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RADIOCHEMISTRY OF URANIUM-SERIES ISOTOPES IN GROUNDWATER

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RADIOCHEMISTRY OF URANIUM-SERIES ISOTOPES IN GROUND WATER

(Chemical Fate of Uranium-Daughter Radionuclides in Recharge Wells, Central Florida Phosphate District)

by

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PERSPECTIVE

GORDON D. NIFONG, Ph.D.

FLORIDA INSTITUTE OF PHOSPHATE RESEARCH

It has long been known that elevated levels of uranium occur naturally associated with the sedimentary phosphate deposits found in central Florida. Mainly because of its low solubility, uranium is not generally considered to be a major environmental hazard, but many of the members within the uranium decay series are more of a cause for concern. These would include radium-226, a radioactive element chemically similar to calcium; radon-222, a gas that is chemically inert but radioactive; several "short-lived" daughter products of radon; and finally two longer-lived decay products -- lead-210 and polonium-210. All of the above are naturally occurring radioactive materials that are ubiquitous in the environment but tend to be elevated in phosphate-related materials.

Since its inception, the Florida Institute of Phosphate Research has been interested in the environmental aspects of the phosphate industry. It is believed that all phases of ore mining, minerals processing and land reclamation can be accomplished in an environmentally acceptable manner. Because of the array of radionuclides found in phosphate ores, much of that concern for the environment has been focused on the issue of radiation. Well over a dozen projects have been conducted or sponsored that directly address the topic of radiation, and numerous other projects have had radiological components as secondary issues. Strong interest exists not only in characterizing natural radionuclides as to their nature, extent and magnitude, but also in determining their effects on the population that lives and works in the phosphate region. The Institute has addressed both concerns.

One of the great natural resources available to the citizens of the State of Florida, but one perhaps too often taken for granted, is a source of plentiful and clean water for domestic consumption and other uses. For most of the people living in central Florida, this source is groundwater, often obtained from shallow, private wells,but more often obtained from public, community wells tapping the Floridan aquifer. The supply is not infinite, however, and continued growth and development of the area depend in part on proper management of this resource, including especially conservation measures and avoidance of pollution. The central Florida phosphate industry requires a great deal of water in the mining and processing of phosphate rock, even though great strides have been made in recent years in the recycling of process water. To mitigate water withdrawals from the Floridan aquifer, the industry has frequently utilized recharge wells, designed to transfer water from surficial zones to the deeper aquifer. Not only does this lessen the overall withdrawal impact on the Floridan, but it aids in the dewatering of land to be mined.

Assessing the quality of water has been a goal of several Institute-sponsored studies. In 1981 the Institute sponsored a study by the state Department of Health and Rehabilitative Services to study radiochemical contamination in shallow drinking water wells in the phosphate region. Later this study was expanded to be statewide in scope. Further water quality studies, done mainly at the University of South Florida and at Florida State University, have looked in detail at the radiological components of groundwater.

In earlier work, the results of which were published by the Institute in 1985, Dr. Upchurch and his co-workers at South Florida found that polonium-210, rather than uranium or radium, was the dominant radionuclide in much central Florida groundwater, especially that from surficial aquifers. That and other findings in his study suggested that a more in-depth chemical and radiological analysis of water from inter-aquifer connector "recharge" wells, and from shallow and upper Floridan aquifers monitoring wells, might provide a basis for better understanding the chemistry of the waters. This in turn could lead to better location and management of recharge wells, perhaps increasing their acceptability. Thus, this current study was initiated.

Dr. Upchurch has now confirmed that polonium does indeed account for most total alpha radiation in groundwater, and that mostly it is found in surficial sources. Polonium in recharge wells is seasonally related to water table fluctuations. High levels of alpha activity are spatially related to fracture traces in the earth's crust. Thus, recharge wells should be more acceptable for use in the central Florida phosphate district if several precautions are taken. They should be located to avoid fracture traces or areas where leached zone material is thick and the water is acidic. Sampling protocols should be designed to avoid contamination from well casing slimes.

Chemical modeling and raw data clearly indicate that conditions for transport of polonium and lead exist in the surficial aquifer, but not in the Floridan aquifer. Therefore, it appears that, with respect to the parameters measured, the quality of receiving Floridan aquifer waters is not jeopardized by the practice of interaquifer connector (recharge) wells.

A central theme that runs through much of the Institute's environmental research is the evaluation of human exposure to radiation dose as contributed by some phase of the natural environment. This work seems consistent with the societal goal of keeping radiation exposures to "as low as reasonably achievable."

EXECUTIVE SUMMARY

Chemical analysis of water from interaquifer connector wells ("recharge wells") and associated monitor wells in the Central Florida Phosphate District has provided a basis for understanding the chemistry of the Surficial and upper Floridan aquifers and of recharge wells. The data are particularly important because they suggest chemical controls on the mobility of uranium and uranium progeny. Time-series and nearest-neighbor analyses of historical data suggest hydrologic conditions that cause mobilization of iron, sulfur, and radionuclides in ground water and provide a basis for recharge-well location and management to minimize risks of failure of water-quality criteria for gross-alpha radioactivity, iron, and color.

Specific findings can be summarized as follows:

1. Twenty three recharge wells were sampled. A total of 51 water samples from recharge wells were analyzed for 31 chemical variables, including uranium-238, uranium-234, radium-226, lead-210, and polonium-210. Three recharge wells had associated Surficial and Floridan aquifer monitor wells. Eighteen samples were analyzed from the monitor wells.

2. Water of the Surficial aquifer is acidic, reducing, and organic rich. Eh-pH data show that the aquifer water is near the hydrogen sulfide-sulfate stability boundary, and sulfides are the major sulfur species in the water. Ferrous iron is the stable iron species. Polonium and, to some degree, radium may be present in activities sufficient to be of concern.

3. Floridan aquifer water is neutral to slightly alkaline and slightly reducing. Sulfate is the dominant sulfur species, and ferrous iron is stable. Activities of radionuclides are low in the Floridan aquifer where sampled, although radium has been shown to be a problem in other studies.

4. Surficial aquifer water is highly variable and ranges from a sodium-sulfate to sodium-calcium-bicarobonate-sulfate compositions. Upper Floridan aquifer water compositions do not vary significantly and the water is a calcium-magnesium-bicarbonate solution.

5. In recharge wells, sulfur is oxidized to sulfate and iron may be oxidized to the ferric state. Ferric hydroxides precipitate if the system is oxidizing, but most of the ferric hydroxide precipitate appears to form on well casings and screens, not in the turbulent flow of the well water. In general, recharge-well water closely

reflects the chemistry of Surficial-aquifer water, from which it is derived.

6. Sampling trials indicate that much of the ferric hydroxide and biomat that causes color and turbidity violations in water quality is adherent on well casings. Sampling with a tripod to prevent contact of the sampling vessel with the walls of the well avoids contamination of the sample with color- and turbidity-causing casing "slimes".

7. Sulfate reduction is initiated at reduction-oxidation (redox) potentials less than -150 mv.

8. Gross-alpha radioactivity measurement techniques are not reliable measurements of true alpha activity because of short-lived radon daughters that may be present in the sample. Gross-alpha radioactivity should only be used as a screening technique to determine if there is a potential for radiation problems.

9. Uranium was low in all samples and is not a problem. Uranium is mobilized as uranyl ion in oxidizing conditions.

10. Radium was not a problem in most samples. Four recharge wells had samples in excess of the 5 pCi/l standard. Radium appears to be mobilized as a sulfate complex. Strontium, and perhaps barium, appears to enhance nucleation of radiocolloids of radium sulfate. All samples were well below chemical equilibrium with respect to particulate radium sulfate.

11. Lead-210 is present in all systems in minor quantities. Soluble lead-210 does not support its daughter polonium-210, so the aqueous polonium is derived from lead sorbed or precipitated on aquifer materials. Isotherms indicate that lead is strongly adsorbed on clays and is precipitated in contact with ferruginous quartz sand and limestone. Lead is slightly mobile in the Surficial aquifer owing to the low pH of the water. In the Floridan aquifer it is controlled by precipitation of lead carbonate (cerussite). Lead-210 activity is not correlated to total lead concentration.

12. Polonium-210 is most abundant in the Surficial aquifer where it constitutes most of the gross-alpha radioactivity. Polonium mobility is controlled by solubility of the radiocolloids formed by complexing of polonium with hydroxyl. In acid, low OH^{-1} water, polonium is mobilized, while in alkaline, high OH^{-1} waters, it forms the radiocolloid. The polonium-hydroxide

radiocolloid coexists and co-precipitates with iron-hydroxy complexes. Movement of the radiocolloid and iron-hydroxy colloids is mechanically inhibited in aquifer systems.

13. High gross-alpha radioactivity is spatially related to fracture traces. Fracture traces are characterized by enhanced vertical leakance, thickened "leached zone", and extreme temporal variability in saturated-zone thickness. Recharge wells within 0.3 km of a fracture trace are most prone to violation of the 15 pCi/l MCL for gross-alpha radioactivity. Therefore, placement of recharge wells over 0.3 km from fractures should minimize water-quality violations.

14. Gross-alpha (polonium) radioactivity in recharge wells is seasonally related to water-table fluctuations (as reflected in precipitation data at a nearby gage). High recharge and water-table conditions lead to dilution of the radioactivity on the scale of weeks to a month. On the longer term, it appears that years with maximum unsaturated zone development (low water table elevations or wide variations in water-table elevation) have low gross-alpha radioactivity in recharge wells. This is because the particulate, polonium-hydroxide complexes (and other metal-iron-hydroxide complexes) are stable, filterable, and, therefore, not transported. In wet years, when the saturated zone is thick (high water table, little variation in water-table elevation), acid conditions develop that break up the hydroxy-complexes and polonium is mobilized to produce high gross-alpha radiation in the wells.

15. It appears that **recharge wells can be utilized in the Central Florida Phosphate District** if simple precautions are taken. First, they should be located to avoid fracture traces or other locations where the "leached zone" is thick and water-table conditions favor acid water. Second, sampling protocols should be carefully designed, in conjunction with regulatory agencies, to avoid contamination from casing slimes.

16. Chemical modeling and raw data clearly indicate that **conditions for transport of polonium and lead exist in the Surficial aquifer, but not in the Floridan aquifer.** Therefore, **it appears that, with respect to the parameters measured, the quality of receiving Floridan aquifer waters is not jeopardized by the practice of interaquifer connector** (recharge) **wells.**

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

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I. INTRODUCTION

STATEMENT OF PROBLEM

Radiation in ground water is a problem of major concern in central Florida. The radionuclides of concern are the daughters of uranium-235, uranium-238, and thorium-232 (Figure I-1), all of which are naturally occurring, and are found throughout Florida. These radionuclides are relatively more abundant in phosphatic sediments (Osmond, 1964), including commercially-important phosphatic strata of the Hawthorn Group, than in most other strata in Florida, and they present potential water-quality problems to the phosphate industry as a result.

Uranium-238 is the most abundant of these and its decay products include several environmentally-important radionuclides. Guimond and Windham (1975) report that uranium-238 and its daughters constitute over 90% of the alpha activity in Florida phosphate deposits. Daughters of principal concern include radium-226, radon-222, lead-210, and polonium-210. These daughters have been found in ground waters in mined and unmined phosphate deposits (Kaufmann and Bliss, 1977; Texas Instruments, Inc., 1977; Upchurch et al., 1984; Humphreys, 1984; and others), and in coastal areas remote to mining or commercial deposits (Kaufmann and Bliss, 1977; Sutcliffe and Miller, 1981; King, 1983; Miller and Sutcliffe, 1985).

There have been several large-scale environmental assessments of radionuclide distributions in the central Florida phosphate-mining district, but none have related the radionuclides to the specific chemical systems of the aquifers present, and most have omitted several of the most important radionuclides (e.g., polonium-210 and lead-210). If valid judgments are to be made about the hazards and management of the radioisotopes in ground water in the district, it is necessary to understand the specific behavior of these isotopes in the aquifer chemical systems, and that requires detailed knowledge of ground-water pH, reduction-oxidation potentials, and chemical equilibria with rock materials. This report addresses these chemical systems, especially with respect to recharge wells.

The use of recharge wells by the phosphate industry is one of the areas of recent concern with respect to the environmental impact of phosphate mining. Some of the water utilized in the recharge process contains radionuclides in excess of state and federal drinking-water standards. In particular, recent data show that some recharge wells contain radium-226 activities in excess of the state and federal 5 pCi/l standard and/or gross-alpha activities in excess of the 15 pCi/l standard (Polk County Health Department, Office of Radiation Control, 1983). In many of the wells, radium-226 activities meet standards, but gross-alpha

activity does not. The gross-alpha radioactivity that is unsupported by radium has been called the "gross-alpha anomaly" (Oural et al., 1986). Oural et al. (1986) have shown that the excess gross-alpha radiation is, in part, a result of excess polonium-210, a radon-222 daughter. Oural et al. (1987, 1989) have shown that uncertainties inherent to the gross-alpha analytical method may also contribute to the "gross-alpha anomaly".

Recharge wells are an important and cost-effective water-management tool because they allow dewatering of the overburden (the Surficial aquifer) for mining, and mitigate water withdrawals from the deeper Floridan aquifer system. Because of popular and regulatory pressures, and in the absence of reliable data on the chemistry of well-water environments and the fates of potentially hazardous radionuclides, most of the phosphate companies have abandoned or temporarily closed existing wells and postponed permit applications for new ones until the radiation issues can be resolved to insure that environmental hazards are minimized. Because significant losses may accrue (1) to the environment if there is a radiation hazard, and (2) to the phosphate industry if recharge well use is deemed hazardous, it is important that the chemical behavior of uranium and its daughters be thoroughly understood.

Purpose of This Report

This document reports the results of a two-year study to investigate the chemical and physical environment of uranium daughters in recharge wells, with particular emphasis on polonium-210 and lead-210. The study also addresses the district-wide distribution of uranium decay products, major elements, and certain minor or trace constituents of waters in recharge wells. This report discusses the chemical causes of radionuclide mobilization in recharge wells and related aquifer systems. It also deals with a number of other, chronic water-quality problems that such wells experience. These chronic problems include violations of water-quality standards for color, turbidity, and iron.

In order to understand the reasons for radioactivity mobilization in the Surficial aquifer and recharge wells, a detailed study of the chemical environment of recharge wells, the Surficial aquifer, and upper Floridan aquifer was undertaken. This study has shown that specific radioactive isotopes (isotopes of uranium, radium, lead, and polonium) are mobilized under unique chemical conditions, some of which may be controllable. Spatial and time-series analyses of existing data from area recharge wells were conducted to determine the geologic and hydrologic conditions under which those unique chemical

conditions exist. A protocol for recharge-well location was developed to minimize radionuclide mobilization. As part of the development of the analytical procedures utilized in this report, significant modifications of the gross-alpha analytical procedure, and of well sampling methodology were developed.

Water-quality problems associated with color, turbidity, and iron are related to precipitation and entrainment of iron oxides in association with bacterial mats on the well casings and screens. Clogging of well screens by microbes and ferric hydroxides is also a widespread problem (LaMoreaux & Associates, Inc. 1978). The chemical processes associated with iron are included because they impact radionuclides in the wells.

To accomplish the goals of this project, the study was organized into five tasks. These tasks were:

Task 1 - Survey radionuclide activities in a regionally distributed subset of the 50 or so recharge wells that remain available in the Central Florida Phosphate District;

Task 2 - Obtain detailed chemical analyses on wells selected to represent the range of conditions in the wells sampled in Task 1;

Task 3 - Obtain detailed chemical analyses through time from recharge wells that have associated, aquifer-specific monitor wells;

Task 4 - Determine adsorption isotherms and precipitation reactions that fix uranium daughters; and

Task 5 - Model the aqueous chemical reactions, rock-water interactions, and dilution/dispersion that affect radionuclides in recharge wells and Surficial and Floridan aquifer waters.

Background

The Florida Institute of Phosphate Research funded a study by us (Oural et al., 1986) in mid-1983 to determine the cause of the excess gross-alpha radiation in recharge wells, and to investigate the suspicions of several phosphate-company representatives that sampling techniques, rather than water quality, cause the reported water-quality problems. Oural et al. (1986) focused on one recharge well so that water quality could be held relatively constant throughout the different tests (Oural et al., 1988). This well was located at the Kingsford Mine of the

International Minerals and Chemical Corporation (IMCC). The results of that study indicated that the problem results from a combination of inconsistent sampling procedures and relatively high polonium-210 activities in the sampled waters.

