EFFECTS OF THREE PHOSPHATE INDUSTRIAL SITES ON GROUND-WATER QUALITY IN CENTRAL FLORIDA, 1979 TO 1980

By Ronald L. Miller and Horace Sutcliffe, Jr.

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DEFINITIONS

Aquifer.--A formation, group of formations, or part of a formation that is water bearing. Also called ground-water reservoir.

Background well.--A well located at a sufficient distance from a gypsum stack, slime pond, or other cultural influence, so that water from a well would represent natural ground-water quality.

Barometric condenser.--A contact condenser that uses a long, vertical pipe into which condensate and cooling liquid flow to accomplish their removal by the pressure created at the lower end of the pipe.

Beneficiation.--Recovery of phosphate particles from the phosphate ore (matrix) by treatment. Treatment includes sieving or flotation.

Cooling pond.--A pond of large surface area that receives effluent process water from a gypsum stack. The warm process water is cooled before returning to the plant. Cooling ponds are generally diked with earth to 10 to 20 feet above land surface.

Diammonium phosphate pond.--Similar to a cooling pond but one which receives effluent process water from the production of diammonium phosphate (DAP). DAP is a major component of some fertilizers.

Gypsum stack.--Large piles of gypsum ($CaSO_4.2H_2O$) produced as an effluent byproduct of the production of phosphoric acid. Gypsum stacks are frequently greater than 100 feet in height and cover several tens of acres.

Matrix.--Phosphate-bearing ore or strata consisting of phosphate particles, clay, and sand.

Phosphatic clayey waste-disposal pond.--A pond constructed above land surface to provide storage of fine to collodial phosphatic material received from a beneficiation plant. Synonymous with "slime pond."

Phosphogypsum.--An effluent byproduct of chemical processing and phosphoric acid production. It is a slurry composed of process water and gypsum. It is disposed of in Florida in a slurry discharge into settling ponds by the wet-stacking method using the upstream method of construction, which results in a gypsum stack.

Piezometer.--The basic device for the measurement of hydraulic head is a tube or pipe in which the elevation of a water level can be determined. In the laboratory, the tube is called a manometer; in the field, the pipe is called a piezometer.

Slime pond.--Synonymous with "phosphatic clayey waste-disposal pond." It is a local term used in the phosphate mining area. A large-volume settling pond used to store clayey wastes (slimes) from a phosphate mine and beneficiation plant.

Slurry.--A pumpable suspension of fine solid material, such as clay and gypsum, in liquid. Also, a mixture of water and phosphate ore (matrix) produced by high-pressure water to facilitate transportation.

Scrubber.--A device for the removal, or washing out, of entrained liquid droplets or dust, or for the removal of an undesired gas component from process gas streams.

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ABSTRACT

Two gypsum (phosphogypsum) stack complexes, the AMAX, Inc., plant at Piney Point in Manatee County and the U.S. Steel Agri-Chemicals plant at Bartow in Polk County, were chosen for intensive study of the movement and chemical modification of process water seeping into ground water. A third site, a slime pond at the International Minerals and Chemical Corporation mine near Bartow, was also selected for intensive study.

The composition of the process water in the entire system of gypsum stacks, ponds, and ditches is virtually the same. This highly acidic water has a dissolved-solids concentration of about 28,000 milligrams per liter, a pH of 1.4 to 1.8 units, and contains sodium, phosphate, fluosilicate, hydrogen, and sulfate ions as major constituents. The concentration of most other ions are also higher in the process water than in the native ground water and surface water of central Florida. The native ground water has a dissolved-solids concentration of less than 500 milligrams per liter and is calcium bicarbonate water with a pH near 7.0 units; the ambient ground water at the plant sites is similar in composition.

Water drawn from shallow, water-table test holes within a few hundred feet of circulating process water reflects the contaminant source by increased concentrations of almost all constituents compared to the native ground water, although no contaminant-enriched ground water sampled showed ionic concentrations as high as the contaminant source. Migration of process water to great distances or into deep artesian zones is less easily recognizable because of dilution and reactions of process water with aquifer

materials. For all wells sampled, water-quality constituents related to health were found to be within safe limits at distances of 1,500 feet or more from a contaminant source except for one sulfate concentration of 750 milligrams per liter. Water from many wells, however, were within safe limits at much shorter distances from a source.

Sodium and sulfate ions are the most mobile of the contaminant-source constituents in process water. Migration of radionuclides, fluosilicates, phosphates, and trace metals is largely controlled by the degree of acid neutralization as the result of reaction with aquifer materials, and is generally restricted to areas immediately adjacent to the source. Iodide, bromide, and ammonium are useful as tracers near gypsum stacks. These tracers may distinguish the contaminant plume of process water where the existence of the contaminant is more subtle because of reduction in overall concentration of the contaminant due to acid neutralization and chemical precipitation. All contaminants are removed or reduced in concentration in the ambient ground water with distance traveled. Concentrations of contaminants are controlled by the degree of reaction with aquifer materials and dilution by native water; thus, the movement and chemical modification of the contaminant-enriched plume can be documented. The mechanisms involved, which includes adsorption, dispersion, dilution, radioactive decay, and other chemical and physical processes, can be inferred for some constituents--the degree of acid neutralization with aquifer materials being the most significant mechanism. Ion indices for the major ions have been developed as an approach to distinguish between native and industrial sources of solute. Results of ion indices and concentrations of selected constituents suggest that both surficial and underlying artesian aquifers are contaminated in the recharge area at the Bartow site and also at the Piney Point site, which can be either a recharge area or a discharge area depending on the time of year.

Phosphate slimes from mining and beneficiation operations were found to contain phosphorus, trace metals, and radiochemicals. These substances were associated with solid materials and were effectively retained by the slime pond. The quality of water of the slime pond after settling was good for constituents determined and satisfies primary (U.S. Environmental

Protection Agency, 1976) and secondary drinking water regulations (U.S. Environmental Protection Agency, 1977). Water with elevated specific conductance was associated with high water levels in the artesian aquifer near the slime pond, indicating that a hydraulic connection exists between the pond and the first artesian aquifer. The spatial distribution of water with high specific conductance with respect to the slime pond and mining pit suggests that the slime pond is contributing some water and, thus, some solute to the surficial aquifer, although solute contributions are much less than that associated with gypsum stacks.

Rainfall associated with haze and stagnant air at Bartow had specific conductances of 290 and 347 micromhos per centimeter. After the atmosphere was cleansed by wind and rain, rainfall samples had specific conductances of 23 and 43 micromhos per centimeter. Calcium, ammonia, bicarbonate, and sulfate were the predominant ions found in rainfall.

Knowledge of local and regional geology and geohydrology are important for site selection and site interpretation. This report documents the nature, magnitude, and extent of the process-water movement into the adjacent ground water. The report will assist the phosphate industry and regulatory agencies in determining the seriousness and significance of this movement as well as managing water resources and the storage of solid waste more effectively.

INTRODUCTION

The Florida phosphate industry is the State's third largest industry. It produced 40 million tons of phosphate rock during 1978. This is about one-third of the world production of phosphate (Florida Phosphate Council, 1979).

Wastes from phosphate mining and beneficiation plants are primarily sand tailings and phosphatic clayey wastes (slimes). The sand tailings, which drain readily, are usually stacked or spread in convenient areas. The slimes, which are difficult to dewater, are pumped as a slurry to waste storage ponds (slime ponds). Most of the water used to transport the slimes is returned to beneficiation plants for reuse.

The main wastes of phosphate chemical plants are gypsum and the process water used to transport the gypsum as a slurry to a gypsum stack where it is stored. The wet-stacking method of disposal of gypsum, a byproduct of chemical processing and phosphoric acid production, uses the upstream method of construction and creates gypsum stacks that are frequently more than 100 feet high and cover tens of acres. The gypsum settles rapidly in the stack. The process water discharges from the stack to earthen cooling ponds and the water is returned to the chemical plant for reuse in gypsum transport, in scrubbers, and in barometric condensers and cooling units. The acidic process water entrained in the gypsum pores, percolating through the gypsum stacks, and contained in the adjoining recirculation ponds and ditches is a potential source of contamination to ground water.

Control of seepage is difficult in humid climates such as Florida. Excess water in flow systems at chemical plants and at mines and beneficiation plants occurs when rainfall and other contributions of water exceed evaporation. The excess water will seep into the ground near the source or must be discharged offsite by natural or artificial means. To prevent contamination at phosphate chemical plants, excess water must be neutralized by liming (or similar treatment processes) or by its chemical reaction with natural basic materials in aquifers.

Lining gypsum stacks, cooling ponds, and slime ponds may not be sufficient to prevent seepage from entering aquifers. It may be necessary to collect seepage where it overflows liners. Water can collect in lined areas to produce a "bathtub" effect (Hughes and others, 1976; Cartwright and others, 1977).

State and Federal agencies charged with protecting water resources are concerned with possible impairment of ground-water supplies by phosphate industry operations. Much attention has been focused on chemical plants because of high concentrations of radionuclides, acid, fluoride, phosphate, and sulfate typically found in process water. Because of this, the U.S. Environmental Protection Agency proposed a requirement for new pollutant sources in the phosphate industry that gypsum stacks be lined "with an impervious material unless it can be demonstrated in the site specific EIS that such lining is unnecessary in protecting ground water from chemical and radiological contamination" (U.S. Environmental Protection Agency, 1978a, v. I, p. 2.3). But, "because of the lack of data on the extent of surface and subsurface seepage and cost information on impervious linings to control this potential source of pollution, effects assessment did not include a quantitative evaluation of this process modification" (U.S. Environmental Protection Agency, 1978b, v. II, p. 2.27).

Purpose and Scope

The primary purpose of the investigation was to document the magnitude and extent of the movement of contaminants into the shallow ground-water system from potential sources of contamination associated with the phosphate industry--mining, processing, and waste disposal. Geologic, topographic, and hydrologic environments were examined in relation to phosphate industry operations. Emphasis was on the effects from gypsum stacks and associated ponds with some additional effort on slime ponds. Test holes were drilled around the ponds and in the area of the ponds at multiple depths to define the extent and magnitude of movement of any contaminants into the surficial aquifer, the intermediate aquifers, the Floridan aquifer, and possibly into nearby surface waters.

Little information exists on the percolation of soluble substances from gypsum (phosphogypsum) stacks, cooling ponds, or slime ponds into underlying ground water. Information was obtained on quality characteristics of water in phosphate industry ponds and gypsum stacks in order to determine the types of substances that migrate from these sources. An important aspect of the investigation was to determine the movement and chemical modification of particular ions with distance traveled rather than documentation of contamination at a specific plant site. A data base was developed to determine some of the chemical reactions that control movement of material from these sources so that the phosphate industry and regulatory agencies can manage storage of solid waste and water resources more effectively (Miller and Sutcliffe, 1982).

Three sites were selected for intensive study (fig. 1). They include two phosphate chemical plants, AMAX Phosphate, Inc. (formerly Borden) near Piney Point, Manatee County, and USS Agri-Chemicals near Bartow, Polk County, and a slime pond at the International Minerals and Chemical Corporation Clear Springs mine near Bartow. The companies are referred to as AMAX, USSAC, and IMC, respectively, in this report.

Water-quality, water-level, and geologic data were collected from September 1979 to October 1980. These data were published in a separate data report (Miller and Sutcliffe, 1982). At each site, water levels were measured at most wells on the same day. Three clusters of wells--one at each site--tapping the upper two or three aquifers were monitored continuously for approximately 1 year. Bulk precipitation (wet and dry) samples were collected at each site. If the volume of rainfall was sufficient, extensive water-quality analyses were made. Water from gypsum stacks, cooling ponds, ditches, and slime ponds was sampled. Water from 78 wells, 31 surface-water sites, 5 rainfall and other sampling sites at the two chemical plants and a mine was sampled. Most sites were sampled once and samples were analyzed for an extensive suite of major constituents, chemical and physical properties, nitrogen and phosphorus species, radiochemicals, trace elements, and organic substances.

Descriptions of each study site and discussions of the quality of water in ponds and in underlying shallow aquifers are given separately in this report. Rainfall data collected at the study sites are discussed in a separate section.

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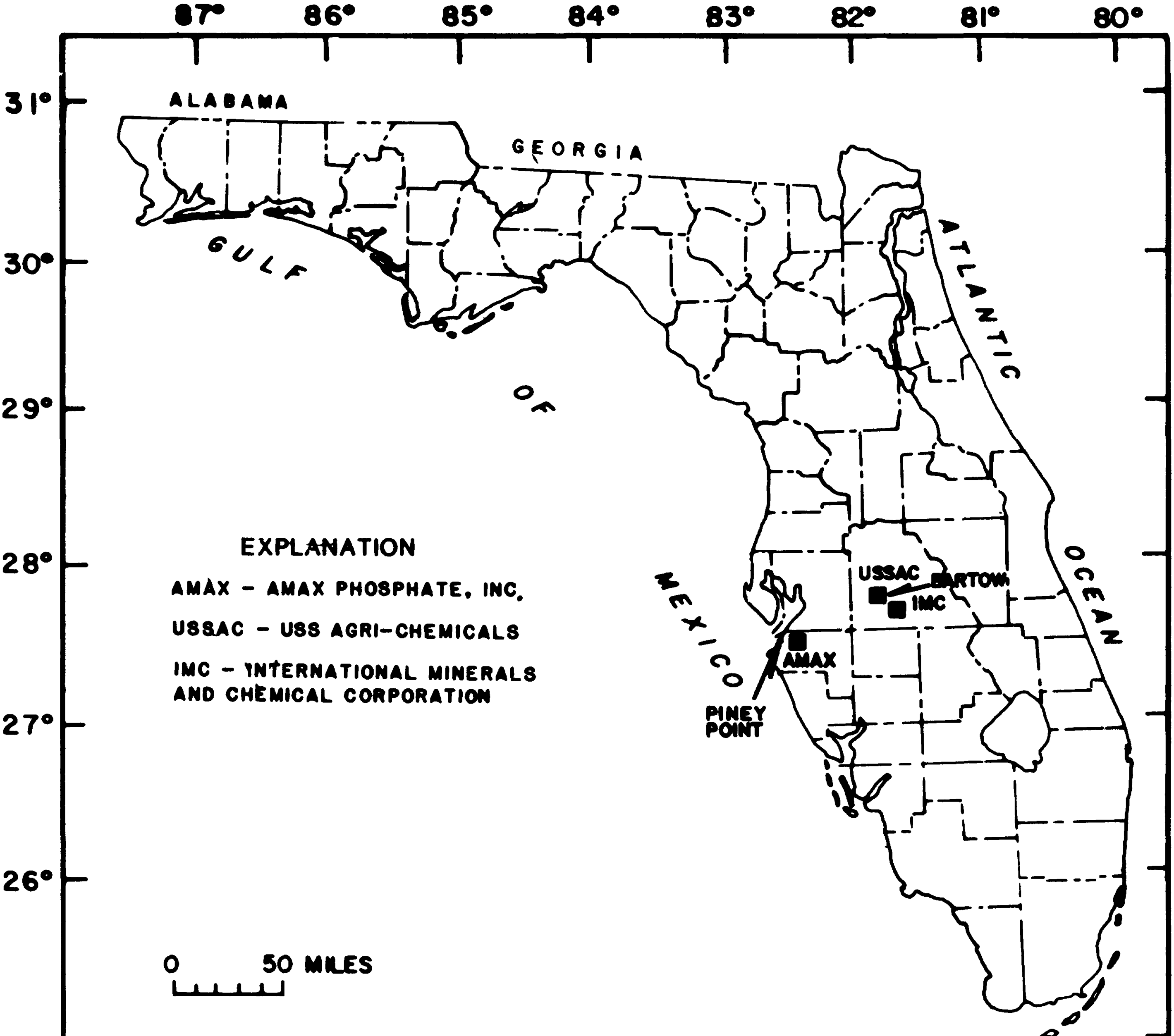

Figure 1.--Locations of study sites in west-central Florida.

Each company provided information and aerial photographs of study sites. Personnel and equipment were provided to assist in drilling of observation and monitor test wells. The companies also provided ready access to their properties for purposes of test drilling and water-quality sampling.

Description of the Area

The study sites (fig. 1) are in the west-central part of Florida or in the midpeninsula physiographic zone as defined by White (1970). Land-surface altitudes range from 10 feet at AMAX to 225 feet at USSAC and IMC. Drainage from AMAX is by way of ditches and a creek to the Gulf of Mexico. Drainage from USSAC is into a creek that flows into the Peace River a few miles east of the USSAC site. Drainage from IMC is by way of canals into the Peace River and eventually to Charlotte Harbor and the Gulf of Mexico. The land surface between the study areas rises from west to east in a series of gently sloping terraces.

Climate of the area is subtropical. Convective thundershowers occur in the summer rainy season; winters and springs are relatively dry. Annual rainfall averages between 50 and 54 inches per year. March, April, and May are dry throughout the area, and are the months of heaviest irrigation of crops.

The AMAX study area is rural. Cattle ranching, row crop vegetable farming, and scattered citrus grove operations are the principal land uses. The USSAC and IMC study areas are urban, being near Bartow, Fla. In areas surrounding Bartow, phosphate mining competes with citrus growing as the principal land use.

Previous Studies

Little literature exists on seepage from phosphate industry gypsum stacks or slime ponds into ground water. The most pertinent studies include those of Ardaman & Associates, Inc. (1978), and Miller and others (1978). These studies were in the vicinity of the Occidental Chemical Company Swift Creek chemical complex in north Florida. The Ardaman and Associates study is similar to this study in west-central Florida. An examination of their data suggests similarities in the characteristics of seepage from gypsum stacks.

The U.S. Environmental Protection Agency (1978d) has compiled a bibliography on geology, mining, chemical plants, environmental effects, and marketing related to the central Florida phosphate industry. Roundy (1941) discussed the geology of phosphate deposits in Florida. Cathcart (1963; 1966) described the economic geology of the Plant City and Fort Meade quadrangles northwest and south of Bartow, respectively. Zellars and Williams, Inc., (1978) evaluated the availability of Florida phosphate deposits and showed locations of known deposits.

County water-resources studies for Polk County (Stewart, 1966), Hillsborough County (Menke and others, 1961), Hardee and De Soto Counties (Wilson, 1977a), and Manatee County (Peek, 1958) cover most of the central Florida phosphate deposits. These reports provide information on geology, aquifer systems, and water quality. Stewart (1963) provided data on water levels and water quality collected during the 1950's.

The areal ground-water flow in the Floridan aquifer is described in Stringfield (1966), Johnston and others (1980), Wilson and Gerhart (1982), and Johnston and others (1981). The areal water quality of the Floridan aquifer is described by Shattles (1965) and by Shampine (1965a,b,c,d).

Wilson (1977b) used a two-dimensional ground-water flow model to predict the effects of phosphate mining on water levels in 1985 and 2000. Zellars and Williams, Inc., (1977) described water use and water balances for central Florida phosphate mines.

Radiochemical studies have been done on: phosphate rock mining and milling operations (U.S. Environmental Protection Agency, 1973); phosphate products, byproducts, effluents, and wastes (Guimond and Windham, 1975); radon daughter products in buildings constructed on mined land (U.S. Environmental Protection Agency, 1975); and effects of mining and phosphate deposits on the concentration of radium-226 in central Florida ground water (Kaufmann and Bliss, 1977).

Considerable information on the impact of the central Florida phosphate industry is available in volumes I, II, and III of environmental impact statements by the U.S. Environmental Protection Agency (1978a,b,c). Much of the information in those reports is extracted from a 10-volume series of working papers (Texas Instruments Incorporated, 1977a,b,c,d,e,f,g,h,i,j).

Muehlberg and others (1977) gave profiles of the phosphate rock and fertilizer industry. Severson and Gough (1979) discussed the emissions of elements from phosphate processing operations in southeast Idaho. Wahba and others (1980) and Slack (1968) described the economics and chemical process of phosphoric acid production. Lamont and others (1975) characterized the settling and dewatering properties and the size distribution of Florida phosphate slimes. Toler (1967) investigated fluoride concentrations in the Alafia and Peace River basins that drain the center of the phosphate mining and processing industry in central Florida.

HYDROGEOLOGIC FRAMEWORK

Ground water in central Florida occurs in two principal aquifers--the surficial aquifer and the Floridan aquifer. The two aquifers are separated by confining bed that in turn contains an intermediate aquifer system (consisting of first and second artesian aquifers within the study area). The Floridan aquifer is underlain by a lower confining bed (table 1). Sand, shell beds, and porous limestone are the most permeable materials in the study area and form the principal aquifers. Clay, marl, sandy or silty clay, and dense limestone or dolomite form the confining beds.

Water in the surficial aquifer is unconfined and the water table rises or falls in response to recharge and discharge. Water in the artesian aquifers is confined (both intermediate and Floridan) by overlying and underlying beds that have low permeability. Water levels in artesian aquifers also respond to recharge and discharge. Recharge to artesian aquifers is generally by lateral flow or by leakage through the confining beds in response to differences in heads between aquifers. The rate of leakage is determined by the difference in head between aquifers and the permeability of the confining beds. The direction of leakage is determined

Table 1.--Hydrogeologic framework

System	Series	Stratigraphic unit	General lithology	Major lithologic unit	Hydrogeologic unit
Quaternary	Holocene, Pleistocene	Surficial sand, terrace sand, phosphorite	Predominantly fine sand; interbedded clay, marl, shell, limestone, phosphorite	Sand	Surficial aquifer
Tertiary	Pliocene	Bone Valley Formation[1]	Clayey and pebbly sand; clay, marl, shell, phosphatic	Carbonate and clastic	Intermediate aquifer system (consists of first and second artesian aquifers)
	Miocene	Hawthorn Formation	Dolomite, sand, clay, and limestone; silty, phosphatic		
		Tampa Limestone	Limestone, sandy, phosphatic, fossiliferous; sand and clay in lower part in some areas		
	Oligocene	Suwannee Limestone	Limestone, sandy limestone, fossiliferous	Carbonate	Floridan aquifer
	Eocene, Paleocene	Ocala Limestone	Limestone, chalky, foraminiferal, dolomitic near bottom		
		Avon Park Limestone	Limestone and hard brown dolomite		
		Lake City, Oldsmar, and Cedar Keys Limestones	Dolomite and chalky limestone, with intergranular gypsum and anhydrite	Carbonate with intergranular evaporites	Lower confining bed of Floridan aquifer

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[1] May also include all or parts of Caloosahatchee Marl and Tamiami Formation (adapted from Wilson and Gerhart, 1980).

by the relative positions of the water table in the surficial aquifer and the potentiometric surface of water in the artesian aquifers.

Recharge to and discharge (excluding pumping) from the Floridan aquifer are principally by leakage through the upper confining bed of the aquifer. Vertical flow between the Floridan aquifer and its lower confining bed is assumed to be negligible (Wilson and Gerhart, 1982).

Gradients of the water-table and potentiometric surfaces indicate generalized directions of ground-water flow. The flow pattern in the Floridan aquifer was first described by Stringfield (1936, 1966). Johnston and others (1980) discussed regional ground-water flow prior to development in the southeastern United States, and Johnston and others (1981) discussed regional ground-water flow after development. Maps from those reports show a recharge area centered in Polk County and a discharge area along Tampa Bay. In the recharge area, flow is generally downward from the surficial aquifer to the Floridan aquifer, whereas in the discharge area, flow is generally upward from the Floridan aquifer to the surficial aquifer. However, according to Wilson and Gerhart (1982, p. 6), most ground-water flow in the surficial aquifer is toward local points of discharge.

Since 1975, the potentiometric surface of the Floridan aquifer in west-central Florida has been mapped semiannually by the U.S. Geological Survey at times of normally highest annual water levels in September and lowest annual water levels in May (Wilson and Gerhart, 1982). The September maps show that discharge is directly to the Gulf of Mexico. The May maps show a reversal of flow along the coast and discharge into a depression in central Manatee County caused by pumping during the winter months.

The AMAX site is in a regional discharge area of the Floridan aquifer and the IMC and USSAC sites are in a regional recharge area (Johnston and others, 1981).

Stratigraphic and lithologic units that make up the general hydrogeologic framework for the study areas are listed in table 1. The areas are covered by surficial sand that range in thickness from 5 to 30 feet. Immediately below the sand are interbedded layers of clay, marl, sandy clay, shell, and phosphatic materials that comprise the Bone Valley Formation, one of the world's most important sources of phosphate. Where grains of fluorapatite in this formation are sufficiently concentrated and near land surface, phosphate can be mined economically. The Bone Valley Formation ranges in thickness from about 20 to 100 feet. Some rocks herein described as the Bone Valley Formation may be part of the Caloosahatchee Marl or Tamiami Formation (Wilson and Gerhart, 1982).

The Hawthorn Formation underlies the Bone Valley Formation. It consists of interbedded limestone, dolomite, sand, clay, and marl and varies in thickness from a few tens of feet to about 100 feet. The Tampa Limestone underlies the Hawthorn Formation. It is similar in lithology to the Hawthorn Formation but contains a greater percentage of carbonate and clay beds. The Tampa Limestone varies in thickness from a few feet to about 100 feet. Grains of fluorapatite also occur throughout the Hawthorn Formation and Tampa Limestone but they are not sufficiently concentrated to be mined economically.

Surficial Aquifer

The surficial aquifer consists of fine to medium sand interbedded with clay, shell, and marl. The aquifer extends from near land surface to the first clay or marl zone that appreciably retards vertical movement of water. Yields from the surficial aquifer differ widely due to variability in thickness of permeable material and percentage of fine-grain material present. In general, yields are small, ranging from about 1 to 10 gal/min. The aquifer is not generally used as a source of water except for lawn irrigation. The aquifer, however, is a source of water for recharge to the Floridan aquifer in central Florida. Conversely, along the Gulf Coast water moves upward from the Floridan and the Floridan is a source of recharge to the surficial aquifer.

Intermediate Aquifer System

The intermediate aquifer system consists of interrelated permeable and poorly permeable material that function regionally as a water-yielding hydraulic unit. Within the study area a persistent confining bed separates the system into two aquifers. The uppermost, or first artesian aquifer, consists of permeable parts of the Bone Valley Formation and the upper part of the Hawthorn Formation. The lowermost, or second artesian aquifer, consists of the lower part of the Hawthorn Formation and permeable parts in the upper part of the Tampa Formation that are in hydraulic contact with the Hawthorn Formation and not the Floridan aquifer. The first and second artesian aquifers are separated from the Floridan aquifer by confining beds. Wells tapping the second artesian aquifer at USSAC are about 100 feet or less above the top of the Floridan aquifer, but at AMAX the second artesian aquifer is more than 200 feet above the Floridan aquifer.

The intermediate aquifers serve as a source of water for irrigation and rural domestic use in the study areas. South of the study areas, where the Floridan aquifer contains mineralized water, the intermediate aquifers serve as a source of water for municipal and most other supplies.

Floridan Aquifer

The Floridan aquifer is the principal artesian aquifer in west-central Florida. The aquifer includes all or parts of the Lake City Limestone, Avon Park Limestone, Ocala Limestone, Suwannee Limestone, Tampa Limestone, and "permeable parts of the Hawthorn Formation that are in hydrologic contact with the rest of the aquifer" (Parker and others, 1955). Recent studies have defined the top of the Floridan aquifer as the horizon below which carbonate rocks persistently occur (Wilson and Gerhart, 1982). The base of the aquifer is marked by the occurrence of intergranular evaporites that generally correspond to the top of the Lake City Limestone. Some test holes drilled for this study at the Bartow site were completed in aquifers that are hydraulically connected to the Floridan aquifer. Although the Floridan aquifer was not directly evaluated as part of this study, the aquifer is important because it is the major source of fresh ground water in the area.

METHODS OF INVESTIGATION

Site Selection and Description

Selection of sites for study was based on the following criteria: (1) the site was active so water from gypsum stacks, cooling ponds, and slime ponds could be characterized and potential water-table mounding near the source could be detected; (2) the site had relatively few nearby ponds that could complicate flow patterns and confuse interpretation of sources of materials; (3) the site had sufficient space on each side of the source pond in order to operate and maneuver a drilling rig; and (4) the site had potential for monitoring a plume downgradient from the source.

The AMAX chemical plant (fig. 1) is on unmined land in an area that has a high water table. It is remote from phosphate mines and other chemical plants. The plant began operation in September 1966 under the ownership of the Borden Chemical Company. On June 30, 1980, ownership was transferred to AMAX Phosphate, Inc. Phosphate ore was originally acquired from Agrico, the Borden Tenoroc mine, and other sources. Since January 1980, the phosphate ore has been acquired exclusively from the Borden Big Four mine. The estimated standing mass of gypsum at AMAX on January 1, 1981, was 11,300,000 tons (James Smith, AMAX, written commun., 1981).

The USSAC gypsum stack is on unmined land, but most of the surrounding land to the north, east, and south near the stack has been mined. An inactive slime pond and a dump are located near the gypsum stack. In general, water levels in the underlying artesian aquifers at USSAC and IMC are deeper below land-surface datum than those at AMAX. Water levels in deep aquifers in the Bartow area have been significantly lowered by nearby industrial and agricultural pumpage from the Floridan aquifer.

No mining was done at the USSAC site during the study period. The chemical plant was originally started in 1946 by the Armour Company. Since about 1967, the plant has belonged to USS Agri-Chemicals. The gypsum stack contained about 1,780,000 cubic yards of material in 1981 (James Carroll, USSAC, oral commun., 1981).

The IMC Clear Springs mine is about 3 miles from the nearest chemical plant. The nearest inactive slime ponds are about 1 mile away. The slime pond sampled is designated as CS-8. Another pond (CS-9) was under construction at the north side of CS-8 and was put into service in early 1980, near the end of field work for the study. The slime pond (CS-8) was placed in service in June 1977 by IMC. During the life of the slime pond, ore was mined within a 2-mile distance of it. During its active life, the pond had an average depth of clear water of 9.6 feet, and the standing volume of water was approximately 1.03 billion gallons (3,150 acre-feet). The cumulative volume of water flowing through the slime pond was 24.86 billion gallons. The volume of slimes accumulated in CS-8 is 13,931 acre-feet of which 1,216 acre-feet is clay (D. M. Smith, IMC, written commun., 1981).

Well Placement

Drilling for this study was designed to obtain information that could be used to determine hydrologic characteristics of the water-bearing materials and to develop wells that would produce water from the unconfined and confined aquifers for water-quality sampling. During the first phase of drilling, clusters of test wells were drilled on each side of a gypsum stack or slime pond. The first well of each cluster was drilled to the second artesian aquifer. Field data on permeability, based on the loss of drilling fluids and on lithology determined from drill cuttings, were used to determine well depths of the surficial and first artesian aquifer wells in each cluster. Most land near the slime pond at the IMC plant had been mined. The original materials of the surficial aquifer and the upper part of the intermediate aquifers had been so disturbed during mining and reclamation that the aquifers are no longer distinct hydrologic units. Hence, only two wells were required in each cluster. The deep test wells at IMC were cased into the Hawthorn Formation below the disturbed materials. The shallow test wells were open to the disturbed materials that were assumed to be generally homogeneous.

During the second phase of drilling, test wells were drilled to determine quality of water from areas unaffected by phosphate industry operations. These test wells are referred to as "background" wells in this report. Also, additional wells were drilled in the surficial aquifer to determine the gradient of the water table, the direction of ground-water flow, and the magnitude and extent of solute migration near the gypsum stacks and slime ponds.

Well Construction

Test wells were constructed so that vertical movement of water would not occur along the outside of the casing. To preserve the integrity of the sampling zone at each well, the following procedure was used for all wells drilled by the rotary method:

(1) Drill an 8-inch hole through the surficial aquifer and first artesian zone to the top of second artesian zone, as indicated by examination of cuttings and loss of drilling fluids.

(2) Set 4-inch plastic polyvinyl chloride (PVC) casing back to surface and pressure grout with neat cement. Hold pressure on casing overnight.

(3) Move rig about 5 to 10 feet and drill an open hole to the top of the first artesian zone as determined by the first hole.

(4) Set 4-inch PVC casing back to the surface and pressure grout. Hold pressure on casing overnight.

(5) Drill out grout plug and drill open hole through the first artesian zone, stopping short of casing depth in first hole.

(6) Move rig over first hole, drill out grout plug, and complete well in the second artesian zone.

(7) Move rig and drill, screen, and case surficial aquifer well using 4-inch casing and screen.

(8) Start development of wells in first and second artesian zones with air lift and pumping while drilling surficial aquifer well.

(9) Develop surficial aquifer well by pumping.

(10) Move to next location and repeat sequence.

By starting the drilling sequence about noon, both grouted casings could be installed in the afternoon and allowed to set overnight. The next day they could be drilled out and the shallow well completed before noon.

Since the cluster wells were within 10 feet of each other, only the cuttings and geophysical logs for the deep hole were required at each location. Determination of casing lengths and screen settings was made from the cuttings and logs. Only one mud pit was required at each location. Bentonite drilling mud was used sparingly since native clays within the hole made their own mud. Each well was flushed with clear water to remove the mud and cuttings from the hole.

Wells were developed directly following drilling by using two air lines from a compressor having a capacity of 85-ft^3/min capacity or a pump for the surficial well. One day of development was generally sufficient at each location. Wells were pumped until the water was clear and the specific conductance was stable for about 1 hour. This procedure was used at all three plant sites during the first phase of drilling.

Most drilling in the surficial aquifer was done with hollow-stem augers because 2-inch PVC casing and screen could be installed through the augers before they were removed from the ground. The drilling sequence was as follows:

1. Rotate augers into the ground until clay encountered (contact with clay determined by sound and feel of drilling machine).

2. Pull inner rods and plug from auger.

3. Install 2-inch PVC screen and casing inside auger.

4. Pick up slightly on auger string and rotate in reverse. This was to pack native material around screen and hold casing in place.

5. Continue reverse rotations as auger removed from hole.

6. Wash screen with clear water.

7. Develop well with pump.

PVC casing and screen were used for all test wells drilled.

Water-Level Measurements

Water levels were measured once in each well to define the water table in the surficial aquifer and the potentiometric surface in the underlying first and second artesian (intermediate) aquifers. Recorders were installed on two to four test wells at each study site to obtain continuous water-levels in each aquifer. The recorders were operated for about 1 year to determine aquifer response to recharge and discharge and the head relations between aquifers.

Water-Quality Sampling

Water-quality was sampled at 107 surface-water and ground-water sites at the phosphate chemical plants or mines. Most sites were sampled once and samples were analyzed for an extensive suite of chemical and physical properties, nitrogen and phosphorus species, radiochemicals, trace elements, and organic substances. Samples from test wells installed primarily to determine water levels were analyzed only for pH and specific conductance. Approximately 5,400 determinations were made. The results are published in a separate data report by Miller and Sutcliffe (1982).

The term "total" is used to indicate that at least 95 percent of the substance present in an unfiltered sample was analyzed regardless of its physical or chemical form. "Total recoverable" means that the sample received mild acid digestion before analysis to solubilize readily dissolved substances. This determination represents something less than the "total" amount. "Dissolved" materials are defined as those that pass through a 0.45 micrometer (μm) membrane filter (Skougstad and others, 1979, p. 4).

The total alpha determinations are reported in picocuries per liter (pCi/L) equivalent to natural uranium. Total beta is reported in picocuries per liter equivalent to strontium-90 and yttrium-90 in secular equilibrium. The uranium (U), thorium (Th), lead (Pb), and polonium (Po) isotopes are "total" determinations that include dissolved and suspended material. Some difficulty was reported in determining total alpha and beta on process water because of the hygroscopic nature of the dried residues. These samples were redried and immediately counted to reduce this type of error.

Radiochemical analyses were made by the U.S. Environmental Protection Agency, Eastern Environmental Radiation Facility, Montgomery, Ala. Nitrogen and phosphorus species, suspended solids, color, turbidity, biochemical oxygen demand (BOD), chemical oxygen demand (COD), total organic carbon (TOC), and dissolved organic carbon (DOC) were determined by the U.S. Geological Survey Water Quality Service Unit, Ocala, Fla. All other laboratory analyses were made by the U.S. Geological Survey National Water Quality Laboratory-Atlanta, in Doraville, Ga. Most analytical methods used by the Geological Survey for inorganic determinations are described by Skougstad and others (1979). Methods used for organic determinations are described by Goerlitz and Brown (1972). Methods of sample preparation are described by Friedman and Beetem (1980).

Data Interpretation

Several conceptual approaches were used to determine whether water being sampled had flowed from a source such as a gypsum stack or slime pond to the sampling point. These approaches were based on: (1) the hydraulic gradient from the potential source to the sampling point; (2) concentrations of substances at the sampling point in relation to concentrations at the source and at background water-quality sites; (3) concentrations of substances such as bromide and iodide that are not normally found in ground water in the study area; (4) relations between constituent concentrations that normally would not be expected to occur in natural waters; (5) variability in concentrations that was greater than that normally found in water of an aquifer, especially if wells are close to a source and each other; (6) recognizable and logical patterns in the distribution of concentrations near a source; and (7) recognizable relations between water levels and concentrations. Migration from a source to a sampling point was considered to be more certain if several of these conditions were met.

Hydraulic gradients of aquifers varied considerably within a season and during a year. The absence of a gradient at the time of water-level measurement or water-quality sampling does not necessarily mean that a hydraulic gradient had not existed at other times and that flow could not have occurred previously from a source.

PRINCIPLES AND PROCESSES

General principles and processes of chemistry, of nuclear and radiochemistry, and of physics are discussed in this section so that these concepts can be referred to in later sections. The concepts discussed were used in interpretation of observed constituent concentrations in water. Many solutes (dissolved substances) that migrate from a source are affected significantly by one or more of the processes described.

The solutes in water from chemical plants or mining operations may react on contact with aquifer material and with native water. Such reactions cause solutes to migrate at much slower rates than the flow of ground water. Different materials in aquifers, such as sands, clays, and a variety of minerals, may be relatively inert toward one solute, but quite reactive toward another. Some solute-aquifer reactions can retard or temporarily halt migration of a solute until the aquifer is locally depleted of reactive materials or aquifer materials are sufficiently coated with precipitate to slow their reactions. When depletion or coating occurs migration will continue. Sands tend to be less reactive with most solutes than clays or carbonate materials. Fluoride ions are reactive with sands, especially at low pH.

Particulate materials, such as gypsum, clays, and organic detritus, filter out of water as it flows through an aquifer. Colloidal material may migrate if velocities are high enough and aquifer voids are large. If the pH of water containing suspended materials is shifted such that the net charge on particles approaches zero, flocculation (formation of larger, more settleable particles) occurs.

The following principles and processes aided in interpretation of observed data. Possible reactions are included.

Dissolution

Dissolution is the process of dispersing a material uniformly in a solvent, such as water, in a form that cannot be settled or filtered. Some materials are readily soluble and will dissolve if given sufficient time. Other substances are relatively insoluble and will dissolve only to a small degree. When this limit is reached, the solution is said to be saturated with respect to that substance.

For relatively insoluble substances such as fluorapatite [$Ca_5(PO_4)_3F$], one of the minerals found in phosphate ore, very little dissolves in water unless acid is added. Stumm and Morgan (1970) and Laitinen (1960) discuss solubility products and the acid-base equilibrium that are involved in dissolution of ionic substances. Some possible chemical reactions involved in dissolution of phosphate ore are given below:

$$6Ca_5(PO_4)_3F + SiO_2 + 30H_2SO_4 + 58H_2O \rightarrow$$

$$30CaSO_4 \cdot 2H_2O \downarrow + H_2SiF_6 + 18H_3PO_4 \qquad (1)$$

$$CaCO_3 + H^+ \rightarrow Ca^{+2} + HCO_3^{-1} \qquad (2)$$

$$HCO_3^{-1} + H^+ \rightarrow CO_2 + H_2O \qquad (3)$$

$$M_2O_X + 2XH^+ \rightarrow 2M^{+X} + XH_2O \qquad (4)$$

Reactions of process water with aquifer materials will dissolve many substances. An increase in bicarbonate ions should be particularly noticeable because of the dissolution of carbonate minerals.

The solubility of a mineral species can be described generally by the product of the activities of the ions released when it dissolves in water. For example, the activity (HPO_4^{-2}) may be considered to be the effective concentration of the ion. The activity is calculated from the total concentration of all phosphate species, [$PO_{4_T}^{-3}$] times its activity coefficient γ_2. If the ions are complexed or protonated (protonation is the addition of a hydrogen ion), then the total concentration must be multiplied by the ionization fraction (α_2) to compensate for those effects. For the HPO_4^{-2} ion, the activity is calculated using equation 5.

$$(HPO_4^{-2}) = [PO_{4_T}^{-3}]\ \gamma_2\ \alpha_2. \qquad (5)$$

The ionization fraction can be represented by

$$\alpha_2 = \frac{[HPO_4^{-2}]}{[PO_4^{-3}] + [HPO_4^{-2}] + [H_2PO_4^{-1}] + [H_3PO_4] + [\text{complexes}]} \qquad (6)$$

where bracketed terms mean concentration in moles per liter. When acid is added, the HPO_4^{-2} is converted to the more protonated forms, $H_2PO_4^{-1}$ and H_3PO_4, and α_2 decreases. The resultant decrease in HPO_4^{-2} concentration allows more phosphate mineral to dissolve. Further understanding of these processes can be obtained from chemistry texts such as Laitinen (1960) and Stumm and Morgan (1970).

Plummer and others (1978) described the solubility equilibrium of fluorapatite using equation 7.

$$(Ca^{+2})^5\ (HPO_4^{-2})^3\ (OH^-)^3\ (F^-) = K_{sp} \qquad (7)$$

The solubility product, for reaction 7 at 25°C and 1 atmosphere pressure is 1.6×10^{-67}. There are several computer programs such as those by Kharaka and Barnes (1973), called SOLMNEQP, and by Plummer and others (1978), called WATEQF available to determine if water is at equilibrium with respect to minerals by using equilibrium expressions such as equation 7. Nordstrom and others (1979) have reviewed the state of the art for mineral equilibrium models.

Equations 1 and 2 define the reaction of two possible components [$Ca_5(PO_4)_3F$ and $CaCO_3$] of Florida phosphate rock with sulfuric acid at a chemical plant. The actual reaction may be in more than one step. Sometimes phosphoric acid is used before sulfuric acid to prevent a coating of gypsum from forming on the phosphate rock. Actually, $CaSO_4 \cdot 2H_2O$ is not the only calcium precipitate formed, but the hemihydrate ($CaSO_4 \cdot \frac{1}{2}H_2O$) and anhydrite ($CaSO_4$) also form in different percentages depending on the reaction conditions (Wahba and others, 1980).

Equation 4 is a generalized reaction of a metal oxide with acid. Similar reaction would occur with most metal oxides, carbonates, and fluorides.

The average composition of Florida phosphate rock as reported by Wahba and others (1980) might be represented by the following mixture of substances

$$1.000\ Ca_5(PO_4)_3F,\ 0.352\ CaCO_3,\ 0.129\ CaF_2,\ 0.0459\ MgCO_3$$

and a mixture of clays and other minerals with the following approximate quantity and composition

$$0.00529 Na_{17}K_2Fe_{16}Si_{72}Al_{24}O_x(CO_3)_9(SO_4)_{13}.$$

The value of x is about 184 on the basis of charge balance or 180 on the basis of the ratio of 8 silica to 20 oxygens as found in many clay minerals.

Neutralization

Neutralization is the combination of an acid and a base to form water and a salt. As process water from a gypsum stack migrates into an aquifer, acids will be neutralized by carbonates, hydroxides, and oxides that are present in the aquifer. This increases the ionization fractions and activities of SiF_6^{-2} and HPO_4^{-2} and dissolves calcium from the aquifer. In the absence of competing reactions, $CaSiF_6 \cdot 2H_2O$ and $CaHPO_4 \cdot 2H_2O$ (Weast, 1976) will probably precipitate and control the migration of silicon, fluoride, and phosphate.

Examples of possible reactions are given below:

$$Ca^{+2} + 2HCO_3^{-1} + 2HF \rightarrow CaF_2 \downarrow + 2H_2O + 2CO_2 \uparrow \tag{8}$$

$$CaCO_3 + H_3PO_4 + H_2O \rightarrow CaHPO_4 \cdot 2H_2O \downarrow + CO_2 \uparrow \tag{9}$$

$$CaCO_3 + HSO_4^{-1} + 2H_2O \rightarrow CaSO_4 \cdot 2H_2O \downarrow + HCO_3^{-1} \tag{10}$$

$$Fe_2O_3 + 2H_3PO_4 \rightarrow 2FePO_4 \cdot 2H_2O \downarrow + H_2O \tag{11}$$

$$Al_2O_3 + 2H_3PO_4 \rightarrow 2AlPO_4 \downarrow + 3H_2O \tag{12}$$

$$CaCO_3 + H_2SiF_6 + H_2O \rightarrow CaSiF_6 \cdot 2H_2O \downarrow + CO_2 \uparrow \tag{13}$$

In equations 8 through 13, water is a product of neutralization. Some minerals hold water of hydration when they form, consequently all or some of the water produced by neutralization may appear as part of a mineral as in $CaHPO_4 \cdot 2H_2O$ in equation 9. The upward arrows indicate formation of a gas and the downward arrows indicate that an insoluble precipitate is formed.

Mineral Precipitation

When the product of activities of ions of a relatively insoluble mineral exceed the solubility product, the solution is said to be supersaturated with respect to that mineral. Usually, precipitation occurs until saturation is reached. The study of the rate of a reaction, such as precipitation, is called kinetics. The kinetics of precipitation are discussed by Stumm and Morgan (1970).

Equations 8 through 13 are examples of precipitation (followed by downward arrow) that result after acids are neutralized. The reaction that controls the migrations of an ion, if more than one reaction is possible, is determined by the relative solubilities of possible precipitates and the relative availability of reactants in the aquifer.

Adsorption

Adsorption from water is the holding or concentrating of a dissolved substance at the surface of a solid. Adsorption may involve replacement of water at the solid-water interface by the adsorbed substance (adsorbate).

Organic molecules can be adsorbed by intermolecular attractions (Van der Waals attraction) that produce physical adsorption and that do not involve strong electrical forces of chemical bonding. Some organic and inorganic substances can be adsorbed by chemical reactions with surface atoms of the solid phase (Stumm and Morgan, 1970).

Ion Exchange

Ion exchange is the exchange of an ion in solution for an equivalent amount of another type of ion that is held by a solid material, such as sand, clay, or metal oxides. At a pH lower than the pH of the zero point of charge (pH_{zpc}) for a specific material, the material acts predominantly as an anion exchanger and as a cation exchanger to a very limited extent. As the pH increases, the cation exchange capacity increases and the anion exchange capacity decreases (Stumm and Morgan, 1970). Parks (1967) discusses the measurement of the zero point of charge and lists values for some common materials. Literature values for the pH_{zpc} vary with the method of determination. Several values are listed in table 2 (Stumm and Morgan, 1970).

Table 2.--Values of pH_{zpc} for selected substances

Substance	pH_{zpc}
α - Al_2O_3	9.1
α - $Al(OH)_3$	5.0
Fe_3O_4	6.5
γ - Fe_2O_3	6.7
$Fe(OH)_3$ (amorphous)	8.5
MnO_2	2-4.5
SiO_2	2.0
Kaolinite	4.6
Montmorillonite	2.5
Albite	2.0

Acidic water from chemical plants will reduce the cation exchange capacity of many ion exchange materials found near a source of process water. Reactions with H^{+1} will release cations such as Ca^{+2}, Mg^{+2}, Na^{+1}, and K^{+1} that were initially held by cation exchangers. If the pH of seepage is below the pH_{zpc} for a mineral in a given chemical environment, the mineral may have a significant increase in its anion exchange capacity. As process water flows away from a chemical plant and is neutralized, cation exchange will again predominate over anion exchange. Even at a near neutral pH, there is a small anion exchange capacity that can reduce sulfate concentrations (Wood, 1978). Data in table 2 indicate that the cation exchange capacity increases significantly for SiO_2, albite, montmorillonite, and perhaps MnO_2 as the pH increases above about 2.0 to 2.5. Above pH of 4.6 and 5.0, kaolinite and α - $Al(OH)_3$, respectively, increase significantly in cation exchange capacity. Above pH 6.5, some iron oxides become important cation exchangers. The pH_{zpc} is affected by other ions in solution, so the data in table 2 can only be considered as approximations. There is some question of the transfer value of laboratory data in table 2 to reactions in aquifers because some listed substances may be dissolved or altered by long-term contact with unneutralized process water.

Because the native water type at the chemical plants is predominantly $Ca(HCO_3)_2$, influx of water that is neutralized and high in sodium ions ($Na+^1$) will result in an exchange of sodium ions for calcium ions (Ca^{+2}) as shown in equation 14.

$$CaX_2 + 2Na^+ = Ca^{+2} + 2NaX \qquad (14)$$

where X represents the charged sites of the ion exchanger. After sufficient ion exchange, the ratio of sodium to calcium in water from a phosphate chemical plant will approach that of native water. Cation exchange alters the proportions of cations, but not the total concentration of cations as reported in milliequivalents per liter. Helfferich (1962) gives an extensive discussion of ion exchange.

Dilution

As seepage from a source, such as a gypsum stack, mixes with native water, the resultant concentration of dissolved substances in the mixture will be between the concentrations of the seepage water and the native water if no reactions occur. The resultant concentration in the mixture of ambient ground water and seepage depends on the relative volumes of each as shown in equation 15.

$$C_m = \frac{C_s V_s + C_n V_n}{V_s + V_n} \qquad (15)$$

where

C_m = concentration of the mixture of waters,

s and n = subscripts for seepage and native water, respectively. The equation applies to fixed portions of water that are well mixed.

The mixing process for flow through porous media, such as an aquifer, is best described in terms of hydrodynamic dispersion. Hydrodynamic dispersion results from the different paths that water can follow as it flows through an aquifer. One particle of water may move in a relatively direct path, whereas another may take a rather circuitous route. Hydrodynamic dispersion is the macroscopic outcome of the movement of individual particles through a porous medium (Bear, 1972). Konikow and Bredehoeft (1978) discuss solute transport in ground water for conservative (unreactive) substances. Grove and Rubin (1976) discuss the effects of chemical reactions, ion exchange, and radioactive decay on solute transport.

Bromide, chloride, and iodide ions are good choices for determining effects of dilution because they are relatively conservative (unreactive) at the pH of water usually found in the aquifers of the study area. Anion exchange can affect concentrations of these anions. Iodide and bromide ions are more readily affected by anion exchange because their concentrations are generally less than that of chloride.

Radioactive Decay

Radioactive decay is the spontaneous change of the mass or charge of the nucleus of an atom. The loss of a helium nucleus is called alpha emission. This reduces the nuclear weight by approximately four atomic mass units (AMU) and reduces the atomic number by two. Beta decay is the ejection of an electron from the nucleus. The change in mass of the atom is small, but the atomic number increases by one. Electron capture is the capture of an orbital electron by the nucleus. The change in atomic mass is small and the atomic number decreases by one. Gamma emission is the loss of high energy electromagnetic radiation. Gamma emission may occur if alpha or beta emissions leave the nucleus in an excited state.

The basic equations used to describe radioactive decay are given in equations 16 through 18.

$$\lambda = \frac{\ln 2}{t_{\frac{1}{2}}} \qquad (16)$$

$$\frac{dN}{dt} = -\lambda N \qquad (17)$$

$$\frac{N}{N_o} = e^{-\lambda t} \qquad (18)$$

where

λ = decay constant,

$t_{\frac{1}{2}}$ = half-life, time for half of the amount of an isotope to decay, and

N = number of atoms of an isotope at time t or time zero (o).

Additional information on radioactive decay is given in standard texts, such as Friedlander and others (1964).

It may be possible to "date" water percolating through a gypsum stack by measuring the ingrowth of isotopes present in the gypsum and estimate the natural permeability of the gypsum stack. For example, for short residence times, the increase in Rn-222 in process water because of decay of Ra-226 in the gypsum might provide an approximate residence time. In practice, it may be difficult to determine the fractions of Rn-222 that are: (1) lost to the atmosphere, (2) trapped with gypsum crystals, (3) dissolved in process water percolating through the gypsum stack, and (4) contributed by process before it percolated into the gypsum stack. Other tracers, such as dyes or noble gases (helium, neon, or argon measured by mass spectrometry), may be more practical and conclusive.

