

BROMIDE AS AN ENVIRONMENTAL TRACER IN GROUND  
WATER OF THE TUCSON BASIN, ARIZONA

by

Eric Norman Koglin

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SIGNED: *E. N. Davis*

APPROVAL BY THESIS DIRECTOR

This thesis has been approved on the date shown below:

*S. N. Davis*  
S. N. Davis  
Professor of Hydrology  
and Water Resources

*March 29, 1984*  
Date

This manuscript is lovingly dedicated  
in memory of  
Corlotta Lee McLean Koglin --  
mother and friend.

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## ABSTRACT

Bromide was used as an environmental tracer to determine the possible sources of natural and man-made recharge to the ground water of the Tucson basin. Numerous well, rainfall, runoff, and sewage samples were collected and analyzed for bromide and chloride. The bromide was determined by neutron activation analysis. Bromide concentrations in the ground water ranged from 0.036 to 2.24 mg/l and the chloride concentrations ranged from 3.2 to 332.2 mg/l. The average Cl/Br ratio of the ground water samples is about 130. The bromide distribution suggests the presence of at least four dominant ground-water zones, each differing in chemical character. This observation agrees with those made in previous investigations which have used different hydrologic and geochemical methods.

Most of the ground water in the basin is recharged by natural sources. However, the influence of man-made sources is well documented locally. The results of the bromide analyses strongly suggest that they can be used to delineate different sources of recharge.

## CHAPTER 1

### INTRODUCTION

The distribution of many natural chemical constituents in ground water can provide information about the dynamics of ground-water systems. These constituents are sometimes referred to as environmental tracers. Obviously, not all constituents are suitable for this purpose. Ideally, highly conservative (mobile and non-reactive) and abundant ions are most useful. The halogen elements chlorine, bromine, fluorine and iodine are of fundamental significance in the study of the chemical cycle of pollution and natural trace elements in natural waters. These elements are generally very soluble in water and relatively conservative properties of the water. With the exception of fluorine, removal of these elements from water by sorption or by mineral precipitation should be limited under natural conditions.

Fluoride, chloride and iodide have been used successfully as environmental tracers in ground-water quality investigations, whereas bromide has not. Although bromide is found in large quantities in sea water (65 mg/l) and brines (up to 3000 mg/l, Hem (1970)), it usually only exists in trace amounts (<.1 mg/l) in most dilute natural waters (ground water, surface water, precipitation and snow). The introduction of bromide to ground water can occur through the dissolution of aquifer materials and/or by recharge of surface water that contains bromide from both natural and anthropogenic sources. Chloride can similarly be

introduced, but is more abundant than bromide ( $>1$  mg/l). Bromide and chloride are the most conservative halogens. However, bromide detection is more difficult due to its chemical similarities to chloride and presence in low concentrations. The relationship between chloride and bromide (Cl/Br ratio) in a given source should be relatively constant, thereby providing a unique "fingerprint" of that source. The impact and migration of a source on a ground-water system can be evaluated by monitoring the Cl/Br ratio distribution of the ground water.

The objectives of this study are: 1) to evaluate the possibilities of using bromide as an environmental tracer, 2) to try to apply the more theoretical tracer concepts to bromide measurements made in the Tucson basin, and 3) to compare the conclusions drawn from my study of bromide to results of previous studies of the Tucson basin.

## CHAPTER 2

### CHEMISTRY AND SOURCES OF BROMIDE AND CHLORIDE

#### Chemical Properties

Although bromide and chloride have some similarities in many natural systems, their chemical properties have some important differences. Elemental bromine and chlorine exist naturally in two different states, as a liquid and a gas, respectively. In their water soluble forms (ionic), bromide and chloride differ only slightly in ionic radius, 1.95 and 1.85 Å, respectively (Weast, 1974). However, bromide is more than twice as heavy as chloride and far less abundant in nature. The stable bromine isotopes are  $\text{Br}^{79}$  and  $\text{Br}^{81}$ . Each accounts for about 50% of the total natural bromine.

Bromide is more readily affected by natural processes than is chloride. Atmospheric bromide is highly susceptible to oxidation to elemental bromine by photochemical oxidation, ozonation and by solar radiation related mechanisms (Winchester et al., 1967). Chloride is subject to these mechanisms but to a much lesser degree. Due to their slightly different chemical characteristics, bromide appears to sorb onto soil particles more readily. Walters and Winchester (1971) analyzed soil samples for halogen content. They recognized three possible "phases" in which halogens could be found: water soluble, surface bound and internally bound. Bromide was found in greatest abundance in the water soluble and surface bound phases. The investigators felt that

this represented an intermediate chemical behavior between bromide ion in the interstitial water and bromine associated with the sediment particles either as  $\text{Br}^-$  held by anion exchange or possibly by covalent bonds with carbon. Chlorine on the other hand is contained primarily in the water soluble phase as chloride ion ( $\text{Cl}^-$ ). Soils and sediments may not act as effective mechanisms for bromide attenuation. If, as expected in many environments, the soils and sediments have reached chemical equilibrium with interstitial water. The exchange sites may be occupied, therefore the bromide ions in subsequent recharging pulses will most likely move conservatively through the unsaturated and saturated zones.

Plants have a slightly greater affinity for inorganic bromide than inorganic chloride. The amount of bromide uptake is highly variable among plants, however, the total bromine content of most plants is generally less than 50 mg/g for dry matter (Maw and Kempton, 1982). Therefore, the net removal of bromide from water infiltrating through the root zone should be negligible. Marine and fresh-water plants also utilize bromide but have not been studied in any detail.

#### Sources of Bromide in Dilute Natural Waters

The occurrence of bromide in dilute natural waters is due to contributions from natural and anthropogenic sources. The primary natural source of bromide in surface water is believed to originate from sea water. Atmospheric moisture, which derives its halogen content from sea spray, is the means by which the halogens enter the surface waters from rainfall. Duce et al. (1963, 1965) studied the atmospheric content

of the halogens: bromine, chlorine and iodine. They concluded that the sea is the most likely source of the halogens, and that transmission to the atmosphere was by emission of aerosols through bubbles breaking on the surface of the sea.

The investigations were conducted in relatively nonpolluted maritime environments in order to eliminate potential interferences from anthropogenic aerosol emissions. Numerous aerosol and precipitation samples were collected and analyzed. The analytical method of choice was neutron activation analysis. For each sample they determined the bromide, chloride and iodide content. From these data the Cl/Br, Cl/I and Br/I ratios were determined and compared to those of sea water. This proved to be a useful technique for the comparison of the data, illustrating the degree of fractionation occurring as a result of the bubble breaking process and atmospheric mechanisms. The factors causing fractionation through the bubble breaking process are thoroughly discussed by Bloch et al. (1966). They found that, generally, the Cl/Br ratios of precipitation and aerosol samples ranged between 25 and 200 which is much less than sea water which has a ratio of about 300.

Ground water has the potential of being affected more by geochemical sources of bromide than surface water. The matrix of crystalline rocks in the earth's crust contain small amounts of the halogen elements. The Cl/Br ratio in crystalline rocks in general is roughly 200 (Vinogradov, 1959). Igneous rocks have a Cl/Br ratio of about 127 (Hem, 1970). The contribution of bromide and chloride from these rock types to ground water is negligible in most cases.

Evaporite deposits characteristically have small amounts of bromide incorporated among the precipitated chloride minerals. After deposition of NaCl, bromide can concentrate in the residual lake brines. The Cl/Br ratio in the precipitated salts can exceed 10,000, while in the brine it is about 30. If, however, the brine does not become concentrated enough to precipitate NaCl, the Cl/Br ratio of the brine should be about the same as the unconcentrated source water. The presence of brines in the subsurface can provide a significant source of bromide and chloride to ground water and surface water (Wittemore et al., 1981). Salts of bromide and chloride differ sharply in solubilities. This is evident by the lack of bromide salts incorporated among the documented evaporite deposits.

Soils and sediments contain appreciable amounts of bromine but little of it is water-extractable bromide. Bromide and iodide have similar properties in soils and sediments. Both are biophilic elements and enriched in organic-rich soils and sediments, showing close correlation with organic carbon content (Yuita et al., 1982; Maw and Kempton, 1982; Fuge and Behler, 1974). Maw and Kempton (1982) analyzed soils and peats for total bromine. The total inorganic bromide varied among the different soil types and between the soils and the peats. A correlation exists between total bromine content and organic content. However, in soils about 6% of the total bromine was inorganic bromide and in the peats it was less than 1%. The majority of the bromine exists in organic form which, as yet, generally remains undefined. Soils and peats are not likely to contribute bromide to infiltrating water

because, as mentioned earlier, the soils are probably in a quasi-chemical equilibrium with the infiltrating water.

In addition to natural sources, bromide is introduced to the environment through a variety of anthropogenic means. The most significant is from the combustion of leaded gasoline. Ethylene dibromide (EDB) is used as a lead scavenger (anti-knock compound) in leaded gasoline. Upon combustion, a number of bromide-rich (and chloride-rich) by-products are emitted with the automobile exhaust. These include:  $\text{PbClBr}$ ,  $\text{NH}_4\text{Cl}\cdot 2\text{PbClBr}$  and  $2\text{NH}_4\text{Cl}\cdot \text{PbClBr}$  (Winchester et al., 1966). Particles that have a sufficiently small diameter to be carried into the atmosphere will be subject to various chemical and physical reactions which strip the bromide and chloride ions from the compound. The likely result is the formation of  $\text{HBr}$  and  $\text{HCl}$ . Aerosols that are too large to be carried in the atmosphere will be deposited on the ground surface, eventually infiltrating into the soil or removed by runoff.

Lininger et al. (1966) and Winchester et al. (1966) used the halogen elements as a means to determine the impact of automobile emissions on the atmosphere. Samples were collected from a variety of locations and different altitudes over large metropolitan areas. The various halogen ratios were determined from the data and compared to those from the earlier work of Duce et al. (1963, 1965), which were assumed to be representative of the natural distributions of bromide, chloride and iodide. Bromide was the one halogen which was consistently higher than natural levels but varied considerably. Due to the similarity in behavior between lead and bromide in the atmosphere, it was concluded that automobile emissions were responsible.

The studies by Lininger et al. (1966), Winchester et al. (1966), and Duce et al. (1963, 1965) were completed before the introduction of unleaded gasoline. Because the number of automobiles using unleaded gasoline today represents the majority of automobiles on the road, the contribution of atmospheric bromide from automobile emissions has probably declined. To date, no further investigations have been done to determine this decreasing contribution.

The bromide and chloride concentrations of ground water and surface water can be increased by the recharge of various types of wastewaters. For example, sewage effluent, cooling tower blowdown water and irrigation return flows represent concentrated forms of the source water. However, sewage effluent may also contain additional amounts of bromide and chloride contributed through disposal of a variety of domestic and industrial wastes (i.e., brine from rejuvenating water softeners and photographic chemicals).

Some pesticides contain an appreciable amount of bromine but no inorganic bromide. The bromine is tied up in organic forms. The by-products of pesticide degradation include  $\text{CO}_2$ , water and mineral salts. Bromide is one of the resultant salts and could represent a miniscule addition to bromide concentrations in surface water and ground water.

#### Previous Attempts

The use of bromide as an environmental tracer has had limited application in previous water-quality studies. Tiffany et al. (1968) investigated natural and pollution sources of bromine, iodine and chlorine in the Great Lakes. Their work supported the idea that significant

amounts of bromide were being introduced into the atmosphere from the combustion of leaded gasoline. They found the bromide and chloride concentrations greatest near the shore and generally concluded that this was due primarily to pollution from the metropolitan areas.

Bathurst (1980) used bromide as an interpretive tool in a groundwater investigation to study pollution movement in a small unconfined aquifer in New Zealand. Two sanitary landfills were located down-gradient from a river but up-gradient from a local water supply. It was feared that bromide contamination of the drinking supply would result from bromide-rich wastes at the landfill sites. Slightly elevated bromide levels were reported near the landfills but, due to dilutional effects, the down-gradient concentrations were not found to be significantly above background levels.

In another case, Tolipano et al. (1982) investigated the water chemistry of a karstic aquifer along the Ionian Coast in Italy. Bromide concentrations are listed among their data base but the significance of the bromide distribution is not discussed.

## CHAPTER 3

### STUDY AREA

The area which I studied is in the central and northern portions of the Tucson basin, which lies in the Basin and Range Province, in southeastern Arizona (Figure 1). The northern boundary of the study area parallels Tangerine Road, the eastern boundary is defined by the Santa Catalina and Tanque Verde Mountains-piedmont Junction, the western boundary is defined by the Tucson Mountains-piedmont junction and the southern boundary roughly parallels a line projected eastward from the southern boundary of the San Xavier Indian Reservation. The area is approximately 1300 km<sup>2</sup>. Tucson, the major population center, and the small communities of Cortaro and Oro Valley are within the area studied.

