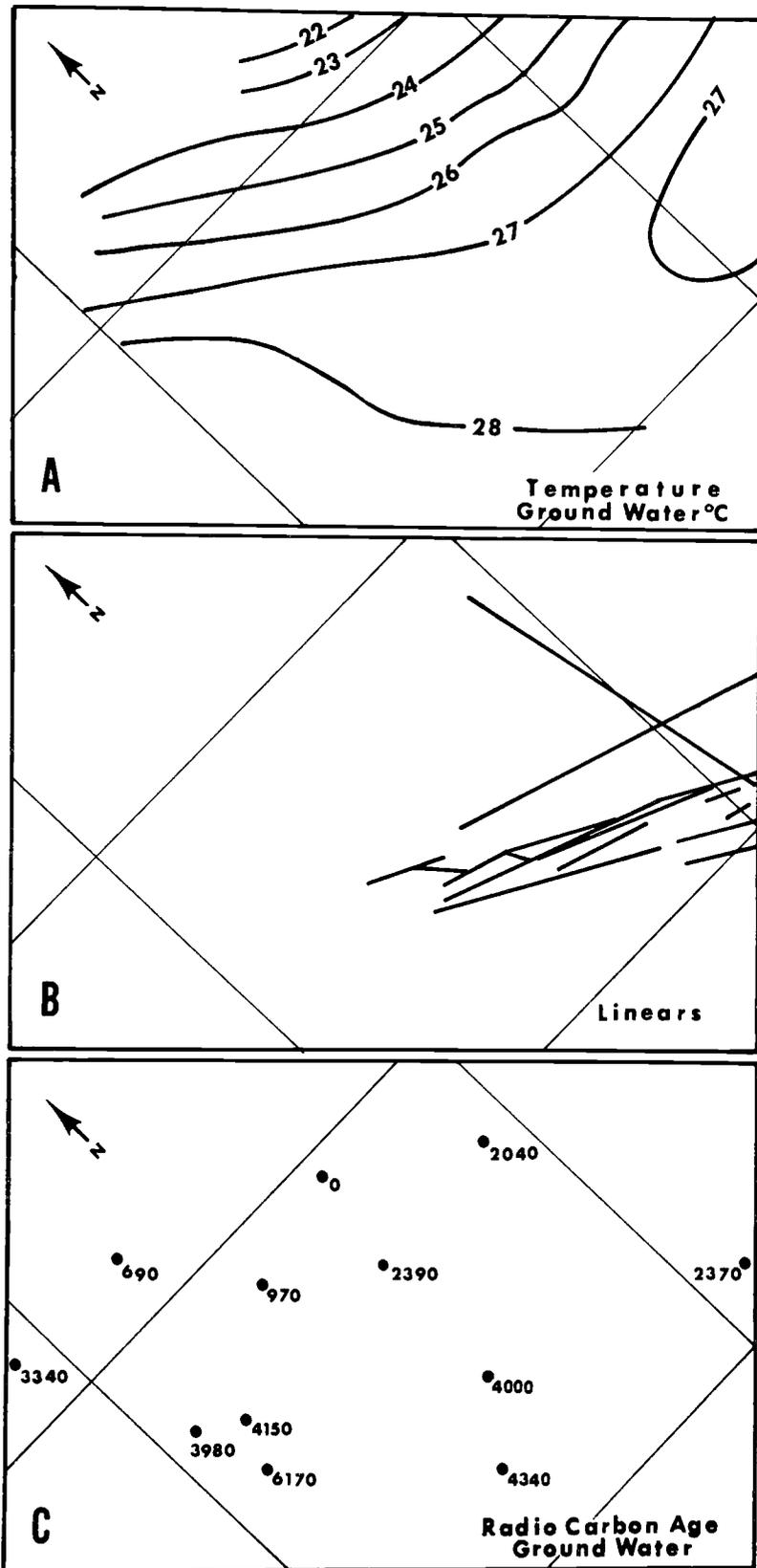


Figure 7. Hydrogeology of the Tucson Basin.

of the aquifer. By the "age" of the ground water is understood the amount of time since the water was last in contact with the  $C^{14}$  reservoir in the atmosphere, presumably at the time of recharge. Ground-water samples from the basin-fill aquifer in the central part of the basin have yielded apparent ages up to 6000 radio carbon years (Figure 7C). Carbon-14 activity is determined primarily from bicarbonate in the water sample. The radiocarbon ages of ground water plotted in Figure 7C have not been corrected for exchange reactions involving this anion.

### III. THE CONCEPT OF HYDROCHEMICAL FACIES

#### Introduction

The concept of hydrochemical facies has been used by Back (1960, 1966) to denote the chemical character of ground water in hydrologic systems. Hydrochemical facies reflects the effects of chemical processes in the lithologic environment and the prevailing ground-water flow patterns. The lithologic framework determines which facies will develop and the flow pattern of the ground water controls the distribution of the facies. The hydrochemical facies concept therefore may provide a model for explaining the distribution and origin of the principal chemical types of ground water in selected areas (Back and Hanshaw, 1965).

Significant parameters of hydrochemical facies can be illustrated by techniques and procedures similar to those used in lithofacies studies of sedimentary basins. Back (1960, 1966) has adapted and applied some of these methods to mapping of hydrochemical facies during the course of his work on ground water in sediments

underlying the Atlantic Coastal Plain. In this study he demonstrated the regional relationship between chemical character of ground water, the lithology of the sediments, the topography of the area and the ground-water flow patterns. Subsequently, Seaber (1965), Morgan and Winner (1962), and Maclay and Winter (1967) have used the same concept to study the chemical character of ground water in various parts of the United States.

The term facies has been applied to a variety of geological problems and its use is sometimes controversial and ambiguous (Teichert, 1958, Krumbein and Sloss, 1963). Some of this controversy is also reflected in the development of the term hydrochemical facies in the ground-water literature. In geology, facies has been used in reference to rather different concepts. Not including some non-stratigraphic applications the term, in general, has been used to denote:

1. The physical and chemical characteristics of a rock.
2. The environment in which the rock was formed.
3. The association of fossils in the rock.
4. The association of living fauna in the environment of deposition.

Originally, facies referred to the sum of lithologic and paleontologic characteristics of a sedimentary rock from which its origin and the environment of its formation may be inferred. However, later the term facies was applied to designate environmental conditions of deposition. Others developed the term into a diversity of meanings by applying the concept in a completely different context to different geological fields. The metamorphic and mineral facies proposed by Eskola (Mason, 1958), for example, are conceptually different from and unrelated to its use in the original stratigraphic sense.

The term hydrochemical facies probably found its original use in the U.S.S.R. where it naturally evolved from geochemical studies of sediments. "Geochemical facies" has been used by Teodorovich (1949) and Pustalov (1952) to define different sedimentary environments by means of specific mineral indicators of Eh and pH. Other Russian literature defines geochemical facies as "a part of the earth surface throughout which exists the same physico-chemical and geochemical conditions of accumulation and formation of sedimentary rocks" (Teichert, 1958). Keith and Degens (1959) used the term "chemofacies" to designate

all the chemical elements that are collected, precipitated, or adsorbed from the aqueous environment, or fixed by chemical reactions in the bottom muds, as a basis for differentiating between marine and fresh water sediments.

Chebotarev (1955) used "hydrochemical facies" to indicate concentration of dissolved solids, from low to high saline facies. In the Russian literature frequent references are made to hydrochemical zoning involving large continent-sized areas (Schoeller, 1959) and sometimes the chemical differentiation of water with depth of occurrence (Chebotarev, 1955). As presently used in ground-water studies, hydrochemical facies may be a well defined concept but it refers to an inadequately understood geochemical situation occurring in the ground-water body. In this study of the hydrochemical facies of ground water of the Tucson Basin it has been found useful to keep in mind some of the suggestions made by Krumbein and Sloss (1963) concerning the operational concept of facies in stratigraphic analysis.

## Operational Concept of Hydrochemical Facies

To the hydrogeologist the problem of finding an appropriate definition for the term hydrochemical facies as applied to ground-water studies is analogous to that encountered by the stratigrapher using primarily subsurface data for lithofacies studies. The geologic information from subsurface sources is largely quantitative in nature and as a result, the facies concept in subsurface stratigraphy tends to give greater emphasis to discrete observable lithologic variations than the more subjective and abstract interpretations of environment. Similarly, chemical analysis of ground-water samples are also expressed in some kind of numerical form and the study of hydrochemical facies should stress the use of discrete measurable data.

Subsurface information on the chemistry of ground water consists of a number of separate observations, composed of variable amounts of chemical constituents, from different localities. Samples from each well require separate analysis, and little environmental interpretation can be made until samples from many different locations have been examined. In the present study of hydrochemical facies of ground

water in the Tucson Basin, a vast amount of information is available and an operational definition, formulated to serve the needs of the problem is desirable to interpret this information. In this area it is customary to complete water wells by slotting the casing over the entire thickness of penetration of the saturated zone. Standard chemical analysis of groundwater samples collected at the well head are assumed to be representative of the entire thickness of penetration into the saturated section of the aquifer.

#### Operational Definition of Hydrochemical Facies

Hydrochemical facies are the lateral variations in chemical character of ground water in a hydrologically defined ground-water body. A number of corollaries modified after the suggestions of Krumbein and Sloss are implicit in this definition.

1. Facies occupy mutually exclusive areas bounded by arbitrarily and preferably quantitatively determined units.
2. A single facies may comprise one or several types of water that occur in vertical succession or are intertongued. The facies in a given ground-water body

exclusively occupy the complete thickness of the ground-water unit, and are neither vertically successive nor inter-tongued within that ground-water body.

3. Facies boundaries are fence-like surfaces passed from top to bottom through the ground-water body. These boundary surfaces may be considered essentially vertical planes. This simplification becomes less objectionable if one keeps in mind the difference in scale between average well depth and the size of the area under investigation. The average well depth is less than 500 feet and the average well penetration of the aquifer is about 200 feet. The area under study exceeds 70 square miles. At this scale the water body samples are merely a relatively thin layer of water and each chemical analysis does not represent more than a point.
4. The projection of a facies boundary to the surface is a line. Therefore, the distribution of facies is ideally represented by isopleths on a map. According

to Hem (1959) the chemical quality of ground water in widespread uniform basin-fill aquifers of the Basin and Range Province in the Western United States can be successfully studied through isopleths of individual chemical constituents. Moreover, the nature of the data collected from this area does not permit a three-dimensional study of the hydrochemical facies.

A more general definition of hydrochemical facies may be formulated by: hydrochemical facies are those chemical aspects of a ground-water solution from which chemical processes involving water and the geologic and hydrologic environment may be inferred. The definition is a modification of the one given by Back in that it does not restrict itself by referring to chemical processes taking place within the aquifer only. In the Atlantic Coastal Plain study the main controls on the chemistry of the ground water are probably the physical properties and the mineralogic composition of the aquifers. In the Tucson Basin, factors outside the aquifer may play an important role and the chemical quality of ground water may, therefore, also be a

reflection of chemical processes acting on the water before and during recharge to the actual ground-water body or aquifer.

#### IV. THE CHEMICAL QUALITY OF GROUND WATER IN THE TUCSON BASIN

##### Introduction

The initial phase of this study involved the collection and organization of the chemical analyses already available from the Tucson area followed by a preliminary interpretation of the regional variation of water quality data. This part of the investigation was done in cooperation with Arlen Feldman, who presented the results of the early part of this study in a master's thesis (1966). Unfortunately, most of the data available are from a relatively small area of intensive ground-water development. For large sections of the Tucson Basin the information on the hydrologic and geologic characteristics of the basin-fill sediments is extremely limited.

Because of this the present study is restricted to an area in the north central part of the basin where information available on the hydrology and geology of the basin-fill aquifer is more reliable. This area covers most of Township T14S-R14E and some adjacent

sections (Figure 2). The basin-fill aquifer underlying this area has been developed intensively for municipal supply and there are many wells with chemical analyses. The chemical analyses used in this study are all from wells which derive water from the basin-fill aquifer only.

Previous students of ground-water quality in the Tucson Basin (Professor Schwalen, personal communication) had noted that sometimes the chemical composition of the ground water from wells of approximately equal depth varies greatly within a relatively small area. On the other hand, some wells many miles apart would bear a striking resemblance to one another in chemical quality. Numerous chemical analyses available and representative of the basin-fill aquifer suggest, in general, a relatively low mineral content less than 500 ppm total dissolved solids. The occurrence of extreme local variation over a limited range of values in the chemical character of ground water in the Tucson Basin often makes it difficult to interpret the regional variation of ground-water quality by isochemical contour maps. This specifically seems to be the case if a relatively small area, the size of a township or smaller, restricted by the availability of sampling points or

bound by arbitrary political limits is considered for study. Only by taking a large enough area with known natural boundaries and by knowing or inferring a regional trend of chemical quality satisfactory results may be achieved. This type of approach of interpreting regionally distributed data is also known as interpretive contouring (Krumbein and Sloss, 1963). Mechanical contouring techniques such as can be performed by a computer-plotter combination would not always yield satisfactory results unless a preference for a certain "grain" or trend in the map is incorporated in the computer program.

#### Chemical Analyses of Water Samples

Most of the chemical analyses used in this investigation were made in the Soil and Water Testing Laboratory of the Department of Agricultural Chemistry and Soils at the University of Arizona. Many of these chemical analyses have been published in reports compiled by the Agricultural Experimental Station (Reports 217, 223) and a complete set of data is available from the files of the same agency. The data used specifically for statistical studies in this report are given in Appendix A.

The chemical analyses used in this study are reported in parts per million. Besides the amount of total dissolved solids, the following major ionic species are reported:  $\text{Ca}^{++}$ ,  $\text{Mg}^{++}$ ,  $\text{Na}^+$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{--}$ ,  $\text{HCO}_3^-$ , and  $\text{F}^-$ . Water samples were collected by the author for trace element determination. The elements to be determined were Fe, Mn, Cr, Ni, Cu, Zn, Pb, Cd, Co, and Sr. Concurrently, samples were also taken for standard chemical analysis, and pH and temperature were measured in the field. In addition, these samples were also analyzed for  $\text{NO}_3^-$  and  $\text{K}^+$ .

A brief resume of the laboratory methods and their limitations follows. The degree of accuracy of the chemical analyses on the water samples were learned through George Draper, Chemist, Soil and Water Testing Laboratory, the University of Arizona. For details of the chemical methods employed, the reader is directed to standard reference works on water analysis such as Rainwater and Thatcher (1960) or the Standard Methods for the Examination of Water and Wastewater, published by the American Public Health Association (1960).

Total dissolved solids (TDS) is usually the sum of ions determined. Sometimes total dissolved solids are also measured by determining the weight of the residue left after evaporation.

Prior to about 1955, calcium and magnesium were determined by the soap titration method. After this time, the versenate titration method has been used. The accuracy of the soap titration method is poor and such an analysis can only be used to characterize the sum of the two ions. Almost all wells used in this study were City wells, sampled after 1955 and analyzed by the versenate method. The versenate method is accurate to  $\pm 5$  percent. Magnesium is usually present in relatively small amounts and is determined by subtracting calcium, which is determined directly, from the total calcium and magnesium.

Sodium content traditionally has been determined by the difference of the sum of the milliequivalent weight of calcium and magnesium and the sum of the milliequivalent weights of the anions. The result not only includes potassium but also the sum of errors of determination of all other ions. The sodium data incorporated in the factor analysis were obtained in this fashion. For the study of sodium as a single constituent and its relationships to other constituents, only sodium values, directly determined by flame photometry, are used.

Chloride is determined by titration with silver-nitrate using 5 percent potassium chromate solution. This method is usually accurate.

Sulfate is determined by the turbidimetric method. It is precipitated as barium sulfate and stabilized with gum arabic. This method is accurate to  $\pm 10$  percent.

Bicarbonate is determined by titration with sulfuric acid using the mixed indicator brom-cresol green-methyl red. Unless careful precautions have been taken to prevent loss of  $\text{CO}_2$  from the sample, it is doubtful whether determination of bicarbonate in the laboratory can be considered representative of actual conditions in the aquifer. To achieve greater accuracy as to approach field conditions, bicarbonate should be determined in the field. Bicarbonate values used in the factor analysis were determined in the laboratory and little is known concerning the mode of sampling. In the trend surface analysis and the calcite equilibria calculations, only bicarbonate values from carefully and uniformly obtained samples were used. The sampling of water wells was done during the hot summer months in the daytime, the only time when all City wells are running almost continuously. Careful sampling in the

field, storing the sample in sealed bottles and prompt analysis in the laboratory may represent true groundwater conditions more adequately than field determination carried out under adverse conditions of a hot summer day. Bicarbonate data, perhaps, do not fully represent actual field conditions, but at least the error in the analysis is consistent as to justify the use of these data for chemical calculations.

Fluoride concentration is determined by the Scott-Sanchis color comparison method. Accuracy here is about  $\pm 10$  percent.

Nitrate was determined by the phenol-disulfonic acid method with an accuracy of about  $\pm 10$  percent.

Potassium was determined by atomic absorption spectrophotometry using a Perkin-Elmer-303. The accuracy by this method is good, up to  $\pm 1$  percent.

Strontium was also determined by the same method using a Jarrell Ash Model 86-360 atomic absorption spectrophotometer with an accuracy of  $\pm 1$  percent.

Zinc was also determined by the same principle on the Jarrell-Ash unit. No limits of accuracy are available. The zinc data were used because it was thought to be reasonably reliable compared to the results obtained for other trace elements.

Other trace elements were not incorporated in this study because no reliable results were available at the time of writing of this report.

### Regional Variation of Ground-Water Quality

The interpretation of regional variation of ground-water quality in the basin-fill aquifer on the basis of isopleth maps of dissolved constituents sometimes leads to ambiguous results. This is not only due to the irregular spacing of sample localities but also due to local variation of the data. Under such conditions reasonable success in contouring the data can only be assured by applying an averaging or smoothing process to the data according to some predetermined pattern. A generalized water quality map in the report by Schwalen and Shaw (1957) shows that some chemical constituents represented by hardness and total dissolved solids can be traced from its source in the Cienega Gap area to the central portion of the basin. Feldman (1966) mapped the following chemical constituents in ground water of the Tucson Basin using all available chemical analyses; total dissolved solids, calcium plus magnesium, chloride, sulfate, bicarbonate and fluoride. He made the assumption that the ground-water quality

pattern had a general tendency to parallel the direction of ground-water movement. Sodium was not mapped because of questionable accuracy of the data.

An examination of the isochemical maps by Feldman (1966) shows similarity in the regional variation of concentration of all ions and total dissolved solids. The fact that all magnitudes vary similarly perhaps indicates that changes in the ground water chemistry are controlled by regional factors simultaneously affecting all constituents (Feldman, 1966). Mechanisms that selectively change the concentration of individual ions without affecting the concentrations of other ions apparently are of little significance. However, this may also be explained by the fact that once the quality of ground water has been established in the recharge area, little happens to upset the chemical composition of the ground water as it moves further in the basin.

The changes in subsurface lithology of the basin-fill aquifer as interpreted by Ganus (1965) (Figure 4A, 4B, 4C) do not seem to noticeably affect the quality of ground water. Therefore, it appears likely that the chemical quality of ground water in the basin-fill aquifer, as determined from chemical analyses, is only

partially controlled by the lithology of the sediments through which the water moves, and the time involved in this movement. The difference in chemical character must also be due to differences in recharge conditions and the chemical composition of the rock and soil in the drainage basin before recharge. On a scale involving the entire Santa Cruz Valley and including aquifers of different lithology from greater depth, many of the variations in chemical quality may be explained in terms of the variations in mineralogic composition of the different geological formations containing the water (Kister and Hardt, 1961). Within the upper basin-fill, however, the main causes for the differences in chemical composition based on present evidence, seem to be independent from the lithology of the basin-fill sediments.

In the area selected for detailed study, two distinct types of water quality can be recognized; one of relatively low ionic concentrations occupying the northeast half of the area and one of moderately high ionic concentration occupying the southwest half of the area. The water of relatively low mineral concentration carries fewer than 500 ppm total dissolved solids and probably originated from the high mountains,

composed predominantly of crystalline gneiss, to the north and the east of the basin. The water in the southeastern half of the area has an average total dissolved solid content between 500 and 1000 and a predominance of calcium and magnesium and sulfate ions over the other ions. This water has passed through a relatively low-lying area between the Rincon Mountains to the north and the Empire Mountains to the south before being recharged to the Tucson Basin. This area is drained by the Cienaga Creek and is underlain by limestone and formations containing gypsum deposits.

The direction of change in chemical quality of ground water in the north central part of the basin appears primarily along a trend perpendicular to the general direction of ground-water movement. Little progressive change in ground-water quality in the direction of ground-water flow is apparent. Sometimes abrupt changes in chemical quality are found over a relatively small distance normal to the direction of ground-water flow, suggesting that, perhaps, mixing of water of different water quality underground is not significant. However, wells used in this study are not spaced sufficiently close to draw any valid conclusions concerning the mixing process in ground water of the Tucson Basin.

The fact that the pattern of ground-water quality seems to have a tendency to parallel the general direction of ground-water flow is contrary to the observations of some hydrogeologists working in the Basin and Range Province of the Western United States (P. Cohen, U.S.G.S., personal communication) and is some other arid areas of the world (Cheboratev, 1955, Schoeller, 1962). This calls for an investigation of possible bias in the regional interpretation of the quality data. It is also of interest to investigate the more fundamental reasons why the regional distribution of water quality in the Tucson Basin is anomalous compared to basins in desert areas elsewhere.

No distinct changes in ground-water quality seem to have resulted from the lowering of the water table in the Tucson Basin. Heavy withdrawals of ground water in the central part of the basin have significantly altered the flow pattern. This, no doubt, has changed the course of waters of different qualities previously flowing in the direction of the natural gradient. The velocity of ground-water flow apparently has been too slow to result in significant diversions of water quality from the previously established pattern. Chemical analyses of samples taken at time intervals of several

years apart fail to show any significant deterioration or improvement of water quality due to changes in the direction of ground-water flow (Feldman, 1966).

Schwalen (personal communication) thinks that in some parts of the basin, the quality of water has actually improved over the years. There is no evidence of upward flow of water of inferior quality from formations underlying the basin-fill aquifer due to lowering of the potentiometric surface of the ground water (W. Ganus, former graduate student, University of Arizona, personal communication).

The distribution of ground-water temperature in the basin-fill aquifer suggests a relationship between water of relatively higher temperature and the occurrence of linear structures which have been reported in the Tucson Basin (Figures 7A, 7B). This leaves open the possibility that at least water of different temperature might have come up from deeper formations. However, the hydraulic head measured in a well of the Tucson Gas and Electric Co., penetrating the upper basin fill only, is considerably higher than the head of a well in the same area tapping deeper lying formations (S. Turner, private consultant, Phoenix, Arizona, personal communication).

In the Tucson Basin, return flow to the ground-water reservoir resulting from irrigation might be considerable (Schwalen and Shaw, 1957). Changes in chemical quality of ground water in irrigation areas with time might be due to recycling of irrigation waters.

## V. A MODEL OF HYDROCHEMICAL FACIES DISTRIBUTION OF GROUND WATER IN THE TUCSON BASIN

### Introduction

The spatial change in chemical quality of ground water in an aquifer can be a function of many parameters. Preliminary investigation of the regional variation of the chemical character in ground water of the basin-fill aquifer in the Tucson Basin suggest that the distribution pattern of dissolved constituents in this aquifer may be organized in a specific manner and is not random. The assumption is made that the distribution patterns of dissolved constituents in ground water of the basin-fill aquifer may be related to a few dominant factors.

In the search for the dominant factors that control the regional distribution of chemical quality of ground water in a basin, it is useful to consider process-response models (Krumbein and Graybill, 1965). Initially, such a model may be only conceptual in scope but it serves the purpose of organizing the essential features of a complex hydrogeologic system into a framework to which observations may be referred. In a

study of regional variation of ground-water quality a conceptual process-response model is a qualitative expression relating the most pertinent hydrogeologic elements of the basin to the distribution of dissolved constituents in ground water. For most ground-water basins the processes that result in a certain distribution of ground-water quality cannot be directly observed or measured. Consequently, the relationships that link the dominant controls with the chemical quality of ground water are not always clear. However, a critical evaluation of the response elements or chemical quality data should make it possible to discriminate between correct and incorrect process-response models.

#### A General Conceptual Process-Response Model for Hydrochemical Facies in the Tucson Basin

A conceptual process-response model of hydrochemical facies of ground water of the basin-fill deposits in the hydrogeologic setting of the Tucson Basin may be entirely qualitative and be expressed by a schematic diagram (Figure 8). Such a conceptual process-response model would contain elements that produce chemical quality of ground water and also the final products themselves, viz., the chemical quality

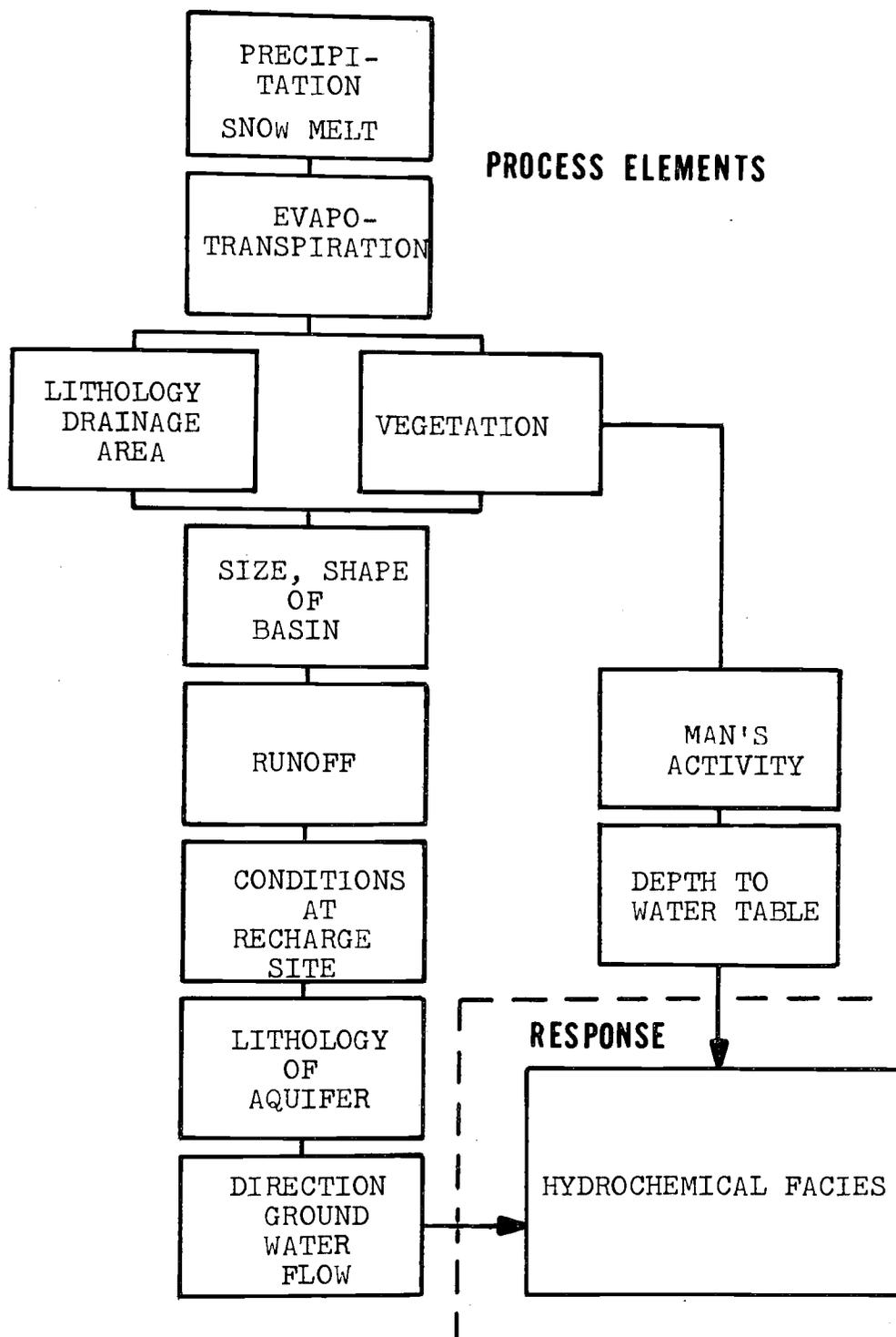


Figure 8. Schematic diagram of sequential process-response model for the origin of hydrochemical facies of ground water in the basin-fill aquifer, Tucson Basin.

data. In its most general form the interactions of the hydrology and geology of the basin are the process elements, and the chemical quality data, expressed by hydrochemical facies, the response elements.

Some of the more relevant process elements that control the chemical character of ground water in the Tucson Basin are:

- (1) Climatologic factors: amount and distribution of precipitation, rates of evapotranspiration, as a function of time and space.
- (2) The chemical composition of the rock and soil of the drainage area before recharge and of the site of recharge of water to the ground-water basin. The vegetative cover of the watershed.
- (3) Geometric properties, such as size, shape and topography of the drainage basin and drainage net.
- (4) Runoff characteristics and sediment load of the streams.
- (5) Location of the principal recharge and discharge areas.

- (6) Mineralogy and texture of the basin-fill sediments. Hydraulic properties of the aquifer.
- (7) Direction of ground-water flow.
- (8) Depth to the water table.
- (9) Natural change in watershed characteristics.
- (10) Man's activity resulting in modification of watershed characteristics, change in the direction of ground-water flow and the recycling of irrigation waters.

The process elements usually are time and space dependent and many of them interact. Time lag between the process event and the response element now observed in the basin is common. Because of the complex interrelationships amongst the process elements, it is difficult to exclusively isolate the dominant causes. Little quantitative information is available on the process elements and almost all the data we have are response elements, represented by the chemical quality data. However, the ultimate aim remains to link a specific set of process elements with a specific set of response elements. By study of the response elements in the correct reference frame of time and space, we may be able to infer the processes that formed them.

Results of ground-water quality studies of regional aquifers representing a wide variety of hydrogeologic environments indicates that commonly the chemical character of the ground water changes progressively in the direction of the hydraulic gradient (Schoeller, 1962, Henningsen, 1962, Morgan and Winner, 1962, Seaber, 1964, Maderak, 1964, Back, 1966, Maclay and Winter, 1967). As a rule, water increases its mineral concentration down gradient. H. Schoeller pointed out that this tendency is particularly strong in desert areas, not only because water dissolves mineral constituents as it moves through the aquifer, but also because of evapotranspiration. The increase in concentration through dissolution of mineral constituents is more appreciable with increasing length of flow path and time of contact with the surrounding rock formation. The direct effect of evaporation is probably negligible if the water table is at depth greater than about 12 feet (Gardner, 1960).

H. Schoeller (1962), who made intensive studies of ground-water quality in desert areas, has commonly found the following progressive changes in chemical composition as water moves down the gradient. Total dissolved solids and chloride concentrations increase

down the hydraulic gradient. The  $\text{SO}_4^{--}/\text{Cl}^-$  ratio in general will decrease down gradient, since chloride dissolves at a faster rate than sulfates. The  $\text{Mg}^{++}/\text{Ca}^{++}$  ratio usually has a tendency to increase down gradient because calcium carbonate reaches saturation more readily than magnesium carbonate.

The progressive increase or change in mineral concentration apparently is directly proportional to time and surface area contact with solid rock aquifers. M. Schoeller (1964) studied the effect that length of flow path and ground-water velocity have on the rate of change of salt concentration. He found that in particular the regional distribution of chlorides is directly proportional to the length of ground-water flow path and the degree of evapotranspiration from the aquifer and inversely proportional to the ground-water velocity. If the chemical character of the ground water changes progressively in the direction of the hydraulic gradient, the resulting pattern of isopleths would be essentially normal to the direction of ground-water flow and parallel to the water table contours.

Kister and Hardt (1961) report that the chemical quality of ground water in the alluvial basins of

Southern Arizona is controlled by the mineralogy and texture of the subsurface formations through which the water flows. This seems, in general, to be the case for ground water in alluvial materials filling large basins of tectonic origin in the western United States (Davis and DeWiest, 1966). This type of situation is particularly evident if we compare samples representative of formations which are not only widely different in lithologic makeup but are also from different depths in the basin. The work by Ganus (1965) on the lithology of the basin fill deposits (Figures 4A, 4B, 4C) does not indicate that the general nature of the sediments changes abruptly with depth at any particular location in the central part of the Tucson Basin. Not until more detailed information concerning depth relations of water quality and lithology becomes available can we test the assumption that depth of well and water quality are independent from one another. As far as the water quality of wells tapping the basin-fill aquifer only, regional variation in ground-water quality is much greater than local variation, and it appears, therefore, that depth does not play a very important role in this respect.

### Proposed Conceptual Model

The development of a conceptual model to explain hydrochemical facies or the chemical character of ground water in the Tucson Basin requires some a priori knowledge of the hydrologic system. Preliminary interpretation of the distribution patterns of some of the major ionic species, in particular calcium and magnesium summed together, sulfate and total dissolved solids, suggests a tendency for alignment parallel to the general direction of ground-water flow. This alignment in the distribution pattern is also shown by chlorides and bicarbonate, but less clearly. On the basis of this preliminary evidence, it appears that within the basin itself the direction of ground-water movement is the most important factor controlling the distribution of chemical quality in the basin-fill aquifer. Outside the basin-fill aquifer the chemical composition of derivative rocks in the drainage basin and conditions at the recharge site seem to be primary factors in determining the chemical character of the ground water in the aquifer. Superimposed on the general patterns parallel to the flow line direction are effects most likely associated with lithologic

Figure 9. Conceptual models of the hydro-geologic environment representing process-elements related to quality of ground water in the basin-fill aquifer of the Tucson Basin.

- (A) Water in the northeastern part of the basin is primarily recharged through alluvial channels.
- (B) In the southeastern periphery of the basin water is primarily recharged through alluvial fans.

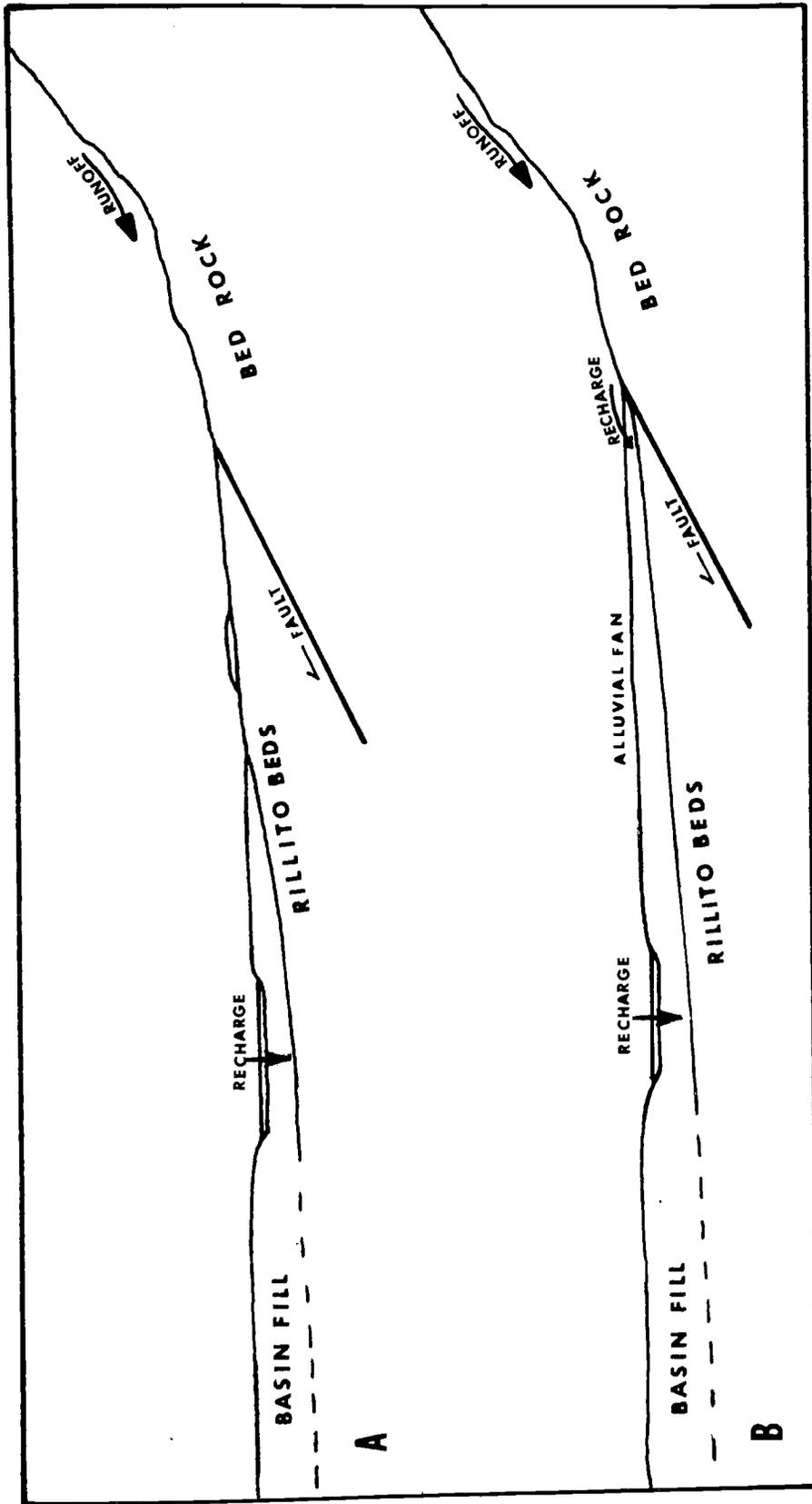


Figure 9. Conceptual models of the hydrogeologic environment.

differences in the basin-fill material. The most relevant process-elements of the physical system related to the quality of ground water in the basin-fill aquifer are shown by simple conceptual models of the hydrogeologic environment (Figure 9A and 9B).