All naturally occurring elements with atomic numbers higher than 83 are radioactive and belong to the uranium, thorium, or actinium series (Friedlander and others, 1964). Each of these series begins with a long-lived parent isotope and go through a series of decay processes until a stable lead isotope is reached. Friedlander and others (1964) and other texts show these series.

Radioisotopes in process water from gypsum stacks are predominantly members of the uranium series. At the AMAX site, the concentration of uranium-235, the parent isotope of the actinium series, was 68 pCi/L, whereas the concentration of uranium-238, the parent isotope of the uranium series, was 1,937 pCi/L. The concentration of thorium-232, the parent isotope of the thorium series, was 14 pCi/L. The percentages of the total radioactivity from parent isotopes are summarized below.

Source	U-238 (percent)	U-235 (percent)	Th-232 (percent)
Process water, AMAX	95.9	3.4	0.7
Process water, USSAC	93.1	6.2	.7
Phosphate rock, USSAC	85.3	9.2	5.5
Phosphate rock, Florida[1]	94.6	4.4	1.0
Gypsum, Florida[1]	91.0	4.9	4.1

[1] Guimond and Windham, 1975.

Guimond and Windham (1975) state that radionuclides in the uranium and actinium series are in secular equilibrium in phosphate ore and that members of the thorium series are close to equilibrium. An ore sample from USSAC indicated that the uranium series was approximately at secular equilibrium to lead-210. The activity of polonium-210, the last radioactive member of the series, had an activity of about 64 percent of its parent, uranium-238.

Equilibrium of the uranium series is not maintained in process water. Thorium-230 activity in process water at AMAX was 56 percent of that for uranium-238. Dissolved radium-226 activity was only 2.4 percent. Both of these isotopes are consequently enriched in the gypsum (Guimond and Windham, 1975, p. 17).

Isotopes initially in solution, those that redissolve from gypsum, and those that become available for solution as the result of radioactive decay (alpha particle recoil) in gypsum have the potential for migrating from the gypsum stack. For example, of all the radioisotopes given by Guimond and Windham (1975), radium-226 has a considerably higher activity in gypsum. The daughter isotope of radium-226 is radon-222, an inert, gaseous alpha-emitter. One might expect radon-222 to be quite mobile. This mobility was not determined, because gross alpha determinations for water samples do not measure radon-222 as it is lost during evaporation of water and drying of solid residues before alpha activity is measured.

Determination of uranium and thorium isotopes (Miller and Sutcliffe, 1982, table 7) indicates that these elements are not mobile at the AMAX plant. Likewise, very little radium appears to migrate from the gypsum stack. Protactinium-234 may contribute to some of the migrating beta emitters at AMAX, but most of it probably comes from daughter isotopes of radon-222 and radon-219 from the uranium and actinium series, respectively; namely, lead-214, bismuth-214, lead-210, bismuth-210, lead-211, and thallium-207. Lead-210, because of its longer half-life (22 years), may be a candidate for migration, despite the relatively low solubility of lead. Only 1.3×10^{-11} mg/L (6.2×10^{-17} moles/L) of lead-210 is required to produce 1 pCi/L of activity.

Migration of radioactive isotopes from the AMAX gypsum stack might occur in the following manner. Using Guimond and Windham's (1975) concentration of 33 pCi/g of radium-226 in gypsum and a standing gypsum mass of 1.13×10^{7} tons (James Smith, AMAX, oral commun., 1981) at the AMAX site, there are about 3.4×10^{14} pCi of radium-226 in the gypsum stack. This produces 4.3×10^{10} pCi of radon-222 each minute. Most radon-222 may remain trapped within gypsum crystals because the volume of gas produced in a 1-milliliter cube of the gypsum stack is about 5.7×10^{-18} mL per minute at 1 atmosphere of pressure. Actual pressures are probably much greater than 1 atmosphere and volumes of trapped gases very small. Probably some small fraction of this escapes into the atmosphere from the unsaturated zone or dissolves in water percolating downward or laterally through the saturated parts of the stack. Also, as radon migrates through the surficial aquifer, some is lost to the atmosphere through degassing. The remainder decays quickly through four short-lived isotopes to lead-210 that in turn decays through bismuth-210 to polonium-210 (half-life 138.4 days). Both lead and polonium would migrate at very low concentrations until they are removed from solution by ion exchange, adsorption, or substitution into mineral lattices or they undergo radioactive decay. In summary, a normally undetected alpha emitter could migrate, producing beta emitters.

Ion Indices

Increases in concentrations of solutes in ground water near a phosphate chemical plant above background levels probably originate from one of two sources. One source is minerals in the aquifer. Local variations in abundances of minerals in the aquifer could produce natural variations in concentrations especially in the surficial aquifer. For example, rainfall percolating into a surficial aquifer that is composed mainly of silica sands could produce water of low dissolved-solids concentration, but where pockets of calcite or gypsum occur in the aquifer, their dissolution may produce water containing significantly greater concentrations of some solutes. The concentrations of solutes in deep aquifers where residence times of water are long would not be expected to vary greatly over short distances unless overriding local effects occur. A second source of solutes in ground water is process water from gypsum stacks, cooling ponds, and associated drainage ditches.

To determine which of these two sources may be responsible for observed increases in major ions in the vicinity of the chemical plants, an index of nonmineral input (INMI) was developed. The principle is that natural sources of solutes generally increase the concentrations, in milliequivalents per liter, of specific cations and anions in essentially equal (stoichiometric) amounts. For instance, seawater will increase sodium and chloride concentrations by similar amounts. Hem's (1970) analysis of normal seawater gives a mineral imbalance of 12.5 percent, so this must be considered where saline water is present. Gypsum will increase concentrations of calcium and sulfate equally. Calcite will increase concentrations of calcium and carbonate species equally and dolomite increases concentrations of calcium plus magnesium the same as the carbonate species. Ion exchange can alter the ratios of some ions, but this effect should be minor for native water flowing short distances, especially if the native water is near equilibrium with respect to ion exchangers in the aquifer.

The predominant species in process water are H^+, Na^+, $SO_4{}^{-2}$, $HSO_4{}^{-2}$, H_2SiF_6, and H_3PO_4. Contact of process water with an aquifer usually removes most of the H^+, H_2SiF_6, and H_3PO_4. The main solutes to migrate in the aquifer are Na^+ and $SO_4{}^{-2}$. Thus, near the solute sources, an increase in Na_2SO_4 would likely indicate that seepage had occurred. After migrating for a sufficient distance, Ca^{+2} will tend to exchange with Na^+ and appear as an increase in Ca^2 and SO_4.

The index of nonmineral input (INMI) measures the percentage increase in concentrations of Na^+ above Cl^- and $SO_4{}^{-2}$ plus alkalinity above Ca^{+2} plus Mg^{+2} compared to background concentrations. Equation 19 is used to calculate the index.

$$\text{INMI}=\frac{\left|(Na_S-Na_B)-(Cl_S-Cl_B)\right|+\left|(Ca_S-Ca_B+Mg_S-Mg_B)-(SO_{4S}-SO_{4B}+Alk_S-Alk_B)\right|-\left|C_S-A_S\right|-\left|C_B-A_B\right|}{C_B+A_B}\times 100 \qquad (19)$$

where

INMI = index of nonmineral input, in percent above background,
Alk = alkalinity, in milliequivalents per liter,
C and A = cation and anion sums, in milliequivalents per liter, and
S and B = subscripts for sample and background concentrations.

The vertical lines in equation 19 and following equations mean that the absolute value of the quantity between them is taken before further calculations are performed, that is all results are given a positive sign.

Equation 19 can be rewritten to simplify the calculations as shown in equation 20.

$$\mathrm{INMI}=\frac{\left|(\mathrm{Na}_S-\mathrm{Cl}_S)-(\mathrm{Na}_B-\mathrm{Cl}_B)\right|+\left|(\mathrm{Ca}_S+\mathrm{Mg}_S-\mathrm{Alk}_S-\mathrm{SO4}_S)-(\mathrm{Ca}_B+\mathrm{Mg}_B-\mathrm{SO4}_B-\mathrm{Alk}_B)\right|-\left|C_S-A_S\right|-\left|C_B-A_B\right|}{C_B+A_B}\mathrm{x}100 \quad (20)$$

For any given hydrologic zone, the terms with subscript B are assumed constant for a limited area. An example of application of the equation and of other indexes are described later.

In the absence of availability of background water-quality data, a percentage mineral imbalance (PMI) can be calculated to determine the source of solutes in ground water using the following equation:

$$\mathrm{PMI}=\frac{\left|\mathrm{Na}_S-\mathrm{Cl}_S\right|+\left|\mathrm{Ca}_S+\mathrm{Mg}_S-\mathrm{SO4}_S-\mathrm{Alk}_S\right|-\left|C_S-A_S\right|}{(C_S+A_S)}\mathrm{x}\ 100 \quad (21)$$

where

PMI = percentage mineral imbalance,

C and A = cation and anion sums, in milliequivalents per liter, respectively, and

S = subscript for sample concentrations.

The PMI is less sensitive to the effects of seepage than is the INMI. The PMI duplicates information contained in the INMI.

The values of INMI and PMI are affected by the accuracy of analytical data, so the terms $\left|C_S - A_S\right|$ and $\left|C_B - A_B\right|$ are subtracted to correct for some types of analytical error. Values significantly above analytical error can usually be attributed to man's influence. Values of INMI and PMI greater than 5 percent are considered by the senior author to be above background levels at the study sites. Values less than 5 percent could be significant if analytical data are very accurate.

In addition to the INMI and PMI, the percentage increase in ions (PII) above background concentrations can be calculated using equation 22.

$$\mathrm{PII} = \frac{(C_S + A_S) - (C_B + A_B)}{(C_B + A_B)} \mathrm{X}\ 100 \qquad (22)$$

where

PII = percentage increase in ions,

C and A = cation and anion sums, in milliequivalents per liter, and

S and B = subscripts for sample and background concentrations.

Specific conductance data could be used to show patterns similar to PII.

The relative values of PII near a source of solutes, such as a gypsum stack, may reveal the direction of solute migration even though the composition of the major ions has been greatly altered. If calculated values of INMI and PII are significantly above background, it probably indicates that seepage has not been altered completely by ion exchange. If the INMI is low while the PII is high, it may indicate that seepage has been altered by the exchange of calcium for sodium or there is some other cultural or natural source of minerals. These indices were useful for interpreting water-quality data because they summarize the relation between six major ions (and indirectly other ions). When values for the indices are plotted or tabulated, they are helpful in determining the occurrence or trends of solute migration.

To demonstrate the use of equations 20 through 22, calculations for surficial aquifer well 9 near the gypsum stack at AMAX are given as follows.

$$\mathrm{INMI} = \frac{\left|(31.320 - 1.241) - (1.392 - 1.326)\right|}{(7.183 + 7.115)} \mathrm{x}\ 100$$

$$+ \frac{\left|(10.978+13.162-10.190-45.804)-(4.691+1.069-4.795-0.979)\right|}{(7.183 + 7.115)} \mathrm{x}\ 100$$

$$- \frac{\left|55.894 - 57.298\right| + \left|7.183 - 7.115\right|}{(7.183 + 7.115)} \mathrm{x}\ 100 = 422 \text{ percent from equation 20.}$$

$$\mathrm{PMI} = \frac{\left|31.320 - 1.241\right| + \left|10.978 + 13.162 - 10.190 - 45.804\right|}{(55.894 + 57.298)} \mathrm{x}\ 100$$

$$- \frac{|55.894 - 57.298|}{(55.894 + 57.298)} \times 100 = 53.5 \text{ percent from equation 21.}$$

$$\text{PII} = \frac{(55.894 + 57.298) - (7.183 + 7.115)}{(7.183 + 7.115)} \times 100 = 692 \text{ percent from equation 22.}$$

As calculated, the INMI for water from well 9 is unusually high when the cations and anions are compared to that of background water. The high percentage indicates the influence of seepage from the gypsum stack. Other surficial aquifer wells adjacent to the gypsum stack at AMAX had INMI's in the range of -0.8 to 1,300 percent. Wells in the first and second artesian aquifers adjacent to the gypsum stack had INMI's that ranged from -1.1 to 18 percent. In general, water from wells at phosphate chemical plants that had an INMI of more than about 5 percent may be assumed to have been affected by seepage of process water.

The PMI for well 9 is also high. The imbalance indicates that the water has been influenced by seepage from the stack. In general, waters from other surficial aquifer wells near the gypsum stack had a PMI that ranged from -0.3 to 79 percent. Water samples from wells in the first and second artesian aquifers adjacent to the gypsum stack had INMI's that ranged from 0.0 to 9.9 percent. As for INMI, percentage imbalances of more than 5 percent indicate that the water sample was probably affected by seepage, unless influenced by other natural sources.

The percentage increase in ions (PII) in water from well 9 is also high. This indicates that solutes have been added to natural water and the mineral content increased. PII for other surficial aquifer wells near the gypsum stack had PII's that ranged from -19 to 1,600 percent.

For subsequent discussions of specific phosphate areas, these three indices are used to assess whether the water from a site had been affected by some industrial influence. The implication that a particular index percentage reflects a cultural rather than natural influence is based on limited data in the Bartow area (USSAC and IMC sites). Nevertheless, the basic assumption that natural water in the areas studied are "well balanced" with respect to minerals is supported by calculated values of PMI for background wells at AMAX. The PMI for each aquifer is given in table 3.

Table 3.--Percentage mineral imbalance for background wells at AMAX

Aquifer	Well No.	Percentage mineral imbalance
Surficial	39	+0.08
First artesian	40	- .12
Second artesian	6	- .83

The values of PMI for background samples are less than 1 percent. Seven wells under or near the AMAX gypsum stack were sampled in May 1966, 4 months before the plant began operations. The wells were open to depths ranging from 98 to 587 feet. Depth of three wells were unknown. PMI for the seven wells ranged from -1.1 to 5.1 percent and averaged 1.6 percent. These low values increase confidence that at phosphate chemical plants a PMI greater than 5 percent results from process water. A low PMI cannot prove that seepage (cultural influence) is not present, but only that its effects are not obvious because water from phosphate chemical plants or mines will react with aquifer materials and reduce the PMI. Negative values of PMI result because the correction term (last term) in equation 21 is greater than the imbalances calculated in the first two terms.

Chemical Reactions with Aquifers

As process water from gypsum stacks contacts aquifer water and materials, especially carbonates and oxides, it is neutralized and the pH is raised. The pH of neutralized process water would be expected to tend toward 6.0 to 6.4, where the maximum buffering capacity of carbonate species occurs (Stumm and Morgan, 1970, p. 140). The major cations released are calcium and magnesium as the result of dissolution of limestone and dolomite in the aquifer by the process water.

The first contact of process water with an aquifer increases sodium concentration because of dissolution of sodium-bearing minerals or exchange of H+ for Na+ initially held by ion exchangers in the aquifer. As the pH is raised, sodium concentrations are controlled by dilution and ion exchange.

Silica and fluoride in process water are rapidly and simultaneously lost because of their association in H_2SiF_6. Either contact with native silica or neutralization and precipitation are responsible for this loss, as shown in equations 23 or 13, respectively.

$$2H_2SiF_6 + SiO_2 \rightarrow 3SiF_4 \uparrow + 2H_2O \qquad (23)$$

Some chemical plants take advantage of this reaction to defluorinate phosphoric acid. Silica is added to the acid and a partial vacuum applied using barometric condensers. Because of the high vapor pressure of silicon tetrafluoride (SiF_4) and the ubiquity of silica in soils, equation 23 probably describes the loss of fluoride and silica, at least at a low pH. At USSAC, the loss was observed to occur at a pH of less than 2.3, which tends to support the reaction indicated in equation 23 at low pH. The formation of insoluble fluosilicates (equation 13) may be responsible for loss of some fluoride and silica at higher pH values. Insoluble fluosilicate deposits are suspected to occur in at least one waste injection site in Florida. Weast (1976) lists $CaSiF_6 \cdot 2H_2O$ as a slightly soluble crystalline solid that dissolves in hydrochloric and hydrofluoric acids. Both reactions (evolution of SiF_4 and precipitation of $CaSiF_6 \cdot 2H_2O$) may occur; their relative importance is determined by the relative abundance of $CaCO_3$ to SiO_2 in the aquifer. Equation 13 would be expected to predominate if acidic wastes contacted a limestone aquifer that was low in silica. Equation 23 would be expected to predominate if acidic wastes contacted a sand aquifer that was low in carbonate.

Sulfate concentrations in water from gypsum stacks are quickly reduced in aquifers by precipitation to about 2,000 to 2,600 mg/L by reactions with calcium dissolved during neutralization of acids. This reaction also takes place at a pH of less than 2.3. Approximate solubility calculations verify that calcium and sulfate are near equilibrium with gypsum for some water samples collected near gypsum stacks. Once sulfate concentrations are reduced to about 2,000 mg/L, the concentrations appear to be affected mainly by dilution. Some small fraction may be lost to anion exchange (Wood, 1978). Bacteria may reduce some sulfate to hydrogen sulfide once conditions in an aquifer are conducive to their growth.

Phosphate concentrations decrease until the pH reaches the range of 2.3 to 3.3. The cause of this decrease is probably not due to fluorapatite precipitation because of the low pH and the loss of fluoride at lower pH values. In the pH range of 2.3 to 3.3 at which orthophosphate was observed to precipitate, it occurs predominantly as $H_2PO_4^{-1}$. As pH is elevated, a small fraction of the orthophosphate will occur as HPO_4^{-2} and probably cause precipitation of brushite ($CaHPO_4 \cdot 2H_2O$), or similar compounds, as shown in equation 24.

$$H_2PO_4^{-1} + CaCO_3 + H^+ + H_2O \rightarrow CaHPO_4\ 2H_2O \downarrow + CO_2 \uparrow. \tag{24}$$

After process water undergoes neutralization to about pH 5 and the loss of most of major species (H^+, H_2PO_4, H_2SiF_6, SO_4^{-2}), the concentration of HCO_3^- increases due to the reaction of remaining CO_2 that was formed at lower pH values, as shown in equation 25.

$$CO_2 + CaCO_3 + H_2O \rightarrow Ca^{+2} + 2HCO_3^{-1} \tag{25}$$

This reaction caused high alkalinity concentrations (510 and 2,910 mg/L) in AMAX wells 9 and 13.

If a metal ion, Me^{+Z}, does not form complexes, the logarithm of its concentration is a linear function of pH if insoluble oxides or hydroxides control solubility. Equation 26 describes this behavior (Stumm and Morgan, 1970).

$$\log [Me^{+Z}] = \log {}^{c}K_{so} + ZpK_{w} - ZpH \qquad (26)$$

where

${}^{c}K_{so}$ = the solubility product for Me $[OH]_{z}$,

Z = the valence of the metal, and

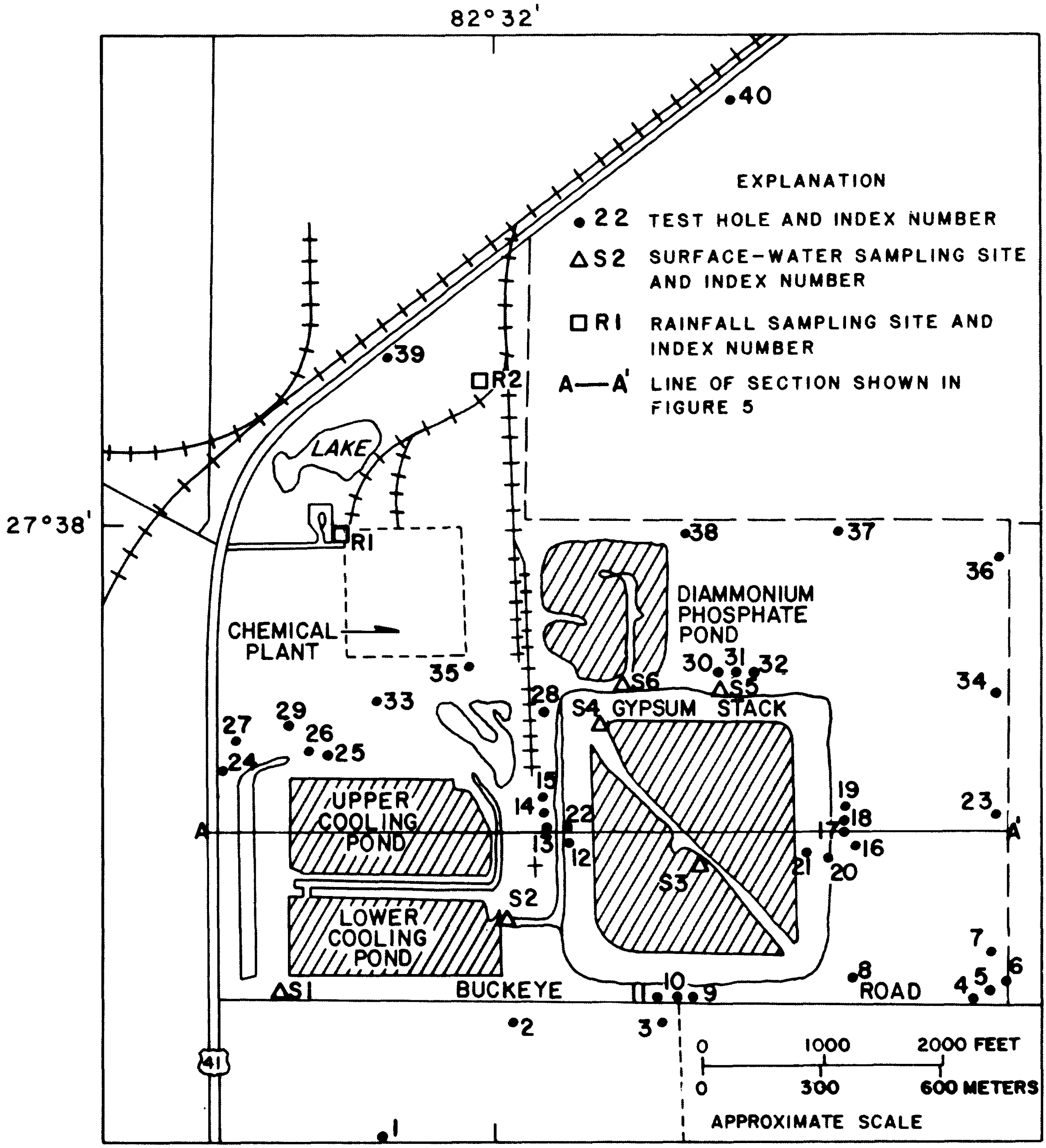
K_w = the ion product of water.

Since ${}^{c}K_{so}$ and K_w are constant for a given temperature and pressure, the logarithm of metal ion concentrations vary with a slope of -Z as pH increases. The log ${}^{c}K_{so}$ can be determined from extrapolation of the linear part of the plot where log $[Me^{+Z}] = 0$. At this point, log ${}^{c}K_{so}$ is equal to difference of two known terms, ZpH - ZpK_w.

Some metals, especially iron, aluminum, and zinc, form hydroxyl and other soluble complexes that complicate the simple behavior described by equation 26. Examination of trace metal data (Miller and Sutcliffe, 1982) indicates that precipitation of metals in ground water affected by process water from the USSAC gypsum stack generally begins by about pH 2.3 except for iron and aluminum, which begin below a pH of about 2.9. Controlled laboratory reactions of process water with aquifer samples may determine whether oxide formation, cation exchange, or precipitation control metal concentrations and migration rates.

AMAX PHOSPHATE, INC., CHEMICAL PLANT

AMAX Phosphate, Inc. is situated in the Gulf Coastal Lowlands in northwestern Manatee County (White, 1970). Natural land surface altitudes range from about 10 feet above sea level at the northwest corner of the plant's property to about 30 feet above sea level in the southeast corner. Altitude of the gypsum stack is 50 or more feet higher than the adjacent land surfaces (Miller and Sutcliffe, 1982). The plant layout, locations of process water ponds, the gypsum stack, and sampling sites are shown in figure 2. The plant processes phosphate from mining operations in nearby counties. Water from the plant is discharged to a gypsum stack. The impact of seepage from the stack on the surficial and intermediate confined aquifers was studied.



BASE MAP FROM AMAX PHOSPHATE, INC.

Figure 2.--Plant layout and locations of data-collection sites at the AMAX plant.

Descriptions of the 40 test wells at the site, including their depth, construction, and water levels, are included in the report by Miller and Sutcliffe (1982). The depth of most wells ranged from 15 to 150 feet, although wells as shallow as 2.5 feet and as deep as 950 feet were drilled or were available for use. Depths to water were plus 4 to minus 15 feet above and below land surface. Because of the potential for ground-water contamination around the gypsum stack, most wells were drilled to determine the quality of water near the stack. In addition to data obtained from the wells, five surface-water sites were sampled for water-quality analysis and rainfall was collected for quality analysis at two sites.

The AMAX phosphate plant was selected for study because the site is in nearly pristine condition with respect to disturbance of the geologic materials and the presence of other sources of contamination. Excavation that would disturb the aquifer system had not been done on or near the site prior to or during this study.

Climate in the general area of the AMAX plant is characterized by warm, humid summers and mild, moderately dry winters. The mean annual temperature is about 72°F; mean monthly temperatures range from 60°F to 80°F. The average annual rainfall is about 55 inches. The rainy season, June through September, accounts for about 60 percent of the annual rainfall. Figure 3 shows monthly rainfall at the AMAX plant and at the National Oceanic and Atmospheric Administration, Bradenton weather station, which is about 15 miles south of the AMAX plant.

Hydrogeology

Ground water has been developed for water supply in the AMAX area for many years. Initially 6- to 10-inch diameter wells supplied water for irrigation of crops; between 1951 and 1954, 29 of these wells were inventoried by the U.S. Geological Survey near the AMAX site (Peek, 1958). Most wells flowed. The wells ranged in depth from 400 to 600 feet and were finished or opened to the intermediate and Floridan aquifers. The potentiometric surface of the Floridan aquifer was about 24 feet above sea level in September 1954. Water from most wells had chloride concentrations of about

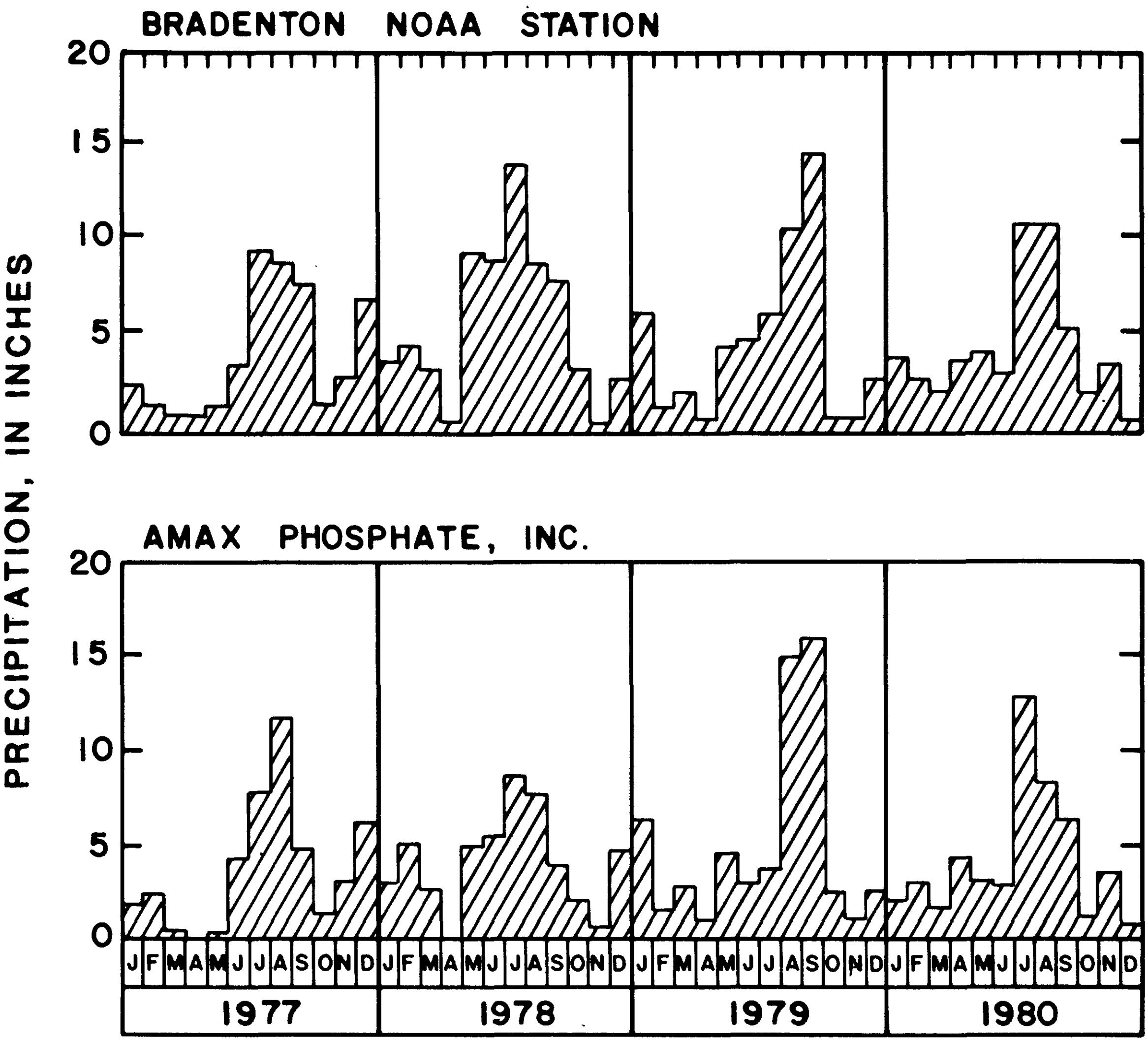


Figure 3.--Monthly precipitation at the AMAX plant and at Bradenton, 1977-80.

50 mg/L, but a few concentrations were as high as 100 mg/L. The common practice of drilling was by cable-tool method in which the casing was driven into the ground until it encountered firm limestone. Subsequently, drilling of open hole continued until a sufficient quantity of water was flowing from the well. As a result, most wells had short casings and long reaches of open hole. Except for wells plugged in 1966 and 1967 by the Borden Company and those within the highway right-of-way that were plugged when U.S. Highway 41 was widened, the wells still exist.

Early in 1966 the U.S. Geological Survey and the Florida Bureau of Geology collected data from several abandoned irrigation wells at the site where the AMAX plant is now located. Geophysical logs were obtained from the wells, and water samples were collected at varied depths from these and other domestic and irrigation wells. Analyses of water from three representative wells are as follows:

Well depth (ft)	Casing length (ft)	Specific conductance (μmho)	Sulfate (mg/L)	Fluoride (mg/L)
98	35	780	106	0.6
284	170	810	202	1.0
548	248	1,080	332	1.1

Well 26 (fig. 2) was one of the wells inventoried in 1966. Several of the wells are located under the present gypsum stack and cooling ponds; it is not known if all these wells were plugged. If the wells had not been plugged, there may be a direct connection between the gypsum stack and the intermediate and Floridan aquifers. The driller's log of the well indicates some hydraulic characteristics of the rocks of the area. At depths of 139 to 149 feet limestone occurs, and the well flowed at the rate of 240 gallons per hour (gal/h). At depths of 169 to 174 feet, blue clay occurs; at 170 feet the well flowed at the rate of 480 gal/h. At a depth of 225 feet limestone occurs, and the well was pumped at the rate of 500 gal/h with 31 feet of drawdown. From depths of 225 to 245 feet limestone occurs; the well was pumped at the rate of 500 gal/h with 30 feet of drawdown. At depths of 280 to 300 feet limestone occurs; the well flowed at 60 gal/min and was pumped at the rate of 120 gal/min with 15 feet of drawdown.

The caliper log of nearby well 2 (fig. 4) indicates that a producing zone occurs between 540 and 660 feet. The zone, in the Suwannee Limestone in the Floridan aquifer, is heavily used in the area for irrigation water. Because large amounts of water can be developed from this zone, few wells are drilled to the underlying Ocala Limestone or the Avon Park Limestone (a large producer in other areas). The Avon Park Limestone may produce saline water in this area (Wilson and Gerhart, 1982).

Pumpage for irrigation is considerable in the area. Potentiometric surface maps of the Floridan aquifer show that water levels decline appreciably during the irrigation season and recover during the wet season. Water levels rose from 5 to 12 feet between May and September 1980 (Yobbi and others, 1980a,b). Water use northeast of the AMAX plant causes a depression in the potentiometric surface of the Floridan aquifer to below sea level in that area, creating ground-water flow to the east and northeast at the AMAX plant near the end of the irrigation season (Wilson and Gerhart, 1982). Flow in the Floridan aquifer is to the west during the remainder of the year.

Of primary interest in this study was the upper part of the rock column (table 1, and figs. 4 and 5). The head relations between the surficial aquifer and the first and second artesian aquifers are shown in figure 6. The figure illustrates the depths of well casing and depth of screen or open hole of each test hole drilled, as well as the water levels in July 1980. Each well in the group of cluster wells was about 10 feet apart. Each monitors a different water-bearing zone that is effectively separated from adjacent zones by confining beds. Well locations are shown in figure 2.

Water-level recorders installed on wells 9 to 11 provided continuous data so that the relation between aquifers in response to rainfall and hydrologic stresses could be observed. Surficial well 9 is affected by two nearby ditches that stabilize its water levels.

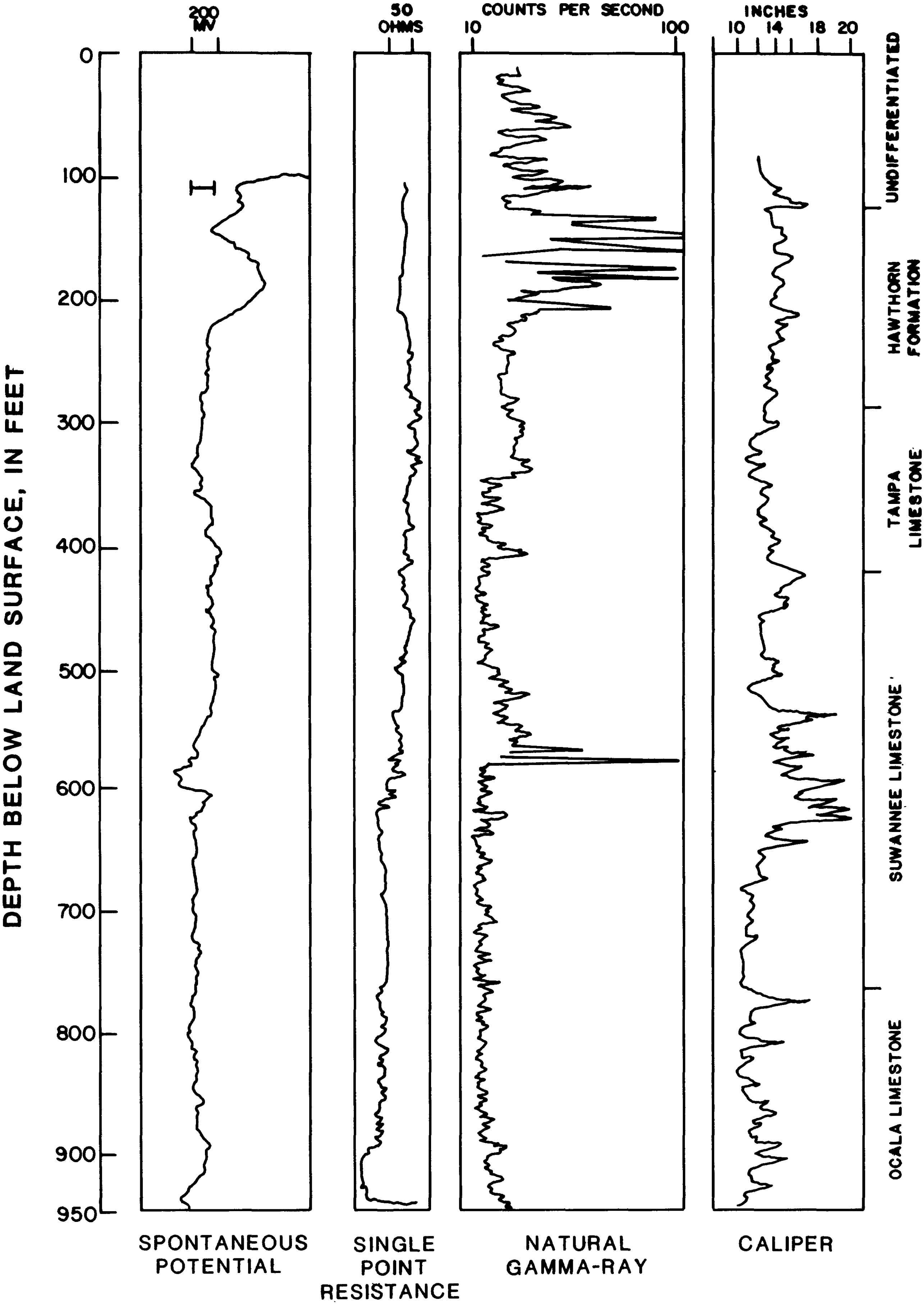
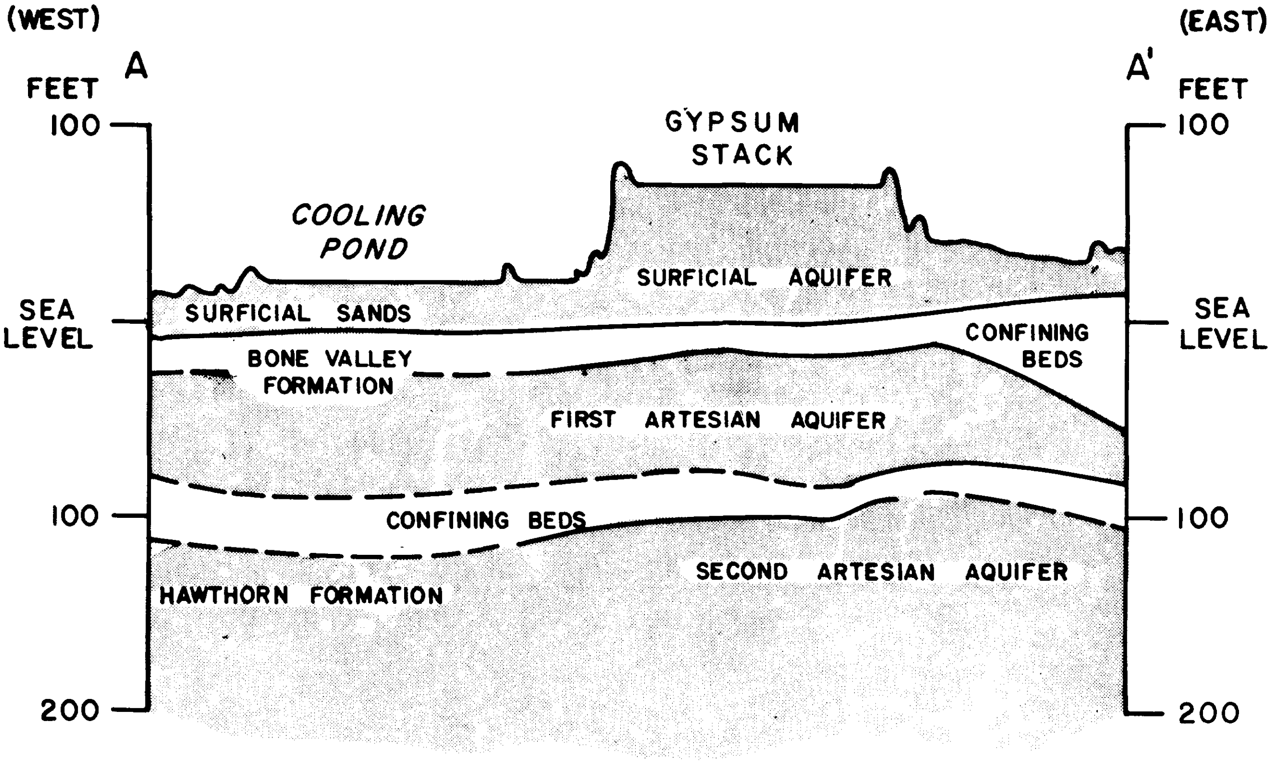


Figure 4.--Geophysical logs for well 2 at the AMAX plant.



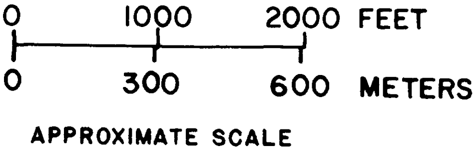


Figure 5.--Generalized geologic section underlying the AMAX plant. (The Bone Valley Formation may include all or parts of the Caloosahatchee Marl and Tamiami Formation. Location of section shown in figure 2.)

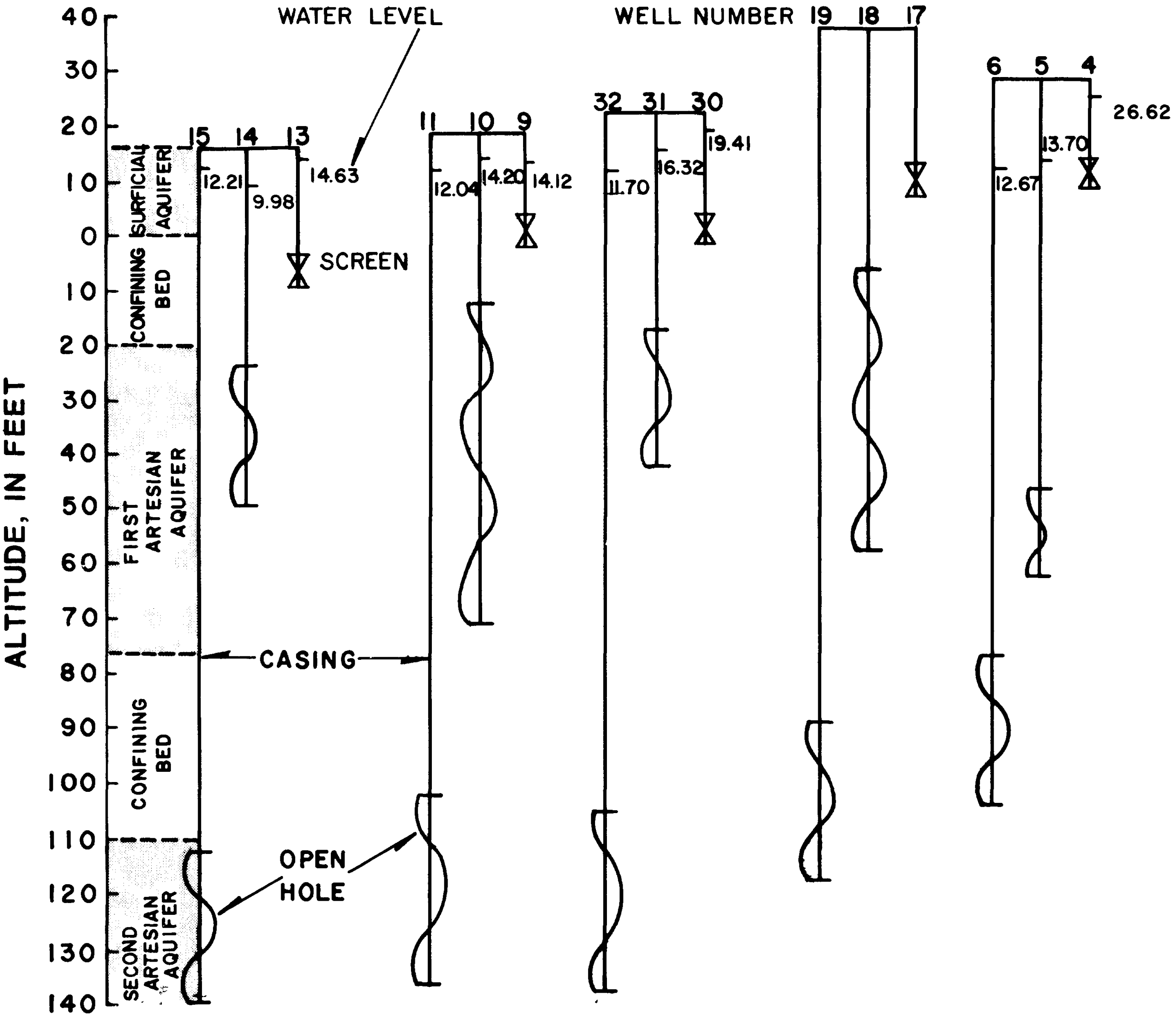


Figure 6.--Relation of water-bearing zones penetrated by cluster wells at the AMAX plant.

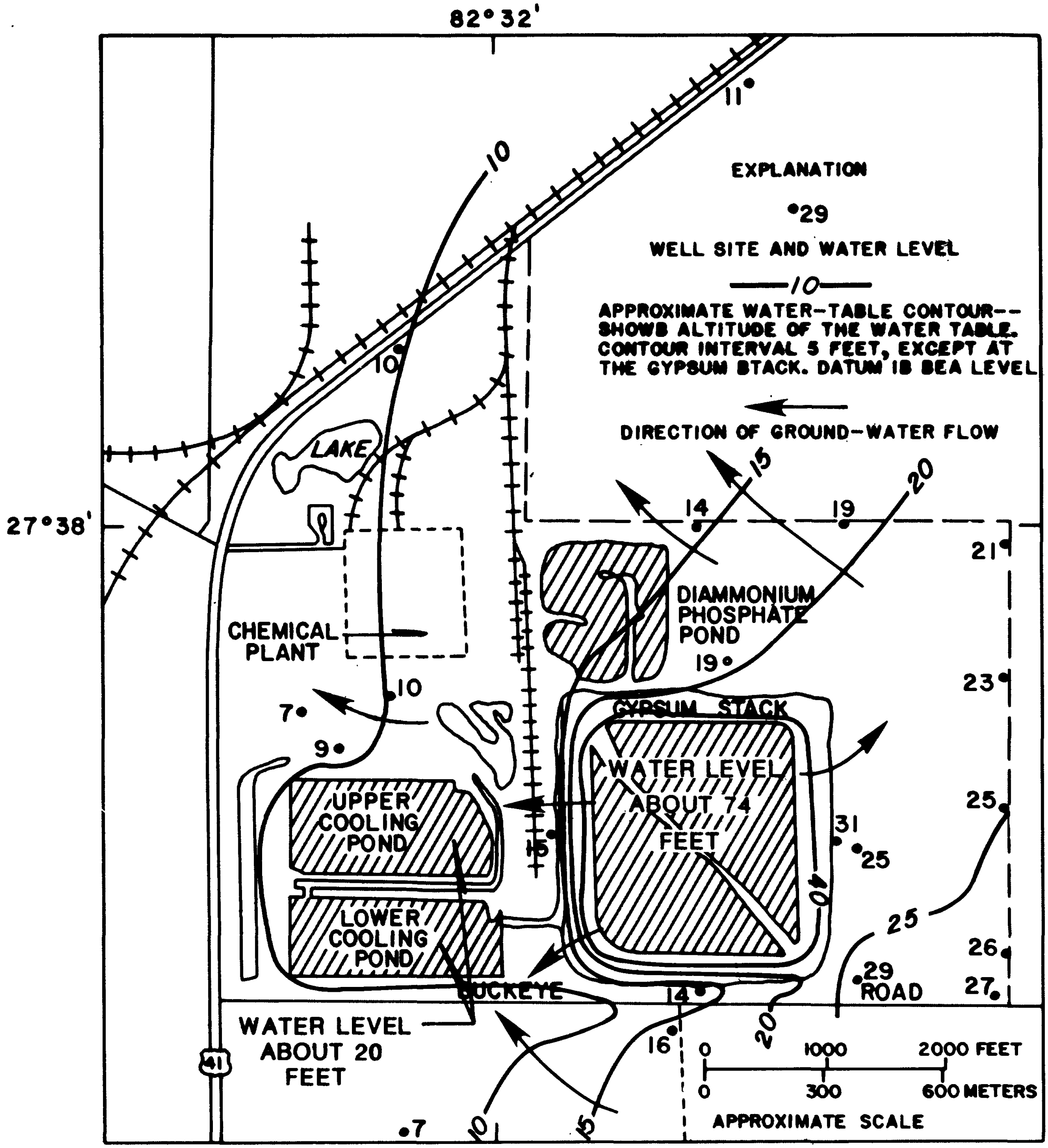
Driller and lithologic logs indicate that there is fine sand within 15 to 20 feet of land surface and that clay and phosphorite content increase with depth. At about 30 feet below land surface, most material is clay with some sand and phosphorite. Below 30 feet, thin lenses of limestone are interbedded with clay. At greater depths, limestone increases until solid limestone of the lower part of the Hawthorn Formation and the Tampa Limestone is reached. Figure 5 illustrates the thickness of the uppermost formations and the tops of the first and second artesian aquifers. The delineation for section A-A' is inferred from data for wells 2, 6, 15, 19, 24, 26, and 32 (fig. 2) adjacent to the section. Lithologic and gamma ray logs (Miller and Sutcliffe, 1982) were used to construct figure 5. The top of the first limestone was determined from lithologic logs. The geophysical definition of high natural gamma-ray activity of the top of the Hawthorn Formation for well 2 (fig 4) was also the method used as the basis for defining the top of the formation elsewhere. Assuming that the amount of phosphate in a rock column is proportional to natural gamma emissions, the gamma logs were used in conjunction with drillers and lithologic logs to determine rock types.

Delineation of rock materials in the subsurface indicates that there is a formational slope to the west and that the slope generally parallels land surface. This is also true for the base of the first confining beds except in the east where overlying clays are thicker. The top of the Hawthorn Formation generally parallels and is more than 100 feet below land surface.

Surficial Aquifer

The surficial aquifer at AMAX ranges in thickness from about 20 to 30 feet. The water-bearing part of the aquifer consists of very fine to fine white to brown sand. North and west of the gypsum stack the aquifer contains some shell. Phosphate pebbles and coarse sand near the base of the aquifer are interbedded with clay at the top of the confining bed.

Surface drainage systems control the ground-water levels to some extent. Figure 7 shows the generalized configuration of the water table of the surficial aquifer and indicates that flow is generally westward.



BASE MAP FROM AMAX PHOSPHATE, INC.

Figure 7.--Generalized water table of the surficial aquifer at the AMAX plant, July 18, 1980.

First Artesian Aquifer

The first permeable rock encountered below the upper confining clay beds forms the first artesian aquifer at AMAX and is a thin friable limestone. The top of the aquifer was reached less than 50 feet below land surface except near the eastern boundary where it was about 80 feet below land surface. Figure 6 shows the sections of hole open to the aquifer and the relation between various zones. The permeable zones ranged from 20 to 60 feet in thickness. Figure 8 shows the potentiometric surface of the first artesian aquifer wells based on measurements of July 18, 1980. A mounding of the potentiometric surface occurs in the vicinity of the gypsum stack.

In general, water at AMAX flows downward from the surficial to the first artesian aquifer. This is shown by water levels of 26.62 feet above sea level for surficial aquifer well 4 and 13.70 feet for first artesian aquifer well 5 (fig. 6). Surficial well 30 had a water level of 19.41 feet and adjacent first artesian aquifer well 31 had a water level of 16.32 feet. Surficial wells 9 (14.12 feet) and 13 (14.63 feet) were affected by ditches and had similar water levels. The water level under the gypsum stack is 31.30 feet above sea level (well 20) and 74 feet above sea level at the top of the stack. The estimated head under the gypsum stack indicates the potential for movement of process water into any of the first three aquifers. For instance, a horizontal pipe (S5) about 10 feet below land surface flowed with water that had the same pH and specific conductance as process water in the gypsum stack. A sample of cuttings from the confining bed between the surficial and first artesian aquifers foamed obviously when mixed with process water indicating that carbonates in the confining layer are readily dissolved by process water. Therefore, carbonates have been dissolved at least to the depth of the pipe and there is a potential for process water to penetrate the first confining bed. A following discussion of the chemical data collected during this study presents further evidence that process water has reacted with aquifer materials and entered the first artesian aquifer.