#### Climate

The climate of the Tucson basin, within the Sonoran Desert, is semiarid. Winter (November-April) and summer (May-October) temperatures average 10°C and 30°C, respectively (Sellers and Hill, 1974). The average yearly pan evaporation (for the time period January 1929 through December 1979) is 240 cm per year. The pan coefficient for this area is between .65 and .70 (U.S. Department of Commerce, 1982).

Precipitation is almost equally divided between the summer and winter seasons. The average yearly precipitation is between 380 mm and 310 mm. Higher elevations in the mountains receive as much as 640 mm annually. The rainfall occurring in the summer season is usually

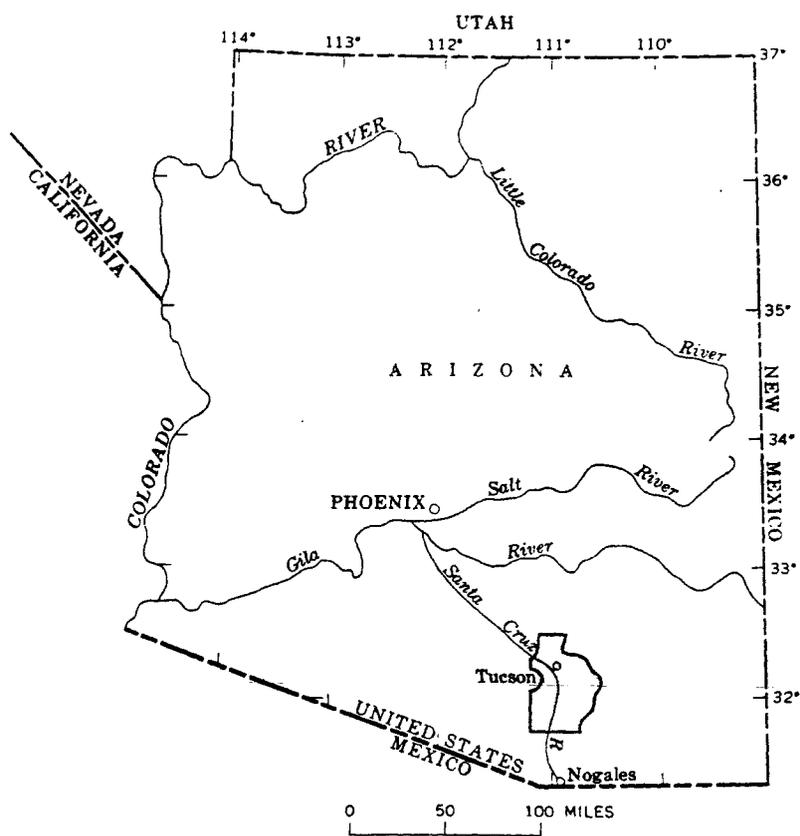


Figure 1. Location of study area (map from Davidson, 1973).

associated with convective storms. Moisture originating in the Gulf of Mexico precipitates in the Tucson basin as localized, often times intense, storms of short duration. Ninety-three percent of the peak streamflows occur during this time of the year (Condes de la Torre, 1970). The winter precipitation is associated with frontal type storms. The storms are widespread and of mild to moderate intensity. The precipitate moisture originates in the northwestern United States and moves eastward with the winter cyclonic storms.

#### Drainage

The Tucson basin is one of a number of sub-basins which are part of the larger Santa Cruz River Basin. The reach of the river lying in the Tucson basin follows the eastern flanks of the Tucson Mountains. Within the Tucson basin there are two principal tributaries which drain into the Santa Cruz River--Canada del Oro in the north and the Rillito River which drains the east-central portion of the basin (Figure 2, in pocket). The river system has formed a gently northwesterly-sloping plain. The altitudes vary from about 884 m at the inlet of the basin, to 610 m at the outlet, Rillito, Arizona. At its widest, the basin is 24-32 km in the central and southern portions and narrows to 6.5 km at the outlet. Overall, 81 km of the Santa Cruz River lie within the Tucson basin.

Rivers in the Tucson basin flow only during and shortly after significant rainfall. However, since 1970 the county wastewater treatment facilities, lying in the northern portion of the study area, have been annually discharging about  $5.1 \times 10^7 \text{ m}^3$  of treated effluent into

the Santa Cruz River channel (Esposito and Thurnblad, 1981). The average annual streamflow out of the basin at Rillito was about  $2.1 \times 10^7 \text{ m}^3$  during the period 1936-1963.

### Geohydrology of the Tucson Basin

#### Rock Units Along the Margin of the Basin

The principal rock units which crop out along the margins of the Tucson basin consist of nonporous, low-permeability crystalline intrusive and metamorphic rocks, moderate to highly porous volcanic and interbedded sedimentary rocks and moderate to highly porous sedimentary rocks (Davidson, 1973). The least permeable of these rocks are generally the most resistant, forming the surrounding mountains and the basement complex of the basin.

The Santa Catalina and Tanque Verde Mountains are composed of fractured metamorphic and intrusive igneous rocks. These mountains form the eastern boundary to the study area and represent, along with the Rincon Mountains, the largest mass of low-porosity and low-permeability material bounding the Tucson basin. Recoverable ground water is contained only along the fractures. These fractures serve as conduits which transmit water to the basin, either as surface flow (i.e., springs) or subsurface basin recharge. The Tucson Mountains are formed principally of low-permeability volcanic rocks. The northern and eastern slopes are underlain by volcanic and sedimentary rocks that are moderately permeable and porous (Davidson, 1973). Wells pumping from these units, however, yield amounts sufficient only for domestic purposes or stock-watering.

## Aquifer

The basin-fill sediments have been divided by Davidson (1973) into three units (in ascending order): Pantano Formation, Tinaja Beds, and the Fort Lowell Formation. The oldest sedimentary unit, the Pantano Formation, is a thick, reddish, claystone-mudstone unit. The upper beds of the Pantano Formation are mainly silty sandstones to gravels and weakly cemented with calcium carbonate. This formation yields small to moderate quantities of water to wells. It crops out locally at certain points along the perimeter of the basin, is believed to be over 1830 m thick in the central portion of the basin, and is severely faulted and tilted. Despite its massive thickness, the Pantano Formation is deeply buried in the central portions of the basin, most likely owing to the severe deformation which occurred during Pantano time (Tertiary). The degree of faulting is well illustrated in the Cortaro area (Wilson et al., 1983). Dramatic differences were reported (>90 m) in the elevation of the top of this unit throughout various wells in the area. This unit has been documented in well cuttings as far south at Township 15 and 16 South, Range 14 East by Laney (1972).

The Tinaja Beds unconformably overlie the Pantano Formation. Near the margins of the basin the unit consists of gravel and sand, grading laterally into a thick sequence of gypsiferous clayey silts and mudstones. The clasts are predominantly derived from volcanic rocks. In the northern portion of the basin, the Tinaja Beds are between 27 and 106 m thick, while along the center of the basin they vary from 60 to 120 m. The Upper Santa Cruz Fault is a northwest-southeast trending fault originating southwest of Tucson and continuing to about 11 km

southeast of Sahuarita, Arizona. East of the fault, the Tinaja Beds are greater than 360 m thick, resulting from down thrusting east of the fault (Schmidt, 1982). To the west of the fault, the Tinaja Beds are approximately 90 m thick. The Tinaja Beds store large amounts of water and yield small to large volumes of water to wells (Davidson, 1973).

The uppermost units in the Tucson basin are layers comprising the Fort Lowell Formation. The Fort Lowell Formation unconformably overlies the Tinaja Beds. Near the margins of the basin, the unit consists of gravel-sized material and grades to a weakly cemented silty-gravel in the central basin. The Fort Lowell Formation is extremely layered and is so characterized by its vertical and horizontal variability in lithology, texture, sorting and grain-size distribution. These layers are stream channel, floodplain, terrace and alluvial fan deposits. The complex interfingering of these layers makes correlation between wells, even those in close proximity to each other, extremely difficult. Structurally, the unit is only slightly faulted, and is between 90 and 120 m thick throughout most of the basin. The Fort Lowell Formation is the thickest highly permeable unit in the Tucson basin and is currently supplying most of the ground water extracted from the basin.

Transmissivities throughout the basin are highly variable. Fogg et al. (1979) reported values ranging from 278 to 6318 m<sup>2</sup>/day in the northern portion of the basin. A zone of high transmissivity exists along the Santa Cruz River floodplain north of the Rillito River junction. The Upper Santa Cruz River Basin Task Force (1983a) reported values ranging from 50 to 1863 m<sup>2</sup>/day in the southern and south-central

reaches of the basin. Schmidt (1982) and Fogg et al. (1979) agree that the specific yield (storage coefficient) ranges from 0.1 to 0.3 and that the finer sediments east of the Upper Santa Cruz Fault may be less than 0.1.

#### Ground-Water Pumpage and Recharge

The annual volume of ground water pumped from the Tucson basin has undergone about a five-fold increase since 1940 (Figure 3). Initially, the majority of the water was used for irrigation, but by 1980 ground-water usage was evenly divided between agricultural, industrial and municipal uses (Figure 3). The Tucson area currently uses some  $2.5 \times 10^8 \text{ m}^3$  of ground water annually.

Recharge primarily occurs along the ephemeral stream channels, either following a rainfall event or snowmelt. Figure 2 (in pocket) shows the basin-wide water table elevations. The contours indicate that a significant amount of recharge occurs along the Santa Cruz River channel and from the eastern reaches of the basin, which are drained by the Pantano Wash, Tanque Verde Creek, and the Rillito River. In the extreme northern portions of the basin, water flows from the Oracle Junction area southwesterly to the Santa Cruz River, paralleling Cañada del Oro. Recent investigations have verified earlier suggestions that an important part of the basin recharge is contributed along the mountain front areas (Olson, 1982; Mohrbacher, 1983; Thorne, 1983; and Merz, 1983). Man-made recharge sources primarily are the sewage effluent discharged to the Santa Cruz River and irrigation return flows.

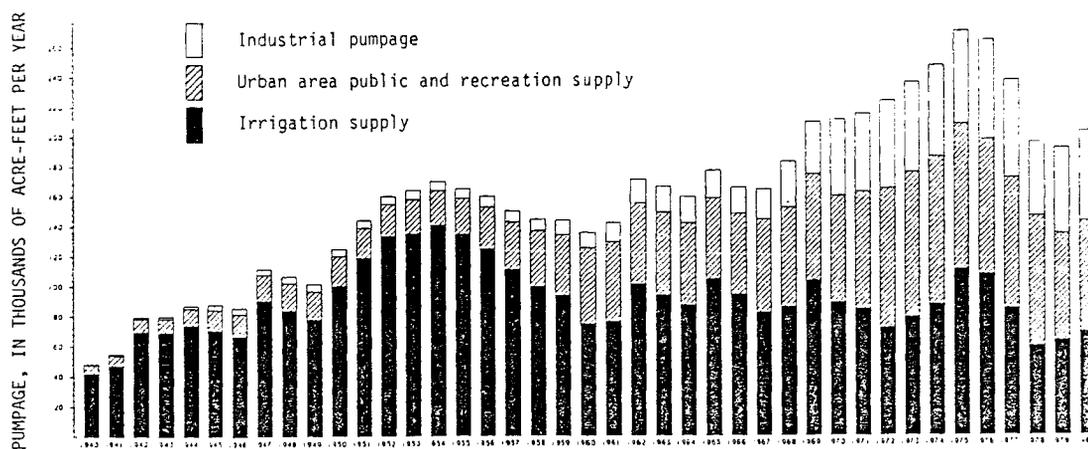


Figure 3. Annual ground-water pumpage in the Tucson basin, 1940-1980 (from Babcock et al., 1982).

Due to the significant overdraft of the ground-water supplies, the ground-water levels have undergone a steady decline since the early 1940's. The depth to water in the basin is highly variable. The shallowest depths occur along the Santa Cruz River (15-30 m), while in the higher elevations along the perimeter of the basin the depth to water can exceed 150 m.

### Ground-water Quality Characteristics of the Tucson Basin

#### Previous Investigations

The first major effort to define and characterize the chemical quality of ground water of the Tucson basin was conducted by Laney in the later 1960's. It was a basin-wide study extending from the Pima-Santa Cruz County line northward to the Rillito Narrows. In this study, Laney illustrated the impact that lithology and land use have on the chemical quality of the ground water. Since this investigation, much more information has been amassed and a number of other studies have been undertaken. The recent studies have been conducted on a more local scale. Figure 2 depicts roughly the areal extent of some of the study areas.

Wilson et al. (1983) investigated the impact that land use has on the chemical quality of the ground water in the Cortaro area (region A, Figure 2). An extensive sampling network was established to update the data base which already included all of the available historical water quality information from this area. From these data they were able to characterize each source, define three different ground-water quality zones and, most importantly, establish a multistage approach for

assessing the impact that surface waste sources have on the ground-water quality.