Samples of ground water from the basin-fill aquifer in the central part of the basin have been dated by Carbon-14 method (Bennett, 1965). Ground water from the west-central part of the basin that, based on flow line analysis, must have been recharged in alluvial fans at the southeastern periphery of the basin has yielded dates of approximately 6000 radiocarbon years. Water closer to the assumed recharge areas becomes proportionally younger (Figure 7C). From this evidence, it may not be unreasonable to assume that almost all ground water presently occurring in the basin-fill sediments is less than 10,000 years old. Older water recharged before that period probably has been displaced by younger water.

There is little evidence available to contradict the assumption that the general configuration of the basin has been significantly altered during the last 10,000 years (E. Davidson, U.S.G.S., personal

communication). We may therefore also assume that the general direction of ground-water flow during that time has not been much different from the present conditions. The oldest water now present in the basin-fill aquifer was probably recharged in alluvial fans (Figure 9B) which extend from the southeastern edge to the central part of the basin. Areal photographs show a large system of overlapping alluvial fans extending from the northern Santa Rita Mountains and the Cienega Gap area into the Tucson Basin. It may be noted that the alluvial fan associated with the Cienega Gap area clearly extends into the study area. These alluvial fans serve as a relatively slow transmission medium for water recharged in the periphery of the basin.

The drainage area supplying the alluvial fan system in the southeastern part of the basin consists of a variety of geologic rock formations. The conceptual model proposed in this paper implies that in the basin-fill aquifer the quality of ground water, that was recharged through the alluvial fans in this area, will reflect the variability of the derivative rocks even after flowing through almost the entire length of the basin.

The Catalina and Tanque Verde Mountains are exclusively made up of granitic gneiss producing a type of water generally low in dissolved solids. The type of water produced after contact with granitic gneiss is probably distinctly different in quality than water derived from contact with the great variety of rock types in the southeastern part of the basin. Alluvial fans formerly extending from the base of the Catalina and Tanque Verde Mountains have been largely eroded away exposing less permeable formations underneath (Figure 9A). Recharge of ground water at the base of these mountains is probably small because of the lack of permeable alluvial material to receive and transmit water to the basin. Most of the water drained from the Catalina and Tanque Verde Mountains is carried directly into the basin by surface runoff and recharge to the ground-water reservoir, presumably, takes place primarily through stream channels. Therefore, the water recharged to the basin by way of stream channels is probably younger than water recharged through alluvial fans in the periphery of the basin.

Incorporated in the conceptual model are also the results of the preliminary study on chemical quality suggesting that once the quality of ground water at the

recharge area in the alluvial fans or in the stream channel has been established, little change appears to take place as water moves through the basin-fill aquifer. This view does not necessarily imply that the lithology of the basin-fill aquifer does not affect the major ionic species at all. As a matter of fact, some chemical constituents are clearly more affected than others. The distinct advantage of a conceptual model, as a guide for a suitable design of a water sampling program, is not utilized. Most of the information on water quality of the Tucson Basin was collected before formulation of the conceptual model. Often, no samples are available from areas where the availability of analyses would be desirable. This situation, however, is not uncommon in groundwater studies where observation points usually depend on wells drilled to suit the need for water supply rather than for hydrologic data.

The correctness of the interpretation described by the conceptual model may be evaluated statistically if a mathematical model can be constructed on the basis of the real world of data which corresponds to the distribution of hydrochemical facies predicted from the conceptual model. Most of the measured data

available from the real system are chemical quality data or response elements. Hence, the next step is to find a mathematical model that will represent as quantitatively as possible the regional distribution of chemical quality data.

## VI. TREND SURFACE ANALYSIS OF GROUND-WATER QUALITY DATA

### Introduction

The postulated model of hydrochemical facies of ground water in the basin-fill aquifer of the Tucson Basin implies that the distribution patterns of major ionic species concentrations should show a tendency to parallel the direction of ground-water movement. Lateral variation of the lithology of the aquifer also imposes some effects on the chemical quality of ground water. If changes in chemical quality are somewhat regular and systematic, the regional distribution of chemical constituents may be represented by some suitable mathematical model. Trend surfaces are simple mathematical models of planes or curved surfaces that represent general, regular trends. Simulation of the regional distribution of chemical constituents by such a mathematical model may be accomplished through fitting of polynomial trend surfaces to the data. This quantitative model may then be used to test the proposed hypothesis on the distribution pattern of ionic

species in ground water of the basin-fill aquifer in the Tucson Basin.

### Trend Surfaces

The sample locations in this ground-water study are restricted to available well sites and are, therefore, irregularly spaced. In such cases it is common practice to fit successively higher order polynomial surfaces to the data. A trend surface fits a simple mathematical model to ground-water quality patterns as a function of location only. A well location from which a sample is taken and analyzed represents information that can be used as a variable. A least square polynomial surface is fitted to chemical quality data such that the chemical analyses  $Z$  are a function of arbitrary geographic coordinates  $X$  and  $Y$ . In other words, a trend surface can be described mathematically in terms of  $Z = f(X,Y)$  by a power series fitted to the data by a least square method. This study is limited to linear, quadratic and cubic surfaces. Complete trend is defined by Grant (1957) as the polynomial of best fit and this polynomial of best fit may not be identified by their three low order surfaces. A trend surface may be visualized as a smooth surface

showing the systematic pattern of variation of a mapable variable  $Z$  from one map edge to the other (Figure 10, Table 1). First degree surfaces are planes that contain linear terms only; generalized second degree surfaces contain both linear and quadratic terms and are paraboloid planes. Third degree surfaces are more complex, containing linear, quadratic and cubic terms. These planes can be conveniently represented by contour maps. Geologic and hydrologic characteristics of the basin are the causal factors of hydrochemical facies as a function of location. Trends in regional variation of dissolved constituents may suggest relationships between chemical character of ground water and the dominant factors that control water quality. A significant trend may be helpful in predicting occurrence of water quality in unsampled areas.

Trend surface analysis can be used to separate large scale systematic changes in regionally distributed data from essentially non-systematic small scale variations due to localized effects (Krumbein and Graybill, 1965). Small scale fluctuations, such as caused by local variations or by analytical errors of chemical analysis, and superimposed on the trend as non-systematic components, or residuals, are subdued. It is known

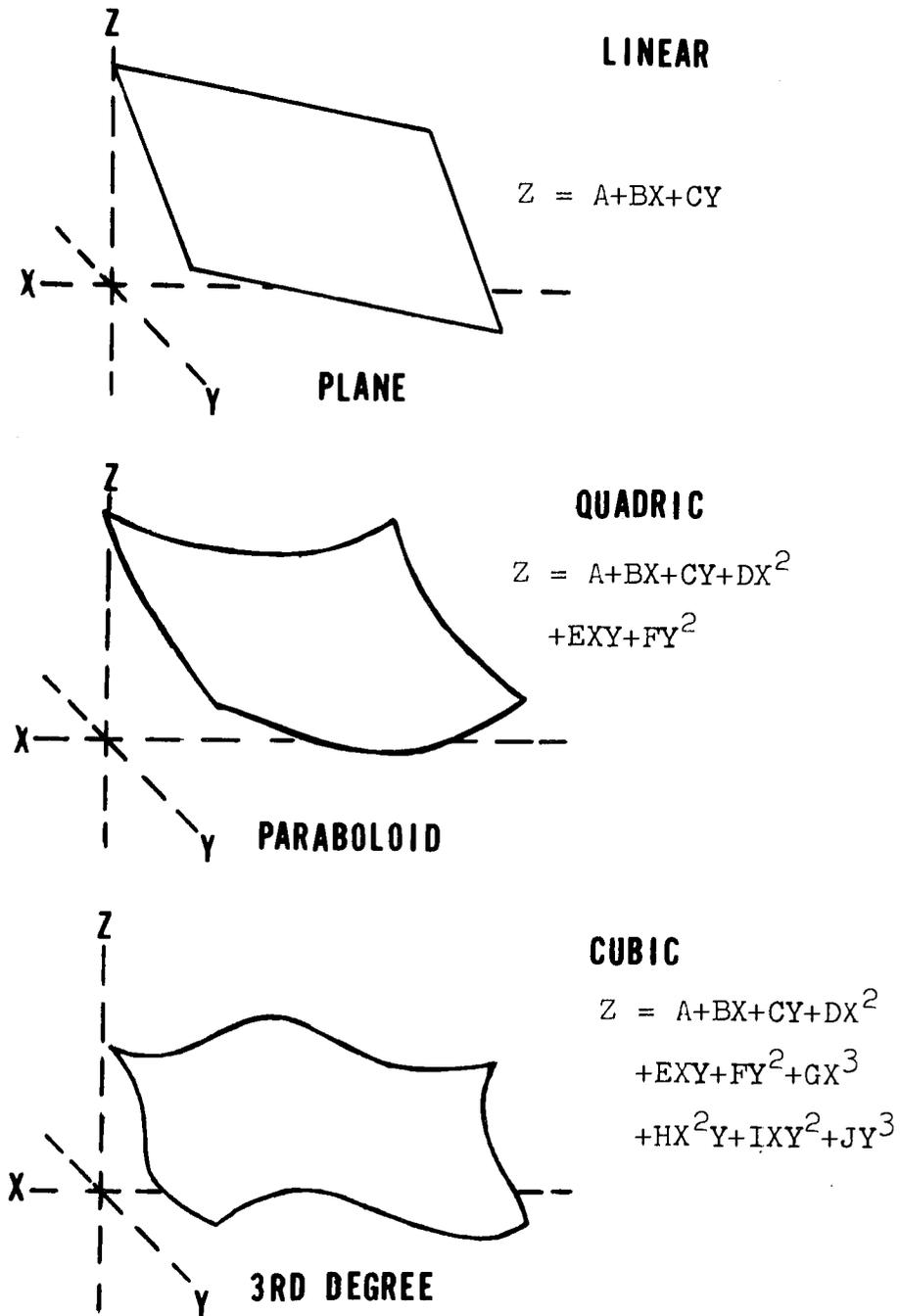


Figure 10. Geometric representation of linear, quadric and cubic surfaces and their generalized equations (after Harbaugh, 1964).

Table 1. General classification of trend surface equations in which components are grouped according to degree. Letters A through J represent constants of equations, and X and Y, independent variables; Z is dependent variable (Harbaugh, 1964).

	Dependent Variable	Base	Linear Component	Quadratic Component	Cubic Component
First degree (plane)	Z =	A +	BX + CY		
Second degree (Paraboloid)	Z =	A +	BX + CY +	$DX^2 + EXY + FY^2$	
Third degree	Z =	A +	BX + CY +	$DX^2 + EXY + FY^2 +$ $GX^2 + HX^2Y$ $+ IXY^2 + JY^3$	

that parts of these non-systematic components may become systematic at higher order trend analyses. Improvement of fit by higher order models will, in general, be the result. Trend surfaces have been used to simulate and analyze geophysical data, regional structure, sedimentary facies, ore distributions and the occurrence of plant and animal species. For review of the theory and applications of trend surface analysis to other geologic problems, including practically all the references to the recent literature, the reader is referred to Krumbain and Graybill (1965, p. 319-357).

#### Selection of Data Points

In this study, trend surfaces are fitted to chemical quality data primarily to test the hypothesis that the regional distribution of chemical quality data shows a tendency to parallel the direction of ground-water flow. In addition the objective is to show to what extent the lithology of the aquifer affects the quality of ground water. This study, therefore, is necessarily restricted to an area where the natural flow pattern can be reconstructed and where adequate information on the chemical quality of ground water and the lithology of the aquifer is available. Most

of the reliable data on ground-water levels, and hence on the direction of ground-water flow, and chemical quality are from the area of most intensive ground-water development in the north-central part of the basin (Figures 11A, 11B). Almost all major wells in this area are owned and operated by the City of Tucson and almost without exception, these wells are completed in what is known as the basin-fill aquifer.

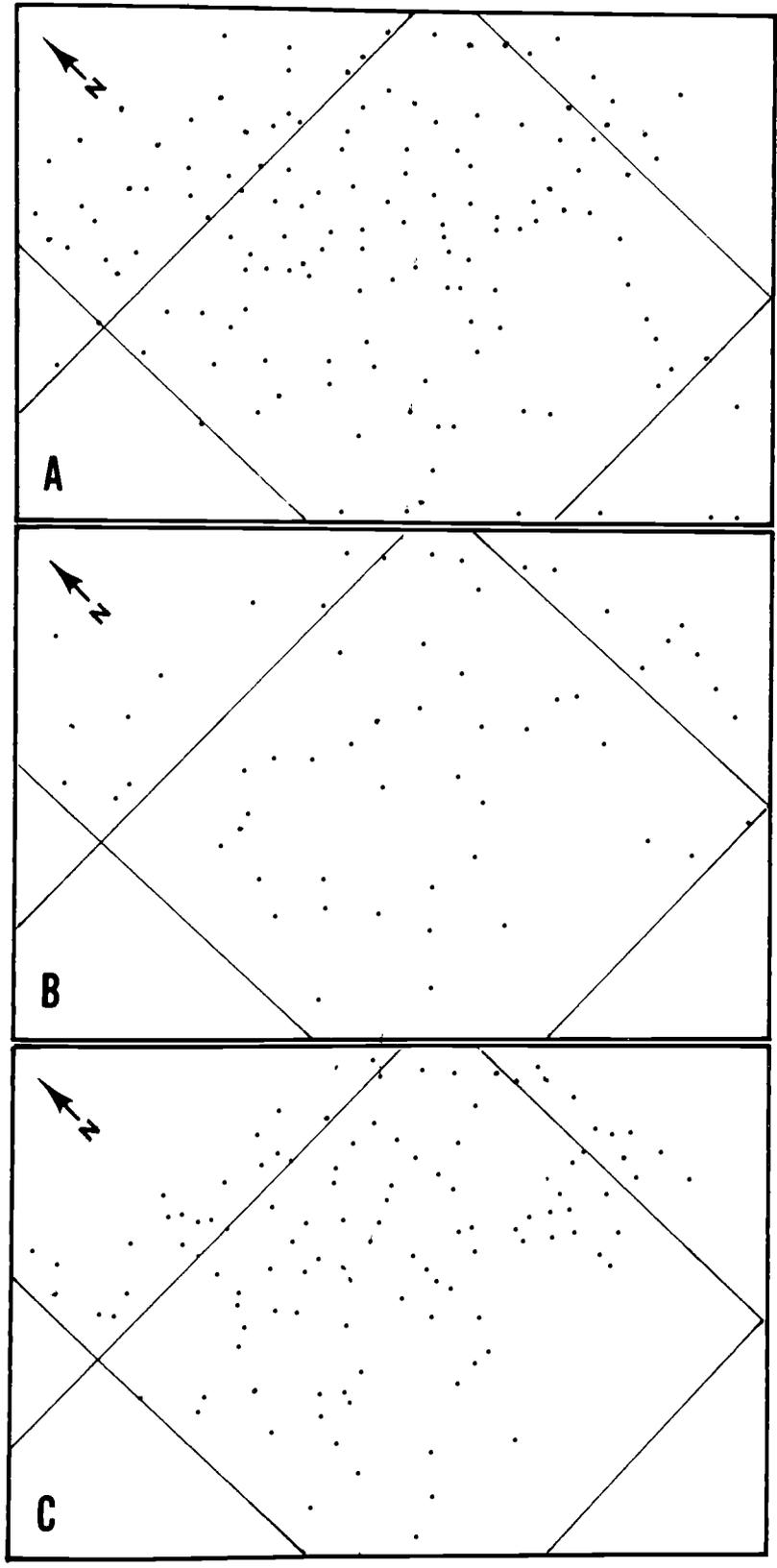
No interpretation in quantitative terms is available on the lithology of the basin-fill aquifer. Specific capacities of individual wells may indirectly give an indication as to the hydraulic and related textural properties of the aquifer. Qualitative information is provided by the lithologic interpretations of the drillers' logs (Figures 4A, B, C).

For trend surface analysis it is desirable that the data points are more or less evenly distributed within the mapped area. They should not be clustered in some places and spread apart elsewhere, because clustered data give undue weight to the areas containing them. In areas of sparse development the spacing of wells is too large and hence the available ground-water quality data too limited to detect changes in water quality over relatively short distances. The map

Figure 11. Maps showing location of wells used in trend surface analysis. Perpendicular solid lines indicate Township T14E-R14E.

- (A) Location of data points used in trend surface analysis of old quality data from 144 wells.
- (B) Location of data points used in trend surface analysis of new quality data from 59 wells.
- (C) Location of data points used in trend surface analysis of specific capacity data of 123 wells.

TREND SURFACE ANALYSIS



INDEX MAP OF WELL LOCATIONS

FIGURE 11

coordinates, expressed in miles, were selected normal and parallel to the general direction of ground-water movement. The coordinates selected for trend surface analysis of specific capacity data were north-south and east-west because of the availability and distribution of the data.

In this study two sets of water quality data from the same area have been used; old data assembled from the files and the published literature and new data from samples collected by the author. Old data usually are from samples submitted by the well owners and little is known about the mode of sampling. Errors inherent to an unknown method of collecting samples might be considerable. The advantage of using the old data is that more wells with analyses (144) are available (Figure 11A). The only reliable parameters of chemical quality of the older samples, perhaps, are total dissolved solids, calcium, chloride and sulfates. New data are from analyses of samples collected by the author from 59 wells of the same area (Figure 11B). Special attention was given to uniform and careful sampling of the wells and chemical analysis was performed immediately after delivery of the samples to the laboratory. For reasons of comparison, calcium,

chloride and sulfate were run using both the old and new data. Magnesium, sodium, bicarbonate and fluoride were analyzed using the new data only. As for the other parameters, pH, potassium, strontium, zinc and nitrate, only analyses from the new samples are available. Of these, zinc data are probably the least reliable. The analyses of other trace elements originally included in this study are not yet available.

#### Computation of Trend Surfaces

Computation of trend surfaces and display of the results can be accomplished by computer. Several programs to this effect have been written (Whitten, 1963, McIntyre, 1963, Harbaugh, 1964, Good, 1964), but none of these programs can be run directly on the IBM 7072-1401 system presently available at the University of Arizona. The computer program used in this study is an adaptation of a FORTRAN II program, developed by Good (1964) for use on IBM 1620. This program accepts irregularly spaced data points and fits first, second and third degree trend surfaces to the data.

The program executes the following operations:

- (1) Calculation of trend surface values and

residuals for each (X,Y) coordinate of the data set.

- (2) Printing of the equation for each trend surface.
- (3) Calculation and print out of the error measures of the trend surfaces.
- (4) Contouring of the trend surfaces.
- (5) Plotting of the original data and residual values.

Details concerning the program and its printed output are explained by Special Publications 11 (Merriam and Harbaugh, 1964) and 14 (Good, 1964) of the Kansas State Geological Survey.

### Statistical Appraisal of Trend Surfaces

#### Frequency Distribution of Chemical Quality Data

Frequency histograms of the original data are shown by a series of histograms (Figure 12). Most of the distributions of the original data are somewhat skewed with most of the values falling in relatively few classes. At this time little can be said about the geochemical and statistical significance of these distributions. However, it may be noted that frequency

Figure 12. Frequency histograms of original values of chemical quality data used in trend surface analysis.  $N$  = number of samples ( $N = 144$ , old samples,  $N = 59$ , new samples).  $\bar{X}$  = mean.  $S$  = standard deviation. Also given are class intervals. Values are in parts per million unless otherwise indicated.

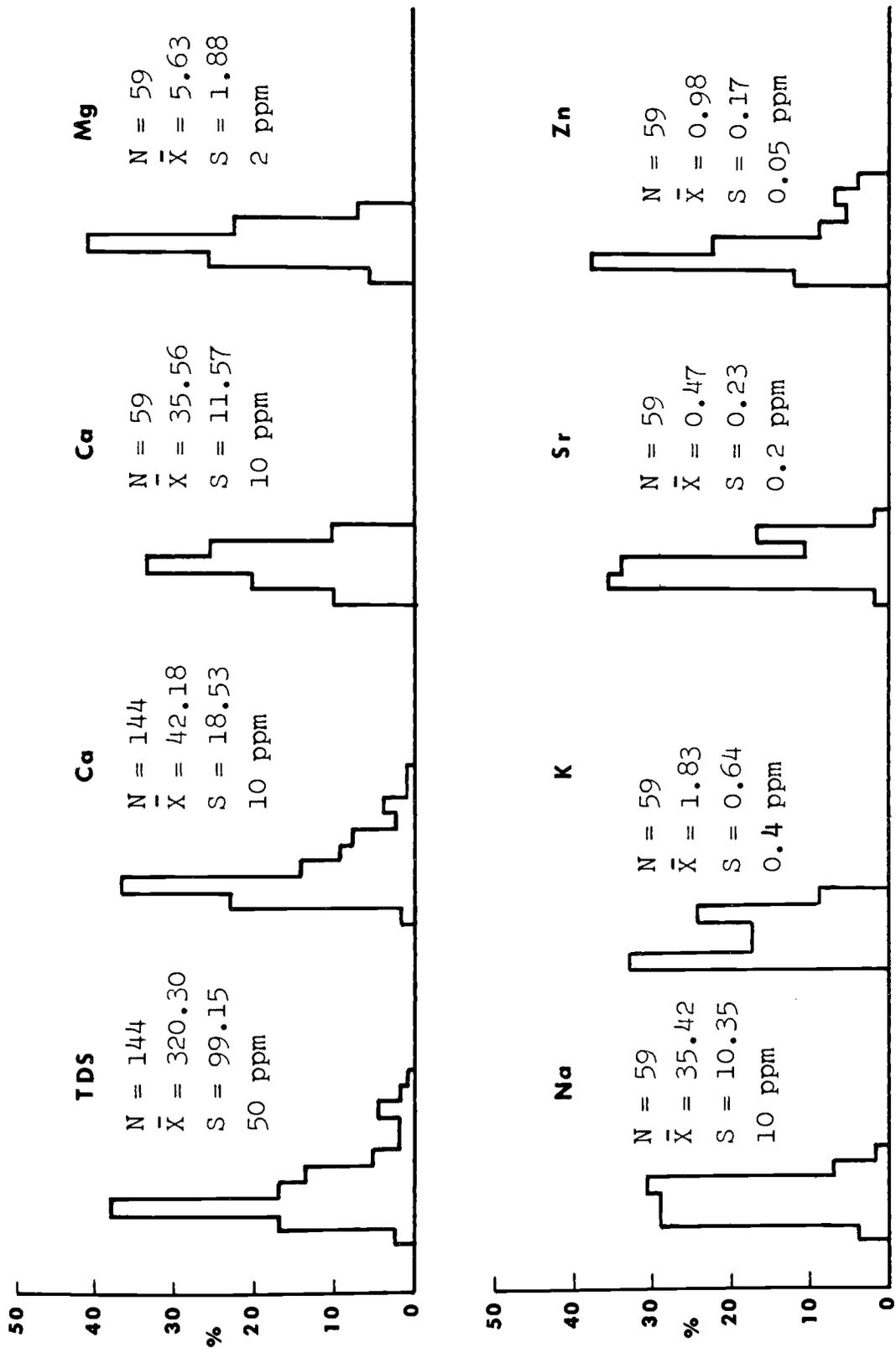


FIGURE 12

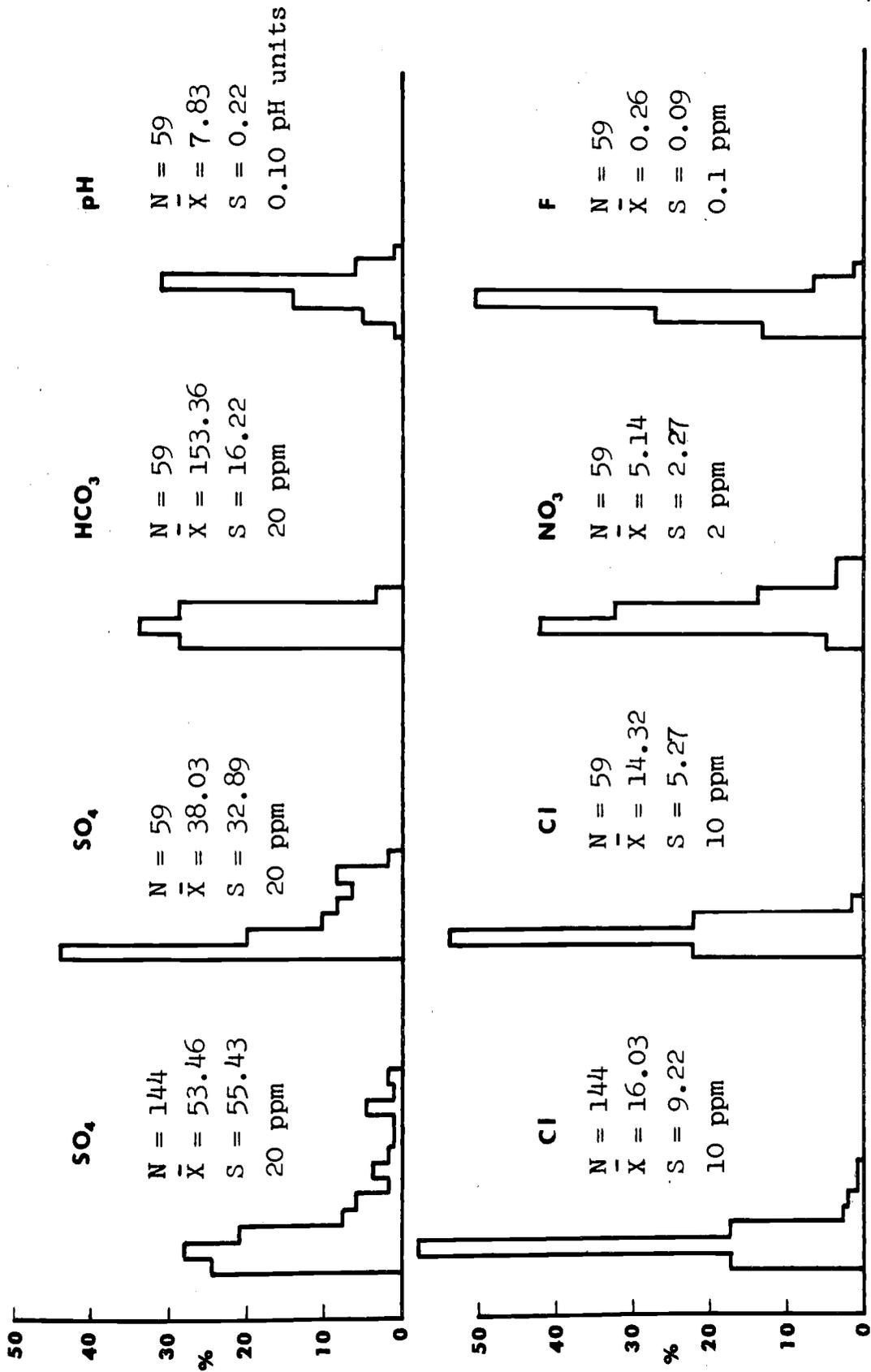


FIGURE 12. Continued

distributions of chemical quality data from the entire Tucson Basin and representative of many different locations have a strong tendency to be positively skewed; that is, the mean is displaced to the right or high value side of the median. This is also the case if we plot composite histograms of chemical quality data from different parts of the State of Arizona.

### Analysis of Variance

Analysis of variance may be used to determine statistical significance of the different trend components (Krumbein and Graybill, 1965). The degree of confidence for each component of the trend surfaces are an indication whether the linear, quadric and cubic components are statistically significant or could be due to chance alone. The degree of confidence or "confidence level" is expressed in percent. On this basis absolute certainty is 100 percent and absolute uncertainty is 0 percent. For example, a confidence level of 99 percent for a particular component would indicate 99 percent certainty that the component represents a real effect and not chance.

The data needed for calculation of confidence levels by analysis of variance include (a) sum of

squares that are apportioned among the linear, quadric and cubic components, (b) sums of squares associated with the deviations or residuals, and (c) number of degrees of freedom associated with the components and deviation. These data, in turn, permit (d) calculation of the mean square of the components and deviations and (e) calculation of F-values. (f) The confidence level in percent is obtained by reference to F-tables (Krumbein and Graybill, 1965, Table A6).

Interpretation of the F-values assumes that the residuals are independent or do not contain systematic effects, and are normally distributed. This assumption may not be satisfied for the data used in this study. The techniques necessary to ascertain complete independence of the residuals are quite involved and are not performed in this study. Neither were the deviations tested for fit to a normal distribution. F-ratios, however, may be used in the relative sense to judge the degree of fit for various trends (Connor and Miesch, 1964). Confidence levels computed for all trend components are given in Table 2.

Table 2. Confidence Levels of Trend Components in Percentage of Certainty that the Linear, Quadric and Cubic Components are Statistically Significant or are Due to Chance Alone

Constituents	No. of Samples	Confidence level of trend components in percent		
		Linear	Quadric	Cubic
TDS	144	99.9	99.9	50.0
Ca	144	99.9	99.9	99.9
Ce	59	99.9	75.0	99.9
Mg	59	97.5	75.0	99.9
Na	59	99.9	99.9	99.9
Cl	144	99.9	99.9	90.0
Cl	59	99.9	<50.0	75.0
SO <sub>4</sub>	144	99.9	99.9	95.0
SO <sub>4</sub>	59	99.9	99.9	95.0
HCO <sub>3</sub>	59	90.0	95.0	90.0
pH	59	97.5	99.9	99.9
F	59	99.9	99.0	99.0
K	58	99.9	75.0	99.0
NO <sub>3</sub>	59	90.0	95.0	75.0
Sr	59	99.9	99.9	99.9
Zn	59	75.0	<50	<50

Percentage Total Sum of Squares

The goodness of fit of any trend surface can be determined by calculating the percentage reduction of total sum of squares. It is a measure of the degree to which the trend approaches the observed data and may be defined by the expression (Merriam and Harbaugh, 1964):

$$100 \frac{\sum X_{\text{trend}}^2 - \frac{(\sum X_{\text{trend}})^2}{n}}{\sum X_{\text{obs}}^2 - \frac{(\sum X_{\text{obs}})^2}{n}} \quad (6.1)$$

where  $X_{\text{trend}}$  = computed trend surface values at location of data points.

$X_{\text{obs}}$  = observed data values.

$n$  = number of data values.

A perfect fit of the surface to the data points would give 100 percent of the total sum of squares. Any less perfect fit would yield a correspondingly smaller percentage sum of squares. There is a general relationship between the percent total sum of squares associated with that component. If there is a marked increase in percent total sum of squares when a new

component is included, a high confidence level is generally associated with that component (Harbaugh, 1964). A substantial increase in the percentage and total sum of squares is usually required to justify use of a higher order surface as representative of the trend. Table 3 gives the percentage total sums of squares accounted for by trend surfaces fitted to chemical quality data of the Tucson Basin. To avoid confusion in the terminology, it should be remembered that linear surfaces contain linear components only. Quadric surfaces include linear and quadric components and cubic surfaces include linear, quadric and cubic components.

#### Trend Surface Analysis of Specific Capacity Data

To test the reliability of the interpretation of the regional distribution of specific capacities of wells in the basin-fill aquifer (Figure 7C), trend surfaces up to the third degree were fitted to specific capacity data. The percentage total sum of squares explained by the cubic surface amounts to only about 30 percent, suggesting large local variation. The level of confidence that the cubic surface represents a real effect is 90 percent. Nevertheless, there is

Table 3. Percentage of Total Sums of Squares Represented by Trend Surfaces Fitted to Chemical Quality Data

L = Linear Component, Q = Quadric Component,  
C = Cubic Component

Constituent	No. of Samples	L	L + Q	L + Q + C
TDS	144	43.8	68.9	69.8
Ca	144	26.2	50.7	57.6
Ca	59	29.3	35.9	60.2
Mg	59	15.0	30.0	52.1
Na	59	25.6	53.6	67.2
Cl	144	15.8	23.4	28.0
Cl	59	60.1	60.6	65.7
SO <sub>4</sub>	144	55.7	79.1	80.6
SO <sub>4</sub>	59	62.1	79.8	83.6
HCO <sub>3</sub>	59	9.4	22.6	35.4
pH	59	13.0	42.3	63.4
F	59	36.9	48.9	60.5
K	58	46.0	50.7	63.5
NO <sub>3</sub>	59	10.0	22.3	32.0
Sr	59	46.1	63.6	75.3
Zn	59	5.7	6.5	9.4

a definite resemblance between the computed cubic surface (Figure 13C) and the interpretation of specific capacity distribution shown by Figure 7C. The occurrence of high specific capacity values in the basin fill is simulated by the saddle-shaped contours of the cubic surface. The shape of these contours supports the hypothesis that high specific capacities might be associated with a paleo-stream channel system (Ganus, 1965). This is a good example of how trend surface fitting techniques can be applied to test a geologic model. This method of testing is particularly appropriate if "noisy" data such as specific capacity values of wells lead to subjective and ambiguous regional interpretations.

#### Trend Surface Analysis of Chemical Quality Data

Trend surface analysis in this study is conducted with the primary purpose to test a conceptual model of distribution of chemical quality data in the Tucson Basin. Commonly, however, trend surfaces are also used as a predicting device and it is necessary to carefully distinguish between these two modes of application (Allen and Krumbain, 1962). In the case trend surfaces are also used as a predicting device,

**SPECIFIC CAPACITY**

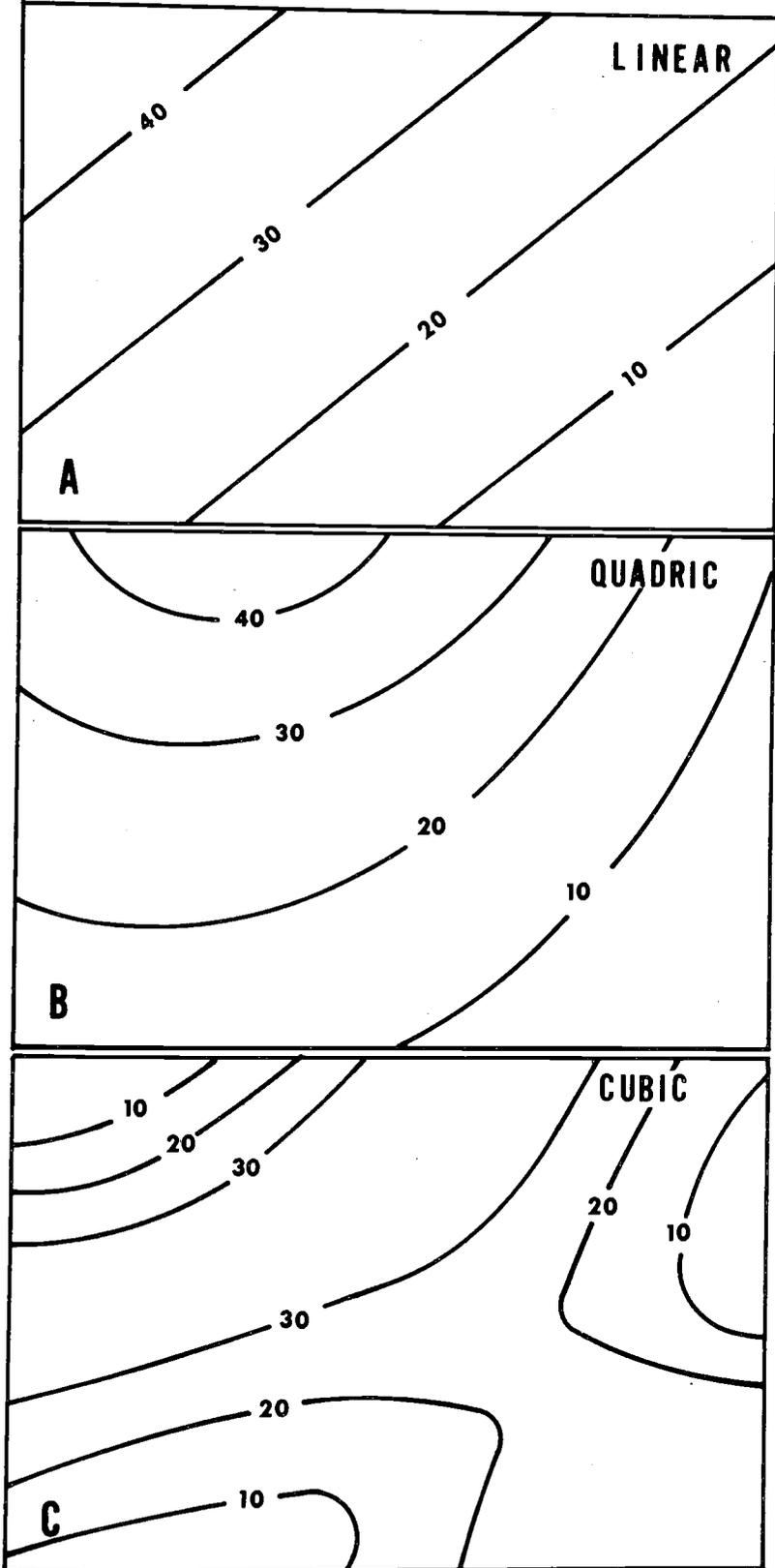


Figure 13. Contour maps of trend surfaces (A-C) fitted to specific capacity data in gallons per minute per foot of drawdown.

consideration as to how good a predictor a surface may be, becomes important.

Computed trend surfaces may be used as a predicting device when the trend surfaces account for a large percentage of the variability expressed by the percentage total sum of squares. Local fluctuations may then simply be considered as noise which, unfortunately, imposes a degree of uncertainty about the prediction. A polynomial surface accounting only for about 30 percent or less of the variability is probably extremely weak and constitutes a poor predictor. A relatively large content of local fluctuations widens the confidence band about the predicted value.

Trend surfaces are fitted to data from groundwater samples that do not necessarily represent the whole target population. Hence, trend surface fitting is strongly affected by the errors inherent in a poorly designed sampling program. It has been mentioned previously that there is little hydrologic or statistical basis to the sampling design of ground-water quality data in the Tucson Basin. Statistical conclusions about the target population in such a case by using trend surfaces as a predictor become at least hazardous. Trend surfaces usually can only be applied to continuously

variable systems (Whitten, 1963a). Not enough is known about the nature and the distribution of ground-water quality to ensure that this is the case in ground-water basins. Conventionally, polynomial functions have been used to fit trend surfaces but there is no reason, theoretically, why a variety of other functions could not be employed to represent the distribution of ground-water quality data (Whitten, 1963a, Preston and Harbaugh, 1965, James, 1966).