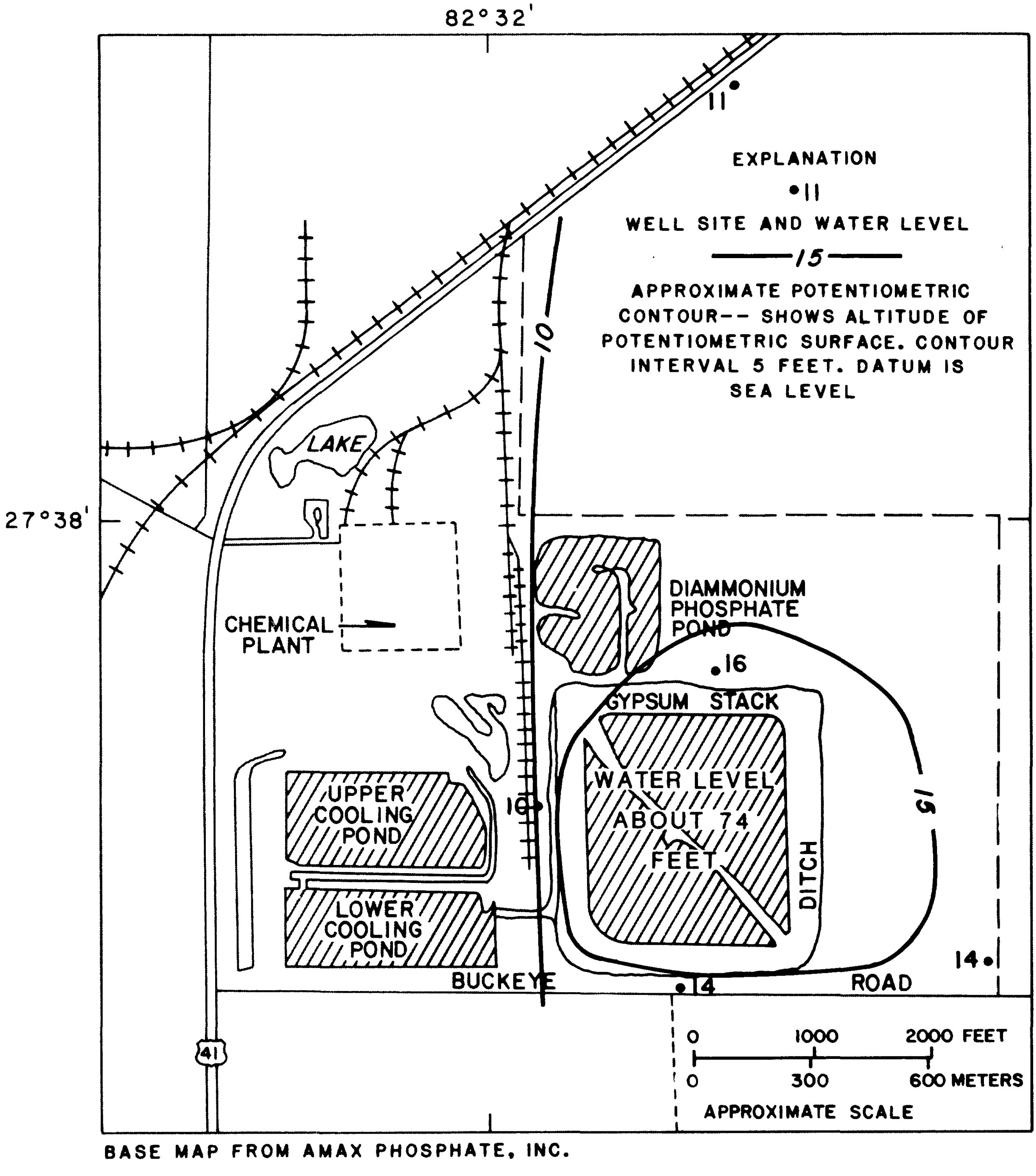


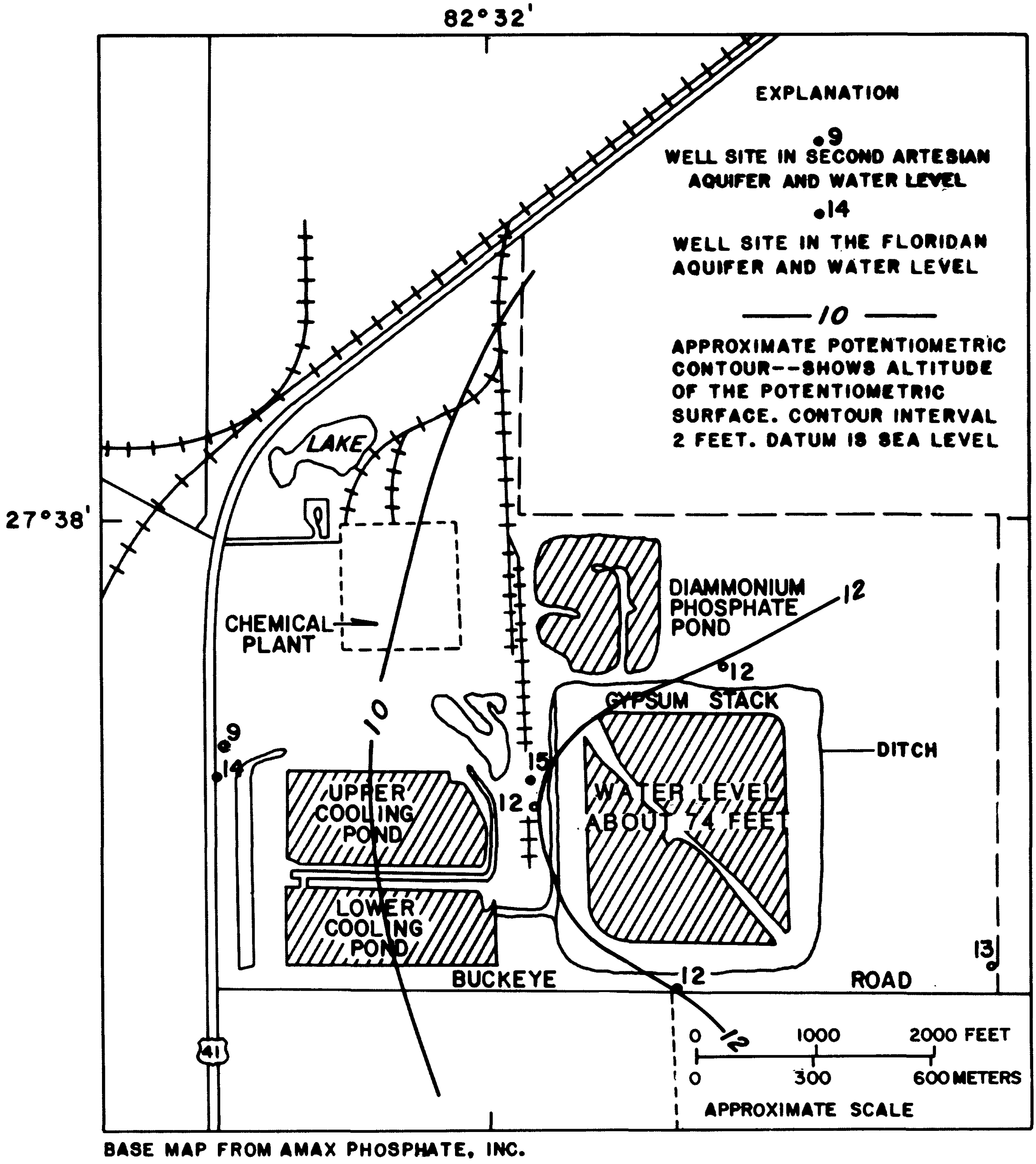
Figure 8.--Potentiometric surface of the first artesian aquifer at the AMAX plant, July 18, 1980.

Second Artesian Aquifer

Figure 9 indicates that the configuration of the potentiometric surface for the second artesian aquifer is similar to that of the first artesian aquifer (fig. 8). Because of good hydraulic connection through the leaky confining bed separating the aquifers, their water levels generally parallel each other. The lateral direction of flow in both aquifers is not well defined within the study area. However, the direction of flow in the second artesian aquifer changes with the seasons depending on withdrawals from and recharge to the underlying Floridan aquifer.

Figure 10 shows water levels for 1980 from the four aquifers underlying the AMAX site. The hydrographs indicate that the water table (well 9) fluctuates about 2.5 feet and remains relatively stable within that range. Although the hydrograph also illustrates that the confined aquifers have higher water levels than the water table at well 9 most of the time, measurements at other surficial aquifer wells in the immediate area indicate the opposite. The water table at well 9 is influenced by the adjacent ditches. Water-level trends in the first and second artesian aquifers parallel each other, but lag behind those in the Floridan aquifer. This indicates that there is not a direct hydraulic connection between the Floridan and the overlying aquifers. Most of the time, water levels in the Floridan aquifer throughout the AMAX area are higher than those in the overlying aquifers indicating the potential for upward leakage. During times of heavy pumping from Floridan aquifer wells, the Floridan potentiometric surface is depressed and a downward-directed gradient results, reversing the potential-leakage direction.

Figure 9 also shows the water levels for the Floridan aquifer based on data at two sites. Fluctuation in the potentiometric surface of the aquifer in figure 10 shows the effects of pumpage on water levels in the aquifer. These effects are masked in the second artesian and higher aquifers because of delay in response time.



BASE MAP FROM AMAX PHOSPHATE, INC.

Figure 9.--Potentiometric surface of the second artesian aquifer at the AMAX plant, July 18, 1980.

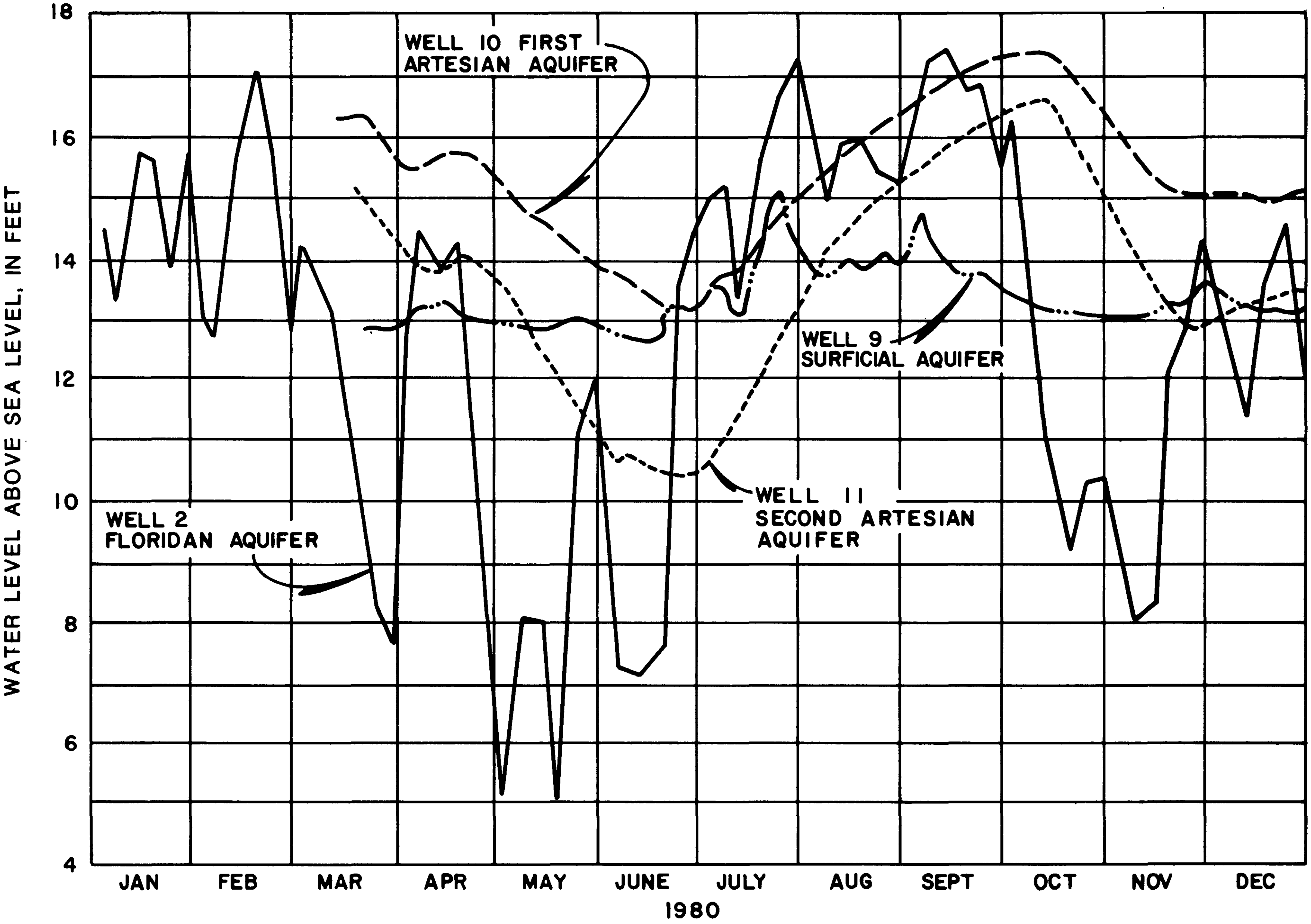


Figure 10.--Water levels in wells at the AMAX plant.

Water Quality

Process Water

Process water from the AMAX chemical plant has accumulated soluble matter from its repeated contact with gypsum and its residual acid and with gases in plant scrubbers. Because process water is recycled, its composition is relatively stable for many parameters until rainfall or changes in plant operation occur.

Figure 11 illustrates the concentrations of major species in process water based on four samples collected at the plant between October 1979 and March 1980. The samples were collected at the inflow and outflow of the gypsum stack (sites S4 amd S3), in the lower (southernmost) cooling pond (site S2), and in the diammonium phosphate pond (site S6). The predominant cations are H^+ and Na^+. Most of the hydrogen ion is combined with HPO_4^{-2}, SiF_6^{-2}, and SO_4^{-2}. Only about 20 me/L of free H^+ is present at pH 1.8. Results of these analyses and those for other samples collected at the plant are given in the report by Miller and Sutcliffe ,(1982). The reaction of HF with SiO_2 is essentially complete. The amount of H_2SiF_6 was determined by calculation of which reactant (SiO_2 or HF) would be depleted first.

An idealized analysis of process water at the plant is shown in table 4. The analysis best represents the composition of process water using available data and the concept of ionic balance between cations (positively charged ions) and anions (negatively charged ions). Calcium concentrations (about 20 mg/L) were controlled by high sulfate concentrations (4,700 to 5,200 mg/L). Chloride concentrations ranged from 11 to 15 mg/L (Miller and Sutcliffe, 1982).

The gypsum slurry, about 10 feet below its outfall into the gypsum stack (S4, fig. 2), contained 31,700 mg/L of suspended solids. In the solid phase, it contained 1,900 pCi/L of undissolved radium-226. The suspended solids concentration of the slurry decreased to 75 mg/L by the time it reached the outflow from the stack (S3). Dissolved radium-226 concentrations in the liquid phase of the process water ranged from 29 to

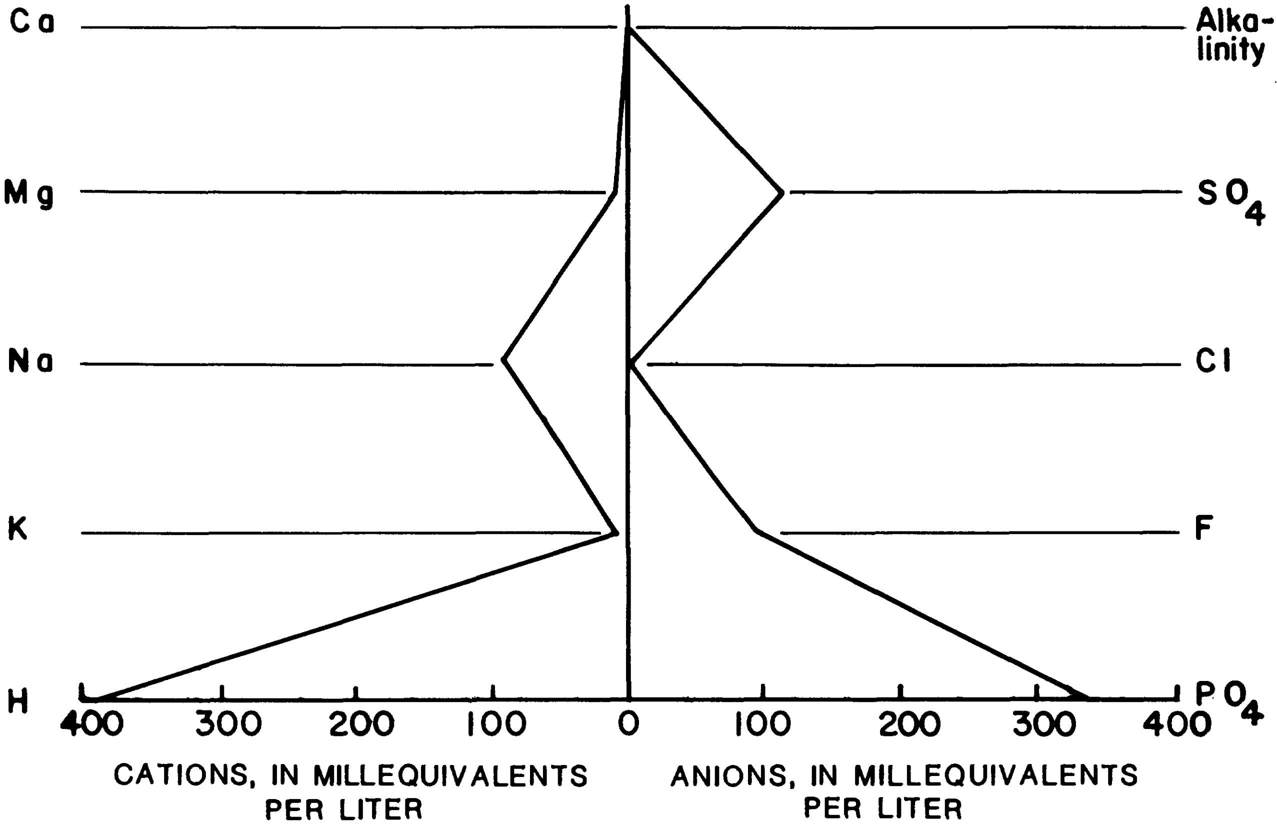


Figure 11.--Modified Stiff diagram showing concentrations of principal ions in process water from the AMAX plant.

Table 4.--Idealized analysis of AMAX process water
[mg/L, milligram per liter; me/L, milliequivalents per liter]

Cations			Anions		
Species	Concentration (mg/L)	Concentration (me/L)	Species	Concentration (mg/L)	Concentration (me/L)
H^+	393 ~~19,500~~	390	SO_4^{-2}	5,200	108
Na^+	2,000	87	SiF_6^{-2} (as F)	5,300	93
Mg^{+2}	75	6	HPO_4^{-2} (as P)	5,350	333
K^+	220	6	Cl^{-1}	12	0
Ca^{+2}	20	1			
NH_4^+ and others	--	44			
Total		534	Total		534

55 pCi/L and had an arithmetic mean of 42 pCi/L. This is lower than the range of 60 to 100 pCi/L reported by Kaufmann and Bliss (1977, p. 32) for leachate from gypsum stacks. Chemical oxygen demand and concentrations of silica, mercury, and total organic carbon in process water decreased during their residence in the gypsum stack due to settling or precipitation. Other substances determined in process water did not decrease in concentration in the liquid phase of the process water during their stay in the gypsum stack.

Specific conductance of process water ranged from 21,200 to 22,500 µmho. This range is approximately equal to the expected measurement error. The concentrations of dissolved solids (residue) ranged from 27,900 to 28,800 mg/L. This is also within the expected range of measurement error. The pH of each sample was 1.8, suggesting that the composition of dissolved solids is relatively stable, buffered, and homogeneous throughout the process-water system. Ammonia is an exception and varies from one part of the process-water system to another. The arithmetic mean concentrations of some constituents are listed in table 5.

Table 5.--Concentrations of selected constituents in process water from the AMAX plant

[TR, total recoverable; mg/L, milligrams per liter; µg/L, micrograms per liter]

Constituent	Arithmetic mean concentration	Constituent	Arithmetic mean concentration
Aluminum, TR (µg/L)	56,000	Boron, dissolved (µg/L)	2,900
Iron, TR (µg/L)	79,000	Cadmium, TR (µg/L)	490
Manganese, TR (µg/L)	6,200	Chromium, TR (µg/L)	700
Bromide, dissolved (mg/L)	3.1	Cobalt, TR (µg/L)	180
Ammonia, total (mg/L as N)	750	Copper, TR (µg/L)	240
Organic nitrogen, total (mg/L as N)	460	Lead, TR (µg/L)	92
Organic carbon, total (mg/L as C)	140	Lithium, dissolved (µg/L)	870
Phenols (µg/L)	24	Molybdenum, TR (µ/L)	57
Methylene blue active substances (mg/L)	.5	Nickel, TR (µg/L)	1,500
Arsenic, total (µg/L)	770	Zinc, TR (µg/L)	2,600
Antimony, dissolved (µg/L)	92	Beta, total (pCi/L)	1,370

Concentrations of silica in process water ranged from about 3,000 to 5,000 mg/L. Concentrations of nitrate, nitrite, mercury, selenium, and oil and grease in process water were relatively low or not detectable and were not evaluated further. The process water had a brownish-yellow appearance; color was 160 platinum-cobalt units and resembled that of water in Florida swamps. Tannin and lignin concentrations were 13 to 17 mg/L, but the method of analysis was not specific for these substances. The process water had a distinct and characteristic chemical odor that was similar at all central Florida phosphate chemical plants visited.

Background Water Quality in the Surficial Aquifer

Well 4, a surficial aquifer well (depth 20 feet) in the extreme upgradient (southeast) corner of the AMAX property, was installed to provide background information on the quality of natural water in the surficial aquifer. Well 39, about 0.4 mile north of the chemical plant, was also installed to provide background water-quality data and was used as the background data well in this report. The analysis of water from well 39 was very similar to that for well 4. This similarity increases confidence in background water-quality data for the surficial aquifer despite a large variability in parameter concentrations in other shallow wells.

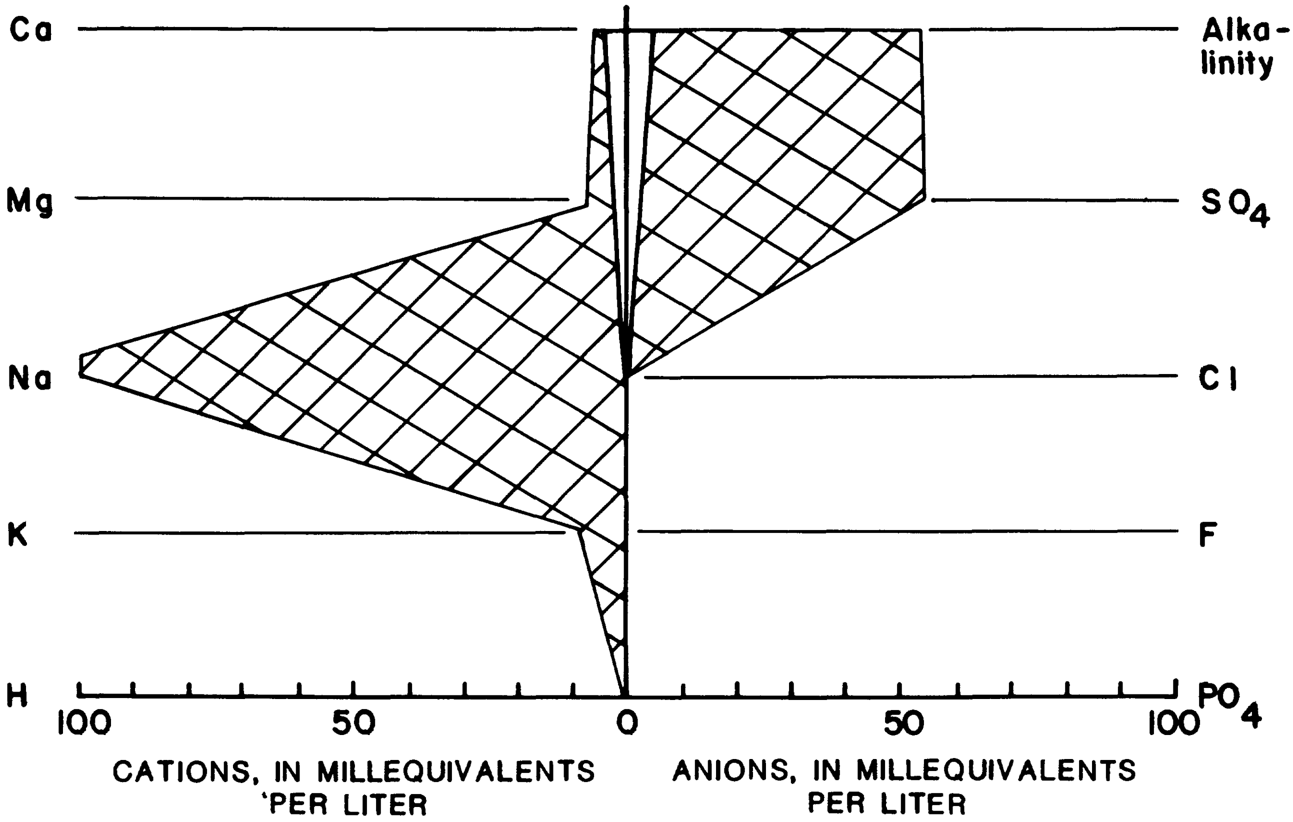
The heavy, dark, near vertical line in figure 12 illustrates the quality of background water from well 39. The hatchured field shows the observed range of concentrations for water samples from surficial aquifer wells 9, 13, 17, and 30 that are on each side and adjacent to the gypsum stack.

Background water was predominantly a $Ca(HCO_3)_2$ type with small amounts of $MgSO_4$ and NaCl. The specific conductance of the background water was 670 µmho/cm and the pH was 6.9. The orthophosphate concentration was 0.22 mg/L as P and total nitrogen was 0.87 mg/L as N. Activities of total alpha, total beta, and dissolved radium-226 were 1.1, 3.9, and 0.90 pCi/L, respectively. Concentrations of trace metals, other than iron (250 µg/L) and strontium (560 µg/L), were at or near their detection limits.

Background Water Quality in the First Artesian Aquifer

Well 40 is on private property, 0.9 mile north of the AMAX gypsum stack (fig. 2), and corresponds to wells finished in the first artesian aquifer. The well was utilized to provide background water-quality data. Well 5 in the southeast corner of AMAX property was also drilled to obtain background water-quality samples. Water-quality analyses indicated that net ground-water flow in this aquifer is to the southeast. Data indicate that water from well 5 had a mineral imbalance of 11 and may have been affected by seepage from the gypsum stack.

Water from well 40 had a low PMI of 0.1 and probably was not influenced by seepage from chemical plant operations. Despite its metal well casing, concentrations of trace metals in water from well 40 were similar to those in water from well 5. Concentrations of trace metals in water from well 5 may be close to background levels despite its mineral imbalance. Metals are readily absorbed once process water is neutralized by the aquifer.



EXPLANATION

— BACKGROUND WATER QUALITY

▨ RANGE IN CONCENTRATIONS FOR SAMPLES ADJACENT TO THE GYPSUM STACK

Figure 12.--Modified Stiff diagram showing concentrations of principal ions in water from surficial aquifer wells adjacent to the AMAX gypsum stack and a background well.

The heavy line in figure 13 illustrates the quality of water for well 40. The hatchured field on the figure shows the observed range of major ions for wells 10, 14, 18, and 31 that are on each side of the gypsum stack (fig. 2).

Water from well 40 contained about the same amount of $Ca(HCO_3)_2$ as water from well 5, but concentrations of $MgSO_4$ and NaCl were approximately half of that in well 5. Samples from both wells indicate that the waters were predominantly $Ca(HCO_3)_2$ type waters.

Water from well 40 had a specific conductance of 669 umho and a pH of 7.2. The orthophosphate concentration was 0.01 mg/L as P and the dissolved nitrogen concentration was 0.43 mg/L as N. Total alpha, total beta, and dissolved radium-226 activities were 7.7, 1.0, and 1.0 pCi/L, respectively. Concentrations of trace elements, other than strontium (320 μg/L) and boron (104 μg/L), were at or near their detection limits.

Background Water Quality in the Second Artesian Aquifer

Well 6, 132 feet deep, was completed in the second artesian aquifer and was drilled to define background water-quality characteristics. Water from the well contains a mixture of $Ca(HCO_3)_2$, $Mg(HCO_3)_2$, and NaCl water types, as shown by the heavy line in figure 14. The hatchured field shows the range of concentrations observed for deep wells 11, 15, 19, and 32 on each side of the gypsum stack (fig. 2). High concentrations of major ions suggest that the quality of water in the background well may have been influenced by water from the gypsum stack.

Water from well 6 had a specific conductance of 930 μmho and a pH of 7.6. The orthophosphate concentration was 0.05 mg/L as P and the total nitrogen concentration was 0.81 mg/L as N. Total alpha, total beta, and dissolved radium-226 activities were 2.5, 12, and 3.5, respectively. Concentrations of trace metals, other than iron, copper, lithium, strontium, and zinc, were at or near their detection limits. The elevated concentration of copper (93 μg/L) may have resulted from contamination by grease used to lubricate the drilling rods during well construction.

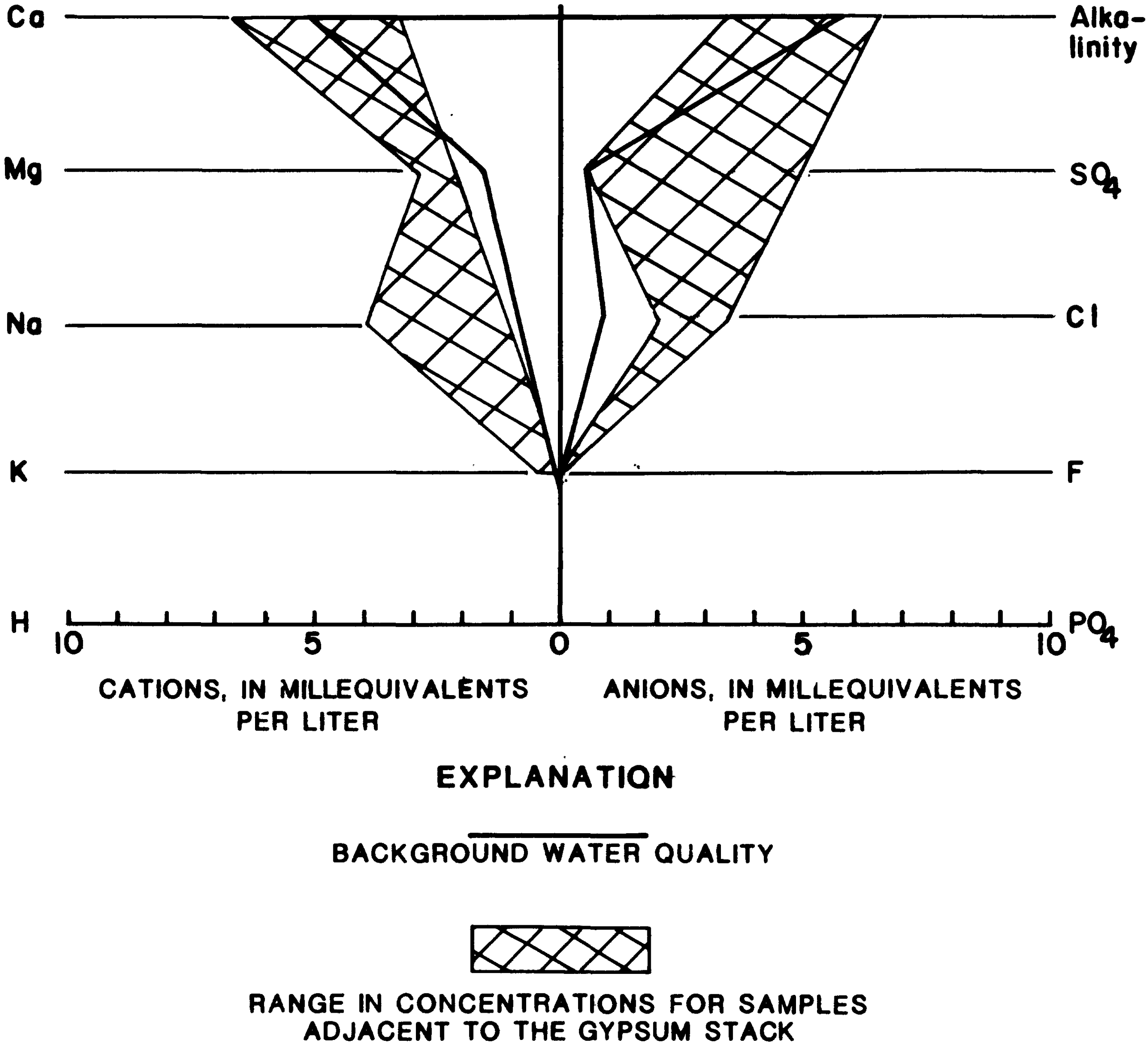


Figure 13.--Modified Stiff diagram showing concentrations of principal ions in water from first artesian aquifer wells adjacent to the AMAX gypsum stack and background well 40.

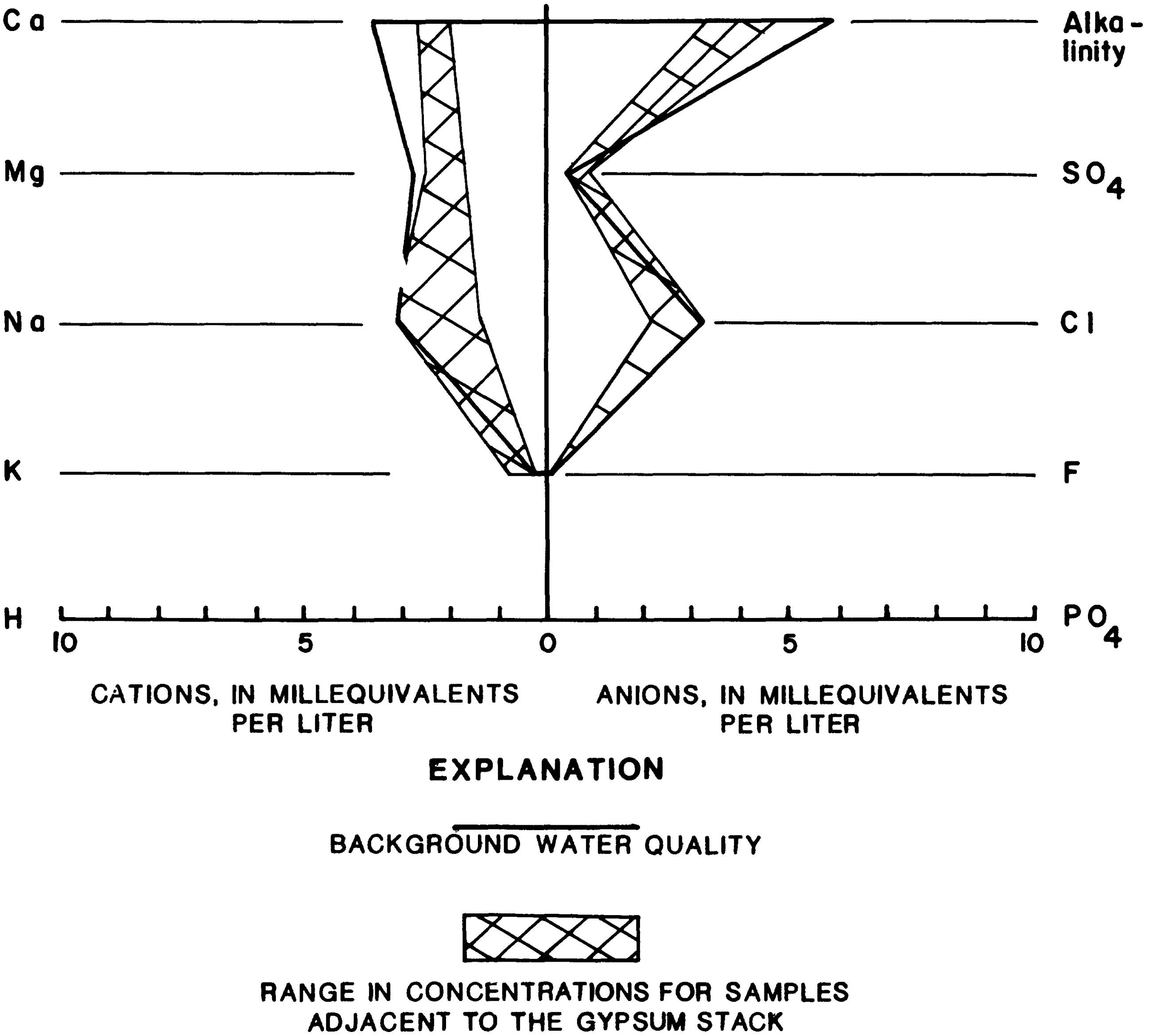


Figure 14.--Modified Stiff diagram showing concentrations of principal ions in water from second artesian aquifer wells adjacent to the AMAX gypsum stack and a background well.

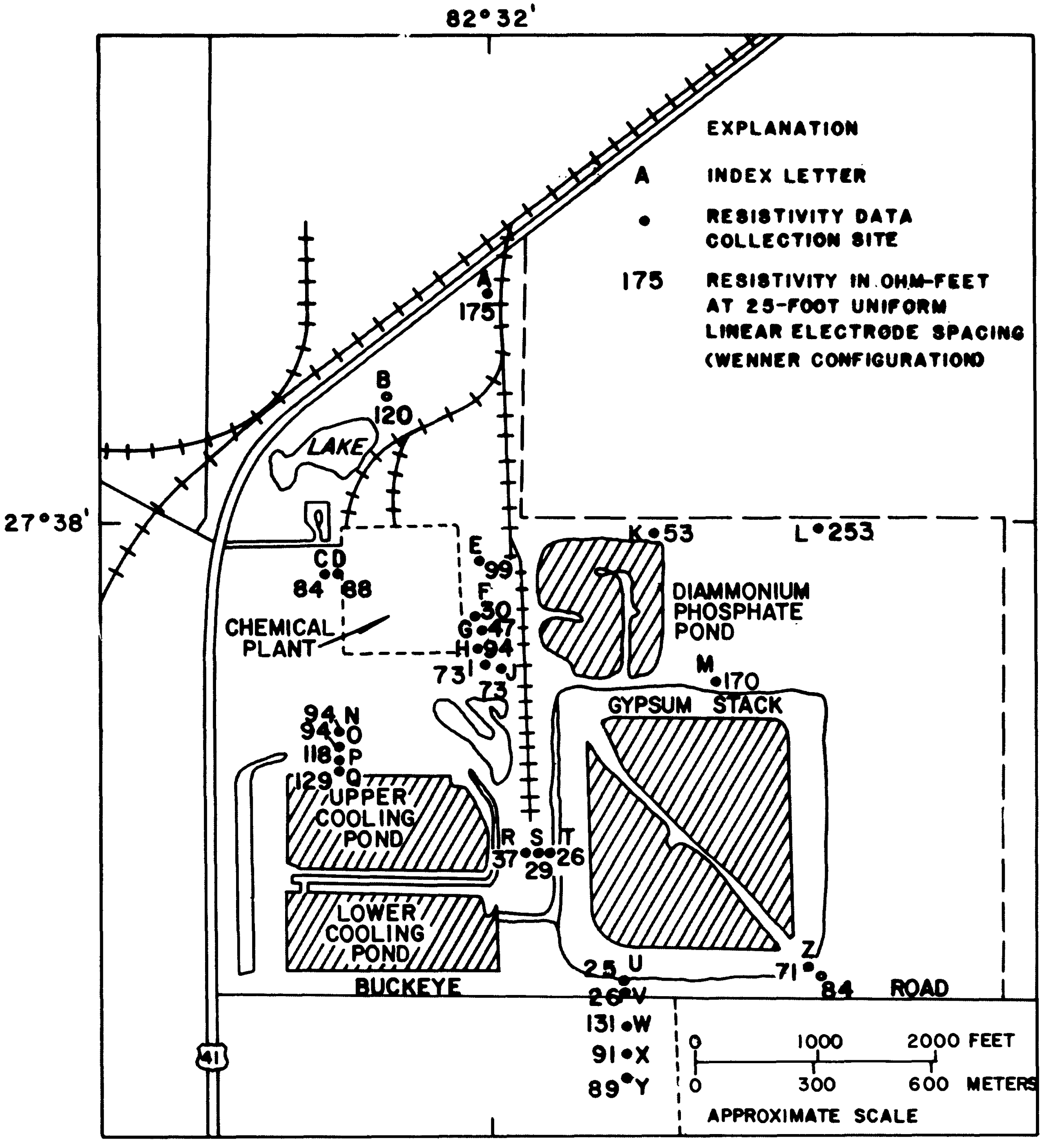
Soil Resistivity

To aid in interpretation of water-quality data for the surficial aquifer, soil resistivity data were obtained. Resistivity data give an integrated measure of the electrical resistance of shallow earthen layers. Factors that affect soil resistivity are: (1) composition of the soil, sand, and rock material; (2) depth to water table and moisture content of soil above the water table; and (3) specific conductance of water in the aquifer. Dry soils are more resistive than moist soils, and pure water is more resistive than water with dissolved minerals. Values of resistivity are higher away from a source and lower near a source, such as a gypsum stack where the water table and specific conductance are high.

Resistivity data collected for this study were made using a 25-foot uniform linear electrode spacing (Wenner configuration) except for soundings that used several spacings. Resistivity data in figure 15 are useful in defining the extent of seepage of process water in the surficial aquifer when correlated with water-quality data. For example, high resistivity corresponds to water with low specific conductance; low resistivity corresponds to water with high specific conductance. Zohdy and others (1974) and Dobrin (1976) discuss the theory of direct-current resistivity methods.

Vertical sounding of resistivity at sites U and V (fig. 15), made about 30 and 60 feet south of the gypsum stack, indicate that the most likely depth for seepage from the stack to occur would be between 4 and 20 feet. Results of the soundings are given below:

Site	Approximate distance south of gypsum stack (feet)	Resistivity of layer 1 (ohm-feet)	Thickness of layer 1 (feet)	Resistivity of layer 2 (ohm-feet)	Thickness of layer 2 (feet)	Resistivity of layer 3 (ohm-feet)
U	30	180	3.5	18	18	73
V	60	68	4.5	14	14	68



BASE MAP FROM AMAX PHOSPHATE, INC.

Figure 15.--Soil resistivity at the AMAX plant.

Although a quantitative interpretation of data in figure 15 is not warranted, some general statements are possible. Resistivities within 100 feet of the gypsum stack or cooling pond were 30 ohm-feet or less. Measurements further away from process water sources usually were 90 or more ohm-feet. Water samples collected from the surficial aquifer near sites T and U had specific conductances of 11,600 and 4,840 µmho, respectively. This indicates that water with specific conductance of 4,000 µmho or more usually occurs in areas that are less than 100 feet from a source, which agrees with the water-quality data discussed earlier.

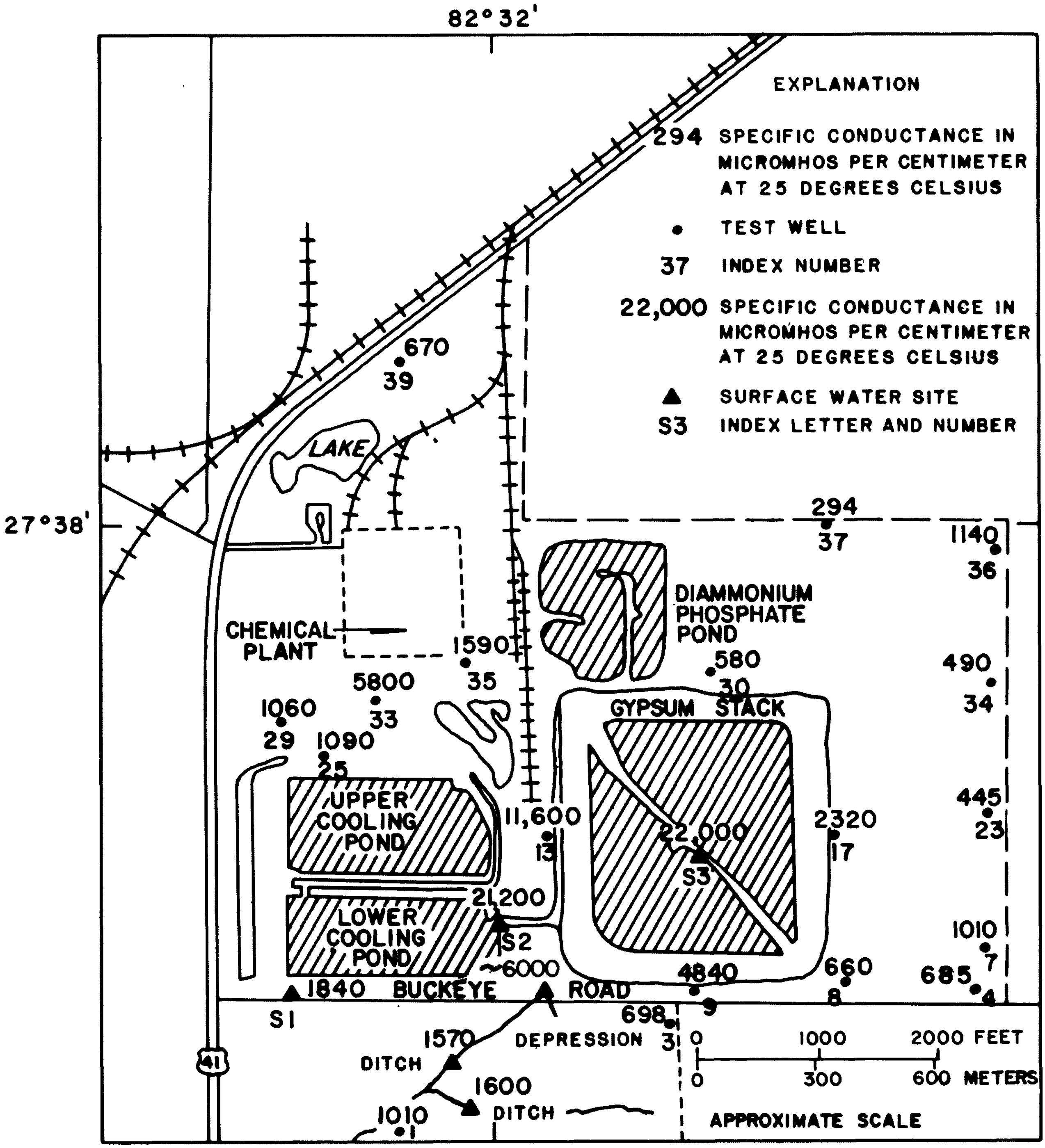
Water Quality in the Surficial Aquifer

Specific Conductance

The specific conductances of water from surficial aquifer wells and surface-water sampling sites at the AMAX plant are shown in figure 16. Water-level and specific conductance data indicate that flow from the gypsum stack is generally in a westerly direction.

Water from a surface depression near Buckeye Road, just east of a ditch near the southwest corner of the gypsum stack, had a specific conductance of about 6,000 µmho. Water from ditches near well 1, also in the southwest part of the study site, had specific conductances of 1,570 and 1,600 µmho. A water sample from a ditch between Buckeye Road and the lower cooling pond in the southwest corner of the area had a specific conductance of 1,840 µmho. The three samples were collected on March 19, 1981. The distribution of specific conductance data and soil resistivity data indicate that some high conductance water is migrating southwesterly from the gypsum stack.

The quality of water from well 35 is probably affected by water from a diammonium phosphate pond and from the gypsum stack. Water from well 33 is affected by process water in a ditch about 20 feet away. The high conductance water from wells 7 and 36 in the eastern part of the area may be related to chemical plant activity or to construction of a new gypsum stack in that area. Calcium and sulfate concentrations in water from wells 7 and 36 were higher than those for nearby wells 23 and 34. Sulfate concentrations of



BASE MAP FROM AMAX PHOSPHATE, INC.

Figure 16.--Specific conductance of water from the surficial aquifer and surface-water sampling sites at the AMAX plant.

water from surficial aquifer wells near the gypsum stack were generally higher than those in the lower artesian aquifers. This was not true for water from wells 4 and 30 that were farther from the gypsum stack.

In general, specific conductance of water from wells and surface-water sites to the north and east was lower than that to the west and southwest. This difference agrees with the general direction of water movement from the gypsum stack.

Major Constituents

The range in concentrations of selected major constituents in water from surficial aquifer wells adjacent to the gypsum stack is shown in figure 12. Migration of dissolved substances from the stack was evident in water from wells 9, 13, and 17 (fig. 2) that had sulfate concentrations of 2,200, 2,600, and 1,000 mg/L, respectively. Concentrations of sulfate are quickly reduced to about 2,000 mg/L by chemical precipitation, after which dilution and anion exchange slowly reduce its concentration. Of the major anions--orthophosphate, fluosilicate, and sulfate--sulfate is the most mobile. As the pH of the water increases to about 4 by neutralization, most water-soluble fluoride and orthophosphate are removed by reactions with the aquifer.

Chloride concentrations of water in the surficial aquifer are probably relatively unaffected by process water at AMAX because the process water is thought to be low in chloride. (Note.--The laboratory reported analytical difficulties in determining chlorides in highly acidic samples.) Fluoride and silica in process water are associated in the forms of $HSiF_6^{-1}$ and SiF_6^{-2}. They are rapidly lost as process water contacts the aquifer materials (see equations 13 and 23). These processes are so effective that the fluoride concentration in water from well 13 was only 2.2 mg/L, though well 13 was more affected by process water than any other well at the AMAX site. This reaction is dependent upon neutralization of process water by the aquifer.