The Upper Santa Cruz River Basin Task Force (1983a, 1983b) focused their efforts on the southwestern portion of the basin (region B, Figure 2). The two investigations conducted were similar in scope. Basically, their goal was to define the region-wide ground-water quality characteristics. Little historical information is available in this area, so these studies were conducted over an extended period of time in order to establish any time dependent characteristics. This work provides a comprehensive summary of the ground-water quality characteristics.

The remaining areas denoted on Figure 2 (C, D, E and F) are completed, or soon to be completed, masters' theses (Mohrbacher, 1983; Olson, 1982; and Merz, 1983). The primary objective of all these theses is to quantify the volume of mountain-front recharge entering the Tucson basin on the basis of the in situ ground-water quality parameters. These theses afford a large amount of current data and informative interpretations of areas which previously were not considered as significant sources of recharge.

Some duplication exists in these investigations. However, as can be noted in Figure 2, a large majority of the basin has not been investigated. The most likely cause of this is the lack of wells which can be sampled. The southeastern portion of the basin is practically devoid of any wells. Those that are available produce limited quantities of water and may not be representative of the ground-water conditions.

## Overview of the General Chemical Quality

Generally, the chemical quality of the ground water in the Tucson basin is adequate for most purposes. The zones of heaviest pumpage (the shallowest zones) usually contain less than 500 mg/l of dissolved solids and the principal inorganic ions are calcium, sodium and bicarbonate. The deeper ground water (>213 m) also contains less than 500 mg/l total dissolved solids, however the principal ions are sodium and bicarbonate. Ground water from depths greater than 300 m generally has fluoride concentrations in excess of the recommended health standard (Laney, 1972).

Zones of poor-quality ground water have been noted primarily along the Santa Cruz River channel and some of its tributaries. Concentrations of TDS, chloride, sulfate, calcium, nitrate and bicarbonate tend to exceed the basin averages in these areas. The origin of these poor-quality zones could be due to the dissolution of relict salts along the stream channels, upward leakage of ground water from the Pantano Formation through the complex fault system or deep percolation of leachate emanating from wastewater treatment facilities and sanitary landfills.

Laney (1972) divided the ground water of the basin into 6 distinct types. The dominant type is a calcium-sodium-bicarbonate water. The poor-quality water is either a calcium-sulfate or sodium-sulfate (with more than 50 mg/l chloride present) type.

### Selected Major Constituents

The geographic distributions of the major ions characterized by Laney (1972) have been shown by more recent studies to have remained relatively unchanged. This section discusses briefly the distribution of five important constituents in the ground water of the Tucson basin: total dissolved solids (TDS), fluoride, chloride, nitrate and sulfate. The reader is referred to Laney (1972), Wilson et al. (1983), Upper Santa Cruz River Basin Task Force (1983a, 1983b) and Thurnblad (1983) for more detailed discussions and illustrations of these and other dissolved constituents.

Total Dissolved Solids. The total dissolved solids content of the shallow ground water in the Tucson basin is generally between 300 and 500 mg/l. The zones of highest TDS are parallel to the Santa Cruz River channel, in the Pantano Formation and Tinaja Beds along the north-east margin of the basin and along the major stream channels. Along the northern reach of the Santa Cruz River channel (north of Grant Road, in the Cortaro area) the origin of the zone of high TDS is probably due to the dissolution of relict salts, infiltration of sewage effluent and irrigation return flows. In the south, it could also be due to these factors in addition to some upward leakage of ground water from the Pantano Formation along the Upper Santa Cruz Fault. In the Region Wide Study area (Upper Santa Cruz River Basin Task Force, 1983a, 1983b) high TDS values were reported near the mine tailings ponds, near the Sierrita Mountain-piedmont junction. Down gradient from these areas, toward the Santa Cruz River channel, the TDS concentration decreases to about 300 mg/l, however the data suggest that some anomalously high concentrations

exist locally. In the Cortaro area (Wilson et al., 1983), anomalously high values have been noted near the Roger Road Wastewater Treatment facility, the septic tank areas to the west and northwest and in the vicinity of the I-10-Miracle Mile interchange.

The vertical distribution of TDS concentration is discussed by Laney (1972). It is primarily a function of lithology. Wells which are cased in or near the gypsiferous mudstones will yield poor-quality water, while those in the coarser basin-fill will usually yield water of much higher quality (<500 mg/l TDS).

Fluoride. Fluoride content of the shallow ground water is usually less than 0.5 mg/l throughout most of the Tucson basin. Elevated fluoride levels are common along the previously mentioned poor-quality zones and additionally along the mountain front areas. Ground-water samples from very deep wells (>300 m) have had fluoride concentrations in excess of 4 mg/l. Based on a limited amount of information, Laney noted that fluoride increases with depth throughout the basin, but not uniformly. A linear relationship between pH and fluoride has been recognized. The origin of the fluoride in the ground water is probably a result of the dissolution of minerals in the fluoride-rich volcanic rocks which are the dominant clasts comprising the Tinaja Beds and the Pantano Formation.

Chloride. The chloride content of the ground water generally does not exceed 30 mg/l except in the poor-quality zones. In the Cortaro area, shallow ground water paralleling the Santa Cruz River channel has a wide and high range of chloride concentrations (98-232 mg/l). High chloride concentrations are most likely a result of the

infiltration of sewage effluent and irrigation return flows. This band of water having high chloride concentrations does not extend very far on either side of the channel. West of the river the chloride values are within the basin norm. However, there are a number of local anomalies. The most prominent is an area which is significantly impacted by deep percolation of septic tank leachate (Wilson et al., 1983). High chloride concentrations in ground water are also associated with the gypsiferous mudstone units. Along the northeast margin of the basin a number of wells which are cased in the Tinaja Beds and the Pantano Formation yield water with very high chloride content. Thorne (1983) delineated a band of poor-quality water within and paralleling the Tucson Mountains (>200 mg/l chloride). Even though the ground water flows easterly from this region, toward the Santa Cruz River channel, the chloride content of the water in the adjacent basin-fill material does not exceed 50 mg/l. This suggests that the movement of this poor-quality water is restricted.

Nitrate. Nitrate content of the ground water in the basin usually does not exceed 5 mg/l. Nitrate concentration is highest in ground water close to irrigated farmlands, unsewered areas and the Santa Cruz River. High nitrate in the Cortaro area is a result of infiltration of sewage effluent, application of nitrogen fertilizers and septic tank leachate. Highest nitrate concentrations in this area are found in the septic tank area west of the river (40-94 mg/l) and represent some of the highest recorded in the basin. In the Region Wide Study area, a moderately sized plume of ground water with high nitrate content is detected north of Green Valley, parallel with the Santa Cruz River. The

most apparent cause is the sewage treatment facility at the southern end of this plume.

Concentrations of nitrate, unlike that of other constituents in the ground water, decrease vertically in the basin. Hem (1970) pointed out that most nitrate in ground water is organically derived and is most commonly the final product of the decomposition of organic matter. An abundance of plant life was at one time associated with the continually flowing Santa Cruz River. As the ground water levels declined, so did the plant life. The formerly abundant swamps may still be contributing to the high nitrate concentrations in the ground water along the river.

Sulfate. Sulfate concentration in ground water of the Tucson basin is highly variable. Principal natural sources of sulfate include the gypsiferous mudstone units and/or a constituent of the rock detritus that was deposited in the area. Sulfates are lowest in the northeastern portion of the basin and highest along the Santa Cruz River. The highest values of sulfate recorded in the Cortaro area are associated with the Roger Road wastewater treatment facility, the septic tank areas and cooling tower blowdown water. In the eastern portion of the Cortaro area, sulfate content is about 10 mg/l. In the Region Wide Study area, sulfate concentrations are highest in ground water along the Sant Cruz River and ground water affected by mine tailings pond leachate. In the eastern portion of the Region Wide area the sulfate content is roughly about 100 mg/l.

## CHAPTER 4

### DATA ACQUISITION

Samples were collected and analyzed from 107 wells throughout the study area (Figure 4, in pocket) in order to characterize the bromide-chloride relationship in the ground water of the Tucson basin. The ground water is recharged by runoff, occurring as a result of the winter and summer rains, and sewage effluent discharged into the channel of the Santa Cruz River. Bromide concentration of these waters is a function of natural processes and the activities of man. Therefore, two precipitation, six urban runoff and two sewage effluent samples (one from the outfall at each facility) are included in the sample network. The field work was conducted from December 1982 through October 1983. The following discussion includes the criteria for well and source selection, the field sampling methods and the analytical techniques employed.

#### Well Selection Criteria

The primary concern in collecting ground-water samples was to select and sample only those wells which were pumped a sufficient amount of time so as to yield representative ground-water samples (eliminate effects of surface contamination and sampling of stagnant water). Most of the wells sampled penetrate the upper 300 m of the basin-fill. The aquifer is assumed to be unconfined, but due to the complex origin of the sediments (extensive layering of silts, clays, sands and gravels) it

may behave in a locally confined manner in many places. Consequently, the various confined zones may have different aquifer and water quality characteristics. Ideally, defining the vertical distributions of chloride and bromide concentrations would prove useful to the overall interpretation. Unfortunately, the casings of most wells in the Tucson basin are perforated throughout their entire length below the water table. As a result, interpretation of the results is based on composite groundwater samples without the desired vertical control.

The greatest density of wells is in the central and northern portions of the basin. In the sparsely populated portions of the basin (particularly southeast of Tucson) wells which meet the requirements for sampling were hard to find. The four types of wells sampled in the study area are: municipal, irrigation, industrial and domestic. Thirty percent of the wells are domestic wells having small discharges, sampled only as a last resort when wells with a large discharge were not available. The remaining seventy percent are high discharge wells.

#### Field Sampling Methods

To minimize the possibility of sample contamination all the wells were sampled as close to the well head as possible. Only with rare exception was any sample drawn from a storage tank (well 37). Samples collected from the municipal, irrigation or industrial wells were usually taken after two hours of pumping. Domestic wells were not pumped for extended periods. Usually the owner would release water from the storage tank in order to allow the pump to engage. The pump was allowed to run as long as possible (5-30 minutes) before collecting the

sample. Water samples were collected and stored in 2-liter polyethylene bottles. No preservation was required for bromide or chloride. The samples were stored at room temperature (approximately 25°C).

At each well site electrical conductance (EC), pH, alkalinity and temperature measurements were made. A standard field sheet was filled out, noting, when possible, discharge, well depth, location, date, field parameter values and miscellaneous comments.

#### Surface Water Site Selection and Sampling

Selection of sites for runoff samples was primarily dependent on the location of the storms because the convective nature of the summer storms made it impractical to preselect a precise location for sampling. All runoff samples were collected within a two week period extending from July 26, 1983 to August 9, 1983. Samples which were judged to be representative of water which was eventually recharged were collected from ponded depressions at various locations throughout the study area. A standard field sheet was filled out at each site and samples were collected and stored in 2-liter polyethylene bottles. No field parameters were measured.

Samples of sewage effluent were collected from both the Ina Road and Roger Road wastewater treatment facilities. Each facility discharges treated effluent directly into the Santa Cruz River channel. The samples were collected from the large ponded areas formed by the discharging effluent. A sample was collected in a 2-liter polyethylene bottle after a few rinses with the effluent. No field parameters were measured.

The samples of precipitation were collected during two different storms at a site in the northern end of the City of Tucson. The collection device consisted of a plastic sheet draped over a wooden frame which created about  $1 \text{ m}^2$  of surface area. The sheet was set at an angle of approximately  $70^\circ$  off the horizontal. Precipitation ran off the sheet into a plastic-lined catchment from which the sample was taken. A large amount of time was required to accumulate a sufficient volume of sample. The precipitation samples were collected and stored in 2-liter polyethylene bottles. No field parameters were measured.

#### Analytical Methods

One of the important objectives of this study was to investigate the available techniques used for the analysis of bromide in aqueous solutions. Many of the analytical techniques reviewed were applied in cases where bromide was present in large amounts ( $>1 \text{ mg/l}$ ) and/or in solutions other than water. The concentration of bromide in ground water, precipitation and surface water is usually in trace amounts ( $<0.1 \text{ mg/l}$ ). Most of the analytical techniques are not designed for trace analysis, therefore lacking the necessary sensitivity and selectivity to insure a reasonable level of precision and accuracy in the results. The most frequently referenced techniques are: spectrophotometric (colorimetric) methods, high performance liquid chromatography (HPLC), gas chromatography (GC), specific ion electrode, neutron activation analysis (NAA), and X-ray fluorescence. Of these only the HPLC, NAA, GC, and the specific ion electrode were attempted. The following discussion

summarizes briefly the application of NAA and the bromide specific ion electrode.

Chloride detection was accomplished by titration with mercuric nitrate. This method is also summarized briefly in the following discussion.