Keeping these pitfalls in mind, an attempt is made to meaningfully interpret the trends computed for the different chemical quality data. Interpretation of the results of trend surface analysis of chemical quality data is based on the percentages of total sum of squares accounted for by the surfaces (Table 3) in conjunction with analysis of variance of trend components computed for each chemical constituent (Table 2). Contour maps of linear, quadric and cubic surfaces fitted to chemical quality data are plotted by the line printer and are shown in Figures 14-29.

The discussion also draws heavily on the information included in Chapter II on the hydrogeologic setting of the Tucson Basin. Specifically, reference is made to those aspects that play a significant role

in the nature and distribution of chemical quality of ground water in the basin-fill aquifer and are shown by the following diagrams. First, the generalized geologic map of the basin (Figure 2) and the lithology of the basin-fill aquifer (Figures 4A, B, C). Next, the direction of ground-water flow (Figure 6A) and the distribution of specific capacity of wells producing from the basin-fill aquifer (Figure 6C, Figure 13C).

#### Total Dissolved Solids

The distribution of total dissolved solids (TDS) in ground water of the basin-fill aquifer (Figure 14) shows a strong tendency to parallel the general direction of ground-water movement. The linear surface accounting for about 44 percent of the variability at 99.9 percent level of confidence shows a gradual increase in the direction normal to the flow lines. The quadric surface that accounts for 69 percent of the variability at an equally high level of confidence clearly shows an area of general low mineral content associated with area of predominantly coarse-grained sediments in the northeastern part of the map area. The flow net indicates that the water in all likelihood was recharged in surface channels and has been derived

**TOTAL DISSOLVED SOLIDS**

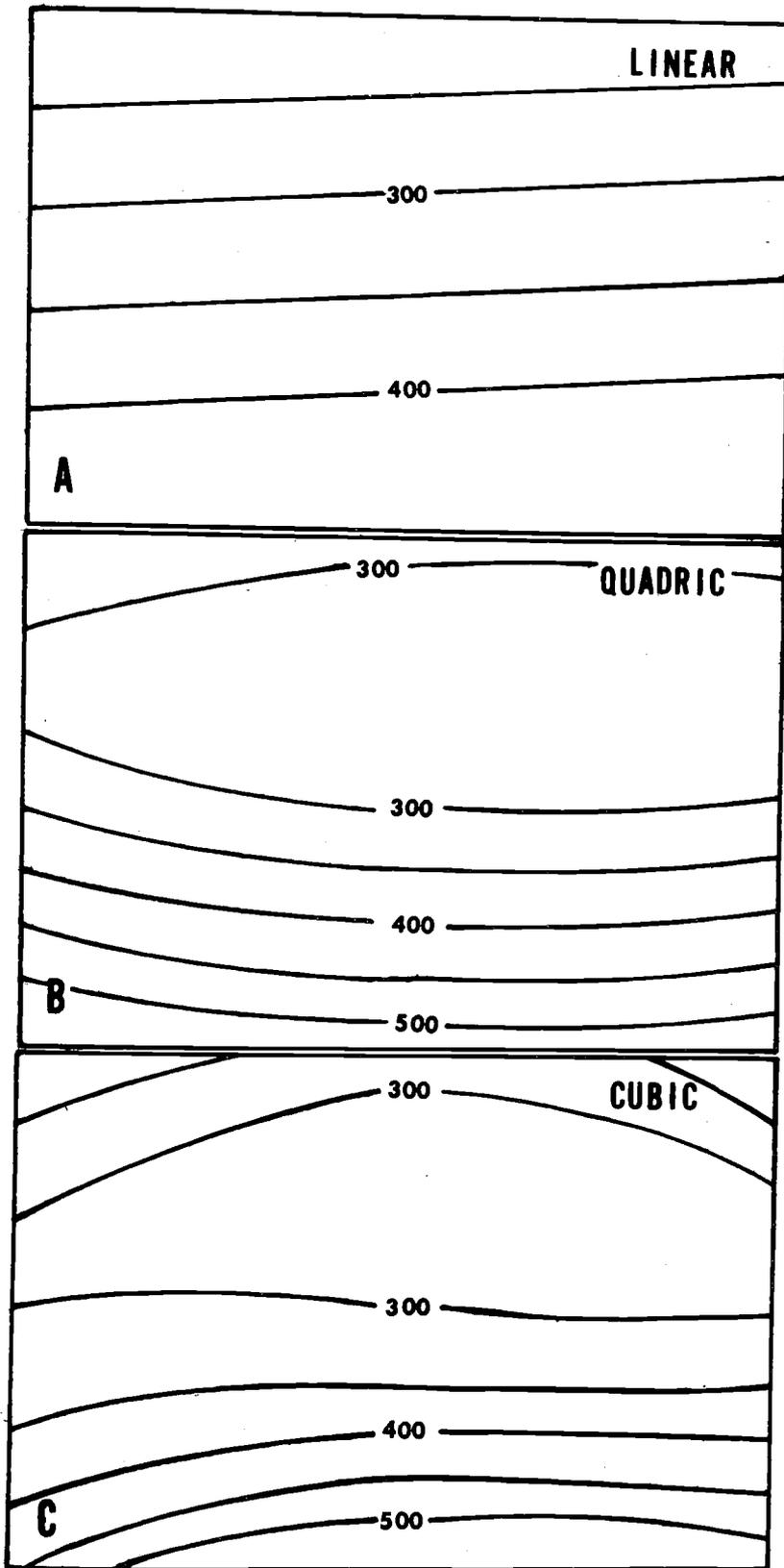


Figure 14. Contour maps of trend surfaces (A-C) fitted to total dissolved data, in ppm. Old samples.

from the gneissic Catalina and Tanque Verde Mountains. The water, higher in total dissolved solids content in the southwestern part of the map area, presumably, has been recharged in the alluvial-fan system extending from the Cienaga Gap area into the basin. The rocks exposed in the Cienaga Gap area and surrounding mountains are predominantly sedimentary, including carbonates and evaporites, producing water with a higher mineral content than water derived from granitic terraines.

In the area of pronounced banding parallel to the flow lines little seems to affect the total dissolved solids content of the ground water. The cubic surface fitted to total dissolved solids data does not add much to explain the variability, and the confidence limit associated with the cubic trend component is low (50 percent). However, it may be noted that even for the cubic surface banding parallel to the flow line persists. This seems to indicate that bulk total dissolved solids content does not change very much in ground water of the Tucson Basin as it moves down the hydraulic gradient.

### Calcium

Calcium trends based on the old analyses from 144 well locations (Figure 15) show a strong tendency

CALCIUM

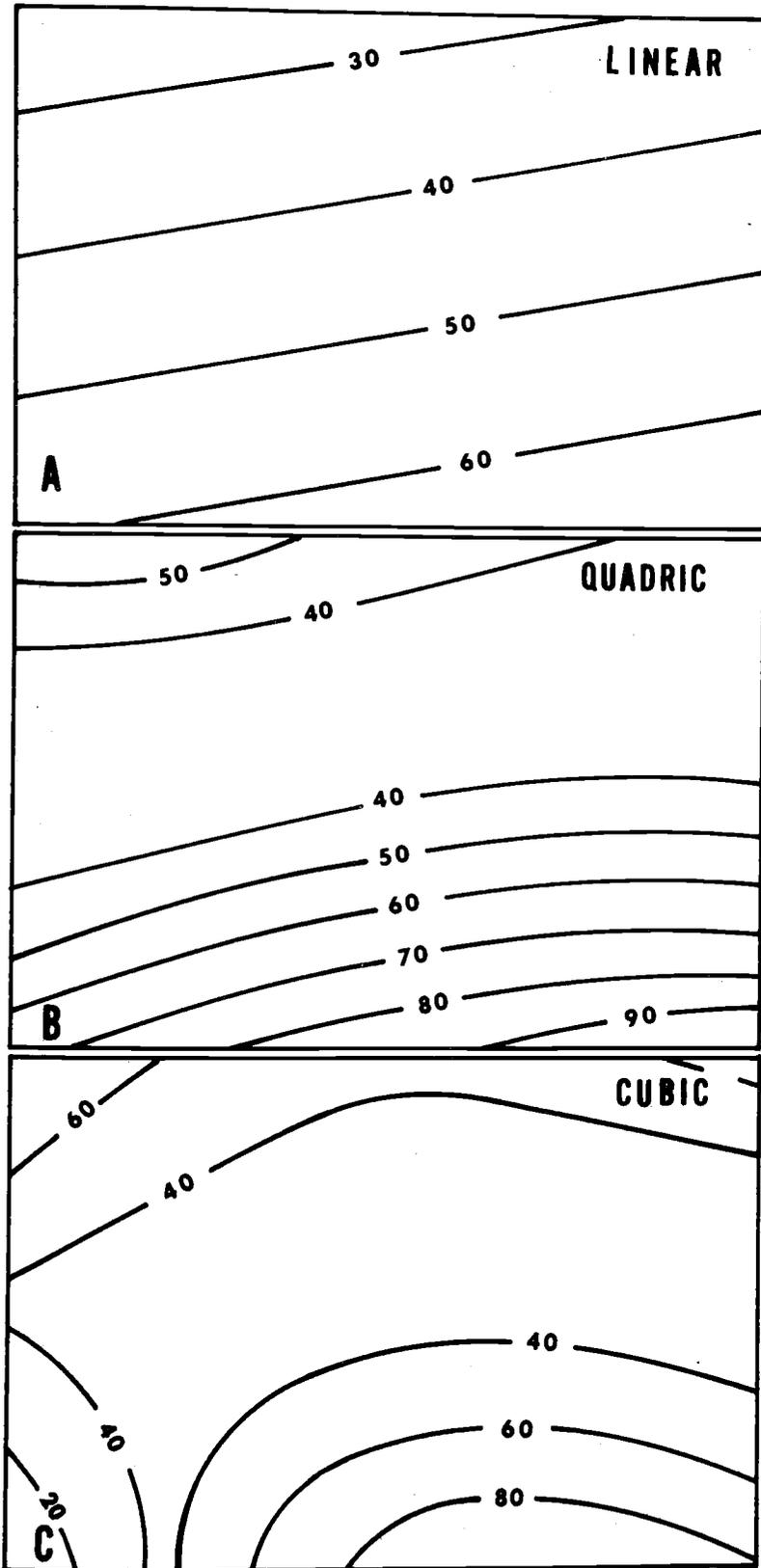


Figure 15. Contour maps of trend surfaces (A-C) fitted to calcium data, in ppm. Old samples.

to parallel the direction of ground-water flow. The linear surface explains about 29 percent of the variability. Considerable improvement in fit is provided by the quadratic surface accounting for more than 50 percent of the total sum of squares. The cubic surface accounts for an additional 7 percent. The confidence levels associated with all three trend components is more than 99.9 percent. Again, low calcium values seem to be associated with the area of predominantly coarse sediments. This is also water most likely derived from the Catalina and Tanque Verde granite-gneiss complex. Water in the southwestern part of the map area is probably derived from the Cienaga Gap area.

Trends are also fitted to calcium data from 59 wells covering the same area (Figure 16). Water from these wells was collected by the author and analysis of water quality was performed immediately after delivery of the samples to the laboratory. The surface fitted to the new, more accurate, but less numerous data are somewhat different than the same surfaces fitted to the old data. The new calcium data have a smaller range of values and have a lower mean value than the older data (Figure 12). The tendency for banding parallel to the flow lines is much less

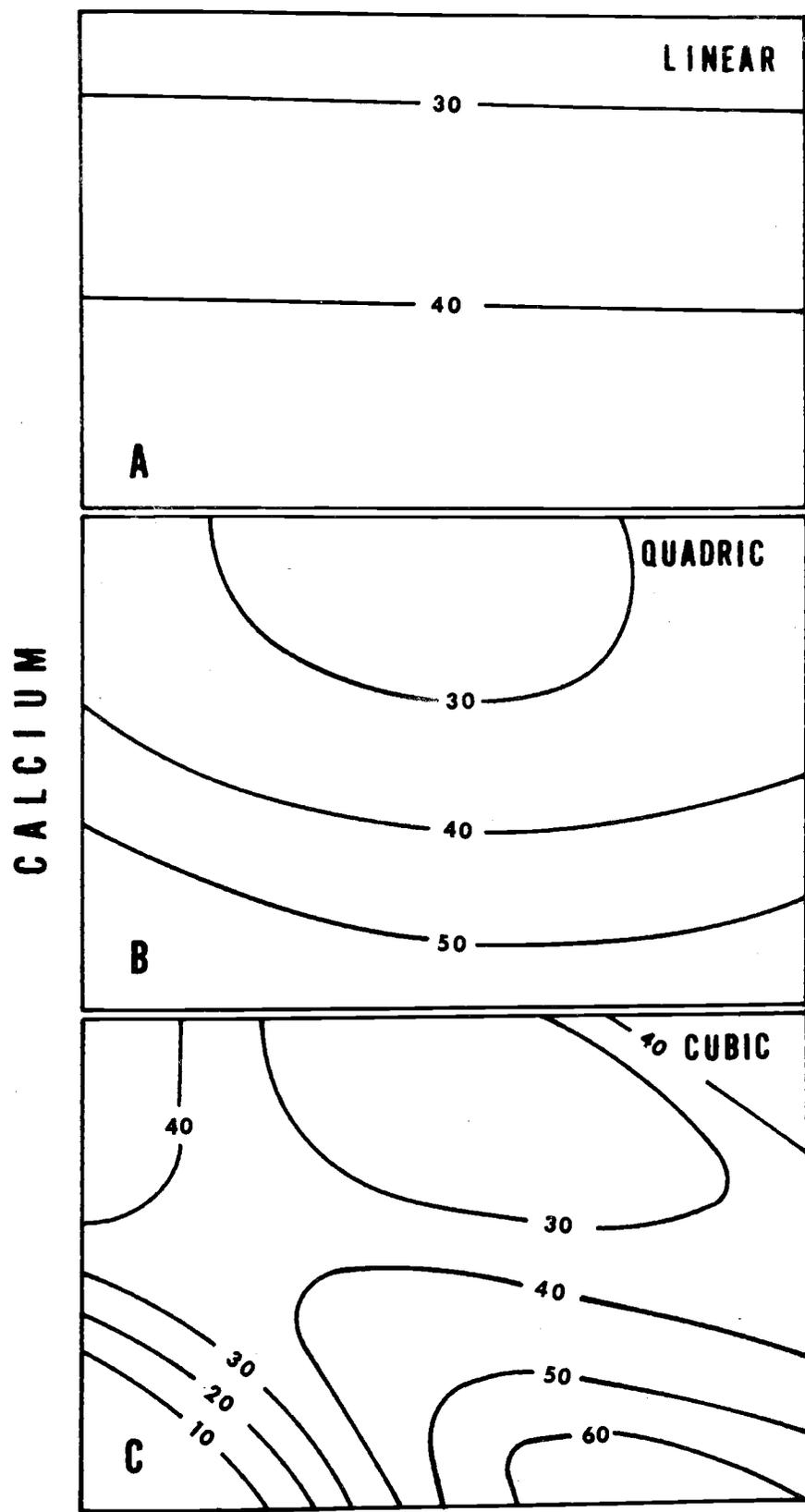


Figure 16. Contour maps of trend surfaces (A-C) fitted to calcium data, in ppm. New samples.

pronounced indicating that, perhaps other factors besides the direction of ground-water flow such as lithologic variation may play an important role. Low calcium values have some tendency to be associated with coarse-grained sediments and high calcium values with finer grained sediments but these relationships are not clear cut. Because of the inadequate representation of data in some corners, the cubic surface tends to "blow up" at the margins with values that are not real (very high or negative values). Neither the analysis of variance nor the percentages sums of squares gives us any clues as to which of the two sets of surfaces more correctly explains the distribution of calcium in ground water of the basin. Trends computed for the old data seem to favour control by the direction of ground-water flow and trends computed for the new data seem to favour the effects imposed on calcium content by the lithology of the aquifer.

### Magnesium

Not much can be said about the distribution of magnesium values (Figure 17) except that banding parallel to the direction of ground-water flow is not very pronounced. Magnesium content is not determined directly

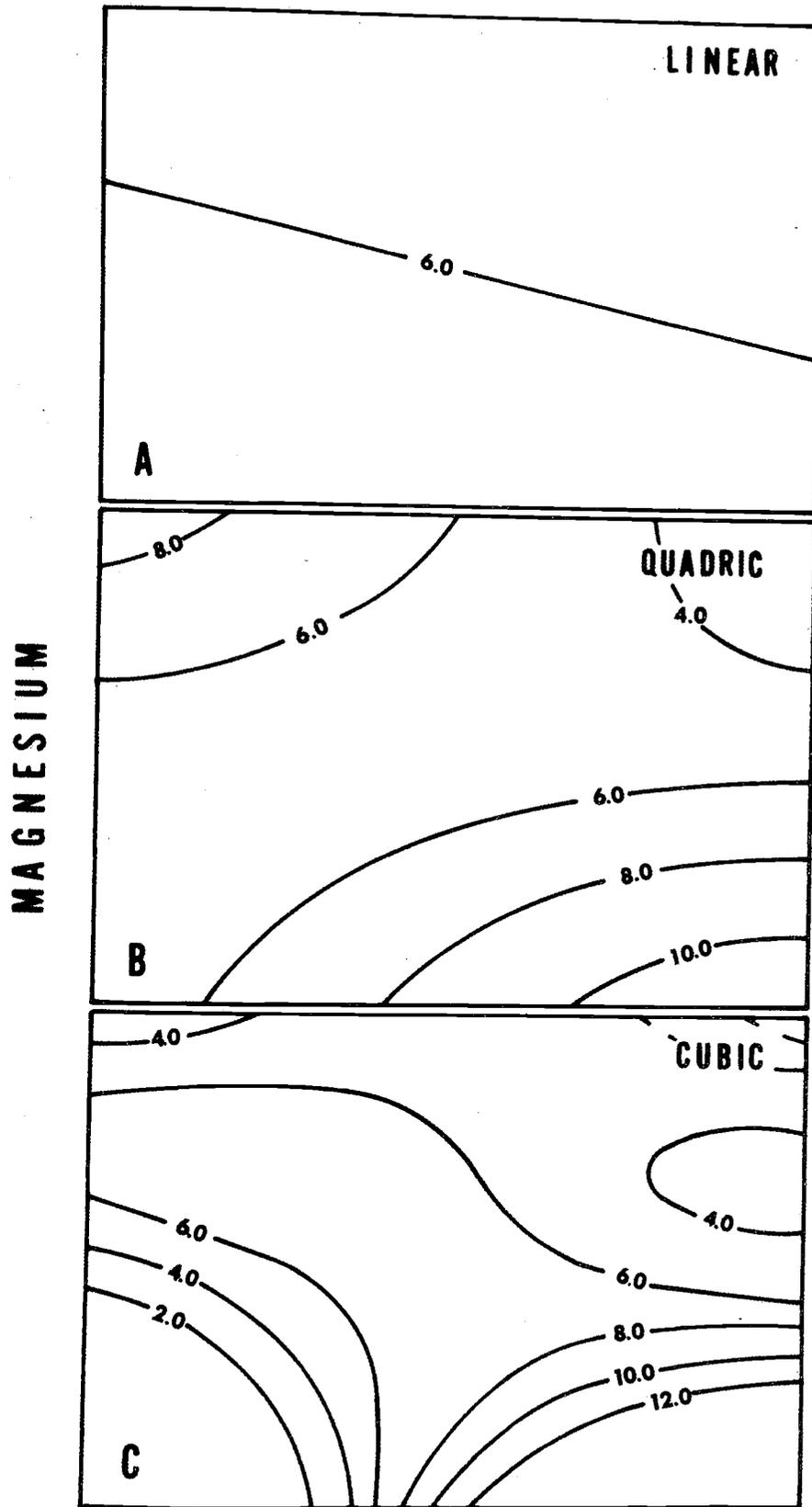


Figure 17. Contour maps of trend surfaces (A-C) fitted to magnesium data, in ppm. New samples.

but arrived at by subtracting calcium from total calcium and magnesium. There is some resemblance between the cubic surfaces of magnesium and calcium.

### Sodium

The distribution of sodium as represented by quadric and cubic contours (Figure 18) shows a fair tendency to parallelism to the direction of groundwater flow. Low sodium values seem to be associated with coarser grained sediments in the northeastern part of the map area. Elsewhere this relationship is less clear. The quadric and cubic surfaces explain 54 and 67 percent of the variability, respectively, and confidence limits are 99.9 percent for both surfaces.

### Potassium

The distribution of potassium (Figure 19) shows a striking resemblance to the distribution pattern of calcium (Figure 16) from the same samples. There is no apparent reason why the distributions of potassium and calcium should resemble one another. It seems, however, that concentrations of potassium and calcium might be controlled by similar mechanisms.

SODIUM

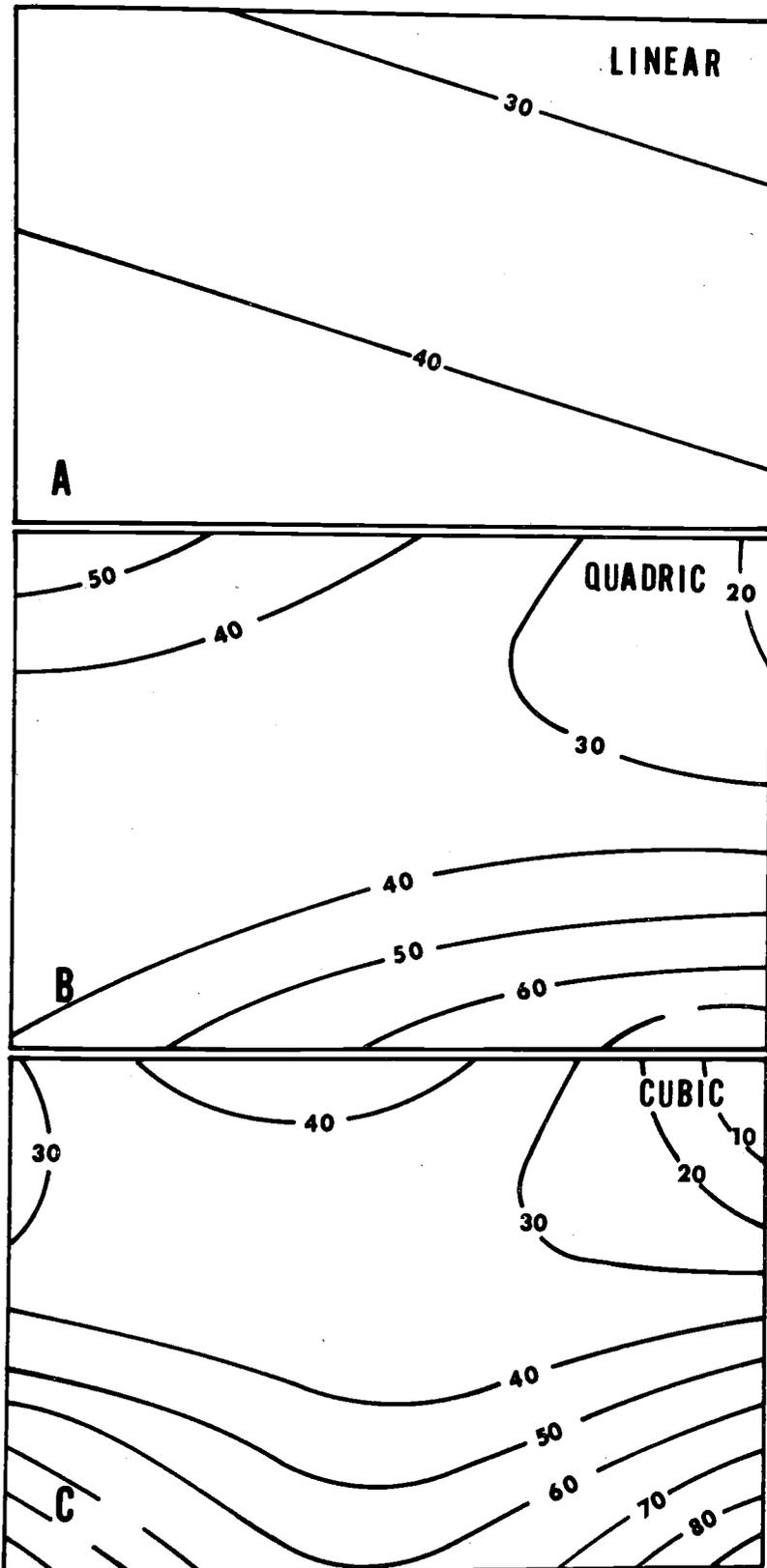


Figure 18. Contour maps of trend surfaces (A-C) fitted to sodium data, in ppm. New samples.

POTASSIUM

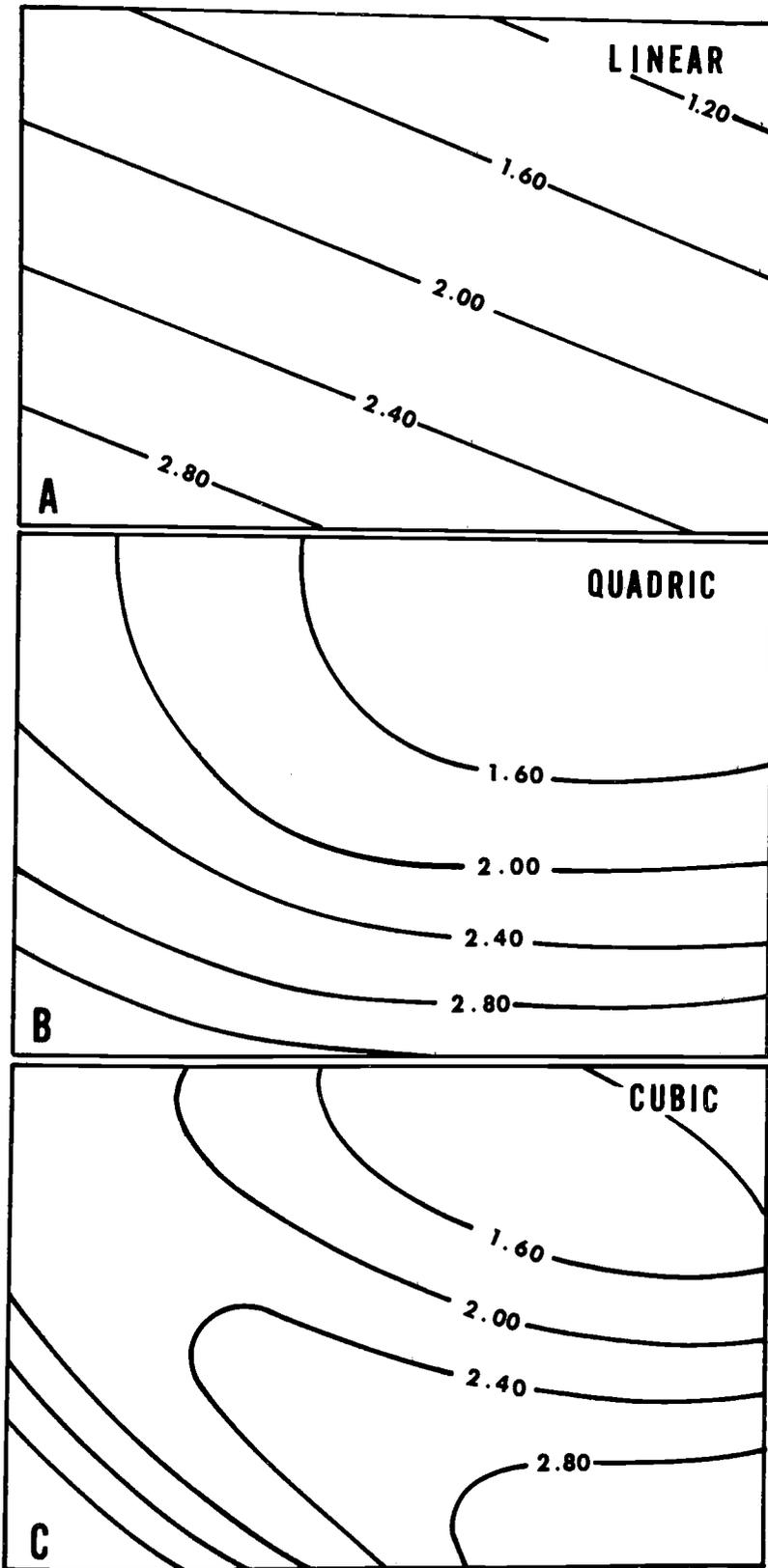


Figure 19. Contour maps of trend surfaces (A-C) fitted to potassium data, in ppm. New samples.

## Chloride

Two sets of chloride data were also subjected to trend surface analysis. The older data (Figure 20), more numerous, failed to yield sufficiently high percentages of total sums of squares for all three surfaces. No large scale systematic trends are apparent because of high local variation. This may either be due to local processes affecting the chloride content of ground water or due to "noise" generated by non-systematic analytical errors.

The linear surface (Figure 21A) fitted to the new data, however, shows a definite trend of progressive increase of chloride content in the direction of ground-water flow. This is a large scale and systematic feature because the linear trend accounts for more than 60 percent of the variability. Quadric and cubic trend components add very little to explain more of the variance and are statistically of low significance. This trend of progressive increase in chloride content down gradient supports the model of gradual increase in chloride values in the direction of ground-water movement proposed by H. Schoeller (1962). This model finds its basis primarily on data from arid zone

**CHLORIDE**

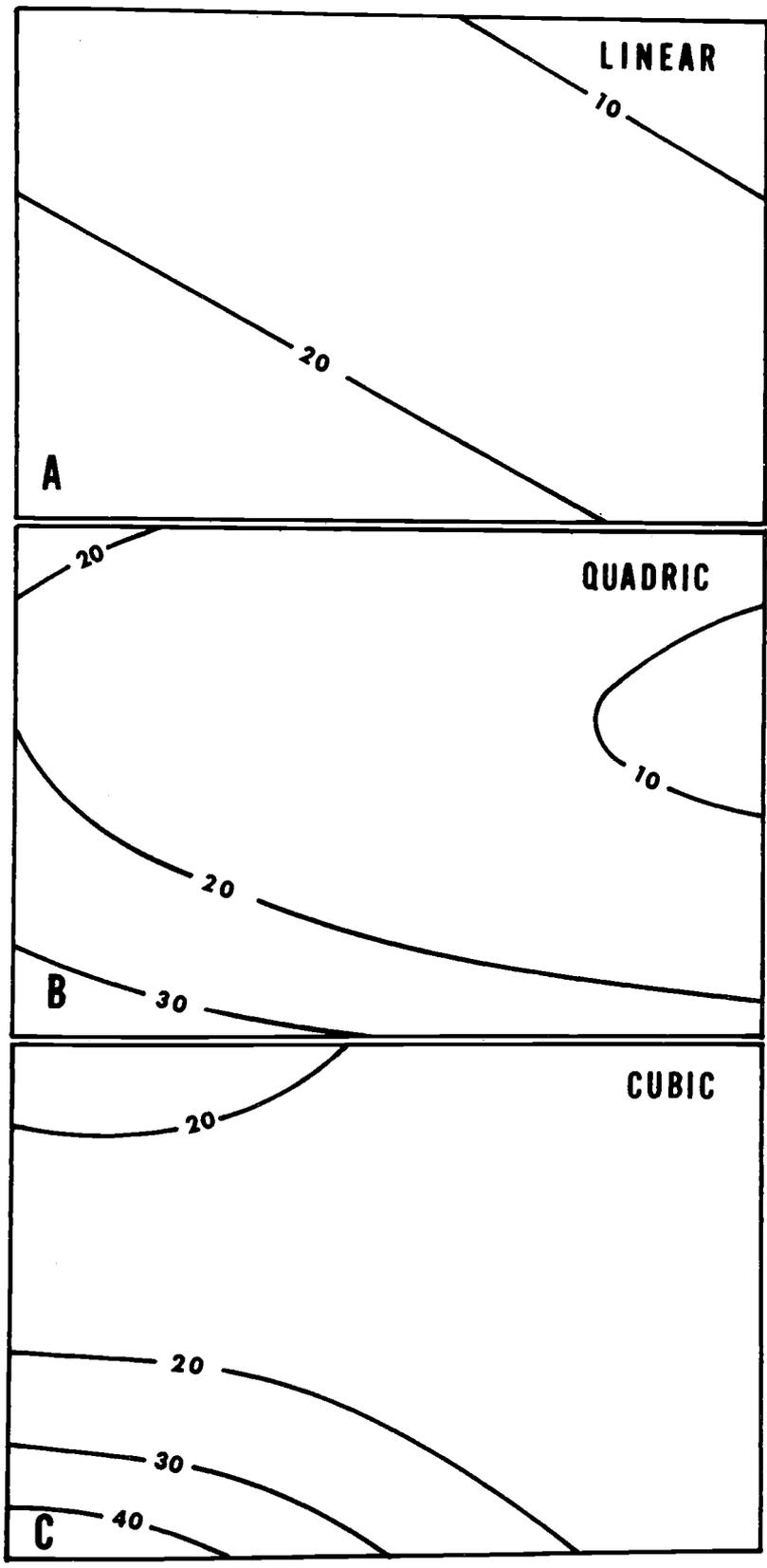


Figure 20. Contour maps of trend surfaces (A-C) fitted to chloride data, in ppm. Old samples.

## CHLORIDE

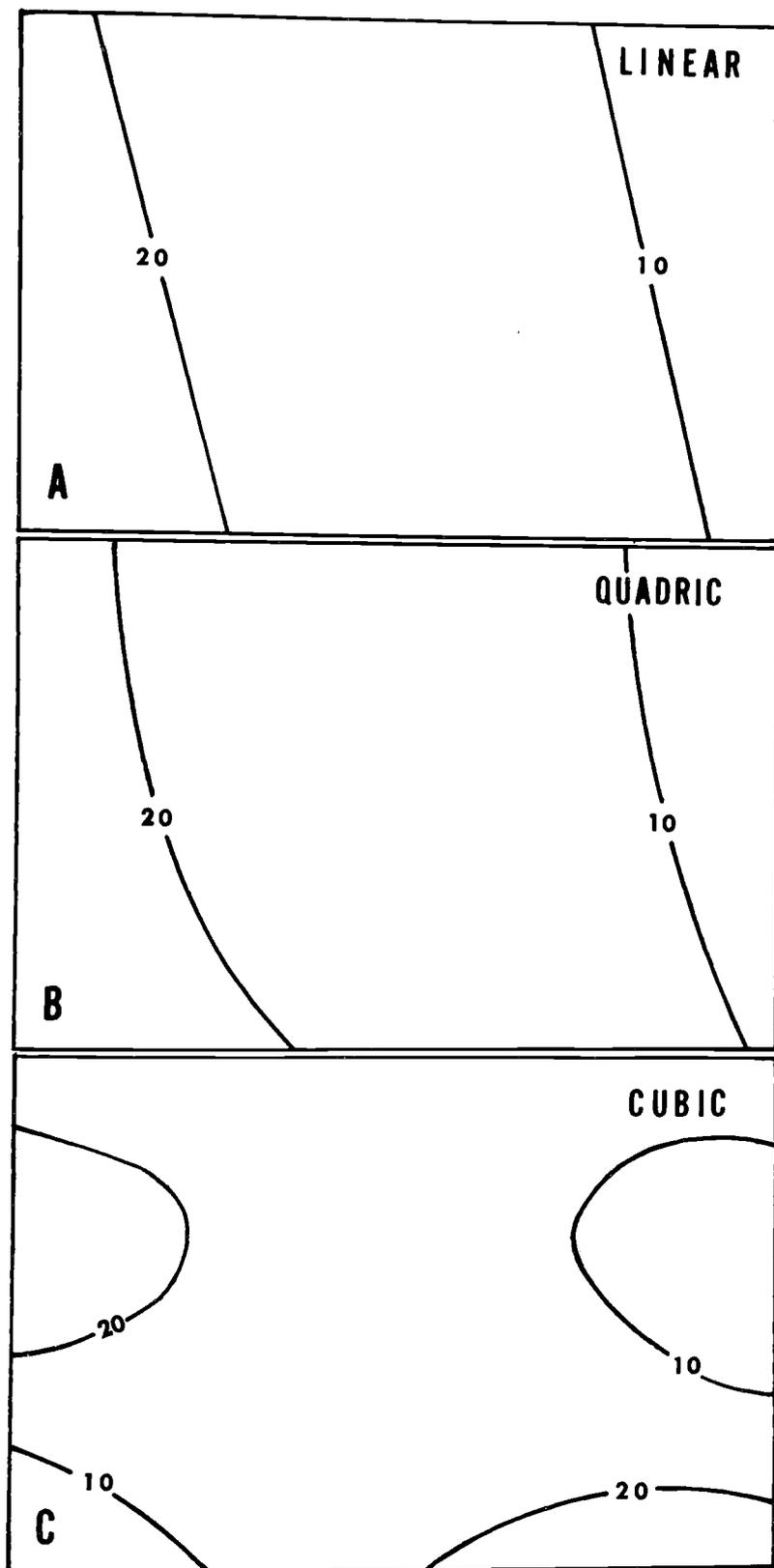


Figure 21. Contour maps of trend surfaces (A-C) fitted to chloride data, in ppm. New samples.

basins with ground waters of generally much higher chloride and total dissolved mineral content than found in the Tucson Basin. Chloride content and total dissolved solids content in the basin-fill aquifer are clearly independent. Increase in chloride does not necessarily imply increase in total dissolved solids content. It is significant to note that the use of two different sets of data of the same chemical constituents from the same area may yield entirely different results.