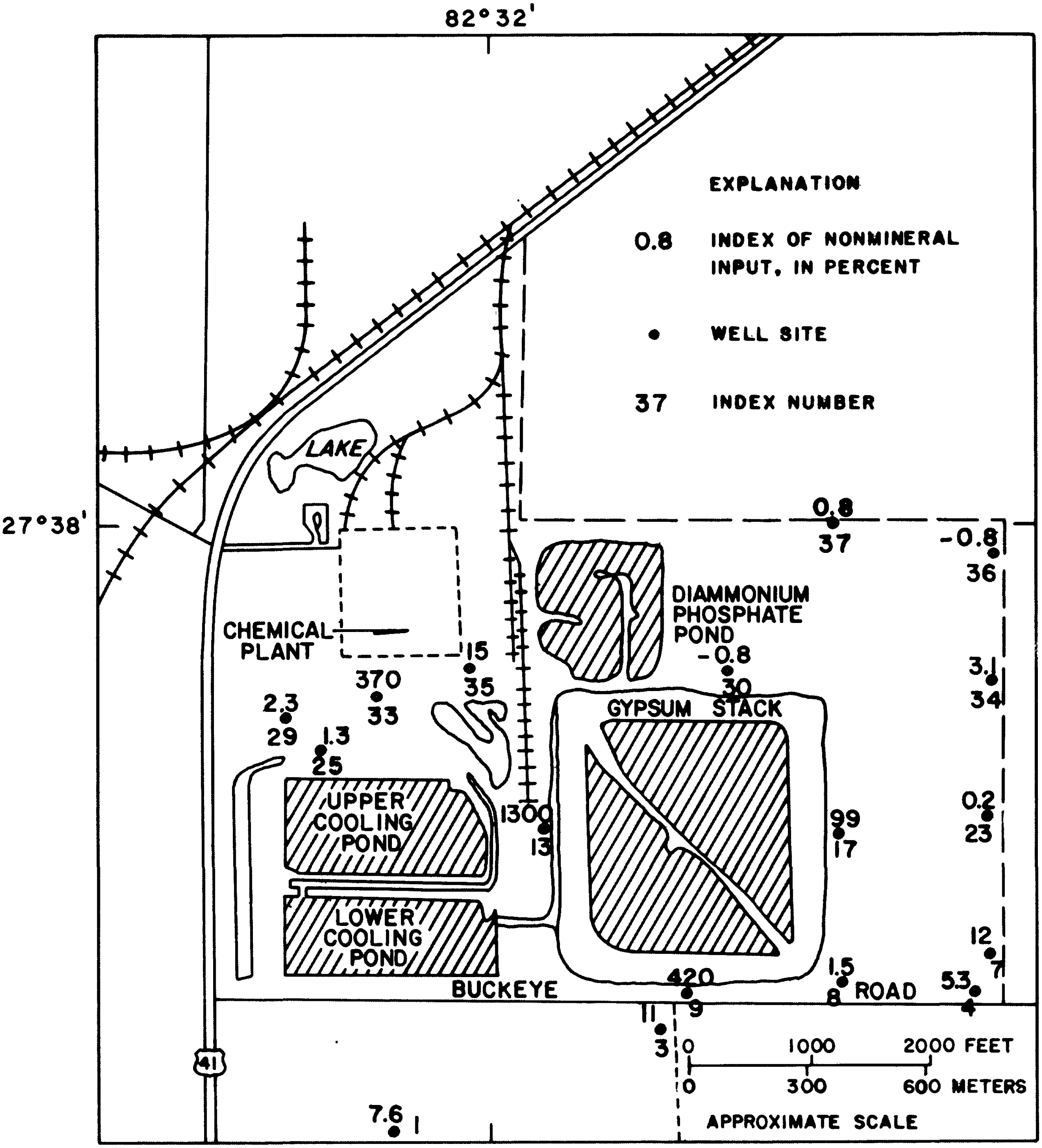
Sodium and potassium migrate downgradient from the gypsum stack. Concentrations of sodium and potassium in water from well 13 were the same as concentrations in the process water. Solubility controls do not retard their movement, only cation exchange and dilution are involved. Sodium and potassium concentrations in water from well 33 were about 30 percent of those in the process water.

Magnesium does not precipitate as readily as calcium, and thus, elevated concentrations were found in water from wells 9, 13, and 33. Some magnesium near the gypsum stack probably originated from dissolution of magnesium minerals by the process water and from ion exchange with sodium and potassium.

Calcium concentrations in water from the surficial aquifer were suppressed by high sulfate concentrations in process water. As acidic process water dissolved calcium minerals in the native carbonate rocks, calcium concentrations increased but only to the limits permitted by its formation of insoluble sulfate, fluoride, and phosphate salts. In wells influenced by process water, calcium concentrations ranged from 14 mg/L in well 13 to 280 mg/L in well 35 where sulfate and phosphate concentrations are significantly lower.

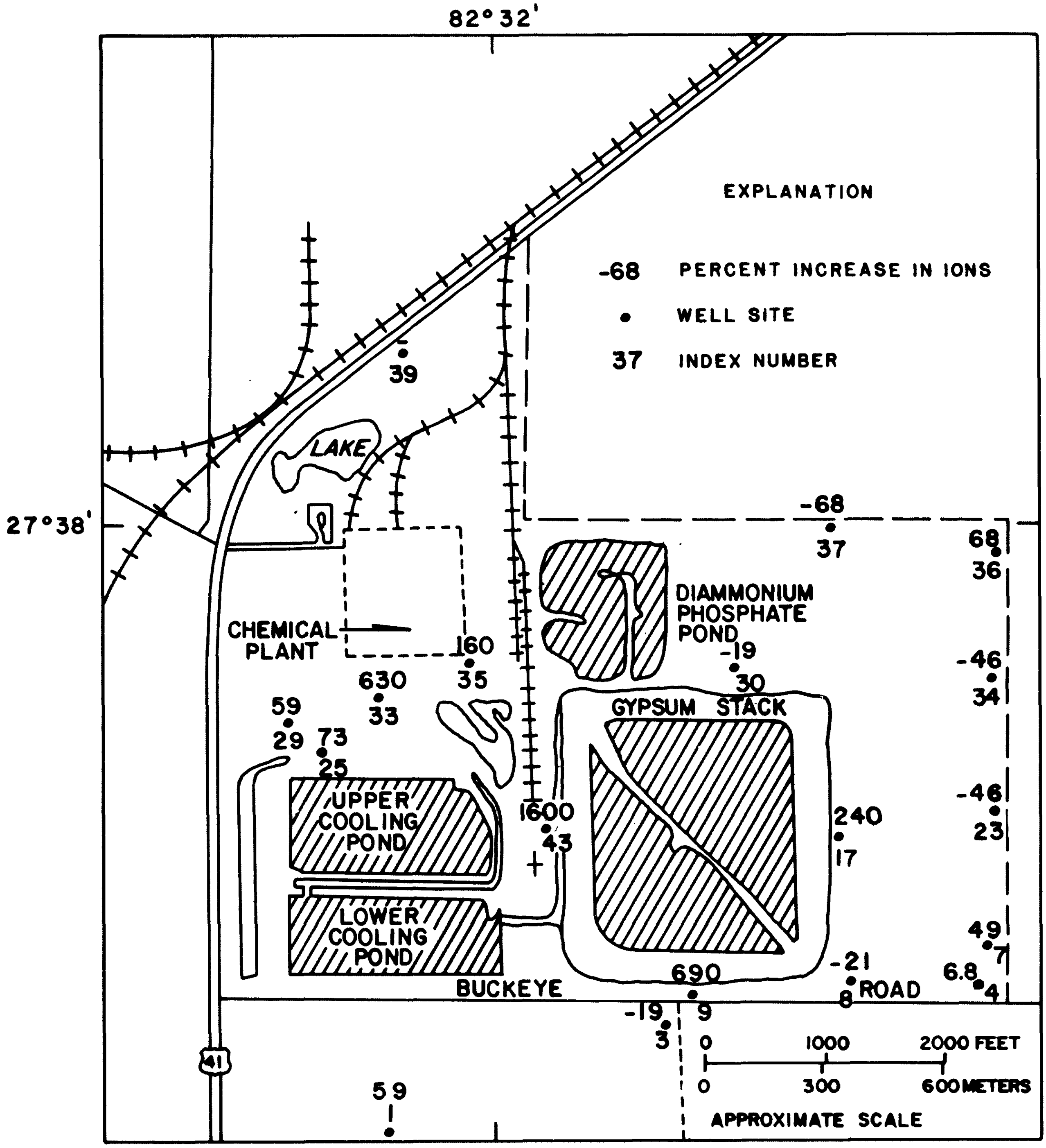
Figure 17 shows the index of nonmineral input (INMI) for wells at the AMAX plant. Values of INMI above about 5 percent are thought to be high enough above analytical error to be significant, considering that some analytical error is compensated for by a correction term (see section on "Principles and Processes").

Figure 18 shows the percentage increase of ions (PII) above that of the background well 39. The PII of several wells (3, 8, 23, 34, and 37) decreased (negative percentages) with respect to the background well. This may be related to recharge from rainfall in these shallow (most are screened from 10 to 15 feet below land surface) wells. The PII for wells 1, 7, and 36 are significantly higher with respect to the background well. The elevated INMI for wells 1, 4, and 7 (fig. 17) strongly suggest a cultural influence. Even though the INMI is low for well 36, it is doubtful that variations, as observed for wells 34, 36, and 37 within short distances of each other (about 1,000 feet), would occur without some cultural influences.



BASE MAP FROM AMAX PHOSPHATE, INC.

Figure 17.--Index of nonmineral input for water from the surficial aquifer at the AMAX plant.



BASE MAP FROM AMAX PHOSPHATE, INC.

Figure 18.--Percentage increase in ions for water from the surficial aquifer at the AMAX plant.

A low INMI and a high PII for well 35 near the chemical plant suggests that the water had interacted with aquifer materials (for example, ion exchange reactions) or that the increases in solute concentrations (PII) were not because of the migration of process water.

The influence of process water on at least one of the indices is noted for water from wells 9, 13, 17, 25, 29, 33, and 35. Well 17 is about 30 feet from the seepage ditch around the base of the gypsum stack and is affected because of ground-water mounding under the gypsum stack and consequential outward flow from the stack. Well 30 is farther from the stack and at a right angle to flow lines. The only indication of process water from well 30 was an elevated iodide concentration (0.12 mg/L).

The pattern of indices for wells in the surficial aquifer is caused by: (1) local mounding and outward flow near the base of the gypsum stack and its seepage ditch; (2) a general west and southwest flow of water from the gypsum stack and cooling ponds; and (3) irregular surface or subsurface transport of some material to wells 4, 7, and 36. Well 1 may be influenced by activities in nearby citrus groves or by transport of material from the chemical plant by way of ditches.

Nitrogen and Phosphorus

Well 13 contained 470 mg/L of ammonia as N and 350 mg/L of organic nitrogen as N. Ammonia and organic nitrogen concentrations in surficial aquifer wells 33, 9, and 17 were significantly above background levels. Nitrate and nitrite concentrations were low throughout the study area and were not considered further.

Orthophosphate concentrations as P were 570, 330, 56, and 0.12 mg/L in wells 13, 33, 9, and 17, respectively. This indicates that, although phosphate is not lost as rapidly as fluoride, its migration is limited to a relatively short distance from the source. Well 33 is 20 feet from a ditch containing process water. Well 17 has a sulfate concentration of 1,000 mg/L, but the orthophosphate concentration had been reduced to about 0.002 percent of that found in process water. Phosphorus occurs mainly as orthophosphate in the process water and in the surficial aquifer. Occasionally particulate matter containing phosphate minerals or precipitate was entrained with the water during sampling. This elevated the total phosphorus concentrations above orthophosphate concentrations.

Radiochemicals

Gross alpha activities were greater than 15 pCi/L in four samples from the surficial aquifer at the AMAX plant. Apparently most of the alpha emitters are coprecipitated with the sulfate, fluosilicate, or phosphate as they react with the aquifer. One of the higher alpha activities observed in water from well 37 is shown in figure 19. This activity is believed to be of natural origin as the sample had a specific conductance of 294 µmho and a pH of 3.9. Lithologic logs indicate that phosphate pebbles occur at depths of about 10 to 20 feet where many of the surficial aquifer wells were screened or opened (Miller and Sutcliffe, 1982). These phosphatic deposits would release radioactive isotopes if they were dissolved by natural low-pH waters.

Water from wells 7, 25, and 35 had elevated gross alpha activities. Each well was affected by process water, but not to the same extent as wells with significantly lower alpha activities. This suggests that gross alpha activities observed at the wells are either dissolved from natural phosphatic deposits by water that is aggressive to them, were generated as daughter isotopes of radon-222 (as discussed in the section on "Principles and Processes"), or were transported more readily to these wells because reactions of the process water with the aquifer are different along their flow paths than for other wells.

Figure 20 shows gross beta activities determined for water samples from the surficial aquifer. The beta emitters are mobile near the gypsum stack, but they are reduced to less than about 20 pCi/L by reactions with the aquifer within about 50 feet of the stack.

Figure 21 shows the dissolved radium-226 activities for water samples from the surficial aquifer wells. Activities of radium-226 for all but one sample were less than 6.0 pCi/L. Radium-226 concentrations in water samples

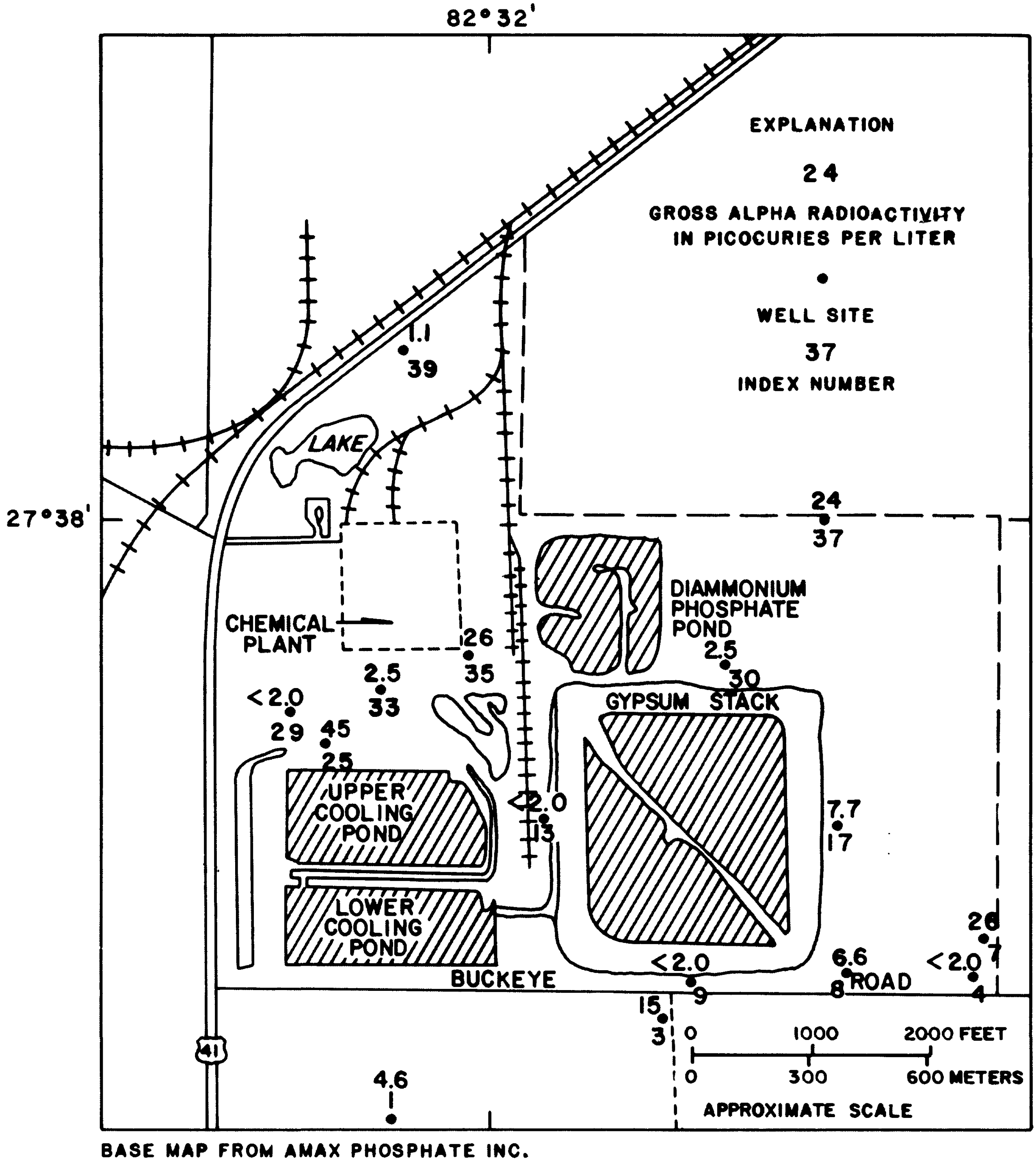


Figure 19.--Gross alpha radioactivity for water from the surficial aquifer at the AMAX plant.

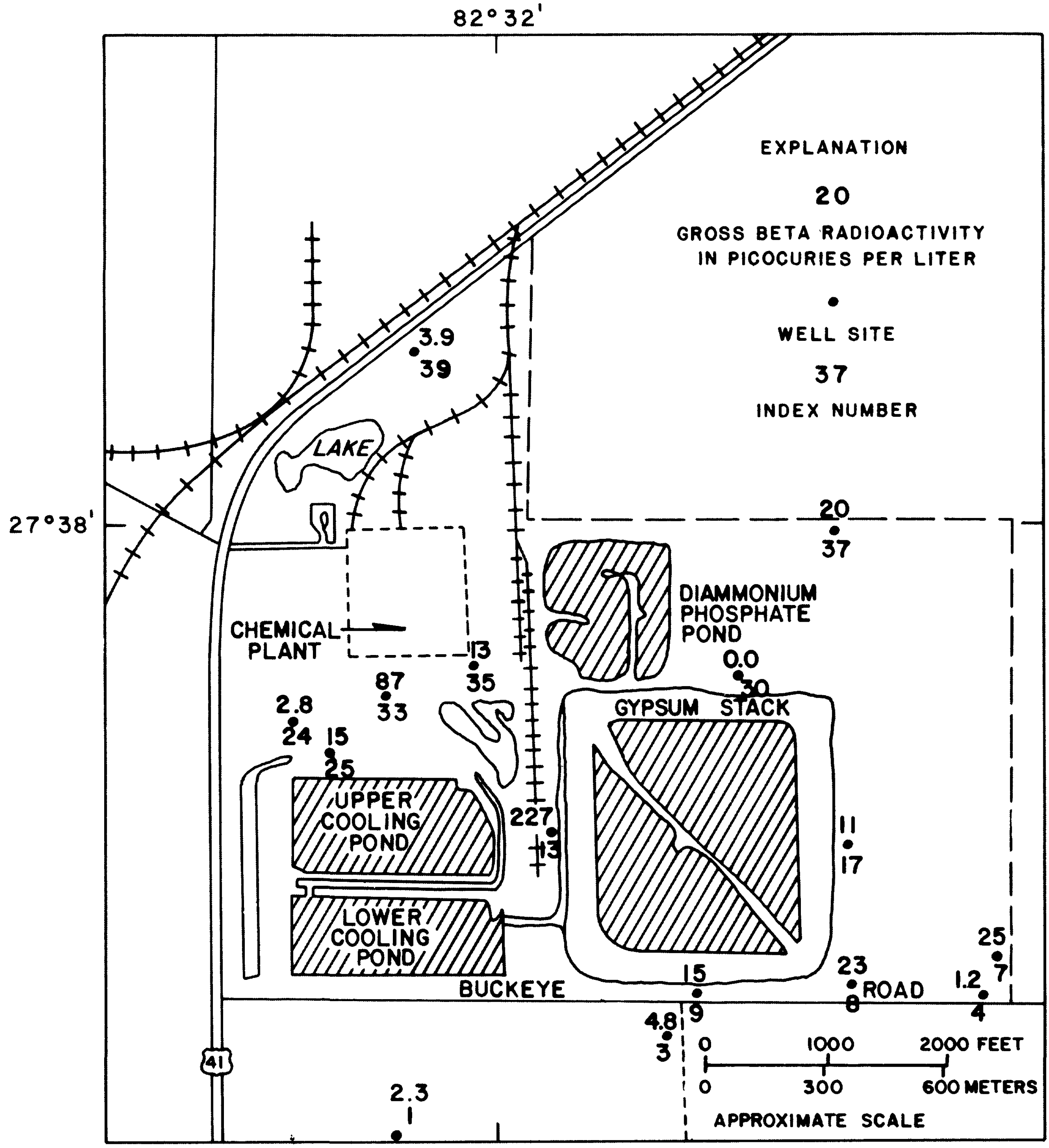
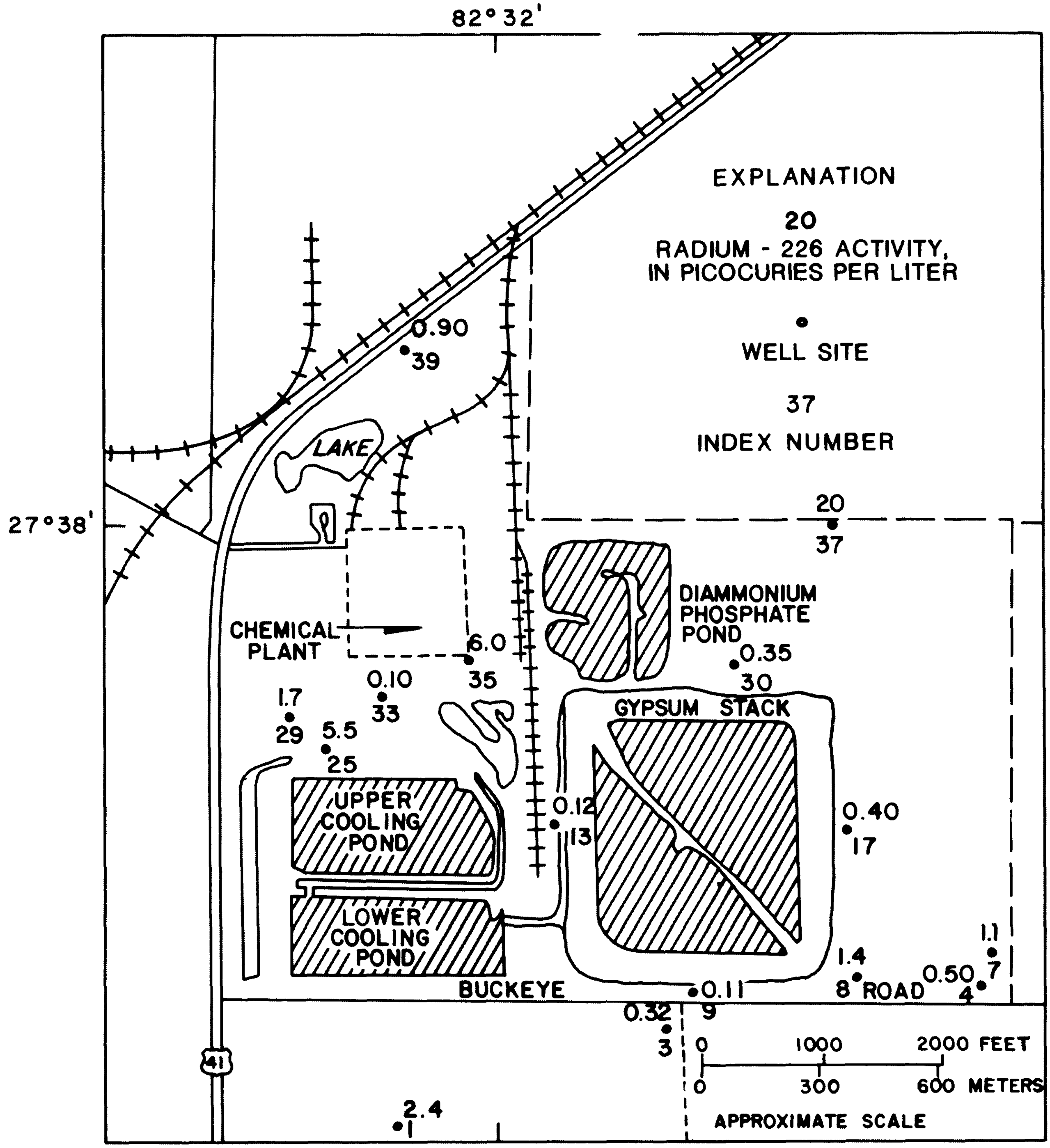


Figure 20.--Gross beta radioactivity for water from the surficial aquifer at the AMAX plant.



BASE MAP FROM AMAX PHOSPHATE, INC.

Figure 21.--Radium-226 activity for water from the surficial aquifer at the AMAX plant.

from shallow wells adjacent to the gypsum stack were 0.40 pCi/L or less. The interaction of process water and the aquifer effectively reduces radium-226 activities to less than about 1 percent of that in the process water. The highest radium-226 activity (20 pCi/L) was for water from well 37 northeast of the gypsum stack. This is believed to be unrelated to the operation of the chemical plant and is because of natural processes.

Trace Elements

Iron concentrations greater than 24,000 μg/L were found in wells 3, 7, 9, and 17 east and south of the gypsum stack. The natural concentration of iron was highly variable in the surficial aquifer because of the swampy environment of much of the AMAX site. Well 37, which had an iron concentration of 5,600 μg/L, is believed to be unaffected by the chemical plant. Iron concentrations greater than about 10,000 μg/L may indicate the effects of seepage at the AMAX plant.

Comparison of concentrations of several trace elements with those listed in the National Interim Primary Drinking Water Regulations (U.S. Environmental Protection Agency, 1976) shows that arsenic and chromium exceed the regulations only in water from well 13 which is 8 feet from a ditch containing process water. Barium, cadmium, lead, mercury, and selenium do not exceed the regulations in water from any of the surficial aquifer wells.

Lithium migrates into the surficial aquifer and, in wells 13 and 33, it equals or exceeds concentrations that were measured in process water. This situation probably arose for one or more of the following reasons: (1) matrix effects caused the measured concentration for process water to yield low analytical results; (2) some substances found in water from the wells were dissolved in the aquifer by the acidic process water; (3) concentrations in the process water were lower at the time of sampling then they may have been in the past; or (4) the precision of analyses is low enough that the apparent lower concentrations in the process water are not statistically valid. Migration of lithium in the surficial aquifer is limited by ion exchange so that the concentration in well 17 is near the background concentration.

Background concentrations of strontium range from 250 to 560 μg/L. Wells with high sulfate because of seepage of process water have suppressed strontium concentrations. Well 13, which is strongly influenced by the process water, contained 190 μg/L of strontium. As sulfate concentrations decrease, strontium concentrations increase to 1,000 to 2,000 μg/L because of dissolution of strontium from the aquifer.

Boron concentrations are elevated above background levels mainly in wells 9, 13, and 33. Boron does not appear to migrate at high concentrations.

Bromide and iodide concentrations were determined to see if they would serve as tracers or indicators of seepage from the sources of process water. Although either could be used, iodide appears to be the superior choice because (1) its sensitivity is greater using U.S. Geological Survey analytical procedures; (2) background concentrations were slightly lower; and (3) concentrations found in water from wells 9, 13, and 17 are more easily distinguished from background levels. Figure 22 shows the ratios of concentrations of bromide, iodide, sodium, and sulfate in wells 9, 13, 17, and 35 to the concentrations of those constituents in the process water (background concentrations were subtracted from each). For bromide, the process-water concentration is for water from a seepage pipe in order to provide data consistent with well 13 and with observed iodide concentrations. Bromide and iodide migrate at similar rates, perhaps because they react similarly with aquifer materials or because they migrate almost conservatively (unhindered by reactions) at least for short distances from the stack. Below concentrations of about 2,000 mg/L, sulfate ions behave similar to bromide and iodide. Anion exchange will affect each of these anions, but much of this occurs in clay beds between aquifers where permeabilities are low rather than in sand and limestone aquifers.

Manganese, cobalt, copper, molybdenum, nickel, zinc, aluminum, and antimony occur in easily detected concentrations in the process water but do not appear to migrate to any significant degree.

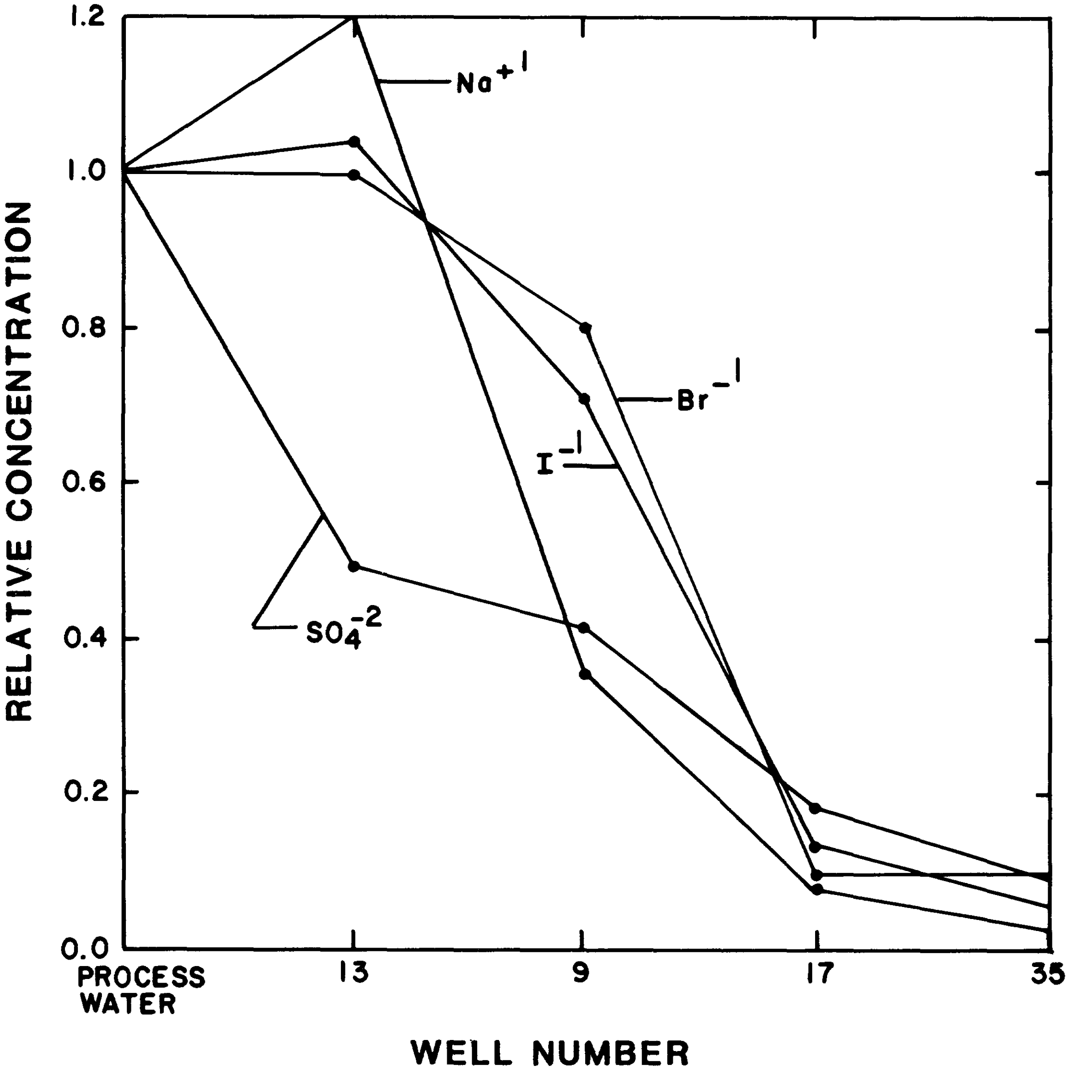


Figure 22.--Relative concentrations of bromide, iodide, sulfate, and sodium in water from four surficial aquifer wells at the AMAX plant.

Organic Compounds

Background concentrations of total organic carbon in the surficial aquifer ranged from 9.3 to 11 mg/L compared to 110 to 160 mg/L in the process water. Total organic carbon concentrations greater than about 25 mg/L may indicate that the water had been influenced by chemical plant operations. None of the samples from wells at the AMAX plant had concentrations of that magnitude.

Concentrations of phenolic compounds ranged from 0 to 2 μg/L in water in the surficial aquifer and from 9 to 34 μg/L in the process water. These traces of phenolic material in water in the surficial aquifer appear to be of natural origin because water from wells near the gypsum stack did not contain any phenolic compounds, whereas water from the deeper aquifers contained significantly higher concentrations.

Concentrations of methylene blue active substances (MBAS), which include synthetic detergents and surfactants, were low in the process water and in water from the surficial aquifer. Concentrations greater than 0.10 mg/L at wells 13, 17, and 33 can probably be attributed to chemical plant activities or seepage of process water.

Oil and grease were not found in the process water. The 1 mg/L (lowest nonzero value reported) for wells 19 and 28 is probably because of normal analytical error rather than because of the presence of oil and grease.

Water Quality in the First Artesian Aquifer

Wells 5, 10, 14, 18, 31, and 40 (fig. 2) at the AMAX plant are open to the first artesian aquifer. The wells range in depth from 63 to 95 feet. Casings were about 30 to 45 feet deep. Well 40 is an abandoned private well about 0.9 mile north of the gypsum stack.

Major Constituents

Figure 13 shows that there is considerable variability in concentrations of calcium, sodium, alkalinity, and sulfate in water in the first artesian aquifer. The variability can result from natural variations in geology or hydrology of a local nature and from the effects of seepage from the gypsum stack. Water that is below the surficial aquifer usually has been in contact with minerals in that hydrologic zone for lengthy periods of time and would not be expected to vary considerably over short distances unless an overriding local influence is present.

The (INMI), (PII), and (PMI) are given in table 6 to aid in interpretation of major constituent data. Ion indices indicate that water from wells 5, 14, and 18 may have been influenced by sodium and sulfate from process water. Water from wells 10 and 31 appear to be influenced by process water that has undergone ion exchange.

Table 6.--Ion indices for water from wells in the first artesian aquifer at the AMAX plant

Well No.	Index of nonmineral input (percent)	Percentage increase in ions	Percentage mineral imbalance
5	17	57	11
10	1.7	29	1.4
14	7.6	- 2.6	8.6
18	18	87	9.9
31	- .8	64	.0
[1]40	--	--	- .1

[1] Background well to which the index of nonmineral input and percentage increase in ions are compared.

Figure 13 shows that sulfate concentrations vary considerably in the first artesian aquifer. The wells listed in order of decreasing sulfate concentration are 18, 5, 31, 14, and 10. Water from well 10 has about the same sulfate concentration as water from well 40, which represents background conditions, but contains more sodium chloride. The other wells had sulfate concentrations that were two to eight times higher than that in well 40.

During times of high pumpage near the AMAX plant, the direction of ground-water flow is from the gypsum stack to the east in the underlying Floridan aquifer. Because these Floridan aquifer wells are often cased shallow (40-60 feet), similar behavior is expected in the first artesian aquifer because the Floridan wells also pump the shallower aquifers.

Resistivity data show that high conductance water occurs from about 4 to 22 feet below land surface at the south side of the gypsum stack and water of lower conductance occurs at depths greater than about 22 feet. Specific conductance data support the resistivity data. The conductance for water from well 9 (screen depth 16 to 21 feet) was 4,840 µmho, for well 10 (open hole depth 32 to 90 feet) it was 933 µmho, and for well 11 (open hole depth 121 to 155 feet) the conductance was 803 µmho. This corresponds to about 4 feet of unsaturated zone (4.9 feet measured with a tape), a surficial aquifer of high conductance water from depths of about 4 to 22 feet, and lower conductance water in the first and second artesian aquifers (below depths of 22 feet).

Nitrogen and Phosphorus

No indication of migration of phosphorus species into the first artesian aquifer was noted at the AMAX plant. Orthophosphate concentrations ranged from 0.01 to 0.12 mg/L in the first artesian aquifer. Ammonia concentrations were within about 0.5 mg/L of background concentrations, but distribution patterns of ammonia are similar to those of other constituents that had seeped into the first artesian aquifer indicating the possibility that traces of ammonia migrated into the aquifer.

Radiochemicals

Gross alpha radioactivities were lower (<2.0 to 5.4 pCi/L) in the first artesian aquifer wells adjacent to the gypsum stack than in background well 40 (7.7 pCi/L). Beta activity was low (7.0 to 12 pCi/L) but was above the background level of <1.0 pCi/L. This may be due to migration of radon-222 and its decay to beta emitters.

Radium-226 activities ranged from 1.0 to 2.3 pCi/L. Radium-226 activity in the background sample was 1.0 pCi/L. This indicates that migration of radium-226 from gypsum stacks did not affect this aquifer. Water from each well tapping the first artesian aquifer next to the gypsum stack contained more radium-226 than the surficial aquifer well in each cluster. The small increases in activity are probably of natural origin.

Trace Elements

Concentrations of most trace elements in the first artesian aquifer were at or near their detection limits. Strontium concentrations ranged from 1,600 to 2,600 μg/L near the gypsum stack. The higher strontium concentrations tend to coincide with low sulfate concentrations. This occurs despite the fact that solubility controls in the first artesian aquifer do not seem to be responsible. Some of the ion products were nearly two orders of magnitude below solubility products found in literature (Bjerrum and others, 1957) for saturated strontium sulfate solutions. It appears that water low in strontium (from the surficial aquifer) is diluting strontium concentrations in the first artesian aquifer below native concentrations.

Iodide concentrations are above background in water from wells 14 (0.46 mg/L) and 31 (0.29 mg/L). The concentration of iodide may be sensitive to the composition of the aquifer where the process water initially contacts the aquifer. If the amount of neutralizing capacity ($CaCO_3$) is low, but the anion exchange capacity (clays) is high, iodide concentrations may be significantly decreased. This occurs because at low pH the anion exchange capacity is high. Conversely, if the neutralizing capacity of the aquifer is high and the clay content low, the pH is rapidly elevated with less loss of iodide ions. Water from a cooling pond could show a shift in iodide ion and INMI compared to gypsum stack waters if the materials initially contacted are different enough.

Water flowing east or southeast from the cooling pond and diammonium phosphate pond towards wells 14 and 31 is higher in iodide concentrations and has a lower INMI than water from wells 5, 10, and 18 that may receive much of their solute from the gypsum stack.

Organic Compounds

Total organic carbon concentrations ranged from 5.7 to 48 mg/L in the first artesian aquifer. The highest concentrations were found to the north and east of the gypsum stack as shown in figure 23. Figure 23 also shows the distribution of phenols and of methylene blue active substances (MBAS). The highest concentration of phenols occurred in water from wells 14 and 18 that are closest to the seepage ditch around the gypsum stack. Phenols were higher in the first artesian aquifer than in the aquifers above and below it. This suggests that seepage from the gypsum stack may be dissolving phenolic compounds from the aquifer. Traces of MBAS (0.1 mg/L) were found in water from four of the wells that had elevated phenol concentrations.

Water Quality in the Second Artesian Aquifer

Deep wells 6, 11, 15, 19, and 32 (fig. 2) are the only wells that are open exclusively to the second artesian aquifer at the AMAX plant. Well 6 was drilled to provide background data for this aquifer, but the percent increase in ions (PII) indicates that the quality of water from the well may be influenced by solute from the chemical plant. Predevelopment flow in the second artesian aquifer is toward the west; however, the flow direction has been reversed in recent years during periods of heavy pumping. Water levels in the well fluctuated about 6 feet between the wet season and the dry season when heavy irrigation occurred.

Major Constituents

Figure 14 shows that concentrations of major ions varied somewhat in the second artesian aquifer. Sodium, alkalinity, chloride, and calcium varied 130, 87, 70, and 54 percent, respectively, between the lowest and highest concentrations. The indices given below aid in understanding the nature and source of the variability.

The percentage increase in ions (fig. 24) suggests that concentrations of major constituent ions increase from west to east. Well 32 may have been affected by seepage from the diammonium phosphate pond. Figure 24

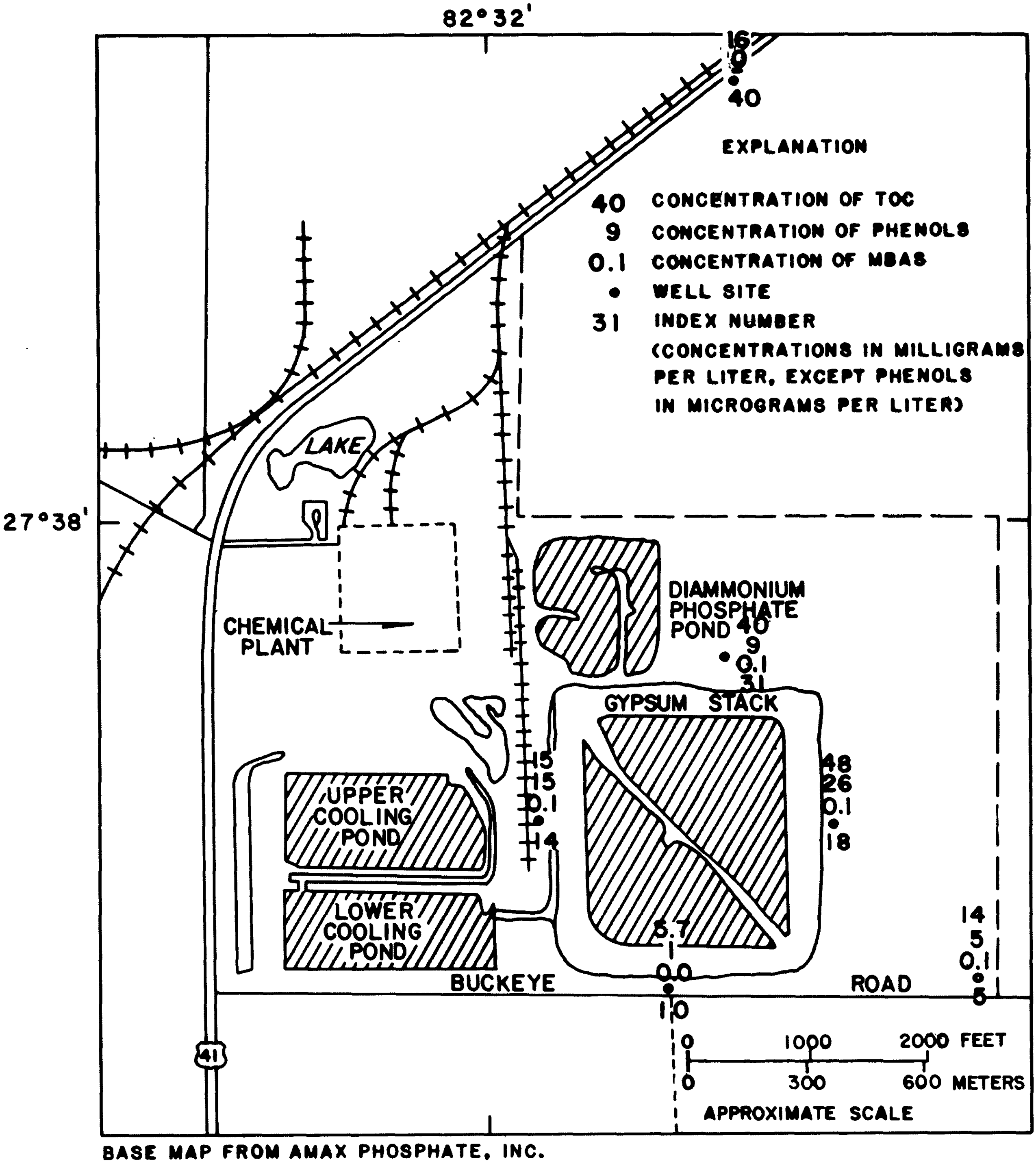


Figure 23.--Concentrations of total organic carbon, phenols, and methylene blue active substances in water from the first artesian aquifer at the AMAX plant.

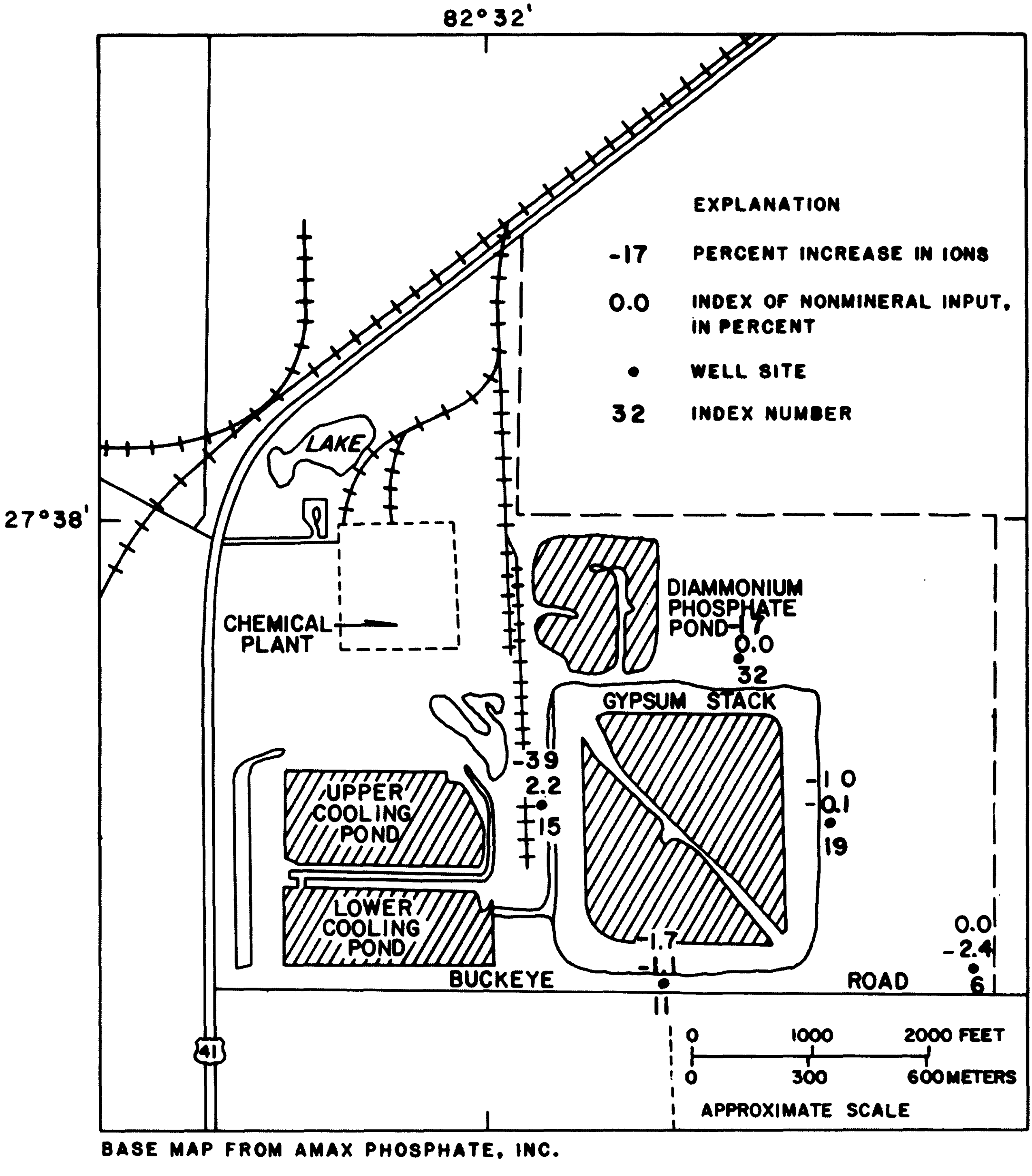


Figure 24.--Index of nonmineral input and percentage increase in ions for water from the second artesian aquifer at the AMAX plant.

shows the increase in ions from negative percentages to 0.0 from west to east because the percentages were calculated with respect to the quality of water from well 6.

The index of nonmineral input (fig. 24) and the percentage mineral imbalance indicate that although the total concentrations of major ions increase because of seepage, the ions had undergone ion exchange in the two overlying aquifers. The amount of exchange was such that the relations of the ions are essentially those of native ground water.

Major constituent data indicate that water that has high concentrations of major ions may have migrated from under the gypsum stacks and cooling ponds to well 6 or beyond.

Nitrogen and Phosphorus

Nitrogen and phosphorus concentrations were relatively low in the second artesian aquifer. Nitrate, nitrite, and orthophosphate concentrations were at or near the detection limits for the methods used. Ammonia and perhaps total organic nitrogen concentrations were in patterns similar to that for major ions and reflect an eastward migration of water from the gypsum stack.

Radiochemicals

Concentrations of radium-226 in the second artesian aquifer ranged from 3.5 to 5.1 pCi/L. Most of the radioactivity is probably of natural origin. In general, water samples from this aquifer contained greater radiochemical activities than water from wells in the upper aquifers.

Gross alpha, gross beta, and radium-226 activities are shown in figure 25. Because radioactive materials do not appear to migrate in significant quantities from the gypsum stack into the overlying aquifers, and because major constituent data indicate that solute from the chemical plant has been displaced east of the gypsum stack, it seems that more radioactive native water has displaced seepage under the gypsum stack to the east. The reactions and flow patterns are complex so that observed activities are not

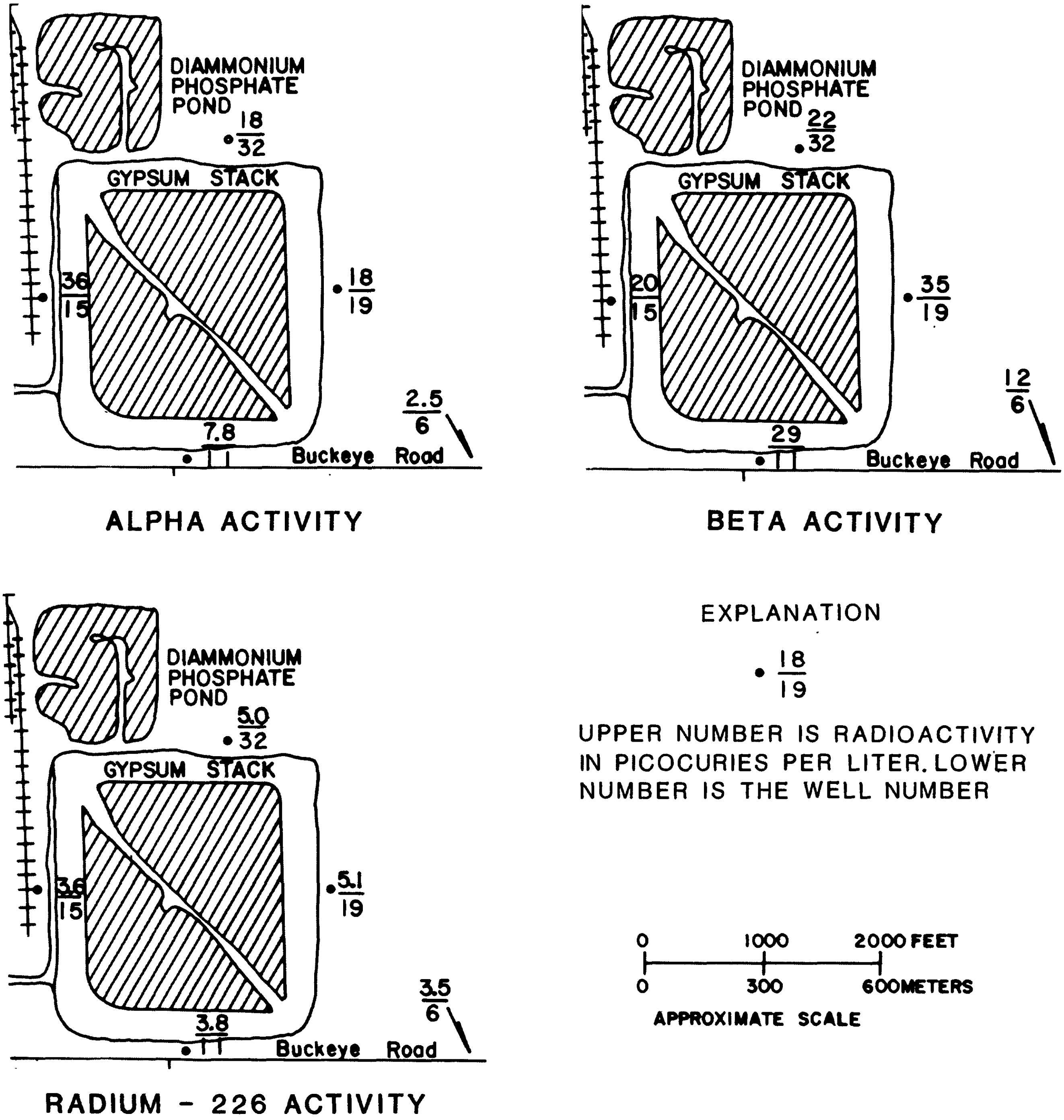


Figure 25.--Gross alpha, gross beta, and radium-226 activities for water from the second artesian aquifer at the AMAX plant.

simple to interpret. Data for the surficial aquifer show that alpha and beta emitters from process water migrate at different rates.

Trace Elements

In general, concentrations of trace metals in the second artesian aquifer were near their detection limits. Exceptions were iron, which ranged in concentration from 50 to 550 µg/L, and strontium, which ranged in concentration from 2,300 to 5,400 µg/L. Bromide and iodide concentrations were essentially constant. Boron concentrations ranged from 80 to 150 µg/L.

Strontium concentrations display a pattern similar to the radiochemicals. Apparently strontium occurs in higher concentrations in native water than in seepage from the gypsum stack.

Organic Compounds

Except for water from well 32 (fig. 2), total organic carbon concentrations found in water from the second artesian aquifer wells at the AMAX plant are similar to those in the first artesian aquifer. Phenols and methylene blue active substances were near their detection limits. Spatial relations suggest that the organic carbon in water is related to its distribution in the aquifer rather than to migration from the chemical plant.