### Neutron Activation Analysis

Neutron activation analysis (NAA) is a method for detection and quantification of the elemental composition of substances. NAA depends on the induction of radioactivity by neutron capture. When a sample is exposed to an intense thermal neutron source (i.e., in the immediate vicinity of a nuclear reactor core), a small fraction of the stable nuclei will capture neutrons, thereby transforming them into unstable, radioactive, ones. The number of these transformed nuclei is proportional to the original number of the parent nuclei and thus to the concentration of the corresponding element. The activity (rate of decay) is in turn proportional to the number of active nuclei. As an unstable isotope decays, gamma, alpha or beta rays may be emitted. Most frequently (in thermal-neutron capture reactions) the decay of an unstable isotope produces a beta particle followed by one or more gamma rays. Specific unstable isotopes can be identified by characteristic gamma ray energy(s) emissions (Wang et al., 1965, and Das et al., 1983).

A germanium-lithium (Ge-Li) detector is usually employed to assay radioactive samples because it has good energy resolution. Through the use of this detector, the energies of the gamma rays emitted by a specific unstable isotope can be quantitized. However, due to various

effects caused by the detector, the resulting signals are distributed around the characteristic peak energies (normal distribution).

Bromine-82, the activated isotope used in this study, has many characteristic gamma rays (Table 1). The gamma rays used in this study had energies of 554.34 keV (72.5 gamma rays/100 decays) and 776.50 (83.2 gamma rays/100 decays), and were selected because they are the most intense of the group.

The analytical process designed for the analysis of water samples required five steps: 1) Preconcentration of all samples (approximately a 10-fold concentration). This step was required to shorten reactor and detector time. 2) Aliquots of the concentrated samples were placed in 8 ml polyethylene vials. These vials were placed in an oven at 90°C in order to evaporate the water sample to dryness. 3) Vials were then sealed and loaded into the reactor. The samples were irradiated for at least 2 hours at a thermal neutron flux of  $7 \times 10^{11}$  neutrons/cm<sup>2</sup>-s. 4) The samples were counted after 4 to 5 days to allow the more intense gamma radiation of sodium-24 to decay to a level which would not interfere with the bromine determinations. Each sample was then placed in the Ge-Li detector for 400 seconds to count gamma ray emissions. 5) The output from the pulse height analyzer was recomputed by hand to determine gross and net counts and standard deviation in the peaks resulting from the 554.34 keV and 776.50 keV gamma rays.

In order to minimize the interference effects from sodium contamination, all vials were soaked in a dilute hydrochloric acid solution overnight, rinsed three times with deionized water, then placed in an oven until dry. Vials were only handled with gloves or tongs.

Table 1. Most probable gamma energies resulting from decay of Bromine-82  
(from Erdtmann and Soyka, 1973).

Gamma energy (keV)	Number of gamma rays/100 decays (%)
554.3	72.5
619.1	39.6
698.4	28.0
776.5	83.2
827.8	24.2
1044.0	28.0
1317.4	27.0
1474.9	17.0

Techniques for the removal of sodium from aqueous solutions were not used in this investigation in order to avoid sample contamination.

A 1-liter stock solution containing 1000 mg of bromide was prepared using potassium bromide and deionized water. Standards of 0.5, 1, 10 and 20 mg/l were prepared by serial dilution, and stored in 500 ml polyethylene bottles. In each sample run, two each of the 1 mg/l and 0.5 mg/l bromide standards were included among the unknowns. Additionally, one empty vial and one blank were included.

The average error in peak detection (counting) was about 8%, and there is as much as 5% error in preconcentration. The total error (~13%) is acceptable. These data are presented in Appendix A. For each sample, the bromide concentration as determined by the 554.34 keV and the 776.50 keV are given with the associated peak detection error. The bromide concentration used in this study is the average of the two peak values.

At the present time, both the cost and time factors are high in comparison with analytical techniques used for other inorganic ions. The preconcentration phase and reactor time are each about 2 hours. Every sample must be analyzed at least once in the Ge-Li detector, therefore a considerable amount of time is also required in this phase. Based on these time factors and miscellaneous equipment costs, the total cost for analysis of an individual sample is about \$40.00. This figure assumes that a large number of samples (>50) are to be analyzed.

### Specific Ion Electrode

The use of a bromide specific ion electrode is one of the most frequently applied techniques for detection and quantification of this ion in water. The accuracy and precision of the method are highly dependent on the abundance of interfering ions, the total ionic strength of the solution and the presence of complexing agents. The operational theory is based on the generation of electrical potential which is a function of the concentration of the specific ion.  $\text{Cl}^-$ ,  $\text{I}^-$  and  $\text{NH}_3$  are some common ions which, if present in sufficient amounts, can interfere with bromide detection, thus impairing the usefulness of the electrode. Preparation of standards requires the addition of a buffer to make the ionic strength roughly equal to that of the unknown sample. The calibration curve is prepared using the adjusted standards. Should a particular sample have an ionic strength which is different than the standards, the calibration curve will yield inaccurate values. The position of the calibration curve can be shifted by increasing or decreasing the total ionic strength of the standards. This suggests that serious error may result by using one calibration curve for all samples. The dominant complexing agents,  $\text{Pb}^{++}$ ,  $\text{Cd}^{++}$ ,  $\text{Ti}^{+++}$  and  $\text{Sn}^{++}$ , are not found in sufficient quantities in ground water to have any significant effect. The lower limit of bromide detection by specific ion electrode is about .4 mg/l. This is inadequate for most of the samples collected in the basin, because bromide concentration is generally less than .1 mg/l. To use this method, most of the samples had to be preconcentrated (approximately 10-fold). This raised the bromide concentration of the samples to within the detection limits of the electrode. Assuming that

the NAA gave the most accurate results, the specific ion electrode had anywhere from 50-100% error.

Chloride concentration was determined by the colorimetric technique recommended by ASTM (1981). Basically, a mixed indicator was added to an aliquot of sample, to which mercuric nitrate was titrated until the color of the solution reached the violet endpoint. The method was standardized for accurate application. The error in analysis was estimated to be about 5%, based on the determination of replicate samples.

## CHAPTER 5

### PRESENTATION AND INTERPRETATION OF RESULTS

The analytical results for the ground-water samples are tabulated in Appendix A. The data for urban runoff, precipitation and effluent samples data are presented in Table 2. The geographic distribution of bromide and chloride concentration and the Cl/Br ratios for the ground water of the Tucson basin are shown in Figures 4 and 5, respectively (in pocket).

#### Sources of Bromide and Chloride in the Tucson Basin

The origins of bromide and chloride in the ground water of the Tucson basin are from both man-made and natural sources. Bromide contributed through atmospheric precipitation is the most widespread source in the basin. The atmospheric bromide and chloride concentrations are due to both natural and man-made emissions. As previously mentioned, the natural bromide and chloride components are derived from sea water, whereas the man-made component is primarily from the combustion of leaded gasoline. The two precipitation samples from the Tucson basin, R-1 and R-2, were collected from two different storms about two weeks apart. These data are listed with chloride and bromide data from selected sites throughout the world in Table 2. With few exceptions, the Cl/Br ratios are relatively constant (30-120) over a wide range of concentrations. Sample R-1 has a Cl/Br ratio of 100 which compares

Table 2. Bromide and chloride concentrations of various sources from the Tucson basin and other parts of the world.

Location	Sample type	Bromide Concentration (mg/l)	Chloride Concentration (mg/l)	Cl/Br Ratio	Date Sampled	Reference
Tucson, Arizona	runoff	.027	4.2	156	8/9/83	1
Tucson, Arizona	runoff	.025	2.2	88	8/2/83	1
Tucson, Arizona	runoff	.12	5.1	43	7/26/83	1
Tucson, Arizona	runoff	.50	12.5	25	8/5/83	1
Tucson, Arizona	runoff	.048	2.2	46	8/17/83	1
Tucson, Arizona	sewage effluent (Roger Road)	.30	82.8	276	10/12/83	1
Tucson, Arizona	sewage effluent (Ina Road)	.18	70.6	392	10/12/83	1
Tucson, Arizona	precipitation	.017	1.7	100	7/20/83	1
Tucson, Arizona	precipitation	.004	2.2	579	8/9/83	1
	sea water	65.0	19000.0	300	-	2
Jerusalem	precipitation	.105	5.7	54	2/16/61	3
Jerusalem	precipitation	.122	5.6	46	2/16/61	3
Tel-Aviv	precipitation	.358	106.0	300	10/62	3
Haifa-Hadar	precipitation	.073	8.9	122	10/62	3
Daphna	precipitation	.061	4.6	76	2/63	3
Ein Harod	precipitation	.201	5.4	27	5/63	3
Sde Boker	precipitation	.261	3.5	13	62/63 (winter)	3
Nicosia	precipitation	.18	8.9	49	10/61	3
Prodromos	precipitation	.17	1.8	11	1/62	3
Hilo, Hawaii*	precipitation	.019	7.1	372	5/24/63	4**
Hilo, Hawaii*	precipitation	.010	1.3	125	5/30/63	4**
Hilo, Hawaii*	precipitation	.009	1.2	129	5/30/63	4**

Table 2. Continued

Location	Sample Type	Bromide Concentration (mg/l)	Chloride Concentration (mg/l)	Cl/Br Ratio	Date Sampled	Reference
Hilo, Hawaii*	precipitation	.007	.739	106	5/30/63	4**
Kulani, Hawaii***	precipitation	.037	7.9	214	6/17/63	4**
Kulani, Hawaii	precipitation	.048	10.8	225	6/17/63	4**
Kulani, Hawaii	precipitation	.09	15.6	170	6/17/63	4**
Kulani, Hawaii	precipitation	.006	.532	89	6/17/63	4**
Kulani, Hawaii	precipitation	.020	2.25	113	6/17/63	4**
Kulani, Hawaii	precipitation	.014	2.42	173	6/17/63	4**
Hamilton, Ontario***	precipitation	.110	5.4	49	1/9/68	5
Hamilton, Ontario	precipitation	.105	7.0	67	1/9/68	5
Hamilton, Ontario	precipitation	.165	14.0	85	1/9/68	5
Hamilton, Ontario	precipitation	.075	6.6	88	1/9/68	5
Hamilton, Ontario	precipitation	.100	7.8	78	1/9/68	5
Hamilton, Ontario	precipitation	.040	3.4	85	1/9/68	5
Hamilton, Ontario	precipitation	.040	2.9	73	1/9/68	5
Hamilton, Ontario	precipitation	.007	.40	57	1/26/68	5
Hamilton, Ontario	precipitation	.004	.32	80	1/26/68	5
Hamilton, Ontario	precipitation	.009	.54	60	1/26/68	5
Hamilton, Ontario	precipitation	.006	.51	85	1/26/68	5
Hamilton, Ontario	precipitation	.012	.35	29	1/26/68	5
Hamilton, Ontario	precipitation	.009	.35	39	1/26/68	5
Hamilton, Ontario	precipitation	.007	.43	61	1/26/68	5
Hamilton, Ontario	precipitation	.004	.25	63	1/26/68	5

\* Collected from same location (ø m altitude), at different times throughout the same storm.

\*\* Only a partial listing of available data from this reference.

\*\*\* This and following samples were collected in approximately the same local except from altitudes of 1000, 2000, 3000, 4000, 1700 and 1700 meters, respectively.

\*\*\*\* From collection stations throughout this area during a given storm.

- 1 This investigation
- 2 Hem (1970)
- 3 Bloch et al. (1966)
- 4 Duce et al. (1965)
- 5 Harriss and Williams (1969)

favorably with other areas, however, sample R-2, with a ratio of 579 indicates an abundance of chloride in the atmosphere. The reason for this is unknown, but is most likely due to analytical error or sample contamination.

Runoff occurs when the precipitation intensity exceeds the infiltration rate. Land use can have a significant impact on the chemical quality of the runoff as the runoff flows over the land surface. Natural runoff represents a large component of the recharge in the Tucson basin, so the quality and the movement of that recharge is of particular interest. Six urban runoff samples were collected from the Tucson basin and analyzed. The bromide and chloride concentrations ranged from 0.025 to 0.5 mg/l and 2.2 to 12.5 mg/l, respectively. The samples were collected from locations where runoff waters had ponded. The ponded waters were not indicative of any one source but represented inflow from a number of local areas. Bromide and chloride concentrations were highest in samples R0-4 and R0-5. These samples were collected from the initial pulses of runoff from their respective storms. Samples collected during the latter stages of a storm tended to have lower chloride and bromide concentrations. The data suggest that some residual bromide and chloride ions must be deposited on the ground surface between rainfall events and that the initial pulses of runoff carry most of it away. The runoff samples collected later in storms have concentrations of bromide and chloride which are comparable to those of precipitation (see Table 2). Therefore, the chemical quality of the runoff samples collected later in the storm are probably the most representative of the recharging runoff.