#### Sulfate

Trend surfaces fitted to the two different sets of sulfate data (Figures 22 and 23) yield almost identical results. In both cases banding parallel to the flow lines is pronounced and the behaviour of sulfate in ground water of the basin fill resembles that of total dissolved solids. It is curious to note that sulfate also is the largest single contributor to the total of dissolved solids. This persistence in sulfate content down gradient is an indication that sulfate is a stable constituent in ground water of the Tucson Basin. The variance explained by the surfaces is 62 percent for the linear, 80 percent for the quadric

**SULFATE**

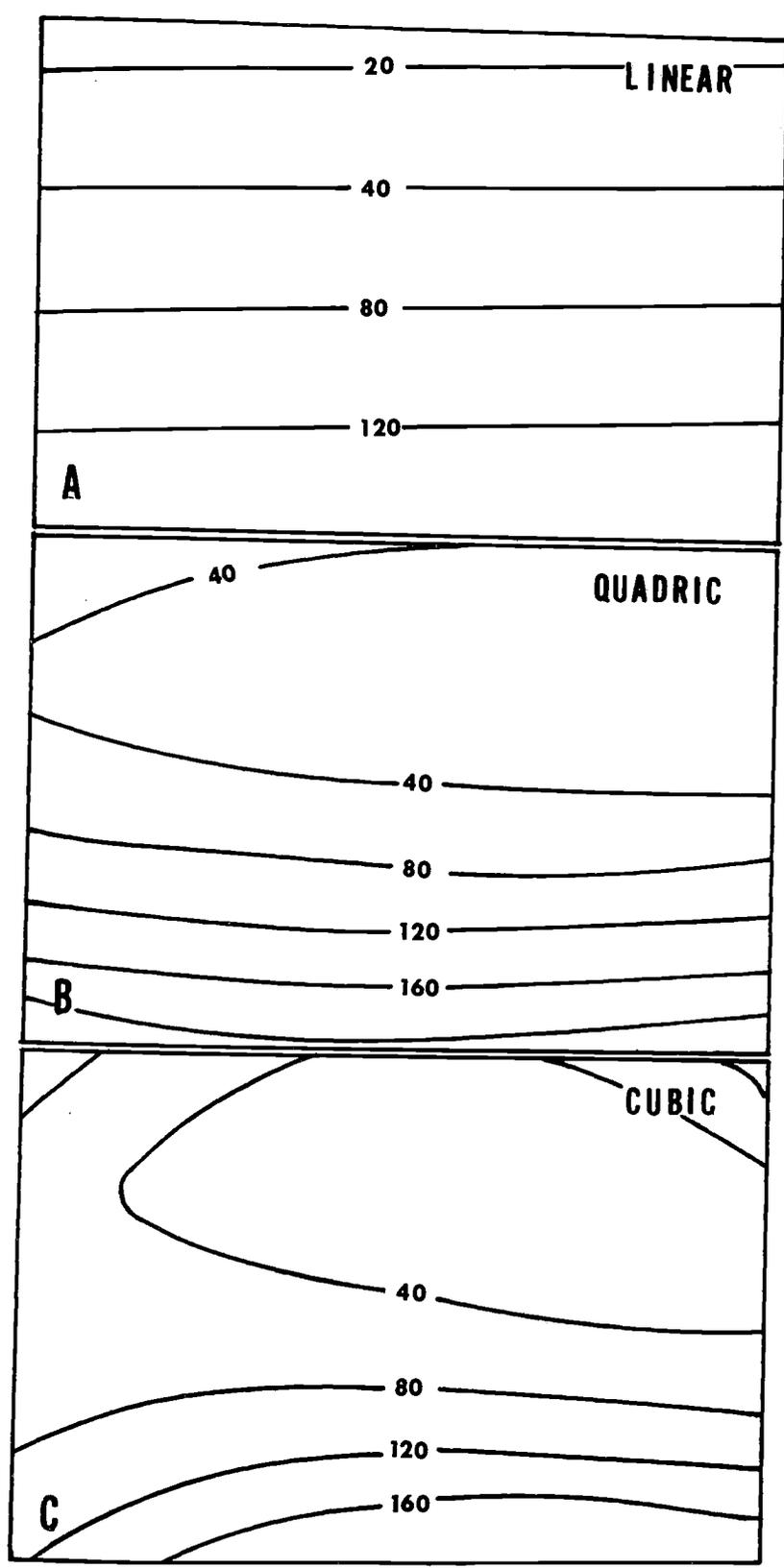


Figure 22. Contour maps of trend surfaces (A-C) fitted to sulfate data, in ppm. Old samples.

**SULFATE**

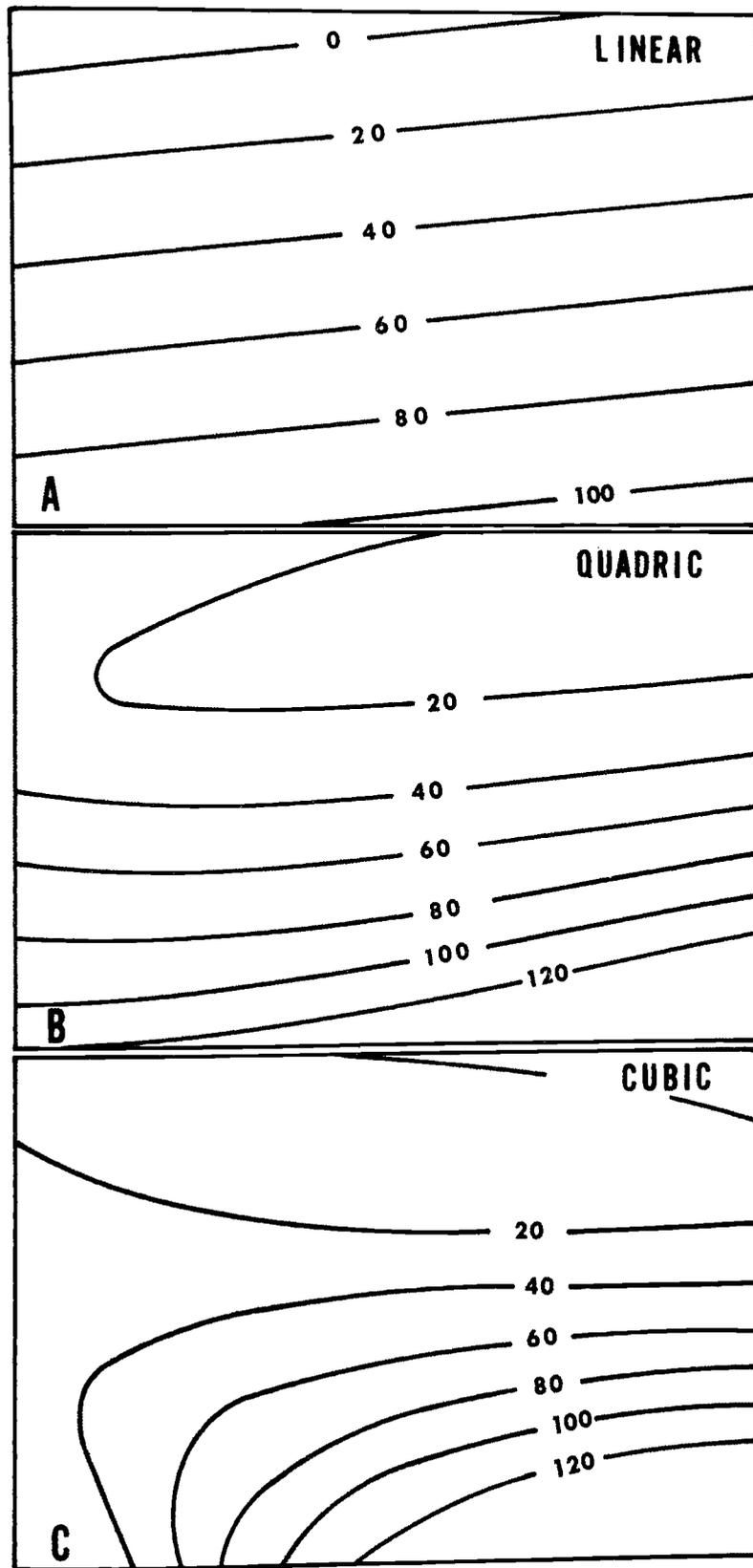


Figure 23. Contour maps of trend surfaces (A-C) fitted to sulfate data, in ppm. New samples.

and 84 percent for the cubic trends of the new data. Variance explained by trend surfaces fitted to the old data are almost the same. Confidence limits for all trend components of both sets of data is uniformly better than 99.9 percent.

### Bicarbonate and pH

Bicarbonate and pH are discussed together because their distributions are clearly related (see also Chapter VIII on calcite equilibria in ground water). Low bicarbonate values are associated with high pH measurements and vice versa (Figures 24 and 25). No clear relationships to the lithology and the direction of ground-water flow is apparent. This indicates that probably some other mechanism controls the distribution of these parameters in ground water of the basin. Trend surfaces computed for pH data which were measured in the field show better fit to the original data than the bicarbonate data determined in the laboratory. This indicates that the bicarbonate data are noisier than the pH data. Trend components for pH distribution are also statistically more significant than the trend components for bicarbonate.

**BICARBONATE**

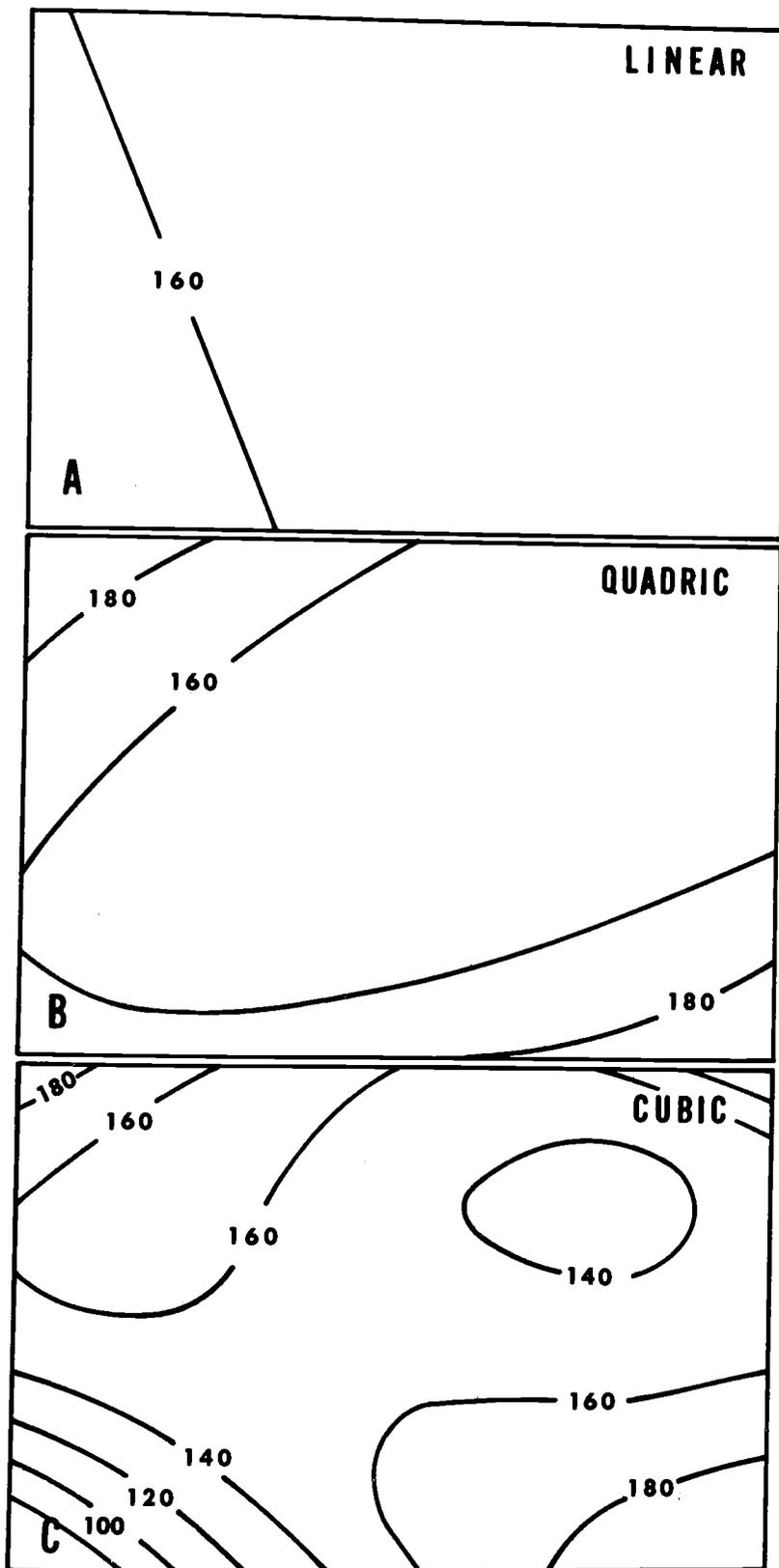


Figure 24. Contour maps of trend surfaces (A-C) fitted to bicarbonate data, in ppm. New samples.

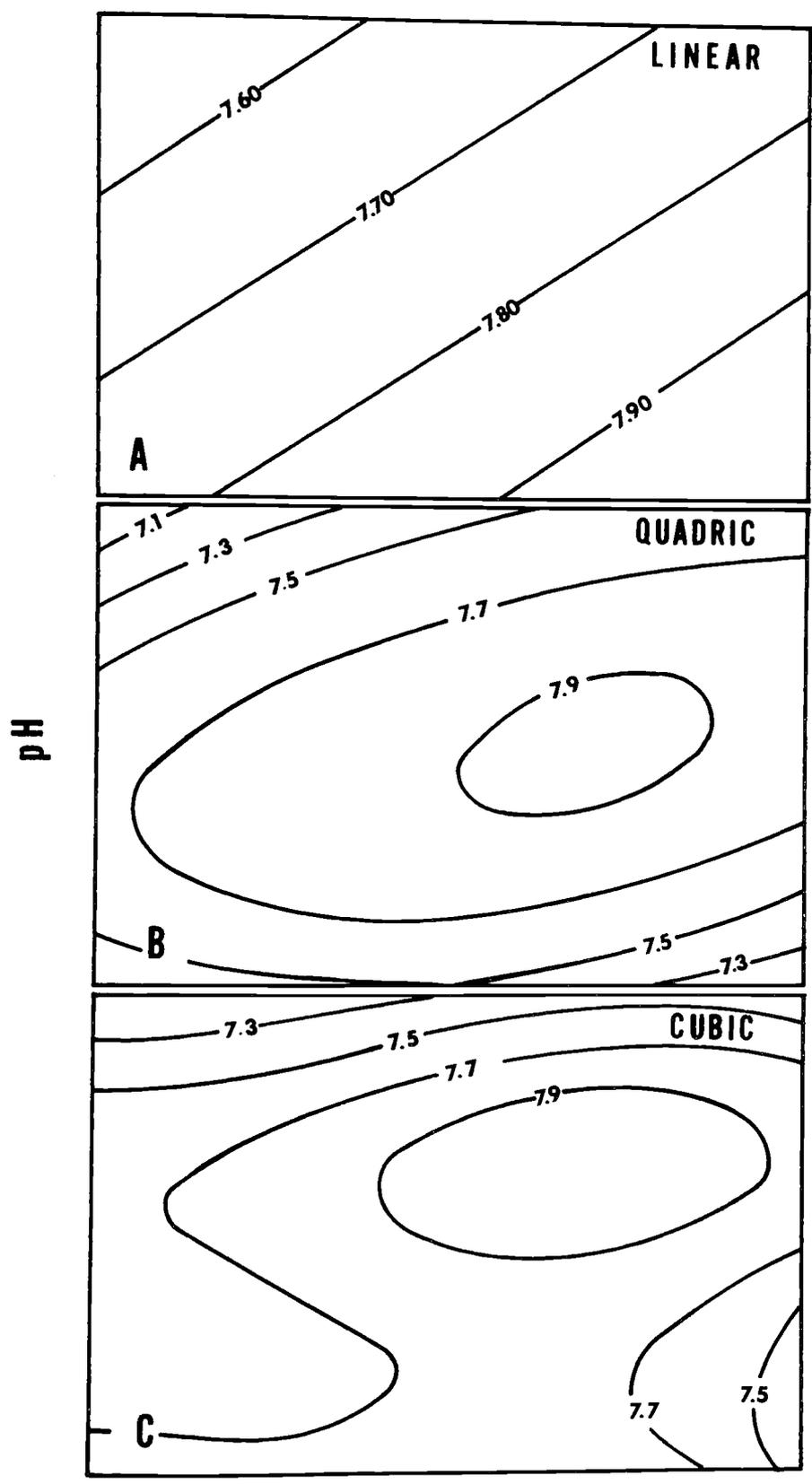


Figure 25. Contour maps of trend surfaces (A-C) fitted to pH values. pH measured in the field.

### Fluoride

Fluoride also shows a reasonably strong trend of distribution parallel to the flow lines (Figure 26). The linear trend explains 37 percent, the quadric trend, 49 percent, and the cubic trend, 61 percent of the observed variability. There is some indication that low fluoride values might be associated with coarser grained sediments derived from granitic terranes. There is a definite increase in fluoride content towards the southeastern part of the map area.

### Nitrate

Nitrate trends (Figure 27) show a very close resemblance to trends computed for the distribution of specific capacity of wells in the basin-fill aquifer (Figure 13). This clearly suggests strong lithologic control on the nitrate content of ground water assuming that specific capacity of wells is related to the lithology of the aquifer. Surprisingly also, high nitrate values are associated with high specific capacities and low nitrate values with low specific capacities. The relatively low percentages of the variance explained by the trend surfaces indicate that

**FLUORIDE**

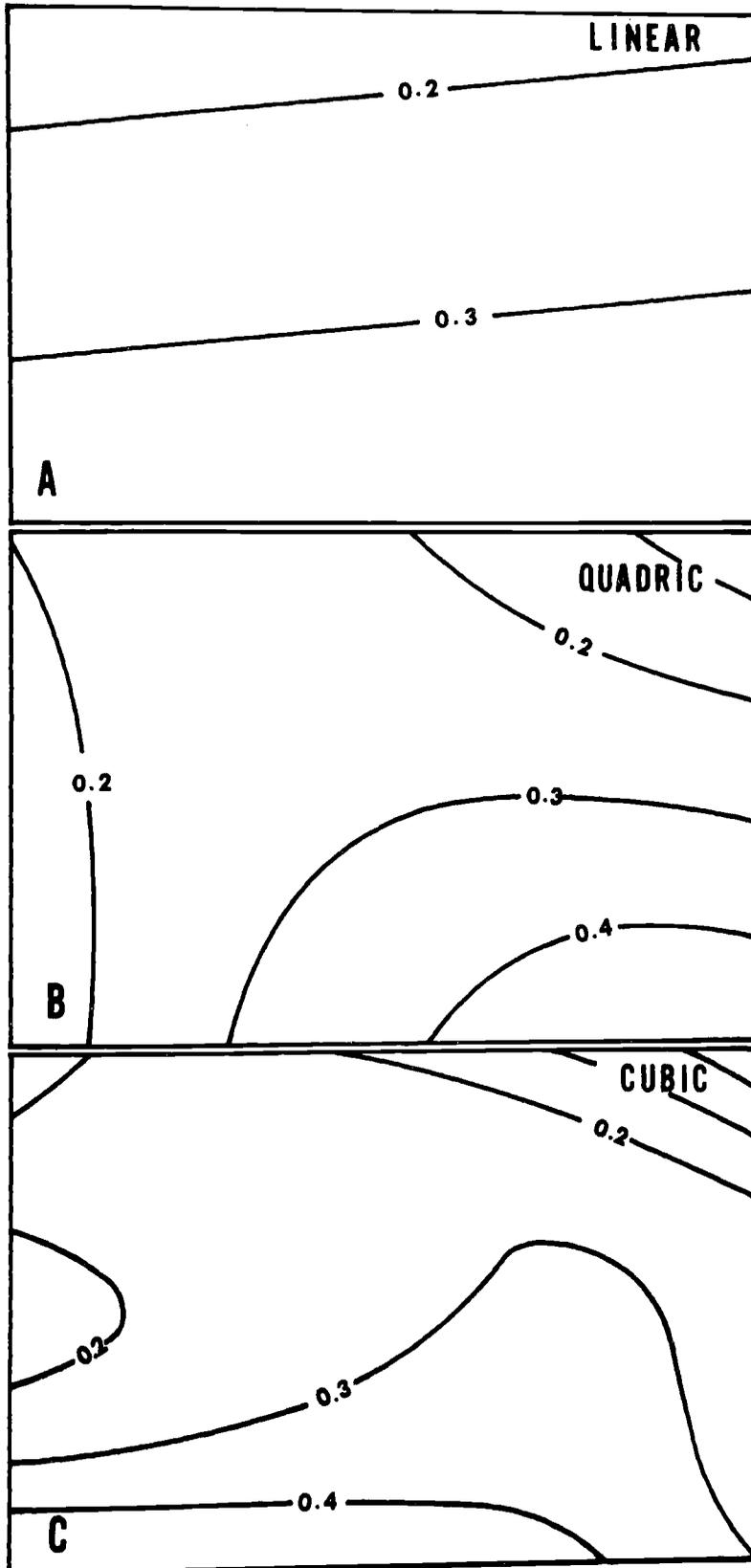


Figure 26. Contour maps of trend surfaces (A-C) fitted to fluoride data, in ppm. New samples.

**NITRATE**

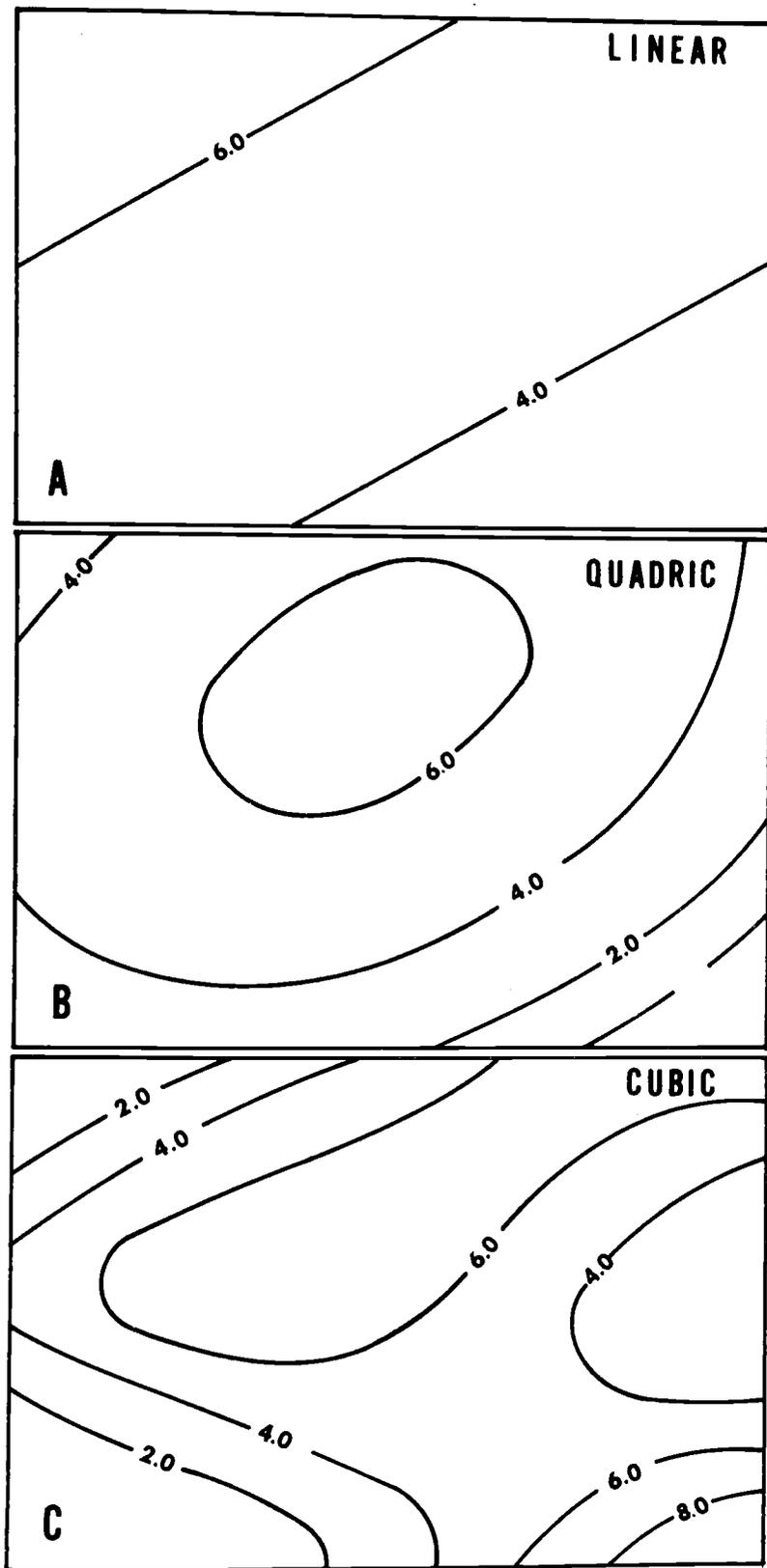


Figure 27. Contour maps of trend surfaces (A-C) fitted to nitrate data, in ppm. New samples.

the local variation might be considerable. This may have something to do with the fact that the lithology is such a determining factor in the nitrate content. Little is known about the sources of nitrate in ground water. If we exclude possible agricultural sources of nitrate in ground water at the depth of water table prevailing in the Tucson Basin, the following sources of nitrate might be suggested. Ancient playa deposits now in the zone of saturation are known to be associated with high occurrence of nitrate in ground water and ground water high in nitrate has also been found in areas where caliche occurs (Feth, 1966). Nitrate in ground water at greater depth may be derived from buried caliche or playa lake deposits. To this may be added that the higher specific capacities are probably associated with old stream-channel deposits. This combination of evidence appears to be a problem of some geologic interest.

### Strontium

Linear and quadric strontium trends show a relatively strong tendency to parallel the direction of ground-water flow (Figure 28). There is some suggestion that coarse-grained sediments contain water

**STRONTIUM**

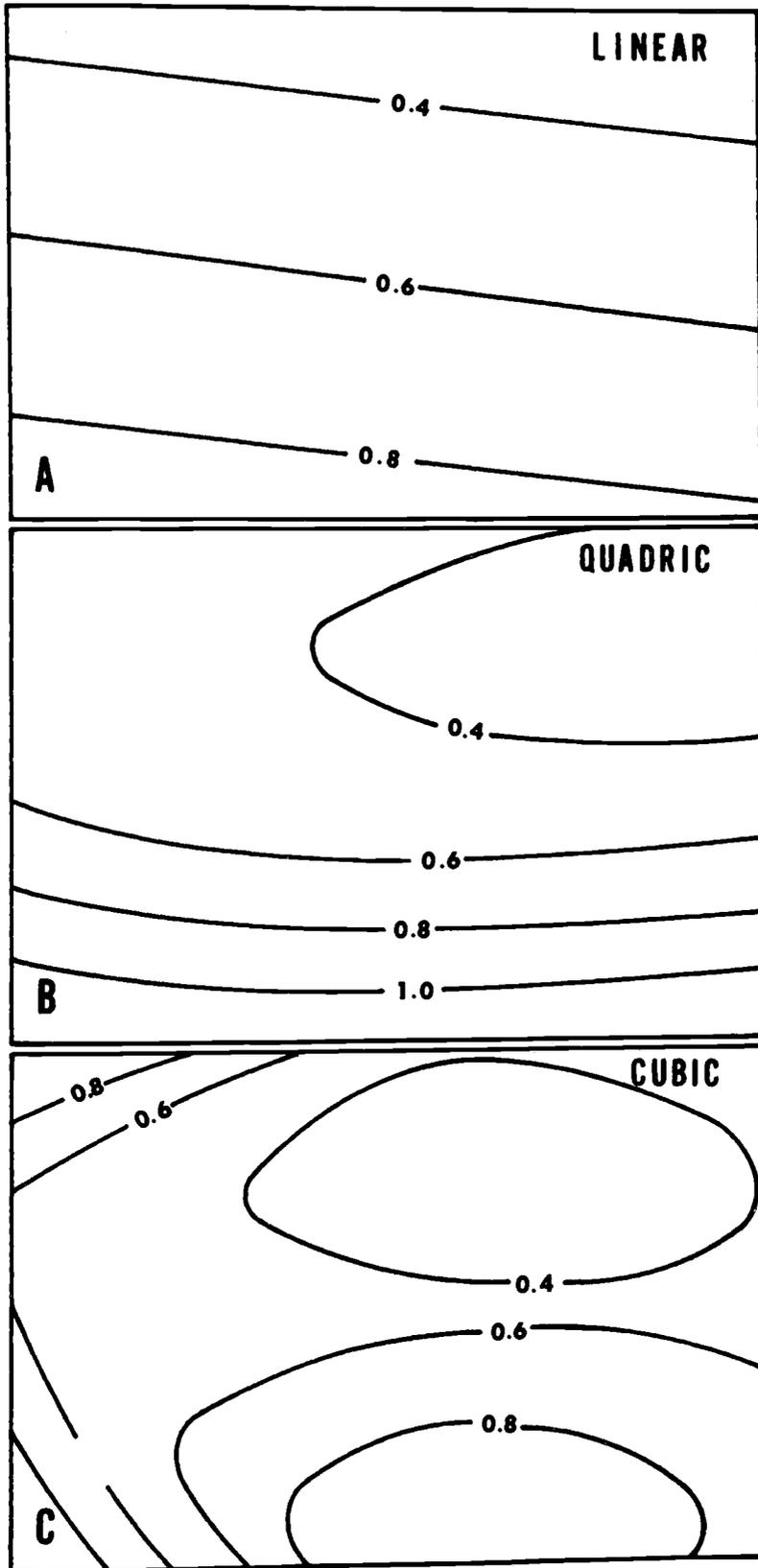


Figure 28. Contour maps of trend surfaces (A-C) fitted to strontium data, in ppm. New samples.

of generally lower strontium content. There is also some resemblance between the strontium and the calcium and potassium trends from the same samples. Linear trend explains 46 percent, quadric trend, 64 percent and the cubic trend, 75 percent of the observed variability. All three trend components have confidence levels of 99.9 percent.

### Zinc

Zinc trends (Figure 29) are very weak and statistically not significant. The lack of large scale systematic variation and the presence of excessive "noise" is probably best explained by the comparatively large analytical errors involved in the determination of zinc. Visual inspection of the trend surfaces suggests that there is some tendency for zinc isopleths to parallel the direction of ground-water flow and for low zinc values to be associated with coarse-grained sediments.

### Conclusions

The application of trend surface analysis to geologic problems is still in an experimental stage. The method as applied to geochemical problems has not

ZINC

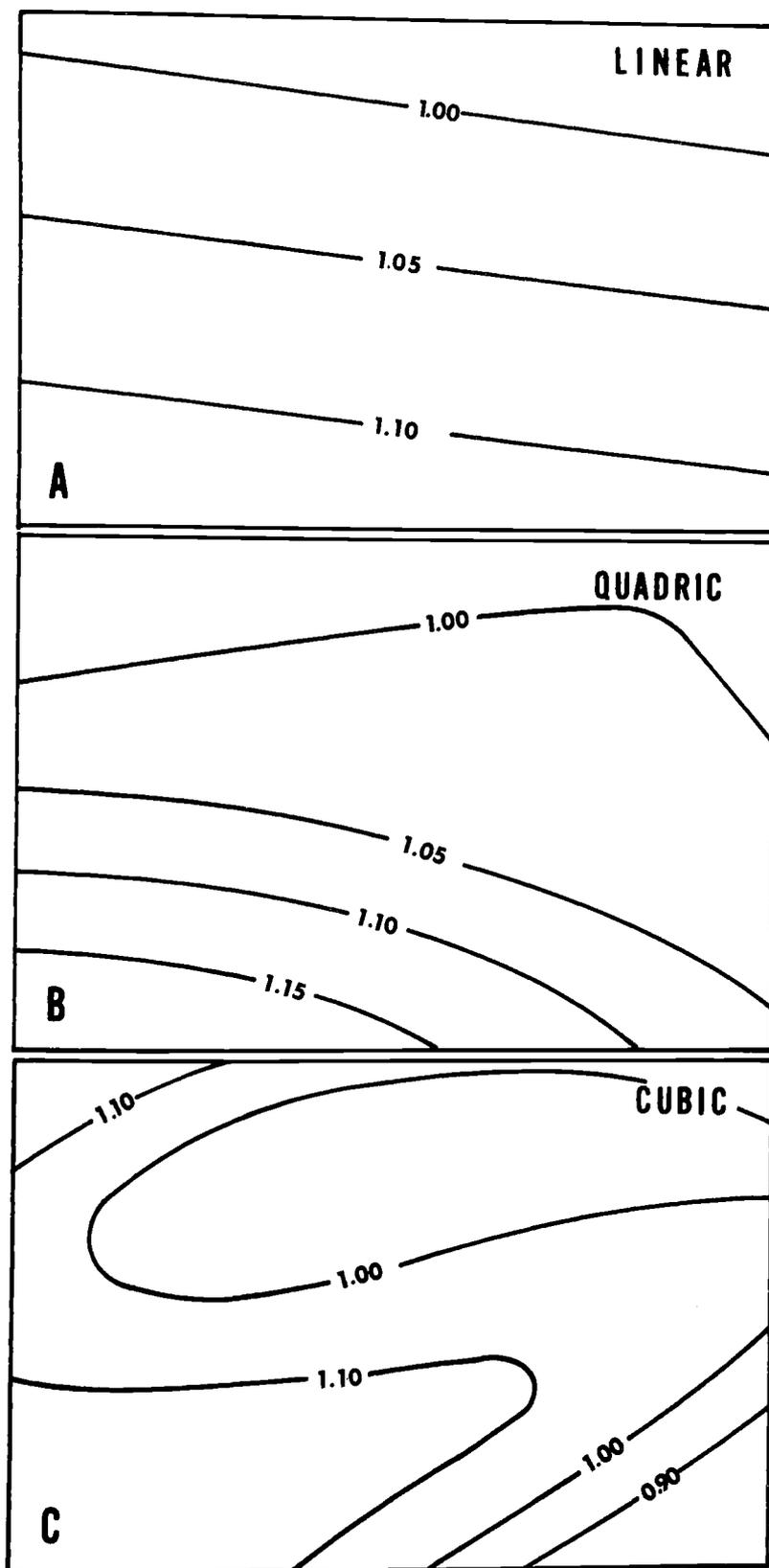


Figure 29. Contour maps of trend surfaces (A-C) fitted to zinc data, in ppm. New samples.

been adequately tested and no report of its use to the study of ground-water quality other than this one has yet appeared in the literature. It seems that several studies of this kind are being contemplated by other investigators and some are currently in progress.

Trend surface analysis here is applied primarily as an indicator of regional gradient to test a conceptual model. The trend surface is evaluated in terms of predictions that arise from the postulated conceptual model. Because of the inherent simplicity of the conceptual model, only large scale systematic effects have been considered. Only if these large scale systematic effects are appreciably strong as indicated by a large percentage of total sum of squares accounted for by the surface use of the trend as a predictor may be justified.

The large scale systematic effects on ground-water quality in the basin-fill aquifer as postulated by the model and identified by the trend surfaces are due to (1) the lithology of the derivative rocks, (2) lateral variation of the gross lithology of the basin-fill aquifer, and (3) direction of ground-water flow. As a testing device of a conceptual model based on a priori and intuitive knowledge of the hydrogeologic

conditions in the basin, trend surface analysis has been successful. This cannot be said for the use of trend surfaces as a predictor because of the generally low percentages (<80 percent) of the variances accounted for by the surfaces, an indication of large local fluctuations.

Trend surface analysis draws attention to some of the limitations and problems involved in the regional interpretation of ground-water quality data. The problem of sampling is probably a main source of errors. Sampling errors include restriction on the selection of sampling sites, faulty sampling procedures, etc. Little is known about appropriate sampling intervals in order to realistically interpret the regional variation of different chemical constituents. Not all chemical constituents are affected equally by the same factors. For a regional interpretation some chemical constituents obviously require fewer samples than others and also a different sampling design.

It has been tacitly assumed that the chemical composition of ground water at a particular locality does not change significantly with time. To what extent change with time plays a part in explaining the differences in trend surfaces of chemical constituents from

water samples of the same area but collected at different times requires further investigation.

In general, it is very difficult to interpret the regional distribution of dissolved constituents in ground water if there is considerable non-systematic local variation. Trend surface analysis can be of valuable help to interpret noisy data as it will bring out general trends. Without any idea as to the trend or grain to anticipate the interpretation of noisy data appears a perilous undertaking, especially if a large number of data are involved. Trend surface analysis is also a fast, objective and inexpensive way to evaluate the regional distribution of large numbers of chemical quality data.

## VII. APPLICATION OF FACTOR ANALYSIS TO THE STUDY OF HYDROCHEMICAL FACIES OF GROUND WATER

### Introduction

Ground-water quality data of the Tucson Basin are given in the form of tabulated chemical analyses of a large number of water samples, each sample representing one well location. The primary objective of using factor analysis in this study is to resolve the array of chemical quality data, referred to as the data matrix, into a simple framework that can be interpreted in terms of what we know of the geology and hydrology of the Tucson Basin. In general, factor analysis seeks this objective by reducing the relationships among a set of variables to a smaller number of fundamental variables or "factors".

For a readable introduction to factor analysis and its application to geologic problems, the reader is referred to recent papers by Imbrie and van Andel (1964), Griffiths (1964, 1966), Harbaugh and Demirmen (1964) and Miesch, Chao and Cuttitta (1966). More theoretical treatments of the subject are covered by

texts such as Cattell (1953), Fruchter (1954), Harman (1960), and Krumbain and Graybill (1965). Dawdy and Feth (in press, 1967) applied factor analysis to the study of ground-water quality data of the Mojave River Valley, California. Wallis (1965) critically discussed general applications of factor analysis to hydrologic problems. Other applications to the field of hydrology are by Fiering (1964) and Maxwell (1964). Matalas and Reihner (1967) have made some judicious comments, and rightfully so, on the uses and abuses of factor analysis.