Quality of Water from Wells Tapping More Than One Aquifer

Four wells, 24, 26, 27, and 28 (fig. 2), at the AMAX plant are open to more than one aquifer. Table 7 summarizes the depth interval of the open hole and relates the interval to the three shallow aquifers.

Wells 24, 26, and 27 were drilled prior to the start of this study. Well 28 was drilled for this study to correspond to what is considered to be the normal water-producing zone for this area.

Wells 24, 26, and 28 that bottom more than 250 feet below sea level had sulfate concentrations that ranged from 240 to 290 mg/L. The percentage mineral imbalance was the only ion index determined for the wells

Table 7.--Depths of open hole for wells 24, 26, 27, and 28 at the AMAX plant

Well No.	Altitude of bottom of casing (feet below sea level)	Casing ends	Altitude of bottom of well (feet below sea level)	Open hole ends	Percentage mineral imbalance
24	74	Bottom first artesian aquifer	550	Below second artesian aquifer	-0.15
26	33	Middle first artesian aquifer	290	Below second artesian aquifer	.39
27	30	Middle first artesian aquifer	141	Bottom of second artesian aquifer	5.32
28	173	About 30 feet below second artesian aquifer	255	Below second artesian aquifer	2.85

because the imbalance does not refer to a background sample as is required for the other two indices. Based on the similar sulfate concentrations, the low percentage mineral imbalance, and an examination of other water-quality parameters, there is no indication of process water seepage into aquifers tapped by these wells. For wells 24 and 26, any seepage of process water into the aquifer monitored by the upper part of the open hole would be diluted by water from greater depths. If the deep zones yield relatively more water because of their greater length of open hole and greater transmissivity, seepage into the first artesian aquifer could be effectively masked.

Well 27 is open from the middle of the first artesian aquifer to the bottom of the second artesian aquifer. The sulfate concentration of water from the well was 20 mg/L, which is similar to that in background well 40 (30 mg/L of sulfate). The percentage mineral imbalance is slightly elevated in well 27, but because of the low sulfate and sodium concentrations, the sample is believed to be unaffected by process water.

Quality of Water from a Drainage Ditch

A water sample was collected from the drainage ditch (site S1, fig. 2) between the southwest corner of the lower cooling pond and Buckeye Road to see if seepage from the cooling pond had occurred. The percentage mineral imbalance was found to be 32 percent, confirming that seepage was entering the drainage ditch. The sulfate concentration of water from the ditch was higher than water from any of the background wells for this area. The ammonia, orthophosphate, nitrate, and nitrite concentrations were elevated to 20, 26, 0.50, and 0.22 mg/L, respectively. These data confirm that water and solute were moving south from the area of the gypsum stack and cooling ponds.

Summary

Migration of radionuclides from the gypsum stack appears to be limited because of solubility controls. Radium-226 activities were below background levels near the gypsum stack.

Elevated concentrations of bromide and iodide ions may indicate that process water has migrated to a sampling site. Their absence does not insure that water has not migrated from the gypsum stack, probably because anion exchange is sensitive to aquifer composition near a source of process water.

Water in the surficial aquifer at the AMAX plant generally flows westerly from the gypsum stack but local variations occur because of mounding of the water table near the stack. The aquifer neutralizes acid present in process water and causes most of the phosphate, silica, fluoride, trace elements, and radioisotopes to precipitate from solution within about 100 feet from the stack. Sulfate concentrations decrease to about 2,000 mg/L within about 50 feet of the stack and then continue to decrease in concentration slowly thereafter. Sodium and sulfate are the most mobile major ions in the process water. Calcium, magnesium, and bicarbonate ions are dissolved from the aquifer. Dilution, ion exchange, and dissolution of aquifer materials gradually change the composition of major ions toward that of native water. Ammonia and orthophosphates occurred in high concentrations near the gypsum stack, but not away from the source.

Seepage in the first artesian aquifer has been displaced eastward by native ground-water flow as indicated by the percentage increase in ions and ammonia concentrations. Low activities and low variability of radioisotopes indicate that their migration into the first artesian aquifer is restricted.

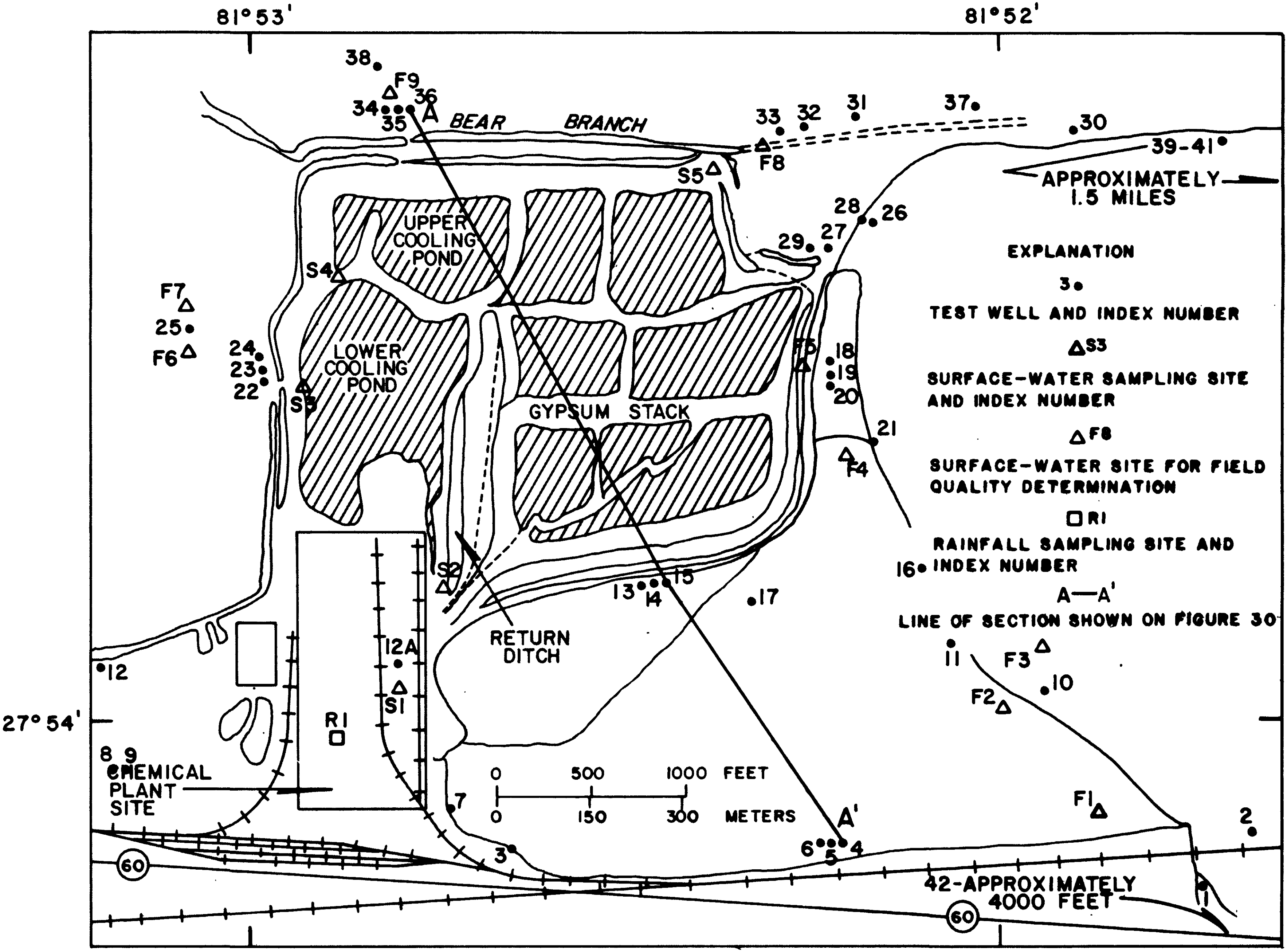
Water in the second artesian aquifer has been displaced farther toward the east than that in the first artesian aquifer. The percentage increase in ions and ammonia concentrations indicate that the highest concentrations of solutes seeping from the chemical plant occur east of the gypsum stack at some undetermined distance. This is caused by as much as 6 feet of drawdown of water levels because of ground-water pumpage to the east. Native ground water in the second artesian aquifer seems to contain more radiochemicals than seepage water from the chemical plant.

USS AGRI-CHEMICALS PLANT

The USS Agri-Chemicals plant is in the Polk Upland area between the Lakeland Ridge and Lake Henry Ridge in central Polk County (White, 1970). Land-surface altitudes at the plant range from 140 to 150 feet above sea level. Altitudes of the gypsum stack are several tens of feet above the adjacent land surface. The plant layout and locations of the gypsum stack, cooling ponds, and data-collection sites are shown in figure 26.

Descriptions of 43 wells and 16 surface-water sites that were sampled are given in the report by Miller and Sutcliffe (1982). In general, well depths ranged from 10 to 100 feet, but were as shallow as 9 feet and as deep as 1,052 feet.

The USSAC site was selected for study because it is in a mined area, but active phosphatic clayey waste-disposal ponds were not present to complicate flow of water and materials. The USSAC site is also in a recharge area of the Floridan aquifer and, hence, heads decrease with depth below land surface.



BASE MAP FROM USS AGRI-CHEMICALS

Figure 26.--Plant layout and locations of data-collection sites at the USSAC plant.

A small ditch (Bear Branch) drains a swampy area bordering the plant on the north and west sides (fig. 26). The ditch flows eastward into McKinney Branch and subsequently to the Peace River, about 2 miles east of the plant.

The general area of the USSAC plant has a humid, subtropical climate with warm, humid summers and relatively dry winters. Average monthly temperatures range from about 62°F in December and January to 82°F in August. The average annual rainfall is about 51 inches, about three-fifths of which occurs from June through September (Stewart, 1966). Figure 27 shows the typical patterns of monthly rainfall as based on data for the NOAA weather station at Bartow. Rainfall patterns are similar to those at Piney Point.

Hydrogeology

The geologic setting at USSAC is similar to that of AMAX. Beneath the surficial aquifer, two artesian aquifers occur within the intermediate aquifers and confining beds. These, in turn, overlie the Floridan aquifer (table 1). However, the geohydrologic setting is different because the USSAC site is in a recharge area of the Floridan aquifer and the AMAX site is in a discharge area of the Floridan aquifer.

Numerous production wells have been drilled at the USSAC site in the past--most are not currently in use. Most of the wells produced water from the Floridan aquifer. The aquifer is most productive at depths between 650 and 1,200 feet below land surface. Yields from the Floridan aquifer of 2,000 gal/min are common in large diameter wells. Well 7 at USSAC (fig. 26) has been reported to yield about 1,400 gal/min.

Continuous water-level recorders were installed on wells open to the surficial aquifer, the first and second artesian aquifers, and the Floridan aquifer (wells 34, 35, 36, and 8, respectively) at the plant, and on a Floridan aquifer well (42) southeast of the plant (fig. 26). Hydrographs of water levels in these wells are presented in figures 28 through 30. The hydrographs indicate that there is a better hydraulic connection between

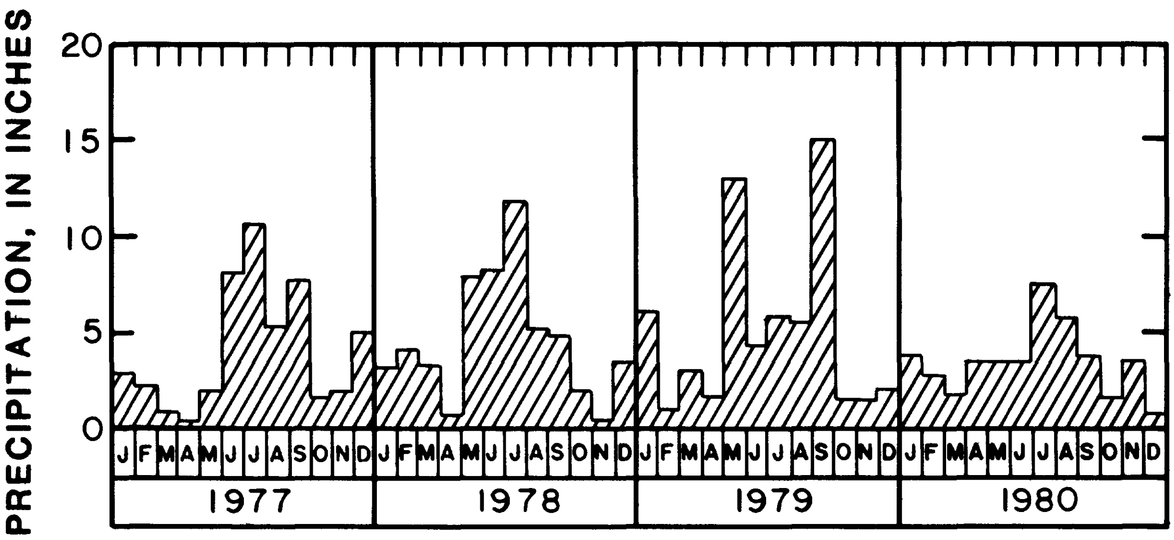


Figure 27.--Monthly precipitation at the National Oceanic and Atmospheric Administration weather station at Bartow, 1977-80.

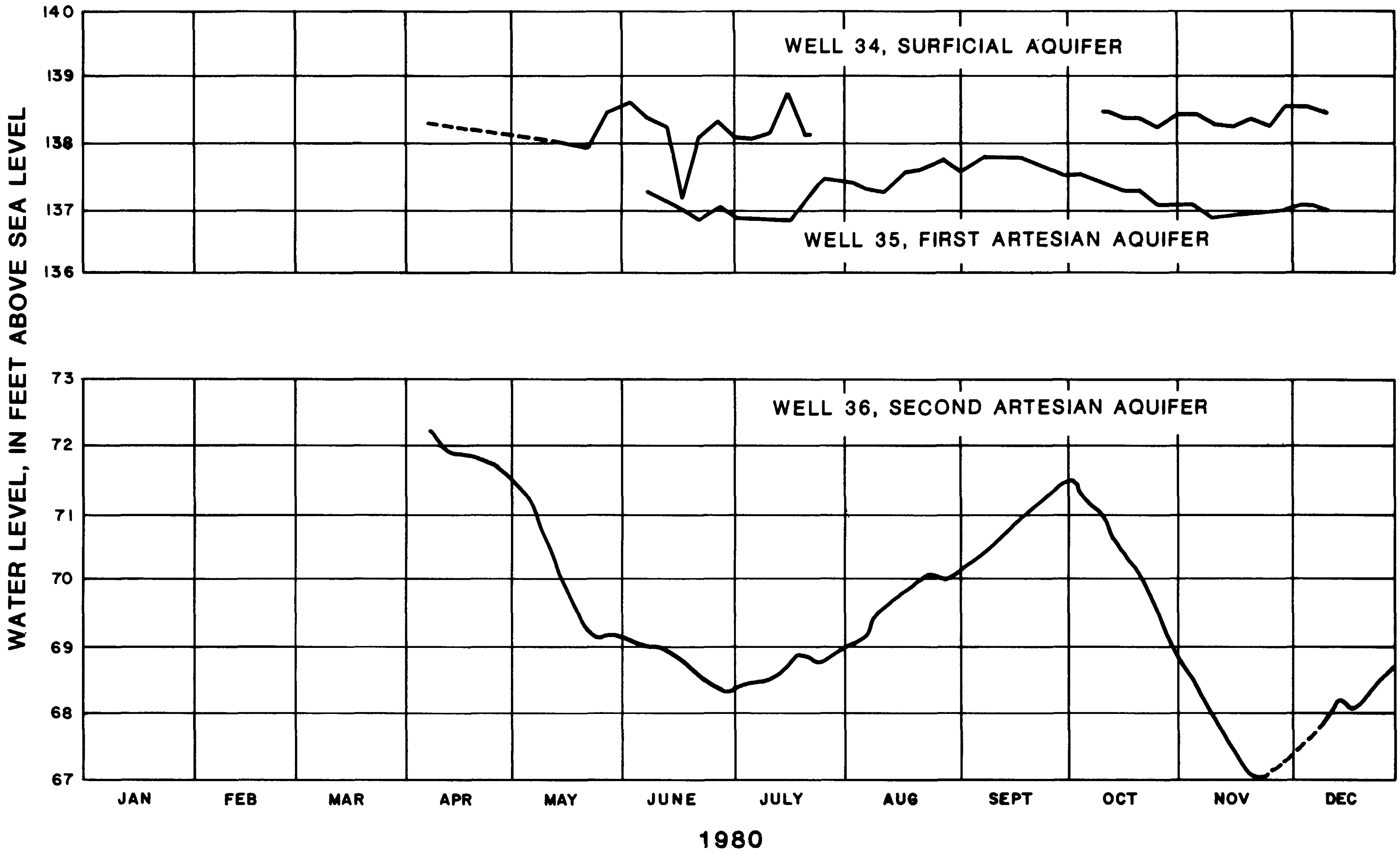


Figure 28.--Water levels in wells 34, 35, and 36 at the USSAC plant.

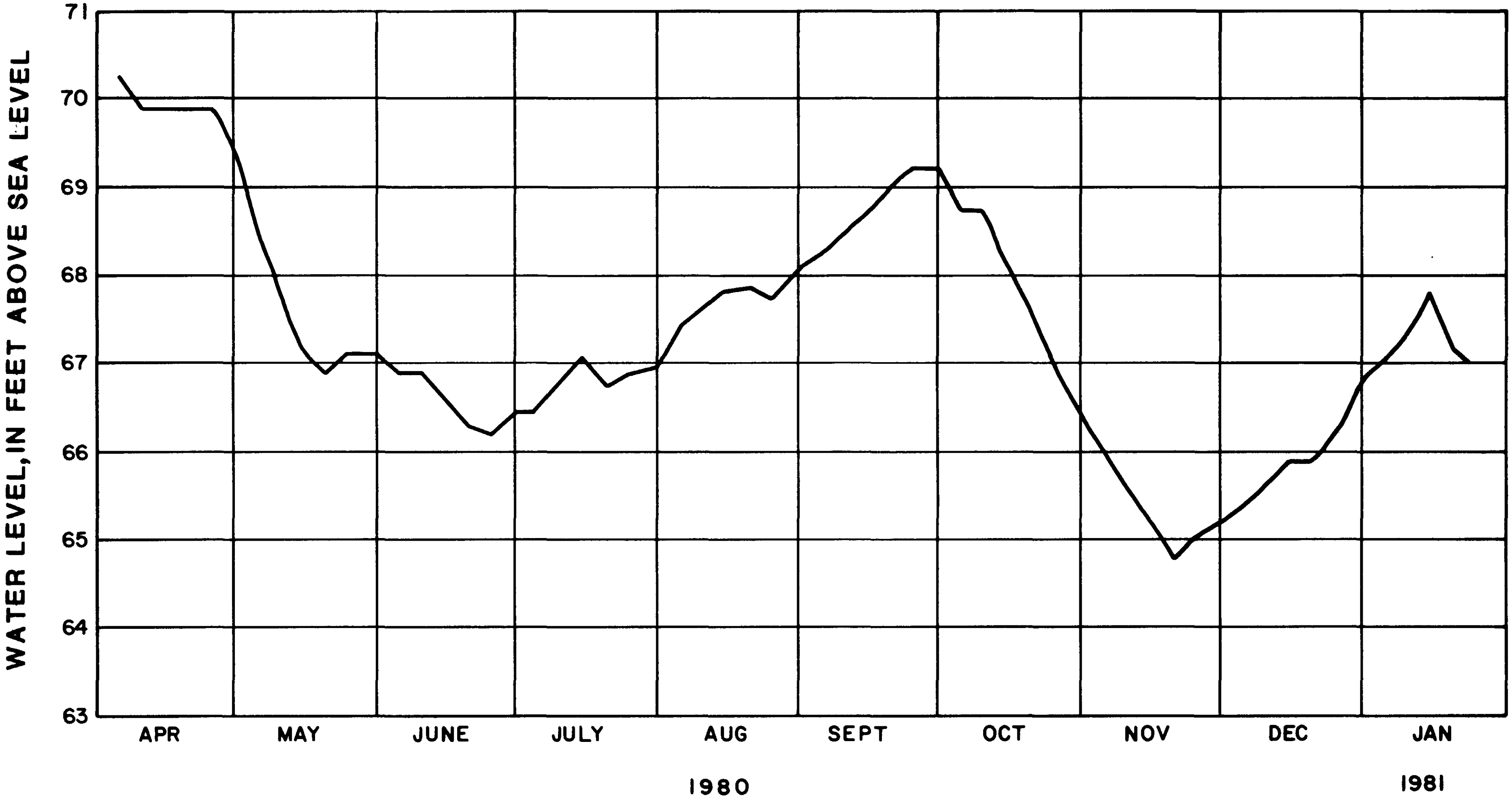


Figure 29.--Water levels in well 8 (second artesian aquifer) at the USSAC plant.

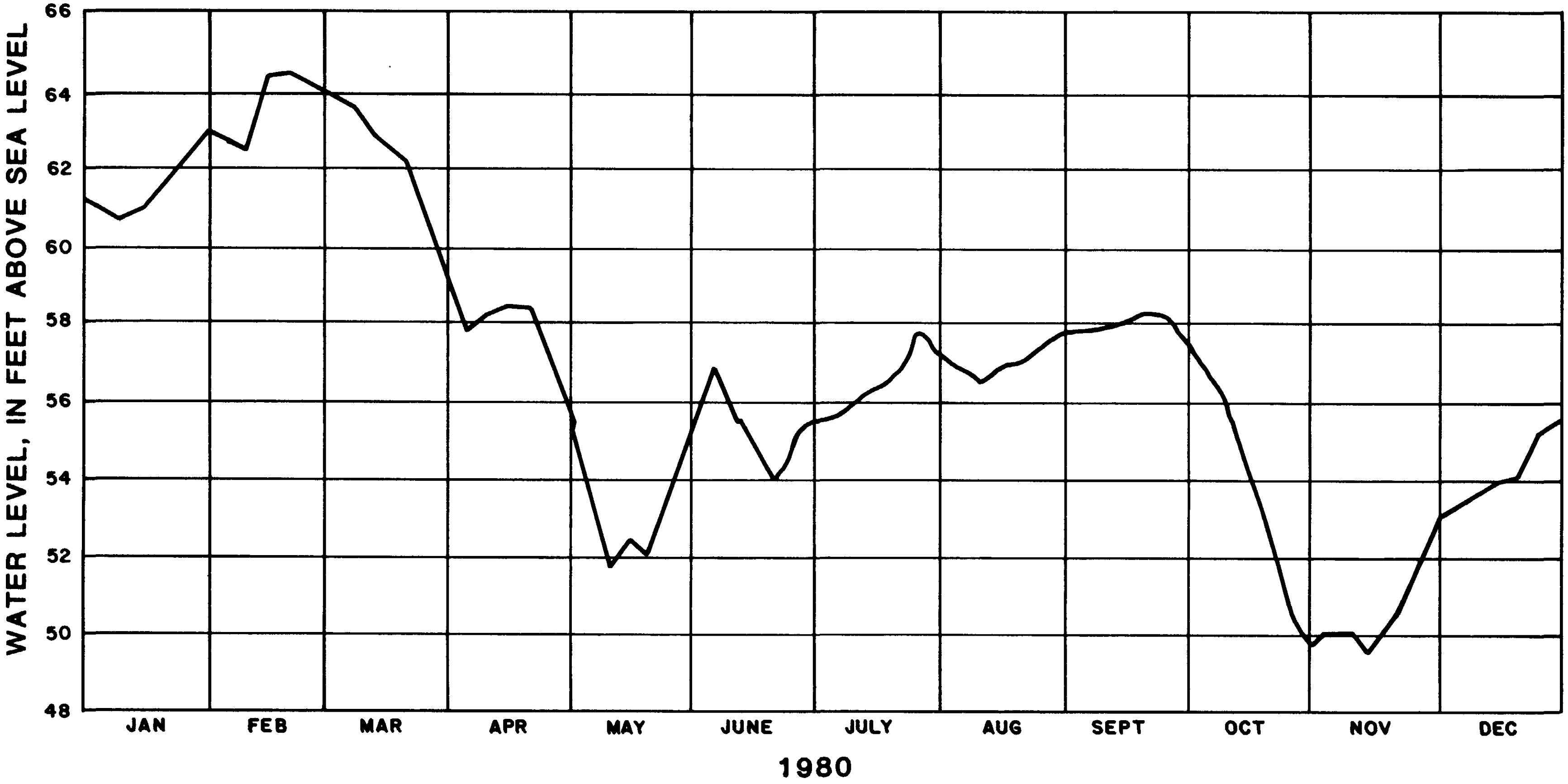


Figure 30.--Water levels in well 42 (Floridan aquifer) near the USSAC plant.

the surficial aquifer (well 34) and the first artesian aquifer (well 35) than between the first and second artesian aquifers as shown in wells 35 and 36. Also, the water level in the first artesian aquifer is nearly 70 feet higher than in the second artesian aquifer. A comparison between water levels in well 8 and well 36 (second artesian aquifer wells) indicate that their levels track each other; however, the water levels in well 8 are about 2 feet lower than levels in well 36. The hydrograph of water levels in Floridan aquifer well 42 shows a wider range of fluctuation than levels in the other wells. The water levels in the Floridan aquifer are 11 to 15 feet lower than those in the second artesian aquifer. This is probably because of nearby pumpage from the Floridan aquifer. Water levels are higher in the uppermost aquifers, indicating that the area is one of recharge to the Floridan aquifer.

At the USSAC plant, the Bone Valley Formation contains a relatively impermeable phosphate ore matrix that separates the surficial aquifer from the first artesian aquifer. Clays and marls at the base of the surficial sands and above the Bone Valley Formation are very thin or absent. For this report, the occurrence of the first limestone below the Bone Valley Formation was considered to be the top of the first artesian aquifer. However, characteristic kicks on gamma ray logs that occur at greater depths have been used to define the top of the first artesian aquifer south of the study site.

A generalized geologic section, figure 31, was constructed using data from wells 4, 7, 8, 15, 24, 30 and 36 (fig. 26). The section shows that there is little change in the thickness and slope of the geologic units. The geologic log for well 42, about 4,000 feet southeast of the study site indicates that the top of the Bone Valley Formation is about 99 feet above sea level and the top of the first artesian aquifer is about 59 feet above sea level. The tops of the formations dip to the southwest.

Surficial Aquifer

The surficial aquifer at USSAC consists of fine to medium sand and sandy clay. In some areas there is an assortment of fill materials that are apparently sand tailings from earlier ore washing activities. Beneath

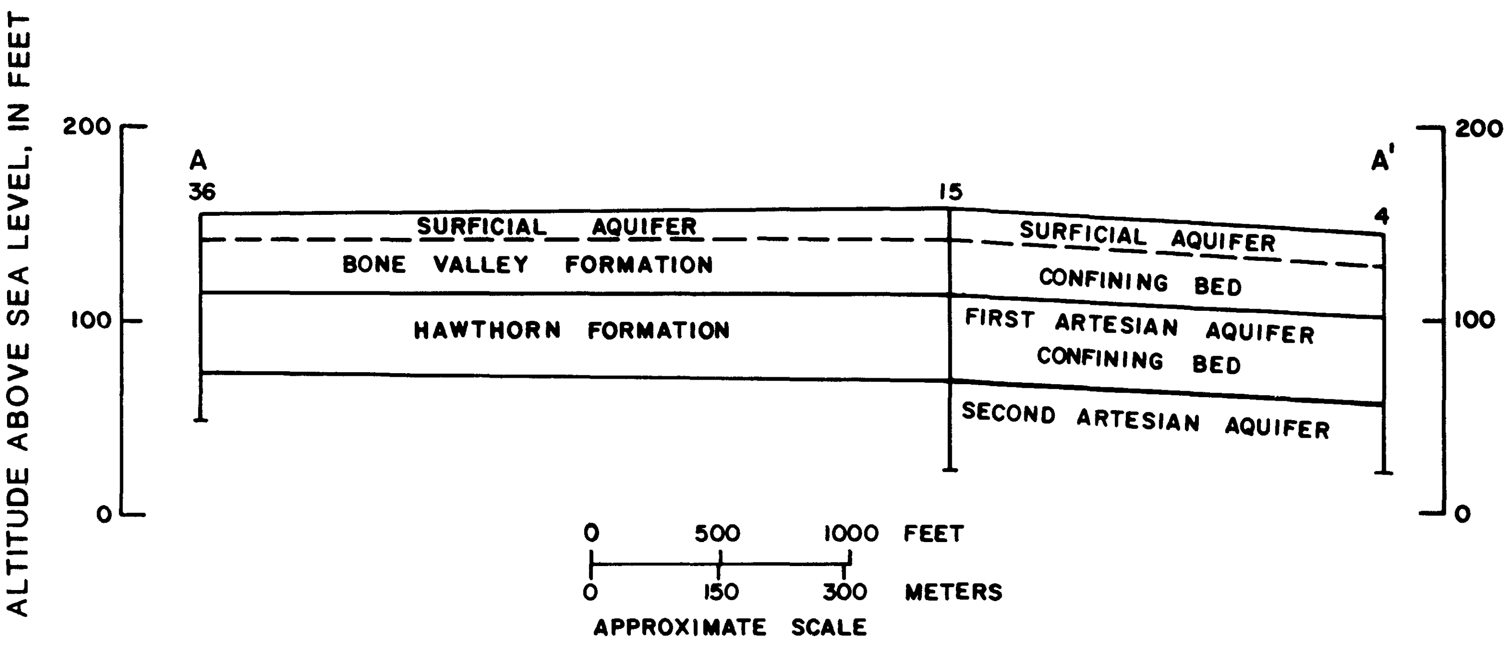


Figure 31.--Generalized geologic section underlying the USSAC plant. (Location of section shown in figure 26.)

the sand is clay and phosphorite of the Bone Valley Formation that confines the predominantly carbonate rock of the first artesian aquifer. The configuration of the water table in the surficial aquifer, as shown in figure 32, is based on water-level measurements of June 17, 1980, the low water-level period in the surficial aquifer for 1980 (fig. 28). The slope of the water table generally follows the slope of land surface except where it has been modified by drainage or by ground-water withdrawals. In general, water flows outward from the high levels that occur in the plant area and southern side of the gypsum stack; the overall direction of flow is easterly.

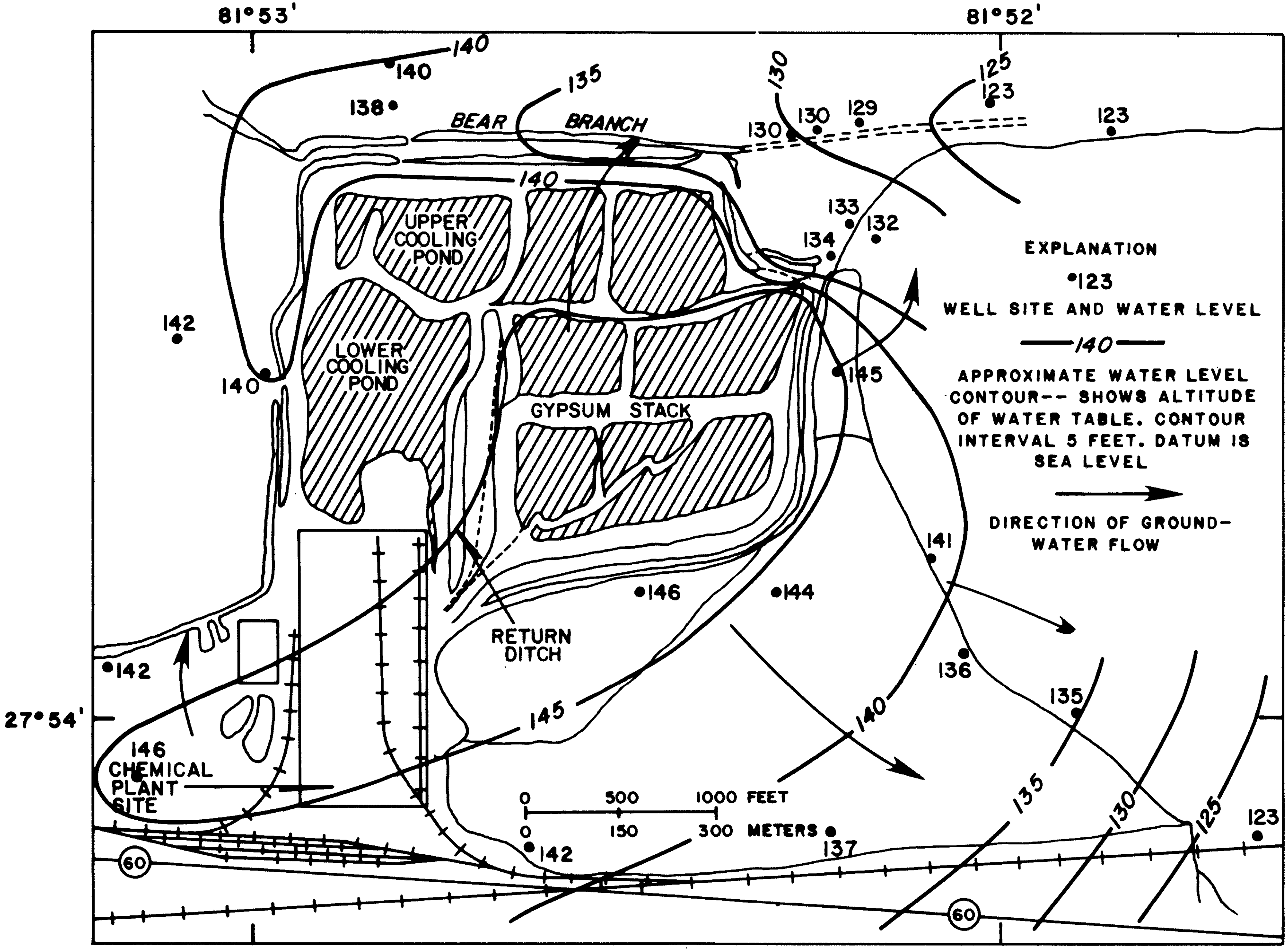
First Artesian Aquifer

The first artesian aquifer is about 50 feet thick and wells developed in it produce up to 5 gal/min. Test wells were constructed so that one or more clay layers separated it from adjacent aquifers. This was done to permit determination of whether vertical migration of fluids occurred between it and adjacent aquifers. Figures 28 through 30 indicate that there is potential for vertical migration of water downward because of head differences between each aquifer. The direction of migration at USSAC is from the surficial aquifer toward the first and second artesian aquifers and then to the Floridan aquifer. Figure 33 indicates that water levels in the first artesian aquifer are highest at the gypsum stack. The closed contours indicate recharge from the gypsum stack. The hydrograph on figure 28 indicates a close relation to the water-table aquifer.

Second Artesian Aquifer

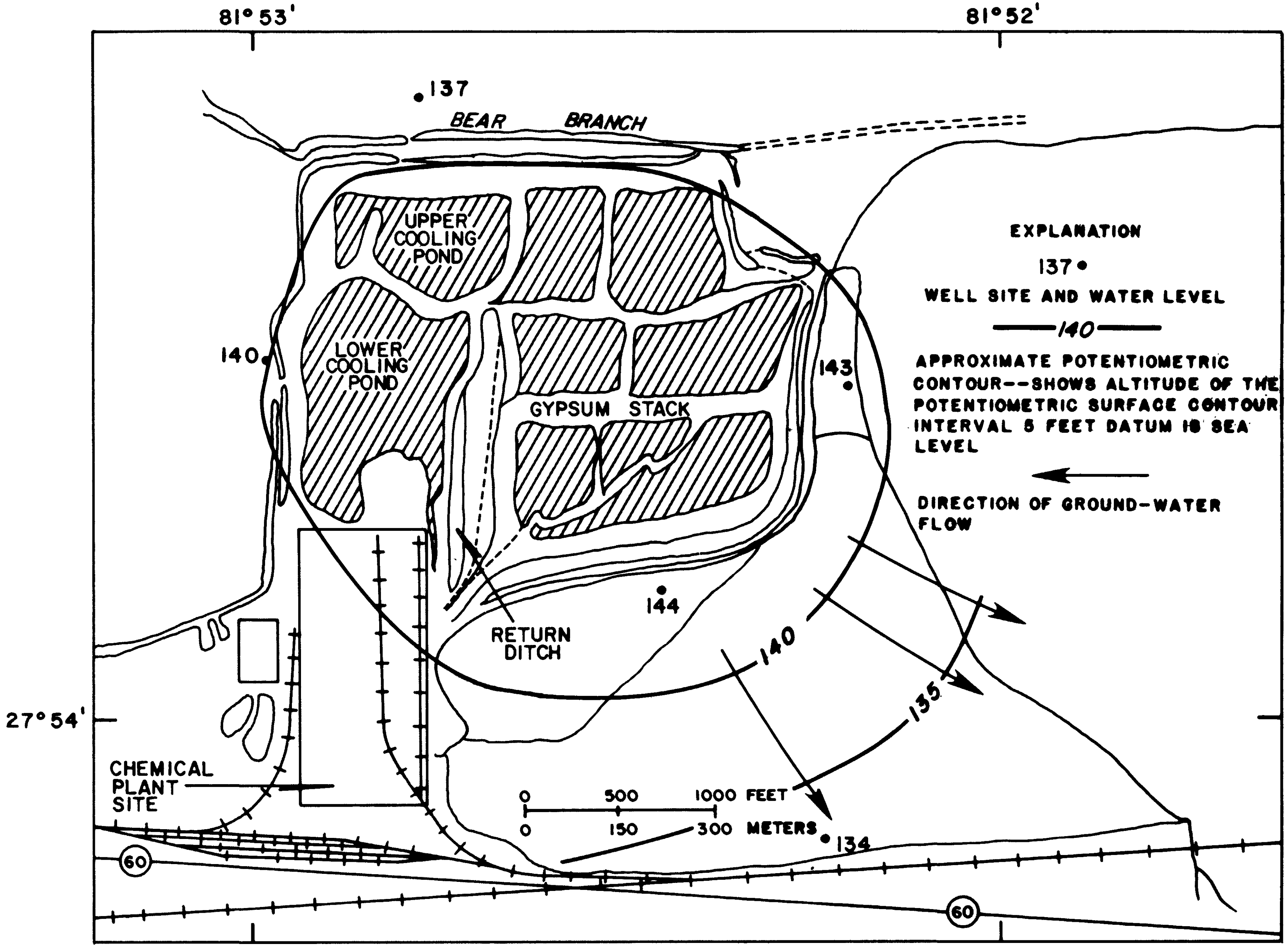
The second artesian aquifer at USSAC is composed of limestone with lenses of clay. One characteristic of the aquifer is the occurrence of small cavities in the limestone. These cavities caused a loss of drilling fluid and cuttings during drilling of wells.

Figure 34 shows the potentiometric surface of the second artesian aquifer. Potentiometric contours appear to close around well 7 because of heavy pumpage from this well. Pumpage from the Floridan aquifer also occurs to the south in Bartow. Hydrographs (figs. 28-30) indicate that water from the second artesian aquifer recharges the underlying Floridan



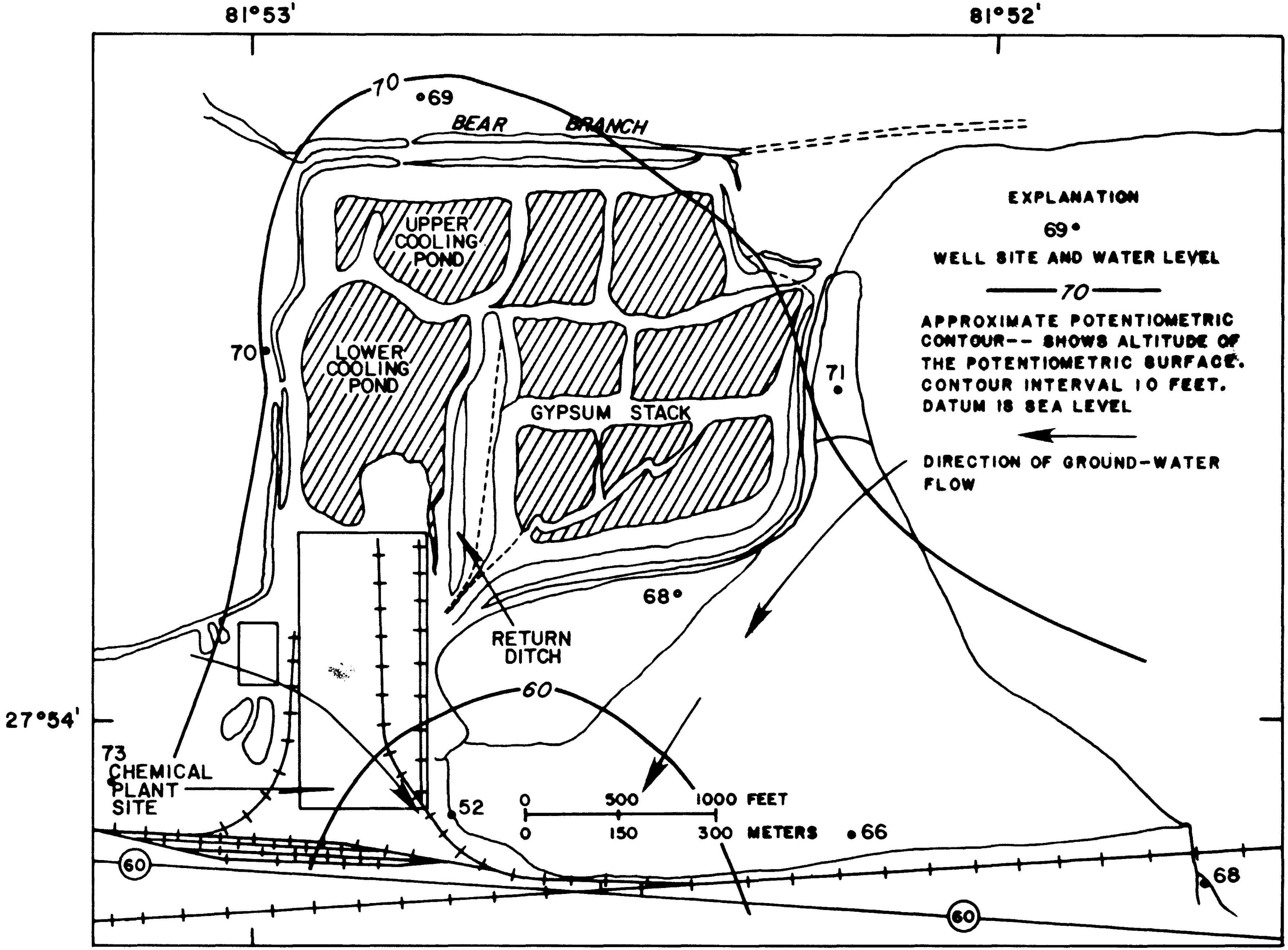
BASE MAP FROM USS AGRI-CHEMICALS

Figure 32.--Generalized water table of the surficial aquifer at the USSAC plant, June 17, 1980.



BASE MAP FROM USS AGRI-CHEMICALS

Figure 33.--Potentiometric surface of the first artesian aquifer at the USSAC plant, June 17, 1980.



BASE MAP FROM USS AGRI-CHEMICALS

Figure 34.--Potentiometric surface of the second artesian aquifer at the USSAC plant, June 17, 1980.

aquifer by vertical leakage and has similar water-level fluctuations. The northward extension of the 70-foot contour indicates the influence of recharge from the gypsum stack area.

Water Quality

Process Water

Process water at USSAC was more acidic (pH 1.4) and contained more fluoride and phosphate than AMAX process water (pH 1.8), but less sodium. Silica concentrations were about the same. At USSAC, about 30 percent of the fluoride occurs as F^- or HF. Table 8 shows an idealized analysis of process water.

Table 8.--Idealized analysis of process water at the USSAC plant

[mg/L, milligrams per liter; me/L, milliequivalents per liter]

Species	Concentration (mg/L)	Concentration (me/L)	Species	Concentration (mg/L)	Concentration (me/L)
H^{+1}	743	737	HPO_4^{-2} (as P)	8,375	541
Na^{+1}	780	34	SO_4^{-2}	5,050	105
K^{+1}	106	3	SiF_6^{-2} (as F)	5,500	96
Ca^{+2}	30	2	F^{-1} (as F)	2,100	110
Mg^{+2}	56	5			
NH_4^{+1} and others	---	71			
Total		852	Total		852

The process water was highly colored and had a characteristic chemical odor and brownish-yellow color. Figure 35 shows concentrations of principal ions in process water. The major constituents are H^+, SO_4^{-2}, SiF_6^{-2}, F^{-1}, and HPO_4^{-2}.

The gypsum slurry was sampled from a slurry tank inside the USSAC plant. The suspended solids concentration was 43,000 mg/L. The slurry

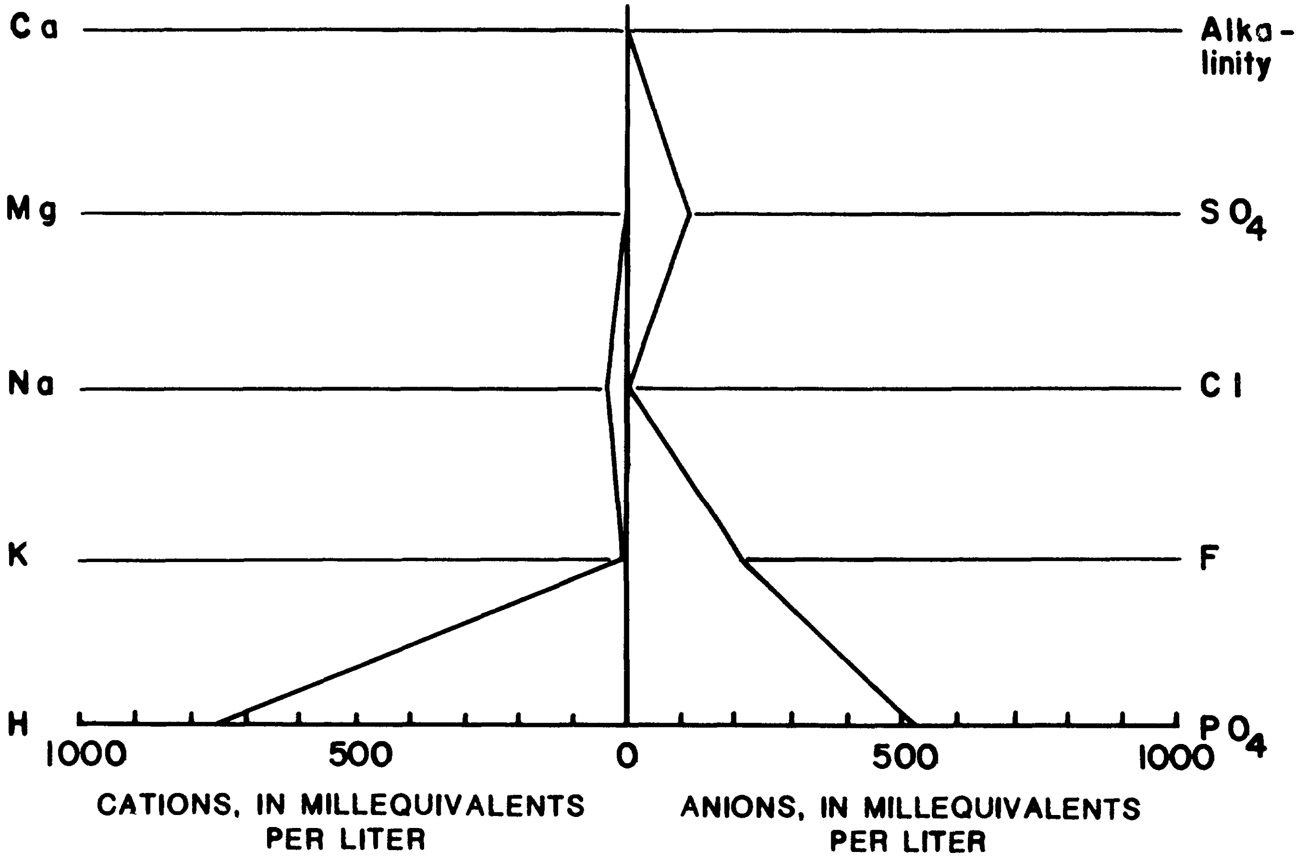


Figure 35.--Modified Stiff diagram showing concentrations of principal ions in process water from the USSAC plant.

contained 2,200 pCi/L of radium-226 which does not differ appreciably from the 1,900 pCi/L of suspended radium-226 found in the AMAX gypsum slurry. The concentration of radium-226 was calculated at 51 and 60 pCi/g of suspended solids at USSAC and AMAX, respectively. Kaufmann and Bliss (1977) reported an average of 33 pCi/g.

The specific conductance of process water ranged from 24,500 µmho in December 1979 to 29,300 in February 1980. The dissolved-solids concentration ranged from 33,200 to 34,700 mg/L. The observed variability in dissolved solids may be due only to analytical error.

Although pH was stable because of the buffering capacity of the process water, specific conductance, orthophosphate, and calculated dissolved solids concentrations indicate that the process water varies in composition with time. The variability could be because of rainfall quantity, time since last rainfall, and variations in plant operations and water use.

The arithmetic mean concentrations of selected constituents in process water from the USSAC plant are listed in table 9.

Table 9.--Concentrations of selected constituents in process water from the USSAC plant

[TR, total recoverable; mg/L, milligrams per liter; µg/L, micrograms per liter]

Constituent	Arithmetic mean concentration	Constituent	Arithmetic mean concentration
Aluminum, TR (µg/L)	400,000	Lead, TR (µg/L)	110
Antimony, dissolved (µg/L)	110	Lithium, dissolved (µg/L)	240
Arsenic, total (µg/L)	630	Manganese, TR (µg/L)	12,000
Beta, total (pCi/L)	4,900 ~~220~~	MBAS (mg/L)	2.0
Boron, dissolved (µg/L)	2,900	Molybdenum, TR (µg/L)	270
Carbon, organic, total (mg/L)	120	Nickel, TR (µg/L)	430
Chromium, TR (µg/L)	2,700	Nitrogen, ammonia, total (mg/L)	68
Copper, TR (µg/L)	550	Nitrogen, organic, total (mg/L)	69
Iron, TR (µg/L)	38,000	Phenols (mg/L)	55
		Zinc, TR (µg/L)	3,400

Concentrations of nitrate, nitrite, mercury, and oil and grease were low and are not discussed further. The gypsum slurry contained 410 mg/L of selenium, most of which probably was suspended because of the low concentrations (1 to 3 mg/L) found in other samples of process water.

Background Water Quality in the Surficial Aquifer

Data from wells 2 (fig. 26) and 39 (fig. 36) were used to define background water quality. Analyses of water from these wells were similar for most parameters except orthophosphate, total alpha radioactivity, iron, manganese, and total organic carbon. Analysis of water from well 2 was used to calculate ion indices because most major constituents in water from the well had lower concentrations than those for well 39 and because both the difference in ionic balance and the percentage mineral imbalance were lower.

The background analysis appears as a straight line near the zero line in figure 37 because of the scale required to present the ranges of constituents observed near the gypsum stack. The background water is predominantly a $Ca(HCO_3)_2$ type. The specific conductance was about 240 μmho and the pH was about 6.1. Fluoride ranged from 0.8 to 1.6 mg/L. Phosphate concentrations of water from wells 39 and 2 were 0.27 and 2.2 mg/L, respectively. Stewart's (1963) data that were obtained during the 1950's, and Miller and Sutcliffe's (1982) data suggest that sulfate concentrations in the surficial aquifer are generally less than 20 mg/L. Because natural sulfate concentrations in the surficial aquifer are low, concentrations of sulfate greater than about 20 mg/L are probably of industrial or cultural origin.

Background Water Quality in the First Artesian Aquifer

A background well (40) was drilled about 2 miles northeast of the gypsum stack (fig. 36). The permeable zone at the site was dry so background water-quality samples could not be obtained there. To calculate ion indices, well 35 was selected as the best alternative for defining background water quality in the first artesian aquifer. The low percentage mineral imbalance (PMI) and the low sulfate and iodide ion concentrations in water from well 35 suggest that the water approaches background quality in its composition.