Bromide and chloride are also introduced to the ground water in the Tucson basin through the recharge of sewage effluent. Effluent samples from both the Ina Road and Roger Road wastewater treatment facilities were collected and analyzed. Most of the municipal and industrial sewage of the region is handled by these two plants. The plants are located in the northern portion of the basin, along the Santa Cruz River in the Cortaro area. The Roger Road plant is south of the Ina Road plant and handles mostly industrial wastes. The bromide concentration of the effluent from the Roger Road facility is 0.30 mg/l. The Ina Road facility predominantly treats domestic waste and the bromide concentration of its effluent is 0.18 mg/l. The chloride concentrations of the two plants are comparable, about 70 mg/l. The bromide concentrations of the effluent discharged by the two plants are higher than the native ground water (<0.1 mg/l), which is used as the transporting medium. This is due to the nature of the wastes delivered to and treated by the treatment plants. Treatment processes do not normally concentrate the influent enough to cause such an effect on the effluent. The Cl/Br ratios of the two effluent samples are higher than ground water, suggesting that some amount of excess chloride is introduced (see Sawyer and McCarty, 1978). Therefore the Cl/Br ratio can serve as a means to tag the impact and movement of the recharging effluent.

There are no identified geochemical sources of inorganic bromide in the Tucson basin. Soluble clasts and sediments (gypsum and anhydrite) can cause increases in the calcium, sulfate and sodium concentrations of the ground water, however, bromide is not a constituent of

these materials. Insoluble clasts may contain bromide, however, groundwater flow velocities are rapid enough (15 cm/day) that the water may not chemically equilibrate with the basin-fill material.

Water recharging the aquifer from the mountain-front areas primarily flows through fractures. The residence time of the water in the fractures is probably not long enough to allow the migrating water to chemically equilibrate with the surrounding media. If by chance the water remained in contact with the porous media (or fractured rock) for a sufficient period of time to allow the dissolution of water soluble ions, the bromide content of most rock types is so low that the increase in bromide content of the water would be negligible.

#### The Distribution of Bromide and Chloride in the Tucson Basin

Based on the distribution of bromide shown in Figure 4, four different water quality zones can be inferred. The central zone is the largest, characterized by bromide concentrations which are less than 0.1 mg/l. This area extends from the Santa Rita Mountains in the southeast to the Tortolita Mountains in the northwest and includes the central portion of the basin. The eastern zone is defined by bromide concentrations which exceed 0.1 mg/l and is along the eastern flank of the central zone. The northwestern zone, along the northern portion of the western flank of the central zone, is characterized by bromide concentrations which generally exceed 0.2 mg/l but are less than 1 mg/l. The southwestern zone lies south of the northwestern zone. The southwestern zone is characterized by bromide concentrations which exceed 0.1 mg/l but are generally less than 0.2 mg/l except for an anomalous area in the

southern end of this zone. The chloride distribution follows the same trends as bromide.

#### Central Zone

The direction of ground-water flow is toward the northwest throughout most of this zone. The underflow comes from the Rincon and northern Santa Rita Mountains. In the section of the central zone north of Grant Road, the ground water flows toward the southwest, coming from the Santa Catalina and Tortolita Mountains and the Oracle Junction area. As the underflow in this region moves toward the basin center it changes flow direction to northwesterly, in the direction of regional ground-water flow.

Land use differs dramatically throughout this zone. Most of the central portion of this zone is classified as urban built up. The amount of surface area available for the infiltration of runoff is severely restricted by the large expanses of asphalt and concrete. Runoff is channeled to the major washes through the streets. The land south of the city is primarily undisturbed desert. The drainage network is comprised of major and minor washes, affording ample opportunity for the infiltration of runoff. North of the city much of the land is under development. All of this area is sewered and there is ample area available for infiltration of runoff, particularly in the areas approaching the northern boundary of the study area.

Despite the differences in land use and sources of recharge throughout the central zone, the bromide and chloride concentrations in the ground water are relatively constant. Ground water in this zone has

the lowest bromide and chloride content in the basin. Bromide concentrations are generally less than 0.1 mg/l while the chloride concentrations vary between 2.5 and 17 mg/l. As can be noted in Figures 4 and 6, the Cl/Br ratios of the samples collected in this zone are relatively constant (130), but greater than those of the runoff samples (25-100). This is attributed to the dissolution of chloride by the infiltrating runoff rather than attenuation of bromide as ground water moves through the subsurface. The data suggest that the central zone is not affected noticeably by activities on the surface and probably best represents the natural background concentrations of bromide and chloride in the ground water of the Tucson basin.

#### Northwestern Zone

The bromide and chloride data suggest that the ground water in the northwestern zone is affected by man's activities. The ground-water flow in this zone is toward the northwest and the land use is highly variable. In the north, agricultural lands dominate. The east-central and southern reaches are sewered and the west-central portion of the northwestern zone has unsewered areas. Bromide concentrations are generally greater than 0.2 mg/l but less than 1 mg/l in this zone. The chloride content of this zone is also higher than the central zone. The elevated bromide and chloride concentrations can be attributed to a number of sources, none of which affects the ground water of the central zone. The sources include: 1) recharge by sewage effluent, 2) irrigation return flows, 3) miscellaneous local pollution sources and 4) underflow of poor-quality water coming from the Pantano Formation.

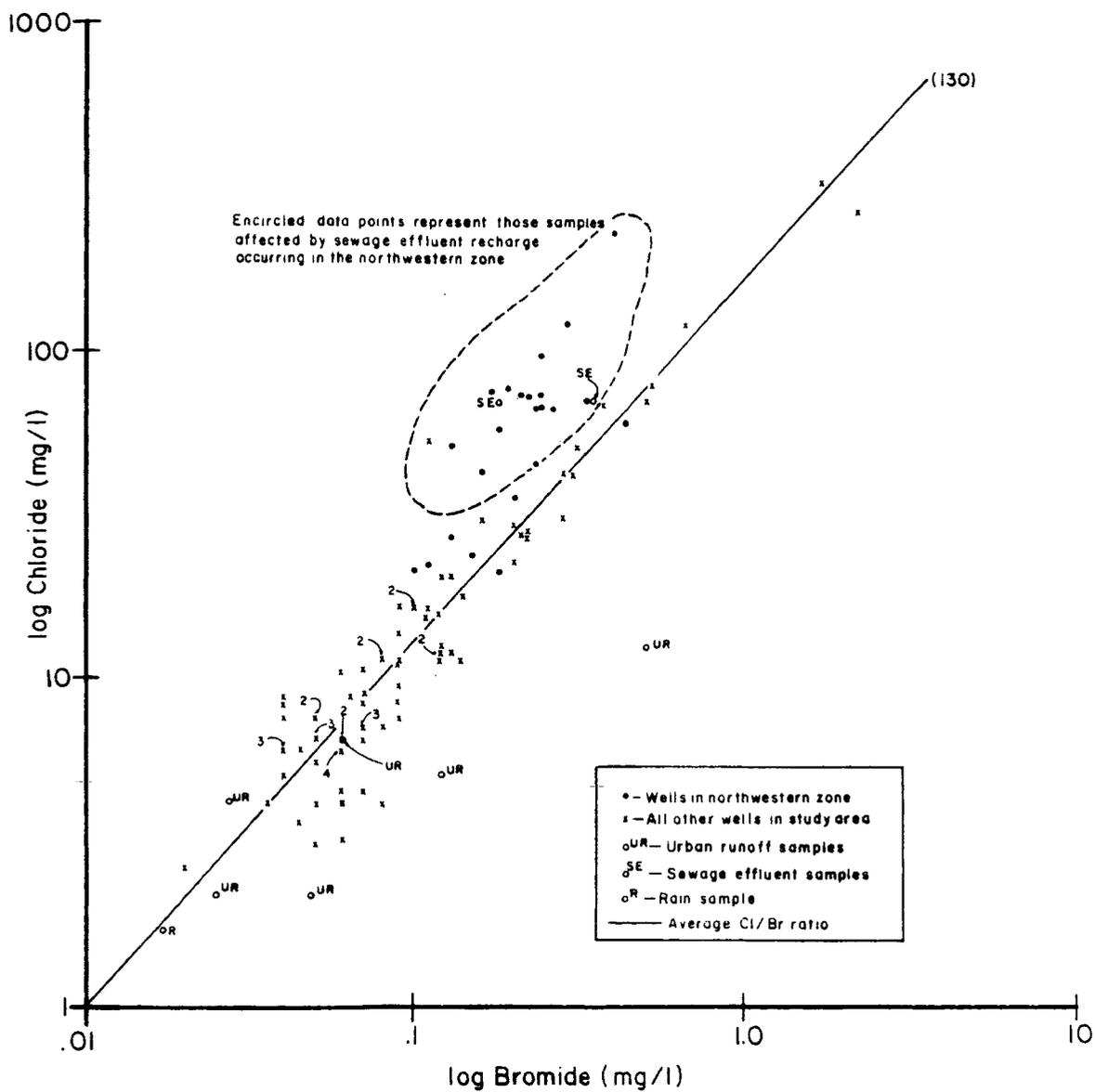


Figure 6. Scattergram of chloride vs. bromide in milligrams per liter.

Wilson et al. (1983) noted the existence of a number of poor-quality surface waters in the northwestern zone which, as recharge, seriously affects the quality of the ground water. The principal types of recharge appear to be irrigation return flows and sewage effluent. Bromide and chloride concentrations in the ground water of this zone illustrate the impact of these two sources. The bromide concentration of sewage effluent from the Roger Road treatment facility is about 0.30 mg/l and that of the Ina Road facility is 0.18 mg/l. Assuming a 1:1 mixture of the two effluents is reaching the ground water, the expected concentration would be about 0.24 mg/l bromide. Indeed, the bromide concentrations of the sampled wells along the Santa Cruz River roughly approach this value. The same effect is noted in the chloride concentrations. The chloride concentration of the Ina Road plant effluent is about 71 mg/l and the Roger Road plant is about 83 mg/l. The expected concentration in the ground water would be about 77 mg/l, which is close to those measured. Irrigation return flows are recognized as a potential source for affecting the general chemical character of the ground water; unfortunately no sample from this source was collected. If the irrigation return flows were contributing bromide and chloride in excess of the effluent, the ground-water samples would have reflected it. The impact of the irrigation return flows on the ground-water quality in this part of the northwestern zone is probably less than that of the sewage effluent.

Historical data from this area suggest that a poor-quality zone existed in the ground water along the Santa Cruz River channel before the recharge of man-made sources played a dominant role (Wilson et al.,

1983). As mentioned earlier, the Pantano Formation is a source of poor-quality water. Due to faulting, the Pantano Formation lies close to the surface along the western side of the Santa Cruz River (Figure 7). Leakage occurs across the vertical interface into the Tinaja Beds and Fort Lowell Formation. However, samples collected from wells in these units do not reflect the leakage.

The distribution of bromide in this region of the basin supports the delineation of the high- and low-quality zones depicted by Wilson et al. (1983, see Plate 16). Their boundary separating high- and low-quality zones coincides with the boundary separating the central zone from the northwestern zone defined in this investigation. Eastward from the Santa Cruz River, the bromide concentration in the ground water abruptly decreases in a short distance. For example, well 9 is 0.6 km from well 10 and the bromide concentrations are 0.21 and 0.09, respectively. The sharp eastern edge of the poor-quality plume of ground water probably results from a combination of factors. The longitudinal extent of the plume is influenced by the northwesterly flow of ground water. The transverse migration of the plume is controlled by the slow ground-water flow and the underflow of higher quality water coming from the northeast. The data suggest that the poor-quality water is displacing the native ground water, with minimal mixing occurring at the interface between the poor- and high-quality waters.