Oural et al. (1986) recommended sampling procedures to standardize data reporting. Adoption of standard sampling protocols will significantly reduce the apparent variability in radium and gross-alpha analyses and provide a basis for better management of water quality in the recharge wells. Some of the high gross-alpha activity values appear to be artifacts of the sampling and analytical procedures. For example, Oural et al. (1986) found that gross-alpha analyses are, at best, estimates of alpha activity. Polonium can be volatile and some appears to be lost in the typical gross-alpha analytical procedures (Oural et al., 1986). Gross-alpha activity measurements are also sensitive to the radon daughters remaining in the sample at the time of counting (Oural et al., 1989). Procedure standardization makes it easy to compare analyses and determine behavior of the radioisotopes, but it does not eliminate the problem of high polonium activities. High polonium activities remain a problem that needs to be properly evaluated before irreversible management policies are set.

The problem, however, may not be as serious as it seems, and it can possibly be mitigated because the activity of polonium can be significantly reduced in the well by either (1) dilution, (2) adsorption on rock material, (3) precipitation, or, possibly, (4) metabolic activity of microbial populations in the well. Similar reactions involving parent isotopes (e.g., lead-210) also govern polonium availability in the aquifers. To evaluate the potential for transport of polonium, and other uranium-daughter isotopes, into the Floridan aquifer by recharge wells, it is necessary to (1) identify the chemical and physical reactions that govern polonium mobility, and (2) determine if the results of Oural et al. (1986) are valid throughout the phosphate district. Management practices must include knowledge of the ultimate fate of these uranium daughters. If it can be shown that lead, polonium, and other radionuclides are immobilized outside of the recharge-well environment in Surficial and Floridan aquifers, then a valid basis for operating the recharge wells exists.

PREVIOUS WORKS

Previous work on the chemistry and distribution of radiation in aquifers in the phosphate district is scant and, for the most part, descriptive in nature. Few researchers have undertaken to model the chemistry of the aquifers involved and relate chemical conditions in those aquifers or in recharge wells to radionuclide mobility. Oural et al. (1986) give a detailed discussion of these

previous studies.

Equilibrium Studies

There are few studies that have attempted to work out the chemical interactions in Florida's aquifers. Back and Hanshaw (1970) and their colleagues at the U.S. Geological Survey have modeled rock-water interactions in the Floridan aquifer on a regional scale. Their work is too generalized to allow specific statements about chemical conditions and causes of radionuclide mobility in the district's ground water. Upchurch et al. (1984) modeled rock-water interactions in the Floridan aquifer in Manatee County with the goal of determining the causes of release of gross-alpha radioactivity when treated water is injected into a potable aquifer horizon. They suggested that desorption from rock surfaces as ionic strength increases is the most probable cause of the increase in gross-alpha radiation. Upchurch and Lawrence (1984) modeled the interactions of water with aquifer materials that occur with recharging of the Floridan aquifer in north Florida.

Radioactive Equilibrium

For any particular radionuclide in a decay series, there is a rate of production via decay of its immediate parent and a rate of loss via decay into the daughter. A condition of equilibrium is established if the entire series is contained in a chemically- and physically-closed system over a sufficiently long period of time. This decay equilibrium is maintained only if the system remains undisturbed.

In ground-water systems, chemical reactions, such as ion exchange, chemical complexing, and equilibration reactions with minerals, and physical processes, such as alpha recoil (Osmond and Cowart, 1976), can cause considerable departures from decay equilibrium. Because of their greater mobility, uranium and radium-226 are usually depleted relative to thorium-230 on the surfaces of soil or rock particles (e.g., minerals and particulate organics). Uranium-238, -234, and radium-226 are, therefore, present in greater abundance in ground water than thorium-230 (Bolch, 1979). Radon-222 enters water by alpha recoil and/or leaching (Osmond and Cowart, 1976), and, because radon is a chemically inert gas, it migrates. Polonium-210 and lead-210 also migrate to a lesser extent, and they show disequilibrium relationships with other isotopes in the uranium-238 series.

Uranium Chemistry and Migration

Uranium is an important trace constituent in marine phosphorite deposits. It is co-precipitated with carbonate fluorapatite (a k a francolite [$Ca_5(PO_4,CO_3)_3F$], the predominant mineral in marine phosphorite deposits) in low-oxygen, reducing environments. Uranium is both incorporated within the crystal lattice of the phosphate mineral (Altschuler et al., 1958) and as a sorbed or chemically-complexed phase on clay minerals and organics. Upon weathering in ground-water environments, uranium is generally conserved (Altschuler et al., 1956) and concentrated in the weathering profile. Thus, the so-called "leached zone", a weathering profile on the upper surface of the phosphatic strata in central Florida, contains elevated uranium concentrations (Cathcart, 1956).

Uranium, which is polyvalent, has complex solubility relationships depending on reduction-oxidation potential and water chemistry (Langmuir, 1977). In reducing waters, at 25°C and with compositions similar to Florida aquifer waters, uranous (U^{+4}) ion forms complexes with fluoride below pH's of 3-4. At higher pH's uranous-hydroxy complexes form. However, the solubility of uranium-oxide and -silicate minerals is low ($U<10^{-4}$ $\mu g/l$), so uranium remains below normal detection limits. In oxidized waters, uranium is hexavalent (U^{+6}). At pH's below about 5, uranyl ion ($(U^{6+}O_2)^{2+}$) and uranyl fluoride predominate. At pH's of 4-7.5, $UO_2(HPO_4)_2^{2+}$ is important. At higher pH's uranyl di- and tricarbonate species are important. Other uranyl complexes with fluoride, phosphate, sulfate, and carbonate form under these conditions, as well. Thus, formation of uranyl greatly increases uranium solubility.

At pH's between 5 and 8.5, uranyl minerals are at minimum solubility and uranyl complexes are readily sorbed on colloidal particles. Preferred sorption sites include organics, ferric hydroxides, Mn- and Ti-oxyhydroxides, and clays, in approximate decreasing order of sorption. Therefore, in environments with high particulate surface area to water volume ratios, such as in ground-water systems, uranyl complexes should tend to obey a sorption-controlled equilibrium with the water.

Radioactive decay influences the sorption-controlled equilibrium somewhat. While uranium chemical activity is determined by ionic strength, chemical species, Eh, and pH, the

distribution of isotopes of uranium is controlled by production or loss through radioactive decay, and decay events. Uranium-238 decays by alpha emission to thorium-234, which has a half life of 24.1 days. Thorium-234 decays to uranium-234 by means of two beta-particle emissions (^{234}Th——β——> ^{234}Pa——β——> ^{234}U). When a sorbed uranium-238 decays, therefore, there is a probability that the alpha particle will emerge towards the sorption surface. Energy transfer to the sorption surface by the massive alpha particle can disrupt the sorption binding energy and cause the daughter thorium-234 to be ejected into the water or air in the adjacent pore space. Therefore, with time, water should become relatively enriched with uranium-234 as compared to uranium-238. The activity ratio (A.R. = $^{234}U/^{238}U$) is a measure of this relative maturity. The activity ratio has been utilized by Osmond et al. (1974), Osmond and Cowart (1977), Cowart et al. (1978) and others to characterize Floridan aquifer flow systems and mixing relationships.

Radium Chemistry and Migration

Of the 16 known isotopes of radium, only two are important in Florida systems. These are radium-226, which is a decay product in the uranium-238 series, and radium-228, which occurs in the thorium-232 decay series. Radium-228 is rare owing to the scarcity of thorium in marine sediments and its relatively short half life. The Polk County Health Department, Office of Radiation Control (1983) analyzed for radium-228 in recharge wells and found that out of 71 wells, 76% had less than 1 pCi/l ^{228}Ra, 22.5% had 1-5 pCi/l, and 1.5% (1 well) exceeded 5 pCi/l. Radium-226 is present in larger quantities and is more widespread (see below) than is radium-228. Therefore, radium-226 is the isotope of principal interest.

Radium-226 forms by the alpha decay of thorium-230, and it has a half life of 1,620 years. The immediate decay product of radium-226 is radon-222. The radium ion is divalent and behaves somewhat like calcium or barium, so it can substitute for calcium in bone tissues. The combination of substitution in calcified tissues and alpha emission causes radium-226 to be carcinogenic and of major health concern. Radium forms strong bonds with sulfate and carbonate. Solubility of radium sulfate is quite low, and limits radium mobility in most systems. There is some indication that radium sulfate does not readily nucleate in the absence of barium (Gilkeson et al., 1983). When barium is present, it co-precipitates with radium sulfate and controls radium solubility through nucleation kinetics. The solubility-product constants of radium sulfate and barium sulfate (barite) at 25°C are similar, with a K_{sp} of $10^{-10.4}$ for radium sulfate and 10^{-10} for barite (Sillen and Martell, 1964; Gilkeson et al., 1983). Radium can also complex with soluble sulfate and carbonate

species. Based on data presented in this study, $RaSO_4^0$ appears to be the most probable complex in the aquifer systems studied.

Radium can enter aqueous systems by ion exchange, leaching, alpha recoil, and possibly microbially induced sulfate reduction'. Numerous studies have documented leaching of radium from weathering profiles (e.g., Cathcart, 1956; Burnett and Deetae, 1987). Changes in ionic strength of ground water in the coastal, salt-water/fresh-water transition zone of Florida have been suggested to cause competition for sorption sites on aquifer walls and encourage release of sorbed radium into ground waters (Upchurch, 1987). Microbial sulfate reduction has been documented in $(Ba,Ra)SO_4$ precipitates produced to remove radium from uranium-mine wastes (Fedorak et al., 1986). Barium, radium, and sulfide were products of the resulting reactions.

There have been many studies of the occurrence of radium in the aquifers of the Central Florida Phosphate District. Kaufmann and Bliss (1977) compared radium in ground waters in coastal areas of Florida with that of the district. Upchurch et al. (1979) compared major element chemistry of waters at the Kingsford Mine with radium-226 activities. Their study included a number of recharge wells. King (1983) and the Polk County Health Department, Office of Radiation Control (1983) included analyses of radium and gross-alpha radiation in ground waters in recharge wells in the district. Kimrey and Fayard (1984) analyzed several recharge wells in the district for radionuclides and other pollutants. Humphreys (1984) and Osmond et al. (1984) have also discussed mobility of radium in waters of the district, including recharge wells.

Radon Chemistry and Migration

Radon is a noble, gaseous element incapable of sorption or equilibration with mineral phases, and considerably greater disequilibrium occurs with respect to its precursors and its daughters than for most other isotopes in the uranium-238 decay series. Because of the great discrepancy between radon activities and the activities of both progeny and parent, radon was not determined in this study. However, the presence of radon in the aquifers is important to this study for three reasons:

1. It is highly mobile, especially with respect to transfer from the aquifer matrix to pore water or soil atmosphere,

2. It a primary means by which decay products within the decay series are redistributed in nature, and

3. It decays to lead-210 and polonium-210, which have relatively long half lives and are the are progeny of interest.

Migration of radon-222 determines the reservoirs of radon daughters from which lead-210 and polonium-210 are derived. Activities of radon in ground-water systems vary from a few picoCuries per liter to well over ten thousand. Therefore, the chemical and physical properties of radon are included below in order to assist in explaining the behavior of polonium.

There are numerous factors that affect the emanation of radon into ground water and soil atmospheres (Rama and Moore, 1984). At the rock or soil pore-space scale, radon activity in the pore water may be approximately equal to activity in the adjacent mineral phases. The reported activity of radon in pore environments is a few disintegrations per minute (dpm) per milliliter of pore fluid. This activity is comparable with that found in an equivalent volume of solids in the aquifer. Thus, ground water receives radon-222 effectively from a volume of solids roughly equal to that of the pore water. It has been further observed that the level of non-gaseous uranium- and thorium-series isotopes in ground water is three to five orders of magnitude lower than that of radon-222.

Belin (1959) related radon solubility to pH and residence time of water in contact with rock sources. Andrews and Wood (1972) have related radon in ground water to rainfall. They suggested that soil moisture dissolves radon, which is then transported in the direction of flow. Panik and Burnett (1987) documented losses of radon in phosphatic rocks of Florida. Dry phosphate rock losses of 3-74 dpm/g were detected. Average loss from dry rock was 18.5 dpm/g or 12.9% of the radium-226-generated radon. In wet rock losses were three times that of dry rock, with a mean of 43.2 dpm/g, or 31.5% of radium-226-supported radon. Therefore, leaching may be an important mechanism for introduction of radon to pore waters.

Rama and Moore (1984) attempted to understand the mechanism of release of radon and other uranium- and thorium-series isotopes into ground water. Tanner (1964) showed that approximately 20% of the radon-222 generated in the solids under investigation emanated into the water. Since the diffusion of radon out of the crystal lattice is negligible (Tanner, 1964), Rama and Moore concluded that radon must come out of the mineral phase in other ways. They proposed that rock or soil mineral grains are permeated with "nanopores", which have opening widths at the grain surface that are less than 1 micron. Radon, they suggested, is being released into these body pores and diffusing out into the intergranular pores, which have dimensions of tens to hundreds of microns. Radon-222 and other, non-gaseous isotopes

are introduced into the nanopores by alpha recoil from the pore walls in approximately equal quantities. Since the nanopore wall area-to-volume ratio is very high, the ionic isotopes are quickly sorbed within the pores, while the radon can pass outward into intergranular pores.. Migration of radon-222 and its progeny through nano-, micro-, and macropores is not well understood. The process, however, explains the accumulation of inert radon in pores in relatively high concentrations.

Radon can migrate from pore to pore under certain conditions and additional accumulation may result. In unsaturated soils, the radon is free to migrate by diffusion or advection, but the short half life of the radon generally limits migration to a few meters. Ogden et al. (1987) showed that radon emanation into homes increases with thickness of the unsaturated zone. In water-saturated soils, radon accumulates in the water because diffusion and degassing are restricted, and transport is limited to flow rates of the water and degassing at the water-table interface. Fluctuations in radon emanation rates were attributed by LeGrand (1987) to pumping action produced by fluctuations in water-table elevation. These processes are exacerbated when radium-bearing aquifer materials are fine grained (Andrews and Wood, 1972). Several workers (Tanner, 1964; King et al., 1982; Krishnaswami et al., 1982) have observed very large amounts of unsupported radon-222 gas in ground waters. The mechanisms of radon migration have been extensively studied because of their impacts on human health and uses in earthquake prediction (Chiang, 1977).

Israel and Bjornsson (1966) suggested that, in the vadose zone, diffusion controls radon migration. Diffusion coefficients may be as great as $1x10^{-2}$ cm^2/sec, depending on porosity, permeability, and soil moisture. They argued that in phreatic (saturated) environments the diffusion coefficient is less than $1x10^{-5}$ $cm^2/sec.$, therefore radon would decay through many half lives before it travelled 10 cm from the source. In phreatic environments, therefore, they suggested that fluid flow and changes in hydrostatic pressure control radon migration. Gingrich (1976) found evidence of radon migration over a distance of 100 m from uranium deposits, which suggests that mechanical transport in flow systems is of importance. Banwell and Parizek (1988) studied radon and helium (alpha particles) associated with fracture traces. Radon activities in ground water were found to be reduced in the vicinity of fractures because of enhanced ground-water flow associated with higher transmissivities in highly fractured rock. Radon activity is also correlated to H_2S, indicating two possible explanations. These are:

(1) In sulfide-rich, reducing waters radium-226, the parent of radon-222, is somewhat soluble and, possibly, transported to the vicinity of the well. Near the well, oxidizing

conditions prevail, and the radium is fixed by sorption on oxyhydroxides. Thus, a reservoir of radium accumulates near the well and H_2S and radon might co-exist.

(2) Deep aquifer waters exist in low transmissivity rocks and are somewhat stagnant. High H_2S waters and radon could co-exist in this environment and produce the observed correlation.

Banwell and Parizek (1988) also monitored helium-4, which comprises the alpha particles produced by uranium-series decay. Since helium-4 is a stable, noble gas, transport over long distances is possible, whereas radon-222 migration is limited by decay. High helium concentrations in ground water delineate the fractures, with highest concentrations above background within a half width of 0.4 km for the fracture-trace center. Their data clearly indicate that fractures have the potential for accumulation of reservoirs of uranium-series isotopes.

Kovach (1945) related radon gas emanation from soils to variations in atmospheric pressure. Rodgers (1954) and Chen et al. (1973) found that increasing temperature decreases radon solubility in water. Arndt (1953) described radon distribution in springs and found that about 40% of the radon is lost to the atmosphere within 4 ft. of the spring emergence.