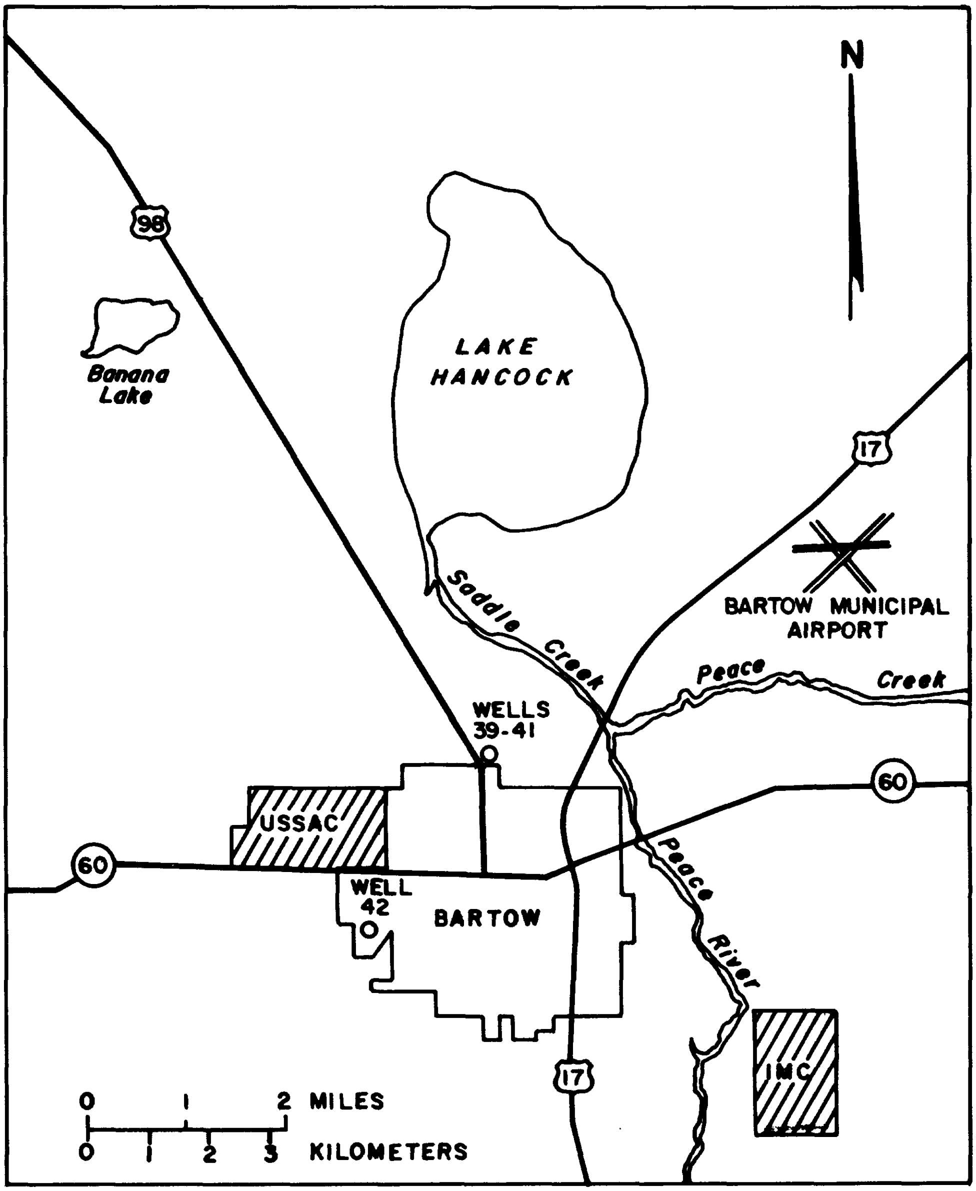


Figure 36.--Locations of background water-quality sampling wells near the USSAC and IMC plants.

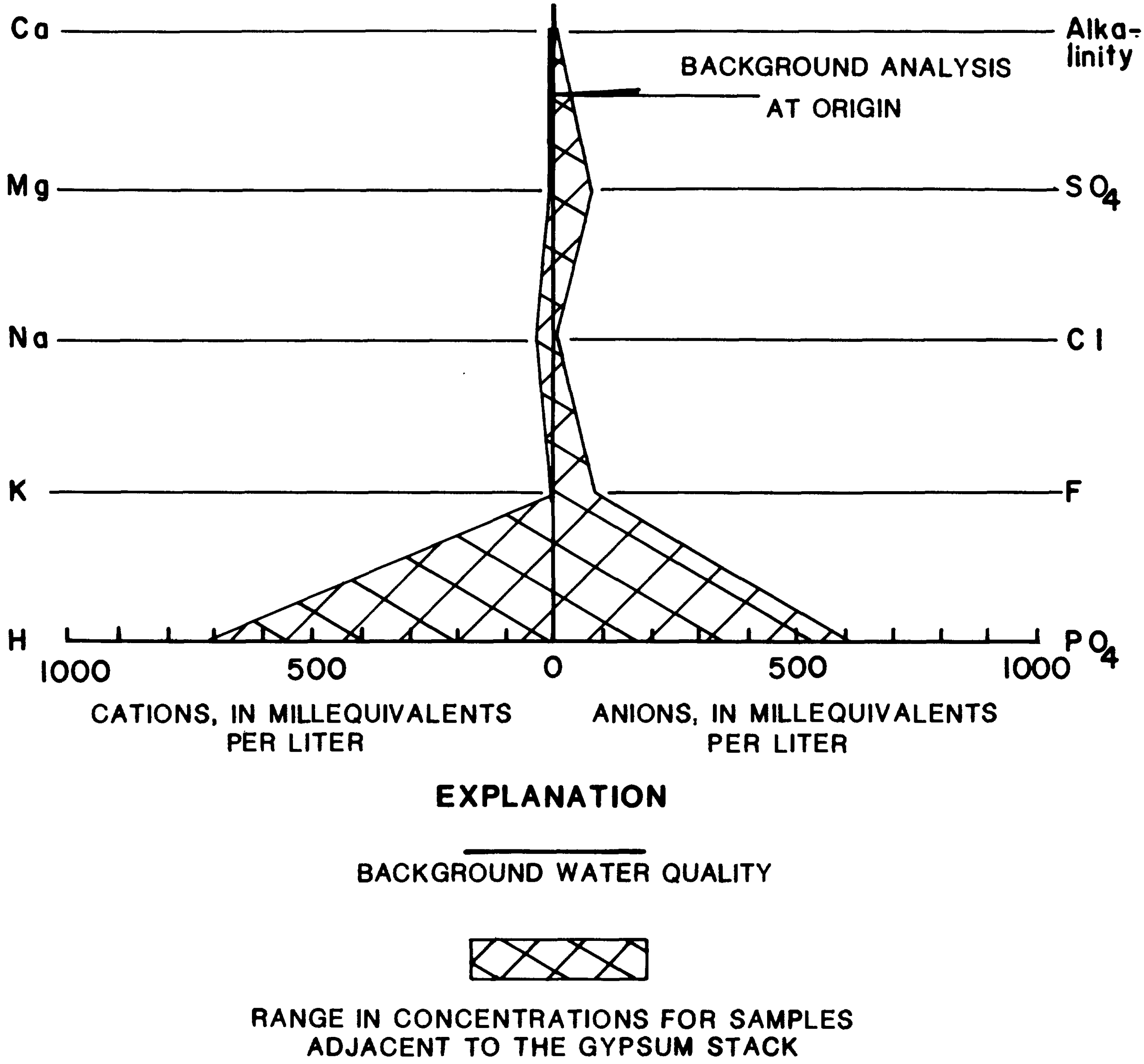


Figure 37.--Modified Stiff diagram showing concentrations of principal ions in water from surficial aquifer wells adjacent to the USSAC gypsum stack and background well 2.

The water type for the background sample was a $Ca(HCO_3)_2$-$Mg(HCO_3)_2$ (fig. 38). Sulfate concentrations ranged from 1 to 4 mg/L. Fluoride concentrations ranged from 1 to 2 mg/L. The concentration of orthophosphate was 0.01 mg/L in water from wells 35 and 23.

Background Water Quality in the Second Artesian Aquifer

Well 41, about 2 miles northeast of the gypsum stack, was sampled to establish background water-quality conditions in the second artesian aquifer (fig. 36). The similarity between analyses of water from wells 41 and 24 increases confidence that they are representative of background conditions.

The background water sample contained predominantly calcium, magnesium, and bicarbonate ions. Fluoride, sulfate, and orthophosphate concentrations were 0.17, 3.9, and 0.05 mg/L, respectively. Figure 39 illustrates the background quality of water for the second artesian aquifer.

Soil Resistivity

Several resistivity soundings were made on March 16, 1980, in the area around the USSAC gypsum stack. In some cases, high resistivity of the dry sands near land surface made quantitative interpretation impractical. However, the approximate depth to water and thickness of layers of high conductance water (the higher the conductance of water, the lower the soil resistivity) could often be estimated for the surficial aquifer.

On a road between well 34 (fig. 26) and the upper cooling pond, a low resistance zone began at a depth of about 25 feet and continued to an undetermined depth. About 50 feet north of that site on undisturbed land about 15 feet lower in altitude, the depth to the low resistance zone ranged from about 2 to 26 feet. About 25 feet south of well 34, the low resistance zone was from about 12 to 26 feet in depth. About 300 feet north of well 34, where the water table is about 5 feet below land surface, there was no apparent zone of low resistance. This indicates that a 20-foot thick solute plume, a few feet below land surface, has migrated to well 34, less than 400 to 500 feet north of the upper cooling pond. Water-quality samples from well 34 showed a 22 percent increase in specific conductance

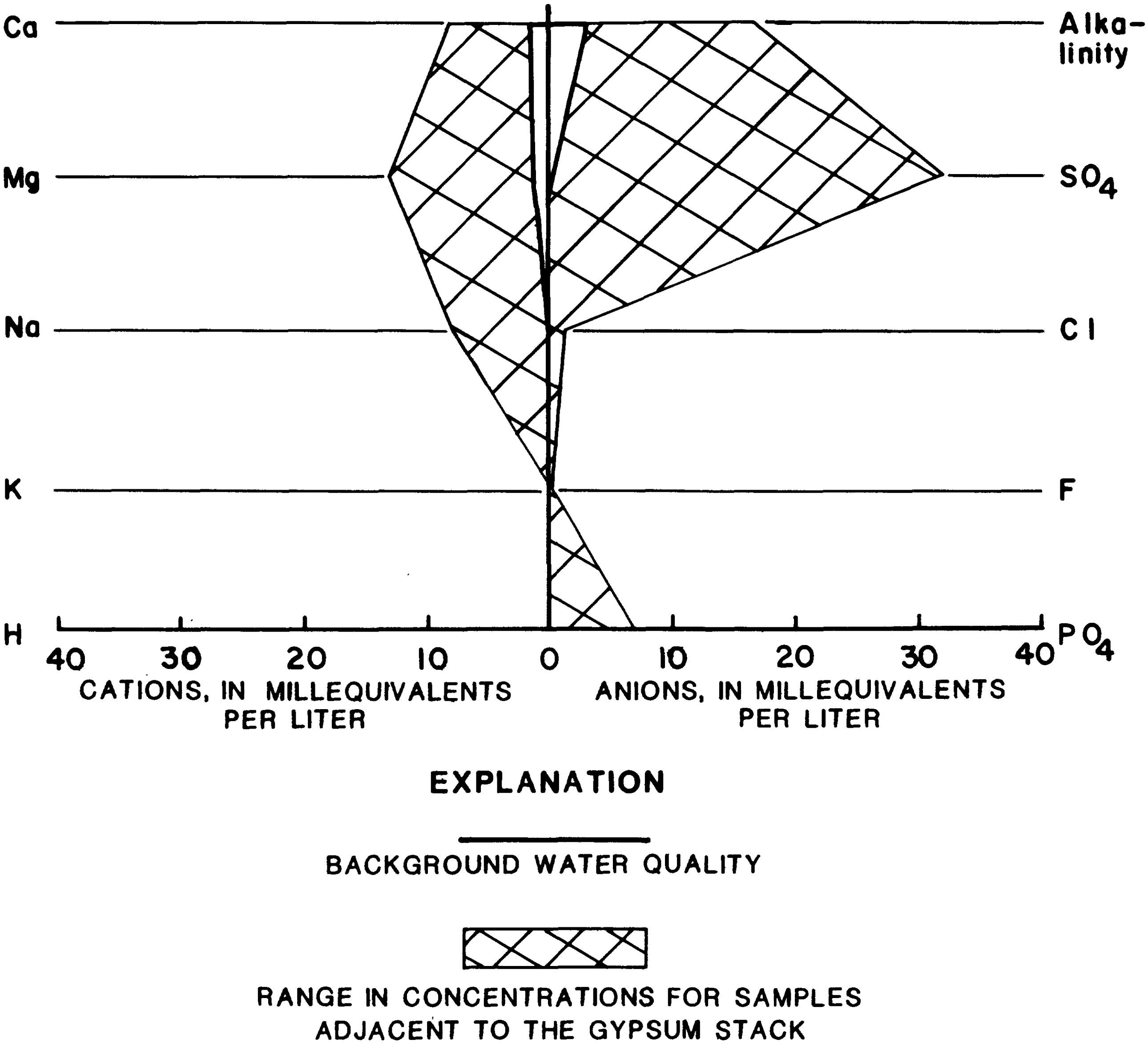


Figure 38.--Modified Stiff diagram showing concentrations of principal ions in water from first artesian aquifer wells adjacent to the USSAC gypsum stack and background well 35.

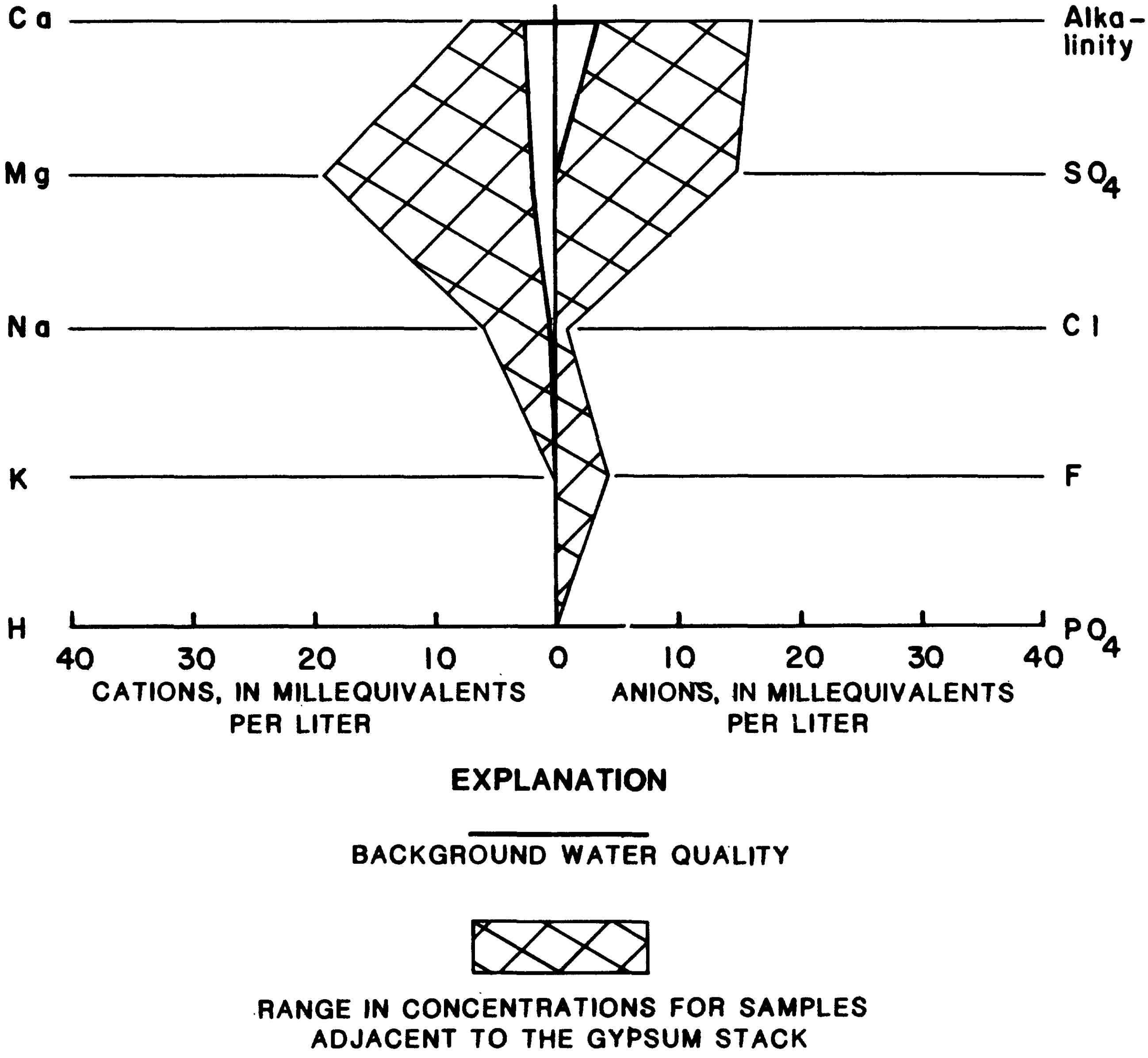


Figure 39.--Modified Stiff diagram showing concentrations of principal ions in water from second artesian aquifer wells adjacent to the USSAC gypsum stack and background well 41.

between December 1979 and June 1980. This increase does not establish a long-term trend, but is possibly the result of temporary hydrologic conditions in the surficial aquifer.

About 15 feet south of well 13, the resistance dropped at least two orders of magnitude at a depth of about 11 feet. The bottom depth of the low resistance zone could not be determined. The water level was 8 feet below land surface in well 13. About 100 feet south of well 13, the low resistance zone started at a depth of about 26 feet. The land surface was about 15 feet higher than near well 13. The water table was about 24 and 10 feet below land surface at about 300 and 400 feet south of well 13, respectively. About 40 feet south of well 5, the low resistance zone was from 4 to 22 feet below land surface. These data indicate that a solute plume occurs in, and has probably moved through, the surficial aquifer to about one-third mile south of the USSAC gypsum stack.

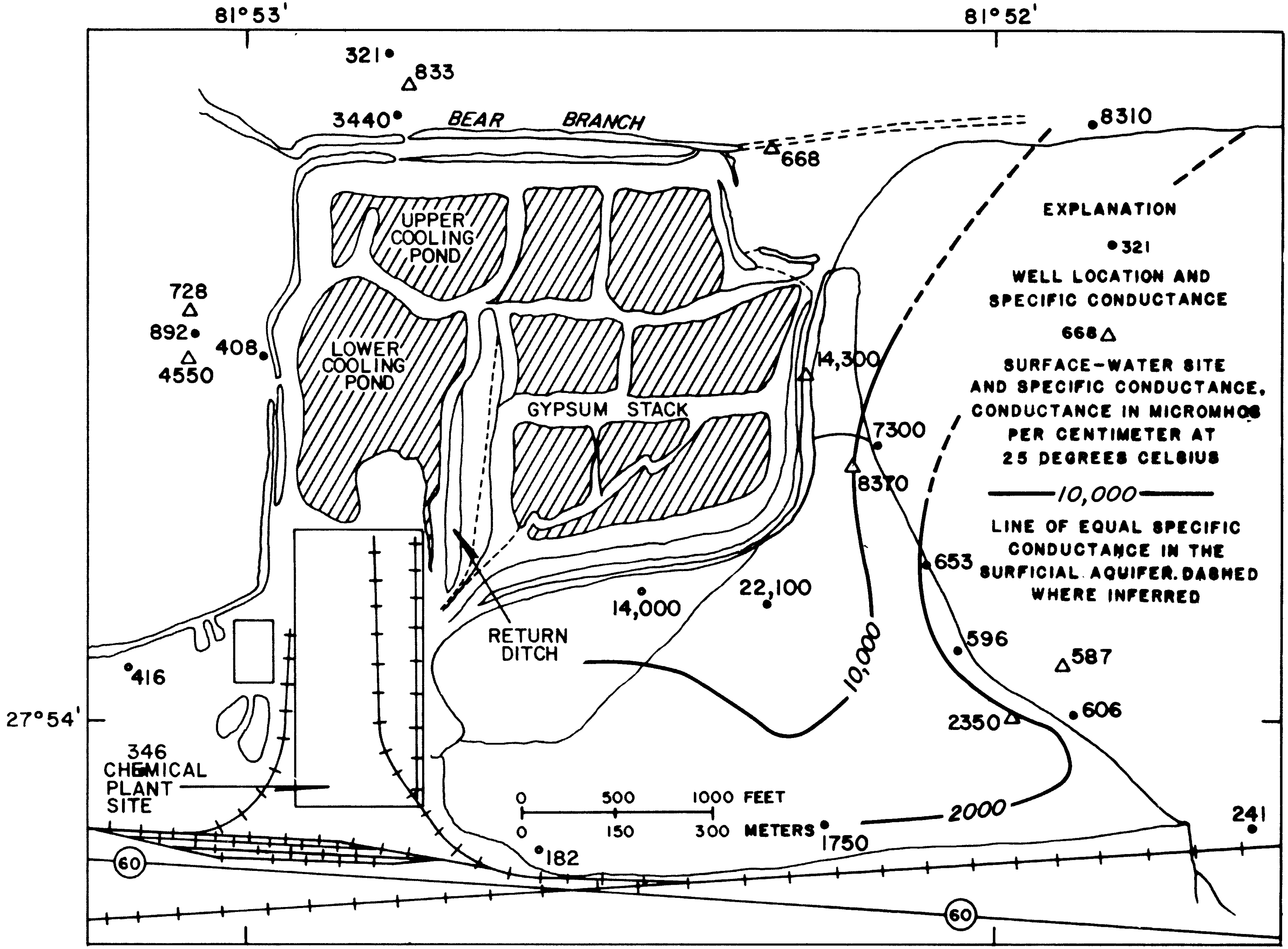
Water Quality in the Surficial Aquifer

Specific Conductance

The specific conductance of water samples from the surficial aquifer is shown in figure 40. Data for several surface-water sites are included to help define locations of high conductance water. All concentrations shown in figure 40 are higher than the background concentration (240 µmho) except at well 3, south of the chemical plant. Many of the ponds contained high conductance water that migrated through the surficial aquifer, traveled as runoff, or was disposed of in the pond.

Only to the east and south of the gypsum stack were there enough data points to contour specific conductance. A plume appears to exist southeast of the gypsum stack. Well 17, which is in a small dump, contains substances derived from process water and materials disposed of in the dump.

Lithologic data for well 15 (fig. 26) indicate that sand fill (tailings) occurs as deep as 43 feet at the south side of the gypsum stack. The high permeability and low acid neutralizing capacity of these sands permit process water to migrate into this area more readily than in other areas.



BASE MAP FROM USS AGRI-CHEMICALS

Figure 40.--Specific conductance of water from surface-water sites and wells in the surficial aquifer at the USSAC plant.

Ground water with a specific conductance of 1,750 µmho (well 5) was found about 1,800 feet south of the gypsum stack, and surface water with a specific conductance of 2,350 µmho (pond F2) was found about 1,800 feet southeast of the gypsum stack.

Major Constituents

Figure 37 compares major constituent ions in a background water sample to those in water from surficial aquifer wells adjacent to the USSAC gypsum stack. All constituents except chloride and alkalinity significantly exceeded background levels in one or more wells. Acidity, sodium, sulfate, fluoride, and orthophosphate concentrations were orders of magnitude above background levels at some wells. The ion indices for surficial aquifer wells at USSAC (see section on "Principles and Processes") are listed in table 10.

Table 10.--Ion indices for water from wells in the surficial aquifer at the USSAC plant

Well No.	Depth (feet)	Percentage mineral imbalance (PMI)	Index of nonmineral input (INMI)	Percentage increase in ions (PII)
[1]2	10	1	--	--
5	20	25	240	870
10	19	29	61	120
11	19	0	-2	220
13	22	[2]50	[2]1,300	[2]4,600
16	17	16	41	190
17	14	64	4,200	4,300
18	22	[2]30	[2]1,200	[2]2,700
21	19	44	760	1,600
22	19	0	3	80
34	21	70	1,600	2,000

[1] Background well used to calculate INMI and PII for other wells.
[2] Estimated.

Figures 41 and 42 show the change in INMI and PII with distance from the gypsum stack. The water levels show that there is a gradient of about 0.8 foot per 100 feet away from the gypsum stack. Some seepage from the stack may be intercepted by a small drainage ditch between wells 2 and 10. Well 10 is near a pond that contains high conductance water (2,350 µmho). The influence of this pond is to elevate the PMI and INMI because those indices are sensitive to input of Na^+, SO_4^{-2}, and H^+. The PII for water from well 10 is in line with other wells.

Figures 43 and 44 show the relative concentrations for several major constituents found in water from wells at several distances from the gypsum stack. The wells are approximately in a line downgradient from the stack. The relative concentration is the observed concentration divided by the concentration shown in table 8 for the idealized analysis of process water. The water sample collected from well 2 is considered to represent background water quality.

Calcium and magnesium concentrations are low in the process water so they increase in concentration initially as the result of dissolution of the carbonates in the aquifer by acidic process water. As the sulfate concentrations decrease, calcium and magnesium are dissolved from aquifer materials by acids. Decreases in concentration of magnesium occurred at least as far as 1,800 feet from the gypsum stack. The sodium concentration in water from well 13 (100 feet from the gypsum stack) is about the same as in process water. Sodium concentrations are near background concentrations in water from well 11 (about 1,000 feet from the gypsum stack). Potassium concentrations near the stack exceed those in process water in one sample shown in figure 44. This may result from dissolution of potassium-bearing clay minerals. Potassium concentrations approach background levels within 1,000 feet from the gypsum stack. Sodium and potassium behave similarly to sulfate except that they are initially higher than sulfate in terms of concentrations relative to the process water. Fluoride concentrations are reduced by reactions with aquifer materials and are near background levels within about 400 feet of the gypsum stack. Water from well 17 (300 feet from the stack) is different in composition perhaps because of the influence of the dump near the well. The water was turbid, brown, and had a putrid odor.

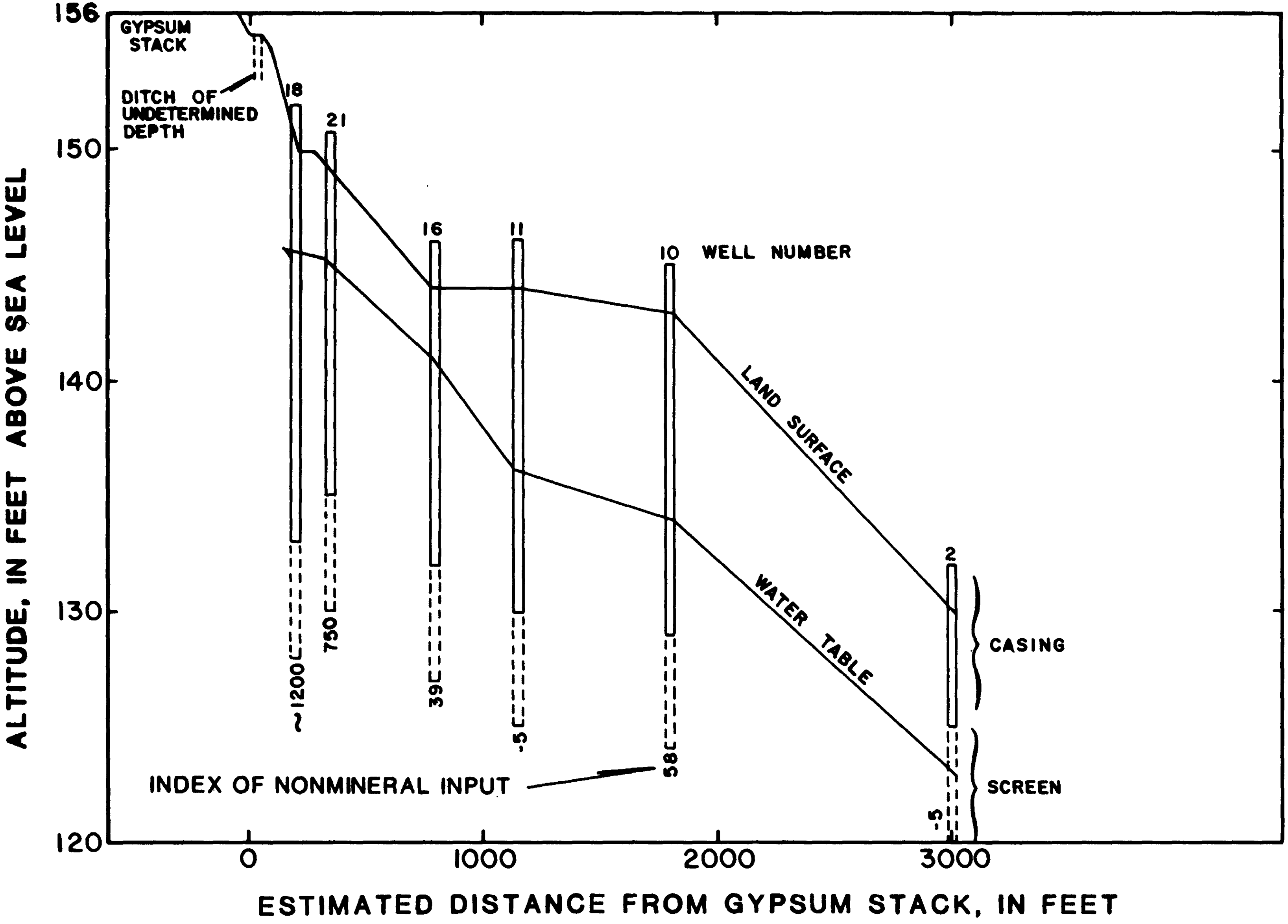


Figure 41.--Index of nonmineral input (INMI) for water from wells in the surficial aquifer at the USSAC plant.

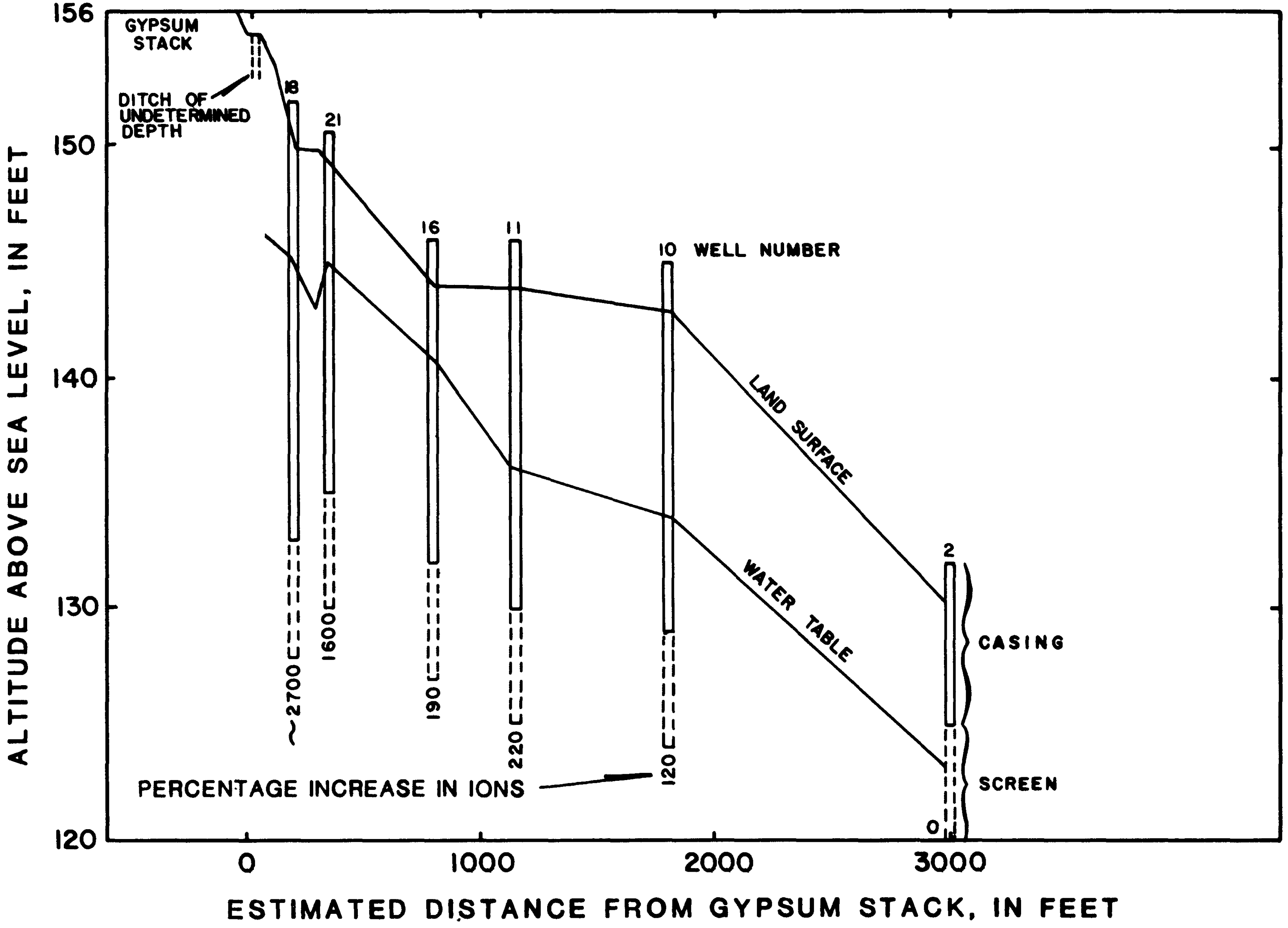


Figure 42.--Percentage increase in ions (PII) in water from wells in the surficial aquifer at the USSAC plant.

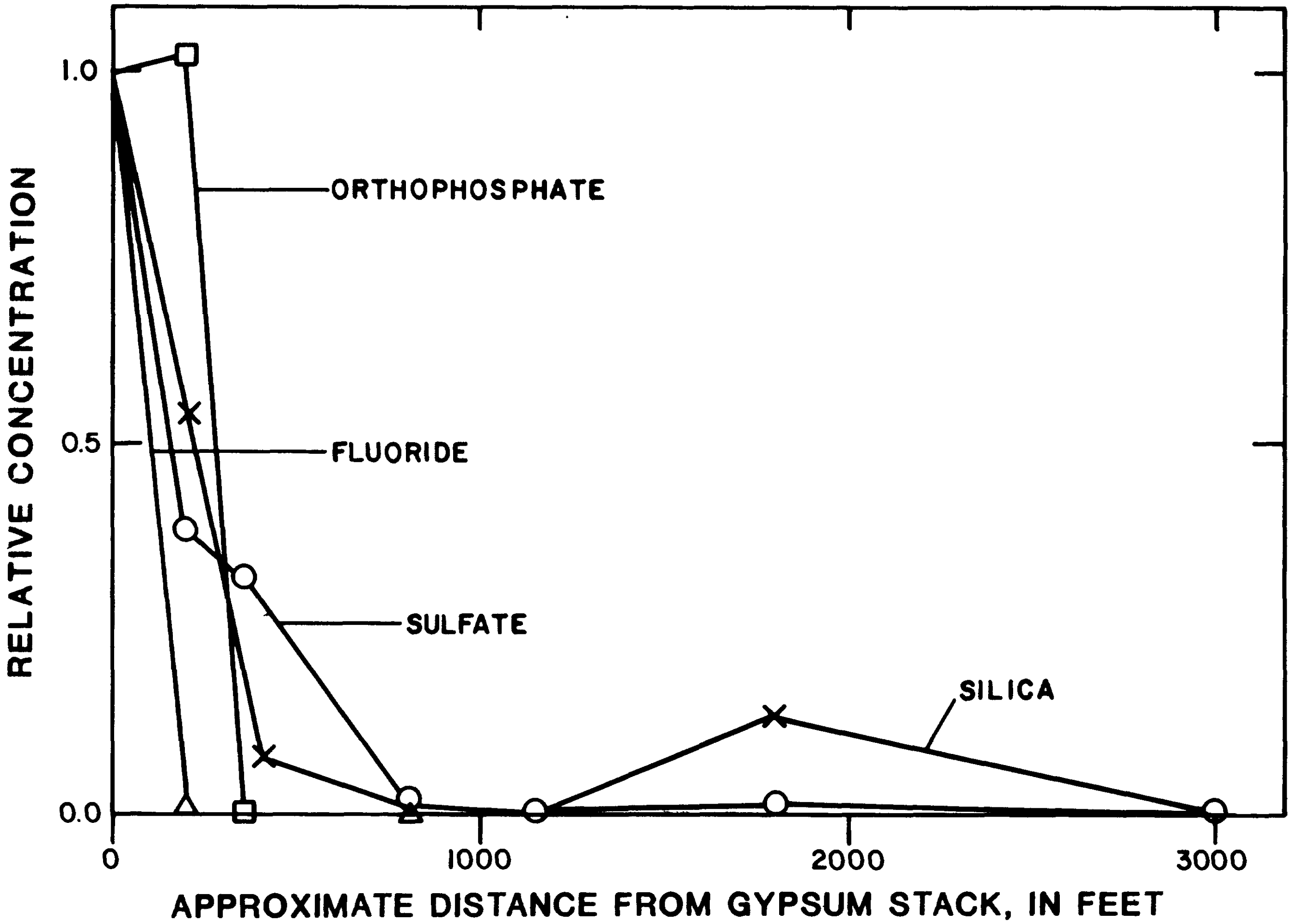


Figure 43.--Relative concentrations of sulfate, orthophosphate, fluoride, and silica in water from the surficial aquifer relative to process water at the USSAC plant.

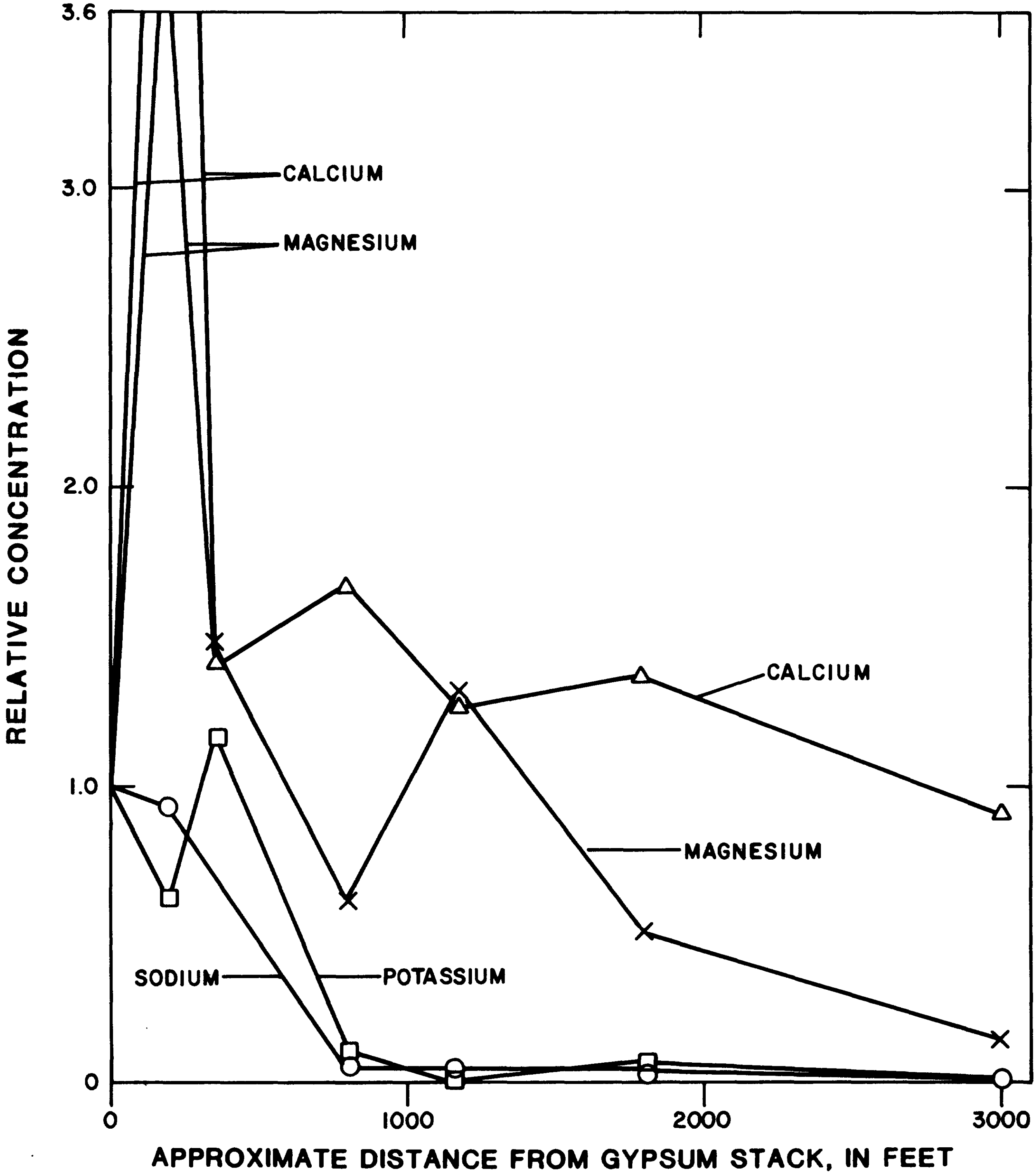


Figure 44.--Relative concentrations of sodium, potassium, calcium, and magnesium in water from the surficial aquifer relative to process water at the USSAC plant.

Sulfate concentrations decrease to about 2,000 mg/L by reactions in the aquifer, but probably migrate readily below this concentration. Water from well 17 is anomalously high in sulfate. The plot (fig. 43) of sulfate concentrations versus distance is nearly linear until about 800 feet from the gypsum stack. This shows that sulfate has migrated 400 to 800 feet from the stack along the line of wells. This also suggests that dilution of these ions with native water is occurring.

Orthophosphate concentrations rapidly decrease to low levels (less than about 2 mg/L) within about 350 feet from the gypsum stack. Silica concentrations decreased rapidly within the first 300 feet, but then showed increases in water from wells 21 and 10.

Nitrogen and Phosphorus

In general, nitrate concentrations were low in water from the surficial aquifer. Nitrate concentrations in water from wells adjacent to the gypsum stack ranged from 0.00 to 0.28 mg/L as N. Water from well 17 (fig. 26), which is in a dump, contained 43 mg/L of nitrate as N.

Most water samples from the surficial aquifer contained elevated ammonia concentrations compared to the background water sample from well 39, which contained 0.01 mg/L of ammonia as N. Water from wells 5, 13, 18, 21, and 34 contained more than 10 mg/L of ammonia. The water sample collected from well 17 contained 4,000 mg/L of ammonia. This is higher than the nitrogen concentration in process water, so some of the substances in the sample must have originated in the dump rather than in the process water. Concentrations of 12 and 9.0 mg/L of ammonia were found about one-third of a mile south of the gypsum stack at wells 5 and 10, respectively.

Organic nitrogen concentrations were also elevated in water from the surficial aquifer. Near the gypsum stack, concentrations ranged from 0.22 to 15 mg/L of total organic nitrogen as N. Water from well 17 contained 500 mg/L of total organic nitrogen. This exceeded the nitrogen concentration in process water.

Elevated orthophosphate concentrations occurred in much of the surficial aquifer at the plant site. At wells 13 and 18, the phosphate concentrations approached that of process water. Concentrations of orthophosphate as P in water from wells 17 and 21 exceeded 3,000 mg/L and from wells 5 and 10 exceeded 100 mg/L.

The nitrogen and phosphorus data indicate that significant concentrations of ammonia, total organic nitrogen, and orthophosphate in the surficial aquifer (well 5) occur as far as one-third of a mile to the south of the gypsum stack.

Radiochemicals

Dissolved radium-226 activities in water from the surficial aquifer ranged from 0.1 to 54 pCi/L. Both background wells (wells 2 and 39, fig. 26) contained 0.2 pCi/L of radium-226. Water from well 18 contained 54 pCi/L of dissolved and 0.6 pCi/L of suspended radium-226. Water from well 13 contained only 2.6 pCi/L of dissolved and 215 pCi/L of suspended radium-226. Particulate matter high in radium-226 may have been entrained during sampling. Such particulate matter could be deposited near this well if the reaction zone for precipitation or coprecipitation of radium-226 occurs there.

High concentrations of radium-226 are limited to two wells (13 and 18) close to the gypsum stack, which indicates some migration of radium-226. Concentrations in the process water and the surficial aquifer appear to be controlled by sulfate concentrations.

Water from well 13 contained the highest gross alpha (2,027 pCi/L) and beta (2,985 pCi/L) activities of all surficial aquifer wells. Water from well 18 contained 861 pCi/L of alpha and 550 pCi/L of beta radioactivity. Gross alpha activities were significantly above background in water from well 17 and were slightly elevated in water from wells 22 and 34. Gross beta activities were significantly above those in background wells 2 and 39. Gross alpha and beta radioactivities that are significantly above background levels are found only in wells that are adjacent to the gypsum stack.

Trace Elements

Higher concentrations of trace elements were detected in water from the surficial aquifer at USSAC than at AMAX. Some of the causes are: (1) greater age of the chemical plant, (2) a sandy soil that probably has less neutralizing capacity and greater transmissivity, and (3) process water that has a lower pH.

Iron concentrations in excess of 20,000 µg/L, as is the case for wells near the gypsum stack, indicate that seepage of process water had occurred. Manganese concentrations above about 1,000 µg/L are probably indicative of seepage. Selected trace metal data (Miller and Sutcliffe, 1982) are presented in table 11 to show the range in concentrations for wells close to the gypsum stack. The pH is the dominant control on solubility and migration of metals that form insoluble oxide, hydroxides, fluorides, sulfates, and carbonates. Ion exchange will affect all the metals if the pH is above the zero point of charge for the aquifer materials. Wells 13 and 18 (fig. 26) were in sandy soil and near the gypsum stack in the downgradient direction.

Table 11.--Concentrations of trace elements and pH data for selected surficial aquifer wells at the USSAC plant

[mg/L, milligrams per liter; µg/L, micrograms per liter]

Well No.	Iron (µg/L)	Manganese (µg/L)	Beryllium (µg/L)	Cadmium (µg/L)	Chromium (µg/L)	Cobalt (µg/L)	Copper (µg/L)	Lithium (µg/L)	Molybdenum (µg/L)
2	14,000	200	0	0	20	4	2	0	2
39	490	10	0	0	<~~1~~10	0	3	0	7
34	25,000	2,500	20	0	60	37	0	80	1
34	39,000	2,800	10	0	70	33	0	110	0
18	110,000	13,000	150	2,100	3,200	230	130	360	130
13	32,000	12,000	130	2,000	---	180	15	470	58
22	3,500	20	20	0	7	2	1	10	7
21	720,000	8,600	10	0	50	0	0	610	2
S2	41,000	13,000	100	(1)	3,000	500	500	230	260

Table 11.--Concentrations of trace elements and pH data for selected surficial aquifer wells at the USSAC plant--Continued

[mg/L, milligrams per liter; µg/L, micrograms per liter]

Well No.	Nickel (µg/L)	Strontium (µg/L)	Zinc (µg/L)	Aluminum (µg/L)	Iodide (mg/L)	Arsenic (µg/L)	Boron (µg/L)	Antimony (µg/L)	pH (units)
2	1	120	10	300	0.03	9	80	0	6.1
39	3	90	20	300	.00	1	20	0	6.1
34	280	1,000	420	---	.12	1	80	0	3.3
34	330	850	1,400	150,000	.17	1	100	0	2.9
18	580	15,000	7,300	---	7.0	1,100	1,600	98	2.3
13	630	2,500	5,200	40,000	9.7	640	1,000	76	2.4
22	12	190	10	300	.00	1	20	0	5.8
21	35	2,600	100	1,100	.05	1	360	0	4.0
S2	420	920	3,700	400,000	2.3	630	2,700	100	1.3

[1] Chemical interference in process water, possible pH adjustment.

The pH in water from the wells was 2.4 and 2.3, respectively. Elevated levels of iron, manganese, beryllium, cadmium, chromium, cobalt, copper, lithium, molybdenum, nickel, strontium, zinc, aluminum, iodide, arsenic, boron, and antimony occur in water from these two wells. In general, elevated levels of trace metals were not found in wells remote from the gypsum stack. Elevated levels of cobalt, nickel, iodide, and arsenic were found in water from well 5, which is about one-third of a mile (1,800 feet) south of the gypsum stack.

Barium, mercury, lead, and selenium do not appear to migrate to any significant degree. Selenium and mercury concentrations are elevated only in the solid phase of the gypsum slurry coming off the filters. Elsewhere, their concentrations are very low.

Organic Compounds

Concentrations of total organic carbon in water from background wells 2 and 39 were 75 and 30 mg/L, respectively. The process water contained in water from the surficial aquifer wells ranged from 1.9 to 379 mg/L. Because total organic carbon can originate from natural sources as well as the process water, it is a poor indicator of seepage into the shallow aquifer. Water from well 17 contained 370 mg/L of total organic carbon, which exceeds the concentration found in process water (120 mg/L). Water from well 17 (fig. 26) contains substances that originated from the dump as well as from the gypsum stack.

The concentrations of phenols ranged from 0 to 1,300 µg/L in water from the surficial aquifer. A water sample from well 2 contained 1 µg/L of phenols. The concentration of phenols in process water averaged 55 µg/L. The highest concentrations of phenols in the aquifer were 22 µg/L in water from well 18, 23 µg/L in water from well 13, and 1,300 µg/L in water from well 17 near the dump site. Other surficial wells contained from 0 to 7 µg/L of phenols.

Methylene blue active substances (MBAS) ranged in concentration from 0.00 to 2.2 mg/L in the shallow aquifer. Both background wells contained 0.10 mg/L of MBAS and the process water contained about 2.0 mg/L. MBAS concentrations greater than about 0.3 mg/L may be an indication of seepage. In general, samples that contained high concentrations of MBAS also contained high concentrations of iodide ions and had high ion indices. Water from wells 13, 18, 17, 21, and 5 are in order of decreasing MBAS concentration.

None of the oil and grease samples contained measurable amounts of the substances. Some apparent tannins and lignins were found in the process water and in water from wells 13 and 22, but no pattern was discernible.

Water Quality in the First Artesian Aquifer

Specific Conductance

Water from well 35 at the USSAC plant (fig. 26) was considered to be the most representative of background water quality for the first artesian aquifer. The specific conductance for two water samples from well 35 averaged 280 µmho. Water from wells 6, 14, 19, and 23 had specific conductances of 332, 2,770, 3,200, and 478 µmho, respectively. These differences conform to information on water levels and indices that show that water in the surficial and first artesian aquifers flows mainly to the northwest and southeast rather than in other directions from the gypsum stack. Water from wells 14 and 19 were affected by process water. Water from wells 6 and 23 appear to be affected to a minor degree based on major constituent and trace element concentrations. The amount of natural variability in specific conductance in the first artesian aquifer cannot be determined from available data.

Major Constituents

Figure 38 compares background water quality to the observed range in concentrations of major constituents for water from wells adjacent to the USSAC gypsum stack. Concentrations of calcium, magnesium, sodium, alkalinity, sulfate, and phosphate all show significant increases above background levels. Water from wells 14 and 19 (fig. 26) were the most affected.

No migration of fluoride was detected in water from any of the first artesian wells. Chloride concentrations at wells 14 and 19 were elevated above background levels. Silica concentrations were elevated to 230 mg/L at well 14 and 240 at well 19.

Ion indices for water from wells in the first artesian aquifer are listed in table 12. The indices show that water in wells 14 and 19 are strongly influenced by seepage from the gypsum stack. Water in wells 6 and 23 show increases in the PII, but the values of PMI and INMI are low. The occurrence of elevated concentrations of iodide ions and the indices show that seepage has affected water at wells 6 and 23, but that the seepage has been altered considerably by reactions in the aquifer.