To explain the application of factor analysis to the study of ground-water quality data, a qualitative discussion of its concepts will be given first. To illustrate its use, Q-mode and R-mode analysis are applied to ground-water quality data of the Tucson Basin. As a further test of its usefulness the results of hydrochemical facies analysis using a conventional approach on the same data will be compared to what can be achieved by factor analysis.

#### Selection of Data Points

The amount of computational labor involved is excessive and factor analysis can only be accomplished

through the use of computers. The nature of the computer program and the size of the computer used limits factor analysis to 100 well locations. The number of chemical constituents considered is either 6 or 8. The 6 constituents are the three major cations,  $\text{Ca}^{++}$ ,  $\text{Mg}^{++}$ ,  $\text{Na}^+$ , and the three major anions,  $\text{Cl}^-$ ,  $\text{SO}_4^{--}$  and  $\text{HCO}_3^-$ . By including total dissolved solids and fluorides, 8 constituents are taken into account.

The restriction to 100 wells influenced the decision to select two sets of data, each 100 wells. One set covers the area of greatest ground-water development underlying the City of Tucson (Figure 30A). This area was also studied by trend surface analysis. The other set covers a larger area which extends to the southeastern part of the basin to give more attention to the problem of tracing ground-water quality from the recharge areas (Figure 30B). This area is referred to as the regional ground-water system.

The selection of 100 wells of the Tucson Basin was accomplished by a random number process of elimination of wells from sections with excess well locations. The larger area of the regional system includes almost all of the smaller area except wells in township T13S - R14 E. To obtain 100 well sites for the larger area,

Figure 30. Maps showing locations of wells used in factor analysis.

- (A) Index map of 100 well locations, City of Tucson area. Solid lines indicate Township T14S-R14E.
- (B) Index map of 100 well locations, regional ground-water system of Tucson Basin.

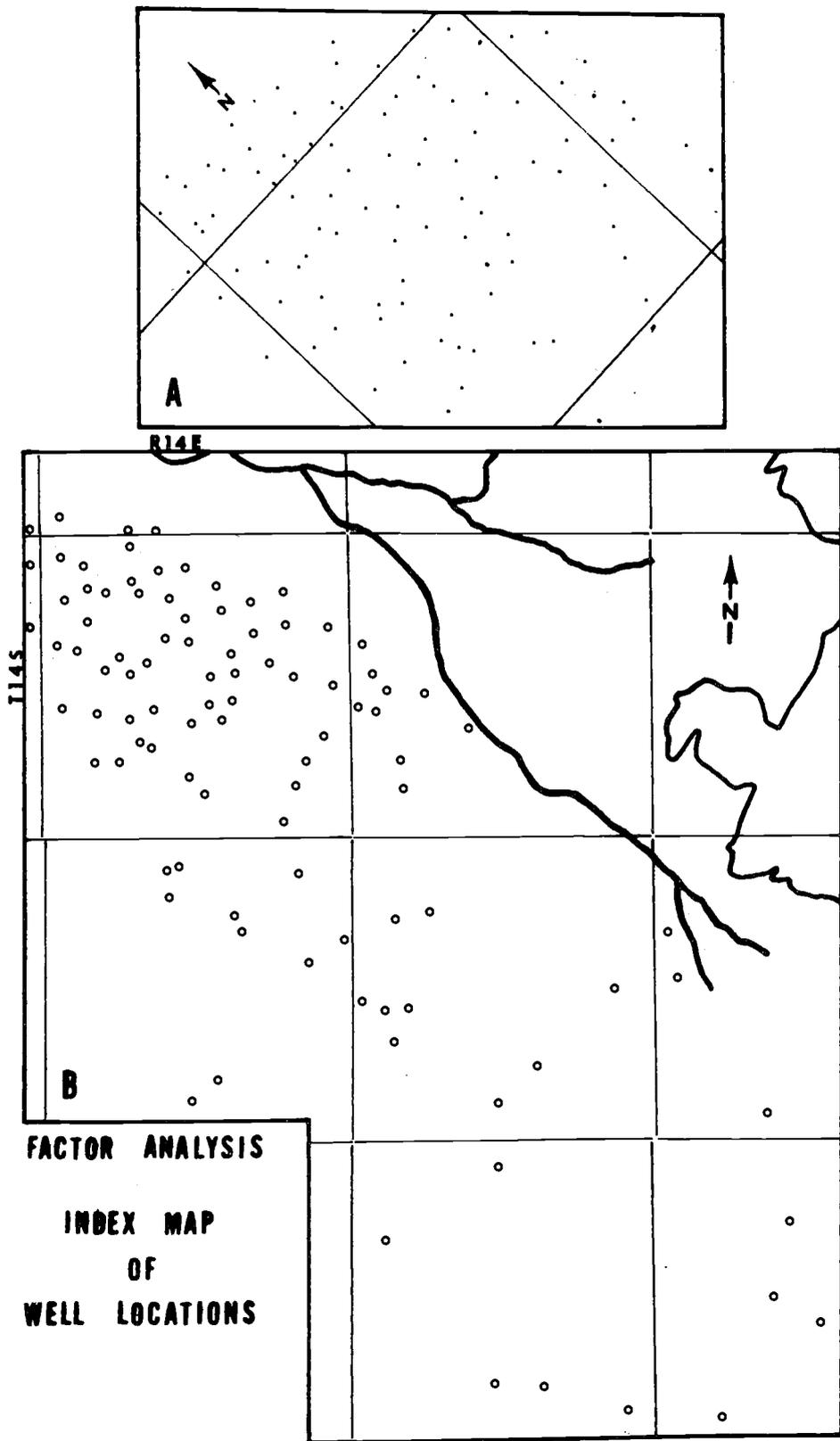


FIGURE 20

wells towards the southeast hydraulically upgradient from the smaller area were selected.

### Conventional Approach to the Study of Hydrochemical Facies

Traditionally, hydrochemical facies of ground water has been classified by graphical means. Most natural ground waters contain relatively few dissolved constituents with cations and anions approximately in electrical balance with one another. The three most abundant cation constituents are calcium, magnesium, and sodium. Potassium also occurs, but ordinarily it is much less abundant than sodium. The three most common anions are chloride, bicarbonate and sulfate. Because of this, the use of trilinear diagrams has been popular in the interpretation of water analyses (Hill, 1942, Piper, 1953, Back, 1961).

Two triangles (Figure 31A) are used, one for cations and one for anions, with each vertex representing 100 percent of a particular ion, expressed in equivalents per million. The chemical character of the water is indicated graphically by single point plottings of cations and anions based on the trilinear coordinates. Each point, therefore, expresses the

Figure 31. Classification of Hydrochemical Facies.

- (A) Water analysis diagram showing hydrochemical facies, in percent of total equivalents per million (after Back, 1966).
- (B) Classification of water types proposed by Piper (1953):
  1. Carbonate hardness exceeds 50 percent; chemical properties of water are dominated by alkaline earths and weak acids.
  2. Carbonate alkali exceeds 50 percent.
  3. Noncarbonate hardness exceeds 50 percent.
  4. Noncarbonate alkali exceeds 50 percent; chemical properties of the water are dominated by alkalis and strong acids.
  5. No cation-anion pair exceeds 50 percent.
- (C) Classification of cation hydrochemical facies (modified after Back, 1966).
- (D) Classification of anion hydrochemical facies (modified after Back, 1966).

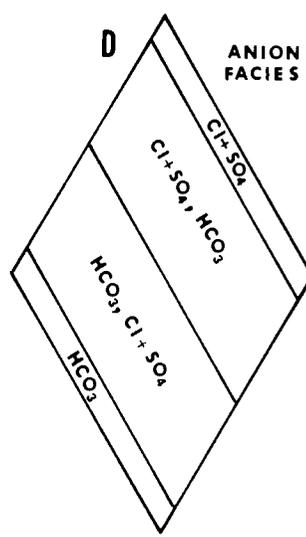
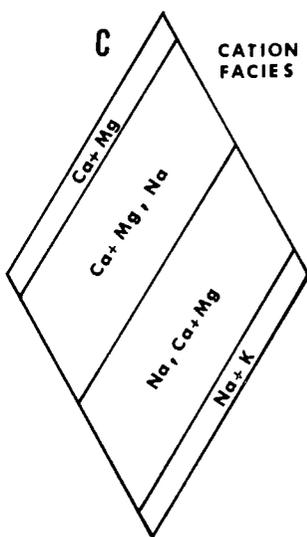
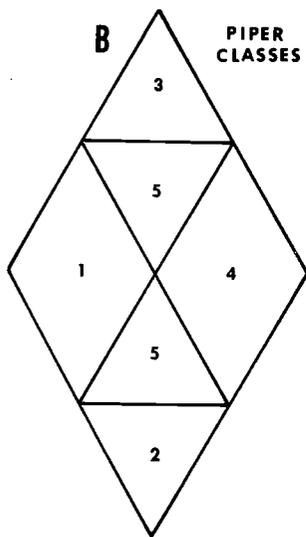
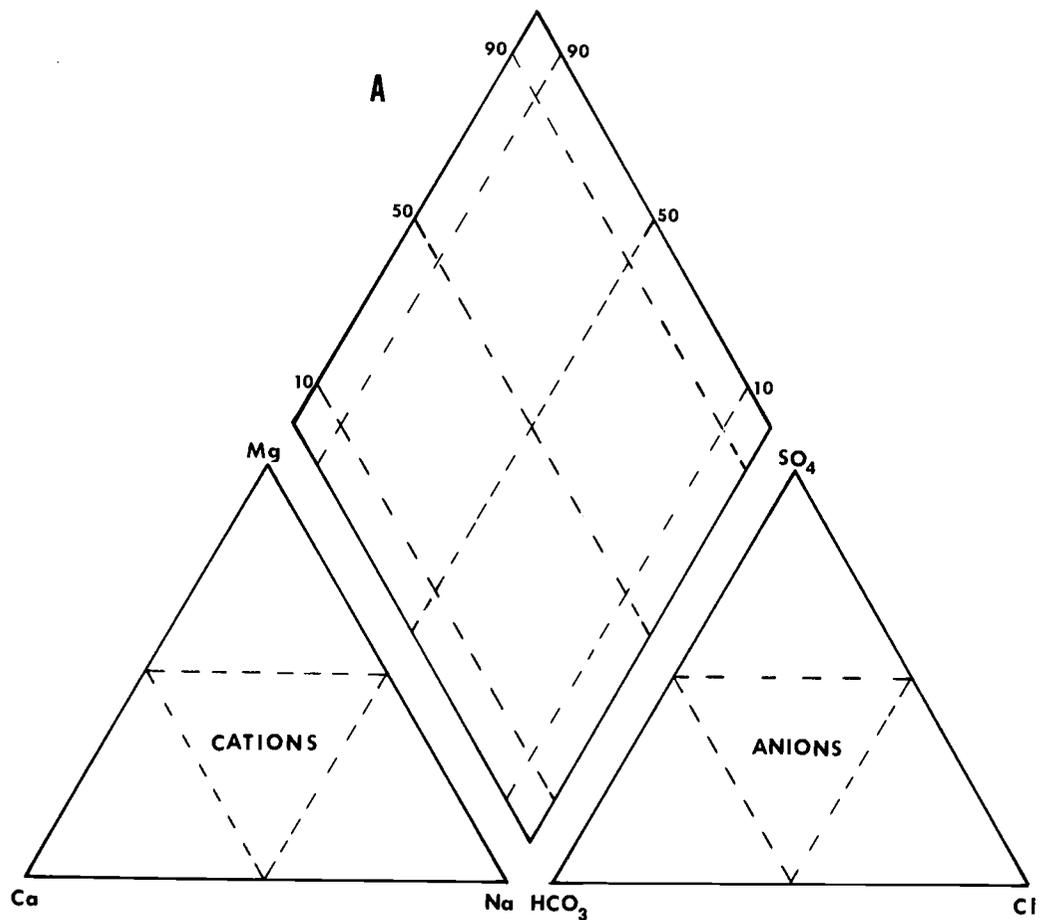


FIGURE 31

relative concentrations of constituents as a percentage of total reacting value. The procedure balances analytical errors automatically.

Hill (1942) added a diamond-shaped area to the two triangles. The two points plotted in the triangles are projected into the diamond and are plotted as a single point. Piper (1953) developed an essentially similar diagram modifying the position of the triangles and the diamond (Figure 31A). Piper also gives a detailed description of the procedures and examples of application of this diagram to the geochemical interpretation of water analyses. The Piper diagram (Figure 31B), with some changes as to the classification of the different water types, has been used by Back (1961, 1966) and others (Seaber, 1962, Morgan and Winner, 1964) to study hydrochemical facies of ground water (Figures 31C and 31D).

The Piper diagram was also used in this study of hydrochemical facies of ground water in the basin. In the part of the basin selected for detailed study, three water types according to Piper's classification scheme can be detected (Figures 31B and 32A). Most of the water is characterized by carbonate hardness (secondary alkalinity) exceeding 50 percent, that is,

Figure 32. Hydrochemical facies of ground water of the basin-fill aquifer, City of Tucson area. Solid lines indicate Township T14S-R14E. For explanation, refer to Figure 31.

- (A) Map showing distribution of different water types based on classifications proposed by Piper (Figure 31B).
- (B) Map showing distribution of cation hydrochemical facies, after Back (Figure 31C).
- (C) Map showing distribution of anion hydrochemical facies, after Back (Figure 31D).

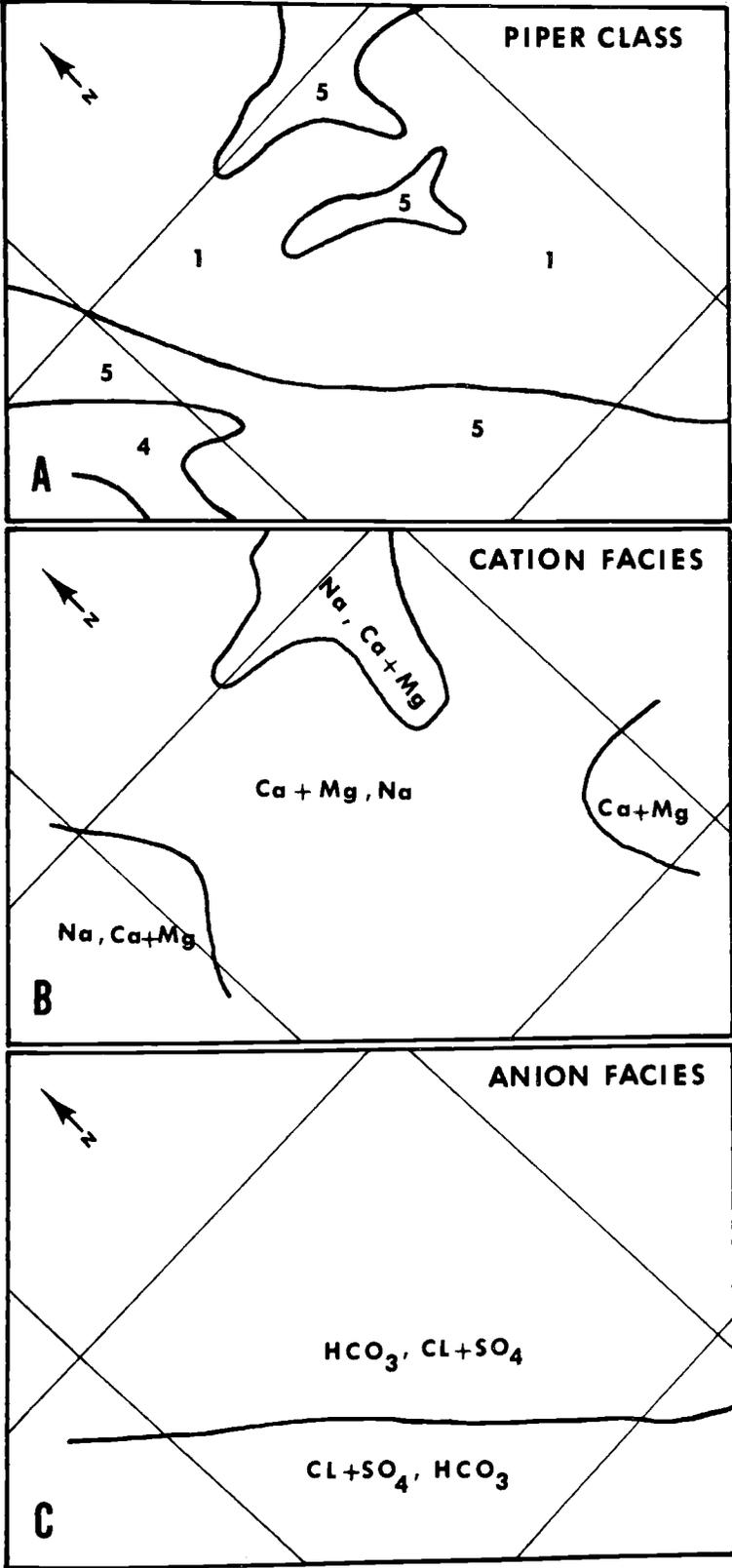


Figure 32. Hydrochemical facies of ground water of the basin-fill aquifer, City of Tucson area.

chemical properties of the water are dominated by calcium and bicarbonate. This water occurs predominantly in the area which is also characterized by relatively low ionic concentrations, less than 500 ppm total dissolved solids. In the southwestern portion of the area under investigation, no one cation-anion pair exceeds 50 percent of the total. The average total dissolved solids content in this area is between 500 and 100 ppm and there is a predominance of calcium, magnesium and sulfate ions over other ions. This water may be part of the area, some water, in which primary salinity or non-carbonate alkali exceeds 50 percent, occurs. In this water, chemical constituents are dominated by alkalies and strong acids.

The data from the same area were also interpreted using Back's (Back, 1961, 1966) classification (Figures 31C and 31D). Percentages of constituents suggested as most informative by this classification are the cation facies and the anion facies. The cation facies expresses sodium (and potassium) as a percentage of total cations and the anion facies expresses bicarbonate as a percentage of total anions.

The cation facies (Figure 32B) produces a pattern which is difficult to interpret in terms of

direction of ground-water flow in the basin. The distribution of percentage sodium values in the basin is not random but fairly well defined areas of high and low occurrences may be outlined. No explanation for these occurrences are presently available and little is known of what the effect of the use of the difference method to determine sodium might be. The cation facies in certain parts of the basin resembles the pattern resulting from the Piper classification.

The anion facies (Figure 32C) also produces a pattern which bears some similarity to the results obtained by the Piper classification. The ground water with average total dissolved solids content below 500 ppm and carbonate hardness exceeding 50 percent is of the bicarbonate, chloride-sulfate type. In the southeastern section where the average total dissolved solids content runs between 500 and 1000 ppm the water is characterized as a chloride-sulfate bicarbonate type.

The results of these graphical methods do not adequately support the hypothesis proposed to explain hydrochemical facies in the Tucson Basin, namely, that water quality does not change significantly as it moves along the hydraulic gradient. The methods are probably

not sensitive enough to bring out significant patterns that identify waters of different quality. The limitations of graphical methods probably are:

- (1) The "pigeon hole" classification employed to differentiate water types is arbitrary.
- (2) The use, in the three component systems, of percentage data that add up to 100 percent total. The chemical character of the water is expressed according to relative rather than absolute concentrations (Chayes, 1960, 1962).
- (3) Restrictions imposed by the two-dimensional space used to interpret the data.

There would be considerable improvement in distinguishing different types of water if we could identify discrete clusters of the plotted points in either the triangular or diamond shaped fields. Optimal classification can only be achieved by directly taking into account all available constituents in absolute concentrations, plotting them in a space not restricted by planar dimensions, and grouping them by identifying clusters of data that belong together. Such a method would only be limited by the type of information available on chemical quality.

In addition to its function as a tool to differentiate water types, Piper has suggested the use of his diagram as a means to study apparent mixing of waters of different chemical quality in the basin. Two waters of different chemical quality mixed in all proportions plot in the three fields as a straight line. Assuming that all products remain in solution, this line joints all the points representing all possible mixtures of the two different waters.

To investigate, at least qualitatively, the possibility of mixing of water in the direction normal to the ground-water flow lines, the chemical quality of wells across the basin was studied using the Piper diagram (Figure 33). Points representative of a series of wells across the basin do not plot on a straight line. Considering anion facies only, there might be a tendency of water to gradually become more of the  $(\text{HCO}_3^-, \text{Cl}^- + \text{SO}_4^{--})$  type from  $(\text{Cl}^- + \text{SO}_4^{--}, \text{HCO}_3^-)$  going from southwest to northeast across the basin. Strictly adhering to Piper's method, large scale mixing across the basin is not apparent. However, it should be pointed out in this context that this method and the data available are probably inadequate to confirm or generally disprove mixing of ground water of different qualities in the Tucson Basin.

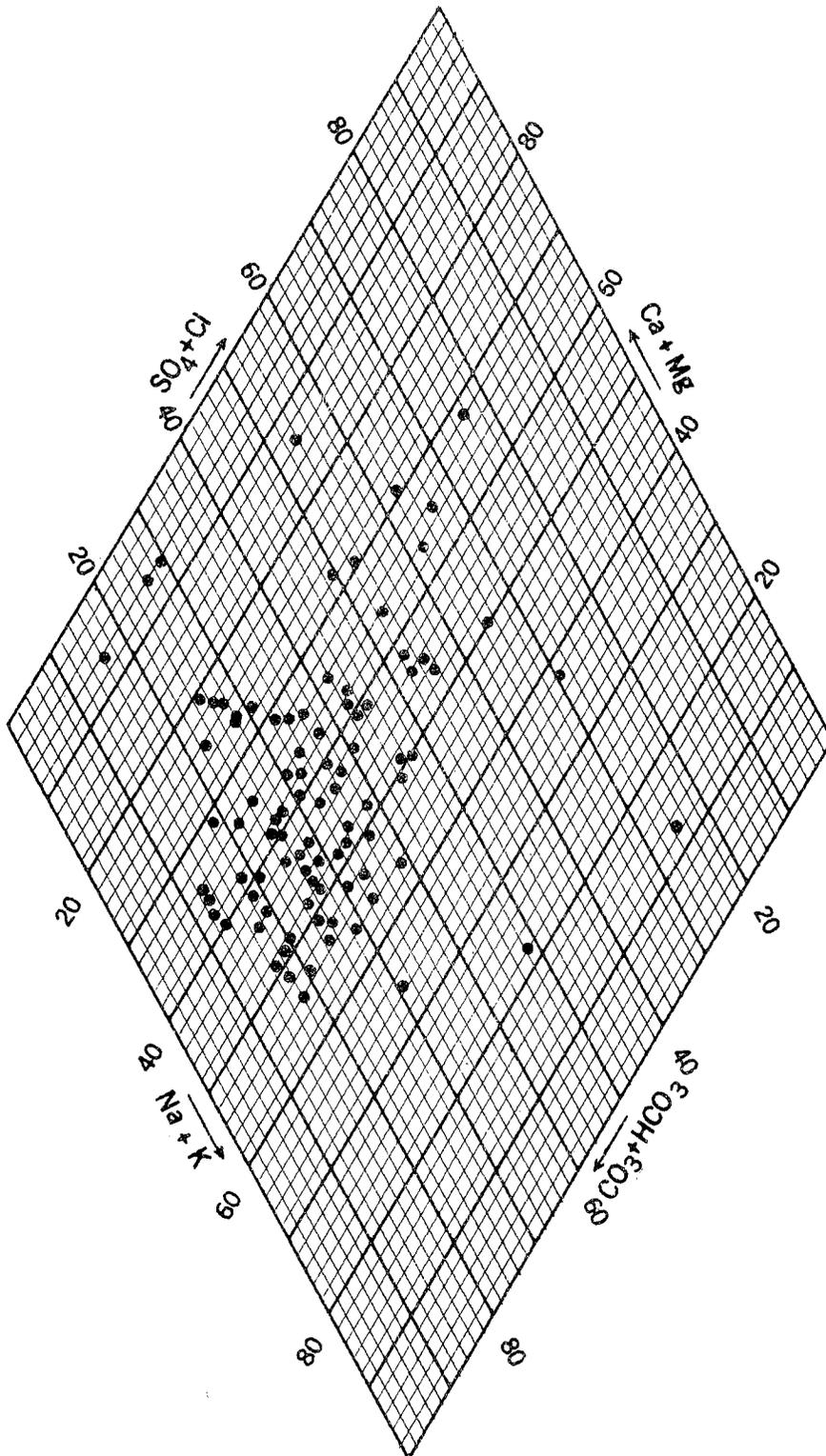


Figure 33. Water analysis diagram of 100 wells in the basin-fill aquifer, City of Tucson area.

## Representation of Data Points in Orthogonal Coordinate System

The position of point X in the plane trilinear diagram of Figure 34A represents the three ratios  $X_A/X_B$ ,  $X_A/X_C$ , and  $X_B/X_C$ . The same information can be displayed in a simple rectangular coordinate system (Figure 34B). Point X in the plane triangle can be represented as a point X in a three coordinate system with orthogonal reference axes A, B, and C. Here the coordinates  $X_A$ ,  $X_B$ , and  $X_C$  fix the position of point X. Each of the reference coordinates A, B, and C represent samples consisting only of end members A, B, and C, respectively. The position of the point reflects the composition of the sample. Samples with nearly identical composition will be clustered together. Samples of dissimilar composition will be located at greater distance from one another.

## Distance Coefficients

As a first step in the factor analysis computation the data are arranged in a matrix form, in which the rows represent water samples from different well locations, and columns represent chemical constituents.

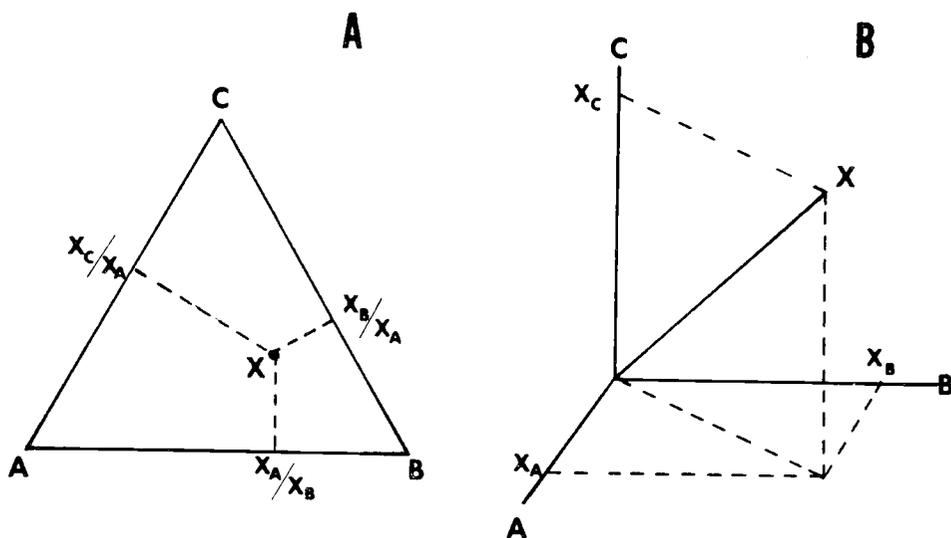


Figure 34. Relationship between representation of a three-component system by trilinear diagram (A) or by an orthogonal coordinate system (B).

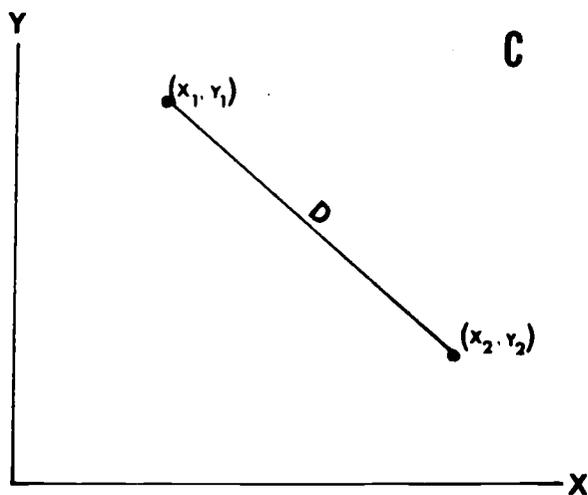


Figure 34C. Computation of distance, D, between two points in two-dimensional coordinate system.

The array of numbers in any row indicate the chemical composition of a sample.

The chemical analyses contained in the data matrix cannot be analyzed directly by factor analysis. It is necessary to compute coefficients that express the degree of similarity between the different pairs of variables, whether they will be well locations or chemical properties. A quantitative measure of the degree of similarity between two variables is provided by the distance that separates them in a rectangular coordinate system (Harbaugh, 1964). The shorter the distance, the greater the similarity and vice versa. Other measures of similarity are the conventional product-moment correlation coefficient (Pearson's R) and the angular measure of similarity proposed by Imbrie and Purdy (1962). The use of distance as a measure of similarity was suggested by Dr. Harbaugh of Stanford University. Sokal and Sneath (1963) have emphasized the usefulness of this measure of similarity in taxonomy.

Distance coefficients are based on the distance between two variables in a rectangular coordinate system in a space of any dimensions. In a two dimensional coordinate system (Figure 34C), the distance,

D, between two points  $(X_1, Y_1)$  and  $(X_2, Y_2)$  is given by the relationship

$$D = \sqrt{(X_1 - X_2)^2 + (Y_1 - Y_2)^2} \quad (1)$$

In the three dimensional case, the distance, D, between  $(X_1, Y_1, Z_1)$  and  $(X_2, Y_2, Z_2)$  is given by

$$D = \sqrt{(X_1 - X_2)^2 + (Y_1 - Y_2)^2 + (Z_1 - Z_2)^2} \quad (2)$$

Likewise, in the n-dimensional case

$$D = \sqrt{\sum_{i=1}^n (X_{i1} - X_{i2})^2} \quad (3)$$

where  $i=1, 2 \dots n$ .

If the coefficient of similarity is going to be analogous to other measures of correlation it should indicate maximum similarity when its absolute value approaches 1.0 and minimum similarity when it approaches zero. In calculating a coefficient that is a measure of similarity, therefore, it is convenient to limit its absolute value to the range 0.0 to 1.0. Generally, distance coefficients should be calculated from data

in which the values are either all positive or all negative and in which the absolute values do not exceed 1.0. Transformations of raw data are generally necessary to satisfy these conditions. The data used in this study are all positive and the raw data are divided by the highest value observed for each variable. This has the effect of giving each variable an equal influence in determining the composition of the water sample. Distance coefficients may be defined by the formula

$$d = 1.0 - \sqrt{\sum_{i=1}^n \frac{(X_{i1} - X_{i2})^2}{n}} \quad (4)$$

where  $d$  = distance coefficient  
 $n$  = number of variables  
 $X_{i1}$  = observations of variable 1 with absolute values not exceeding 1.0  
 $X_{i2}$  = observations of variable 2 with absolute values not exceeding 1.0.

Maximum distance yields a coefficient of zero, minimum distance a coefficient of 1.0.

## Factor Analysis

As the number of variables increases, the number of distance coefficients becomes unmanageably great. It is here that factor analysis becomes a useful tool as a means to simplify the relationship in a matrix of similarity coefficients.

Factor analysis as applied to ground-water quality may be used to study relationships between chemical constituents (R-mode) and between sample localities (Q-mode). The difference between R- and Q-factor analysis is one of objective and the same original data may be used in both techniques. The Q-factor technique can be used to segregate populations of well samples from one another and the R-technique may be applied to subdivide the chemical constituents of a population of well samples. Before the application of factor analysis, little was known as to the nature of the populations of the water samples selected for study. In the discussion of factor analysis applied to water quality data, special attention is focused to Q-mode analysis as a technique to identify groups of well samples that belong together. Material to illustrate these concepts can be found in Appendix B.

The matrix of distance coefficients between any pair of samples or sample properties (chemical constituents) may also be considered in terms of vector relationships in a  $n$ -dimensional space. The distance coefficient between two variables can be represented graphically by using two vectors separated by an angle whose cosine is equal to the distance coefficient between the two variables. If three variables are involved, we may think of three vectors. The cosine of each angle separating the vectors is equal to the distance coefficients between each pair of variables. This procedure can algebraically be repeated for any number of vectors in  $n$ -dimensional space.

The factor analysis method plots  $n$  vectors of unit length in  $n$ -dimensional space. The angle between each vector pair is a function of the distance coefficient between a corresponding pair of variables. Each vector, therefore, represents a variable, either a well location or chemical constituent.

Factor analysis proceeds by placing orthogonal axes within the  $n$ -dimensional cluster of vectors. These orthogonal axes are used as a reference system for describing the orientation of each vector or well sample. The coordinates of these reference axes, also referred

to as factor axes, comprise the factor matrix. By use of the principal component method, the factor matrix of principal components is constructed. The principal component method places the reference axes so that the sums of the squares of the vector projections or factor loadings on factor axis I is a maximum. Factor axis II is perpendicular to factor axis I but oriented so that the vector projections or factor loadings on factor axis II are also maximum. Successive factor axes are also orthogonal to all preceding factor axes, each placed within the n-dimensional space so that vector projections on it are as high as possible (Harman, 1960). Therefore, by the principal component method, the factor axes are positioned so that the first factor represented by factor axis I accounts for as much of the variance as possible. This is the same as saying that the sum of squares of the factor loadings is maximized on this axis. Each successive factor axis is positioned so that it accounts for as much of the remaining variance as possible.

Each row of the principal component factor matrix represents one of n variables and each column refers to one of the reference axes or factor axes. The sums of squares of each of the columns of the factor

matrix, composed of factor loadings for each variable, are equal to the eigenvalues of the distance coefficient matrix. The first eigenvalue, therefore, constitutes the total variance or information accounted for by factor I. The sum of squares of the next column II is numerically equal to the second eigenvalue of the distance coefficient matrix. Eigenvalues, therefore, may be considered as the variance accounted for by each successive factor axis. The first axis, which is the most important and accounts for the largest variance, is associated with the largest eigenvalue. From a table of eigenvalues arranged in decreasing numerical order, we see that each successive factor axis accounts for less and less.

Physically, the eigenvalues indicate the degree of clustering of vectors about each factor axis. If enough vectors cluster about a relatively small number of factor axes, most vectors may be satisfactorily defined in a space less than  $n$ , say  $m$ , dimensions. Inspection of the table of eigenvalues will indicate how many reference vectors or factor axes will be needed to account for a desired percentage of the total variance or information represented by the correlation matrix of distance coefficients. Ideally,

the first  $m$  eigenvalues are all greater than zero and the remaining ones are zero. In reality, due to random error in the data, non-linear relationships not regarded in factor analysis or insufficient data, most of the eigenvalues will be greater than zero. Usually, the first few eigenvalues will be notably higher than the succeeding eigenvalues, suggesting that most of the vectors occupy a relatively small dimensional space. The quantity,  $m$ , associated with this dimensional space, is interpreted as the minimum number of independent factors or components that are required to account for the variation observed in the data (Miesch, Chao, and Cuttitta, 1966). Generally, only few factors may account for some 70-90 percent of the total variance or information (Griffiths, 1966). Griffiths also has suggested to consider only those factor axes whose cumulative total variance accounted for approaches about 90 percent. The rest of the variance may be classed as unassigned or random variation.

After establishing the factor axes or principal component factors, factor analysis attempts to derive from these principal component factors a set of factors of as simple structure as possible (Dawdy and Feth, in

press, 1967). This set of factors may correspond to a structure which has physical meaning in contrast to the entirely theoretical character of the principal component factors. This procedure is accomplished by rotating the factor axes, two axes at a time, around the origin so that the value of each loading on the two axes tends to approach unity or zero. Ideally, the absolute values of the loadings on these factor axes are either high or low, permitting clear cut decisions to be made. In actual practice, intermediate values are commonly obtained, making decisions more difficult. The method of rotation used in this study is the orthogonal varimax rotation. Varimax rotation is similar to the better known varimax method by Kaiser (1959) and the term varimax will, therefore, be used.

Varimax rotation of the principal component factor axes, which now become rotated factor axes, results in a new set of loadings comprising the varimax factor matrix. The varimax factor loadings on relatively few rotated factor axes may provide a basis for constructing a model of regional variation of ground-water quality in the Tucson Basin. This mathematical model may be tested for hydrogeologic

significance if the map pattern resulting from contouring the factor loadings is systematic with respect to known or inferred hydrogeologic parameters as postulated by the conceptual model. Simplicity, however, apparently can only be achieved by sacrificing on completeness. The variance explained by the rotated factor axes is usually less than that explained by the factor axes before rotation.

Imbrie (1963) has made the suggestion that rotation to oblique axes may be advantageous as it enhances the recognition of actual end members. It has been the experience of other workers (Griffiths, Harbaugh, personal communication) that rotation to orthogonal axes only is adequate for most purposes.

#### Computations of Factor Analysis

The computation involved in the execution of factor analysis can only be performed by high speed computers. The calculation of distance coefficient matrix was accomplished by a BALGOL program written by John Harbaugh of Stanford University for IBM 7090 computer in conjunction with a special BALGOL compiler (Harbaugh, 1963). Factor analysis itself was done using a FORTRAN II factor analysis program, "FACTAN",

consisting of a main program and subroutines. This factor analysis program, "FACTAN", is a versatile, general purpose program for principal component analysis and varimax rotation with factor axes maintained at right angles to each other (orthogonal). The program can be run with FORTRAN II compiler on IBM 7090/7094 and should also be readily adaptable to IBM System/360 series.

All computations of factor analysis on water quality data of the Tucson Basin were performed by the writer on IBM 7090 of the Stanford University Computation Center. For additional information on "FACTAN", the reader is referred to John Harbaugh or to the writer. Samples of the output of these programs are listed in Appendix B.

#### Q-Factor Analysis of Chemical Variation Between Localities

Q-factor analysis is used in this study to identify natural groupings of well locations in the Tucson Basin based on the chemical composition of the water samples from these localities. First 100 wells representative of the City of Tucson area were analyzed by this method. This area was also studied by trend

surface analysis of water quality data as individual constituents. Distance coefficients were computed for all possible pairs of 100 well samples based on 6 constituents. The number of computed distance coefficients results in a 100 x 100 matrix consisting of 4450 elements (Appendix B, Table 1A). Before computing the coefficients the data were transformed by dividing each value by the highest value observed for that particular constituent.