Radon can diffuse upward through porous strata. The presence of fractures or other pathways of increased porosity and/or permeability in vadose environments encourages migration. Radon detection has, therefore, been used to locate faults and fractures (Stothart, 1948; Israel and Bjornsson, 1966, Chiang, 1977).

The effects of water flow on radon in systems influenced by operating wells is unknown. LeGrand (1987) described a conceptual model of radon-rich ground-water flow under in influence of well pumpage. He argued for hydraulic pumping of radon in the vadose atmosphere as the water table fluctuates, and for transport of the gas in water moving towards well screens or other discharge points. Therefore, there is good evidence that radon gas can migrate significantly in ground-water systems wherever a radon-concentration or hydraulic gradient exists.

Recharge wells may encourage migration and/or mechanical accumulation of radon gas. There are several possible consequences of recharge-well use that should be investigated. First, by proper selection of the screened interval in a recharge well, it may be possible to avoid naturally high radon, and polonium, horizons of the aquifer. Second, production of a cone of depression in the Surficial aquifer by artificial drainage,

alters a portion of the aquifer from phreatic to vadose. This change in regolith pore filling (water to atmosphere) may have an influence on the radon distribution and on the distribution of sorbed, reactive parents and daughters of radon.

Most of the emphasis on radon and radon daughters at state and national levels has been focused on radon in structures and migration out of the soil. Radon has been found in homes in many areas of Florida, and a state priority has been identified to develop criteria for evaluation of radon risks from measurements of soil radon prior to construction (Nagda et al., 1987). Early studies on the potential for radon in structures in Florida include Guimond et al. (1979), Roessler et al. (1980), and others.

Roessler et al. (1980) and Roessler et al. (1983) studied radiation in the Florida phosphate district. In both papers it was concluded that "debris lands" produced by former mining have the greatest potential for radon emanation into structures. More recently reclaimed lands appear to be less prone to radon hazards, but problem areas may exist. Methods of reclamation and site treatment, such as replacement of overburden over clay wastes and/or "leached zone" materials, were suggested to further reduce hazards. Natural, undisturbed land was found to be at less risk of high radon emanation rates than mined lands.

The most significant radon study in Florida was the statewide radiation study of Geomet, Inc. (Nagda et al., 1987). The Geomet study identified indoor radon risks based on both population and geologic criteria. It identified, by U.S. Geological Survey quadrangle area, regions where there is a probability of hazardous levels of radon emanating into structures. The study also made recommendations for dealing with the problem, including a recommendation that methods of characterizing soil radon be studied in anticipation of development of predictive criteria for high radon risks prior to construction. The study found that homes on reclaimed land in Polk County have 50% higher indoor radon levels that homes on mineralized, unmined lands and that soil radon levels are two times those on unmined lands (Nagda et al., 1987, Table 4-23). Correlation of soil radon with indoor radon for 2,749 homes was 0.52, which is statistically significant (α=0.01), but not strong (R^2 = .27, or 27% of total variability accounted for by the analysis). The correlation was improved to 0.80 when the sample set was limited to quadrangles with 4 or more homes tested.

In 1987, Roessler et al. compiled literature data on radon potential in Florida. They concluded that reclaimed lands have higher potential for radon hazards than do unmined lands based on data from 17 sites on mined land and 61 sites on equivalent, unmined sites. The Florida Department of Health and

Rehabilitative Services (1987) also compared mined and unmined lands for radon potential. Differences in radon activities in their data were less dramatic, and significant differences were not evident.

Bolch et al. (1987) and Nagda et al. (1987) have done most of the pioneering work on methods of characterizing soils for radon potential prior to construction. Bolch et al. (1987) studied radium-226 profiles in soils to a depth of 1.8 m. Near-surface radium-226 was found to be higher in mined lands than in undisturbed lands, where Plio-Pleistocene marine sands form overburden. Clearly, radium-226 profiles in shallow soils provide an indication of potential for radon emanation into structures and indicate that one cannot assume that all lands have the same potential for emanation.

Lead Chemistry and Migration

At the Eh and pH range of most natural waters, lead is divalent (Garrels and Christ, 1964; Hem, 1970). If carbonate is present, lead carbonate (cerussite, $PbCO_3$) is relatively insoluble and controls solubility of lead. Lead sulfate (anglesite, $PbSO_4$) and lead sulfide (galena, PbS) are also relatively insoluble and are likely to precipitate in oxidizing and reducing environments, respectively. Therefore, lead concentrations in natural systems are expected to be in the order of 2 μg/l or less.

Lead-210 is the longest-lived daughter of radon-222. It has a half life of 19.4 years, and it forms by the alpha decay of polonium-214. At the picoCurie activity level, lead-210 is present in such minute quantities that solubility constraints are minimal, unless other lead is present in the system. The longest half life of the four radon daughters that precede lead-210 is 27 min. (^{214}Pb), so lead-210 is quickly made available for transport by radon release into the water, and it may exist in solution in pores or sorbed on pore walls. Owing to the low solubility of both lead carbonate and sulfate/sulfide species, and ability to adsorb onto colloids, clays, and organics, lead is likely to be present in low quantities in most ground-water systems.

There are three sources of lead-210 in soils: (1) upward migration of radon-222, (2) radon-222 trapped in soil minerals, and (3) atmospheric fallout (Moore and Poet, 1976) from decay of radon in the open atmosphere. This fallout was estimated by Moore et al. (1973) to average 0.8 dpm/cm^2 yr in the western U.S. Lead-210 was found to decrease in concentration with depth in soils. The high lead-210 content near the soil surface is partly due to upward migration of radon-222 and partly due to fallout.

Percolating ground water transports some of the fallout-generated lead downward.

Lead-210 essentially controls the fate of its granddaughter, polonium-210. Cowart et al. (1987) compared lead-210 and polonium-210 in aquifers in central Florida. They found that polonium-210 activities greatly exceed lead-210 in water and that lead-210 averages about 3% of the polonium-210 activity. Thus, most of the lead-210 is present as a sorbed or precipitated phase in or on the aquifer matrix, not as an aqueous species.

Polonium Chemistry and Migration

Polonium is a radioactive, polyvalent metal with a number of possible valence states. In natural conditions only the +4 and +2 states are likely, with the +4 state being the most common. The half life of polonium-210, the longest-lived isotope of polonium, is 138 days. Decay of polonium-210 is by alpha emission, and the daughter is stable lead-206. "Crystalline" and colloidal phases can be precipitated in the laboratory, but intense radioactive decay rapidly destroys crystal structure and heats the solid (Bagnall, 1957), which increases solubility. No work has been done on the phases present in natural systems.

In reducing environments, PoS has been shown to precipitate at elevated temperatures with a solubility constant of 10^{-29}. PoS precipitates in the presence of H_2S in dilute acids. It is insoluble in HCl, but can be oxidized.

In oxidizing environments, PoO_2 and $Po(OH)_4$ are the most likely solid phases (Bagnall, 1952; Sedlet et al., 1964). Polonium dioxide is structurally like the uranyl radical. It is relatively insoluble in water, ammonia, or alkali carbonate solutions. Polonium dioxide is soluble in HCl and other hydrogen halides, and the result is volatile $PoCl_6^{2-}$ and $PoCl_4^{2-}$. Volatility of polonium chloride and other halides, is a constraint in analysis (Bernabee and Sill, 1982; Oural et al., 1986). Polonium dioxide is also soluble in nitric acid, with the formation of several nitrate complexes. Polonium hydroxide forms in aqueous, alkaline environments. The hydroxide is slightly soluble in dilute sulfuric acid according to the reaction

$$Po(OH)_4 + 2H_2SO_4 \rightleftharpoons Po^{4+} + 2SO_4^{2-} + 4H_2O. \qquad (I.1)$$

The solubility product constant for the dissociation of polonium hydroxide in water at 25°C

$$Po(OH)_4 \rightarrow Po^{4+} + 4OH^-$$

(I.2)

is 10^{-37} (Ziv and Efros, 1959), so equilibrium activities in pure water would be in the picoCurie range. Polonium hydroxide is also slightly soluble in phosphoric acid. Tetravalent polonium complexes with a number of organic acids, including acetic acid, formates, oxalates, and tartarates. Stability of the complexes increases with acidity of the compound. Therefore, in ground-water systems there is the potential for formation of trace quantities of polonium complexes with sulfate, phosphate, nitrate, chloride, fluoride, and organics.

An important property of polonium is its ability to form "radiocolloids" (Sedlet et al., 1964). Radiocolloids are anomalous particles that form in solutions of radioactive isotopes at concentrations well below equilibrium with solid phases. Thus, the radiocolloid behaves like a solid and is filterable, although the isotope is present in insufficient quantities for chemical nucleation. In ground-water systems radiocolloids may be mechanically filtered as water passes through pore throats in the aquifer or it may be filtered after sample collection. The behavior of polonium as a radiocolloid is controversial. There is not any doubt that radiocolloids form, but reports of the conditions of colloid formation are inconsistent. Acidity of the solution seems to control colloid formation. Sedlet et al. (1964) summarized the literature on polonium radiocolloids. They reported that, in neutral, or nearly neutral, solutions (pH 6-8), polonium is soluble and only 0-20% is filterable on 0.045μm membranes. At pH's near 1 and 12, polonium is nearly completely filtered. In contrast, Haissinsky (1964) reported that polonium acts as a radiocolloid at pH's above 3. Thus, polonium solubility is pH sensitive, but the specific behavior is debatable.

Hansen and Watters (1971) characterized polonium-210 solubilities in soils, including 8 samples from 5 Florida soils. They used a polonium dioxide tracer and found that polonium is fixed in soils, especially in fine-grained soils. Distribution coefficients (K_d) were calculated from the ratio of polonium fixed on the soil sample to that remaining in solution. Distribution coefficients for Florida soils are as follows:

Soil	Horizon	K_d
Adamsville	A_1	26 ± 2
Blanton	A_1	35 ± 3
Lakeland	A_1	25 ± 2
Leon	A_1	17 ± 1
	A_2	15 ± 0.6
	B_h	55 ± 17
	C	77 ± 29
Ruskin	A_1	17 ± 1

These distribution coefficients are low in comparison with sandy loams from elsewhere, where K_d's of 500 to 7000 were reported. However, they do indicate that polonium is effectively immobilized in Florida soils. The highest level of fixation is in the B zone of the Leon sand, which is rich in ferric hydroxides and organics. The lowest levels of fixation are in fine quartz sands of the A_1 zones of the Leon and Ruskin soils. Hansen and Watters (1971) also determined regression equations to predict the distribution coefficients as a function of soil pH and silt content. The data base for the regression equation includes soil samples from all horizons and a diversity of locations throughout the U.S. The equations they obtained are

$$\ln K_d = 3.2 + (0.046 \pm 0.007)(\%\ silt) \qquad \text{(I.3)}$$

for A horizons only, and

$$\ln K_d = -1.3 + (0.034 \pm 0.007)(\%\ silt) + (0.88 \pm 0.20)(pH) \qquad \text{(I.4)}$$

for all soils. The multiple correlation coefficient (R) for equation I.3 is 0.84 (15 df), and R is 0.74 (48 df) for equation I.4. An equation similar to I.4, but using percent clay rather than percent silt, has an R of 0.65, so sorption on clay is somewhat less important than the presence of the silt fraction, which often includes the oxyhydroxides. Since both pH and silt are deemed important in predicting the distribution coefficient, and the correlation (slope) with pH is positive, it appears that sorption on clays is less important to fixation of polonium than is precipitation of radiocolloids and/or co-precipitation of polonium hydroxide with iron and/or aluminum oxyhydroxides.

Factors that mobilize polonium in ground water are unknown. Possible causes of mobilization include (1) decay of soluble lead-210 to produce polonium-210 at levels below equilibrium concentrations, (2) "dissolution" of radiocolloids with change in pH, (3) mobilization as an organic complex, (4) mobilization as an inorganic chemical complex, (5) changes in solubility with reduction or oxidation, (6) ion exchange reactions (desorption)

between water and aquifer matrix, and (7) bacterial metabolism. Decay of lead-210 to polonium-210 is by beta emission, so recoil is not a significant factor in introduction of polonium into ground water.

At the concentrations typical of ground-water systems, lead salts and sorbed lead represent trivial masses in aquifer systems. Decay of lead-210 to polonium-210, therefore, could result in small amounts of a chemically unstable, polonium compound that could go into solution if the water is undersaturated with respect to ithe compound. Also changes in pH, or other chemical parameters, can lead to changes in solubility of the compound. For example, polonium hydroxide can be used to illustrate these conditions. Assuming that the dissolution reaction of polonium hydroxide is

$$Po(OH)_4 \rightleftharpoons Po^{4+} + 4OH^-, \qquad (I.5)$$

and the K_{sp} relationship at 25°C is

$$K_{sp} = 10^{-37} = a_{Po^{4+}} \cdot a_{OH^-}^{4+}, \qquad (I.6)$$

where a is the activity of the species and the activity of particulate polonium hydroxide is assumed to be 1, then the equilibrium polonium activity can be calculated for any OH^- activity. Note that the assumption that the activity of particulate polonium hydroxide is 1 causes underestimation of the particle solubility. Activities should exceed 1 because of (1) the small size and high surface-free-energy of colloid-sized precipitates, and (2) the disruption of order in the interior of the precipitates during radioactive decay.

Examination of equation I.6 indicates that the solubility of polonium hydroxide is quite sensitive to hydroxyl activity, and, by extension, pH. Low hydroxyl activities are associated with low pH's, and, therefore, high solubility of the hydroxide. Conversely, high hydroxyl activities encourage polonium hydroxide precipitation. Assuming that there is excess polonium hydroxide available so that equilibrium can be obtained, and assuming a typical range of hydroxyl activities of 10^{-6}-10^{-3} at 25°C, dissolved polonium radioactivities at chemical equilibrium range from 10^{-6} to 10^{+6} pCi/l. The existing reservoir of polonium hydroxide in most aquifer systems is, however, insufficient to allow radioactivity to rise to 10^{+6} pCi/l, but Burnett et al. (1987) have documented polonium activities in excess of 10^{+3} pCi/l. Clearly, polonium-210 is likely to go into solution in acid waters, while it is precipitated in basic solutions. Polonium activities in water are, however, ultimately limited by

the concentration and decay constant of the parent lead-210 in the system.

Inorganic and organic complexing have not been adequately addressed in the literature. No literature on natural, inorganic complexing can be found. Laboratory studies (see above) clearly indicate that halide, nitrate, and other complexes are possible. Harada et al., 1989 have found a correlation of polonium activity with sulfide oxidation and a relationship with ability to recover polonium in the laboratory. They speculate that complexing and microbial activity may play roles in mobilization of polonium, with highest polonium mobilities in reducing, sulfide-rich waters. Oural et al. (1987, 1989) adjusted the pH of organic-rich ground water to separate humic and fulvic fractions. They estimated that as much as 89% of the recoverable polonium was associated with the fulvic fraction. Their studies suggest that organic complexing may also be important in polonium mobilization.

There is little direct evidence that ion exchange or reduction/oxidation reactions play a role in polonium mobilization. Ion exchange is well documented for major elements in ground-water systems, and the process can be expected to occur, although the low chemical concentrations of polonium in ground-water systems reduces the probability of exchange. Upchurch (1987) suggested that exchange may play a role in polonium mobilization in coastal aquifers; however, his data were circumstantial. The predominant valence state of polonium over the range of conditions prevalent in most aquifers is +4 (Bagnall, 1957). Existing literature does not indicate significant reduction or oxidation of polonium in such systems. Upchurch et al. (1987) suggested that variations in water saturation in the Surficial aquifer in central Florida may lead to reduction/oxidation reactions and variation in polonium mobility. Harada et al. (1989) found that polonium solubility, as indicated by the ability to filter on an 0.2 μm filter, is highest in reducing, sulfide-rich waters, and that particulate polonium increases as sulfide is oxidized, perhaps by sulfur bacteria.