Table 12.--Ion indices and iodide concentrations for water from wells in the first artesian aquifer at the USSAC plant

[mg/L, milligrams per liter]

Well No.	Depth (feet)	Percentage mineral imbalance (PMI)	Index of nonmineral input (INMI)	Percentage increase in ions (PII)	Iodide (mg/L)
[1]35	65	0.78	---	---	0.01
6	70	.45	- 0.16	16	.25
14	75	21	220	960	2.7
19	55	19	250	1,200	4.4
23	62	1.4	3.1	75	.11

[1] Background well to which the index of nonmineral input and the percentage increase in ions are compared.

Nitrogen and Phosphorus

All nitrate and nitrite concentrations were near the detection limits in the first artesian aquifer. Water samples from wells 14 and 19 (fig. 26) contained 2.8 and 1.4 mg/L of ammonia as N. This indicates that a small amount of ammonia has migrated into this aquifer, but its movement over long distances is unlikely. Water from wells 14 and 19 contained elevated concentrations of orthophosphate (100 and 30 mg/L, respectively). Concentrations of orthophosphate in the other wells in the first artesian aquifer were 0.01 or 0.02 mg/L.

Radiochemicals

Dissolved radium-226 activities in water at USSAC ranged from 0.11 to 16 pCi/L in the first artesian aquifer. Only well 19 (fig. 26) exceeded 5 pCi/L of radium-226. The gross alpha radioactivity ranged from 0.9 to 8.4 pCi/L and gross beta radioactivity ranged from 0.0 to 31 pCi/L. Water from well 19 contained the highest activities in the first artesian aquifer, and it is possible that some radiochemicals from the process waters have migrated into the first artesian aquifer.

Trace Elements

Concentrations of trace elements at USSAC were lower in the first artesian aquifer than in the surficial aquifer. This may be because of the water being in contact with limestone and other reactive aquifer materials.

Table 13 shows concentrations of selected trace elements for water samples from the first artesian aquifer wells. Water from wells 14 and 19 (fig. 26) had the highest concentrations of most trace elements. These wells are in the direction of greatest seepage from, and are closest to, the gypsum stack and had the lowest pH. Two factors are involved in the reduction in concentrations of trace elements. One is the degree of reaction with the aquifer and native water. The other is simple dilution by native water. These factors may explain why water from well 19 contained more iodine, lithium, boron, and arsenic, but had a higher pH and lower iron, cobalt, and nickel than water from well 14. Water in the aquifer near well 19 had undergone more reaction with the aquifer, but had been diluted less.

Table 13.--Concentrations of trace elements and pH data for water from selected first artesian aquifer wells at the USSAC plant

[μg/L, micrograms per liter]

Well No.	Iron (μg/L)	Manganese (μg/L)	Cobalt (μg/L)	Lithium (μg/L)	Nickel (μg/L)	Iodide (μg/L)	Arsenic (μg/L)	Boron (μg/L)	pH (units)
6	90	10	0	10	2	0.25	6	20	7.5
14	18,000	110	24	100	110	2.7	4	40	5.4
19	1,700	290	4	160	30	4.4	54	140	6.3
23	1,000	40	0	10	5	.11	1	50	6.8
35	290	30	0	10	0	.01	1	60	7.4

Concentrations of most trace elements in water from well 35 were near the detection limits. The percentage of mineral imbalance and concentration of iodide ions also indicate that water from the well is the most representative of background water quality for the first artesian aquifer.

As table 13 shows, the distribution of lithium concentrations is very similar to that of iodide ion. Most of the other elements show a similar but less distinct pattern. This pattern indicates that process water was the source or that process water had dissolved substances from the aquifer.

Organic Compounds

Concentrations of total organic carbon in water from the first artesian aquifer ranged from 4.9 to 29 mg/L. No concentration patterns were discernible, but the small elevations in total organic carbon at wells 14 and 19 are probably because of migration of process water based on ion indices and concentrations of iodide.

Phenols were not detected in water from any well except well 35, which contained 3 µg/L in June 1980 and 0 µg/L in December 1979. Phenolic compounds do not occur at detectable levels in water from other wells in the first artesian aquifer.

Concentrations of methylene blue active substances were 0.30 and 0.10 mg/L in water from wells 14 and 19, respectively. The substances were not detected in the other wells in this aquifer. Other parameters such as iodide indicate that process water may comprise 20 to 40 percent of the water in wells 14 and 19.

Water Quality in the Second Artesian Aquifer

Specific Conductance

Specific conductance of water from the background well for the second artesian aquifer, well 41 (fig. 36), was 422 µmho. Specific conductances of water from well 8 (321 µmho) and well 36 (318 µmho) were lower than in water from the background well. This is attributed to natural variability in water composition in the second artesian aquifer. Background specific conductance near the gypsum stack is probably less than about 420 µmho and may be as low as 320 µmho. Water from wells 20 (430 µmho) and 24 (367 µmho) were in this range.

Water from well 4 (specific conductance, 594 μmho) appears to be influenced to a small degree by process water. Water from well 15 (specific conductance, 2,340 μmho) is significantly influenced by process water. The indices discussed in the following section support this premise. As the general direction of ground-water flow is toward the south, there is appreciable flow toward these wells. Cavities in the second artesian aquifer are common in this area and were detected in several wells, including well 15, during drilling operations. Well 15 released gases for a few months and bubbling sounds were audible near the well for several weeks after the well was completed.

Major Constituents

Figure 39 compares the background water-quality data for water from well 41 for the second artesian aquifer at USSAC to the observed range in concentrations of major constituents in water from second artesian aquifer wells adjacent to the gypsum stack. Calcium, magnesium, sodium, alkalinity, and sulfate concentrations show significant increases above background concentrations. Water from well 15 (fig. 26) is the most affected.

No significant migration of fluoride was detected in the second artesian aquifer. Silica concentrations were near background levels of 20 to 30 mg/L except for water from well 15, which contained 290 mg/L of silica.

The ion indices in table 14 show that water from well 4 is affected by process water. Well 15 has the highest value for all three indices. Major ions and the PII for wells 8 and 36 suggest that background concentrations for calcium, magnesium, and alkalinity are lower near the plant than at the background well site.

Process water that reaches the second artesian aquifer will be neutralized after flowing short distances and the composition of process water will be altered considerably by reactions with aquifer materials. Obvious effects of process water were found only in water from well 15 at the south side of the gypsum stack. More subtle effects were detectable in water from well 4, one-third of a mile south of the gypsum stack. Most water from wells in the second artesian aquifer had pH values of 7.2 to 7.7.

Water from well 15 had a pH of 6.4. This indicates that process water was nearly neutralized, but the effects of the process water were still detectable.

Table 14.--Ion indices for water from second artesian aquifer wells at the USSAC plant

Well No.	Depth (feet)	Percentage mineral imbalance (PMI)	Index of nonmineral input (INMI)	Percentage increase in ions (PII)
4	119	5.6	9.7	41
8	119	3.1	4.0	-31
15	135	11	83	640
20	103	.5	1.8	3.6
24	116	6.6	7.5	-15
36	105	6.0	6.3	-26
[1]41	82	.3	--	--

[1] Background well to which the index of nonmineral input and percentage increase in ions are compared.

Nitrogen and Phosphorus

Nitrate and nitrite concentrations were all near the detection limits in water from the second artesian aquifer at USSAC. Ammonia concentrations ranged from 0.04 mg/L as N in water from background well 41 to 1.2 mg/L in water from well 15. The highest concentration of organic nitrogen was 0.28 mg/L as N. Total phosphorus concentrations were less than 0.05 mg/L (as P) except for water from well 15, which contained 0.62 mg/L.

Other than the slightly elevated concentration of ammonia and total phosphorus at well 15, the migration of nitrogen and phosphorus species into the second artesian aquifer is very limited.

Radiochemicals

The only water sample with gross alpha, gross beta, and radium-226 activities significantly above background levels was from well 15 and the increases were relatively minor, but may reflect some effects of the process water. Table 15 summarizes the data for water from background well 41, well 15, and the range observed for all other wells in the second artesian aquifer at USSAC.

Table 15.--Summary of radiochemical data for water from the second artesian aquifer at the USSAC plant

[Data in picocuries per liter]

Well No.	Gross alpha activity (pCi/L)	Gross beta activity (pCi/L)	Dissolved radium-226 (pCi/L)
[1]41	2.8	0.4	1.9
15	22	4.4	7.9
All others	.6-4.8	.3-2.5	1.3-1.6

[1] Background well.

Trace Elements

Only a few trace elements were found at concentrations of significance in water from the second artesian aquifer. These data are tabulated in table 16.

The elevated concentrations of lithium, bromide, or iodide in water from wells 4 and 15 suggest that process water is their source. Water from well 8 is low in these three elements, but contained elevated levels of molybdenum, arsenic, and antimony above background concentrations. This suggests that these elements have a source other than the process water, such as ore piles near the well.

Table 16.--Concentrations of selected trace elements in water from the second artesian aquifer at the USSAC plant

[mg/L, milligrams per liter, µg/L, micrograms per liter]

Well No.	Lithium (µg/L)	Molybdenum (µg/L)	Bromide (mg/L)	Iodide (mg/L)	Arsenic (µg/L)	Antimony (µg/L)
4	20	11	0.0	0.50	5	0
8	10	300	.0	.01	160	5
15	130	900	.2	--	18	0
20	10	5	.0	.31	10	0
24	6	50	.0	.01	14	0
36	10	9	.0	.00	8	0
[1]41	0	13	.0	.00	4	0

[1] Background well.

Organic Compounds

Total organic carbon concentrations in water from wells 4, 8, 15, 20, and 36 ranged from 12 to 16 mg/L. Concentrations for background well 41 were 5.7 and well 24 contained 23 mg/L of total organic carbon. These differences may reflect the natural variability in concentrations of carbon in the second artesian aquifer. Well 41 is about 2 miles northeast of the gypsum stack. All of the samples from wells near the gypsum stack were similar in carbon content except for well 24 which borders a swamp.

Phenol concentrations ranged from 1 to 7 µg/L. The observed variations probably reflect the natural variability of phenolic materials in the aquifer as no pattern was discernible. Water from most wells in the first artesian aquifer did not contain any measurable amounts of phenols; therefore, phenols do not appear to have migrated downward from the gypsum stack. Methylene blue active substances were not detected in water from any well except well 15 (0.2 mg/L).

Summary

High concentrations of major constituent ions at the USS Agri-Chemicals plant are found in samples from surficial aquifer wells to the north, east, and south of the gypsum stack. Mounding of the water table near the gypsum stack shows that the direction of ground-water flow is toward wells that contained high concentrations of major ions. The plume of high concentrations appears to extend farthest in a southeast direction from the gypsum stack. Some ponds at the plant site contained water with high specific conductance that may influence water from nearby surficial aquifer wells. Ammonia concentrations of 9.0 and 12 mg/L and very high phosphate concentrations were found about one-third of a mile south of the gypsum stack. Radioactivity was considerably above background levels in water from the surficial aquifer near the south and east sides of the gypsum stack, but activities were lower than background levels away from the gypsum stack. Elevated concentrations of trace elements were found in areas near the gypsum stack where pH was low. Concentrations of methylene blue active substances ranged from 0.0 to 2.2 mg/L in the surficial aquifer.

Water from wells in the first artesian aquifer downgradient (south and east) of the gypsum stack are influenced by seepage. Water from a well one-third of a mile south of the stack contained 0.25 mg/L of iodide ions. Ammonia, orthophosphate, trace metals, and radioactivity did not migrate far from the gypsum stack in the first artesian aquifer.

Ion indices indicate that process water has migrated into the second artesian aquifer just south of the gypsum stack where a cavity occurs. A well one-third of a mile south of the gypsum stack may have been influenced by process water, as shown by a significant INMI and PII and by an iodide concentration of 0.50 mg/L. In general, nitrogen, phosphorus, radioactivity, and most trace elements were near background concentrations in the second artesian aquifer except near the gypsum stack.

INTERNATIONAL MINERALS AND CHEMICAL CORPORATION CLEAR SPRINGS MINE

The International Minerals and Chemical Corporation (IMC) Clear Springs mine is about 1 mile southeast of Bartow and about 6 miles southeast of the

USSAC plant (fig. 36). The phosphatic clayey waste disposal pond (slime pond) that was studied at the IMC mine is 0.8 mile east of the Peace River (fig. 45). The disposal pond (called CS-8) is in the Polk Upland and borders the western side of the Lake Henry Ridge (White, 1970).

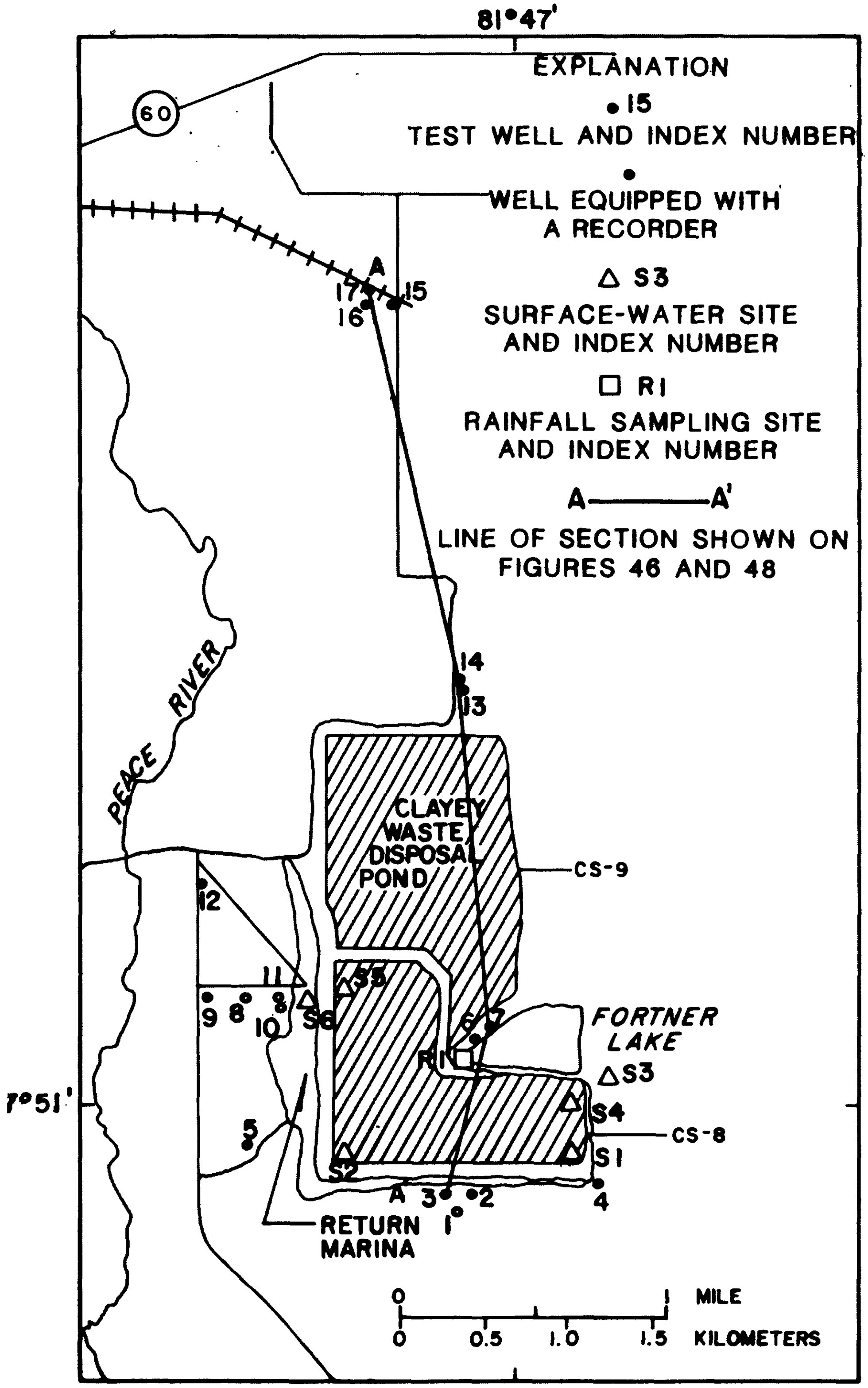
Much of the land north, west, and south of the settling pond has been mined for phosphate. Peat is presently being mined about 0.5 mile south of the pond. A citrus grove and two small lakes are near the eastern side of the pond. The Lake Henry Ridge rises steeply just east of the pond and was used as a natural dike for pond CS-9 that was being constructed during the study. Land-surface altitudes at the mine range from about 100 to 130 feet above sea level. Altitudes of the phosphatic clayey waste disposal ponds are several tens of feet higher than the adjacent land surfaces.

The climatic and rainfall data collected at the USSAC plant are applicable to the IMC study area.

The study at IMC was of a storage site where slimes, or residues from mining and beneficiation or concentration of ore processes, are received and stored. The slimes are principally colloidial particles and fines from the ore matrix that are mixed with water and stored in large pits so that suspended materials can settle out. The water is subsequently recirculated for use in transporting ore to the mill or slimes to the disposal ponds. The general layout of the IMC site and locations of sampling sites are shown in figure 45. Figure 36 shows the relative locations of the IMC and USSAC study sites near Bartow and the locations of wells 40 and 42 that were used for determining background water quality.

Hydrogeology

The geology at the IMC site is very similar to that at the USSAC site with the exception that some land is reclaimed and filled with overburden material and the phosphate ore matrix of the Bone Valley Formation has been mined out. A generalized geologic section of the IMC site, based on data from wells 3, 7, 14, and 17, is shown in figure 46. Figure 47 illustrates the configuration of the top of the first artesian aquifer, which illustrates a general dip toward the northwest. Figure 48, a profile across the slime



BASE MAP FROM INTERNATIONAL MINERALS AND CHEMICAL CORP.

Figure 45.--Plant layout and locations of data-collection sites at the IMC plant.

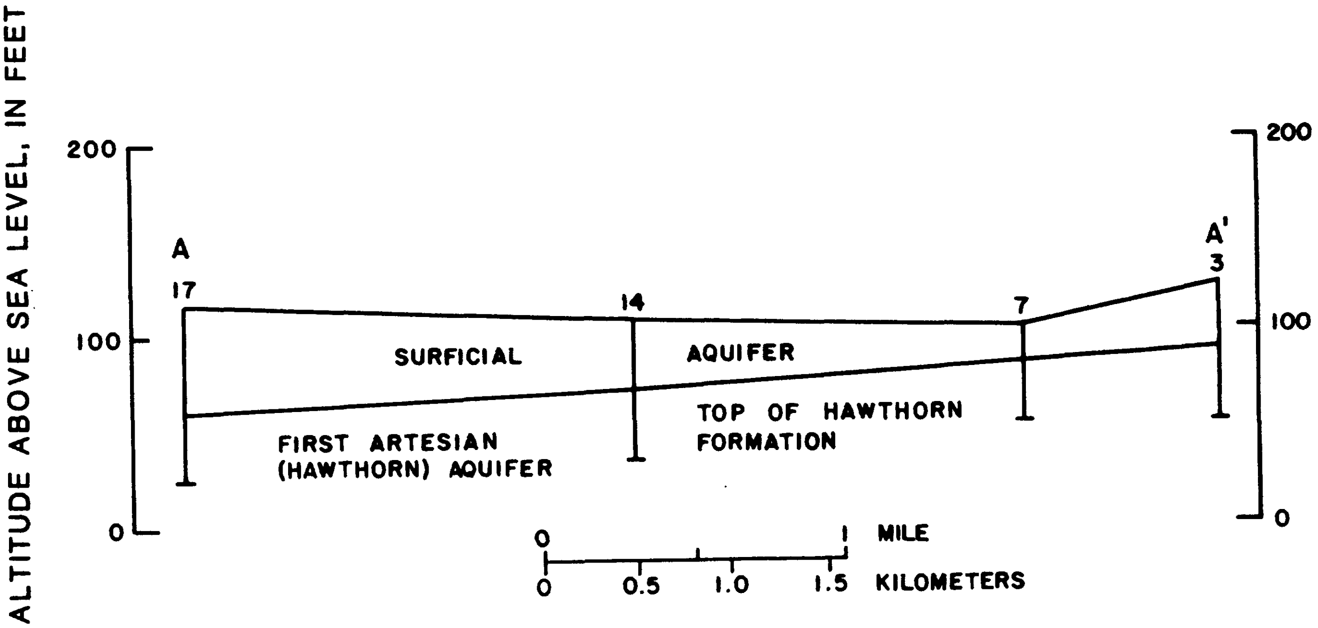


Figure 46.--Generalized geologic section underlying the IMC plant. (Location of section is shown in figure 45; enlarged view of section A-A' is shown in figure 48.)

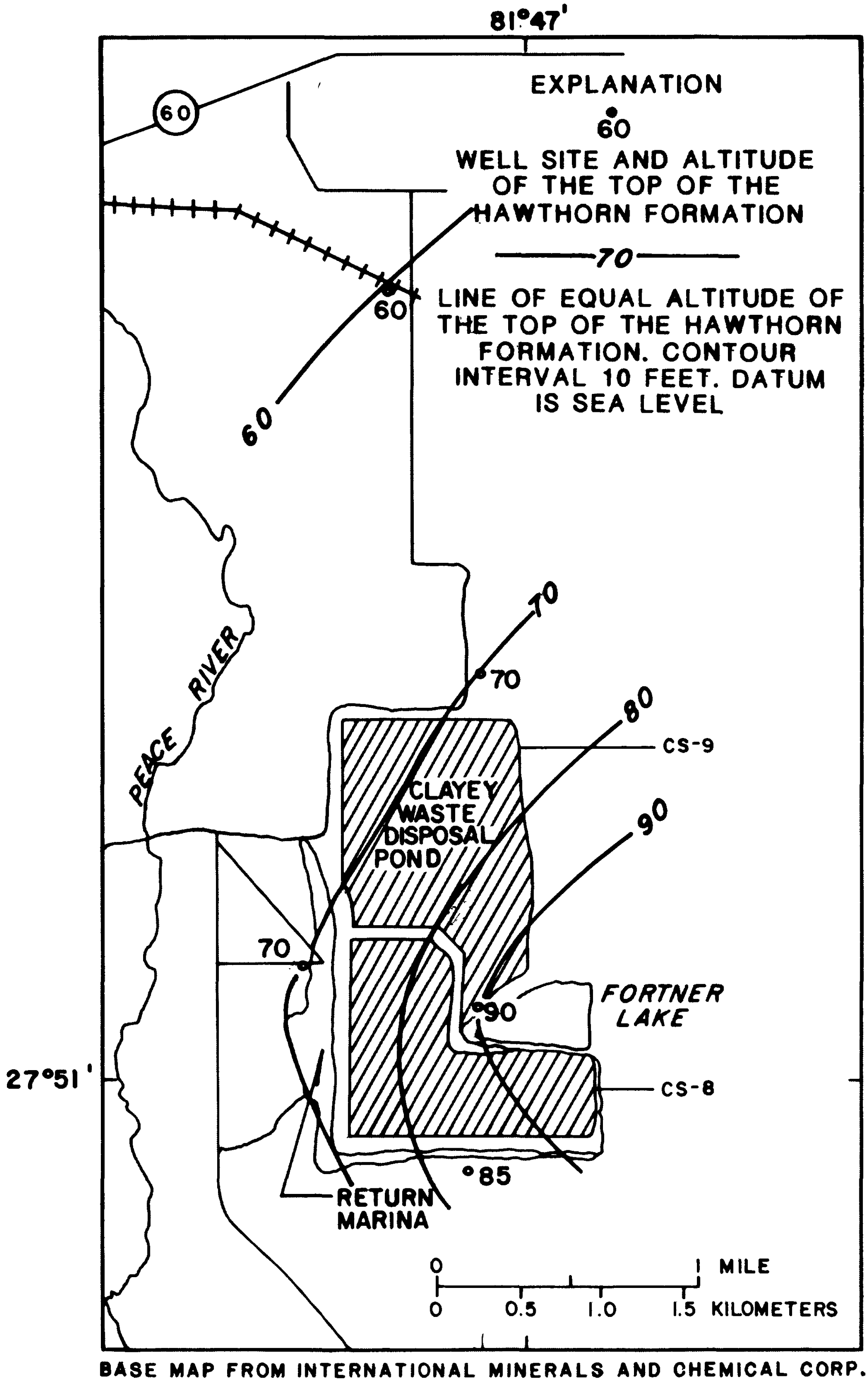


Figure 47.--Configuration of the top of the first artesian aquifer at the IMC plant.

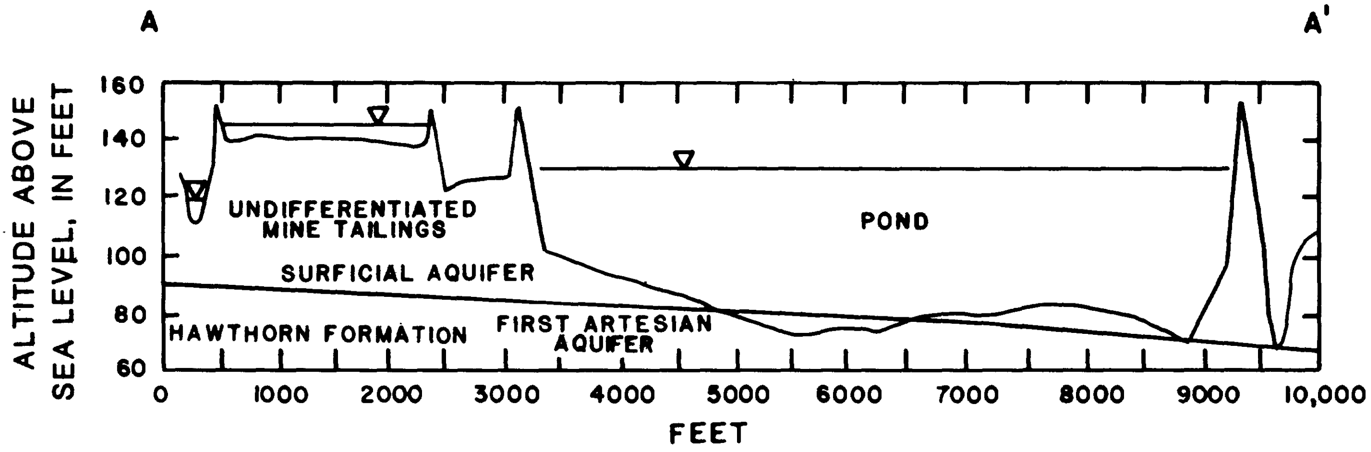


Figure 48.--Profile across the phosphatic clayey waste disposal ponds and generalized geologic section at the IMC plant. (Location of section is shown in figure 36; horizontal scale is approximately two times that of figure 36.)

ponds, shows the relation between the base of the slime pond and the top of the first artesian aquifer as determined from data on test wells. In general, the base of the pond corresponds to the top of the first artesian aquifer, thus providing a direct connection between the pond and the first artesian aquifer. No wells were drilled to a second artesian aquifer at this site for this study.

Well 11 (fig. 45) first encountered limestone at 35 feet. The limestone was marly and clayey to a depth of 48 feet where circulation was lost during drilling. The hole was subsequently cased to 42 feet and grouted. Drilling was then continued, but circulation was again lost at 52 feet. These characteristics also occurred at other wells.

Water levels in the surficial aquifer fluctuated only slightly during the study. Figure 49 shows the hydrographs of water levels for well 10 (surficial aquifer) and well 11 (first artesian aquifer). The rise and fall of water levels in wells 10 and 11 indicate that they are responding similarly to local pumpage, but effects are considerably dampened in well 10. Delineation of altitudes of the water levels of the surficial aquifer is difficult because of the nonhomogeneous nature of the mined sediments and the steep slope of the land surface. Figure 50 shows altitudes of the water table in areas where they could be delineated south of the ponds.

Water levels in the upper part of the second artesian aquifer at the USSAC plant (well 36, fig. 28) have been shown to closely follow water levels in the Floridan aquifer (fig. 30) although heads between the aquifers are different. The water level in the upper part of the first artesian aquifer at IMC, as reflected in water levels in well 11 (fig. 49), compare closely with water levels in well 36 (fig. 29) at the USSAC plant that is open to the second artesian aquifer, although levels in well 11 fluctuate more widely. Apparently, local pumpage is affecting water levels at the IMC plant. There are several large irrigation wells in citrus groves east of the IMC site and also large industrial wells west of the site. A comparison of water levels for Floridan aquifer well 42 at USSAC (fig. 30) and well 11 at IMC (fig. 49) indicates that they roughly follow each other, but levels in well 11 fluctuate more because of the influence of nearby pumpage

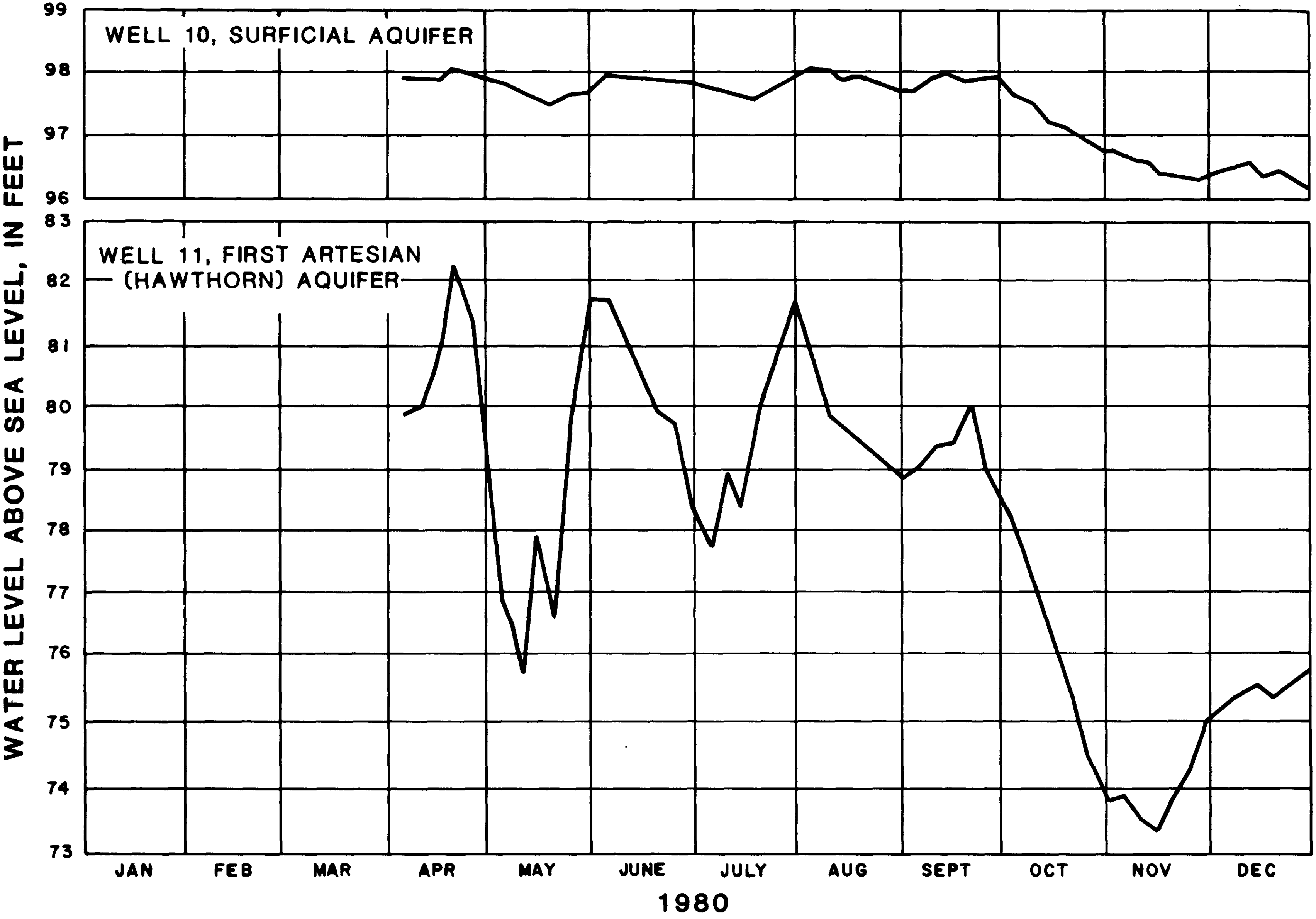
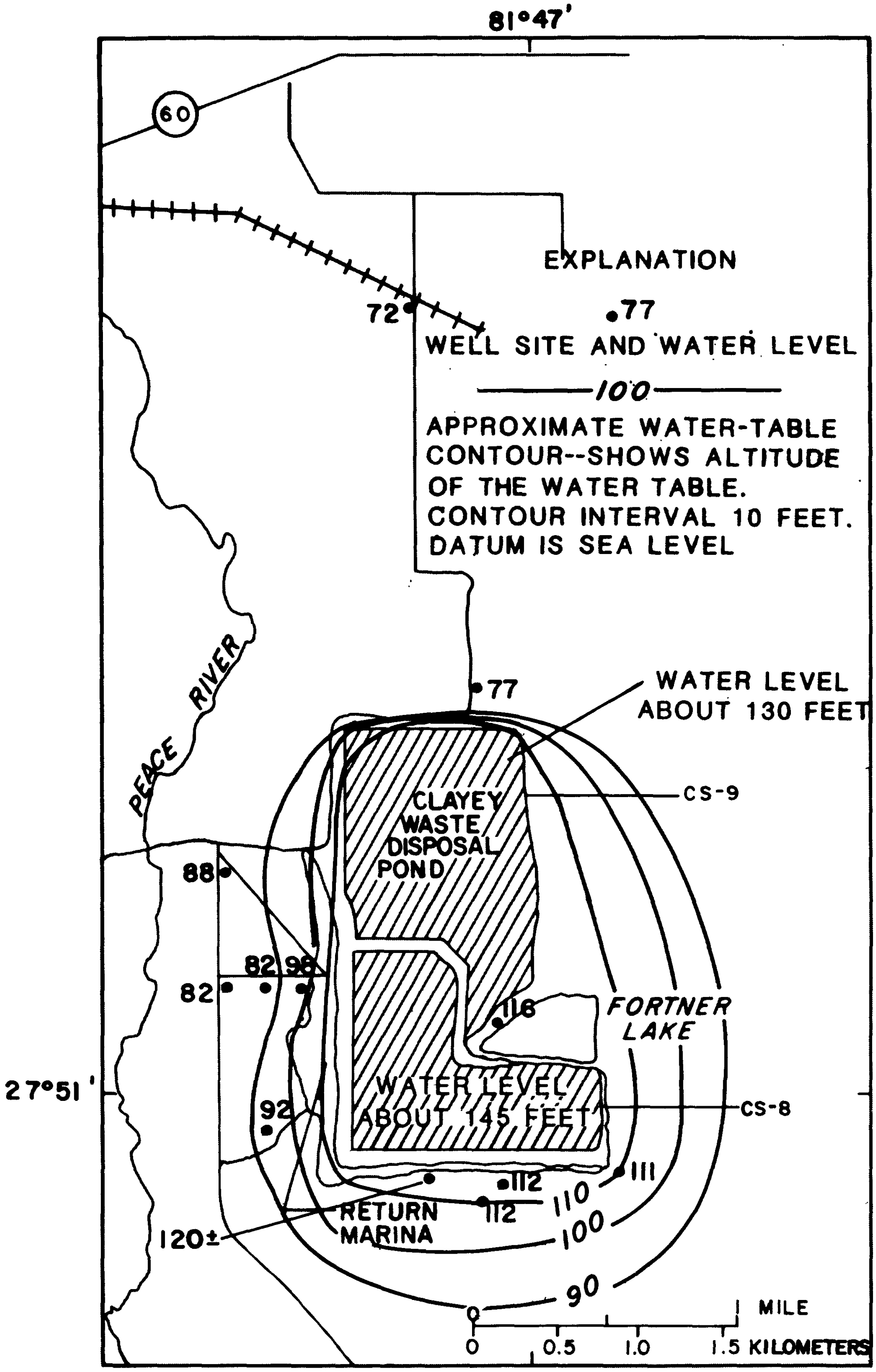


Figure 49.--Water levels in wells 10 and 11 at the IMC plant.



BASE MAP FROM INTERNATIONAL MINERALS AND CHEMICAL CORP.

Figure 50.--Water table of the surficial aquifer at the IMC plant, July 18, 1980.

and its level is about 20 feet higher. The close relation between water levels of the first artesian aquifer at IMC to nearby Floridan aquifer wells suggests direct hydraulic connection between the aquifers.

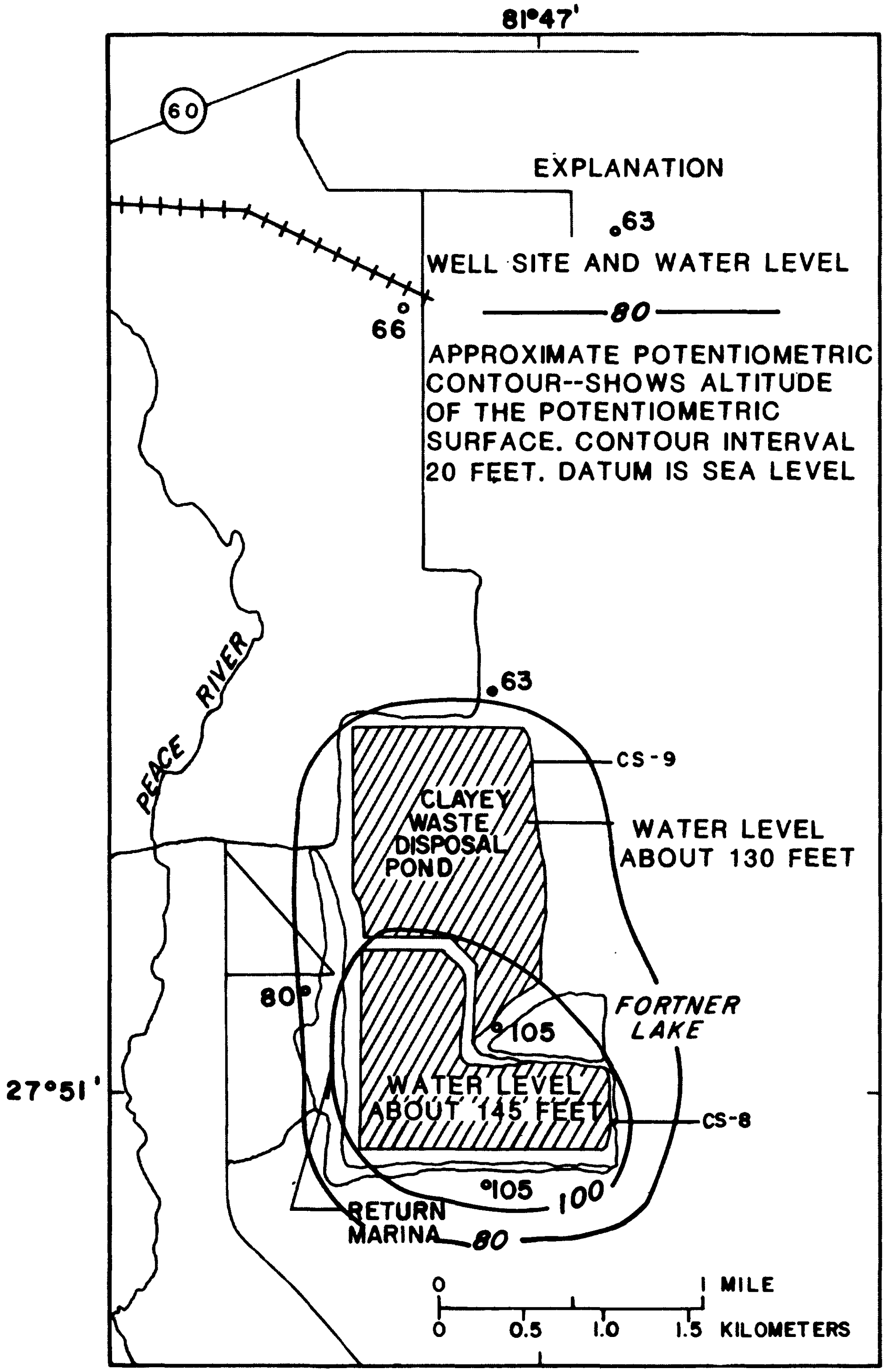
Water levels in the first artesian aquifer are shown in figure 51. Although figure 46 shows the pond breaching the top of the aquifer, figure 51 indicates that water flow between the pond and the first artesian aquifer is impeded by clays in the bottom of the pond. The general direction of flow of the aquifer is to the west and northwest. This is expected because of the high ridge to the east of IMC that acts as a source of recharge for the aquifer. Wells near the slime pond show that mounding occurs in the first artesian aquifer; consequently flow may occur outward in all directions near the slime pond.

Water Quality

Pond Water

Water that transports clay slurry (slimes) to the slime pond (CS-8) was sampled at the inflow to the pond, at three outfalls, at the culvert that drains Fortner Lake into the return marina, and at the return marina near where the slurry is pumped into the slime pond (sites S5, S1, S2, S4, S3, and S6, respectively). Reconnaissance samples collected in October 1979 indicate that some fluctuation in nitrogen and phosphorus species occurs. The specific conductance averaged 483 μmho, which is not significantly different from the average of 499 μmho determined in January 1980 when more extensive sampling was undertaken. This suggests that the concentrations of major dissolved ions are relatively constant.

Table 17 shows an idealized analysis for major ions in water from the slime pond. Five samples from the slime pond and return water had an arithmetic mean for the percentage mineral imbalance (PMI) of 14.1 percent and a standard deviation of 0.37 percent. This is caused by an increase in $NaHCO_3$ or Na_2SO_4. Figure 52 shows the composition and water type for the slime pond water. No significant mineral imbalance was found in most



BASE MAP FROM INTERNATIONAL MINERALS AND CHEMICAL CORP.

Figure 51.--Potentiometric surface of the first artesian aquifer at the IMC plant, July 18, 1980.

samples collected from wells near the slime pond. In an earlier study by the U.S. Bureau of Mines, analytical data for supernatant water from "as-received slimes" (Lamont and others, 1975, p. 19) indicate that a significant mineral imbalance existed at all three IMC mines, at the Agrico mine, at the Grace mine, and at the Cities Service mine in 1972. Samples from other slime ponds did not have any significant mineral imbalance.

Table 17.--Idealized analysis of water from the slime pond at the IMC plant

[mg/L, milligrams per liter; µg/L, micrograms per liter]

Cations			Anions		
Species	Concentration (mg/L)	Concentration (me/L)	Species	Concentration (mg/L)	Concentration (me/L)
Ca^{+2}	44	2.196	SO_4^{-2}	140	2.195
Na^{+1}	29	1.261	Alkalinity	70	1.399
Mg^{+2}	15	1.234	Cl^{-1}	17	.480
K^{+1}	1.6	.041	F^{-1}	1.7	.089
Sr^{+2}	.14	.002	NO_3^{-1}	.92	.066
NH_4^{+1}	2.8	.200			
Total		4.935	Total		4.949

On January 29, 1980, the slurry flowing into the slime pond contained 16,000 mg/L of suspended solids, 1,460 pCi/L of gross alpha, and 3,480 pCi/L of gross beta radioactivity. The suspended material in the inflow water contained about 91 and 220 pCi/g of alpha and beta radioactivity, respectively, that was effectively trapped by the slime pond. Less than 0.5 percent of the radioactivity was transported to outflow from the slime pond in the return water.

The total phosphorus concentration of the slurry was 690 mg/L; whereas, the orthophosphate concentration was only 0.46 mg/L. Similar relatively low concentrations were observed for several trace metals. Most elevated

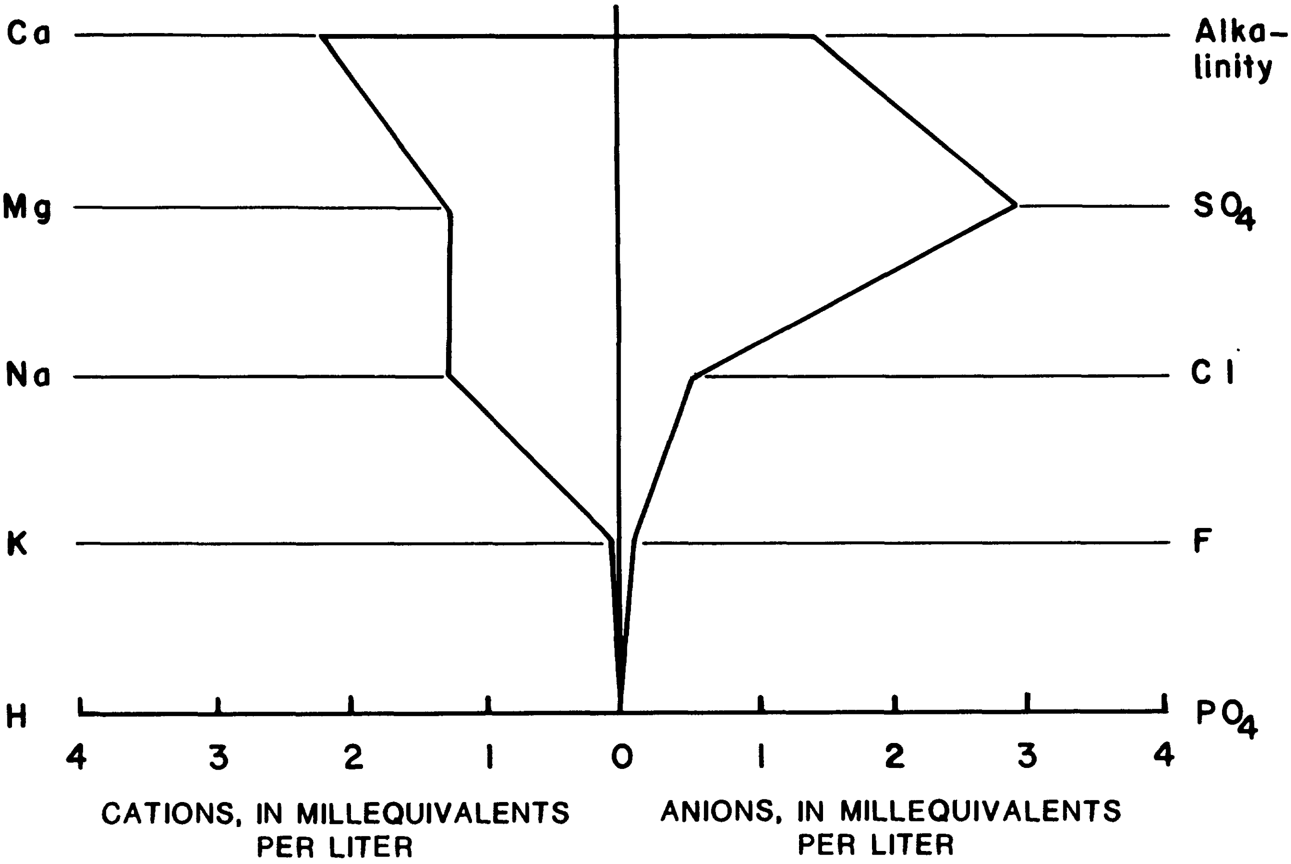


Figure 52.--Modified Stiff diagram showing concentrations of principal ions in water from the IMC slime pond (CS-8) and return marina at the IMC plant.

concentrations of material are associated with the solid phase and do not appear at the outflows from the slime pond. Concentrations of selected trace elements in the inflow and outflow to the slime pond are summarized in table 18. Also shown are the percentage of the constituents determined in the inflow that appeared at the outflow. Aluminum, arsenic, barium, cadmium, chromium, cobalt, copper, iron, lead, manganese, nickel, selenium, and zinc are all reduced to low levels during passage through the slime pond. Thus, these elements would be reduced to low levels in water that leaks from the slime pond if pH and Eh conditions in the pond do not solubilize settled materials. Other than increases in nitrogen and phosphorus species and in the PMI, most differences between water leaving the slime pond and natural ground water are small according to data collected during the study.

Table 18.--Concentrations of selected trace elements in the inflow and outflow of the IMC slime pond (CS-8)

[T, total; TR, total recoverable; μg/L, micrograms per liter]

Element	Inflow concentration (μg/L)	Mean of two outflow concentrations (μg/L)	Percentage reaching outflows
Aluminum, TR	420,000	60	0.01
Arsenic, T	26	4	15
Barium, TR	3,600	100	3
Cadmium, TR	430	0	0
Chromium, TR	1,500	3	0.2
Cobalt, TR	66	0	0
Copper, TR	350	2	.6
Iron, TR	100,000	60	.06
Lead, TR	72	0	0
Manganese, TR	5,600	70	1
Nickel, TR	750	5	.7
Selenium, T	8	0	0
Zinc, TR	3,000	10	.3

Background Water Quality in the Surficial Aquifer

The background well (USSAC-39, fig. 36) is about 5 miles northwest of the slime pond. Well 13 (2.5 miles north of CS-8) was originally intended to be the background well, but it was dry during the study.

The background sample (USSAC-39) was predominantly a $Ca(HCO_3)_2$ water with lesser amounts of $MgSO_4$. The specific conductance of the water was 242 µmho and the pH was 6.1. Concentrations of fluoride, orthophosphate, and sulfate were 1.6, 0.27, and 15 mg/L, respectively.

Total alpha, total beta, and dissolved radium-226 activities were 8.2, 0.0, and 0.2 pCi/L, respectively. Most trace element concentrations were at or near their detection limits, except for iron (490 µg/L), molybdenum (7 µg/L), strontium (90 µg/L), and aluminum (300 µg/L). The background water quality sample contained less sodium, calcium, chloride, and sulfate ions and more alkalinity than water from the slime ponds.

Background Water Quality in the First Artesian Aquifer

Well 14 (fig. 45), used to define background water quality was about 1 mile north of the CS-8 slime pond, but downgradient of the pond. Originally well 17 was intended to be the background well, but it was found that water from the well contained high nitrate concentration (7.1 mg/L) resulting from application of fertilizers to nearby citrus groves to the east. Water from well 14 contained a mixture of $Ca(HCO_3)_2$ and $Mg(HCO_3)_2$ with a lesser amount of NaCl. Sulfate was not detected in the sample. The PMI was 0.3 percent. Concentrations of fluoride and orthophosphate were 0.3 and 0.18 mg/L, respectively. The specific conductance and pH were 340 µmho and 6.7, respectively.

Total alpha, total beta, and dissolved radium-226 activities were 0.8, 0.6, and 0.3 pCi/L, respectively. Most trace element concentrations were at or near their detection limits except for iron (2,100 µg/L), manganese (70 µg/L), chromium (6 µg/L), strontium (140 µg/L), iodide (0.08 mg/L), and arsenic (3 µg/L).