The distance coefficient matrix is subjected to a principal component analysis, resulting in a principal component matrix. Inspection of the table of eigenvalues associated with the distance coefficient matrix of 100 wells representative of the City of Tucson area (Appendix B, Table 2A) clearly shows that the first eigenvalue is much larger than any of the successive eigenvalues. More than 81 percent of the variance in the distance coefficient matrix may be explained by one factor. A two factor model only explains an additional 4 percent and a three factor model, another 2 percent.

Varimax rotation produces a new set of factor loadings (Appendix B, Table 4A), which can be used as a basis to group the well locations, using chemical

quality as a criterion. The first step is to identify a group of wells representing a water quality type which may serve as a reference group or end member for all other water samples considered. The samples representing an end member group have the highest loadings on a factor axis (Imbrie, 1963). Inspection of the varimax rotated factor matrix for the wells from the City of Tucson area shows that only the first rotated factor axis has high enough loadings to provide a suitable end member group. The generally low and intermediate loadings on the other rotated factor axes makes determination of clear cut physically meaningful end members difficult.

The factor loadings on the first rotated factor axis, which has the highest factor variance, can be contoured and the resulting map is shown in Figure 35A. The end member group consisting of wells with high ( $>0.8$ ) loadings on the first rotated factor axis is found in the northeast half of the study area. The water associated with this end member group is generally characterized by low dissolved solids and low sulfates. Two distinct tongues or intrusions of water of different quality than the end member type can be recognized, extending from the direction of Rillito

Figure 35. Q-factor analysis of ground-water quality data, City of Tucson area. Perpendicular solid lines indicate Township T14S-R14E.

- (A) Map showing distribution of loadings on rotated (varimax) factor axis I, based on 6 constituents.
- (B) Map showing distribution of loadings on rotated (varimax) factor axis I, based on 8 constituents.

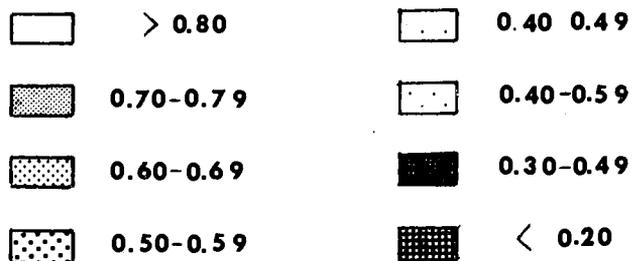
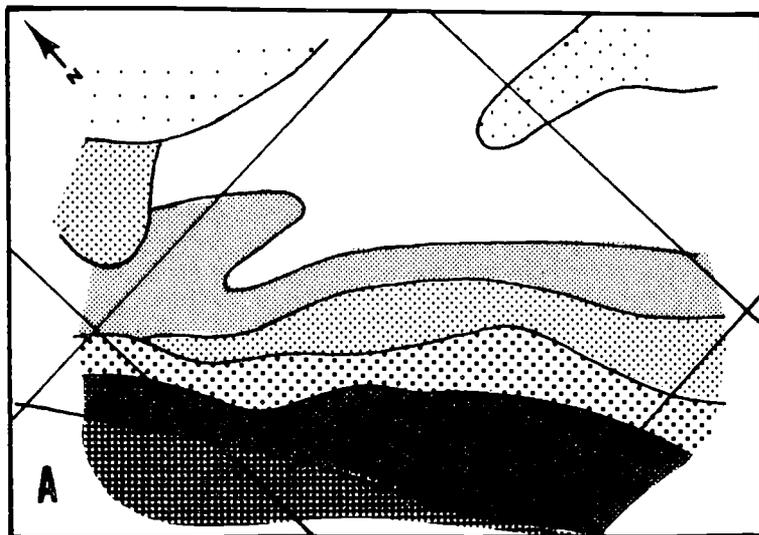


Figure 35. Q-factor analysis of ground-water quality data, City of Tucson area.

Creek and another extending from the channel of Pantano Wash. It may be noted that the quality of water in the intrusion extending from Rillito Creek is slightly different from the water in the tongue associated with Pantano Wash. I believe that these intrusions of water different in quality from the end member type represent water recharged in the surface channels of the Rillito and Pantano. The slight difference in Rillito and Pantano water may be accounted for by the difference in conditions at the recharge site and the somewhat different origin of surface water in both surface channels. The difference would probably have been more pronounced if Rillito Creek and Pantano Wash would not have been connected. The alternative, but in my opinion, less likely explanation, would be the difference in lithology of the aquifer penetrated by wells in the areas with ground water of different chemical quality than the end member type. This possibility appears not entirely unlikely in the area characterized by low loadings associated with Rillito Creek. This area also has wells of relatively low specific capacity, indicative perhaps of the presence of finer grained materials. That this is actually recharged Rillito water is confirmed by a considerable

rise of the water table in this area as a result of the winter rains and snow melt during the winter of 1965-1966.

In case of the intrusion-like body of ground water of different quality extending from Pantano Wash, the situation also appears a little ambiguous. The occurrence of water of different quality coincides with an area of wells of high specific capacities. Unfortunately, no data are available to ascertain whether or not the stream channel shaped area of higher specific capacities extends under Pantano Wash. However, if it does, the area of higher specific capacities serves as a preferred avenue of recharge. Otherwise, it would be difficult to explain why high specific capacities are associated with low factor loadings.

The end member water which is used as a reference for the system is probably water originating from the high mountain ranges consisting of granite and gneiss to the north and northeast of the basin. Recharge of this water probably took place through a different system of surface channels in the past or through alluvial fans, now partially eroded away, at the foot of these mountains.

A band of water of greater chemical diversity characterizes the southwestern portion of the area under study. This water of a relatively heterogeneous character with respect to the end member water, shows a distinct pattern parallel to the direction of the ground-water flow lines. The regional ground-water flow net suggests that this water most probably emanates from the area at either side of the Cienaga Gap. This area has a more diversified geology than the relatively homogeneous Catalina and Tanque Verde Mountain ranges, and the water coming from this area will acquire different quality types depending on the geology of the drainage basin and the conditions in the area of recharge.

The map showing contours of factor loading on the first rotated factor axis based on 8 constituents, 6 major ions plus total dissolved solids and fluorides (Figure 35B) does not differ very much from the contour map of first factor loadings based on 6 constituents only. In both cases, no meaningful results could be obtained by grouping wells on the basis of factor loadings on other rotated factor axes, which account for much smaller variances.

Factor analysis in the Q-mode is also applied to the larger area, more representative of the regional

system. Contours of factor loadings on the first rotated (Figure 36A) factor axis also shows distinct banding of water-quality types parallel to the general direction of the ground-water flow lines. No noticeable differences can be detected in the distribution of the first rotated factor loadings by using either 6 or 8 constituents. It may be noted that the water associated with Pantano Wash at the northeastern edge of the regional area and distinctly different from the end member water (loadings  $>0.9$ ) resembles ground water at the southwestern margin of the area. The latter water probably originated as precipitation in the mountain area of the Santa Ritas and was recharged in the alluvial fans extending from this mountain range into the basin.

Because of the greater diversity of ground-water quality in this larger area, factor loadings on the second rotated factor axis, that accounts for the next largest variance, are still sufficiently high to yield a second end member group of wells. Contours of these second rotated factor loadings also produce a pattern approximately parallel to the ground-water flow lines (Figure 36B). The second rotated factor axis explains considerably less of the variance than

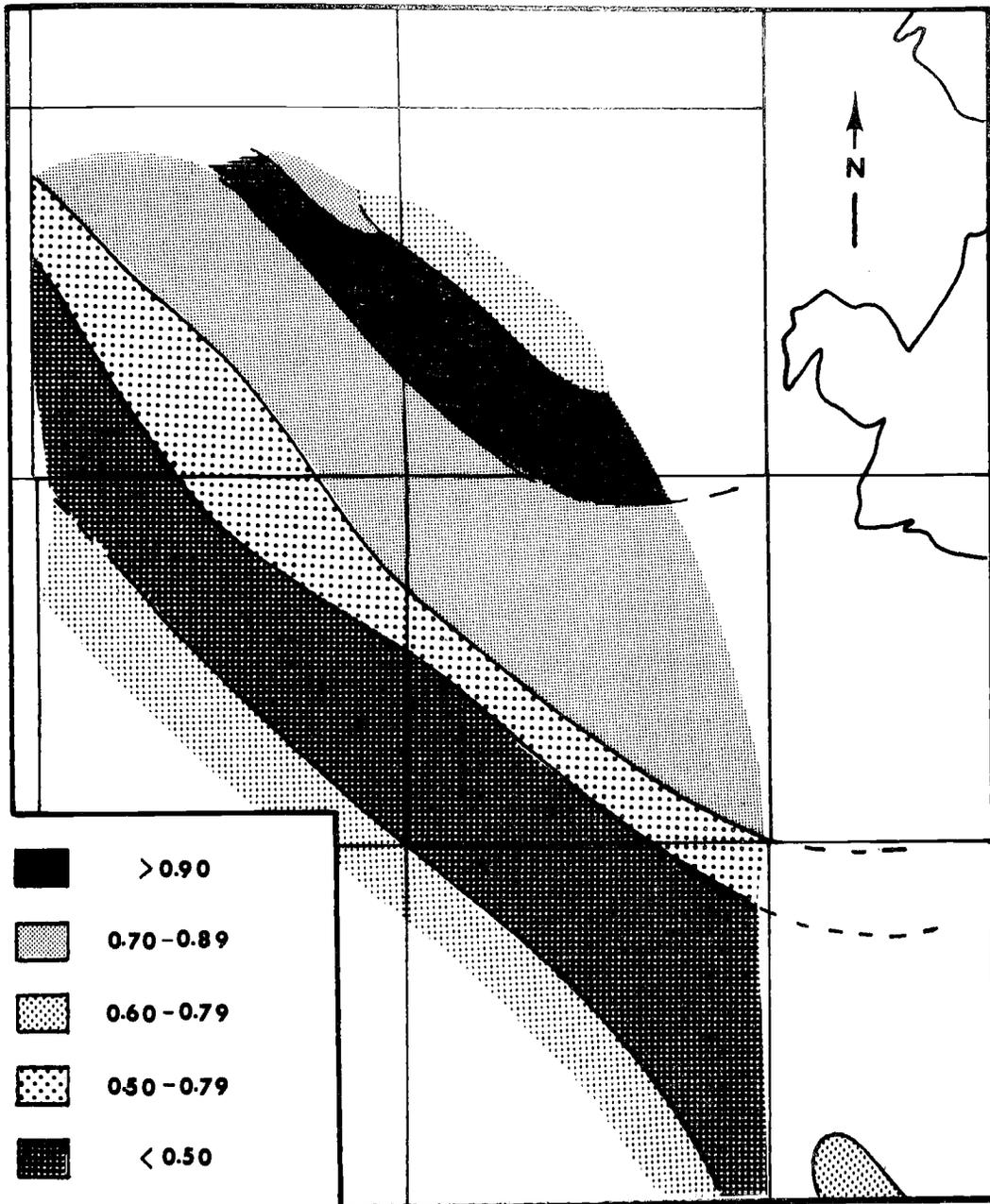


Figure 36A. Q-factor analysis of ground-water quality data, regional ground-water system of Tucson Basin. Map showing distribution of loadings on rotated (varimax) factor axis I, based on 6 constituents.

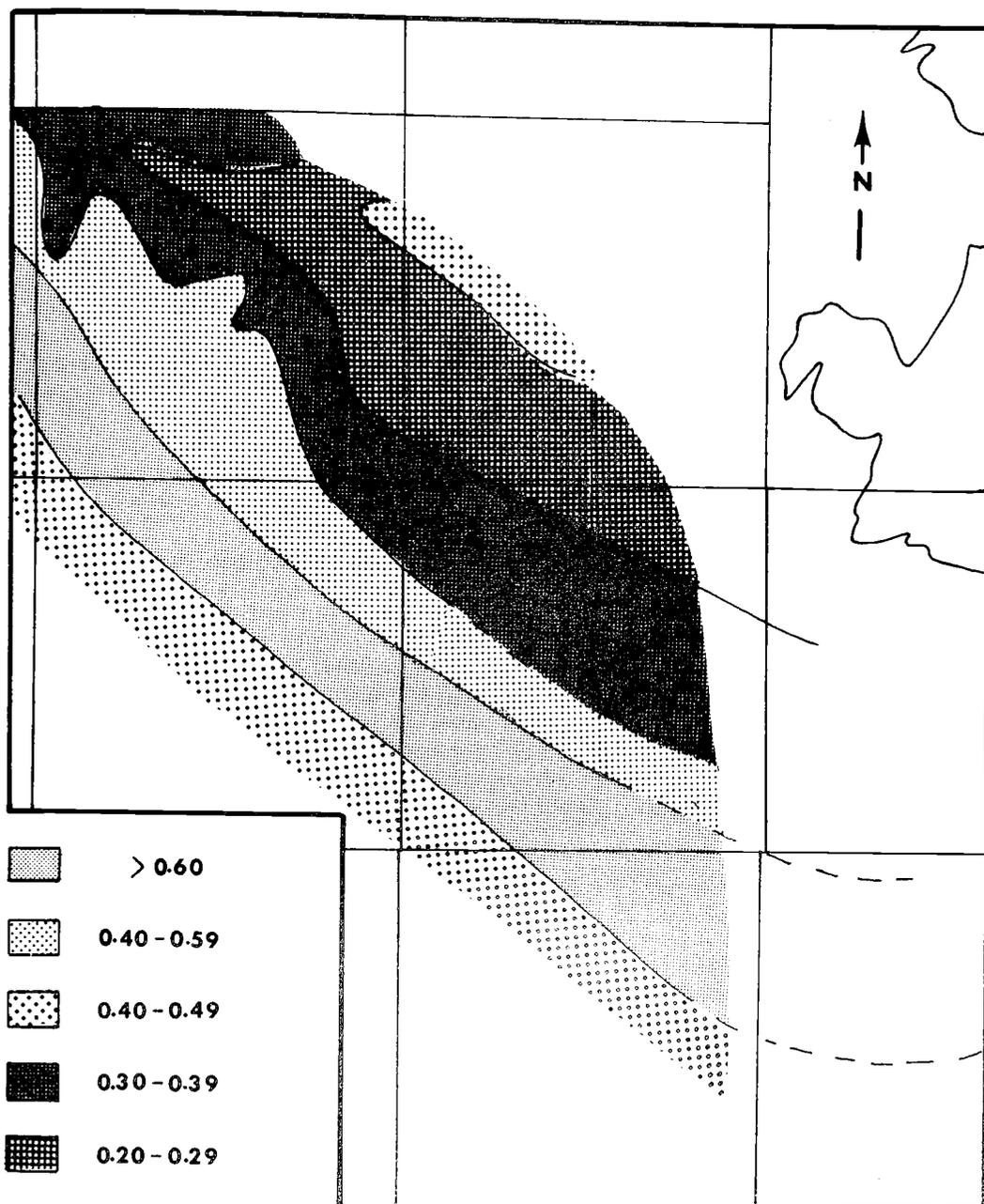


Figure 36B. Q-factor analysis of ground-water quality data, regional ground-water system of Tucson Basin. Map showing distribution loadings on rotated (varimax) factor axis II, based on 6 constituents.

the first rotated factor axis (Appendix B, Table 5). The physical meaning of the differences produced by the contours of the first and second rotated factor loadings cannot be explained.

#### R-Factor Analysis Applied to the Geochemical Interpretation of Ground-Water Quality

In the R-mode of analysis, attention is focused on the chemical constituents of ground water as a variable. Dawdy and Feth (in press, 1967) have applied R-factor analysis to ground-water quality of the Mojave River Valley, California. Their objective was to find the minimum possible number of variables which may adequately describe the chemical quality of ground water in the basin. This can be achieved by grouping chemical constituents together that are closely related. This might lead to an insight in the geochemical relationships among the chemical constituents analyzed from the water samples of the basin. R-mode analysis is applied to study the relationships of 8 chemical constituents from the same two sets of 100 wells. Because the results in both cases are nearly identical, only R-mode analysis on data from the regional system will be discussed. The output is listed in Appendix B.

Again, the first step is to compute a matrix of similarity coefficients expressing the quantitative relationship between all pairs of chemical constituents. The degree of similarity between every pair of constituents can also be expressed by distance coefficients. The relationship amongst every pair of chemical constituents is summarized in a matrix of distance coefficients. Interpretation of these relationships is complex if the data are interdependent. If this is the case, R-mode analysis becomes less valuable (Imbrie and van Andel, 1964). The distance coefficient matrix is a measure of how well the variance of each chemical constituent can be explained in relationship to each of the others. Factor analysis takes the explained variance of the distance coefficient matrix and distributes it among a set of fewer variables or factors.

The eigenvalues of the R-mode distance coefficient matrix expresses the variance accounted for by each successive principal factor axis. From the table of eigenvalues, we see that the first factor axis accounts for by far the largest variance, almost 80 percent. After rotation by varimax method the first factor accounts for a far lesser proportion of the

variance than before rotation. This transferring of unexplained variance from the first to the later factor axes apparently is the price paid for simple structure of the relationships.

Inspection of the rotated varimax matrix and the table of factor variances after rotation shows that most of the variance in the chemical properties of the system may be accounted for by the  $\text{Cl}^-$  and  $\text{F}^-$ . The fact that these two chemical constituents both have high loadings on the same factor axes suggests a relationship between  $\text{Cl}^-$  and  $\text{F}^-$ .

The second largest variance, but almost equal to that of the first factor, is explained by the factor that contains high loadings for total dissolved solids, calcium and sulfates. These constituents, therefore, appear related. The remaining factor axes contain single high loadings for  $\text{HCO}_3^-$ ,  $\text{Na}^+$  and  $\text{Mg}^{++}$ , respectively. These three constituents apparently are independent from any other constituent in the system.

Calcium sulfate water with high total dissolved solids content expressed by the same factor is present in the southwestern portion of the map area. The close association of  $\text{Ca}^{++}$  and  $\text{SO}_4^{--}$  in this water may

be an indication that this water derives  $\text{Ca}^{++}$  and  $\text{SO}_4^{--}$  by solution of anhydrite or gypsum. The presence of gypsum deposits in the southeastern part of the basin near the Cienaga Gap area has been reported.

The generally poor correlation between  $\text{Na}^+$  and  $\text{Cl}^-$  indicate that  $\text{Na}^+$  and  $\text{Cl}^-$  may not originate from the solution of  $\text{NaCl}$  only. There is the possibility that ion exchange mechanisms play a role. Unfortunately, the analytical inaccuracy of  $\text{Na}^+$  determinations used here and the generally low values of  $\text{Na}^+$  and  $\text{Cl}^-$  make inferences concerning the origin and behaviour of  $\text{Na}$  based on these data doubtful.

The high level of interdependence of the chemical constituents results in relatively few high loadings on the rotated factor axes and a relatively equal distribution of the variance explained among the factors extracted. The main reason for interdependence is probably the uniform nature of water quality of the water samples used in this study. Because of this, there is considerable doubt as to the validity of the interpretation of the geochemistry of ground water of the Tucson Basin based on R-mode analysis of the chemical constituents.

## Conclusions

Factor analysis can be applied to the study of ground-water quality data in a twofold way. Q-mode factor analysis serves the purpose of grouping well samples into "natural" classes using all chemical constituents as criteria on an equal basis. R-mode analysis can be used to study geochemical relationships among chemical constituents from the same ground-water body by grouping associated chemical components.

Through application of Q-mode factor analysis of ground-water quality to a set of well locations, different water types in the basin can be more clearly delineated than is achieved by conventional graphic methods. Q-factor analysis has resulted in considerable improvement and refinement in the interpretation of the regional variation of ground-water quality in the basin-fill aquifer. The technique makes it possible to bring out subtle differences between water types that may be meaningful hydrologically and that may otherwise remain concealed. The differentiation of ground-water quality types based on Q-factor analysis strongly supports the hypothesis that the overall chemical character of ground water in the basin-fill aquifer does not change substantially as ground water moves

through the basin. Slight differences between water that has been recharged by way of surface channels and water already present in the aquifer are accentuated. One may claim that the geochemical significance of the factor loadings in terms of the chemical constituents is still far from clear. However, it should be pointed out that the objective of using Q-factor analysis in this case is not so much to study the geochemical nature of the different water types than to clearly distinguish different water types.

It is notable that a similar result was also achieved by Imbrie and van Andel (1964) in their application of Q-factor analysis to the regional distribution of heavy mineral data from the Gulf of California and the Orinoco-Guayana Shelf. Through factor analysis, they were able to show distinct banding of heavy mineral assemblages parallel to the main current system. This conclusion based on contours of factor loadings did not become apparent from interpretation using graphical means only.

There are arguments that factor analysis is most useful when we know little about the nature of the observed variables (Matalas and Reihner, 1967). This is not likely as no mathematical model can replace

an intelligent a priori statement of the problem based on sound hydrologic and geologic reasoning. The mathematical factor model, however, can reveal a structure of the observed variables that will support or reject a preconceived idea or hypothesis incorporated in a conceptual model.

The fundamental difference between factor analysis and conventional graphical methods in classifying samples is that factor analysis uses actual samples or groups of samples as end members as contrasted to a pigeon hole classification based on the relative amounts of chemical constituents present in the sample. Factor analysis is capable of accomodating a large number of constituents and use these effectively in discriminating between samples. Because of this feature, it becomes particularly useful if a large number of chemical parameters such as trace elements is going to be included to differentiate between water types. The decision to develop factor analysis as a tool to analyze ground-water quality was primarily motivated by the original plans to incorporate trace elements in this study.

The disadvantage of orthogonal Q-factor analysis is that the factor loadings cannot be directly

related to observable variables. Oblique rotation of the factors (Imbrie, 1963) identifies a particular sample as an end member. Further work along these lines is needed but it appears that the first factor loading contours for data of the City of Tucson area somewhat resembles the distribution of sulfates and total dissolved solids, in the same area. However, the main thing is that factor loadings do represent differences in ground-water quality. In this study, Q-factor analysis primarily serves the purpose of testing a postulated model of regional distribution of ground-water quality based on known and inferred hydrogeologic parameters.

Time proven graphical methods have some advantages such as visual clarity and simplicity of use. However, in a trilinear diagram, the sum of the percentages of chemical components always add up to 100 percent. Under these conditions, the data are considered a "closed" system (Chayes, 1960, 1962). Strong correlations may develop among closed variables even in the absence of any correlation if an open system is used (Krumbein, 1962). Using closed data for the purpose of classification by graphical projection in a trilinear diagram and then again into

a diamond shaped field is subject to several statistical restraints, as yet unexplored, and the physical meaning of this procedure is not entirely clear, either.

R-mode analysis of the same data as a means to explain the geochemical relationships of the chemical constituents is probably less successful. The table of distance coefficients between every pair of chemical constituents shows a moderate to high degree of correlation, implying covariance between the variables. Imbrie and van Andel (1964) have pointed out that R-mode studies are less valuable in cases where there is a relatively high interdependence of the data. Results as that obtained by factor analysis can probably also be arrived at by ordinary regression analysis. However, a practical aspect of factor analysis is that quantitative statements can be made concerning the amount of information accounted for by each component or factor axis of the system.

Hopefully, this application shows that R-mode analysis at least potentially offers a valuable tool to interpret chemical quality data of ground water in the geochemical sense. This tool again becomes particularly useful if many more constituents such as trace

elements are going to be included in the study of water quality. Another interesting application would be to also consider other quantitative information, for example on the mineralogy and the hydraulic properties of the aquifer at the same location, to test a conceptual cause and effect relationship.

VIII. CALCITE EQUILIBRIA OF GROUND WATER  
IN THE TUCSON BASIN

Introduction

The chemical composition of ground water in the basin-fill sediments of the Tucson Basin is affected by factors inside and outside the aquifer. The lithology of the aquifer interacts more strongly with some chemical constituents than with others. In general, within the aquifer, the quality of ground water is a complex system consisting of several mineral phases, represented by the solid aquifer matrix, an aqueous phase and a gas phase. In a situation of this kind, there is little choice but to abstract an idealized segment from the complexity of the natural system, for example, by way of a simple chemical equilibrium model. Chemical equilibrium models have the advantage that they are amenable to rigorous theoretical treatment and present an efficient method of approach to the study of dilute aqueous solutions. Comparison of the equilibrium model with data representative of the natural groundwater system allows certain inferences to be drawn

concerning chemical processes taking place in the aquifer. For a review of the applications and its limitations of chemical thermodynamic models to natural water systems the interested reader is referred to a discussion on the subject by Morgan (1966).

### Calcite and Ground Water

The chemical behaviour of calcium carbonate in ground water has received some attention in the geologic (Weyl, 1959, Garrels and Christ, 1965) and hydrologic literature (Back, 1961a, 1963, Barnes, 1964, 1965, Hem, 1961, 1963). These studies have indicated that the problem of calcium carbonate saturation in ground water can be approached with a reasonable degree of success through the application of simplified chemical equilibrium models, based on the principles of chemical thermodynamics.

One of the best formulated and tested equilibrium models available and applicable to the study of ground water in situ is the system calcite-water. Back (1963) has investigated on a regional scale the departure of ground water from equilibrium with calcite in limestone aquifers of Florida. The objective of the present study is to investigate the applicability of

the principles underlying chemical equilibrium models of calcite and water to the study of calcite saturation of ground water in an arid zone alluvial basin without the abundant presence of limestone.

The objective of studying calcite equilibrium in ground water is to determine theoretically the state of saturation of ground water with respect to calcite. This may provide a means to predict the behaviour of calcite and water with respect to the problem, whether calcite is being precipitated or dissolved, in the real aquifer system. The fact that the basin-fill aquifer is porous and permeable to water indicates that ground water is not grossly supersaturated as to cause cementation of the pores. There is little petrographic evidence available indicating that solid calcite is present in large quantities in the basin-fill sediments either as detrital material or as cement. However, routine checks with HCl on well cuttings from the basin have shown that calcium carbonate is present, at least in small amounts, throughout the basin-fill aquifer.

Measurements of pH and temperature were made in the field at 65 well locations during the summer of 1966. These wells (Figure 11B) are more or less evenly

distributed over the northern part of the Tucson Basin and represent approximately the same area also studied by trend surface and factor analyses. At the same time, water samples were taken at these well sites for analysis in the laboratory of major ionic species and trace elements. In this study of calcite equilibrium only the results of the analyses of major ionic species are taken into consideration.

Water temperature and pH of the ground-water system were measured at the well head after the well had been pumping continuously for at least several hours. The average of the temperatures measured was  $26.3^{\circ}\text{C}$  and all the temperatures fell in a range between  $20^{\circ}\text{C}$  and  $30^{\circ}\text{C}$ . The temperature distribution in ground water in the basin-fill aquifer is shown in Figure 7A. Errors in pH determination have considerable implications on the calculations concerning calcite equilibria. Laboratory determinations of pH usually are a poor representation of the field conditions because of the changes in  $\text{CO}_2$  content and temperature during storage and transportation of the samples. In order to approach conditions in the ground-water reservoir as closely as possible, determination of pH in the field is imperative. In the field, a battery operated Beckman Model N

meter was used for pH determination. In the laboratory, a line operated Beckman Model 76 was used. Figure 37 shows the difference between pH as measured in the field and pH measured in the laboratory. If there are no discrepancies between the two sets of data, all points would plot on the 45 degree line. However, there is considerable scatter, indicating that some samples have a higher, others a lower laboratory pH than field pH. There is an equal number of samples showing a drop or increase in pH in the laboratory and there is no way to predict which sample will remain stable and which will decrease or increase in pH after collection. The difference between field and laboratory pH is generally considerably less than one pH unit but the average drop in pH in the laboratory is greater than the average increase. The regional distribution of pH of ground water in the basin-fill aquifer is shown in Figure 38A and the relationship, temperature and pH is illustrated by Figure 39.

The calcium and bicarbonate content of most ground water is usually relatively stable and samples of water collected and handled with care give values on analysis that may be assumed to represent the composition of water in the aquifer. Work by Back (1963)

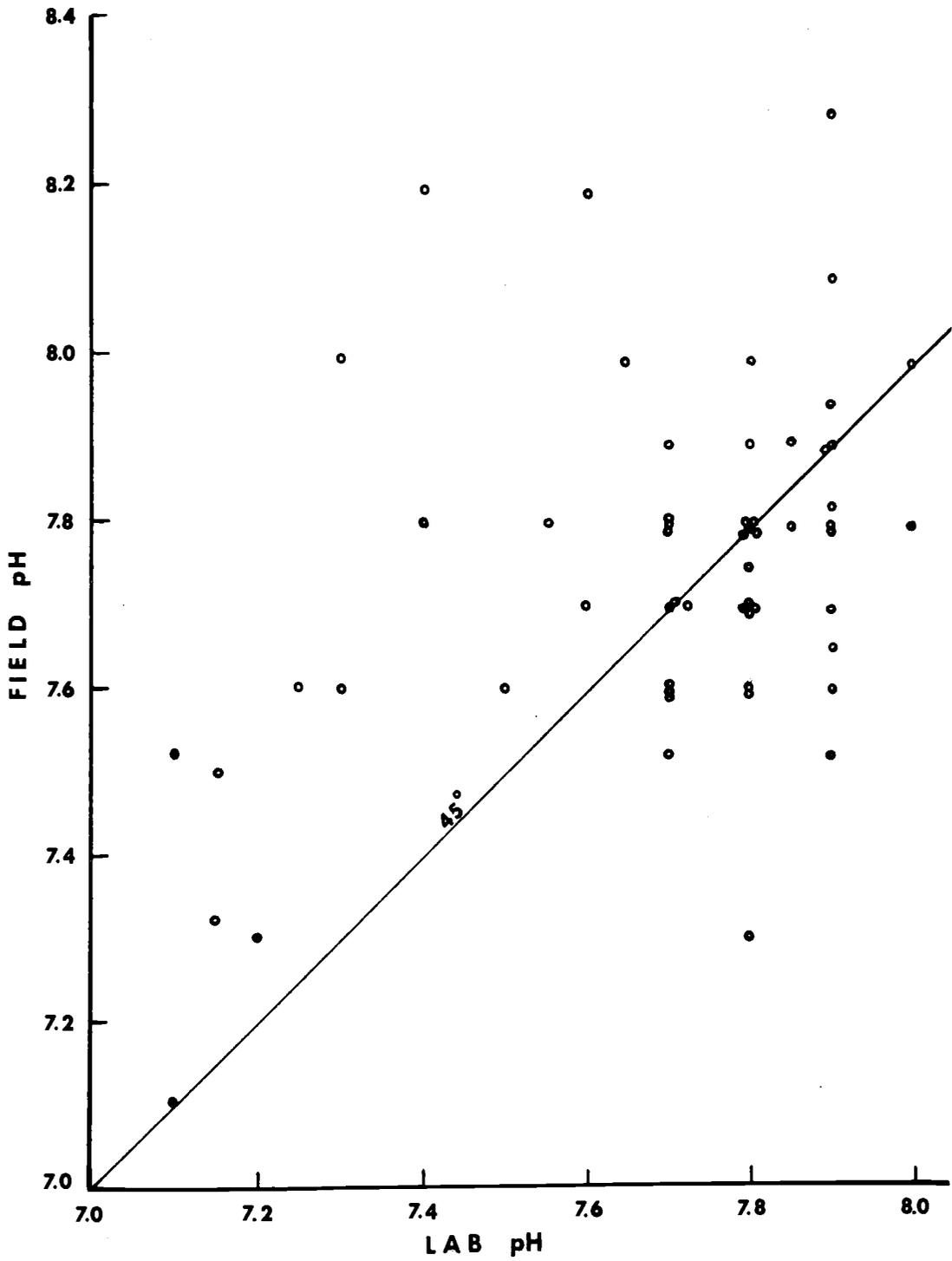


Figure 37. Comparison of pH measured in the field and in the laboratory.

Figure 38. Regional distribution of data representative of ground water in the basin-fill aquifer and used in calcite equilibrium studies. Perpendicular solid lines indicate Township T14S-R14E.

- (A) Map showing distribution of pH values in ground water of the basin-fill aquifer.
- (B) Map showing distribution of calcium concentrations, in ppm, in ground water of the basin-fill aquifer.
- (C) Map showing approximate distribution of bicarbonate concentrations, in ppm, in ground water of the basin-fill aquifer.

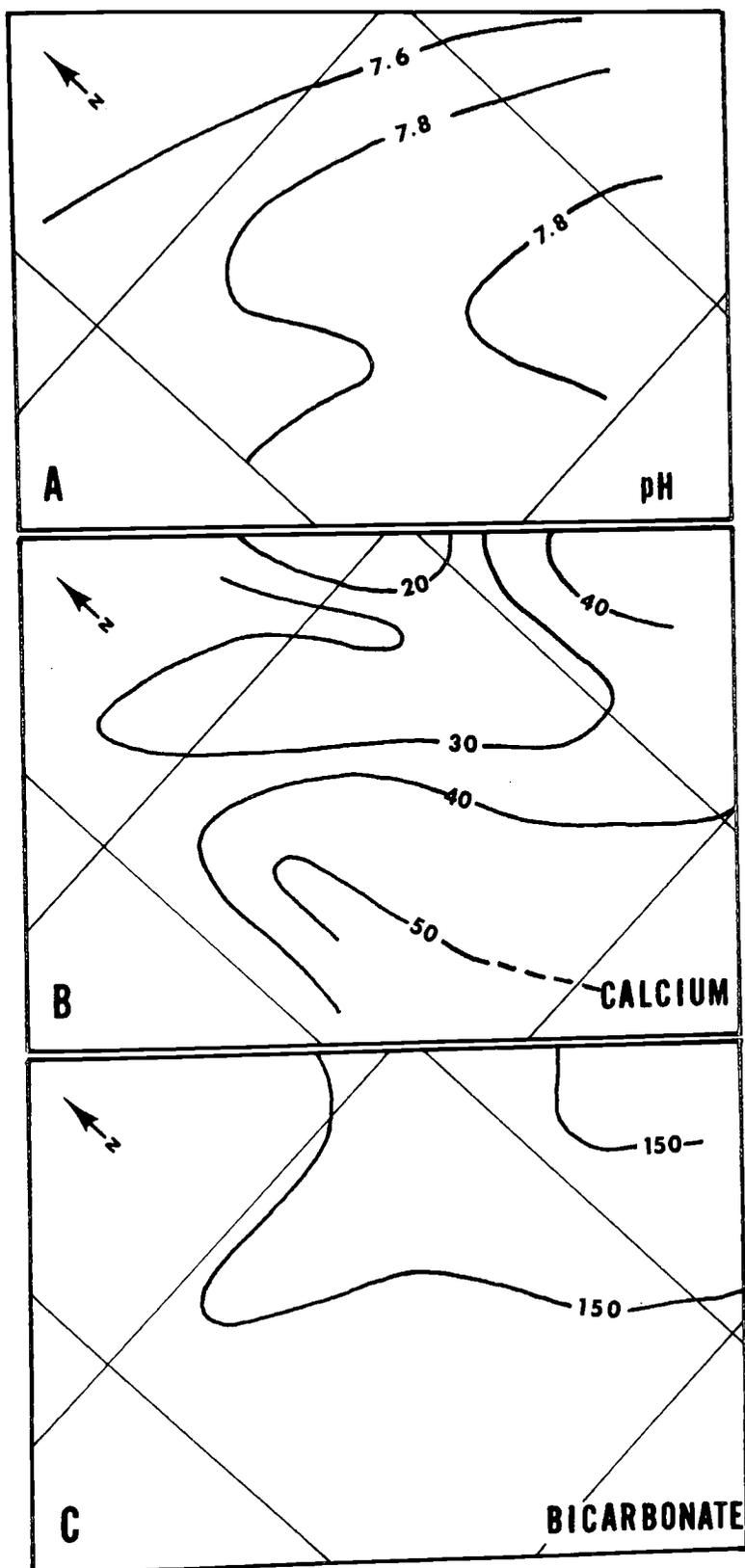


Figure 38. Regional distribution of data used in calcite equilibrium studies.