Polonium-210 has been shown to be present in large quantities in Surficial aquifer waters in Florida (Oural et al., 1987; Chin et al., 1987; Upchurch et al., 1987; Burnett et al., 1987; Cowart et al., 1987; Harada et al., 1989). Chin et al. (1987) found that polonium in the Central Florida Phosphate District can be well above the state and federal Maximum Contamination Limit (MCL) of 15 pCi/l gross-alpha radiation, with a maximum of 500 pCi/l in filtered water and 2,500 pCi/l in unfiltered water. Polonium chemistry and migration modes in the Central Florida Phosphate District have been characterized by Upchurch et al. (1987). They suggested that polonium-210 mobility

is controlled by complexation with soluble organics and maintenance of a saturated zone with net chemical reduction of the polonium to its divalent state. Upchurch (1987) compared uranium-daughter occurrences within aquifers in central Florida and found that high levels of polonium-210 are limited to sand aquifers that are characterized by organics and variable redox potentials. In Lee County, Florida, high polonium activities were limited to the Surficial aquifer and the upper Hawthorn Group sandstone aquifer. Burnett et al. (1987) and Cowart et al. (1987) reported on a private well in southeast Hillsborough County, Florida. They found polonium-210 in excess of 2500 pCi/l in unfiltered samples and 500 pCi/l in filtered. These values represent the highest polonium activities in ground water known.

Iron Chemistry and Migration

While understanding iron behavior in the aquifer systems and recharge wells is not a major goal of this study, much data is available and some observations may be helpful. Iron and sulfur are associated with bacterial activity in ground waters, so color associated with ferric hydroxide precipitates, iron colloids, and bacterial activity cause related problems. For example, Gordon Palm and Associates (1983), in a water quality survey of the Central Florida Phosphate District, found that 16% of the shallow-well samples from mine areas violated the water-quality standards for color and 20% violated standards for iron. In deep wells, 13% violated the color standard and 10% violated iron standards. Recharge wells are particularly susceptible to problems. The well screens plug with bacterial mats and ferric hydroxides, and color and iron standards are frequently violated.

Iron has two valence states, +2 and +3, and is highly susceptible to reduction/oxidation reactions. Hem (1970) has summarized the stability relationships of iron in sulfur-rich systems. In general, the sources of iron in ground waters include (1) oxidation of pyrite (FeS_2), (2) oxidation of organic compounds, and (3) dissolution of iron oxide and silicate minerals.

In general, in acid, reducing waters $FeS_{2\,solid}$ is the stable iron phase. In acid, oxidizing waters ionic Fe^{2+} and Fe^{3+} should go into solution. In basic, reducing waters, pyrite ($Fe^{2+}S_2$) and siderite ($Fe^{2+}CO_3$) are stable solids. And, in basic, oxidizing waters, amorphous $Fe(OH)_3$ should precipitate and then mature to goethite ($FeO(OH)$). In the ground-water systems under investigation, reducing environments tend to mobilize iron as the ferrous (2+) ion. In oxidizing waters, ferric hydroxide precipitates. The color problem is a result of this

precipitation.

Iron is regularly reported in water-quality data from the phosphate district. However, no published studies exist that deal with the problem. LaMoreaux and Associates (1978) conducted a short study of iron in recharge wells. They found a crude relationship between reduction/oxidation potential and iron precipitation.

Sulfur Chemistry and Migration

Rightmire et al. (1974) examined the origin of sulfates in the Floridan aquifer on the basis of sulfur isotope composiiton. They found that sources of sulfate include (1) recharge of sulfate-rich maritime rainfall, (2) dissolution of intraformational gypsum at depth, and (3) mixing with ocean-like saline water. The maritime rainfall component, of course, passes through the Surficial aquifer and constitute a major source of sulfate in that aquifer as well. Isotopic fractionation during sulfate reduction leads to a relative increase in $\delta^{34}S$ in the data. Thus, sulfate reduction in the Floridan was documented. Rye et al. (1981) studied the isotopic composition of sulfide in the Floridan. They found that sulfide in the Floridan results from slow, in situ microbial sulfate reduction. Sulfide concentrations increase down flow paths and with increased residence times. The source of the sulfate in long flow path waters was attributed to dissolution of gypsum in the underlying confining beds. Waters in the study area were found to be low in dissolved sulfide and sulfate as a result of short flow paths and residence times. Harada et al. (1989) studied the relationship of sulfide oxidation in the Surficial aquifer (?) to polonium mobilization. They suggested that polonium is mobile in waters in which sulfide is present. Upon oxidation of the sulfide to sulfate the polonium forms filterable colloids.

REGIONAL HYDROGEOLOGY

The Central Florida Phosphate District can be characterized by three hydrostratigraphic horizons, using the terminology developed by the Southeastern Geological Society, Ad Hoc Committee on Florida Hydrostratigraphic Unit Definition (1986). These are: (1) the Surficial aquifer system, (2) a complex of locally-confined aquifers and semipermeable layers of the Miocene Hawthorn Group, which is called the Intermediate aquifer system and confining unit, and (3) the Floridan aquifer system (Hutchinson, 1978).

Lithologic summaries of these horizons are based on core

data obtained as part of the monitor-well program of this study. Core logs are presented in Appendix A.

Surficial Aquifer System

The Surficial aquifer consists of clean quartz sand to clayey sand of eolian and marine origins. The age of these deposits varies from Plio-Pleistocene to Recent. Organic and ferruginous B horizons and hard pans are locally present. Near the base of the aquifer, phosphate grains may be reworked from the underlying Bone Valley Member of the Peace River Formation (Hawthorn Group). The thickness of the Surficial aquifer is highly variable, and ranges from a few centimeters to over 75 m (Stewart, 1966) in Polk County. In the study area, the thickness of the surficial deposits that overlie the confining unit ranges from 7 to 15 m (Wolansky et al., 1979). The Surficial aquifer constitutes the principal portion of the overburden removed during mining. Cathcart (1963, 1966) mapped overburden thicknesses in the study area, and found that overburden thickens near fractures and other depressions in underlying units.

Cathcart (1963, 1966) also characterized the thickness and extent of the "leached zone". The "leached zone" is a discontinuous weathering profile developed on top of the underlying phosphatic material of the Hawthorn Group. It is enriched in aluminum phosphate minerals, such as wavellite ($Al_3(PO_4)_2(OH)_3.5H_2O$) and crandallite ($CaAl_3(PO_4)_2(OH)_5.H_2O$), and in uranium and uranium daughters. The "leached zone" has variable thickness, with thickness tending to increase over depressions in the underlying material. Some linear and circular thickening patterns appear to be related to development of alluvial dolines (sediment-choked sinkholes) and fractures. Where present, the "leached zone" forms the base of the Surficial aquifer, and it has the potential of introducing high levels of radioactivity, fluorides, and other unwanted constituents to ground waters.

The Surficial aquifer is unconfined, and receives recharge directly from precipitation and from surface-water bodies. It is seldom utilized as a source of potable water, and the primary use is small, low-yield domestic wells.

The sand, which comprises most of the Surficial aquifer, is not cohesive and tends to slump when water saturated. Because of the impact of slumping on mine cut stability and because of excess water that the Surficial aquifer transmits to the mine cut, it is desirable to dewater the Surficial aquifer prior to mining. This is one of the primary motivations for use of recharge wells to dewater the aquifer in lands scheduled to be mined by the phosphate industry. Recharge wells are designed to

extract water from porous and permeable sandy zones in the Surficial aquifer by means of gravity flow through slotted casing (Figure I-2). The slots are located above the underlying confining unit and/or "leached zone" to limit potential contamination of receiving waters in the Floridan aquifer.

In general, Surficial aquifer waters are acid, lower in dissolved ions, and lower in radium-226 than the other hydrostratigraphic horizons. The water is sometimes colored with organics, and has the odor of sulfides, which indicates reducing conditions (Upchurch et al., 1979a,b). Radon-222 migrates upward from the phosphatic strata below and enriches the Surficial aquifer in both radon and radon daughters, such as polonium-210.

Intermediate Aquifer System and Confining Unit

The Intermediate aquifer system and confining unit includes the Peace River Formation and portions of the underlying Arcadia Formation (Hawthorn Group, Miocene to Pliocene). The entire section is phosphatic to varying degrees. The Peace River Formation is predominantly clastic in texture, and is composed of sand and gravel beds, argillaceous sands, silts, and clays. Silt and clay beds include siliciclastic particles and silt-sized dolomite. The Peace River Formation includes the Bone Valley Member (previously the Bone Valley formation) and phosphate rich zones which represent the "ore" or "matrix" mined by the phosphate industry. The Arcadia Formation also contains extensive clastic horizons, but it is characterized by dolostone and limestone. The Tampa Member (old Tampa formation) occurs near the base of the Arcadia. These carbonate units have developed varying degrees of cavernous porosity. The Tampa Member has a clay unit near its base that separates the unit from the underlying Floridan aquifer. The "leached zone" is usually included with this horizon. Thickness of the confining unit ranges from 30 to 120 m (Buono et al., 1979).

The coarse clastic units and cavernous carbonate units serve as local aquifers. Artesian conditions exist in many of these horizons. The individual production zones in the clastic part of the system are discontinuous and limited in extent. These horizons have been called the "uppermost artesian aquifer" (Stewart, 1966). The cavernous carbonates may be more extensive. The Tampa Member serves as a local aquifer throughout the phosphate district. It has been called the "upper Floridan aquifer", "Intermediate aquifer system", "secondary artesian aquifer", or the "shallow artesian aquifer" (Southeastern Geological Society, Ad Hoc Committee on Florida Hydrostratigraphic Unit Definition, 1986). The intermediate-aquifer portion of the Tampa Member is separated from the underlying Floridan aquifer system by a thick, regionally

extensive clay.

The "uppermost artesian aquifer" is seldom used as a source of water because of its limited extent. The "secondary artesian aquifer" is widely used as a source of industrial and potable water. Head distribution is generally below the water table and above the potentiometric surface of the underlying Floridan aquifer. Depth to the "secondary artesian aquifer" is variable, with depths averaging 45 to 60 m.

Recharge wells are cased through the clastic section of the Intermediate aquifer and confining system (primarily the Peace River Formation) to avoid problems of caving, turbidity, and contamination of the underlying aquifers. Waters in the "uppermost artesian aquifer" are typically rich in sulfides, iron, fluoride, phosphate, and, possibly radium and polonium (Upchurch et al., 1979a,b; Upchurch, 1987). The wells are commonly cased into solid dolostone or limestone of the Arcadia, and they are open hole well into the underlying Floridan aquifer. Cavernous zones in the "secondary artesian aquifer" of the Arcadia, therefore, receive discharge from the Surficial aquifer, and in many of the wells reported upon in this report the "secondary artesian aquifer" may be taking a significant portion of this discharge. Waters of the "secondary artesian aquifer" have a typical carbonate-aquifer chemistry, with calcium, magnesium, bicarbonate, and sulfate/sulfide. Fluoride may be slightly elevated and radium-226 may be present at activities near the 5 pCi/l MCL.

Floridan Aquifer System

The Floridan aquifer system is the principal aquifer in Florida, and it is one of the most productive aquifers in the world. It includes limestones, with minor dolostone and clastic strata, of Miocene to Eocene age. Formations involved include the lowermost Arcadia Formation, Suwannee Limestone, Ocala Group, Avon Park Limestone, and Oldsmar Limestone. The gypsiferous Cedar Keys Limestone forms the lower confining unit at the base of the aquifer.

Depth to the top of the Floridan aquifer varies from -15 to -75 m MSL in the study area (Buono and Rutledge, 1979). Depth to the base of the aquifer ranges from -365 to -425 m MSL (Wolansky, Barr, and Spechler, 1979). The Floridan is primarily a fractures and karstic aquifer, with flow through cavernous porosity, fractures, and, to a lesser extent, intergranular and moldic porosity. The aquifer is confined and artesian in the study area, and water rises in wells in excess of 30 m above the top of the aquifer in many areas. The potentiometric surface is below that of the Surficial aquifer, so localized recharge to the

Floridan by means of leakance through the confining beds and by direct connection in active fractures and/or karst conduits occurs. Recharge wells take advantage of this head difference to drive downward discharge of the Surficial aquifer.

Water quality in the Floridan is variable. The water is dominated by calcium, magnesium, and bicarbonate (Back and Hanshaw, 1970), with significant amounts of sulfate. The pH averages 7.6 in the study area. Portions of the upper aquifer that are highly fractured and permeable have relatively low ionic strengths, sulfate, and radium. Upper Floridan aquifer waters in low permeability blocks and deep aquifer waters are elevated in sulfates, radium, and ionic strength (Upchurch et al., 1979a,b).

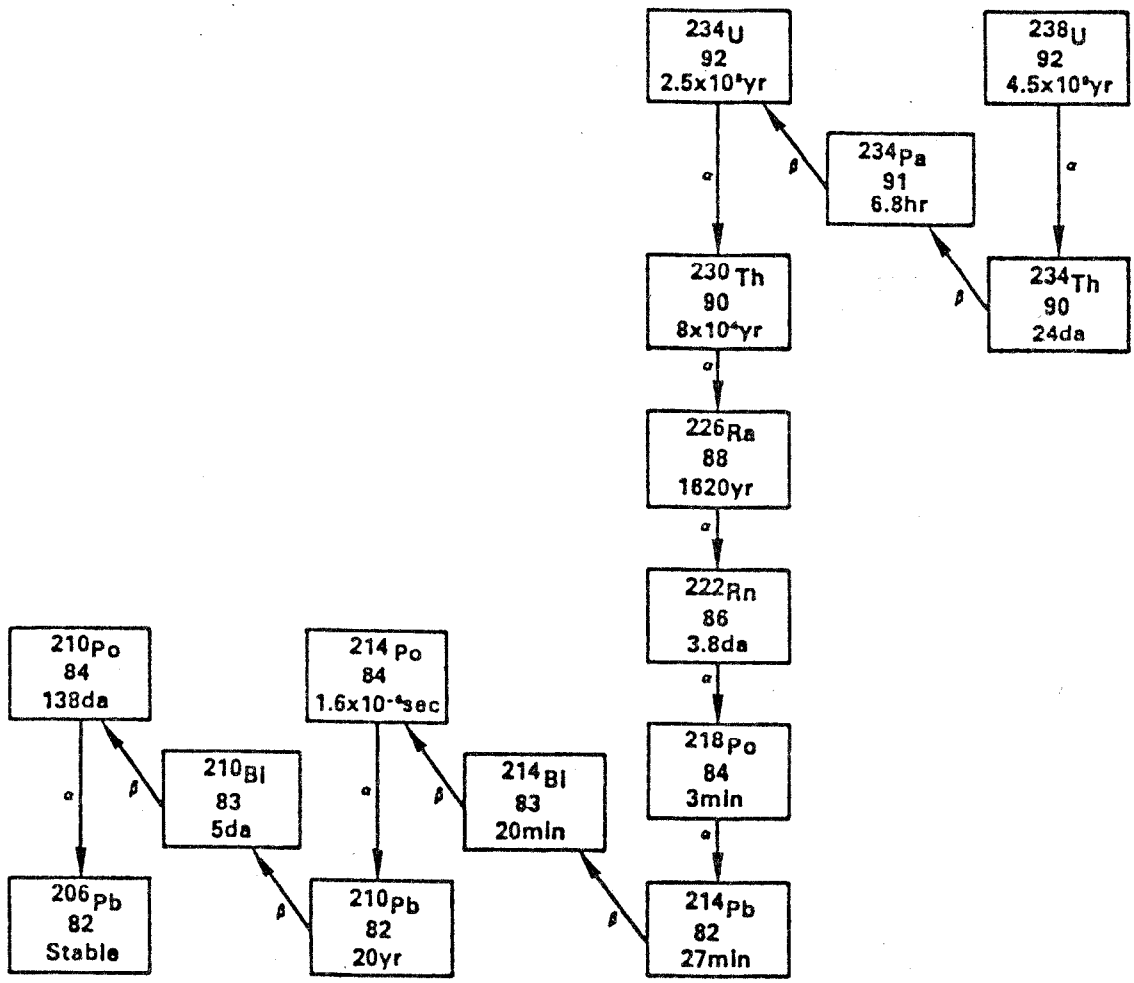


Figure I-1. Uranium-238 decay series.