The Cl/Br ratios of the ground-water samples collected north of the Roger Road treatment plant indicate that the sewage effluent is the dominant form of recharge to the aquifer in this area. In Figure 6, a cluster of samples are shown which have significantly greater Cl/Br

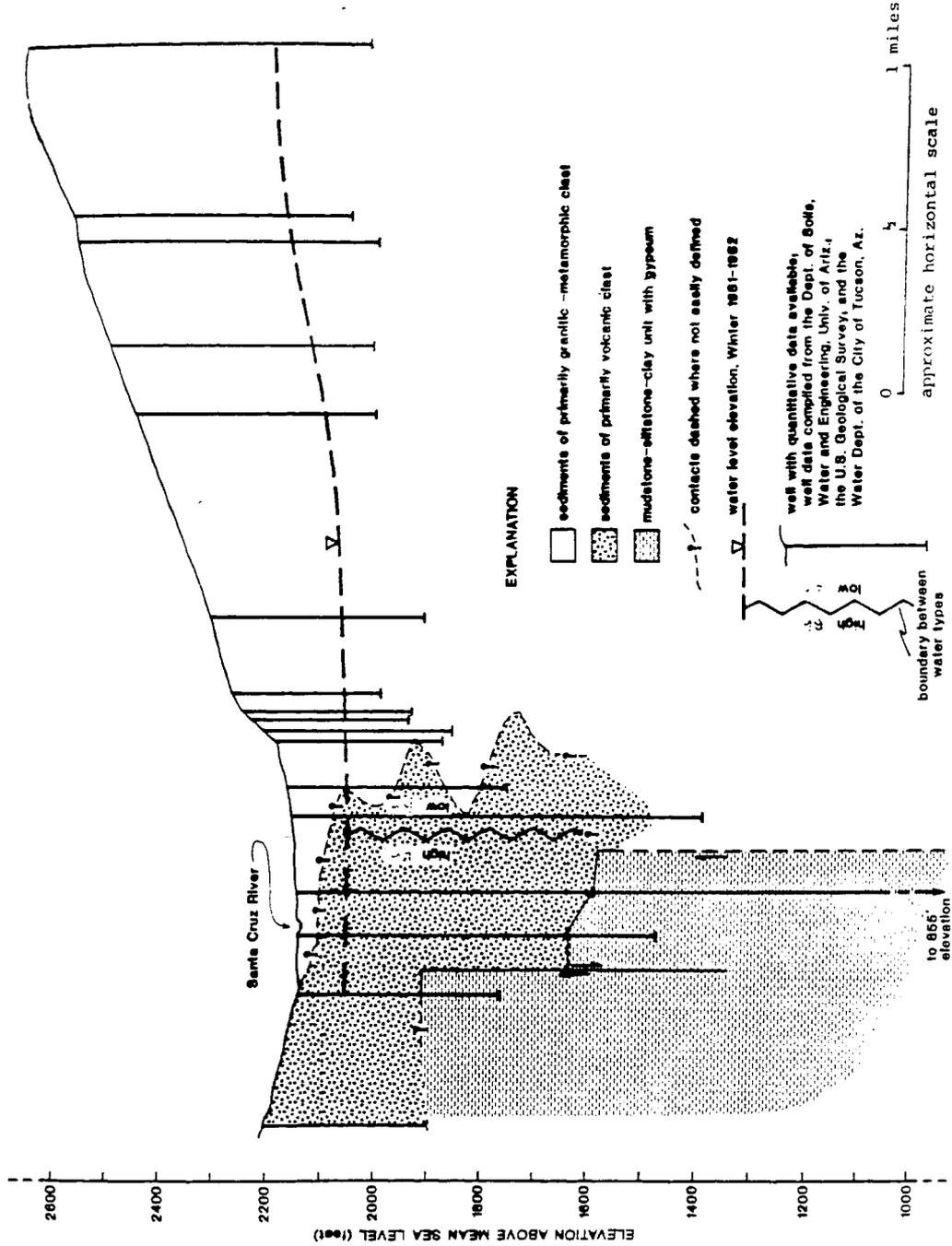


Figure 7. East-west cross-section through a portion of the northwestern zone (adapted from Wilson et al., 1983).

ratios than the average ratio in the basin. All the samples in the cluster are from wells north of the Roger Road treatment plant, along the channel of the Santa Cruz River. The Cl/Br ratios of the samples of effluent are included in this figure. These data also lie within the previously mentioned cluster of well data. This suggests that ground water in the northwestern zone is most affected by recharge of sewage effluent.

Ground water upgradient (south) of the sewage treatment plants should not be affected by the recharging sewage effluent. Wells 38, 39, 40, 42 and 43 lie east and south of the Roger Road treatment plant. The bromide and chloride concentrations are high and the Cl/Br ratios are all above the average basin ratio. The wells lie in an area which was formerly irrigated farmland. Despite the fact that there is no longer any irrigation in this area, the ground water may still be affected by remnant return flows which are, as yet, migrating through the unsaturated zone. However, the effect is probably small. The magnitude of the Cl/Br ratios of the wells suggests a source similar to the wells north of the Roger Road treatment plant; however, it is not likely that the effects of the sewage effluent recharge could have migrated this far east and south. There may be some previously unrecognized point source which is affecting the ground water in this area or possibly some lithologic influence. A lack of samples from this area prevents the testing of either hypothesis.

Well 44 lies south of the Roger Road treatment plant and has an anomalously high Cl/Br ratio. About 0.5 km southeast of this well, cooling tower blowdown water is discharged into the Santa Cruz River

channel. Water used in this capacity generally becomes concentrated a number of times and, in addition, additives are used which inhibit scale formation on the towers. Although no sample was collected, the proximity of this source to well 44 suggests it may affect the quality of the ground water.

Thorne (1983) investigated the quality of the ground water along the eastern flanks of the Tucson Mountains. Although outside the present study area, underflow coming from the Tucson Mountains could be affecting the ground water in the basin-fill material. Thorne collected a number of water samples from wells in both the bedrock and adjacent basin-fill material. The data indicate that a band of poor-quality water exists in the bedrock, paralleling the flanks of the mountain and, in some places, extending into the basin-fill material. Bromide and chloride results are included in the data base; however, the bromide data may not be accurate (the analytical technique used was the specific ion electrode). He concluded that brines or bitterns trapped in the fractured volcanic rocks may be the cause of the poor-quality band of ground water. No wells were sampled in this area to substantiate his conclusions.

#### Eastern Zone

The eastern zone is characterized by high concentrations of bromide and chloride in the ground water. Bromide concentrations generally exceed 0.1 mg/l and have been recorded as high as 2.24 mg/l. Few available wells are in this area of the basin; thus, the areal extent of this zone is rather poorly defined, especially along the southwest

facing flank of the Santa Catalina Mountains. The underflow in the zone emanates from the Molino Canyon area in the Santa Catalina Mountains and flow is toward the west. One characteristic which makes this zone different from the other areas in the basin is the widespread outcrop of the Pantano Formation and Tinaja Beds (see Figure 4).

Land use in the eastern zone is principally undeveloped desert. Industrial activities do not exist in the eastern zone, therefore groundwater samples should be representative of the natural system.

North of Tanque Verde Creek there are twelve wells which have a wide range of high bromide concentrations. Wells 49, 53, 54, 55, 57 and 59 are screened in either the Pantano Formation or the Tinaja Beds and wells 52, 56 and 58 are screened in the Fort Lowell Formation. Wells 49, 50 and 51 only pump water from the fractured gneissic bedrock. The unperforated casing extends from the land surface to the top of the bedrock. The remainder of the well consists of an open hole, from which the supply is drawn.

A simplified north-south cross section of the area in question is depicted in Figure 8. Recharge to the aquifer is from either surface infiltration or the baseflow from the mountains. Most of the surface runoff flows over the low-permeability Pantano Formation and Tinaja Beds and infiltrates the coarser basin-fill sediments. Precipitation entering fractures in the bedrock at higher elevations may recharge the aquifer as underflow. Because the low-permeability units are in direct contact with the bedrock, recharging water must flow through the low-permeability units to the coarser basin-fill material. However, Mohrbacher (1983) pointed out that flow across the interface between the

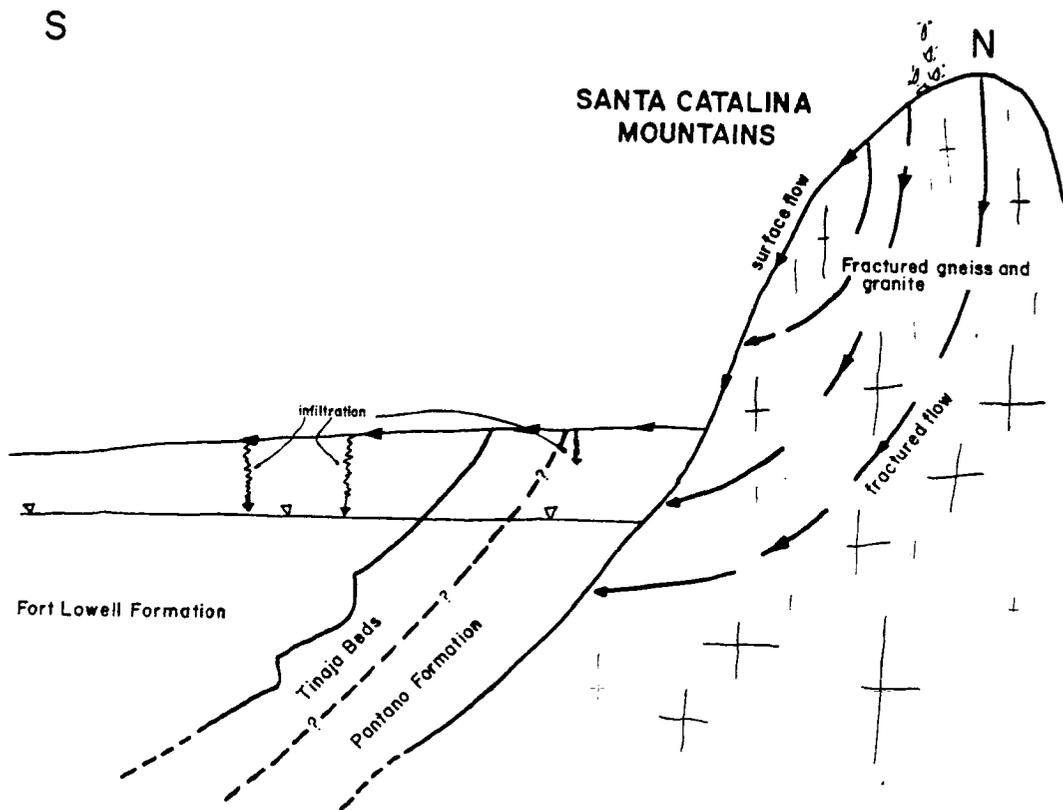


Figure 8. Simplified north-south cross-section through a portion of the eastern zone.

low- and high-permeability units is probably negligible. General chemical quality of ground water in the eastern zone is poor. Previous interpretations of the source of the poor-quality zone usually focus on lithologic effects. However, the distribution of bromide with respect to chloride reveals another possible interpretation.

As can be noted in Figure 4, the distributions of bromide and chloride do not appear to follow any regional or local trends. The absolute concentrations of the two ions are considerably higher than any sample from the central zone. The three wells cased in the fractured bedrock have the lowest concentrations in the area, but are still higher than those found in the central zone. However, the Cl/Br ratios of the ground-water samples in the eastern zone are not significantly different from the basin average (130). It can be suggested that ground-water pumped from the low-permeability sediments of the eastern zone represents a concentrated form of the atmospheric water recharging the basin. However, there are no surface impoundments which concentrate runoff and periodically allow it to recharge the ground water in this area.

The sediments comprising the Pantano Formation and the Tinaja Beds were deposited in playas which inundated this area during Tertiary time. Numerous gypsiferous mudstone units in the Pantano Formation indicate that playa water must have concentrated sufficiently to allow the precipitation of gypsum and anhydrite. The Cl/Br ratio of waters which recharged the playas is unknown, but was probably similar to recent ratios. Recharge to these playas was probably infrequent, allowing the stagnant waters (brines) to evaporate, thereby concentrating the chemical constituents (Blatt et al., 1972). Chloride and bromide are

not volatile and therefore would not be removed during evaporation. The Cl/Br ratio would have remained relatively constant. Some of the brines may have been entrapped within the pore spaces as these playas filled with sediment. The high bromide and chloride content of ground-water samples collected from wells 52, 56 and 58 suggest that a plume of poor-quality water is emanating from the low-permeability units into the coarser basin-fill material. The ground-water velocity through low-permeability units is probably very slow, therefore displacement of the poor-quality water by more recent, higher-quality, recharge through the subsurface is negligible. Those wells pumping from the low-permeability units may be pumping the old brines.

Interpretations of the source of poor-quality water in the northeastern part of the eastern zone which focus on lithologic effects may only apply to certain dissolved chemical constituents in the ground water. The dissolution of gypsum will cause increases in calcium and sulfate content of the ground water. It is expected that little, if any, chloride or bromide would be available from dissolution of these units. Crystalline rocks make up a majority of the clasts in the coarser basin-fill sediments and are not expected to yield significant quantities of bromide and chloride. Water passing through the clasts probably does not remain in contact long enough to allow chemical equilibrium. There are no known lithologic units which can contribute appreciable amounts of bromide through dissolution. The evidence does heavily favor the hypothesis that old brines may be the source of the poor-quality water.

Wells 77, 78, 79, 82 and 83 lie south of the Tanque Verde Creek and are cased in the coarser basin-fill material (Fort Lowell Formation) (Laney, 1972). With the exception of well 77, all the wells have bromide and chloride concentrations which are intermediate between the central and eastern zones. The ground-water quality in this area may be a result of mixing between poor-quality water emanating from the Pantano Formation and higher-quality storm runoff. The Cl/Br ratios of these wells are close to the average basin ratio, therefore suggesting no contribution from anthropogenic sources. Well 77 is located close to Tanque Verde Creek and may be pumping recent meteoric water which has not been in contact with the low-permeability sediments.