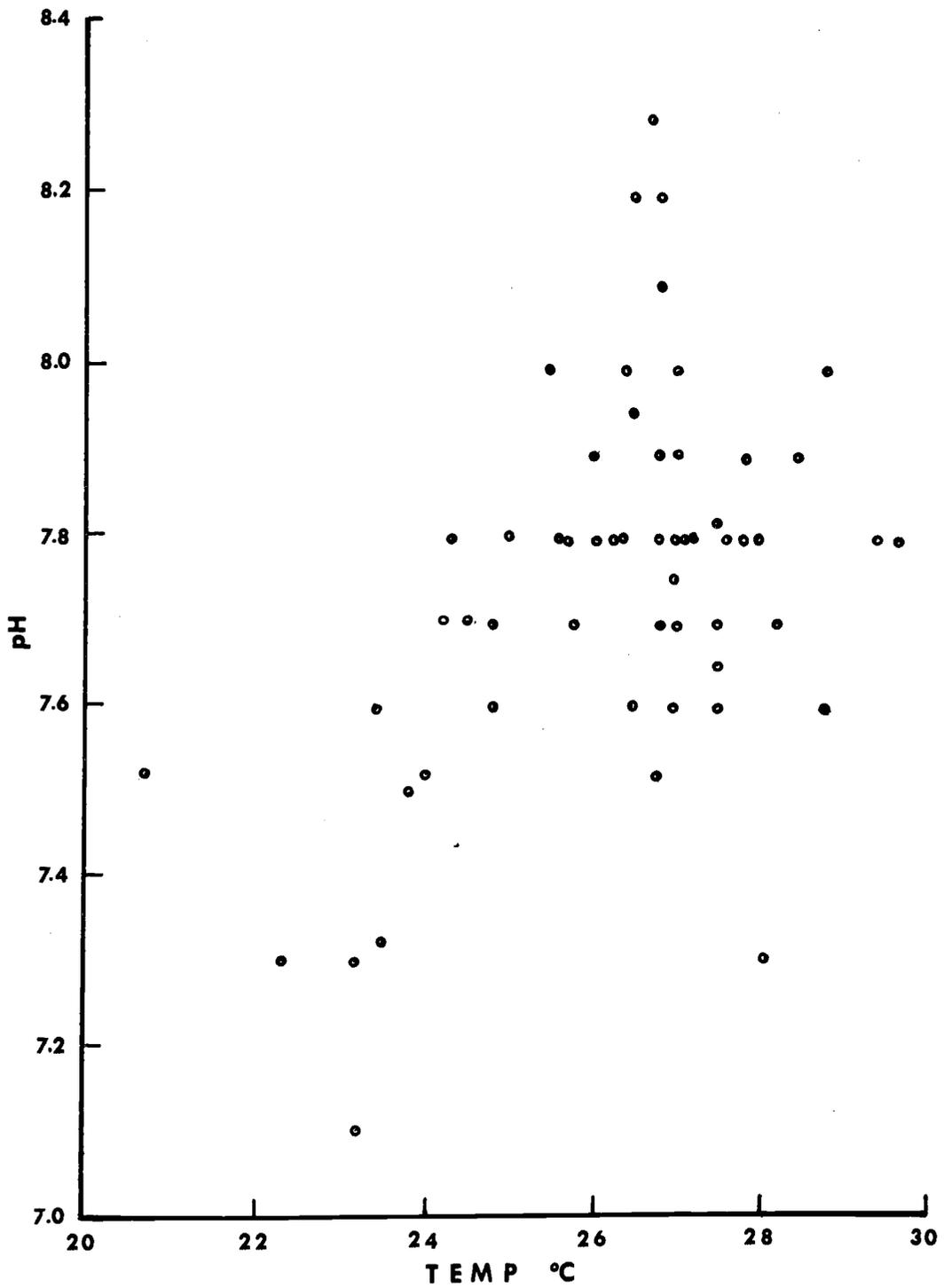


Figure 39. Relationship of temperature and pH in ground water of the basin-fill aquifer.

has indicated that field bicarbonate determinations have, as a rule, slightly higher values than determinations in the laboratory. This decrease in bicarbonate content is mainly due to the loss of  $\text{CO}_2$  gas and the precipitation of calcium carbonate in the sample bottle. Keeping the sample sealed from air and prompt analysis in the laboratory probably more than adequately offsets the advantages of field determination on a hot summer day.

Calcium and bicarbonate in ground water of the basin-fill aquifer are shown in Figures 38B and 38C. The calcium concentrations range from less than 20 ppm to about 60 ppm. Calcium concentrations, therefore, are relatively low, with a tendency of lower values to cluster in the northeastern part of the area. Resemblance of this map to the contour map of the cubic surface fitted to the same data (Figure 16C) is good. Bicarbonate distribution is more difficult to interpret in detail because the relatively high level of local variation. Here, trend surface fitting is helpful in the regional interpretation and to bring out its relationship to pH. In the Florida study by Back (1963), a decrease in bicarbonate in the direction of groundwater movement is noted. The bicarbonate content in

ground water of the northeastern half of the area appears to be lower than in the southwestern half, suggesting a somewhat opposite trend. This feature is only weakly supported by the linear trend fitted to the data (Figure 24A).

### Equilibrium Constants and Free Energy

The driving force of any chemical reaction can be measured by the Gibbs free energy function,  $\Delta G$ . The Gibbs or standard free energy of reaction,  $\Delta G_R^\circ$ , is the net sum of the free energies of formation of the products minus the free energies of formation of the reactants, at standard states.

$$\Delta G_R^\circ = \Delta G_f^\circ \text{ products} - \Delta G_f^\circ \text{ reactants} \quad (1)$$

The equilibrium constant,  $K_{eq.}$ , can be calculated from the Gibbs standard free energy of reaction by the relationship:

$$\Delta G_R^\circ = -RT \ln K_{eq.} \quad (2)$$

where  $R$  is the gas constant and  $T$  is the temperature in degrees Kelvin ( $^\circ K$ ).

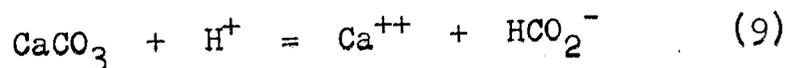
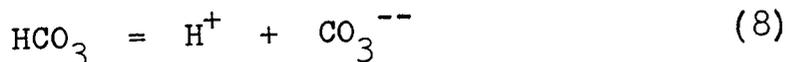
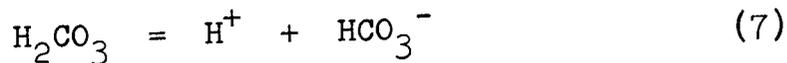
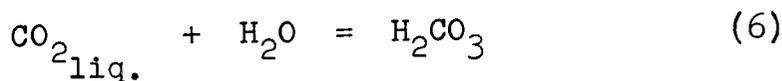
The standard state for the calculation of free energy values is usually taken as the pure substance at 25°C (298.15°K) and 1 atm. total pressure. Under these conditions, we may also write relationship (2) in the form:

$$\Delta G^{\circ}_R = -1.364 \log_{10} K_{eq}. \quad (3)$$

This relationship between  $\Delta G^{\circ}_R$  in kilocalories and the equilibrium constant,  $K_{eq}$ , is the special case of the relation between the Gibbs standard free energy of reaction and the activities of products and reactants for a system at equilibrium. Standard free energies of formation,  $\Delta G^{\circ}_f$ , for many substances, including most ions found in ground water, can be obtained from tables in Garrels and Christ (1965) or Latimer (1952). For a more detailed treatment of the thermodynamic concepts of chemical equilibrium, the reader is referred to standard texts such as Klotz (1964) and Moore (1962); for applications to geology and hydrology, Garrels and Christ (1965) and Back and Hanshaw (1965) are relevant.

Chemical Equilibrium and Solution and Deposition of Calcite

The solution and precipitation of calcite in ground water can be related to the equilibrium of calcite in contact with water containing  $H^+$  ions and the associated ions in solution that result. The chemical reactions pertinent to the state of calcite saturation in ground water are given by the following equilibrium equations:



The equilibrium constant for reaction (9) is

$$K_{\text{CaCO}_3} = \frac{\langle \text{Ca}^{++} \rangle \langle \text{HCO}_3^- \rangle}{\langle \text{H}^+ \rangle \langle \text{CaCO}_3 \rangle} \quad (10)$$

whereby unit activity is assigned to  $\text{CaCO}_3$ . The values between the brackets represent activities which can be computed from concentrations expressed in ppm by applying the Debye-Hueckel theory (Garrels and Christ, 1965).

Pure calcium carbonate or calcite is readily soluble in water, provided there is an abundant supply of  $\text{H}^+$  ions (9). Carbon dioxide combines with water to form carbonic acid (6) which, in turn, supplies  $\text{H}^+$  ions (7) to react with calcite (9). Because of this, the solubility of calcite in water depends on the presence of  $\text{CO}_2$ , the activity of which is a function of temperature and pressure of  $\text{CO}_2$  in equilibrium with its surroundings. At constant temperature, an increase in  $\text{CO}_2$  pressure will increase the solubility of calcite and at constant pressure the solubility of calcite will increase with decreasing temperature. In the presence of abundant  $\text{CO}_2$ , dissociation of carbonic acid will only proceed until the bicarbonate state (6). If pH increases, the ratio  $\text{CO}_3^{--}/\text{HCO}_3^-$  increases and

calcium carbonate may be precipitated. The dissociation of bicarbonate to carbonate (8) is largely effective above pH 8.2. Below a pH 8.2, the reaction (8) will primarily proceed to the left. In most ground waters, concentration of carbonate ions usually lies below analytical detection.

The Gibbs standard free energy of reaction for equilibrium equation (9) may be computed by substituting the free energy values involved in this reaction in (1).

$$\begin{aligned} \Delta G^{\circ}_R &= \Delta G^{\circ}_f \text{Ca}^{++} + \Delta G^{\circ}_f \text{HCO}_3^- - \Delta G^{\circ}_f \text{H}^+ \\ &- \Delta G^{\circ}_f \text{CaCO}_3 = (-132.18) + (-140.31) \\ &- (-0) - (-269.78) = -2.71 \text{ kilocalories} \end{aligned}$$

The equilibrium constant,  $K_{\text{CaCO}_3}$  for equilibrium equation (9) can be derived by substituting  $\Delta G^{\circ}_R = -2.71$  K cal in relationship (3):

$$\Delta G^{\circ}_R = -1.364 \text{ Log}_{10} K_{\text{eq.}}$$

$$-2.71 = -1.364 \text{ Log}_{10} K_{\text{CaCO}_3}$$

$$K_{\text{CaCO}_3} = 10^{1.986} = 0.986 \times 10^2$$

The mass action equation (10) for equilibrium equation (9) can be written in the form

$$\begin{aligned} \text{Log } K_{\text{CaCO}_3} &= \text{Log } \langle \text{Ca}^{++} \rangle \langle \text{HCO}_3^- \rangle \\ &- \text{Log } \langle \text{H}^+ \rangle \end{aligned} \quad (11)$$

Relationship (11) permits computation of the equilibrium pH for reaction (9):

$$\text{pH}_{\text{eq.}} = -\text{Log} \frac{\langle \text{Ca}^{++} \rangle \langle \text{HCO}_3^- \rangle}{K_{\text{CaCO}_3}} \quad (12)$$

If the ground water is in equilibrium with calcite the calculated equilibrium pH should closely agree with the pH determined in the field. Hem (1961, 1963) has computed from equation (12) the equilibrium pH for water in contact with calcite in relation to dissolved calcium and bicarbonate activities (Figure 40).

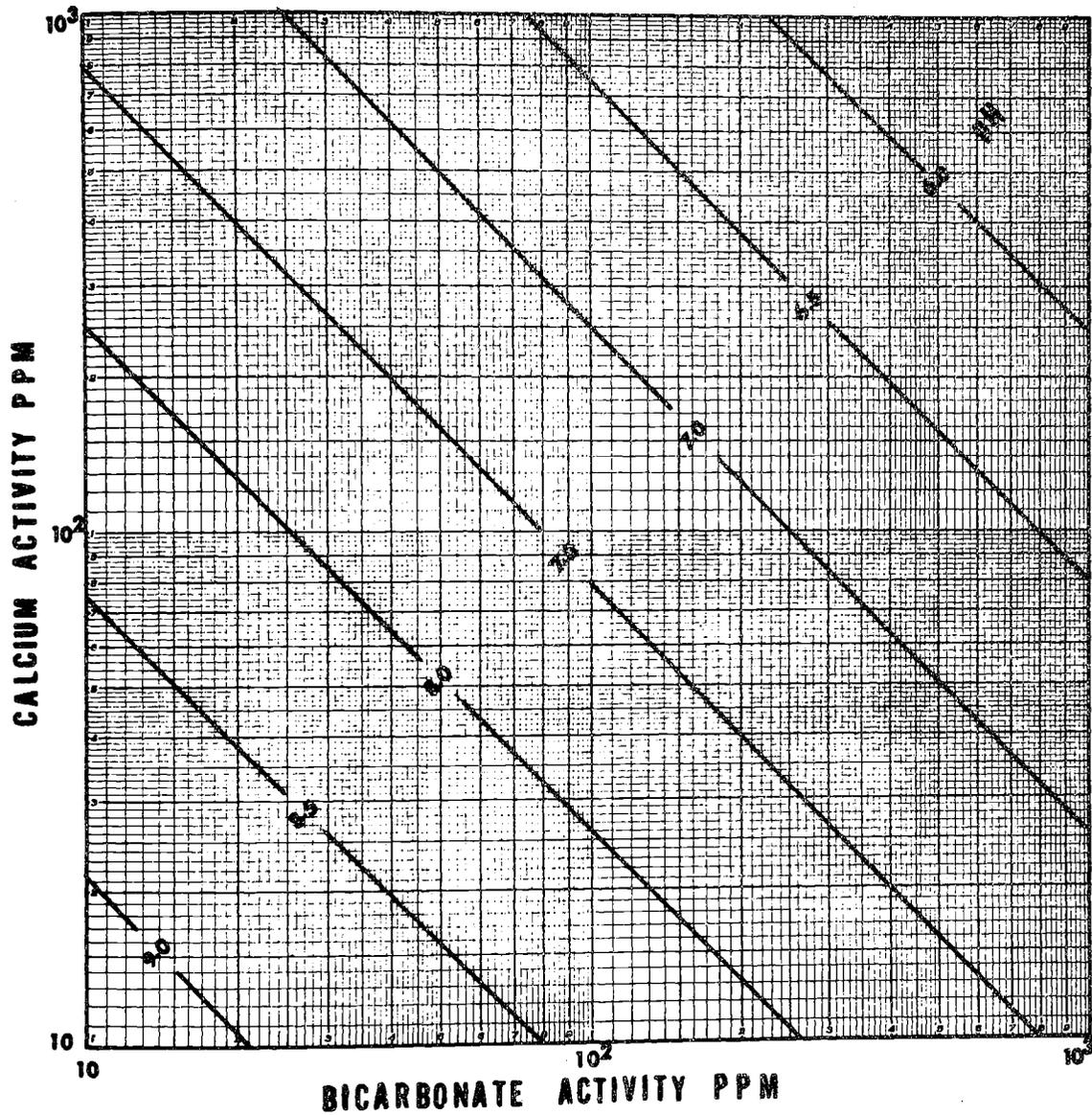


Figure 40. Equilibrium pH for calcium and bicarbonate activities, in ppm, in water in contact with calcite at 20°C and 1 atmosphere pressure (modified after Hem, 1961).

Assuming constant  $\text{CO}_2$  pressure, the solubility of calcite decreases with increasing temperature. However, temperature corrections were not considered necessary in the application of equation (12). The range of ground-water temperatures in this study is within 5 degrees centigrade from  $25^\circ\text{C}$ . Refinements by correcting equilibrium constants for temperature using van't Hoff's equation (Back and Hanshaw, 1965) is probably not justified in view of the fact that other sources of error in the computation of the equilibrium pH (12) are much greater. Therefore, the equilibrium constant computed for  $25^\circ\text{C}$  is used in all cases to calculate the equilibrium pH.

The difference between the actually measured field pH and the calculated equilibrium pH (Table 4) is an index of departure from equilibrium and can be plotted on a map and contoured (Figure 41A). If the assumptions of this simple chemical model are correct, this map should be indicative of the regional distribution of the state of calcite saturation in the basin-fill aquifer. Equilibrium conditions are approximated near the 0-line of pH differential. If the actual pH measured in the field exceeds the computed equilibrium pH, there is an apparent shortage of  $\text{H}^+$  ions. To

Table 4. Departure from Equilibrium of Ground Water in Contact with Calcite in Wells of the Basin-Fill Aquifer. Calculations are based on: (A) The Difference Between pH Actually Measured in the Field and the Calculated Equilibrium pH, (B) Ratio of Calcium Activity Determined Analytically and the Computed Calcium Activity at Equilibrium Conditions. Sample Numbers Refer to Water Samples Collected by the Author.

Sample No.	t °C	pH	(A) pH <sub>field</sub> - pH <sub>eq.</sub>	(B) $\frac{Ca^{++}_{anal.}}{Ca^{++}_{eq.}} \times 100$
PS 1	28.0	7.80	+0.070	132
PS 2	27.5	7.65	-0.040	101
PS 3	27.5	7.82	+0.120	144
PS 4	29.4	7.80	+0.210	196
PS 5	27.5	7.60	-0.030	102
PS 6	27.5	7.70	+0.140	152
PS 7	27.5	7.60	+0.010	114
PS 8	26.8	7.80	-0.130	79
PS 9	26.8	7.90	-0.020	103
PS 10	26.8	7.70	-0.140	77
PS 11	28.1	7.30	-0.390	46
PS 13	27.0	7.80	+0.060	122
PS 14	26.8	7.52	-0.210	65
PS 15	24.8	7.60	-0.030	90
PS 16	24.8	7.70	-0.140	70

Table 4. Continued

Sample No.	t °C	pH	(A) $\text{pH}_{\text{field}} - \text{pH}_{\text{eq.}}$	$\frac{\text{Ca}^{++} \text{ (B) anal.}}{\text{Ca}^{++} \text{ eq.}} \times 100$
PS 17	24.0	7.52	-0.190	60
PS 18	25.5	8.00	-0.010	98
PS 19	25.0	7.70	+0.100	123
PS 20	24.6	7.70	-0.240	43
PS 21	20.7	7.52	-0.010	77
PS 22	23.4	7.60	-0.240	51
PS 23	22.3	7.30	-0.890	11
PS 24	23.2	7.10	-1.170	6
PS 25	23.5	7.32	-0.900	11
PS 26	23.8	7.50	-0.620	21
PS 27	24.3	7.80	-0.190	60
PS 28	26.0	7.90	-0.370	43
PS 29	26.5	8.20	+0.230	179
PS 30	25.6	7.80	-0.020	95
PS 31	25.7	7.80	-0.160	70
PS 32	27.0	8.00	+0.215	178
PS 33	27.0	7.90	+0.164	158
PS 34	27.2	7.80	+0.188	169
PS 35	29.7	7.80	+0.103	156
PS 36	27.8	7.90	+0.224	188

Table 4. Continued

Sample No.	t °C	pH	(A) pH <sub>field</sub> - pH <sub>eq.</sub>	(B) $\frac{\text{Ca}^{++} \text{ anal.}}{\text{Ca}^{++} \text{ eq.}} \times 100$
PS 37	28.2	7.70	+0.084	137
PS 38	28.8	8.00	+0.295	232
PS 39	28.5	7.90	+0.037	119
PS 40	28.8	7.60	-0.141	84
PS 41	26.8	8.20	+0.208	173
PS 42	26.7	8.30	+0.337	232
PS 43	26.8	8.10	+0.092	132
PS 44	27.0	8.00	+0.027	115
PS 45	27.1	7.80	-0.174	73
PS 46	27.0	7.75	-0.145	76
PS 47	27.8	7.80	-0.121	84
PS 48	27.6	7.80	-0.024	105
PS 49	26.4	8.00	+0.096	137
PS 50	26.5	7.95	+0.119	144
PS 51	26.4	7.80	-0.107	85
PS 52	27.0	7.80	+0.126	145
PS 53	26.0	7.80	+0.240	180
PS 54	25.8	7.70	+0.113	132
PS 55	25.0	7.30	-0.355	43
PS 56	25.8	7.70	-0.073	85

Table 4. Continued

Sample No.	t °C	pH	(A) pH <sub>field</sub> - pH <sub>eq.</sub>	(B) $\frac{Ca^{++} \text{ anal.}}{Ca^{++} \text{ eq.}} \times 100$
PS 57	24.5	7.70	-0.156	66
PS 58	24.2	7.70	-0.220	56
PS 59	26.3	7.80	+0.460	302
PS 60	26.5	7.60	+0.127	142
PS 61	26.3	7.80	+0.126	140
PS 62	23.2	7.30	-0.123	68
PS 63	27.0	7.60	-0.131	80
PS 64	27.0	7.60	-0.086	89
PS 65	27.0	7.70	-0.048	97
PS 66	25.0	7.80	+0.041	108

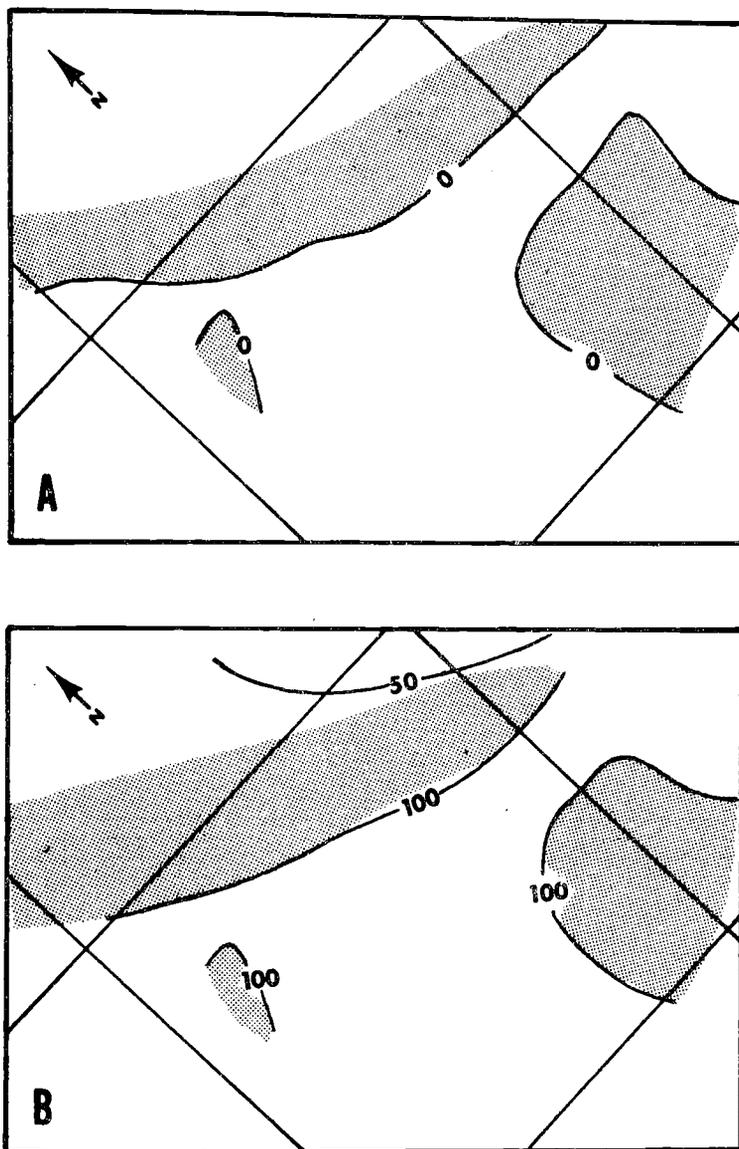
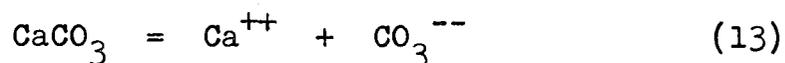


Figure 41. Maps showing departures from equilibrium of ground water in contact with calcite in the basin-fill aquifer based on: (A) difference between pH determined in the field and computed equilibrium pH; (B) ratio of calcium activity determined analytically and computed calcium activity at equilibrium. On the basis of the equilibrium model the shaded areas are theoretically undersaturated.

meet equilibrium requirements (10), reaction (9) will shift to the left and precipitation of  $\text{CaCO}_3$  will be the result. At the other hand, apparent excess of  $\text{H}^+$  ions occurs if the actual pH values fall below the equilibrium pH. In this, the water is undersaturated with respect to calcite and reaction (9) shifts to the right.

An alternative approach to determine the behaviour of calcite in ground water is a chemical equilibrium model based on the following chemical equations.



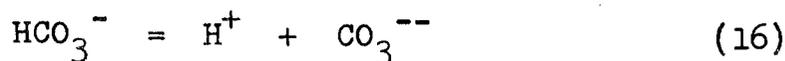
and its equilibrium constant

$$K'_{\text{CaCO}_3} = \frac{\langle \text{Ca}^{++} \rangle \langle \text{CO}_3^{--} \rangle}{\langle \text{CaCO}_3 \rangle} \quad (14)$$

whereby  $\langle \text{CaCO}_3 \rangle$  is assigned unity. Calcium activity at equilibrium conditions is computed by transposing (14).

$$\langle \text{Ca}^{++} \rangle = \frac{K'_{\text{CaCO}_3}}{\langle \text{CO}_3^{--} \rangle} \quad (15)$$

From reaction



and its equilibrium constant

$$K_{\text{HCO}_3^-} = \frac{\langle \text{H}^+ \rangle \langle \text{CO}_3^{--} \rangle}{\langle \text{HCO}_3^- \rangle} \quad (17)$$

carbonate ion activity can be calculated by transposing (17).

$$\langle \text{CO}_3^{--} \rangle = \frac{K_{\text{HCO}_3^-} \langle \text{HCO}_3^- \rangle}{\langle \text{H}^+ \rangle} \quad (18)$$

Back (1961a, 1963) and Garrels and Christ (1965) use these relationships to compute the state of calcite saturation in ground water. The ion activity product for reaction (13),  $K_{\text{iap}}$ , can be calculated from calcium and carbonate activities. Calcium activities are computed directly from laboratory analyses, but carbonate activities, usually below analytical detection, are computed from (18). The computed ion activity product,  $K_{\text{iap}}$ , can be compared with the equilibrium

constant,  $K'_{\text{CaCO}_3}$ , corrected for temperature. This ratio can also be used as an index for departure from equilibrium with respect to calcite. Another way is to calculate the calcium activity required to satisfy equilibrium conditions for reaction (13). The computed equilibrium calcium activity can then be compared with the calcium activity determined analytically. The ratio of analytically determined to calculated equilibrium calcium activity is numerically similar to the ratio ion activity product to equilibrium constant.

The equilibrium constants (14) and (17) used in this approach to calculate departures from calcite equilibrium can be obtained from free energy values. However, carefully determined and computed data on these equilibrium constants are available from the published literature (Garrels and Christ, 1965) and these data agree very closely with data obtained from free energy values and thermodynamically corrected for temperature (Back, 1961).

Harned and Scholes (1941) have made careful determinations of the ionization constants for the reaction  $\text{HCO}_3^- = \text{H}^+ + \text{CO}_3^{2-}$  in the temperature range 0-50°C. Larson and Buswell (1942) used the values for

this reaction to compute equilibrium constants for the reaction  $\text{CaCO}_3 = \text{Ca}^{++} + \text{CO}_3^-$  using data on solubility of calcite from Frear and Johnston (1929). Back (1963) has recomputed and interpolated the pertinent equilibrium constants for the range 20-35°C, adequately covering the range of observed temperature of ground water from the study area (Table 5). Using the equilibrium constants from this table, tabulated in logarithmic form for convenience, the equilibrium calcium activities are calculated. The ratio analytical calcium activity to calculated equilibrium calcium activity (Table 4) is plotted and contoured in Figure 41B, showing lines of equal departure from equilibrium with calcite. Equilibrium conditions are approached by values close to 100. Very low values represent undersaturation and percentages significantly exceeding 100 represent supersaturation.

The two maps showing departure from equilibrium are almost identical in appearance. One is based on the difference between pH actually measured in the field and the computed equilibrium pH (Figure 41A). The other is based on the ratio of calcium activity determined analytically and the calcium activity computed for equilibrium conditions (Figure 41B). This is not surprising

Table 5. Equilibrium Constants for Calculation of Calcite Saturation (after Back, 1963).

$t$ °C	Log $K_{\text{HCO}_3^-}$ (1)	Log $K'_{\text{CaCO}_3}$ (2)
20	-10.376	-8.277
21	-10.367	-8.289
22	-10.356	-8.302
23	-10.347	-8.314
24	-10.338	-8.321
25	-10.329	-8.338
26	-10.320	-8.350
27	-10.312	-8.362
28	-10.304	-8.374
29	-10.296	-8.386
30	-10.288	-8.398

(1) Harned and Scholes (1941)

(2) Larson and Buswell (1942)

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The percentage total sum of squares for the linear surface is more than 51 percent. The linear surface, perhaps, is not a very good predictor but suggests some interesting relationships (Figure 42A). Waters of lower temperature and lower pH have a tendency to be undersaturated. At lower temperatures, solubility of calcite increases (Weyl, 1959). An increase in hydrogen ion concentration (lower pH) also enhances solubility of calcite. Under these conditions, there is a good chance that the ion activity product of calcite is less than the solubility product required to satisfy equilibrium conditions. Conversely, this diagram also confirms the fact that at higher temperatures and at higher pH, supersaturation is more likely to occur because of decreasing solubility of calcite under these conditions. Quadric terms contribute little to reduce the variance and because of this, little significance can be attached to the quadric trend surface (Figure 42B).

### Discussion

The behaviour of calcite in ground water can be studied through the application of chemical equilibrium models based on the principles of chemical

Figure 42. Functional relationships of pH, temperature, and departure from equilibrium of ground water in contact with calcite in the basin-fill aquifer.

- (A) Linear trend of departure from equilibrium of ground water in contact with calcite as a function of pH and temperature.
- (A) Quadric trend of departure from equilibrium of ground water in contact with calcite as a function of pH and temperature.

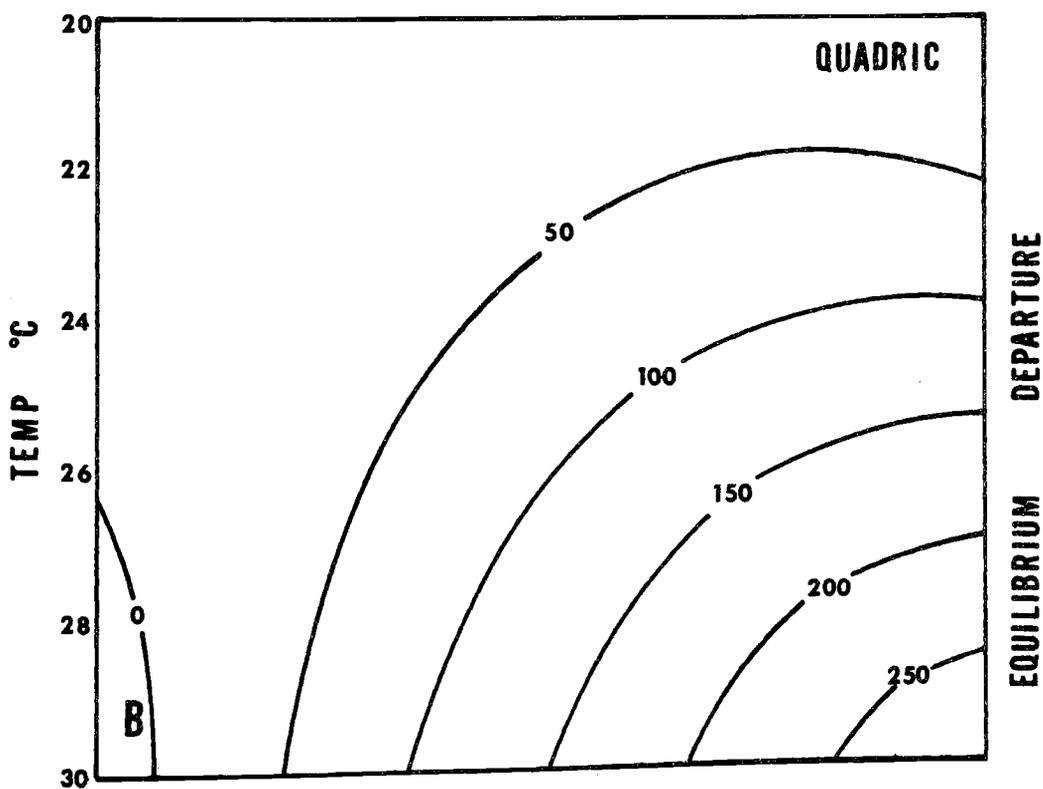
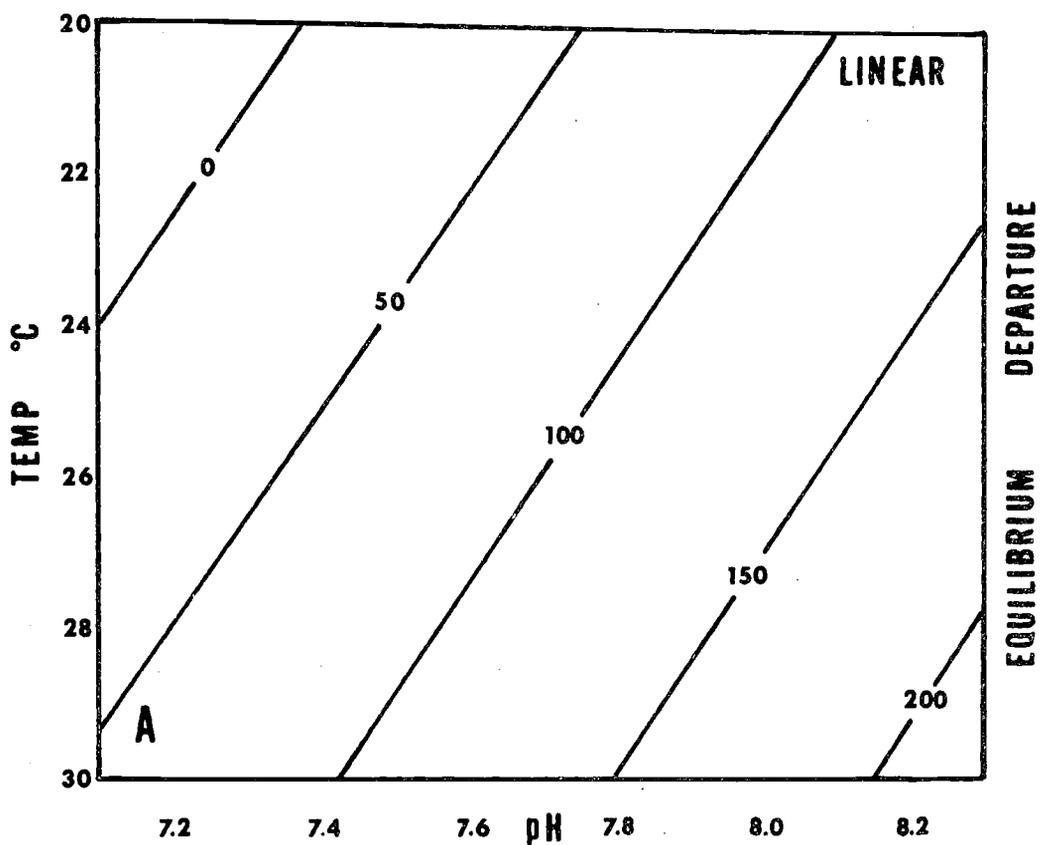


FIGURE 42

thermodynamics. The assumption underlying this approach is that by comparing data representative of the real system with results computed for the theoretical equilibrium model, we may be able to predict the chemical behaviour of ground water in contact with calcite in the aquifer. This requires considerable simplification of the real system. Presence of other ions in solution affect chemical reactions involving calcite and water and not all pertinent chemical equilibria have been included in the model. For example, the effect of sulfates and chlorides are not considered. Hall (1963) has attempted to investigate calcium carbonate equilibria including sulfate and chloride ions in the system. Unfortunately, his assumptions are not applicable to the relatively dilute ground-water solutions of the basin-fill aquifer. Another simplifying condition is the assumption that calcium carbonate is present as pure calcite and evenly distributed throughout the aquifer.

Presently, no systematic body of evidence, based on actual observations, is available giving information on where calcite is being precipitated or dissolved in the basin-fill aquifer. Whether or not predictions based on the chemical equilibrium model

are in accord with the real behaviour of calcite and water in the aquifer remains a matter of speculation. The value of chemical equilibrium models lies primarily in providing an aid for the interpretation of the observed reality. Conversely, only real facts can test the validity of the model. Hence, detailed work on the mineralogy of the aquifer is probably needed to indicate whether the equilibrium model assumed in this study is useful or perhaps an oversimplification of the real picture.

Where ground water has established equilibrium with respect to calcite, changes in temperature, pH, calcium or bicarbonate activities will trigger renewed chemical reaction. Lowering of pH will cause more calcite to dissolve and an increase in pH will cause calcite to precipitate. The pH is controlled primarily by dissolved carbon dioxide, which, in turn, depends on temperature and pressure. Reduction in pressure may release carbon dioxide, and decrease in the dissolved carbon dioxide content may raise the pH of the water sufficiently to bring about precipitation of the calcium carbonate. If ground water is brought to the surface, the latter process is more likely to occur in water that appears relatively supersaturated with respect to

calcite than in water from areas of apparent under-saturation with respect to calcite.

## IX. SUMMARY AND CONCLUSIONS

It has been generally assumed that the primary controls on the chemical character of ground water are the lithology of the aquifer and the flow pattern of the ground water. The lithology of the aquifer determines which facies will develop and the flow pattern controls the regional distribution. If chemical equilibrium between water and the aquifer material has not been attained and an excess of soluble material is available in the aquifer, an increase in dissolved solids content may be the result as water moves down the hydraulic gradient. In the case that the aquifer contains minerals with absorptive or exchange capacities for certain chemical constituents, change in chemical quality may be expected perpendicular to the general direction of ground-water movement.

Factor analysis in the Q-mode on data from the basin-fill aquifer in the Tucson Basin indicates that the overall chemical character of the ground water does not change substantially as it moves through the basin. However, some chemical constituents are clearly more affected by lithology than others as suggested by trend

surface analysis of individual dissolved constituents. The chemical character of the water as it enters the basin-fill aquifer can be traced in the basin over considerable distances. It is likely that a large part of the chemical character of ground water was acquired during contact with various rock types in the drainage basins before recharge. Chemical analysis of a surface-water sample taken from Cienaga Creek indicates a chemical composition similar to that found in the ground water basin many miles down gradient. It appears that in the Tucson Basin the lithology of the basin-fill aquifer only plays a secondary role in determining the overall chemical character of the ground water. The results of this study show that the conceptual model proposed to explain the distribution of dissolved constituents in ground water of the basin-fill aquifer is basically correct.

The methods used by Back (1966) and other investigators of the U. S. Geological Survey to study hydrochemical facies do not appear adequate in explaining the relationships of chemical character of ground water in the basin-fill aquifer and the hydrogeologic environment of the Tucson Basin. This investigation has demonstrated that trend surface analysis and factor

analysis, employing digital computers, can be applied usefully to the study of water quality in a ground-water basin. The use of these two multivariate techniques appears promising and deserves further testing and application in ground-water quality studies of other areas. The success of the application of statistical models to other geologic problems (Krumbein and Graybill, 1965) suggests that regional investigations of ground-water quality could benefit equally from a similar approach. A recent move by several federal and state agencies (Morgan, Dingman and McNellis, 1966) to put all their chemical quality data on IBM cards will certainly encourage the use of computer techniques in the study of ground-water quality.