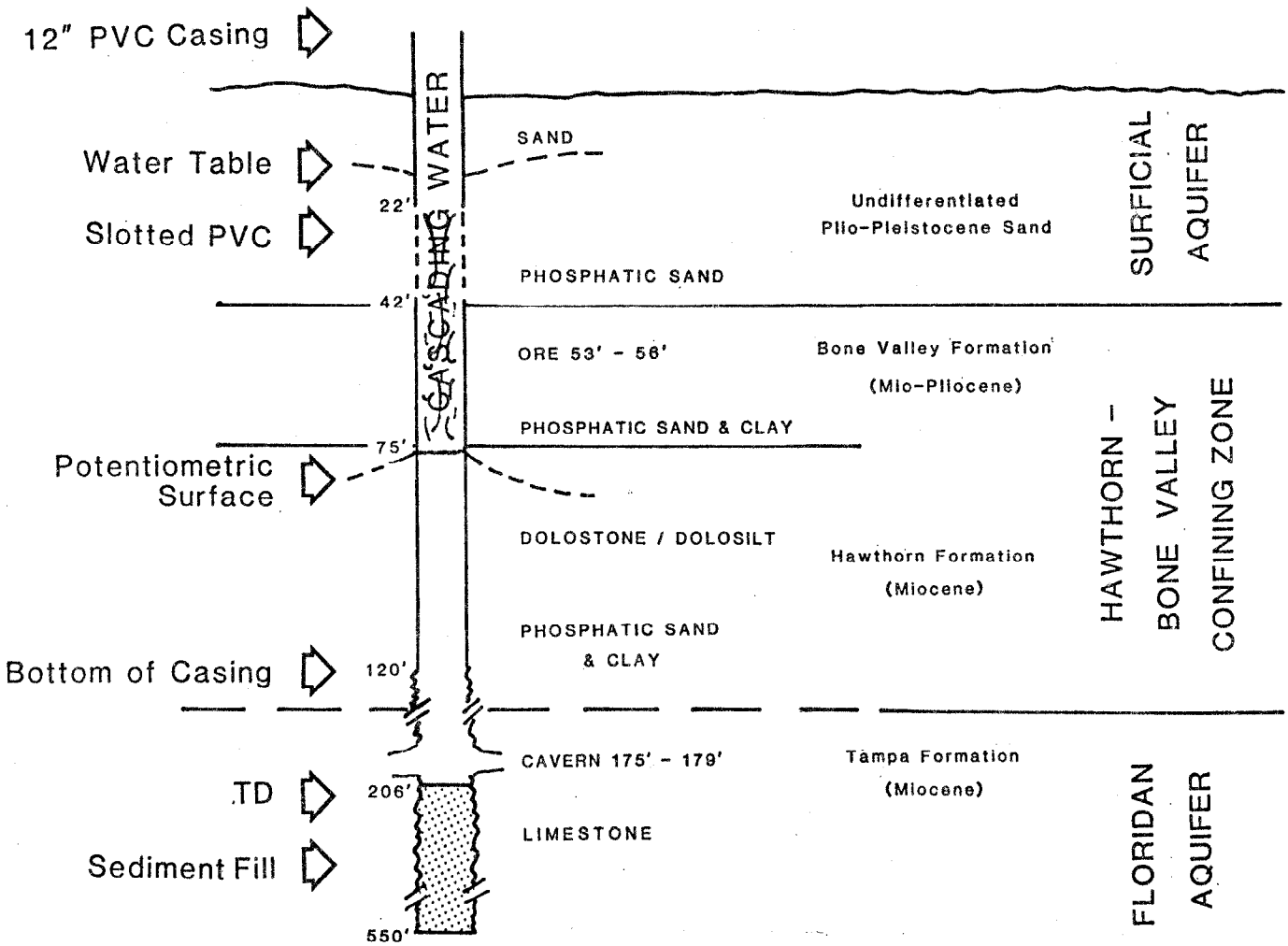


Figure I-2. Diagram showing the design of recharge well KR-98B and the hydrostratigraphy of a typical recharge well.

II. METHODS

SAMPLE COLLECTION

Well Selection

Two sets of recharge-well data were utilized as part of this study. A set of 30 existing wells was selected for detailed chemical analysis, and a larger set of 270 historical well records was used for time-series analysis. The set of 270 wells is based on radiation records (gross alpha and radium-226 activities) submitted to the Southwest Florida Water Management District by the phosphate companies from 1976 through 1986. This data set includes virtually all recharge wells in existence during that 10-year interval. The 270-well data set is discussed in Chapter V.

The number of recharge wells available for the chemical study was limited by three factors. First, there were only about 50 wells remaining in the district, and many of them are clustered, so areal coverage was reduced. Second, wells scheduled for abandonment were excluded in order to maximize the time available for sampling. Third, a few companies declined us access to wells. Given these constraints, 31 recharge wells were selected for analysis. Locations of these wells are listed in Table II-1.

Monitor Wells

In addition to sampling of the recharge wells, monitor wells were installed adjacent to several recharge wells. Four monitor wells were installed for us at recharge well KR-98B in January, 1984 by International Minerals and Chemical Corp. These wells, which consist of 4 in. (0.10 m) PVC, have been described by Oural et al. (1986). Deep and shallow monitor wells were installed both up-gradient and down-gradient from the recharge well. Regional gradient is from northeast to southwest. The shallow wells, which are designated KR-98B-US and -DS (Up-Shallow, Down-Shallow), were cased to a depth of 0.6 m (20 ft.), and had 0.6 m of slotted PVC screen. The screen was set at the same horizon as the screen in recharge well KR-98B. The deep wells were completed into the upper portion of the Floridan aquifer with total depths of 63 m (207 ft.) for the south, down-gradient well (KR-98B-DD), and 63.7 m (209 ft.) for the north, up-gradient well (KR-98B-UD). In both deep wells, casing was set and cemented to 36.6 m (120 ft.), which is within the Arcadia Formation dolostones. The open-hole portion of the deep monitor wells coincides with the portion of the recharge well that was receiving the falling water. In fact, geophysical logs (Oural et al., 1986) indicate that a cavernous zone at 53-54.6 m (175-179 ft.) below land surface is the primary

receiving zone and that the recharge well was "silted up" to a depth of 63.7 m. Shallow monitor wells were intended to be within the "cone of depression" of the recharge well and were within 8 m of the recharge well. Deep wells were designed to be within the "cone of impression" of the recharge well and were within 30 m of it. Geophysical logs of recharge well and monitor wells were provided by the Florida Department of Environmental Regulation, Southwest Florida Water Management District, and International Minerals and Chemical Corp. The recharge well and all monitor wells were plugged and abandoned in the summer of 1988 just prior to mining. Appendix A gives lithologic logs of KR-98B.

The Florida Department of Environmental Regulation installed monitor wells on recharge wells KR-83 and KR-127 (Table II-1) in cooperation with this study. These wells were installed in early 1985. Each recharge well had a Surficial aquifer and a Floridan aquifer monitor, each located to be within the influence of the recharge well. Notation used to indicate the monitor wells is -S for Surficial aquifer monitor and -D for Deep aquifer monitor. All monitor wells are within 30 m of the recharge wells. Shallow monitor wells are 0.05 m (2 in.) in diameter. KR-83-S has 6 m (20 ft.) of black-iron casing and a 1.5 m (5 ft.) stainless screen. KR-127-S has 8.5 m (28 ft.) of black iron casing and 1.5 m (5 ft.) of wound-wire stainless steel screen. Pea gravel pack was used opposite the screen and the casing was cemented to the land surface. Deep monitor wells are 0.10 m (4 in.) in diameter. KR-83-D was drilled to a depth of 80.8 m (265 ft.) and was cased to 39 m (128 ft.). KR-127-D was drilled to 82.8 m (271.75 ft.) and cased to 52.7 m (173 ft.). The wells are "open hole" below casing, which is cemented to the land surface. Casing is "Tri-Lock" PVC, with the deepest 1.5 m (5 ft.) consisting of stainless steel casing in order to allow seating of a packer when using bladder pumps for sampling. The deep monitor well at KR-127 can be shown to be in direct communication with the recharge well as cavitated gas is forcibly discharged from the monitor well. These well complexes were removed and the wells were abandoned prior to mining in 1989.

All wells were developed by air lift and allowed to stabilize for at least 4 weeks prior to sampling.

Sampling Protocols

Recharge wells were sampled at several horizons. Oural et al. (1986) showed that there is a minor change in water chemistry from falling water, to standing water, to bottom of the well. These changes are a result of mixing of recharging water with host water and, possibly, leakage from the Intermediate aquifer into the recharge-well bore. After examining water chemistry and difficulties in obtaining valid samples from falling water, it

was determined that a sample of standing water, just below the potentiometric surface or peak of the "cone of impression", and a sample from the bottom of the well would suffice to characterize "end-member" compositions in the recharge wells.

Because of having to pass through the cascading water, it is difficult to operate bladder pumps in the recharge wells, so stainless steel bailers with PVC check valves were designed. The bailers were constructed with 0.04 and 0.10 m (1.5 and 4.0 in.) diameters. The bailers were designed with a seated, conical, PVC valve in either end of the stainless-steel tube. Tension on the rope from which the bailer was suspended was used to keep the valve seated during lowering and raising of the bailer. The check valves were opened by releasing tension when the bailer was at the desired depth and closed for retrieval of the sample, thus preventing contamination. The top of each bailer was designed to shed water and debris from the well casing. In spite of the closed bailer, considerable difficulty was encountered in micropore filtering the water samples owing to extreme turbidity. The turbidity was a result of ferric hydroxide and microbial filaments scraped off the casing as the bailer was lowered by hand. It was discovered that use of a tripod to center the bailer over the recharge well and a gasoline-powered "cat-head" to smoothly lower and raise the bailer eliminated the problem. Since the recharge wells are constantly flowing, there was no need to purge the wells before sampling.

Monitor wells and a number of recharge wells were sampled by means of Well Wizard bladder pumps powered by a portable, gasoline-powered air compressor/controller. The Surficial aquifer monitor wells were sampled with 0.05 m (1 7/8 in.) pumps, and the Floridan aquifer monitors were purged with a 0.08 m (3 in.) diameter pump and sampled with a 0.05 m (1 7/8 in.) pump. All pumps have Teflon bladders, PVC shells, and stainless fittings, and are fitted with an inflatable packer 0.15 m above the top of the pump. The Surficial aquifer monitor wells were "packed off" just above the top of the screened interval, and 5 well volumes purged before sampling. The Floridan well monitors were first purged by means of a 0.08 m air-lift pump, then "packed off" against the casing just above open hole. Then the bladder pump was allowed to pump for a minimum of 15 minutes prior to sample collection.

The monitor wells were sampled at the same time as the recharge wells in order to determine Surficial and Floridan aquifer water compositions before and after being disturbed by the free-fall down the recharge well.

All samples were archived and "chain-of-custody" procedures maintained to insure sample validity. Forms were used to track sample analysis and record results at all stages of the study.

ANALYTICAL METHODS

Table II-2 lists the parameters measured as part of the chemical study. All measurements were made using standard methods unless otherwise indicated.

Field Methods

In the field, notation was made of well designation and condition, weather, and other factors that might affect sample results. Depth to the pump or bailer was determined from the amount of line in the well. Water temperature, specific conductivity, pH, Eh, dissolved oxygen, and alkalinity were determined at the time of sample collection.

Temperature and conductivity were determined with a calibrated YSI S-C-T meter and temperature was checked with a laboratory thermometer. When the bladder pumps were used, Eh and pH were measured in a closed reservoir with constant replenishment. When bailers were used, these measurements were made as quickly as possible from an undisturbed sample. Eh was measured with a platinum electrode calibrated in the field to Zobel's standard solutions. The pH was measured with a combination glass electrode calibrated to NBS pH=4 and 7 standards in the field. Dissolved oxygen was measured with a YSI DO meter, however, the results are inconsistent and were not used in further interpretation of the data. Alkalinity was determined by titration at the time of sample collection.

Laboratory Methods

Table II-2 lists the methods used for most analytical procedures. Metals were analyzed from samples filtered at the time of collection on a 0.045 μm micropore filter and then acidified according to specified protocol (see references in Table II-2).

All chemical analytical procedures included running of standards every fifth analysis. Radioisotope analyses used internal standards. All standards can be traced to U.S. Environmental Protection Agency (USEPA)-approved procedures and/or standard solutions. USEPA check samples were included in each procedure. Replicate samples were analyzed on the average every four samples. Analyses were redone if analytical errors exceeded those indicated in the published method, or if the USEPA check sample concentration disagreed with the measured concentration allowing for published confidence limits.

Radioisotope analytical methods are described in detail in Oural et al. (1986). Only modifications to these methods are discussed below. There were no modifications to the uranium-238 and uranium-234 procedures.

Gross-alpha radiation method is the procedure specified in American Society for Testing and Materials (1981). The method used is D 1943-66(1977). Allowed sample storage time is 1 year. The gross-alpha method is considered to be a screening procedure at best, and results presented in this report indicate that it is highly unreliable in comparison with isotopic analysis. For example, Oural et al. (1988) have shown that, if polonium-210 represents a major proportion of the alpha-emitting isotopes in the water, gross-alpha activity can underestimate actual activity because of volatilization of polonium during evaporation on the planchet. In addition, the short-lived radon daughters can significantly influence gross-alpha analytical results (Oural et al. 1987, 1989). Presumably, radon is lost through agitation and degassing at the time of sample collection, or during evaporation on the planchet. The alpha-emitting daughters are not entirely lost and, until they decay to a level supported by radium in the water, a time-dependent alpha activity that has little correspondence with actual water chemistry results. Consequently, the length of time required for evaporation of the water on the planchet can affect gross-alpha activity. Low total dissolved solids (TDS) waters are evaporated over a long period of time in order to accumulated sufficient alpha activity to optimize counting statistics. The radon daughters deposited early in the evaporation have time to decay to lead-210, those deposited later in the procedure do not. In contrast, the volume of high TDS waters that can be deposited on the planchet is limited because of self-absorption problems of the residue. Therefore, short-lived radon daughters may not have time to decay away prior to counting and the resultant analysis is high. This leads to the often-described correlation between TDS and gross-alpha activity. Finally, the holding time of the sample and/or planchet affects activity measurement. Samples collected, prepared and run immediately can have high alpha activities because of the presence of radon progeny. Samples held for a few weeks, or prepared and then stored for a few days have relatively low alpha activities because of loss of radon daughters. These problems are discussed and modeled in Oural et al. (1987, 1989).

It would be most desirable if gross-alpha samples could be analyzed immediately so that maximum exposure potential could be evaluated. Unfortunately, laboratories cannot operate on such a short "turn-around" time, so the only alternative is to avoid providing inconsistent analyses by allowing the radon daughters in each sample to grow-out before analysis. This was done for the gross-alpha analyses reported herein.

Lead-210 was analyzed by first precipitating metals from the sample with ammonium hydroxide. Lead and polonium co-precipitate with ferric hydroxide in the sample, and the precipitate can be stored indefinitely without fear of losses from sorption on sample container walls. To analyze for lead-210, which is a beta emitter and difficult to determine, the precipitate was stored for 6 months to allow polonium-210 that is supported by lead-210 to grow in. Analysis for polonium-210 in sample splits soon after precipitation (t=0) and after the "grow-in" period (t) allows determination of lead-210 by the analytical expression

$$A_{01} = \frac{A_2(\lambda_2 - \lambda_1) + A_{02}e^{-\lambda_2 t}(\lambda_1 - \lambda_2)}{\lambda_2(e^{-\lambda_1 t} - e^{-\lambda_2 t})}, \qquad \text{(II.1)}$$

where A_{01} = activity of lead-210 at time t = 0, A_{02} = activity of polonium-210 at time t = 0, A_2 = activity of polonium-210 at time t, and λ_1 and λ_2 = decay constants for lead-210 and polonium-210, respectively.

The method utilized for polonium-210 is described in Oural et al. (1986). The method was modified slightly by addition of a oxidant to break up organic complexes that were thought to interfere with recovery of polonium. These complexes were described in Oural et al. (1987, 1989). To destroy these complexes 1-1.5 ml of 30% H_2O_2 was added to each liter of sample upon return to the laboratory. After allowing the sample to react for 3 days, the polonium was coprecipitated with ferric hydroxide according to the published method. Addition of hydrogen peroxide significantly enhanced recovery of the polonium.

Improved accuracy and counting statistics were obtained by adopting the radium-recovery technique of Moore and Reid (1973). This method involves preparation of manganese oxide-dioxide impregnated acrylic fibers. These fibers quantitatively extract radium from water, and can be utilized for analysis of radium in ground water (Michel et al., 1982). Eight to ten liters of water were passed through a cuvette of manganese-treated fibers to extract the radium. Analysis of fibers from a second cuvette in line with the first indicates complete removal of the radium on the first cuvette. The fibers were then removed, ashed to reduce volume and improve counting geometry, and sealed in a tin "snuff can" for analysis by gamma spectroscopy (Michel et al., 1982).