#### Southwestern Zone

The flow of ground water in the southwestern zone is toward the north-northwest, roughly paralleling the Santa Cruz River channel. Based on water elevation data (Figure 2), most of the ground water originates south of the basin, however, some mountain-front recharge comes from the Sierrita and southern Santa Rita Mountains. The southwestern zone is characterized by bromide concentrations which exceed 0.1 mg/l but are less than 0.2 mg/l.

Land use in the southwestern zone, and just outside of it, is quite varied. A large expanse of agricultural land has been developed along the Santa Cruz River channel south of the City of Tucson. Northward, toward Tucson, the area is urbanized. The boundaries of the zone are limited to the extent of the sampling network; however some of the land use practices outside of this zone need to be mentioned. A

number of large mine tailings ponds are in operation in the higher elevations along the flanks of the Sierrita Mountains, southwest of the southwestern zone. A few small communities discharge their sewage effluent into the Santa Cruz River channel south of the southwestern zone. The sewage effluent is primarily domestic wastes.

The anomalous bromide and chloride concentrations measured in ground-water samples collected in the southern reach of the southwestern zone are probably caused by irrigation return flows, because the sampled wells were close to agricultural lands. Ground water which is used for irrigation will concentrate through evaporation and transpiration before percolating. The result is a poor-quality water which will affect the chemical quality of native ground water. Cl/Br ratios of the samples from this area are close to the average basin ratio. This contrasts with water from irrigation wells in the Cortaro area which have higher Cl/Br ratios and are affected by recharge by sewage effluent and irrigation return flows.

Coverage of the rest of the southwestern zone is sparse but the trend of higher bromide and chloride concentrations in ground water is apparent (wells 60, 61, 62, 63, 64, 98, 99, 100). The elevated levels suggest a source of bromide and chloride in addition to atmospheric contributions. The general ground-water quality along this reach of the Santa Cruz River is poor (Laney, 1972). Upward leakage along the Upper Santa Cruz Fault is frequently pointed to as being the means by which poor-quality water is transmitted to the shallow ground water.

Cl/Br ratios of samples collected in the southwestern zone are close to the basin average, suggesting that ground water in this zone

has a common origin with those of the central zone. The higher bromide and chloride concentrations imply that during some stage of evolution the source waters were concentrated. It may be possible that upward leakage from the Pantano Formation or the Tinaja Beds is brackish or saline water from old lake sediments. There are no samples from wells in the more mountainous terrain to the west, so the quality of the mountain-front recharge along the western boundary of the southwestern zone is unknown.

#### Summary

The purpose of this study was to investigate the use of bromide as an environmental tracer. Bromide is a conservative ion, existing in ground water in trace amounts. Due to its conservative nature, it should be a useful indicator of the migration of both surface and sub-surface sources of recharge to an aquifer. However, the bromide distribution in ground water has seldom been used in this capacity. This is likely due to the lack of an analytical technique which can accurately and precisely detect bromide in trace amounts.

In order to fulfill the objective of this study, the bromide distribution of the ground water in the Tucson basin was measured. Ground-water samples were collected and analyzed for bromide and chloride content from throughout the basin. Additionally, samples of sewage effluent, urban runoff and precipitation were similarly treated. Neutron activation analysis was used to detect and quantify bromide in all samples. From the data, a hydrogeological interpretation was prepared

and compared to interpretations from previous investigations in the basin.

The bromide concentrations in the ground water of the Tucson basin range from 0.036 mg/l (well 34) to 2.24 mg/l (well 55) and for chloride concentration the range was from 3.2 mg/l (wells 22 and 27) to 332.2 mg/l (well 54). The average basin Cl/Br ratio is 130. Based on the geographic distribution of bromide, four ground-water zones are defined. Each is distinctly defined, characterized by differing degrees of influence from natural and/or anthropogenic sources of recharge.

The central zone, besides being the largest region, has the lowest concentrations of bromide and chloride in the Tucson basin. The average Cl/Br ratio is 130, comparing favorably with the precipitation and runoff samples. The ground water in this zone most likely represents the natural background conditions.

The data indicate that the ground water in the northwestern zone is affected the greatest by man's activities. Bromide concentration is greater than 0.1 mg/l and the Cl/Br ratios are significantly greater than the average basin ratio. The bromide and chloride concentrations and the Cl/Br ratios of effluent samples are similar to the ground-water samples collected in the northwestern zone, illustrating the influence of effluent recharge. This compared favorably with the interpretations by Wilson et al. (1983). However, the influence from other sources they noted were not detected.

Although the number of samples defining the eastern zone is small, a great deal of information was gained. The ground water in this zone, like the central zone, is affected only by natural sources of

recharge. The similarity of the Cl/Br ratios in the eastern zone to the central zone attests to this interpretation. However, the bromide and chloride concentrations are an order of magnitude higher. The source of the highly concentrated water is believed to be from brine filling the pore space of the low-permeability playa sediments. Laney (1972) and Mohrbacher (1983) noted the presence of poor-quality ground water in this area but attributed it to lithologic effects.

The southwestern zone is characterized by bromide concentrations which, except for an anomalous region in the south, are greater than 0.1 mg/l but less than 0.2 mg/l. Cl/Br ratios are close to the average basin ratio, suggesting that natural sources of recharge are impacting the ground water. However, the anomalously high concentrations in the southern portion of this zone are probably caused by irrigation return flow. The remainder of the area may be affected by upward leakage from the low-permeability units along the Upper Santa Cruz Fault.

## CHAPTER 6

### CONCLUSIONS

The results of this study substantiate the hydrogeologic interpretations drawn by previous investigators. This suggests that bromide can be effectively used as an environmental tracer. Further, the Cl/Br ratios can be used to evaluate the extent of the effect of various types of recharge on ground water. Neutron activation analysis proved to be the most accurate and precise analytical method for detection and quantification of bromide in dilute natural water.

APPENDIX A

WELL AND SOURCE SAMPLE DATA

Table A1. Well sample data

Well Number	Location	FIELD PARAMETERS				BROMIDE CONCENTRATION BY NAA (mg/l)									
		Electrical Conductivity (µmhos)	pH	Temperature (°C)	Alkalinity (mg/l as CaCO <sub>3</sub> )	Total Depth of Well (m)	Chloride Concentration (mg/l)	Concentration Ratio*	554 key Error	Percent Error	776 key Error	Percent Error	Average	** C1/Br Ratio	Date Sampled
1	12-12-8 dba	900	7.11	22.7	215	261	74.5	-	.21	9.7	.24	9.7	.220	298	3/14/83
2	16 bba <sub>1</sub>	700	7.16	22.8	161	270	57.9	-	.17	11.8	.18	11.6	.176	290	3/14
3	16 bba <sub>2</sub>	660	7.32	22.8	167	700	51.5	-	.14	13.1	.13	14.6	.130	396	3/14
4	16 bdc	700	7.30	24.5	156	586	42.8	-	.14	13.8	.18	11.4	.160	268	3/14
5	16 bcb	920	7.20	22.7	219.5	242	68.2	-	.26	8.8	.22	10.7	.240	284	3/14
6	17 daa	920	7.33	23.7	202	661	66.7	-	.24	9.9	.28	8.8	.260	257	3/14
7	21 baa	950	7.23	24.1	210	566	67.7	-	.22	10.1	.24	10.3	.230	294	3/14
8	21 cad	1050	7.23	-	250	198	75.5	-	.16	13.5	.17	14.5	.170	444	7/28/83
9	21 dcd	990	7.22	22.1	237	300	73.6	-	.25	9.3	.18	13.5	.210	350	3/14/83
10	22 ddb	270	7.57	25.9	108	1033	7.6	10.16	.81	7.2	.94	7.0	.087	87	3/14
11	24 cad	250	8.00	27.3	102	610	4.6	12.95	.77	8.0	.86	8.3	.063	73	3/1/83
12	26 bca	580	7.21	24.5	136	312	27.1	11.85	1.60	4.3	1.55	5.1	.133	204	3/14/83
13	34 cac	495	7.00	23.0	-	200(?)	21.3	12.15	2.08	4.7	2.30	5.0	.180	118	12/20/82
14	34 d	620	7.53	25.0	-	178	35.4	-	.20	9.5	.19	10.2	.200	177	12/20
15	36 cca	970	7.07	21.0	-	362	73.6	8.18	2.00	3.3	1.90	3.8	.240	307	12/21/82
16	12-13-1 adc	230	7.60	23.9	103	-	4.2	-	.05	22.0	.06	19.0	.052	81	3/1/83
17	12 caa	232	7.37	22.5	101	-	6.6	10.00	.59	5.8	.52	7.2	.056	132	3/1

Table A1. Well sample data, Continued

Well Number	Location	FIELD PARAMETERS				BROMIDE CONCENTRATION BY NAA (mg/l)									
		pH	Electrical Conductivity (umhos)	Temperature (°C)	Alkalinity (mg/l as CaCO <sub>3</sub> )	Total Depth of Well (m)	Chloride Concentration (mg/l)	Concentration Ratio*	554 keV	Percent Error	776 keV	Percent Error	Average**	Cl/Br Ratio	Date Sampled
18	12 cbc	7.37	230	22.5	105	-	6.6	-	.06	16.5	.03	32.0	.048	132	3/1
19	13 aca	6.57	250	18.4	90	-	6.6	11.89	.62	5.1	.58	6.0	.05	132	3/1
20	13 adb	-	129	19.0	-	575	5.1	10.95	.43	6.8	.42	7.5	.039	138	12/21/82
21	17 dca	7.65	232	25.7	86	500	6.1	10.28	.56	6.3	.60	6.2	.056	109	3/14/83
22	20 cba	7.20	220	25.0	-	-	3.2	9.51	.57	8.3	.62	8.8	.062	52	12/20/82
23	21 ddd	7.37	258	25.1	92	665	4.2	10.30	.74	7.4	.83	7.7	.076	107	8/15/83
24	23 add	6.73	180	19.5	-	445	6.1	8.41	.38	9.4	.38	10.3	.045	136	12/21/82
25	23 ccc	7.03	215	23.0	72	776	6.1	11.40	.63	7.4	.65	8.0	.057	107	8/5/83
26	26 dad	6.73	138	21.5	-	715	7.6	9.35	.48	6.6	.44	7.7	.049	155	8/5
27	28 ddd	7.20	192	23.5	39(?)	526	3.2	10.30	.54	7.9	.53	9.1	.052	62	8/5
28	30 aaa	7.04	230	24.0	-	-	7.1	11.15	.85	6.3	.90	6.9	.079	90	12/20/82
29	32 ccb	6.90	305	23.9	130	604	7.1	10.22	.77	6.2	.70	7.8	.071	100	8/5/83
30	13-13-1 bbb	7.03	350	27.4	129	500	11.5	10.48	1.42	3.8	1.47	4.1	.140	43	8/5
31	2 bbb	7.12	210	25.8	82	465	6.6	8.84	.45	7.5	.51	7.4	.054	122	8/5
32	9 bcc	6.70	670	22.7	187	470	19.8	10.10	1.18	3.8	1.16	4.1	.120	165	8/5
33	14 adc	6.95	358	21.7	115	395	9.0	9.36	.59	5.2	.63	5.5	.065	138	8/5
34	15 dbd	6.94	200	18.0	-	360	4.2	10.68	.41	6.9	.35	8.8	.036	117	12/30/82

Table A1. Well sample data, Continued

Well Number	Location	FIELD PARAMETERS				BROMIDE CONCENTRATION BY NAA (mg/l)									
		Electrical Conductivity (umhos)	pH	Temperature (°C)	Alkalinity (mg/l as CaCO <sub>3</sub> )	Total Depth of Well (m)	Chloride Concentration (mg/l)	Concentration Ratio*	554 keV	Percent Error	776 keV	Percent Error	Average	C1/Br Ratio	Date Sampled
35	16 bdb	480	6.90	22.5	-	-	23.7	8.94	1.30	5.2	1.30	5.9	.145	163	12/21/82
36	18 abb	1000	7.21	22.0	-	200	77.5	-	.19	12.3	.20	12.9	.194	399	12/21
37	20 dcd	-	-	-	-	-	45.7	-	.22	11.3	.25	11.7	.230	183	12/21
38	22 aac	343	7.21	25.0	124	515	21.3	9.18	.95	6.1	.89	7.4	.100	213	1/11/83
39	22 dcb	660	7.22	25.8	112	410	97.0	-	.23	9.5	.25	9.2	.240	404	1/11
40	22 dda	610	6.67	26.8	115	616	22.2	9.25	1.00	5.8	.96	6.8	.106	209	8/2/83
41	23 abc	283	6.80	20.4	110	585	6.1	8.87	.34	7.7	.34	8.2	.038	161	8/2
42	26 cbc	1380	6.66	27.5	80	380	120.5	-	.31	9.5	.28	10.9	.290	416	8/2
43	26 cda	1090	6.90	27.5	100	658	80.9	-	.33	7.6	.33	8.1	.330	245	8/2
44	34 caa	-	7.42	23.0	172	300	230.0	-	.45	7.6	.36	10.8	.400	575	7/30/83
45	13-14-1 cbd	-	-	-	-	-	42.2	-	.28	7.8	.27	8.5	.280	151	-
46	31 dba	330	7.34	26.5	-	600	11.5	9.15	.81	4.8	.87	5.1	.092	125	1/4/83
47	32 aad	360	7.50	24.7	152	627	7.6	10.53	1.25	5.6	1.11	7.1	.112	68	3/1/83
48	32 bab	365	7.23	24.0	-	500	12.0	9.19	.95	4.9	.99	5.2	.105	114	1/4/83
49	13-15-14 bcb	-	-	-	-	0	29.1	-	.19	13.3	.21	14.0	.200	182	-
50	16 aba	-	-	-	-	144	30.2	-	.16	16.3	.16	19.0	.160	189	-