The advantage of using digital computers to solve problems in regional studies of ground-water quality can perhaps be more appreciated if the research can be organized before commencing the data collection part of the program. Organization of a research program requires adequate formulation of the problem and setting up of one or more hypotheses. Evaluation of hypotheses concerning the origin and distribution of chemical quality of ground water often involves the use of multivariate models. Digital computers are capable

of handling the laborious computation and data manipulation common in testing of multivariate hypotheses.

A chemical process of hydrogeologic interest that takes place in aquifers is the precipitation and dissolution of calcite. Because it is not directly observable underground, little is known about the nature and behaviour of calcite in the basin-fill aquifer. This problem can be approached indirectly by setting up a chemical equilibrium model of the system, calcite-water. Assuming certain simplifying conditions, the theoretical state of saturation of ground water with respect to pure calcite can be calculated by comparing data representative of the actual conditions in the aquifer with results computed for the equilibrium model. However, detailed study of the mineralogy is required to verify the assumption that the computed state of saturation, based on the equilibrium model, can be used directly to predict precipitation or dissolution of calcite in the aquifer.

APPENDIX A  
BASIC DATA

Table 1. Chemical analyses of ground water from the basin-fill aquifer of the Tucson Basin, City of Tucson area. Well numbers refer to base map on file in the Hydrology Laboratory, Department of Geology, The University of Arizona. Wells 1 - 100 are used in factor analysis of ground-water quality data. Wells 1 - 144 are used in trend surface analysis. Source of data are the files and publications of the Agricultural Experiment Station, The University of Arizona. Most analyses were made by the Soil and Water Testing Laboratory at The University of Arizona. Data are in ppm.

Well No.		TDS	Ca <sup>++</sup>	Mg <sup>++</sup>	Na <sup>+</sup>	Cl <sup>-</sup>	SO <sub>4</sub> <sup>-</sup>	HCO <sub>3</sub> <sup>-</sup>	F <sup>-</sup>
1	H 1	422	43	7	67	20	95	190	.1
2	D 50	311	29	2	72	12	40	156	.1
3	I 16	224	38	12	5	18	5	151	.3
4	E 24	285	32	6	38	8	50	151	.2
5	E 23	319	42	7	36	18	30	186	.1
6	E 22	289	37	5	34	10	20	183	.1
7	E 21	329	39	4	51	14	35	190	.1
8	E 49	270	60	4	5	18	22	161	.4
9	E 20	290	34	6	38	16	40	156	.2
10	E 17	292	37	9	30	12	48	156	.2
11	E 57	263	24	12	31	12	38	146	.4
12	E 26	338	49	2	61	30	35	161	.1
13	E 27	298	39	5	36	20	20	178	.1
14	I 17	281	36	7	32	16	34	156	.1
15	I 24	291	39	4	35	12	40	161	.3
16	I 21	313	42	4	39	12	55	161	.1
17	I 19	312	15	2	75	18	73	129	.1
18	I 22	389	41	7	60	18	90	173	.1

Table 1. Continued

	Well No.	TDS	Ca <sup>++</sup>	Mg <sup>++</sup>	Na <sup>+</sup>	Cl <sup>-</sup>	SO <sub>4</sub> <sup>-</sup>	HCO <sub>3</sub> <sup>-</sup>	F <sup>-</sup>
19	I 98	415	11	2	118	48	148	84	.8
20	H 7	567	52	6	116	76	168	147	1.4
21	I 68	391	51	6	52	18	110	154	.1
22	I 25	303	44	1	40	11	40	168	.5
23	I 15	183	32	1	31	10	11	132	.3
24	I 11	283	37	7	29	12	20	178	.2
25	I 12	304	32	5	45	16	40	166	.1
26	E 31	309	35	4	47	20	50	153	.1
27	E 30	274	39	3	33	20	20	159	.1
28	E 25	265	32	2	38	9	32	151	.3
29	E 18	302	35	7	40	24	40	156	.1
30	E 15	371	56	10	30	20	40	215	.2
31	E 16	366	55	13	24	20	30	224	.2
32	E 29	277	29	5	41	16	35	151	.1
33	E 33	297	29	5	47	20	30	166	.1
34	E 50	270	30	1	46	12	50	132	.2
35	E 35	278	27	3	45	16	20	166	.1
36	I 9	230	27	4	31	12	10	146	.2
37	I 10	301	36	5	38	16	25	181	.2
38	I 32	234	25	4	17	14	10	164	.2
39	I 27	260	24	4	42	14	10	166	.3
40	I 31	284	29	5	42	10	30	168	.1
41	I 63	316	44	7	33	14	55	163	.1
42	I 64	260	33	5	33	14	55	120	.3
43	I 65	366	47	6	47	10	90	166	.2
44	I 66	371	48	8	44	10	90	171	.1
45	I 70	454	68	4	71	52	88	171	.3

Table 1. Continued

	Well No.	TDS	Ca <sup>++</sup>	Mg <sup>++</sup>	Na <sup>+</sup>	Cl <sup>-</sup>	SO <sub>4</sub> <sup>-</sup>	HCO <sub>3</sub> <sup>-</sup>	F <sup>-</sup>
46	I 72	396	50	6	54	10	120	156	.2
47	I 69	591	80	14	71	16	220	185	.2
48	I 71	434	60	1	69	28	148	127	2.0
49	I 73	374	83	1	21	14	102	154	.2
50	I 60	375	47	6	50	24	65	183	.2
51	I 62	314	46	4	35	16	45	168	.1
52	I 58	279	39	3	33	20	20	164	.2
53	I 43	262	30	1	40	10	25	156	.1
54	I 34	269	27	4	42	10	30	156	.1
55	I 41	231	30	5	24	6	10	156	.2
56	I 6	278	30	5	41	16	40	146	.1
57	I 3	259	30	1	39	14	10	164	.1
58	I 5	295	36	5	39	14	50	151	.1
59	I 4	258	30	4	34	11	30	138	.2
60	E 58	250	27	2	40	12	23	146	.3
61	E 32	345	75	8	7	30	25	200	.3
62	E 36	436	76	6	33	29	23	269	.3
63	E 39	242	21	4	41	14	25	137	.1
64	I 1	224	30	3	37	8	28	118	.2
65	I 2	263	34	4	31	16	10	168	.2
66	I 38	299	29	3	50	16	40	161	.2
67	I 45	293	57	6	30	9	45	162	.1
68	I 97	367	61	8	27	17	42	212	.1
69	I 44	293	27	5	47	16	15	183	.3
70	I 49	225	26	5	28	12	10	144	.2
71	I 53	245	25	4	36	14	12	154	.2
72	I 61	316	39	3	45	16	35	178	.2

Table 1. Continued

	Well No.	TDS	Ca <sup>++</sup>	Mg <sup>++</sup>	Na <sup>+</sup>	Cl <sup>-</sup>	SO <sub>4</sub> <sup>-</sup>	HCO <sub>3</sub> <sup>-</sup>	F <sup>-</sup>
73	I 76	356	39	5	54	20	50	188	.2
74	I 75	270	42	6	38	9	61	126	.2
75	I 77	339	44	7	39	8	70	171	.1
76	I 74	374	54	7	40	10	90	173	.1
77	I 99	474	105	4	21	24	137	183	.2
78	I 87	425	60	8	49	12	130	166	.1
79	I 88	408	51	5	60	18	125	149	.2
80	I 89	568	82	13	65	40	200	166	.7
81	I 91	742	121	16	80	100	256	157	.1
82	I 86	423	62	12	40	14	131	164	.1
83	I 92	299	45	4	1	16	56	171	.2
84	I 85	240	38	4	4	20	5	168	.3
85	I 84	233	38	1	23	10	20	132	.4
86	I 82	237	29	1	34	14	10	149	.2
87	J 48	280	32	1	25	12	20	171	.2
88	J 40	219	27	4	26	6	10	146	.2
89	J 37	219	30	4	23	6	10	161	.2
90	J 33	232	30	4	26	6	10	156	.2
91	J 35	386	63	9	27	10	50	277	.1
92	J 31	385	60	8	31	6	60	220	.1
93	J 19	269	32	3	36	10	30	154	.2
94	J 17	283	38	5	33	16	25	166	.1
95	J 70	389	52	4	53	20	60	198	.2
96	J 39	218	28	4	24	6	10	146	.2
97	J 49	283	32	3	44	20	40	144	.3
98	J 50	250	30	1	36	12	10	161	.2
99	I104	330	60	1	30	30	25	181	.2

Table 1. Continued

Well No.	TDS	Ca <sup>++</sup>	Mg <sup>++</sup>	Na <sup>+</sup>	Cl <sup>-</sup>	SO <sub>4</sub> <sup>-</sup>	HCO <sub>3</sub> <sup>-</sup>	F <sup>-</sup>
100 M 6	542	78	17	52	16	208	171	.2
101 E 2	318	62			16	40		
102 E 5	280	42			16	17		
103 E 12	306	42			26	10		
104 E 19	316	37			24	45		
105 E 34	263	29			16	20		
106 E 37	378	60			26	53		
107 E 48	197	33			7	25		
108 D 43	322	30			16	64		
109 D 69	296	35			32	30		
110 H 19	502	53			28	180		
111 I 14	282	26			16	30		
112 I 7	260	38			16	40		
113 I 9	230	27			12	10		
114 I 13	278	30			16	25		
115 I 40	210	38			8	16		
116 I 42	162	26			7	6		
117 I 46	256	26			5	4		
118 I 47	243	25			6	3		
119 I 79	230	26			10	14		
120 I 93	342	39			8	70		
121 I 96	267	40			19	12		
122 I100	590	82			40	210		
123 I103	585	94			22	214		
124 I105	352	52			18	65		
125 J 32	334	51			12	28		

Table 1. Continued

	Well No.	TDS	Ca <sup>++</sup>	Mg <sup>++</sup>	Na <sup>+</sup>	Cl <sup>-</sup>	SO <sub>4</sub> <sup>-</sup>	HCO <sub>3</sub> <sup>-</sup>	F <sup>-</sup>
126	J 34	232	29			6	10		
127	M 12	563	82			16	212		
128	M 36	348	41			16	60		
129	M 39	647	99			25	244		
130	N 2	370	38			8	90		
131	DM 6	362	42			8	80		
132	I 26	230	27			12	10		
133	I 29	274	25			20	10		
134	I 36	290	27			12	40		
135	I 50	214	25			6	10		
136	I 52	253	30			14	10		
137	I 54	274	52			8	20		
138	I 55	250	28			12	15		
139	I 57	291	42			8	45		
140	I 59	268	30			14	15		
141	I 83	237	27			12	10		
142	I102	619	93			26	214		
143	J 18	265	32			12	34		
144	I 28	203	32			9	61		

Table 2. Chemical analyses of ground water from the basin-fill aquifer of the Tucson Basin, regional ground-water system. Well numbers refer to base map on file in the Hydrology Laboratory, Department of Geology, The University of Arizona. These 100 wells, 1 - 132, are used in factor analysis of ground-water quality data. Many wells of Tables 1 and 2 are the same. Source of the data are the files and publications of the Agricultural Experiment Station, The University of Arizona. Most analyses were made by the Soil and Water Testing Laboratory at The University of Arizona. Data are in ppm.

Well No.	TDS	Ca <sup>++</sup>	Mg <sup>++</sup>	Na <sup>+</sup>	Cl <sup>-</sup>	SO <sub>4</sub> <sup>-</sup>	HCO <sub>3</sub> <sup>-</sup>	F <sup>-</sup>
1 H 1	422	43	7	67	20	95	190	.1
2 D 50	311	29	2	72	12	40	156	.1
3 I 16	224	38	12	5	18	5	151	.3
4 E 24	285	32	6	38	8	50	151	.2
13 E 27	298	39	5	36	20	20	178	.1
14 I 17	281	36	7	32	16	34	156	.1
15 I 24	291	39	4	35	12	40	161	.3
16 I 21	313	42	4	39	12	55	161	.1
17 I 19	312	15	2	75	18	73	129	.1
18 I 22	389	41	7	60	18	90	173	.1
19 I 98	415	11	2	118	48	148	84	.8
20 H 7	567	52	6	116	76	168	147	1.4
21 I 68	391	51	6	52	18	110	154	.1
22 I 25	303	44	1	40	11	40	168	.5
23 I 15	183	32	1	31	10	11	132	.3
24 I 11	283	37	7	29	12	20	178	.2
25 I 12	304	32	5	45	16	40	166	.1
26 E 31	309	35	4	47	20	50	153	.1

Table 2. Continued

	Well No.	TDS	Ca <sup>++</sup>	Mg <sup>++</sup>	Na <sup>+</sup>	Cl <sup>-</sup>	SO <sub>4</sub> <sup>-</sup>	HCO <sub>3</sub> <sup>-</sup>	F <sup>-</sup>
37	I 10	301	36	5	38	16	25	181	.2
38	I 32	234	25	4	17	14	10	164	.2
39	I 27	260	24	4	42	14	10	166	.3
40	I 31	284	29	5	42	10	30	168	.1
41	I 63	316	44	7	33	14	55	163	.1
42	I 64	260	33	5	33	14	55	120	.3
43	I 65	366	47	6	47	10	90	166	.2
44	I 66	371	48	8	44	10	90	171	.1
45	I 70	454	68	4	71	52	88	171	.3
46	I 72	396	50	6	54	10	120	156	.2
47	I 69	591	80	14	71	16	220	185	.2
48	I 71	434	60	1	69	28	148	127	2.0
49	I 73	374	83	1	21	14	102	154	.2
50	I 60	375	47	6	50	24	65	183	.2
51	I 62	314	46	4	35	16	45	168	.1
52	I 58	279	39	3	33	20	20	164	.2
53	I 43	262	30	1	40	10	25	156	.1
54	I 34	269	27	4	42	10	30	156	.1
55	I 41	231	30	5	24	6	10	156	.2
66	I 38	299	29	3	50	16	40	161	.2
68	I 97	367	61	8	27	17	42	212	.1
69	I 44	293	27	5	47	16	15	183	.3
70	I 49	225	26	5	28	12	10	144	.2
71	I 53	245	25	4	36	14	12	154	.2
72	I 61	316	39	3	45	16	35	178	.2
73	I 76	356	39	5	54	20	50	188	.2
74	I 75	270	42	6	38	9	61	126	.2

Table 2. Continued

	Well No.	TDS	Ca <sup>++</sup>	Mg <sup>++</sup>	Na <sup>+</sup>	Cl <sup>-</sup>	SO <sub>4</sub> <sup>-</sup>	HCO <sub>3</sub> <sup>-</sup>	F <sup>-</sup>
75	I 77	339	44	7	39	8	70	171	.1
76	I 74	374	54	7	40	10	90	173	.1
77	I 99	474	105	4	21	24	137	183	.2
78	I 87	425	60	8	49	12	130	166	.1
79	I 88	408	51	5	60	18	125	149	.2
80	I 89	568	82	13	65	40	200	166	.7
81	I 91	742	121	16	80	100	256	157	.1
82	I 86	423	62	12	40	14	131	164	.1
83	I 92	299	45	4	1	16	56	171	.2
84	I 85	240	38	4	4	20	5	168	.3
85	I 84	233	38	1	23	10	20	132	.4
86	I 82	237	29	1	34	14	10	149	.2
87	J 48	280	32	1	25	12	20	171	.2
88	J 40	219	27	4	26	6	10	146	.2
89	J 37	219	30	4	23	6	10	161	.2
90	J 33	232	30	4	26	6	10	156	.2
91	J 35	386	63	9	27	10	50	227	.1
95	J 70	389	52	4	53	20	60	198	.2
96	J 39	218	28	4	24	6	10	146	.2
97	J 49	283	32	3	44	20	40	144	.3
98	J 50	250	30	1	36	12	10	161	.2
99	I104	330	60	1	30	30	25	181	.2
100	M 6	542	78	17	52	16	20	171	.2
101	M 37	612	94	13	64	28	228	183	.2
102	M 11	554	78	14	62	20	212	168	.2
103	M 36	348	41	16	32	16	60	183	.1
104	J 42	383	53	11	32	4	56	227	.2

Table 2. Continued

	Well No.	TDS	Ca <sup>++</sup>	Mg <sup>++</sup>	Na <sup>+</sup>	Cl <sup>-</sup>	SO <sub>4</sub> <sup>-</sup>	HCO <sub>3</sub> <sup>-</sup>	F <sup>-</sup>
105	N 6	213	27	14	10	20	7	135	.4
106	N 4	229	31	7	20	12	8	151	.3
107	M 40	316	30	4	58	40	50	134	.2
108	M 33	637	98	8	69	6	254	202	.1
109	M 12	563	82	19	49	16	212	185	.1
110	M 39	647	99	16	64	25	244	197	.2
111	M 42	377	42	9	50	19	56	201	.3
112	M 22	416	46	12	55	22	75	207	.3
113	N 15	615	94	20	52	25	223	199	.2
114	N 14	602	96	22	41	16	220	207	.1
115	N 16	432	64	8	48	20	131	159	.2
116	N 18	632	102	22	45	16	240	207	.1
117	N 12	634	86	18	69	16	230	215	.4
118	N 11	302	60	4	15	16	30	176	.5
119	R 1	870	127	7	110	32	372	220	.3
120	R 6	365	68	4	24	26	30	210	.4
121	R 3	375	9	17	75	24	72	176	.8
122	R 4	355	37	15	41	16	63	176	.6
123	R 5	829	98	1	155	40	367	163	.6
124	S 9	377	44	13	38	14	30	232	.8
125	S 5	756	78	33	89	18	250	288	.2
126	S 6	652	29	12	146	28	183	254	.8
127	S 1	649	91	29	44	10	170	305	.1
128	O 9	238	29	9	22	6	30	142	.3
129	O 5	254	41	5	20	10	24	146	.2
130	N 9	299	41	9	27	8	50	154	.1
131	O 2	200	32	6	12	6	20	124	.6
132	N 1	238	29	9	22	6	30	142	.3

Table 3. Chemical analysis of ground water sampled by the author from wells tapping the basin-fill aquifer of the Tucson Basin. Well numbers commencing PS refer to field numbers and City numbers refer to well-numbering system of the City of Tucson Water Department. The analyses are also on file with the Agricultural Experiment Station, The University of Arizona. All analyses were made by the Soil and Water Testing Laboratory at The University of Arizona. Data are in ppm.

Well No.	City No.	Temp <sup>o</sup> C	Field pH	Lab pH	Ca	Mg	Na
PS 1	B 1	28.0	7.80	7.80	39	2	41
PS 2	B 2	27.5	7.65	7.90	44	5	38
PS 3	B 4	27.5	7.82	7.90	42	7	36
PS 4	C 2	29.4	7.80	8.00	49	8	36
PS 5	B 13	27.5	7.60	7.90	49	6	39
PS 6	B 14	27.5	7.70	7.60	58	7	47
PS 7	B 19	27.5	7.60	7.70	56	9	45
PS 8	B 55	26.8	7.80	7.70	27	4	41
PS 9	B 54	26.8	7.90	7.90	29	5	26
PS 10	B 42	26.8	7.70	7.90	34	7	31
PS 11	B 8	28.1	7.30	7.80	46	3	42
PS 12	B 76	30.8	7.60	7.80	71	10	120
PS 13	B 21	27.0	7.80	7.90	38	5	46
PS 14	B 10	26.8	7.52	7.90	39	6	31
PS 15	A 9	24.8	7.60	7.80	50	7	36
PS 16	A 1	24.8	7.70	7.80	32	4	28
PS 17	A 7	24.0	7.52	7.70	38	10	33
PS 18	F 1	25.5	8.00	7.65	21	5	37
PS 19	F 4	25.0	7.70	7.72	47	5	28
PS 20	A 19	24.6	7.70	7.70	18	8	29
PS 21	B 73	20.7	7.52	7.10	52	6	32

Table 3. Chemical analysis of ground water sampled by the author from wells tapping the basin-fill aquifer of the Tucson Basin. Well numbers commencing PS refer to field numbers and City numbers refer to well-numbering system of the City of Tucson Water Department. The analyses are also on file with the Agricultural Experiment Station, The University of Arizona. All analyses were made by the Soil and Water Testing Laboratory at The University of Arizona. Data are in ppm.

Well No.	K	Cl	SO <sub>4</sub>	HCO <sub>3</sub>	F	NO <sub>3</sub>	Sr	Zn
PS 1	3.8	16	40	163	.2	5	.63	1.18
PS 2	2.4	20	60	159	.3	8	.68	1.06
PS 3	2.3	20	44	161	.3	9	.81	1.16
PS 4	2.3	24	42	183	.3	8	.52	1.45
PS 5	2.7	16	79	166	.3	4	.91	0.97
PS 6	13.0	14	105	171	.3	3	.93	0.97
PS 7	3.6	16	104	166	.3	3	.92	1.00
PS 8	1.7	20	16	139	.2	5	.36	1.03
PS 9	1.7	16	16	134	.2	7	.34	0.99
PS 10	1.8	24	17	139	.3	10	.51	0.93
PS 11	2.8	20	75	152	.3	3	.91	2.17
PS 12	3.6	104	246	120	1.8	2	1.41	0.95
PS 13	2.0	16	28	161	.2	8	.54	0.93
PS 14	2.0	20	26	161	.2	6	.48	0.97
PS 15	2.2	32	54	159	.2	3	.56	1.04
PS 16	1.9	20	26	149	.1	2	.38	1.11
PS 17	3.3	20	28	176	.3	4	.39	0.93
PS 18	1.7	16	28	151	.4	5	.51	0.97
PS 19	2.4	20	18	181	.3	6	.58	1.15
PS 20	2.0	22	12	163	.2	4	.49	0.95
PS 21	1.3	11	12	193	.2	6	.59	0.99

Table 3. Continued

Well No.	City No.	Temp <sup>o</sup> C	Field pH	Lab pH	Ca	Mg	Na
PS 22	B 77	23.4	7.60	7.25	24	6	62
PS 23	B 27	22.3	7.30	7.20	15	3	34
PS 24	C 23	23.2	7.10	7.10	12	5	62
PS 25	C 52	23.5	7.32	7.15	14	4	38
PS 26	C 56	23.8	7.50	7.15	16	5	41
PS 27	C 26	24.3	7.80	7.55	22	5	38
PS 28	C 40	26.0	7.90	7.85	12	5	33
PS 29	C 55	26.5	8.20	7.40	26	5	25
PS 30	C 33	25.6	7.80	7.70	34	5	26
PS 31	C 32	25.7	7.80	7.80	26	6	20
PS 32	C 44	27.0	8.00	7.80	35	5	48
PS 33	C 45	27.0	7.90	7.80	38	7	33
PS 34	C 14	27.2	7.80	7.90	54	10	41
PS 35	C 10	29.7	7.90	7.80	47	7	48
PS 36	C 15	27.8	7.70	7.80	46	9	41
PS 37	C 8	28.2	8.00	7.80	57	9	41
PS 38	C 3	28.8	7.80	7.80	48	8	55
PS 39	B 33	28.5	7.90	7.90	34	7	62
PS 40	B 3	28.8	7.60	7.80	40	4	40
PS 41	C 41	26.8	8.20	7.60	24	4	28
PS 42	C 16	26.7	8.30	7.90	26	5	31
PS 43	D 1	26.8	8.10	7.90	24	4	30
PS 44	D 9	27.0	8.00	7.30	26	2	27
PS 45	D 2	27.1	7.80	7.70	25	4	30
PS 46	D 3	27.0	7.75	7.80	30	4	25
PS 47	D 13	27.8	7.80	7.90	30	2	23
PS 48	D 28	27.6	7.80	7.85	34	3	22
PS 49	D 5	26.4	8.00	8.00	30	5	22

Table 3. Continued

Well No.	K	Cl	SO <sub>4</sub>	HCO <sub>3</sub>	F	NO <sub>3</sub>	Sr	Zn
PS 22	1.6	16	8	193	.2	7	.68	0.97
PS 23	1.3	10	8	134	.2	4	.42	0.95
PS 24	1.3	16	8	144	.2	3	.41	0.99
PS 25	1.1	12	12	136	.2	5	.39	0.97
PS 26	1.1	14	14	151	.2	5	.35	0.93
PS 27	1.9	22	24	156	.3	8	.42	0.95
PS 28	1.0	12	10	139	.3	6	.27	0.95
PS 29	1.9	10	8	132	.3	6	.29	0.99
PS 30	1.3	14	16	146	.3	12	.37	1.04
PS 31	1.1	10	8	134	.3	6	.27	0.97
PS 32	1.6	12	34	161	.3	4	.49	0.98
PS 33	1.7	14	48	166	.3	4	.48	0.97
PS 34	2.2	18	100	166	.3	5	.89	0.98
PS 35	2.3	14	94	151	.3	3	.87	0.97
PS 36	2.3	16	80	166	.3	4	.87	0.97
PS 37	2.5	16	104	156	.4	4	1.00	0.99
PS 38	2.4	20	120	151	.4	4	.95	0.93
PS 39	2.2	18	108	146	.5	3	.64	1.11
PS 40	2.2	14	58	156	.3	5	.90	1.04
PS 41	1.1	10	12	137	.4	6	.27	1.11
PS 42	1.0	10	14	137	.4	5	.36	1.04
PS 43	1.0	8	8	132	.3	4	.33	1.04
PS 44	1.0	8	6	132	.2	5	.44	0.99
PS 45	1.1	8	12	137	.2	5	.35	0.99
PS 46	1.2	8	14	137	.3	3	.16	1.04
PS 47	1.3	8	10	129	.3	4	.35	0.96
PS 48	1.4	8	12	144	.3	6	.47	0.97
PS 49	1.3	8	12	134	.3	4	.24	0.97

Table 3. Continued

Well No.	City No.	Temp <sup>o</sup> C	Field pH	Lab pH	Ca	Mg	Na
PS 50	D 6	26.5	7.95	7.90	34	4	23
PS 51	D 7	26.4	7.80	7.80	31	4	19
PS 52	D 29	27.0	7.80	7.80	46	4	22
PS 53	D 19	26.0	7.80	7.80	51	6	29
PS 54	D 18	25.8	7.70	7.70	48	6	24
PS 55	D 22	25.0	7.30	7.80	45	6	25
PS 56	D 21	25.8	7.70	7.90	37	7	24
PS 57	C 21	24.5	7.70	7.80	32	6	30
PS 58	B 50	24.2	7.70	7.80	28	6	32
PS 59	D 24	26.3	7.80	7.40	97	19	45
PS 60	D 25	26.5	7.60	7.50	77	15	41
PS 61	D 26	26.3	7.80	7.70	42	6	20
PS 62	G 3	23.2	7.30	6.93	73	9	46
PS 63	*DM 2	27.0	7.60	7.30	39	8	44
PS 64	*DM 6	27.0	7.60	7.70	42	7	47
PS 65	*DM 4	27.0	7.70	7.80	28	6	55
PS 66	C 51	25.0	7.80	7.80	42	6	38

\* Davis Monthan Air Force Base

Table 3. Continued

Well No.	K	Cl	SO <sub>4</sub>	HCO <sub>3</sub>	F	NO <sub>3</sub>	Sr	Zn
PS 50	1.3	10	14	142	.1	1	.34	0.93
PS 51	1.2	8	6	129	.2	3	.20	0.95
PS 52	1.7	8	22	156	.1	1	.66	1.07
PS 53	1.7	12	28	188	.1	18	.49	1.05
PS 54	1.9	8	26	185	.1	12	.42	1.01
PS 55	1.6	12	28	169	.1	8	.42	1.07
PS 56	1.4	12	20	151	.1	6	.42	1.01
PS 57	1.3	12	34	144	.1	5	.37	1.09
PS 58	1.5	14	30	144	.1	3	.30	1.06
PS 59	2.7	22	200	195	.1	3	1.18	1.15
PS 60	2.7	18	152	169	.2	3	1.20	1.06
PS 61	1.3	10	18	171	.1	6	.41	0.99
PS 62	1.2	26	84	195	.4	10	.56	1.06
PS 63	2.0	8	70	166	.3	4	.55	1.15
PS 64	2.3	8	80	171	.3	4	.56	1.04
PS 65	2.3	8	90	166	.3	4	.72	1.04
PS 66	2.1	16	60	146	.3	8	.33	1.01

Table 4. Specific capacity data of wells penetrating the basin-fill aquifer underlying the study area. Well numbers refer to well-numbering system of the City of Tucson Water Department. UA 1 and UA 4 are wells owned by The University of Arizona. Sources of data are the City of Tucson Water Department and the University of Arizona Agricultural Experiment Station. Specific capacity values are in gallons per minute per foot of drawdown.

Well No.	Spec. Cap.	Well No.	Spec. Cap.
A 1	17.5	B 48	43.3
A 2	46.2	B 50	24.3
A 3	16.9	B 51	49.2
A 5	14.9	B 52	33.0
A 7	38.4	B 53	31.4
A 10	77.0	B 54	27.2
A 17	16.0	B 55	28.7
A 18	26.9	B 56	21.5
A 27	80.9	B 57	63.2
B 2	15.8	B 59	33.0
UA 1	46.4	B 70	25.7
UA 4	32.0	B 73	14.9
B 3	12.3	B 76	57.4
B 4	10.1	B 75	7.1
B 5	13.0	B 77	44.7
B 6	15.5	B 78	16.3
B 7	12.6	C 1	17.9
B 8	18.3	C 3	17.2
B 10	22.6	C 4	22.2
B 11	8.9	C 6	16.9
B 12	14.4	C 7	32.0

Table 4. Continued

Well No.	Spec. Cap.	Well No.	Spec. Cap.
B 13	12.9	C 8	26.8
B 14	10.1	C 9	10.1
B 15	7.5	C 10	12.8
B 16	9.9	C 14	39.1
B 19	11.3	C 15	32.6
B 21	9.9	C 16	7.5
B 22	18.9	C 17	7.2
B 23	9.1	C 18	7.7
B 24	16.5	C 19	23.5
B 26	31.1	C 20	39.5
B 27	63.8	C 21	57.6
B 33	11.0	C 22	21.2
B 35	13.1	C 23	5.2
B 42	23.5	C 24	12.8
B 43	30.5	C 26	79.0
B 44	32.6	C 26	13.3
B 45	49.0	C 30	33.6
B 46	26.9	C 31	42.8
B 47	26.3	C 32	31.6
C 33	49.7	D 1	16.3
C 36	56.8	D 3	14.9
C 38	42.3	D 3	29.9
C 39	30.0	D 4	5.4
C 40	23.1	D 5	2.1
C 41	13.2	D 6	3.0
C 42	26.5	D 8	7.8
C 43	14.9	D 9	12.4

Table 4. Continued

Well No.	Spec. Cap.	Well No.	Spec. Cap.
C 44	29.9	D 10	12.9
C 45	31.8	D 11	8.3
C 46	51.3	D 12	4.7
C 48	61.3	D 13	4.4
C 49	33.8	D 15	8.2
C 50	36.6	D 16	14.1
C 51	41.7	D 17	24.2
C 52	12.6	D 18	17.0
C 53	22.6	D 19	13.2
C 54	60.0	D 21	38.2
C 55	61.3	D 22	32.7
C 56	46.4	D 23	16.2
C 58	73.0	D 28	3.7
		D 31	8.5

## APPENDIX B

### FACTOR ANALYSIS

This appendix contains examples of sets of data used in factor analysis of ground-water quality data of the Basin-fill aquifer. Because of space limitations the data are only partially listed. A complete set of input and output data of factor analysis on water-quality data of the basin-fill aquifer in the Tucson Basin is on file in the Hydrology Laboratory, Department of Geology, The University of Arizona.

Table 1A. Partial listing of lower half of matrix of distance coefficients between all possible pairs of rows (water samples) of original data array (Appendix A, Table 1) based on 6 constituents and used as input for Q-factor analysis

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1.000							
.816	1.000						
.696	.647	1.000					
.834	.841	.790	1.000				
.848	.801	.811	.896	1.000			
.818	.830	.779	.907	.934	1.000		
.861	.877	.722	.882	.904	.927	1.000	
.726	.732	.777	.824	.841	.853	.809	1.000

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Table 1B. Lower half of matrix of distance coefficients between all possible pairs of 8 chemical constituents of the original data array (Appendix A, Table 2) and used as input for R-factor analysis.

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1.000							
.867	1.000						
.801	.757	1.000					
.849	.768	.754	1.000				
.765	.716	.767	.795	1.000			
.900	.814	.792	.822	.784	1.000		
.787	.805	.760	.773	.679	.718	1.000	
.689	.638	.728	.733	.830	.721	.629	1.000

---

Table 2A. Q-factor analysis. Table of first five eigenvalues of Q-mode distance coefficient matrix (Appendix B, Table 1A).

	EIGENVALUES	PERCENT	CUMULATIVE PERCENT
1	81.256	81.26	81.26
2	4.226	4.23	85.48
3	2.379	2.38	87.86
4	1.400	1.40	89.26
5	1.132	1.13	90.40

Table 2B. R-factor analysis. Table of first five eigenvalues of R-mode distance coefficient matrix (Appendix B, Table 1B).

	EIGENVALUES	PERCENT	CUMULATIVE PERCENT
1	6.367	79.59	79.59
2	0.522	6.52	86.12
3	0.300	3.75	89.87
4	0.245	3.07	92.94
5	0.199	2.49	95.43

Table 3A. Q-factor analysis. Partial listing of the factor matrix of principal components for Q-mode analysis based on original data in Table 1, Appendix A. Row numbers refer to samples and column numbers to principal component factors.

Row/Col	I	II	III	IV	V
1	0.88385	0.26926	-0.11255	-0.03559	-0.17896
2	0.89303	-0.08585	-0.23663	0.00959	-0.13267
3	0.81573	0.11804	0.30438	-0.16936	0.16008
4	0.95355	-0.02462	0.02035	-0.17199	-0.00662
5	0.93962	0.08524	0.16656	-0.02457	-0.11942
6	0.95119	-0.06220	0.13015	0.01652	-0.09458
7	0.94119	-0.00945	-0.01137	0.07421	-0.21200
8	0.88948	-0.01806	0.16749	0.19093	0.16975
9	0.96194	-0.02477	0.04005	-0.14391	-0.04082
10	0.91682	0.11996	0.15674	-0.20089	0.03345
11	0.84373	0.14034	0.17663	-0.29052	0.08119
12	0.90425	-0.01366	-0.18979	0.14826	-0.10374
13	0.95569	-0.04578	0.09728	0.02637	-0.10390
14	0.94941	0.01008	0.11646	-0.15486	0.00410
15	0.96700	-0.09297	0.00824	0.00407	-0.01954

Table 3B. R-factor analysis. Factor matrix of principal components for R-mode analysis based on original data in Table 2, Appendix A. Row numbers refer to chemical constituents and column numbers to principal component factors.

Row/Col	I	II	III	IV	V
1	0.93542	-0.17632	-0.18793	0.01606	0.01293
2	0.89330	-0.28439	-0.03488	0.01380	-0.29449
3	0.89113	0.01804	0.16823	0.37537	0.16735
4	0.91115	-0.00024	-0.07436	-0.27065	0.25120
5	0.88704	0.32647	-0.01292	-0.05259	-0.05550
6	0.92012	-0.04495	-0.28859	0.08866	0.02730
7	0.86150	-0.27786	0.36896	-0.13864	0.00865
8	0.83330	0.47313	0.10073	-0.03688	-0.13247

Table 4A. Q-factor analysis. Partial listing of rotated (varimax) factor matrix for Q-mode analysis based on original data in Table 1, Appendix A. Row numbers refer to samples and column numbers refer to rotated (varimax) factors.

Row/Col	I	II	III	IV	V
1	0.50342	0.43709	-0.24345	0.03515	-0.05900
2	0.73308	0.23887	-0.29376	0.09130	-0.05117
3	0.53723	0.54755	-0.06504	0.06679	0.01180
4	0.74624	0.35911	-0.12968	0.06776	-0.03360
5	0.65341	0.55569	-0.12992	0.06268	-0.15836
6	0.76355	0.46279	-0.10669	0.08611	-0.19538
7	0.72028	0.42104	-0.16001	0.08884	-0.20374
8	0.67586	0.46602	-0.07062	0.28449	0.02061
9	0.75156	0.38306	-0.13899	0.06512	-0.09324
10	0.61714	0.48900	-0.11504	0.05929	-0.02883
11	0.55151	0.47260	-0.13027	-0.00220	-0.01196
12	0.69239	0.29716	-0.27370	0.19255	-0.05769
13	0.75593	0.45015	-0.13389	0.09015	-0.20152
14	0.71512	0.43517	-0.12266	0.06833	-0.07686
15	0.80237	0.35259	-0.12171	0.12954	-0.08173

Table 4B. R-factor analysis. Rotated (varimax) factor matrix for R-mode analysis based on original data in Table 2, Appendix A. Row numbers refer to chemical constituents and column numbers refer to rotated (varimax) factors.

Row/Col	I	II	III	IV	V
1	0.65764	0.30948	0.33235	0.33403	0.43765
2	0.74527	0.30620	0.49969	0.21073	0.15394
3	0.34059	0.39428	0.35348	0.73932	0.22058
4	0.34998	0.41569	0.39647	0.22385	0.68519
5	0.35385	0.73195	0.24140	0.26793	0.32925
6	0.65566	0.38283	0.17075	0.37383	0.44180
7	0.33287	0.27075	0.79531	0.28700	0.27535
8	0.24362	0.85382	0.23646	0.24916	0.20233

Table 5A. Q-factor analysis. Factor variances after varimax rotation. Original data in Table 1, Appendix A.

	VARIANCE	PERCENT	CUMULATIVE PERCENT
1	49.436	52.01	52.01
2	16.392	17.25	69.25
3	3.832	4.03	73.29
4	2.503	2.63	75.92
5	0.760	0.80	76.72
6	13.220	13.91	90.63

Table 5B. R-factor analysis. Factor variances after varimax rotation. Original data in Table 2, Appendix A.

	VARIANCE	PERCENT	CUMULATIVE PERCENT
1	1.951	25.56	25.56
2	2.002	26.23	51.79
3	1.418	18.58	70.37
4	1.108	14.52	84.89
5	1.153	15.11	100.00

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