Isotherms

Isotherms are laboratory models that allow approximation of the ability of small amounts of dissolved chemicals to sorb onto

a solid substrate. Briefly, 4-5 solutions of the chemical of interest are prepared in varying concentrations. These are placed in contact with known masses of substrate (rock or soil in this case) and agitated for a fixed length of time. The acidity of the mixtures may or may not be buffered, depending upon the goals of the experiment. After agitation, the supernatant is analyzed for the chemical. The difference between original concentration and final concentration in each solution is the amount adsorbed. The "rate" of sorption as a function of starting concentration is used to characterize the sorptive capacity of the material and approximate a maximum sorption capacity.

Two isotherms are commonly used (Ellis and Knezek, 1972). These are the Langmuir and Freundlich isotherms. The Freundlich isotherm is given by the equation

$$\frac{x}{m} = k \cdot C^{\frac{1}{n}},, \qquad \text{(II.2)}$$

where $\frac{x}{m}$ = the quantity of ions adsorbed per unit weight of adsorber, C = the equilibrium concentration of the adsorbate after adsorption has occurred, k and n = constants. The equation can be rearranged as

$$\log\left(\frac{x}{m}\right) = \frac{1}{n} \cdot \log C + \log k \qquad \text{(II.3)}$$

and a graph of $\log\left(\frac{x}{m}\right)$ versus C yields a straight line with a slope of 1/n and an intercept of k, if the Freundlich isotherm is followed. A limitation of the Freundlich isotherm is that it does not predict an adsorption maximum.

The Langmuir isotherm equation is

$$\frac{x}{m} = \frac{K \cdot M \cdot b}{1 + K \cdot M}, \qquad \text{(II.4)}$$

where $\frac{x}{m}$ = meq of ion adsorbed per 100 g of adsorber, M = activity of ion in question in moles/liter, b = the absorption maximum of ion M in meq/100 g, and K is a constant derived from the ratio of adsorption to desorption rates. Equation II.4 can be rewritten as

$$\frac{M}{\left(\frac{x}{m}\right)} = \frac{1}{K \cdot b} + \frac{M}{b},$$

(II.5)

which can be evaluated by linear regression techniques. The adsorption maximum (b) is the reciprocal of the slope of the regression, and the "adsorption rate" (K) is the reciprocal of the intercept divided by b. K is not a time-based rate, and cannot be used to characterize reaction kinetics.

Polonium sorption has been evaluated by Hansen and Watters (1971), and it was found that, in typical Florida soils, 17 to 77 times as much polonium is sorbed or precipitated as remains in the solution. Since strong sorption is indicated and the results of this study suggest those chemical processes that can cause desorption, it was concluded that sorption isotherms for polonium need not be determined.

A major question remains as to the mobility of the polonium predecessor, lead-210. Isotherms were obtained for lead using (1) slightly argillaceous and ferruginous quartz sand, which is typical of the Surficial aquifer; (2) typical, smectite- and palygorskite-rich, Peace River Formation clay; and (3) calcitic, Suwannee Limestone from cores at KR-98B and KR-127D. Stock solutions of 1, 5, 10, and 20 mg/l lead were prepared from $PbCl_2$ in deionized water. Room temperature was maintained at 26°C. The samples were agitated on a shaker table for 24 hours. The pH of the solutions before and after contact with the adsorbant and the pH of a blank were monitored. Table II-3 gives the conditions of the experiment. Since starting and final pH's are similar to actual field pH's, and buffering of the pH by reaction with carbonate is a predicted reaction as recharge-well water interacts with the Floridan aquifer, no attempt was made to control pH's by addition of buffers. The alkalinity obtained in the experiment using limestone is sufficient to cause precipitation of $PbCO_3$ (cerussite), rather than induce adsorption.

CHEMICAL MODELS

Equilibrium Models

The interactions of the chemical species in ground water are extremely complex and use of simple concentration data often obscures relationships of chemical species in the system. The solutions investigated contain sufficient dissolved ionic species to cause ion pairing. For example, not all calcium is present as Ca^{+2}, some of the calcium is present as chemical complexes with

sulfate, carbonate, bicarbonate, fluoride, and other anionic groups. Thus, when determining the relationship of calcium to other chemical constituents, it is necessary to identify that portion of the total calcium which is actually free calcium ion and available to participate in chemical reactions. The concentration of a free ion, as opposed to total concentration, is known as the activity (a), where activity is related to the concentration by

$$a = \gamma \cdot m, \tag{II.6}$$

where γ = the activity coefficient, and m = molality of the constituent. Molality is the total, analytical concentration, and γ is a proportionality constant that denotes the fraction of the total, analytical concentration that is present in chemical complexes.

The amount of complexing, or γ, of an constituent is a function of the total charge concentration in the solution. This is calculated as the **ionic strength** (I) by the equation (Garrels and Christ, 1965)

$$I = \frac{\Sigma(m_i z_i^2)}{2}, \tag{II.7}$$

where m_i is the molality of charged species i, and z_i is the charge of species i. The γ can then be calculated by a number of different equations. The equation used in this study is the Davies equation, which is best for ionic strengths less than 0.5. The equation is

$$\log \gamma_i = -Az_i^2 R, \tag{II.8}$$

where γ_i = the activity coefficient of species i, A is a constant, z_i is the charge on the ion i, and R is determined from the ionic strength by

$$R = \frac{\sqrt{I}}{1 + \sqrt{I}} - 0.3I. \tag{II.9}$$

For $Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, Cl^{-}, SO_4^{2-}, CO_3^{2-}$, , and HCO_3^{-}, the extended Debye-Huckel equations (Truesdell and Jones, 1974; Drever, 1988) are used. The extended Debye-Huckel equation is

$$\log \gamma_i = \frac{-Az_i^2\sqrt{I}}{1 + B\alpha_o\sqrt{I}} + bI, \qquad \text{(II.10)}$$

where A and B are constants that depend upon pressure and temperature, and α_o is the hydrated ionic radius of the species in question.

To solve the simultaneous equations necessary to calculate the activities of important dissolved constituents and complexes (ion pairs), a computer program, WATEQF, by Plummer et al. (1976) was used. This program calculates activity coefficients and activities of 193 aqueous species and minerals. It also calculates solubility products and degree of saturation of the water with respect to the mineral phases.

Statistical Models

Once the complex ions were identified, chemical models were constructed to explain behavior of the radioisotopes of interest. These models are based on (1) first principles of chemistry, such as basic chemical reactions of major species, and (2) a statistical search for chemical relationships by use of correlation analysis. The correlation analysis search was necessary because the radioisotopes are present in such minute concentrations that the presence of even trivial activities of complex ions may cause unpredicted chemical complexes and mobilization of the isotopes of interest.

Two modes of correlation analysis were undertaken in the search procedure, which involved use of ABSTAT, a commercially-available statistical package (Anderson-Bell, 1987). Pearson product-moment correlation and Spearman rank correlation coefficients were calculated for the monitor-well data and for the recharge-well data.

Pearson product-moment correlation coefficients (r's) require that the data be normally distributed, and they can be rigorously tested for significance (Sokal and Rohlf, 1969). Missing data are omitted from the analysis in a pairwise deletion, so Pearson product-moment correlations allow maintenance of large sample sizes and, therefore, better confidence estimates. Levels of significance of r's were determined by two criteria: (1) reference to a table of significance (Rohlf and Sokal, 1981) for critical levels of r, given an α level of 0.05 (P = 95%) and appropriate degrees of freedom, and (2) calculation of r^2 to determine the amount of covariance accounted for by the correlation. Only correlations

that account for at least 50% of the covariance (r^2 = 0.50, r = 0.707) were accepted as representing a significant relationship.

Spearman rank correlation coefficients (p) are based on principles of nonparametric statistics and do not require normalcy of the data. However, the significance of the correlation coefficient is not easily tested (Sokal and Rohlf, 1969). Also, since the method is a ranking system, missing data are omitted listwise, which eliminates all variables for any sample with missing data. The result is a greatly reduced sample size, and ability to make inference, in comparison to product-moment correlation. Quantiles of the Spearman test statistic were used to test for significance (Conover, 1971). An α level of 0.05 (P = 95%) was used to test for significance.

SEQUENTIAL-DATA ANALYSIS

Task 3 of this study involves determination of the temporal and spatial distributions of gross-alpha radiation in recharge well water. An unique data set exists for this determination. The Southwest Florida Water Management District (SWFWMD) has accumulated analyses submitted by the companies for many years. All totaled, the data set assembled for the time-series analysis included sequential data from 270 recharge wells installed in the Central Florida Phosphate District. A list of these data sources is presented in Section V of this report. Most (48.9%) of the wells were installed in the Keysville Quadrangle. Homeland (13.7%), Bradley Junction (11.5%) and Duette NE (11.5%) quadrangles account for most of the remainder of the available data. Data from the recharge wells range from only 1 gross-alpha radiation analysis to 84 months of data. The average well has 9.4 monthly analyses.

Time-Series Analysis

While most of the records are not suitable for time-series analysis, some are excellent for this purpose. Data sets were selected for time-series analysis according to the following criteria:

1. Only well data from companies shown by Oural et al. (1986) to have good sampling and analytical procedures were used, and

2. Only data sets that have continuous monthly records of at least 24 months were used.

Ten data sets met these criteria. Table II-4 lists the wells used for time-series analysis. Data sets which have single

observations that are anomalously high were avoided because it is likely that the anomalous activities represent interference from short-lived radon progeny and the observations are not comparable to data from other months (Oural et al., 1987, 1989). Attempts at time-series analyses of these "spiky" data sets failed because the peaks are artifacts of sample collection and analysis, and they are randomly distributed throughout the time of data collection.

There were no monitor wells with water-level data from the Surficial aquifer that were suitable for correlation with the gross-alpha data provided by the water management district. There is, however, a well-maintained precipitation gauge at the International Minerals and Chemical Corp. New Wales Chemical Plant located at the northwest corner of the Kingsford Mine, Keysville Quadrangle. Data from this gauge correspond in time and interval with the gross-alpha data, so comparisons with precipitation are possible. By extension, variations in the precipitation data should correspond in a general way with variations in water levels in the Surficial aquifer. These data were used to relate the gross-alpha radiation data to hydrologic conditions in the Surficial aquifer. All of the data used in this paper are from wells within approximately 8 km of the precipitation gauge. Much of the drainage in the mines is internal, so water levels in the Surficial aquifer respond directly to precipitation.

Smoothing, autocorrelation and cross-correlation techniques (Davis, 1973) were used to identify temporal patterns in the data. Correlations with precipitation were used to determine the behavior of the gross-alpha radiation with water-table fluctuations. The smoothing algorithm used in this study is

$$Y_{i,calc.} = 0.1Y_{i-2} + 0.2Y_{i-1} + 0.4Y_i + 0.2Y_{i+1} + 0.1Y_{i+2}, \quad \text{(II.11)}$$

where $Y_{i,calc.}$ is the smoothed value of Y at time i, and $Y_{i-2},\ldots,Y_{i+2}$ are the observed values of Y at times i-2, i-1,...,i+2.

Spatial-Analysis Methods

It is well known that radon gas moves along fracture traces (Oural et al., 1986; Banwell and Parizek, 1988) and, since polonium-210 is a radon daughter, an attempt was made to correlate the locations of wells that chronically exceeded the 15 pCi/l gross-alpha radioactivity MCL with photolinear features, which are presumed to represent fracture traces (Parizek, 1976). Since the majority of the data are from wells on the Keysville

Quadrangle, and since there are two independent fracture-trace studies (Upchurch and Kaufmann, 1979b; Culbreth, 1983) and an excellent geological study (Cathcart, 1963) of that quadrangle, it was selected for spatial analysis. No judgments as to the presence or absence of photolinears were made as part of this study. Cathcart (1963) did not locate photolinear features, but his maps of overburden thickness and thickness of the "leached zone" show linear trends that coincide with many of the features identified by other workers as photolinears, and greatly assist interpretation of the processes operative in the area. No selection was made on the basis of company or sampling and analytical procedure, but the data are from companies found to have adequate procedures (Oural et al., 1986). Only wells with over 10 months of record were used in the spatial analysis.

To clarify any relationship between fracture-trace location and wells that show high gross-alpha radioactivity levels, the shortest distance from each well with at least 10 months of record to the nearest known photolinear feature was measured. This distance, a "nearest-neighbor" statistic, was used to investigate the correlation of proximity to photolinear features with radiation distribution.

Table II-1. - Recharge wells sampled for chemical and radiological analysis in this study. n.d. = not yet determined.

USF Sample Number	SWFWMD Permit Number	SWFWMD Well ID	USGS Quadrangle	Company	Company Well ID	County	Latitude	Longitude	Section, Township, & Range Loc.	Comments
WRG-01-	200029	WRG-4	Myakka City NW	W.R. Grace	RK-01	Manatee	27.28.47	82.11.15	35-34-21	
WRG-02-	200029	WRG-5	Myakka City NW	W.R. Grace	RK-02	Manatee	27.28.55	82.11.01	26-34-21	
APRW-2-	200332	AMX-14	Keysville	AMAX/MOBIL	PRW-2	Hillsborough	27.46.26	82.04.02	24-31-22	
APRW-6-	200332	AMX-18		AMAX/MOBIL	PRW-6		27.43.41	82.04.33		
APRW-9	200332	AMX-22	Duette NE	AMAX/MOBIL	PRW-9	Hillsborough	27.43.56	82.03.20	01-32-22	
APRW-10-	200332	AMX-23	Duette NE	AMAX/MOBIL	PRW-10	Hillsborough	27.43.56	82.04.46	02-32-22	
ATRW-17-	200332	AMX-31	Duette NE	AMAX/MOBIL	TRW-17	Hillsborough	27.43.09	82.04.54	02-32-22	
ATRW-28-	200332	AMX-42	Keysville	AMAX/MOBIL	TRW-28	Hillsborough	27.45.15	82.04.52	26-31-22	
ATRW-29-	200332	AMX-43	Duette NE	AMAX/MOBIL	TRW-29	Hillsborough	27.42.32	82.04.26	11-32-22	
ATRW-30-	200332	AMX-44	Duette NE	AMAX/MOBIL	TRW-30	Hillsborough	27.42.36	82.04.21	11-32-22	
KR-22-	203053	IMC-61	Keysville	IMC	KR-22	Polk	27.49.03	82.00.56	04-31-23	
KR-80-	203053	IMC-65	Keysville	IMC	KR-80	Polk	27.48.45	82.01.28	05-31-23	
KR-83-	203053	IMC-68	Keysville	IMC	KR-83	Polk	27.48.39	82.01.53	05-31-23	Monitor wells
KR-86-	203053	IMC-71	Keysville	IMC	KR-86	Polk	27.48.36	82.02.06	05-31-23	
KR-87A-	203053	IMC-72	Keysville	IMC	KR-87A	Polk	27.48.45	82.02.13	05-31-23	
KR-95-	203053	IMC-76	Keysville	IMC	KR-95	Polk	27.48.52	82.02.50	06-31-23	
KR-98B-	203053	IMC-80	Keysville	IMC	KR-98B	Polk	27.49.10	82.00.55	04-31-23	Monitor wells
KR-117-	203053	IMC-97	Keysville	IMC	KR-117	Polk	27.48.48	82.01.07	04-31-23	
KR-118-	203053	IMC-98	Keysville	IMC	KR-118	Polk	27.48.33	82.01.30	05-31-23	
KR-120-	203053	IMC-100	Keysville	IMC	KR-120	Polk	27.48.31	82.01.21	04-31-23	
KR-122-	203053	IMC-67	Keysville	IMC	KR-122	Polk	27.48.50	82.02.25	06-31-23	
KR-127-	203053	IMC-104	Keysville	IMC	KR-127	Polk	27.48.52	82.02.39	06-31-23	Monitor wells
KR-135-	203053	IMC-112	Keysville	IMC	KR-135	Polk	27.48.33	82.00.35	04-31-23	
NR-2-				IMC	NR-2	Polk				
NR-3-				IMC	NR-3	Polk				
NR-4-				IMC	NR-4	Polk				
NR-5-				IMC	NR-5	Polk				
NR-6-				IMC	NR-6	Polk				
NR-7-				IMC	NR-7	Polk				
NR-8-				IMC	NR-8	Polk				
NR-9-				IMC	NR-9	Polk				

Table II-2. - Variables measured and methods used in the chemical study. APHA = Rand et al., 1976; USEPA = Environmental Monitoring and Support Laboratory, 1979; USGSa = Wershaw et al., 1983; USGSb = Fishman and Friedman, 1985; ASTM = Amer. Soc. Testing and Materials, 1981.