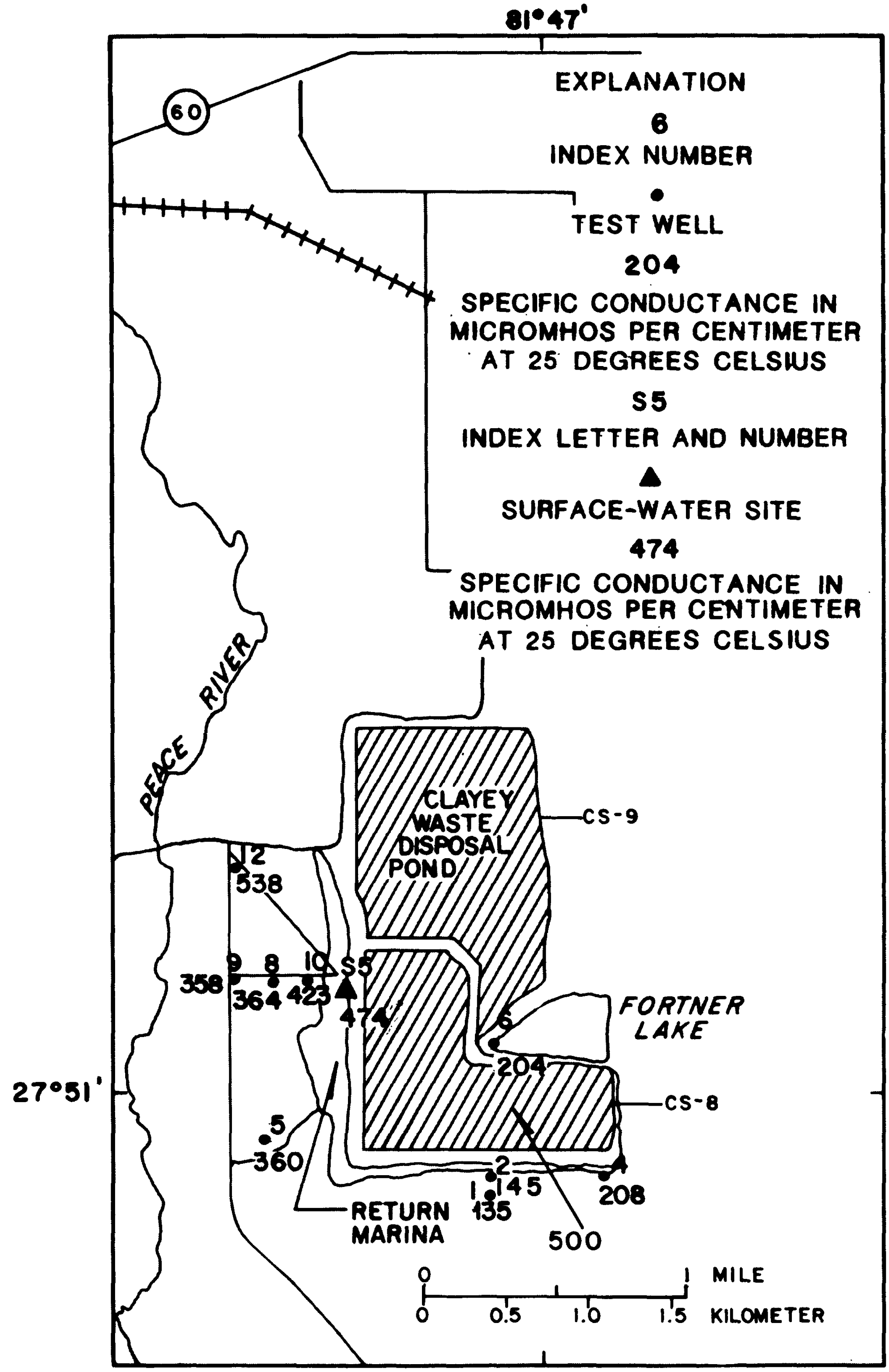
Water Quality in the Surficial Aquifer

Specific Conductance

Specific conductance of water from surficial aquifer wells, the slime pond (CS-8), and the return ditch are shown in figure 53. Specific conductance in ground water appears to increase northward near the west side of the slime pond and is higher in areas of reclaimed land to the west of the pond. A ground-water gradient was probably toward the north to the area of active mining when the samples were collected. Pumpage of water from the mining pit north of the slime pond kept local water levels lower at the mine (about 43 feet above sea level in December 1979) than water levels near the slime pond (about 145 feet above sea level.) Presumably water in the surficial aquifer in this area flows toward the mining pit from the slime pond, and westward toward the Peace River.

Major Constituents

Shallow wells 6, 9, and 10 (fig. 45) are in reclaimed land. Well 2 is in unmined land. None of the water collected from surficial aquifer wells at IMC showed any significant mineral imbalance (PMI) or significant nonmineral input (INMI). The distribution of dissolved solids is consistent with the flow of water toward the mining pit north of CS-9 slime pond. A sample of pond water (CS-8) collected in January 1980 contained about 130 mg/L of sulfate and about 29 mg/L of sodium, which are high relative to water from the surficial and first artesian aquifers. The increases in concentrations of major constituent ions in water from the surficial aquifer are mainly in the form of $Ca(HCO_3)_2$ and lesser amounts of $Mg(HCO_3)_2$. It is possible that concentrations of sulfate are reduced by bacteria and that sodium is exchanged for calcium and magnesium by the plentiful clays near the slime pond. This is supported by the fact that water from well 10, less than 100 feet from the return water marina, had concentrations of sulfate that were about one-tenth and concentrations of sodium that were about one-third of those found in the marina water (S6). Mineral imbalance was probably absent in ground water because the slime pond was young (2½ years) and ion exchange capacity was high. The mineral imbalance may eventually appear in wells near the slime pond.



BASE MAP FROM INTERNATIONAL MINERALS AND CHEMICAL CORP.

Figure 53.--Specific conductance of water from surficial aquifer wells and surface-water sites at the IMC slime pond (CS-8).

Fluoride concentrations ranged from 0.5 to 1.7 mg/L and concentrations of silica ranged from 6.4 to 24 mg/L. Alkalinity, calcium, and magnesium have the greatest variations in concentration (fig. 54). Acidity, sulfate, and chloride had lesser variations.

Nitrogen and Phosphorus

Some variations in the concentrations of nitrogen and phosphorus were observed. The nitrate, ammonia, and orthophosphorus concentrations in water from the surficial aquifer and the slime pond are compared to background water quality (USSAC well 39) in table 19. Water from well 2 (fig. 45), which is in an unmined area, contains about the same concentrations of nitrate (0.78 mg/L) and orthophosphate ions (0.70 mg/L) as pond water, but concentrations of ammonia are much lower. Water from well 10, which is in reclaimed land and about the same distance from the return marina as well 2, contains 0.04 mg/L of nitrate as N and 0.28 mg/L of ammonia as N. The orthophosphate concentration (0.74 mg/L) for water from well 10 is similar to that of pond water. Water from well 9, which is also in reclaimed land but more remote from the slime pond, contains essentially no nitrate, ammonia, or orthophosphate ions. Well 6 is about 50 feet from the slime pond and there are no intervening ditches between the well and the pond. Water from well 6 contained essentially no nitrate and ammonia, but it contained higher concentrations (5.1 mg/L) of orthophosphate than the slime pond (0.62 to 1.2 mg/L). Nitrogen and phosphorus compounds appear to migrate only a short distance into the surficial aquifer.

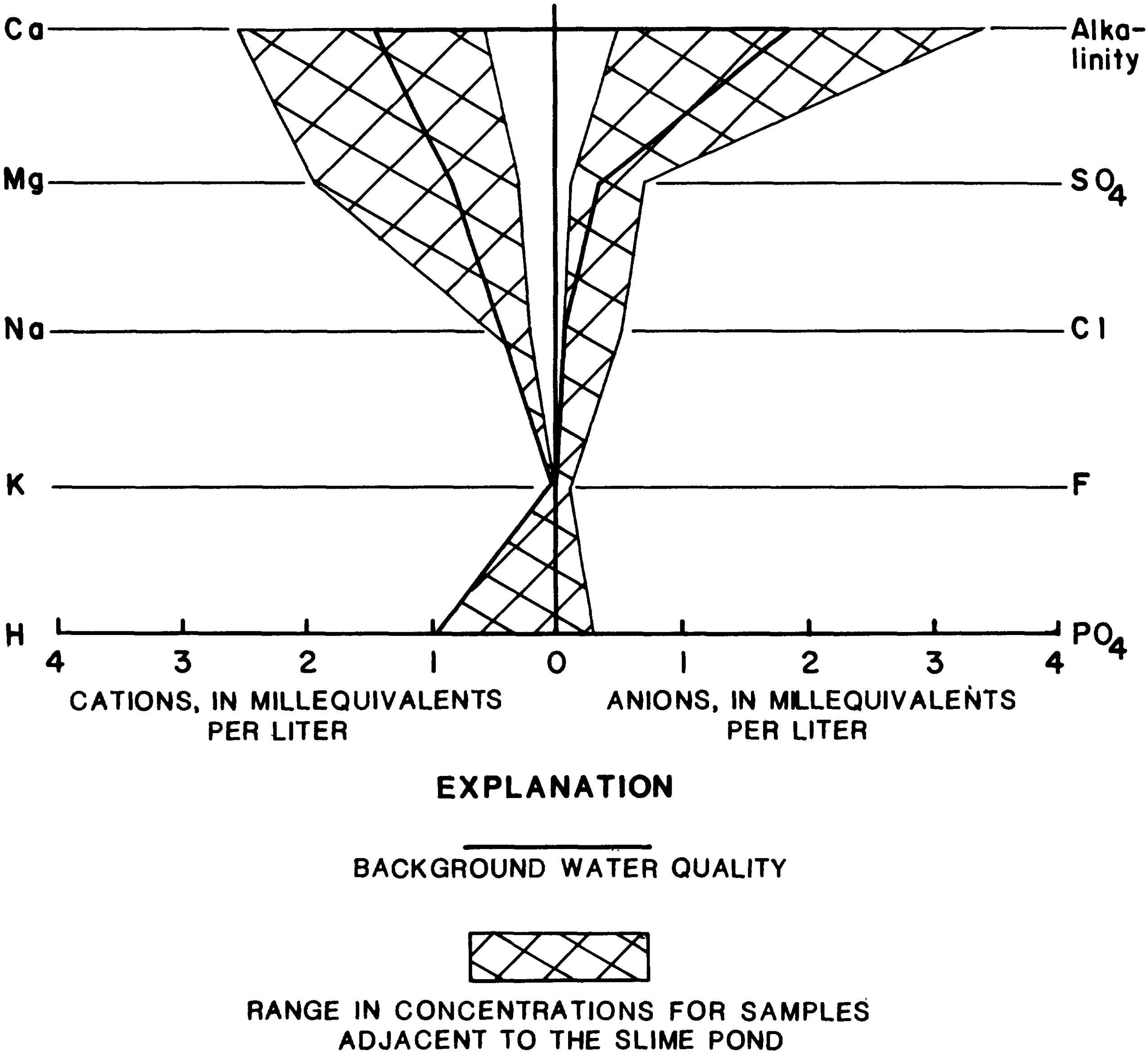


Figure 54.--Modified Stiff diagram showing concentrations of principal ions in water from surficial aquifer wells adjacent to the IMC slime pond and a background well USSAC 39.

Table 19.--Concentrations of nitrogen and phosphorus species in the surficial aquifer and slime pond at the IMC plant

[mg/L, milligrams per liter]

Site No.	Nitrate, mg/L as N	Ammonia, mg/L as N	Orthophosphate, mg/L as N
2	0.78	0.00	0.70
6	.00	.02	5.1
9	.01	.00	.01
10	.04	.28	.74
[1]39	.00	.01	.27
Slime pond	.63-1.1	.45-3.6	.62-1.2

[1] Background water-quality well number 39 near the USS Agri-Chemicals plant (fig. 36).

Radiochemicals

All water samples from the surficial aquifer at IMC met drinking water regulations for gross alpha radioactivity and radium-226 activity. The highest activities were found in water from well 9 in reclaimed land, which had 10, 7.9, and 3.5 pCi/L of alpha, beta, and radium-226 radioactivities, respectively. Water from other surficial aquifer wells contained less than 0.16 pCi/L of radium-226.

Apparently most of the radioactivity in the slime pond is associated with insoluble phosphate ore or clays, and little of this appears in the aqueous phase. Radon-222 may migrate but would be undetected by the analytical methods used during this study. One ore sample analyzed (Miller and Sutcliffe, 1982) indicates that secular equilibrium is approached at least most of the way through the uranium series to lead-210. This means that only a small fraction of the radon-222 escapes from the bulk ore. This may not be true of the fine material associated with slimes. Daughter isotopes of released radon-222 would elevate the gross alpha and beta activities unless the radon-222 escapes into the atmosphere or most of the daughter isotopes are absorbed by the aquifer. The absence of elevated concentrations of alpha and beta emitters in the surficial aquifer water suggest that migration of radon into the aquifer is small.

Trace Elements

Selected trace element determinations are presented in table 20 to show the observed ranges of concentration. Often only one or two concentrations were elevated above the general range of concentrations found for water from other surficial aquifer wells or from the background well. Although only a few patterns might be discerned from these data, some insight can be gained into determinations that may be worthwhile in future studies and the sensitivities that are required.

Iron found in water samples from wells 9 and 10 could not originate from pond water, which contained only about 10 µg/L of iron. In some wells, manganese, mercury, aluminum, bromide, iodide, and boron occur in relatively high concentrations. These high concentrations are somewhat random between wells and no definite pattern is apparent. Some concentrations exceed that found in water from the slime pond. The probable explanations are that: (1) the material is dissolved from the aquifer where local conditions enhance the availability or solubility of the element, (2) seepage through the bottom of the slime pond produces concentrations in excess of that found in the supernatant water, or (3) concentrations in the pond were much higher in the past. The first choice would seem to be the most likely, as the higher concentrations are found in water from wells located in disturbed or reclaimed lands.

Concentrations of iodide ions suggest that some reworked materials found in reclaimed land are dissolving. Thus, iodide may be an indicator of reclaimed land. Concentrations of iodide were low in water from wells that are remote from phosphate industry operations (USSAC wells 2, 39, and 41 and IMC well 15). Concentrations of iodide are also low in water from the CS-8 slime pond, ranging from 0.08 to 0.12 mg/L. Iodide was not detected in water from well 2, which is on unmined land. Water from surficial aquifer wells 6, 9, and 10, which are on mined land, contained 1.4, 0.23,

Table 20.--Concentrations of selected trace elements for sampling sites at the IMC plant

[mg/L, milligrams per liter; µg/L, micrograms per liter]

Well No.	Iron (µg/L)	Manganese (µg/L)	Mercury (µg/L)	Nickel (µg/L)	Vanadium (µg/L)	Aluminum (µg/L)	Bromide (mg/L)	Iodide (mg/L)	Boron (µg/L)	pH (units)	TOC (mg/L)
2	340	10	F0.1	3	6.0	600	0.0	0.00	20	5.9	9.6
3	40	10	.2	2	3.0	30	.0	.03	20	7.2	26
6	40	80	1.8	1	1.0	200	.0	1.4	970	5.3	--
7	80	940	.3	60	1.0	10	.2	.06	10	7.2	4.5
9	25,000	10	.2	3	---	200	.1	.23	40	7.5	9.3
10	19,000	140	1.5	4	1.0	300	.5	2.4	0	5.8	6.8
11	110	20	.6	1	14	30	.0	.16	0	7.3	20
14	2,100	70	.2	2	.0	10	.1	.08	30	6.7	3.7
15	10	0	F.1	1	1.0	100	.0	.00	40	6.4	1.4
[1]39	490	10	F.1	3	---	300	.0	.00	20	6.1	30
S1	60	70	.5	5	7.0	60	.1	.10	20	7.8	8.9

[1] USSAC well.

and 2.4 mg/L of iodide ion, respectively. The highest concentrations of iodide were found in water from wells on mined land close to the slime pond. The method used to analyze for bromide ions was not as sensitive as that for iodide ions, consequently, it is more difficult to distinguish slightly elevated concentrations of bromide ions from background levels. The highest bromide and iodide concentrations were found in water from well 10.

Local variations in availability of trace elements and natural chelating agents, pH, and Eh are probably responsible for the observed distribution of trace elements. High iron concentrations suggest a reducing environment. The iron concentration and pH of water from well 9 suggest that the Eh is -0.4 volts or less (Garrels and Christ, 1965, p. 192). Mercury concentrations for samples from the surficial and Hawthorn aquifers are significantly correlated with pH at the 99 percent confidence level.

Organic Compounds

The total organic carbon (TOC) concentrations of water from surficial wells at IMC ranged from 6.8 to 9.6 mg/L as C. This is similar to concentrations of TOC found in pond water, which ranged from 8.9 to 13 mg/L at the inflow, southeast outflow, and return marina. Concentrations of TOC at the northeast outflow and Fortner Lake were 37 and 52 mg/L, respectively. These higher concentrations may be the result of more biological activity in slow moving water and long residence times in the slime pond. Algal blooms are common in the slime pond. MBAS, oil and grease, and tannins and lignins were all at or near their detection limits in water from wells in the surficial aquifer.

Water Quality in the First Artesian Aquifer

Specific Conductance

Water from well 14 (fig. 45), which best represents background water quality for the first artesian aquifer wells at IMC, had a specific conductance of 340 µmho. Water from well 17 had a specific conductance of 159 µmho. Water from the well is probably young because of local recharge.

Specific conductance of water from deep wells close to the slime pond ranged from 413 to 532 µmho. Water from wells 7 and 3 that are to the east and south of the pond had specific conductances that were about the same as those for the slime pond (520 to 532 µmho). Water from wells 11 and 14, located west and north of the slime pond, had lower water levels than those to the east and south and had lower specific conductances. Wells 7 and 11 are on reclaimed land, but are believed to be open to materials below the mined phosphate matrix. The pattern of lower conductances of water from wells where water levels were lower applies to all four first artesian aquifer wells near the slime pond, and suggests a hydraulic connection between the slime pond and the first artesian aquifer.

Major Constituents

None of the water from first artesian aquifer wells at IMC, other than well 17 (fig. 45), which is believed to be affected by fertilizer, showed a significant PMI or INMI. High values of PII are related to high water levels. This suggests that a hydraulic connection exists between wells 3, 7, and 11 and the slime pond. The chemical composition of water leaving the slime pond and entering the first artesian aquifer probably had been altered by natural processes. Sulfate reduction and ion exchange had probably occurred so that the samples were low in sulfate and did not have any significant mineral imbalances. The slime pond was only 2½ years old during the study period and clays are abundant in and around the pond. Because of these factors many years may be required for ion exchangers (mainly clays) and slime pond water to equilibrate and permit water with a mineral imbalance (PMI) to appear in the surficial and first artesian aquifer wells. The relation between water levels, specific conductance, and percentage increase in ions for first artesian aquifer wells are shown below.

Well No.	Depth open to aquifer (feet)	Water level, feet above sea level[1]	Percentage increase in ions	Specific conductance (µmho)
3	38-72	105	70	520
7	45-71	105	79	532
11	42-47	80	31	413
14	60-87	63	--	340
[2]17	76-90	66	--	159

[1] Water level in slime pond was about 145 feet above sea level and the specific conductance was about 500 µmho.

[2] Remote from slime pond.

Figure 55 shows that increases in alkalinity, magnesium, calcium, and sulfate are mainly responsible for the higher PII and, consequently, the higher specific conductances. Increases in any combination of these constituents does not alter the PMI or INMI.

Nitrogen and Phosphorus

Concentrations of nitrate and nitrite were low in water from the first artesian aquifer wells except for the 7.1 mg/L concentration of nitrate in water from well 17. This was probably because of application of fertilizer to nearby citrus groves. It was not because of the migration of material from the slime pond because the well is too distant, its water level was higher than that at intervening well 14, and it contained more nitrogen that many of the samples from the slime pond.

Concentrations of ammonia for water from wells near the slime pond ranged from 0.02 to 0.61 mg/L. Even though these concentrations are above detection limits for the method of analyses used, no apparent pattern was discernible. Organic nitrogen concentrations were close to the detection limits.

The concentrations of orthophosphate ranged from 0.01 to 0.18 mg/L in water from wells near the slime pond. Wells 3 and 7, which may receive some water from the slime pond, contained only traces of orthophosphate. Water from wells 14 and 17, which had the lowest pH, contained the highest orthophosphate concentrations. This suggests that high concentrations of orthophosphate in the first artesian aquifer are not related to the flow of materials from the slime pond, but to pH and other solubility controls. In the case of water from well 17, the availability of soluble phosphate from fertilizers may have had some influence, but at the depth sampled, solubility was probably the predominant influence.

Radiochemicals

Gross alpha activities and radium-226 activities, but not gross beta activities, demonstrated a pattern similar to that found for specific conductance and PII. The highest activities (radium-226 of 5.5 and 6.6 pCi/L) are associated with the highest water levels.

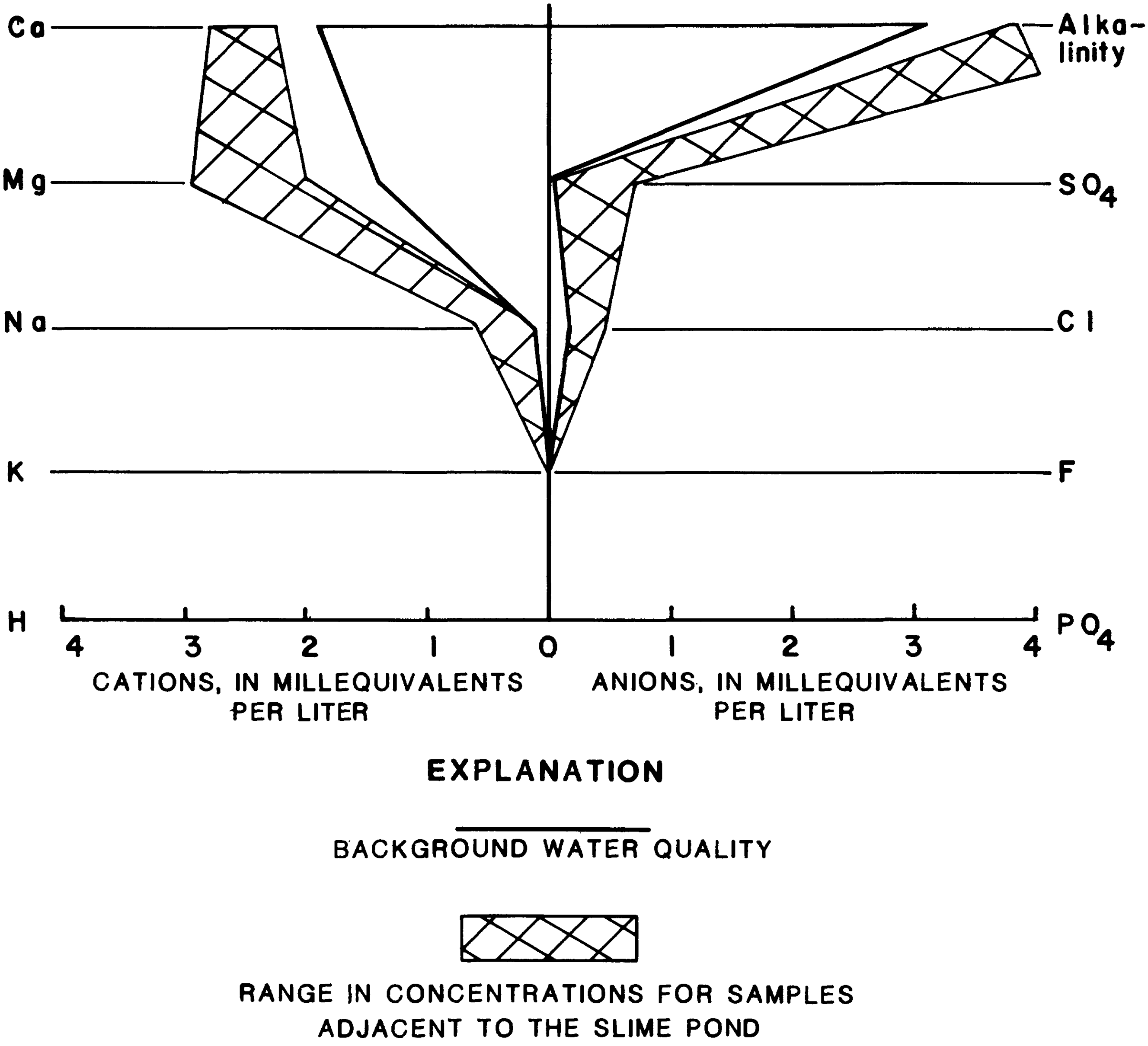


Figure 55.--Modified Stiff diagram showing concentrations of principal ions in water from first artesian aquifer wells adjacent to the IMC slime pond and a background well 14.

The source of the elevated gross alpha and radium-226 activities was not pond water, but probably natural clay layers below the phosphate matrix or the settled slurry in the pond. At each cluster of wells adjacent to the slime pond, water from the surficial aquifer well had a lower activity than water from the first artesian aquifer well next to it. In addition, the pond water and water from wells 14 and 17 were low in alpha and radium-226 activity. As pond water seeps through the clay layers of the slime pond and the underlying surficial aquifer, the dissolution of radium-226 and other alpha emitters occurs through dissolution of aquifer materials or alpha particle recoil.

Beta activity was relatively constant in the first artesian aquifer ranging from 1.1 to 3.2 pCi/L.

Trace Elements

Most trace elements occurred in low concentrations in water from the first artesian aquifer and little variability was observed. Concentrations of a few elements were higher in one or more wells. Examples are iron in well 14 (2,100 μg/L), manganese in well 7 (970 μg/L), and nickel in well 7 (60 μg/L).

Iodide ion concentrations ranged from 0.03 to 0.16 mg/L in water from the first artesian aquifer wells near the slime pond. No iodide ions were detected in any of the surficial or first artesian aquifer background wells that were remote from the industrial operations in the Bartow area. Although this is a small sample from which to draw conclusions, further studies may show that the iodide ion is a useful indicator of phosphate industry operations. At IMC, iodide concentrations may be related to contact time of water with mined land.

Organic Compounds

Concentrations of total organic carbon ranged from 1.4 mg/L for water from well 15 to 26 mg/L for water from well 3. No discernible pattern was found in the occurrence of organic carbon in water from these wells in the first artesian aquifer. Two main sources of organic carbon are possible:

one is the natural organics that may be unevenly distributed (peat is mined south of the slime pond) and the other is seepage of water through the pond. Water within the slime pond varies significantly in organic carbon content. Samples taken at the inflow (S5) and the southeast outflow (S1) contained about 9 mg/L of TOC. Samples from the northeast outflow (S4) and the Fortner Lake outflow culvert (S3) contained 37 and 52 mg/L of TOC, respectively. Interpretation of the distribution of total organic carbon in water from the first artesian aquifer is complicated by: (1) spatial variability in the concentrations of carbon in the slime pond and the aquifer; and (2) undetermined factors such as biologic activity in the pond, its sediments, and the aquifer.

All of the MBAS, oil and grease, and tannin and lignin determinations were at or near the detection limits. Concentrations of phenols were 9, 5, 0, and 0 μg/L at wells 14, 7, 3, and 11, respectively. The nature and origin of these compounds is unknown. The slime pond contained 2 μg/L of phenols. Water from well 14, which is somewhat removed from the pond, contained the highest concentration of phenols in the samples analyzed. Concentrations in water from wells close to the pond were somewhat lower.

Summary

Water from the slime pond had a 14 percent mineral imbalance, which does not appear in water from nearby wells. High concentrations of phosphorus, trace elements, and radioisotopes occur in the solid phase of the slurry from the mine, but most of these materials are effectively retained within the slime pond.

The total concentration of major constituent ions in the surficial aquifer increase in a northerly direction, especially west of the slime pond. Concentrations of ammonia in water from the surficial aquifer were near the detection limits in all but one well. Concentrations of orthophosphate were elevated in water from three wells. In general, radioactivity and concentrations of trace elements and organics were low in the surficial aquifer.

High concentrations of major constituent ions (PII) are associated with high water levels for water from first artesian aquifer wells. This suggests a hydraulic connection between the aquifer and the slime pond. Orthophosphate concentrations seem to be associated with low pH. High gross alpha and radium-226 activities are associated with high water levels and probably dissolve from settled slurry or aquifer materials. Iodide concentration at IMC may be related to contact time of water with aquifer material.

WATER QUALITY OF RAINFALL

Two 11-inch polyethylene funnels and a 5-gallon polyethylene collector were used to collect rainfall for analyses at each of the three study areas. Because refrigeration was not available, samples were collected shortly after rainfall events whenever possible. The parameters determined depended on the available sample volume. All samples were bulk (dry plus wet fallout).

Two samples were collected at AMAX. One was collected by AMAX personnel and the other by U.S. Geological Survey personnel. One large volume sample was collected at the USSAC plant. Another sample was collected at USSAC, but only field pH and specific conductance could be determined. Two samples were collected at IMC.

On June 10, 1980, there was a brown haze over the entire Bartow area. The collectors were set out and a rainfall sample was collected within a few hours after a rainfall event at IMC. The storm was unevenly distributed. Heavy rain fell at IMC and only very small quantities of rain fell at the USSAC collector or at the NOAA weather station in Bartow (0.01 inch). The IMC rainfall sample had an unusually high specific conductance of 347 μmho and a pH of 7.8. A small quantity of rainfall was collected from the USSAC collector the next day, June 11, 1980. Field determinations showed a specific conductance of 290 μmho and a pH of 5.8. These determinations confirm that the atmosphere contained a considerable amount of soluble matter at the time. Figure 56 shows that most of the solute for the IMC sample was calcium, magnesium, and alkalinity (presumably HCO_3^-). Hendry

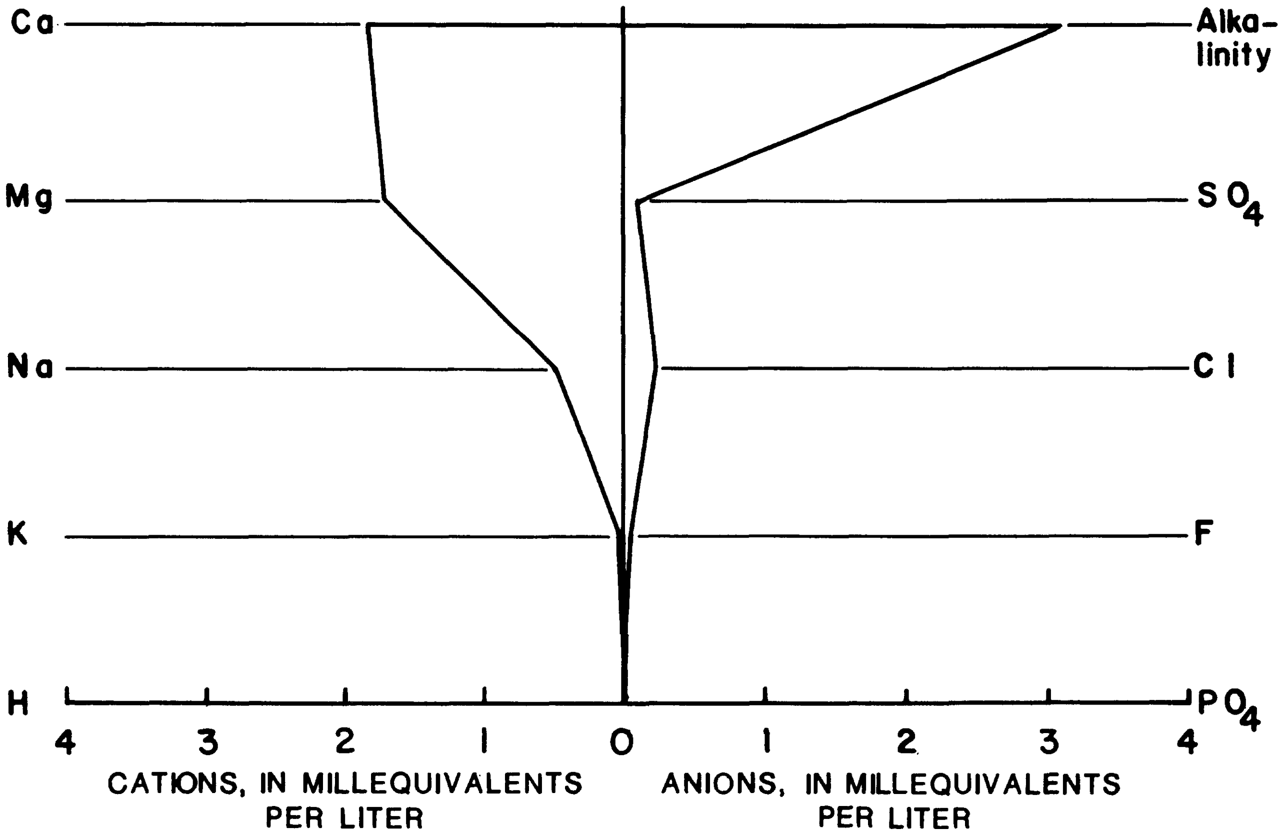


Figure 56.--Modified Stiff diagram showing concentrations of principal ions in rainfall collected at the IMC plant on June 10, 1980.

and Brezonik (1980) suggest that calcium and magnesium in rainfall originate from soil materials. This is believed to have been a rare and atypical rainfall event. The second rainfall sample collected at IMC on June 12, 1980, had a pH of 7.2 and a specific conductance of 23 µmho. The sample was collected after rains and wind had removed high concentrations of airborne solute.

Figure 57 shows the concentrations of major ions for rainfall collected from IMC on June 12, 1980, from USSAC on June 17, 1980, and from AMAX on July 16, 1980. Table 21 summarizes some of the rainfall data collected during this study. The predominant cations and anions are listed in decreasing order of milliequivalents per liter. The April 7 sample from AMAX was only a partial analysis. Ammonium and sulfate ions are known to be important, but may not be the predominant ions for that sample.

The radiochemical determinations shown in table 21 indicate that the activities are quite low. Because the activities are so close to the detection limits, the activities can be considered to be about the same for all three samples.

Only the July 16 sample from AMAX had sufficient water for trace element determinations. All the trace elements determined were too close to the detection limits to be of interest except for low levels of iron (70 µg/L), vanadium (2.0 µg/L), aluminum (50 µg/L), bromide (0.3 mg/L), and lead (7 µg/L). This sample contained predominantly $CaSO_4$, $(NH_4)_2HPO_4$, and some NaCl. These probably originated from airborne gypsum, fertilizer, and sea spray, respectively. The USSAC sample contained about equal amounts of $Ca(HCO_2)_2$ and $(NH_4)_2SO_4$, which may have originated from airborne dust containing $CaCO_3$ (reacted with CO_2) and from the reaction of fugitive ammonia and sulfur trioxide. The IMC sample contained approximately equal amounts of NH_4HCO_3 and $(NH_4)_2SO_4$ with lesser amounts of $NH_4H_2PO_4$. Only the USSAC sample collected on June 17 was acid rainfall. Samples are categorized as acid rain when the pH is less than 5.6 (U.S. Environmental Protection Agency, 1979).

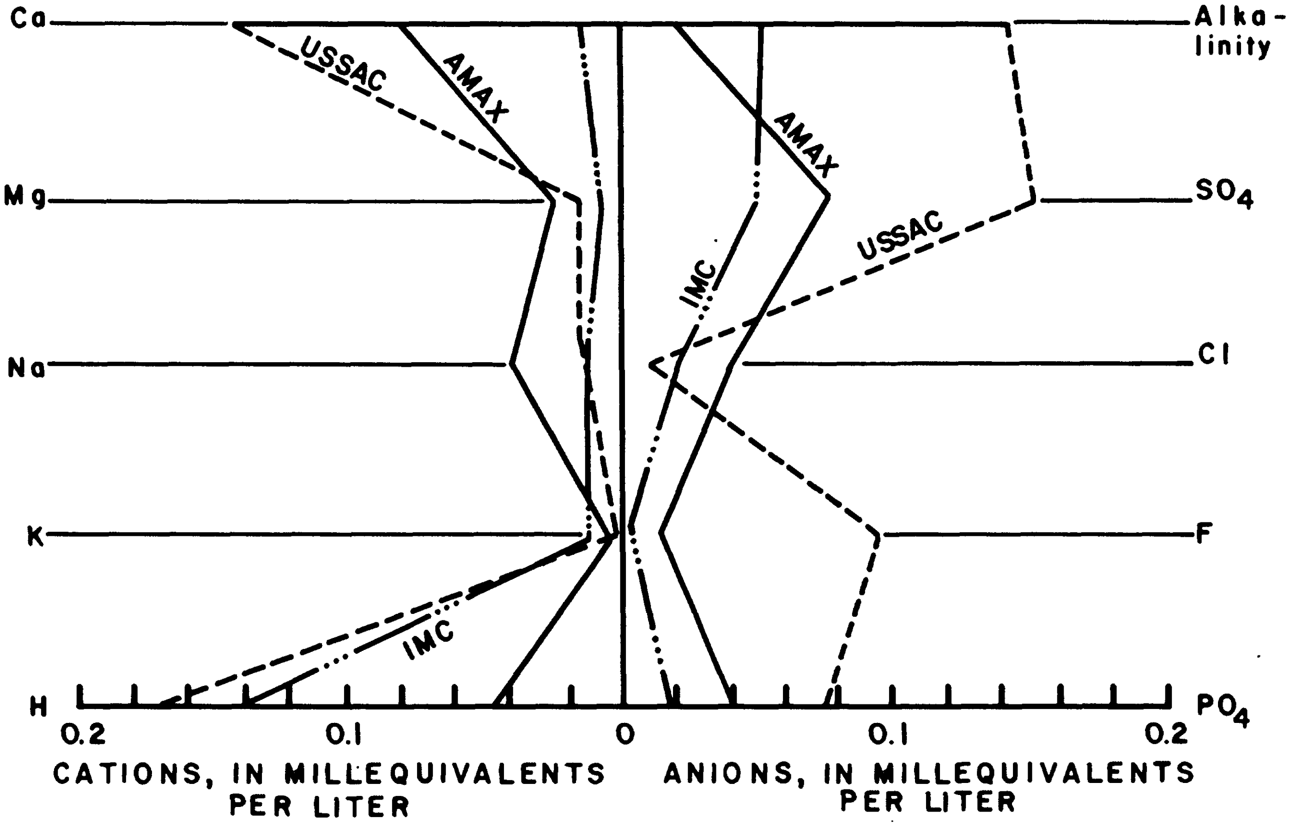


Figure 57.--Modified Stiff diagram showing concentrations of principal ions in rainfall from the three phosphate companies collected during April through July 1980.

Table 21.--Summary of rainfall water quality

Company	Date col-lected (1980)	pH (units)	Specific conduc-tance (µhmo/cm)	Major cations	Major anions	Total alpha (pCi/L)	Total beta (pCi/L)	Radium-226 dissolved (pCi/L)	Radium-226 suspended (pCi/L)
AMAX	April 7	6.5	52	NH^{+1} ?	SO_4^{-2} ?	---	---	---	---
IMC	June 10	7.8	347	Ca^{+2}, Mg^{+2}	HCO_3^{-1}	---	---	---	---
USSAC	June 11	5.8	290	---	---	---	---	---	---
IMC	June 12	7.2	23	NH_4^{+1}	SO_4^{-2}, HCO_3^{-1}	0.1	1.9	0.8	0.1
USSAC	June 17	5.4	43	NH_4^{+1}, Ca^{+2}	SO_4^{-2}, HCO_3^{-1}, F^{-1}, $H_2PO_4^{-1}$	.0	1.6	.14	.1
AMAX	July 16	6.4	23	Ca^{+2}, NH_4^{+1}, Na^{+1}	SO_4^{-2}, $H_2PO_4^{-1}$, Cl	.5	.6	.12	.2

[1] Data from partial analysis suggest these are major ions.

Hendry and Brezonik (1980) reported the results of a 1-year study of the chemistry of precipitation at Gainesville, Fla., about 130 miles north of Bartow. They found that sulfate, ammonium, nitrate, magnesium, and potassium ions were deposited mainly by rain; whereas, dry fallout was of comparable importance in deposition of sodium, chloride, and calcium. Chloride and sulfate were the predominant anions in both bulk and wet-only precipitation. Hydrogen, calcium, sodium, ammonium, and potassium were the major cations in rainfall.

RESULTS AND CONCLUSIONS

1. Water-level and chemical data indicate that water and dissolved materials seep from gypsum stacks, slime ponds, and ditches into underlying aquifers at two phosphate chemical plants and at a phosphate mine and beneficiation plant.

2. Migration of dissolved materials is evident based on analyses of water from most surficial aquifer wells near gypsum stacks. Dissolved materials in water that has migrated any great distance or depth from a source are less evident, but are often recognizable. The requirements of the National Interim Primary Drinking Water Regulations (U.S. Environmental Protection Agency, 1976) are usually met by samples collected at distances of 1,500 feet or more from a source. Water samples from many wells at much shorter distances from a source also met drinking water standards. One water sample from a test well in the surficial aquifer (one-third mile from a gypsum stack) contained elevated sulfate concentrations.

3. Migration of fluoride, phosphate, radioactive isotopes, and trace elements in ground water is retarded once acids contained in process water are neutralized by reaction with aquifer materials. Bromide and iodide are probably the most mobile and easily distinguishable minor elements found in process water.

4. Sulfuric acid used to dissolve phosphate ores results in precipitation of gypsum. Coprecipitation of radionuclides with gypsum and the precipitation of radium sulfate may be responsible for reducing losses of

radioactive materials into the environment. Use of other acids, such as nitric, as used in some European plants, would affect the release of radioactivity into ground water.

5. Sodium and sulfate ions are the most mobile major ions in process water. The index of nonmineral input (an ion index that measures increases of uncommon combinations of major ions above background levels), used to detect increases in sodium and sulfate together, confirms that process water is the source of soluble materials in water from some test wells. The occurrence of bromide, iodide, and ammonium ions also confirms the presence of seepage from gypsum stacks.

6. Water in slime ponds and associated ditches was generally of good quality for parameters determined. High concentrations of phosphorus, trace elements, and radioisotopes associated with the solid phase of the phosphate slimes are effectively trapped in the slime pond, but some material may solubilize after settling and percolate through the bottom of the slime pond.

7. An atypical sample of rainfall, collected on June 10, 1980, southeast of Bartow, had a specific conductance of 347 μmho. Another sample collected a few miles away on the next day had a specific conductance of 290 μmho. After the atmosphere was cleansed by winds and showers, the specific conductance of rainfall was less than 50 μmho. Calcium, ammonium, bicarbonate, and sulfate were usually predominant ions.

8. Application of hydraulics and chemistry to geologic and hydrologic data can explain much of the observed water-quality data and provide direction to future siting and construction of gypsum stacks and cooling ponds. Knowledge of the local and regional geology and hydrology is vital to the understanding of movement of water from the waste-disposal areas and their potential seriousness and significance to the local and regional water supply. Plant location is an important factor in determining the magnitude and extent of the movement of the solutes associated with the waste-disposal site.

9. Neutralization of acids in seepage water or excess process water from phosphate chemical plants after entering ground water aquifers is paramount in limiting the migration of fluoride, phosphate, radioactivity, and many trace elements. Neutralization occurs when acids react with natural carbonate minerals, oxides, or other bases that occur in aquifers.

10. Permeabilities and hydraulic heads control the flow of water from source stacks, ponds, and ditches. Any reduction in permeability at the base of the contaminate source would restrict or hinder movement into the ambient ground water. An impermeable barrier would effectively stop movement; thus, compaction, lining, or sealing of soils underlying future cooling ponds or gypsum stacks would reduce or stop the leakage of water. Barriers and interceptor wells could be used to control seepage from existing gypsum stacks if present conditions require remedial action. Sealants could reduce leakage through the bottom of existing cooling ponds and ditches, but in humid climates excess water tends to overflow lined ponds and ditches.

AMAX Chemical Plant

1. The AMAX chemical plant had been in operation for about 14 years prior to this study in 1980. In general, effects of process water on the surficial aquifer were obvious only in water from wells that were within about 100 feet of the east, south, and west sides of the gypsum stack.

2. Subtle effects of seepage, without public health significance, were observed in water from surficial aquifer wells more than 1,000 feet from the gypsum stack.

3. Most seepage from the waste-disposal site followed the general flow in the surficial aquifer to the west. Water-level contours show that regional ground-water flow is to the southwest from the gypsum stack, and the ion indices and spatial distribution of sulfate, ammonia, phosphate, and bromide indicate that solute migration is greatest southwest of the gypsum stack.

4. Migration of radioactive isotopes is very limited in both distance and magnitude. Water from wells in the surficial aquifer that are definitely affected by the seepage of process water contained less radium-226 and gross alpha activity than samples from less affected wells. Elevated gross beta activities (up to 227 pCi/L) were observed within about 50 feet of ditches containing process water. Elevated gross beta activities (up to 25 pCi/L) were also observed more than 1,000 feet from the gypsum stack. Beta emitters were more mobile than alpha emitters at the AMAX chemical plant.

5. Radon-222, a noble gas, may be an important factor in the migration of radioactivity. Radon is essentially chemically inert toward aquifer materials, but could be absorbed on solid materials. Most radon-222 is probably lost to the atmosphere from the surficial aquifer or decays to daughter products. Analytical procedures used for determining gross alpha radioactivity in water do not detect radon-222. Lead-210 and polonium-210 are expected to occur in aquifers near sources of radon-222.

6. Most trace metals are near background concentrations in ground water in the surficial aquifer. Concentrations of iron and lithium are elevated in water from some test wells that were affected by the seepage of process water. Arsenic and chromium concentrations exceeded limits set in the National Interim Primary Drinking Water Regulations (U.S. Environmental Protection Agency, 1976) in water from one well that was 8 feet from a ditch that contained process water. Concentrations of barium, cadmium, lead, mercury, and selenium did not exceed the regulations in water from any of the surficial aquifer wells. Manganese, cobalt, copper, molybdenum, nickel, zinc, aluminum, and antimony occur in easily detected concentrations in process water, but do not migrate to any significant degree in terms of distance or concentration.

7. The direction of ground-water flow in the first and second artesian aquifers during the rainy season is west toward Tampa Bay. In recent years, however, during periods of heavy agricultural pumpage, the net flow in the second artesian aquifer has been toward the east, as evidenced by chemical data and water-level maps for west-central Florida.

8. Effects of seepage of process water into the first artesian aquifer, as represented by ion indices, are greatest at the east side of the gypsum stack. The second most affected area in the first artesian aquifer is about 1,500 feet east of the south side of the stack. The net effect of ground-water flow since the construction of the gypsum stack has been transport of gypsum stack seepage to the east for some undetermined distance.

9. Fluoride, nitrogen and phosphorus compounds, alpha emitters, radium-226, and most trace metals do not migrate from the chemical plant into the first artesian aquifer at significant levels. Fluoride concentrations were all less than 1.0 mg/L. Gross beta radioactivity was slightly elevated (7.0 to 12 pCi/L) compared to the background activity of less than 1.0 pCi/L.

10. Some ion indices indicate that ground-water flow in the second artesian aquifer may have transported seepage from the gypsum stack. The seepage has reacted with the aquifer such that it is similar to natural water in percentage mineral imbalance, but not in total concentration of ions. Traces of ammonium ion show general increases in concentration from west to east similar to percentage increases in major ions. Other nitrogen and phosphorus species were near their detection limits in the second artesian aquifer.

11. The lowest gross alpha, gross beta, and radium-226 activities were found in water from the test well in the second artesian aquifer that is most affected by process water, as indicated by the ion indices. Water from each second artesian aquifer well contained more gross beta and radium-226 activity than water from the corresponding first artesian aquifer well above it. Gross alpha radioactivity was greater in water from each second artesian aquifer test well than in the corresponding first artesian aquifer test well except for one site where the contrary was true by an insignificant amount. This suggests that native ground water in the second artesian aquifer is more radioactive than seepage from the gypsum stack that has reacted with the shallower aquifers.

USSAC Chemical Plant

1. The USSAC chemical plant was about 34 years old during the data-collection period (1980). The high acidity of the USSAC process water, combined with greater permeability and lower acid neutralizing capacity of the surficial aquifer sands, permitted greater migration of most solutes at USSAC than at AMAX. In addition, the USSAC plant is about 20 years older than the AMAX plant.

2. The effects of process water were observed in water from surficial aquifer test well 5, one-third mile south of the USSAC gypsum stack. The concentrations of sulfate (750 mg/L), sodium (150 mg/L), silica (320 mg/L), ammonium (12 mg/L as N), and orthophosphate (130 mg/L) in water from well 5 were all significantly above background levels.

3. All water from surficial aquifer wells at USSAC had total concentrations of ions (PII) significantly above background levels. Eight of 10 samples also had indices of nonmineral input that were significantly above background levels. The greatest effects of seepage were observed south and east of the gypsum stack, but some migration was observed (less than 500 feet north of the upper cooling pond) northwest of the gypsum stack. Migration of solute to the west of the gypsum stack and cooling pond was limited, but detectable.

4. Either gross alpha or radium-226 activities exceeded limits of 15 and 5.0 pCi/L, respectively, set in the National Interim Primary Drinking Water Regulations, in water from three wells in the surficial aquifer within about 400 feet of the south and east sides of the USSAC gypsum stack. Radium-226 activities appear to be controlled by sulfate concentrations. Gross beta activities greater than 10 pCi/L were limited to water from test wells that were within about 400 feet of the gypsum stack. The highest activities observed in the surficial aquifer were 2,027 and 2,985 pCi/L of gross alpha and gross beta radioactivity, respectively, in water from a well less than 200 feet from the south side of the USSAC gypsum stack. Levels of radioactivity were less than limits set in the National Interim Primary Drinking Water Regulations in water from more remote test wells.

5. Trace metal concentrations were limited by precipitation reactions and ion exchange that were in turn controlled by pH. Elevated levels of iron, manganese, beryllium, cadmium, chromium, cobalt, copper, lithium, molybdenum, nickel, strontium, zinc, aluminum, iodide, arsenic, boron, and antimony were found in water from two surficial aquifer test wells adjacent to the south and east side of the USSAC gypsum stack. The pH of these samples were 2.4 to 2.3. In general, greatly elevated concentrations of most trace elements were not observed in samples from more distant test wells. Elevated concentrations of iron (25,000 μg/L), cobalt (47 μg/L), nickel (78 μg/L), iodide (0.54 mg/L), and arsenic (33 μg/L) were observed about one-third mile south of the USSAC gypsum stack. Barium, mercury, lead, and selenium do not appear to migrate at significant concentrations in the surficial aquifer.

6. Water samples from test wells in the first artesian aquifer near the south and east sides of the USSAC gypsum stack were influenced by process water as determined by ion indices and iodide ion concentrations. Despite this, all fluoride concentrations in the first artesian aquifer were less than 2.0 mg/L.

7. Water from well 19 (east of the gypsum stack) in the first artesian aquifer contained radium-226 activities (16 pCi/L) greater than the limit set in the National Interim Primary Drinking Water Regulations. All other samples had activities that were less than required by the regulations, indicating that little radioactive material had migrated into the first artesian aquifer at USSAC.

8. Other than minor elevations in concentrations of trace elements in water from test wells adjacent to the south and east sides of the USSAC gypsum stack, trace element concentrations were generally low in the first artesian aquifer. The concentrations of arsenic (54 μg/L) in water from a well just east of the gypsum stack exceeded regulations slightly, but concentrations of trace elements elsewhere in the first artesian aquifer met the requirements of regulations.

9. One test well adjacent to the south side of the USSAC gypsum stack indicated that process water had entered the second artesian aquifer. Another test well indicated that subtle influences of process water are detectable one-third mile south of the gypsum stack. Other than near the gypsum stack, levels of radioactivity and fluoride satisfy drinking water regulations. Concentrations of nitrogen and phosphorus species and trace elements were generally low in the second artesian aquifer at USSAC.

IMC Mine

1. The slime pond was about 2½ years old during the data-collection period. A 14 percent mineral imbalance occurred in water in the slime pond at IMC, but was not observed in water from any test wells. Ion exchange by clays and perhaps sulfate reduction by bacteria are responsible for these changes.

2. High water levels (111.1 to 116.0 feet above sea level) associated with low specific conductances (135 to 208 µmho) occur in the surficial aquifer east and south of the slime pond. Low water levels (81.8 to 98.0 feet above sea level) associated with specific conductances that increase in a northerly direction occur west of the slime ponds (CS-8 and CS-9). This indicates that water with low specific conductance from the ridge east of the slime pond is mixing with seepage from the slime pond and flowing toward the mining pit just north of the northwest corner of the CS-9 slime pond.

3. Relations between total major ion concentrations and water levels at the IMC mine suggest that a hydraulic connection exists between the slime pond and the first artesian aquifer.

4. Irregular distributions of trace elements suggest that observed concentrations are related to their availability in the aquifer and to pH and Eh conditions. Mercury concentrations were correlated with pH at the 99 percent confidence level. Iodide concentrations may be related to contact time with the aquifer.

5. Elevated levels of radioactivity, phosphorus, and trace metals occur in the solid phase of the slurry flowing into the slime pond. These solid phase materials are effectively trapped by the slime pond and do not reach outflows.

6. Because dissolved concentrations of health related constituents measured during this study are low in the slime pond, siting of slime ponds to control contamination of ground water should be less critical than siting of gypsum stacks and cooling ponds.

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