Table A1. Well sample data, Continued

Well Number	Location	FIELD PARAMETERS										BROMIDE CONCENTRATION BY NAA (mg/l)						Date Sampled
		pH	Electrical Conductivity ( $\mu$ mhos)	Temperature ( $^{\circ}$ C)	Alkalinity (mg/l as CaCO <sub>3</sub> )	Total Depth of Well (m)	Chloride Concentration (mg/l)	Concentration Ratio*	554 keV	Percent Error	776 keV	Percent Error	Average	** Cl/Br Ratio				
51	16 abb	-	-	-	-	200	53.3	-	.11	24.3	.11	28.8	.110	485	-			
52	17 dcd	-	-	-	-	150	71.0	-	.47	5.7	.56	4.6	.510	139	-			
53	22 cad <sub>1</sub>	-	-	-	-	163	69.2	-	.31	11.8	.43	9.8	.370	187	-			
54	22 cad <sub>2</sub>	-	-	-	-	300	332.2	-	1.78	3.0	1.66	3.5	1.720	193	-			
55	26 dca	-	-	-	-	-	272.3	-	2.23	2.6	2.24	2.8	2.240	122	-			
56	27 baa	-	-	-	-	165	78.1	-	.55	5.2	.48	6.3	.520	150	-			
57	27 ba	-	-	-	-	150	120.9	-	.68	4.2	.65	4.2	.660	183	-			
58	28 adc	-	-	-	-	125	50.1	-	.28	8.1	.33	7.5	.310	162	-			
59	13-16-19 ca	-	-	-	-	110	172.2	-	-	-	-	-	-	-	-			
60	14-13-23 abd	9.05	630	27.0	125	192	16.4	8.85	1.03	6.6	.97	8.3	.110	149	3/15/83			
61	35 caa	7.15	570	23.3	178	295	12.5	9.62	.95	8.5	1.28	7.2	.115	109	1/6/83			
62	35 cal	7.15	840	24.0	201	207	28.1	-	.21	7.2	.22	7.5	.220	128	1/6			
63	36 ccc	7.10	530	24.2	155	517	12.0	10.13	1.19	6.7	1.16	8.0	.115	83	1/6			
64	14-14-5 ddb	7.88	285	31.3	96.0	638	6.1	9.54	.42	9.4	.38	11.2	.042	153	3/1/83			
65	7 dda	7.73	418	28.8	147	555	7.1	9.93	.69	6.6	.68	7.5	.070	101	3/1			
66	9 ddc	7.80	320	30.7	106	695	8.5	10.13	.41	9.2	.42	10.3	.040	213	3/1			

Table A1. Well sample data, Continued

Well Number	Location	pH	FIELD PARAMETERS				Total Depth of Well (m)	Chloride Concentration (mg/l)	Concentration Ratio*	BROMIDE CONCENTRATION BY NAA (mg/l)			C1/Br Ratio	Date Sampled	
			Electrical Conductivity (µmhos)	Temperature (°C)	Alkalinity (mg/l as CaCO <sub>3</sub> )	554 keV				Percent Error	776 keV	Percent Error			Average**
67	11 bac	7.65	325	25.6	142	644	10.5	12.06	.81	5.5	.85	5.9	.069	152	3/3/83
68	11 ccb	7.70	265	27.2	122	800	6.6	9.38	.57	6.1	.45	8.4	.050	132	3/3
69	14 acc	7.83	260	27.6	140	800	5.6	10.85	.50	7.9	.52	8.1	.047	112	3/3
70	21 bcc	7.14	485	26.0	-	434	10.5	-	.05	30.3	.07	23.3	.060	175	1/5/83
71	24 baa	7.26	240	25.0	-	700	4.2	-	.061	20.3	.057	24.1	.059	70	1/5
72	28 dab	7.57	520	28.2	145	504	11.0	8.64	.80	5.6	.72	7.0	.090	122	3/3/83
73	29 acb	7.60	600	26.6	144	478	7.1	10.9	.73	5.5	.84	5.1	.070	101	3/3
74	32 cca	7.10	900	25.3	130	250	69.2	-	.35	8.3	.33	9.2	.340	204	1/6/83
75	35 add	7.03	422	27.5	145	380	6.6	11.6	.69	6.3	.67	7.0	.060	110	8/2/83
76	36 cca	6.93	460	27.5	160	750	7.6	10.31	.51	7.6	.53	8.1	.050	152	8/2
77	14-15-2 dda	6.20	230	18.0	-	490	8.5	-	.08	24.6	.07	23.4	.070	121	1/4/83
78	3 cdc	6.90	310	22.0	96.0	353	12.0	11.11	1.28	5.2	1.34	5.7	.118	102	3/3/83
79	4 dda	7.08	382	22.4	114	500	20.3	9.50	1.22	4.0	1.19	4.5	.127	160	3/3
80	7 bba	7.53	310	23.9	130	534	11.5	10.58	.87	6.9	.85	8.1	.082	131	3/3
81	9 bdd	7.05	305	24.0	-	450	11.5	9.35	1.10	4.6	1.13	5.0	.120	96	1/4/83
82	10 aac	6.52	350	21.0	-	510	15.9	9.89	1.19	5.2	1.08	6.6	.115	138	1/4
83	15 cab	7.07	280	25.0	-	750	11.5	11.26	.83	5.3	.88	5.5	.076	151	1/4

Table A1. Well sample data, Continued

Well Number	Location	pH	FIELD PARAMETERS				BROMIDE CONCENTRATION BY NAA (mg/l)									
			Electrical Conductivity (microhm/cm)	Temperature (°C)	Alkalinity (mg/l as CaCO <sub>3</sub> )	Total Depth of Well (m)	Chloride Concentration (mg/l)	Concentration Ratio*	554 keV	Percent Error	776 keV	Percent Error	Average	** Cl/Br Ratio	Date Sampled	
98	16-14-6 abb	7.54	408	23.8	130	1054	9.5	10.00	.86	8.0	.94	8.5	.090	106	1/8/83	
99	6 bbc	7.40	550	22.6	146	865	17.8	11.61	1.75	4.1	1.41	6.0	.136	131	1/11/83	
100	6 bcd	7.20	600	22.9	138	550	20.3	11.50	1.23	4.7	1.44	4.5	.120	169	1/8/83	
101	17 lcc	7.31	900	22.5	246	360	31.0	11.55	3.30	2.9	3.10	3.4	.280	112	1/8	
102	20 acb	7.07	900	23.6	237	580	27.6	13.89	2.98	2.8	2.82	3.3	.210	131	1/8	
103	21 dbb	7.05	800	25.3	189	650	22.7	9.76	2.06	3.3	1.90	4.1	.203	112	1/8	
104	25 aaa	7.60	408	28.8	140	790	9.0	9.83	.61	9.1	.77	8.4	.070	129	1/13/83	
105	28 ccb	7.04	1250	22.5	280	500	41.8	-	.32	6.5	.29	7.8	.300	139	1/1/83	
106	16-15-18 aac	7.53	463	23.7	140	450	15.9	9.78	1.05	6.1	1.11	6.7	.110	145	3/15/83	
107	17-15-6 bad	7.75	482	25.4	160	315	8.5	9.92	.86	5.3	.86	5.9	.087	98	3/15	

\* - some samples were pre-concentrated before analysis. Bromide concentrations listed under the 554 keV and 776 keV headings are uncorrected.

\*\* - the average is calculated by:  $\frac{Br^- \text{ conc. (554 keV)} + Br^- \text{ conc. (776 keV)}}{2} \times \text{conc. ratio}$

Table A1. Well sample data, Continued

Well Number	Location	FIELD PARAMETERS										BROMIDE CONCENTRATION BY NAA (mg/l)					Date Sampled
		pH	Electrical Conductivity (µmhos)	Temperature (°C)	Alkalinity (mg/l as CaCO <sub>3</sub> )	Total Depth of Well (m)	Chloride Concentration (mg/l)	Concentration Ratio*	554 keV	Percent Error	776 keV	Percent Error	Average	** Ratio	Cl/Br Ratio		
84	18 cda	7.65	272	27.1	125	690	6.6	9.23	.72	7.5	.63	9.7	.073	90	3/3/83		
85	22 abc	7.12	285	25.0	-	750	6.1	9.64	.66	5.7	.59	6.8	.064	95	1/4/83		
86	23 ccb	7.40	287	25.0	-	855	4.6	11.03	.73	5.9	.74	6.9	.067	69	1/4		
87	34 aaa	7.13	390	21.0	168	300	2.7	10.18	.20	9.7	.22	9.8	.020	135	1/7/83		
88	15-13-13 cba	7.33	525	23.3	151	743	16.4	9.80	1.03	7.1	.98	8.4	.102	161	1/7/83		
89	15-14-1 baa	6.73	450	-	96	1100	8.0	12.90	.73	6.2	.74	6.9	.057	140	8/2/83		
90	10 ddc	7.30	675	24.9	143	177	12.0	9.61	1.20	4.4	1.32	4.5	.130	92	1/6/83		
91	25 bda	7.20	600	25.5	165	324	16.9	8.58	.76	5.5	.84	5.4	.092	182	1/13/83		
92	27 ccb	7.23	463	24.9	153	300	13.9	8.95	.85	4.8	.80	5.7	.092	151	1/11/83		
93	31 bbb	7.15	520	22.5	168	552	16.4	11.9	1.13	4.1	1.22	4.2	.098	167	1/8/83		
94	32 abc	7.26	600	24.1	150	400	27.1	-	.22	8.7	.22	9.4	.220	123	1/11/83		
95	15-15-30 ccb	7.93	425	28.3	129	950	7.6	13.61	.56	9.6	.64	9.3	.044	173	3/15/83		
96	36 cdd	7.37	271	22.1	140	585	6.1	9.93	.39	10.2	.47	9.9	.043	142	1/11/83		
97	15-16-19 aaa	7.20	205	20.8	88	600	3.7	10.81	.86	8.0	.94	8.5	.090	106	1/8/83		

Table A2. Source sample data.

Location	Sample Type	Chloride Concentration (mg/l)	Concentration Ratio*	BROMIDE CONCENTRATION BY NAA (mg/l)				Average**	Cl/Br Ratio	Date Sampled
				554 keV	Percent Error	776 keV	Percent Error			
13-12-1 dbb	sewage effluent (Ina Road)	70.6	-	.22	10.4	.15	16.1	.180	392	10/12/83
13-13-20 dda	sewage effluent (Roger Road)	82.8	-	.29	8.9	.32	8.8	.300	276	10/12/83
13-13-24 bcc	runoff	4.2	9.21	.24	6.5	.25	6.5	.027	156	8/9/83
13-13-25 ddc <sub>1</sub>	precipitation	1.7	8.89	.14	8.9	.17	7.0	.017	100	7/20/83
13-13-25 ddc <sub>2</sub>	precipitation	2.2	10.42	.03	29.8	.06	13.4	.004	579	8/9/83
13-14-19 bcb	runoff	2.2	14.60	.37	6.3	.37	7.1	.025	88	8/2/83
13-14-34 baa	runoff	6.6	12.03	.73	3.5	.76	3.6	.062	106	7/31/83
14-14-6 bcc	runoff	5.1	8.63	1.05	2.4	1.10	2.4	.120	43	7/26/83
14-14-18 aca	runoff	12.5	10.33	5.16	1.7	5.14	1.8	.500	25	8/5/83
14-14-18 cdd	runoff	2.2	10.71	.51	4.0	.51	4.2	.048	46	8/17/83

\* - some samples were preconcentrated before analysis. Bromide concentrations listed under the 554 keV and 776 keV headings are uncorrected.

\*\* - the average is calculated by:  $\frac{\text{Br}^- \text{ conc. (554 keV)} + \text{Er}^- \text{ conc. (776 keV)}}{2} \times \frac{1}{\text{conc. ratio}}$

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