Variable	Units	Method Used
Field Measurements		
Temperature	deg. Celsius	APHA (USEPA 170.1)
Eh (redox pot.)	millivolts	Orion Research, 1978
pH	units	USEPA (150.1)
Dissolv. Oxygen	mg/l	USEPA (360.1)
Alkalinity	mg/l	USEPA (310.1)
Laboratory Measurements		
Bicarbonate	mg/l	Calculated from alkal.
Chloride	mg/l	USGSb
Fluoride	mg/l	USEPA (340.2)
Phosphate (sol.)	mg/l	APHA
Silica	mg/l	USEPA (370.1)
Sulfate	mg/l	USEPA (375.1)
Aluminum	µg/l	USEPA (202.2)
Calcium	mg/l	USEPA (215.1)
Iron (tot.)	µg/l	USEPA (236.2)
Lead	µg/l	USEPA (239.2)
Magnesium	mg/l	USEPA (242.1)
Manganese	µg/l	USEPA (243.2)
Potassium	mg/l	USEPA (258.1)
Sodium	mg/l	USEPA (273.1)
Strontium	µg/l	USGSb
Tot. Dissol. Solids	mg/l	USGSb
Tot. Org. Carbon	mg/l	USGSa,b
Tot. Volatile Solids	mg/l	USGSb
Lead-210	pCi/l	See text
Polonium-210	pCi/l	See text
Radium-226	pCi/l	See text
Uranium-238	pCi/l	Oural et al. (1986)
Uranium-234	pCi/l	Oural et al. (1986)
Gross Alpha Radiation	pCi/l	ASTM (D 1943-66)

Table II.3 - Conditions of the lead isotherm determinations.

Sample	pH
Starting solutions	
20 mg/l $PbCl_2$ solution	4.98
10 mg/l $PbCl_2$ solution	5.13
5 mg/l $PbCl_2$ solution	5.28
1 mg/l $PbCl_2$ solution	5.70
Deionized water blank	5.70
Sample SW-6, sl. argillaceous and ferrugineous quartz sand from KR-98B after equilibration	
20 mg/l $PbCl_2$ solution	5.76
10 mg/l $PbCl_2$ solution	5.78
5 mg/l $PbCl_2$ solution	5.78
1 mg/l $PbCl_2$ solution	5.68
Sample of Suwannee Limestone from 267 ft. BLS at KR-127-D after equilibration	
20 mg/l $PbCl_2$ solution	8.92
10 mg/l $PbCl_2$ solution	8.98
5 mg/l $PbCl_2$ solution	8.87
1 mg/l $PbCl_2$ solution	8.70
Sample of Peace River Formation clay from 259 ft. BLS at KR-127-D after equilibration	
20 mg/l $PbCl_2$ solution	5.20
10 mg/l $PbCl_2$ solution	4.91
5 mg/l $PbCl_2$ solution	4.83
1 mg/l $PbCl_2$ solution	4.74

Table II-4. Sources of historical gross-alpha radiation data utilized for time-series analysis. Data are from records collected by the Southwest Florida Water Management District. See Table V-1 for more details.

Well	Record duration	Months of continuous record
a. IMC-68	44 months (1978 - 1985)	35 months
b. IMC-85	40 months (1978 - 1985)	32 months
c. IMC-97	42 months (1978 - 1986)	35 months
d. IMC-104	42 months (1978 - 1986)	37 months
e. AMX-14	37 months (1977 - 1986)	31 months
f. WRG-4	84 months (1978 - 1985)	85 months
g. WRG-5	83 months (1978 - 1985)	84 months
h. MOB-43	25 months (1981 - 1984)	24 months
i. MOB-67	32 months (1982 - 1985)	34 months
j. MOB-69	31 months (1982 - 1985)	33 months

III. - RESULTS - CHEMICAL DATA

DATA EVALUATION

Two sets of data were collected as part of this study. Data from the monitor wells represent undisturbed samples that reflect the ambient chemistry of the aquifer system. These data are important for understanding the chemical environments in which radionuclides are mobilized or fixed, and, therefore, **monitor-well data are the main focus of the interpretation portion of this report.** The recharge-well data reflect water that is in the well environment for a short time, and, therefore, in disequilibrium. These data are best used for determination of the extent of any problem and for determination of any chemical changes caused by recharge.

Monitor-Well Data

Introduction - The chemical data derived from monitor wells are given in Appendix B. These data allow characterization of the Surficial and upper Floridan aquifers outside of the recharge well environment. A detailed chemical analysis of a sample from HK-1, the well with the highest polonium-210 activity yet reported in the state (Cowart et al., 1987), is included for comparison in Appendix B. Table III-1 summarizes chemical conditions in the two aquifers. The aquifers differ significantly in bulk composition. The major-element chemistry of the two aquifers represents the lithologies of the respective aquifer frameworks.

Water Type - Bulk water chemistry is controlled by interactions with rock materials. The bulk chemistry differs greatly from a siliciclastic aquifer, such as the Surficial aquifer, where chemical reactions are minimized owing to the low reactivities of quartz and other minerals, to a carbonate aquifer, such as the Floridan aquifer, where highly reactive minerals are present.

Surficial aquifer. Water compositions from the Surficial aquifer monitor wells range from sodium-sulfate to mixed waters with sub-equal proportions of calcium, magnesium, and sodium and a linear mixture of sulfate and bicarbonate (Figure III-1). Average total dissolved solids (TDS) is 496 mg/l. The Eh-pH conditions average -96.6 mv and 5.3 pH units, with ranges in values of -266.7 mv to +17.6 mv and 4.3 to 6.4 pH. Total organic carbon (TOC) averages 8.3 mg/l, with a range of 6.0 to 13.1 mg/l.

The Surficial aquifer is a quartz sand aquifer with minor

carbonate mineral content. Particulate organics are widely distributed through the aquifer, and are concentrated in organic-rich hardpans. Siliciclastic clays are present and may form argillaceous beds, especially near the base of the aquifer. In the absence of carbonates to buffer the system, the aquifer water tends to be acid and the predominant anions are acid radicals, such as sulfate (Table III-1, Appendix B).

Floridan Aquifer. The upper Floridan aquifer is a karstic limestone that contains calcite and minor dolomite. The upper portions of the aquifer include minor phosphate, siliciclastic clay, and quartz.

Floridan aquifer water is a calcium-magnesium-bicarbonate water (Figure III-1) that averages 289 mg/l TDS. Calcium is slightly predominant(approximately 45% of the cation equivalents), magnesium represents about 40% of the equivalents, and sodium constitutes about 15%. Bicarbonate is the predominant anionic constituent, and represents 90% of the anionic equivalents. Chloride and sulfate are minor constituents. Eh averages -139 mv, and ranges from -235.7 to 64 mv. The pH averages 7.3 and ranges from 7.1 to 7.5. Total organic carbon averages 4.4 mg/l, with a range of 3.4 to 4.9 mg/l.

The high pH and low range in pH values in the Floridan aquifer are a result of buffering by carbonate, where acidity is consumed according to reactions, such as dissolution of calcite

$$CaCO_3 + H^+ \rightleftharpoons Ca^{2+} + HCO_3^-, \qquad \text{(III.1a)}$$

and dolomite

$$CaMg(CO_3)_2 + 2H^+ \rightleftharpoons Ca^{2+} + Mg^{2+} + 2HCO_3^-. \qquad \text{(III.1b)}$$

In reactions of this sort, acidity is consumed and the predominant reaction products include cations, such as calcium and magnesium, and bicarbonate.

Sulfur Species - The distributions of sulfur species, especially sulfate (SO_4^{2-}) and sulfide (S^{2-}) species, is critical to mobility of polonium, and perhaps other isotopes.

Surficial aquifer. The high sulfate content of Surficial aquifer monitor-well water appears to be a result of three

processes: (1) oxidation of pyrite in clay-rich zones of the aquifer, (2) destruction of sulfide- and sulfate-bearing organics, and (3) influx of waters from a nearby waste gypsum disposal area (gypstack) and cooling pond. Hutchinson (1978) included analyses of seven Surficial aquifer water samples in the Alafia RIver basin. He found two calcium-sulfate water samples from wells that are distant from the phosphochemical plants. Therefore, high sulfates are not necessarily a product of fertilizer plants.

Comparison of the Eh-pH conditions of the Surficial aquifer (Figure III-2) indicates that, at 25°C, the water falls at or below the boundary between $SO_{4_{aqueous}}^{2-}$ and $H_2S_{aqueous}$ (Garrels and Christ, 1965), with over half of the samples well within the $H_2S_{aqueous}$ stability field. Equilibrium kinetics between the two sulfur species are dominated by bacteria, and metastable species can exist if bacterial action is inhibited. Connell and Patrick (1968) investigated the stability of sulfate and sulfide in waterlogged soils, such as the Surficial aquifer. They found that microbial sulfate reduction is inhibited and sulfide formation is minimized at redox potentials above -150 mv and at pH's outside the range of 6.5 to 8.5. Since optimal conditions for microbial sulfate reduction may not be present (low pH values and Eh values that tend to be above -150 mv), sulfate, not sulfide, may predominate as a metastable species (Figure III-2).

Floridan aquifer. Sulfate in the Floridan aquifer is formed by oxidation of pyrite or vertical movement of sulfur-rich water. Downward leakance of Surficial aquifer water introduces sulfate and up-coning of waters that have been in contact with gypsum ($CaSO_4.2H_2O$) and/or anhydrite ($CaSO_4$) near the base of the aquifer can be a source, albeit an unlikely one in this data set. Eh-pH relationships (Figure III-2) indicate that sulfate and sulfide are stable in the Floridan in those portions of the aquifer sampled. The low absolute concentrations of sulfate ($\bar{X}$ = 8.3 mg/l, range = 0.0 to 50.0 mg/l) in the Floridan indicate that sulfate reduction, sorption/precipitation reactions, and dilution reduce sulfate in comparison with the Surficial aquifer. The Eh-pH range in the Floridan is suitable for microbial sulfate reduction accoring to the criteria of Connell and Patrick (1968).

Iron Species - As Figure III-3 indicates, iron is also sensitive to Eh-pH conditions. Ferric-hydroxide precipitates are well known scavengers of metals in aqueous systems. Therefore, it is critical to understand how iron speciation affects radionuclide mobility.

Surficial aquifer. Total iron concentrations in the Surficial aquifer average 5.4 mg/l, and range from 1.5 to 11.0 mg/l. Comparison with the Eh-pH stability fields for iron species (Figure III-3) indicates that $Fe^{2+}_{aqueous}$ is the stable iron species. Clearly, iron is soluble and mobile in the Surficial aquifer.

Floridan aquifer. Iron is present in very low quantities in the Floridan aquifer, as compared to the Surficial aquifer. Iron concentrations average 12.6 μg/l, and range from 0.0 to 43.5 μg/l. Eh-pH stability field data (Figure III-3) suggest that $Fe^{2+}_{aqueous}$ is the stable species, so one can only conclude that iron concentrations are reduced en route to the aquifer by precipitation of ferrous sulfide or ferric oxyhydroxides, by sorption on aquifer matrix minerals, or by dilution.

Organics - A very important component of the chemical make-up of Surficial aquifer water is its organic content. Many naturally occurring, soluble organics are strong chelating agents, so metals and radionuclides may be mobilized in the presence of the organics.

Surficial aquifer. Total organic carbon averages 8.3 mg/l. and concentrations as high as 13.1 mg/l were reported. These are very high organic carbon values with respect to natural organics in aquifer systems. Meybeck (1981, 1982) summarized organic carbon in rivers. He estimated that the average dissolved organic carbon content is 5.8 mg/l. Ground waters are generally considered to contain less organic carbon that do surface waters (Hem, 1985). Hem's (1985) citation of an aquifer with exceptionally high organic carbon is the study by Thorstenson et al. (1979) in which TOC's as high as 30 mg/l were reported.

Floridan aquifer. Total organic carbon is low in the Floridan aquifer, as compared to the Surficial aquifer. However, an average of 4.4 mg/l is still high compared to other aquifer systems and the deep Floridan. The TOC present in the Floridan at the monitor wells is probably a result of the influence of the recharge wells. Since there is a significant increase in pH and alkalinity from the Surficial aquifer to the Floridan, humic acids and other pH sensitive organic groups should be flocculated and form advantageous substrates for bacteria in the vicinity of the recharge wells.

Radionuclides - In comparison with the Floridan aquifer, the Surficial aquifer is typically high in polonium-210 and gross-

alpha radioactivity. Other radioisotopes exhibit smaller differences in activity between the two aquifers.

Surficial aquifer. There is little difference in uranium-238 and -235 activities in the Surficial aquifer as compared to the Floridan aquifer. However, the activity ratio ($^{234}U/^{238}U$) averages 2.8, with a range of 1.3 to 4.5. This is significantly greater than the ratio in the Floridan and suggests that there is a significant reservoir of fixed uranium available to the aquifer. While the Eh and pH of the system limit uranium solubility, alpha recoil of ^{234}U in the surficial reservoir causes elevated activity ratios. This reservoir is the "leached zone".

Radium-226 averages 1.6 pCi/l, with a range of 0.2 to 3.4. As indicated earlier, radium can form soluble complexes with sulfate, which may enhance radium mobility. The activities detected in the monitor wells suggest that either radium is limited in availability, or that mobilization is minor because the radium is fixed as a precipitate or is sorbed onto soil particles.

Lead-210 and polonium-210 represent an interesting pair in the Surficial aquifer. Lead-210 is the parent of polonium-210, and the two should be in approximate radioactive equilibrium in the ground water, given similar chemical properties. In fact the average lead-210 activity is 1 pCi/l (range 0.0 - 4.3) and polonium-210 is 18.8 pCi/l (range 0.2 - 54.4). Thus, an average activity ratio of $^{210}Po/^{210}Pb$ is 18.8. That is, polonium-210 is almost 19 times as mobile as lead-210 in the Surficial aquifer. In the Surficial aquifer, chemical conditions favor precipitation and/or sorption of lead. In contrast, the acid, organic-rich Surficial aquifer water enhances mobilization of polonium.

Floridan aquifer. Near the recharge wells, radionuclides are less abundant in the Floridan aquifer than in the Surficial aquifer (Table III-1). Gross-alpha activities are low, which indicates low activities of radium and polonium.

Uranium isotope activities are similar to those in the Surficial aquifer, but the activity ratio is nearer to unity. This indicates that there is less uranium-234 injected into the aquifer waters by alpha recoil, which is probably an artifact of a small reservoir of uranium-238.

Radium is low in activity. Although other analyses (Upchurch et al., 1979a, 1979b) of Floridan aquifer waters in the same general area have shown moderately high radium activities, the data presented herein suggest that the recharge wells studied are not contributing radium to the Floridan. The high radium waters

are found in deep, relatively stagnant portions of the aquifer.

Lead-210 is low owing to precipitation of lead carbonates and polonium is equally low, although the mechanism of fixation is not well known. Polonium hydroxides and radiocolloids are pH sensitive and appear to precipitate in neutral to alkaline waters.

Recharge Wells

Introduction - Chemical data from the recharge wells are given in Appendix B and summarized in Table III-2. Comparison with Table III-1 indicates that recharge well water is chemically similar to water in the Surficial aquifer, which discharges into the wells. Significant differences in Eh of the water, however, affect the behavior of iron and sulfur.

Water Type - The bulk composition of typical recharge-well water is statistically identical with Surficial aquifer water. The water is a sodium-sulfate to mixed water. The average pH of the water from wells associated with the monitor wells is 5.1 (the Surficial aquifer water pH is 5.3). Average Eh, however, is 23.7 mv, with a range of -158.1 to 97.9 mv. This represents a significant increase in oxidation potential within the well as compared to both the Surficial aquifer (mean Eh = -96.6) and Floridan aquifer (mean Eh = -139.1 mv). Examination of the data in Appendix B also shows that most of the recharge-well samples had positive Eh values.

Clearly, the dynamics of water (1) entering the well environment, (2) free falling to the top of the cone of impression, and then (3) flowing down the well to an exit horizon represents potentially rapid changes in chemical environment. As the water enters the recharge well environment it is mildly reducing in nature, as it flows through the well it is turbulent and becomes oxidizing, and then, as it enters the Floridan, it becomes reducing again.

Sulfur Species - The Eh-pH relationships are such that most of the samples fall within the sulfate stability field (Figure III-2). Clearly, there is a strong tendency to oxidize sulfur within the recharge-well environment. Well screens and casings are usually covered by a mat of pale gray, filamentous bacteria and other organisms. These biomats include elemental sulfur, and indicate that sulfate reduction is possible within the protection of the biomat environment.

Iron Species - Iron concentrations in the recharge wells reflect the Surficial aquifer waters. However, the average iron concentration is down from 5.4 mg/l to 1.6 mg/l. This partly reflects precipitation of ferric hydroxides in the oxidizing environment, and partly a larger sample set than the monitor-well set. The hydroxides remain admixed with the biomat and/or as free particles that are removed during microfiltration. Eh-pH (Figure III-3) conditions indicate that ferrous iron ($Fe^{2+}_{aqueous}$) remains the stable iron species in standing water. Cascading water and, possibly, the biomat are the primary loci of ferric oxyhydroxide fixation.

Organic Carbon - Organic carbon is present in the recharge wells in two forms.

Particulate organics are present in the water. These represent the filamentous microbial biomats that thrive on the well screens opposite the Surficial aquifer and on the casing in the splash zone. In sampling, the biomat is disturbed and particulate content of the water increases. Undoubtedly, biomat fragments and unattached microbes are continually entering the water; however, it appears that most of this material is an artifact of sampling. When a tripod was used to center the sampling vessel over the well and minimize scraping along casing walls or when a bladder pump was used, the amount of filterable, filamentous material declined to near zero. From this, it can be concluded that microbe contributions to the recharge-well water are limited.

Dissolved organic carbon averaged 6.4 mg/l, which represents an unusual amount of organic carbon in an aquifer. Note, however, that the average TOC in recharge wells is less than in the Surficial aquifer (Table III-1).

Radionuclides - Radioactivity in the recharge wells also reflects radioactivity in the Surficial aquifer. Average activity ratios calculated by dividing the mean activity in the aquifer of interest by the mean activity in the recharge wells are given in Table III-3. Use of means to calculate the ratios in Table III-3 is somewhat misleading because the sample sizes differ and the recharge-well population includes a number of wells that have little problem with radioactivity, while the monitor well population includes a significant representation from KR-98B, which does have a radioactivity problem. Comparison of the data, however, illustrates an important relationship. That is, for all of the uranium-238 daughters, radioactivity in the Surficial aquifer exceeds or equals radioactivity in the recharge wells, while radioactivity in the Floridan aquifer is less than

radioactivity in the recharge wells.

Comparison of the recharge well data (Appendix B) with state and federal water quality standards indicates that 8 out of 62 samples violated the 15 pCi/l MCL for gross-alpha radiation. These 8 samples were taken from 5 different wells. Clearly, most of the wells that have been chronic violators of the MCL have been closed and abandoned. Four of the well samples in this study violated the 5 pCi/l MCL for radium.

CHANGES IN WATER CHEMISTRY IN THE RECHARGE WELL SYSTEM

Reliability of Monitor-Well Data

There is good chemical evidence to indicate that the Surficial aquifer monitor wells are located within the "cones of depression" of the recharge wells. While there are vertical heterogeneities in the Surficial aquifer because of hardpans and minor clay lenses, lateral flow is through homogeneous media. Therefore, one can assume that flow is essentially radial to the wells. A direct relationship between the recharge wells and monitor wells in the karstic Floridan aquifer is more difficult to establish. Most of the flow in the limestone/dolostone aquifer is through fractures or karst conduits, and, while one can argue that the monitor wells are within the "cone of impression", or mound, developed by recharge, individual monitor wells may not be in the same conduit as the recharge wells they serve. In one case, KR-127, there is little doubt because the deep monitor well discharges gases entrained in the recharge-well water during free fall. As will be illustrated below, there is chemical continuity in the data, which also suggests that the deep monitor wells provide samples that reflect the chemical changes that recharge-well water undergoes upon entering, and mixing with, native Floridan aquifer water.

Chemical Changes During Recharge

Two groups of chemical changes occur as water passes from the Surficial aquifer to the recharge wells and then to the Floridan aquifer. Bulk chemistry changes as the recharge-well water equilibrates with the carbonate minerals of the Floridan, and Eh and pH change at each stage of the path.

Eh-pH Changes - Figures III-2 and III-3 illustrate the changes in Eh and pH along the flow path.

As water passes from the Surficial aquifer into the recharge well, Eh increases, but pH does not change appreciably. There is

insufficient time for pH to change, and buffering by sulfates and organics retard significant changes in acidity. Eh changes because of the aeration induced during free fall in the recharge wells. The net effect of the transition from Surficial aquifer to recharge well is minimal. The only important change is an increase in the stability of sulfate as opposed to hydrogen sulfide (Figure III-2).

Examination of the data in Appendix B and the data of Oural et al. (1986) indicate that there are minor chemical changes from the top of standing water in the recharge well downward. These are a result of mixing with upwardly advected Floridan water or, possibly, Hawthorn Group waters; re-establishment of reducing conditions with depth; and possible sorption on clays and particulate organics.

Once the water enters the Floridan aquifer, Eh quickly returns to a more strongly reducing environment (Figures III-2, III-3), and the pH increases by 1 to 2 units. The increase in pH is a result of equilibration with carbonate minerals in the aquifer according to chemical reactions III.1a and b. The return to more reducing conditions accompanied by an increase in pH has little affect on sulfur or iron species. Radionuclides, however, are greatly reduced by precipitation, dilution, and sorption (see Chapter IV).

Reaction Paths - Figure III-1 shows the bulk chemical reaction paths taken by samples from recharge wells. In general, Surficial-aquifer and recharge-well waters evolve from being enriched in sodium and sulfate to a calcium-bicarbonate water. Most of the chemical change is accomplished by equilibration with the calcite and dolomite and mixing with native water in the Floridan. It is this equilibration that accounts for the increase in pH of the waters in the Floridan. In effect, reaction equation III.1 goes to the right, with consumption of acidity and carbonate minerals, and release of bicarbonate and dissolved calcium, and magnesium if dolomite is involved.

Saturation State of Water

The reaction pathways can be compared by examining the saturation state of the water with respect to certain critical minerals. Saturation state is defined as

$$SI = \log\left(\frac{IAP}{K_{sp}}\right), \qquad \text{(III.2)}$$

where SI = the saturation index, IAP = the ion activity product, and K_{sp} = solubility product constant at environmental temperature. If the SI is negative, the water is undersaturated with respect to the mineral in question. If it is equal to 0.0 ± 0.2, the water is saturated; and if it is positive, oversaturation exists. Note that these calculations, which were done with program WATEQF, do not account for reaction kinetics. Therefore, undersaturation predicts that the mineral will dissolve in the water, and oversaturation predicts precipitation. Neither may necessarily occur.

Table III-4 compares the average SI values at each step of the flow path. The minerals chosen are those likely to play a significant role in changes in water chemistry. Calcite ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$) are the dominant minerals in limestone and dolostone, respectively. Ferric hydroxide ($Fe(OH)_3$), manganese oxide (MnO_2), aluminum hydroxide ($Al(OH)_3$) are examples of amorphous oxyhydroxides that exist in area soils, serve as strong sorption sites for metal ions, and may plug well screens. Boehmite and diaspore are dimorphs with the composition $AlO(OH)$. They, too, form in area soils.

The trend illustrated in Figure III-1 is also indicated by the saturation states of water with respect to calcite and dolomite. Surficial aquifer and recharge-well waters are strongly undersaturated with respect to the two minerals. However, Floridan aquifer waters are very close to saturation, indicating that the recharge-well water reacts with aquifer materials, which are dissolved until equilibrium is obtained.

The oxyhydroxides, boehmite, and diaspore saturation indices show predictable trends. Water is undersaturated with respect to all three phases. However, ferric hydroxide shows an increase in saturation state, which reflects the oxidation present in the recharge-well environment. Aluminum compounds are known to form in area soils as a result of lateritic weathering (Altschuler et al., 1956). The saturation-index data indicate that the Surficial-aquifer water is at or near saturation with respect to diaspore. The water is less saturated in the recharge-well environment, and no aluminum was detected in the Floridan aquifer water. The absence of detectable aluminum in the Floridan is probably a result of dilution.

CHEMICAL SPECIATION

Introduction

Correlation analysis of chemical analytical data indicates

that analytical data (i.e., total concentrations) are not necessarily appropriate for determining the chemical behavior of the system. Correlations are often weak, statistically insignificant, and spurious. Part of the reason that these relationships are obscure is that the radionuclides of interest are present in such small quantities that, if they were not radioactive, they would not be detectable. These isotopes may be strongly affected by chemical complexes that are also present in small quantities. In order to more accurately identify chemical reactions that govern radionuclide mobility, activities of specific species, including ion-pair complexes, were calculated by means of WATEQF. WATEQF calculates chemical speciation based on ionic strength, Eh, pH, temperature, and analytical species present. For example, the samples were analyzed for 14 major and minor constituents (Appendix B). Sulfate was the only sulfur species determined. Calculation of species, however, determined the activity of sulfate (as opposed to analytical concentrations) and identified 8 sulfate-metal ion pairs. Thus, not all analytically determined sulfate is available to function as ionic sulfate in chemical reactions, and only that fraction of the sulfate that can function as simple, ionic sulfate is of importance. By isolating the activities of the various species, much stronger correlations can be identified, and less risk is involved in interpreting the data.

Only those species related to mobilization of the radionuclides are discussed in this report. Pearson product-moment and Spearman rank correlation analysis, and first principles of chemistry (Chapter I), indicate which chemical systems affect the radioisotopes of interest. Only chemical relationships that are statistically significant at $\alpha = 0.05$ and $r^2 \geq 0.50$ are discussed. This section discusses the gross chemical systems. Chapter IV discusses the specific chemistry of the radionuclides of interest.

Sulfate Chemistry

Both sulfate and sulfide, as indicated previously, are thermodynamically favored species at the Eh and pH conditions present in the aquifer systems. Microbial processes and chemical kinetics determine the rates of conversion from one species to the other (Connell and Patrick, 1968; Rye et al., 1981), so metastable sulfur species may be present in the water samples. Harada et al. (1989) have shown that both species may be important in determining polonium mobility. Unfortunately we did not analyze for sulfide, so only the role of sulfate can be documented in this study.

Relationship to Ionic Strength - Examination of the monitor-well

data indicates that the **activity** (as opposed to concentration) of sulfate is closely related to ionic strength (Figure III-4).

Sulfate is one of the dominant anions in the Surficial aquifer, and its activity in the water is a major control on total dissolved solids and ionic strength. The increase in sulfate activity that is documented in these data reflects the high sulfate wells, particularly KR-98B, at the Kingsford mine.

Relationship to Eh-pH - As Figure III-5 indicates there is a negative relationship of sulfate activity with pH. That is, more acid solutions contain higher sulfate activities. In part, this is because oxidation of sulfides produces acid according to the reaction

$$R\text{-}S_2 + 3.5O_2 + H_2O \rightleftharpoons R^{2+} + 2SO_4^{2-} + 2H^+, \qquad \text{(III.3a)}$$

where $R\text{-}S_2$ is a metal-sulfide compound, such as pyrite, containing reduced sulfur, and R^{2+} is a metal that is simultaneously involved in the reaction

$$R^{2+} + 0.25O_2 + 2.5H_2O \rightleftharpoons R^{3+}(OH)_3 + 2H^+. \qquad \text{(III.3b)}$$

If the reaction involves pyrite, $R\text{-}S_2$ is FeS_2 and R is ferrous iron, which is oxidized to ferric iron by reaction III.3b. Thus, production of sulfate and metal oxidation produce hydrogen ion, and reduce the pH. Note that Floridan aquifer monitor well data indicate low sulfate activities and high pH values. Water in the Floridan aquifer is buffered by dissolution of calcium carbonate (calcite), which yields the high pH values. Surficial aquifer water is not buffered in this way.

Sulfate should be related to Eh, because equations III.3a and b are dependent upon the availability of oxygen, or some other electron receptor. Examination of Figure III-2 indicates that the monitor well and recharge well data fall on the boundary between the sulfate and sulfide stability fields. Hydrogen sulfide odor was detected in many wells, and one can conclude that sulfide oxidation is an active process in the system. Figure III-6 shows the relationship of sulfate activity with Eh. Note that, with two exceptions, sulfate does not appear to be important below Eh values of -150 mv. This is in agreement with the findings of Connell and Patrick (1968), who concluded that sulfate reduction in saturated soils is inhibited at Eh's greater than -150 mv. Therefore, one can conclude that those samples with Eh's less than -150 mv are most likely subject to net sulfate

reduction. Only one Surficial aquifer monitor-well sample (11% of sample set), three Floridan aquifer monitor-well samples (33%), and two recharge-well samples (14%) had Eh values of -150 mv or less.

Therefore, sulfate exists at Eh's in which microbial sulfate reduction is inhibited, including Eh's from -150 to 0 mv. This constraint leads to a chemical system in which either sulfuric acid is produced and maintained by sulfide oxidation (eq. III.3) or sulfate is directly introduced to the system by marine aerosols or chemical plant effluents. As sulfates increase, pH decreases and ionic strength increases (compare Figures III-5, III-7). Note in Figure III-7 that the samples from the Floridan aquifer do not participate in this relationship because of buffering with carbonate minerals.

Strontium and sulfate combine to form $SrSO_4$ (celestite) in a manner that is chemically similar to $RaSO_4$. Strontium is not clearly correlated with sulfate. Figure III-8 shows that there is little correlation between strontium and sulfate for the entire data set. The data may indicate several, separate patterns with positive slopes. The pattern of four high-sulfate activities represents data from the monitor wells at KR-98B, which have the highest sulfate values measured in monitor wells. The fact that the data show no coherent pattern suggests that strontium activities are too low for equilibrium reactions to occur. Celestite does not precipitate, and the correlation with sulfate reflects net increase in dissolved salts during equilibration with aquifer matrix. KR-98B is located in a trough that contains significant organics as is near a cooling pond associated with a phosphochemical plant, either of which may constitute the source of sulfate for that well complex.

Iron Chemistry

Iron speciation and solubility are controlled by Eh and pH conditions (Figure III-3). Recharge-well environments approach conditions favorable for ferric hydroxide precipitation. Otherwise, the data indicate that ferrous ion (Fe^{2+}) is stable.

Figure III-9 illustrates the relationship of total iron concentration with pH. Note that the solubility of iron increases with acidity. Thus, in the Surficial aquifer the more acid environments are most likely to contain high iron and to be stripped of particulate, oxyhydroxide compounds, such as ferric hydroxide, by dissolution.

The relationship of iron concentration with Eh is less clear (Figure III-10). In the Surficial aquifer, a positive correlation

exists between the two variables (see regression line on Figure III-10). However, examination of the data indicates that the high iron concentrations are at Eh's greater than -150 mv. This is the threshold predicted by Connell and Patrick (1968) for sulfate reduction, and any samples that show Eh's less than -150 mv are likely to also have low iron owing to precipitation of ferrous sulfides. Iron availability is restricted in the Floridan aquifer because of the high pH's, which encourage precipitation of minerals, such as ferric oxyhydroxdes, carbonates, and phosphates. Thus, no pattern exists in the Floridan-aquifer derived samples.

Organic Chemistry

The humic substances that occur in ground water are affected by pH. Total organic carbon (TOC) was used to estimate the organic fraction. TOC measurements are incapable of distinguishing between humic substances, however. Because many humic substances are known ligands, it is worthwhile to determine the environmental conditions that favor formation and/or preservation of humic substances.

Figure III-11 illustrates the relationship between TOC and pH. Note that the regression line suggests that a weak correlation exists between the two variables within the Surficial aquifer and recharge wells. The most acid samples are from KR-98B and HK-1, where peaty sediments and phosphochemical plant effluents are known to occur nearby. The most basic samples are from the Floridan aquifer, where organics are reduced through flocculation and microbial activity.

The relation with Eh (Figure III-12) shows that TOC's exist at all Eh's. Note that TOC's are highest in the Surficial aquifer and that a very weak negative correlation (not significant at $\alpha = 0.05$) with Eh may exist in the Surficial aquifer samples. Note also that the majority of high TOC samples occur at Eh's near or above -150 mv. This may reflect sulfate reduction processes where, below -150 mv, microbial metabolism, which requires a source of carbon, may consume TOC.

It has been suggested in this study that the high sulfate concentrations in the Surficial aquifer may be a result of release of sulfate from humic substances or by microbial oxidation of sulfide. Figure III-13 shows that there is a negative correlation between TOC and sulfate in the Surficial aquifer. This supports both arguments, which are related, that destruction of organic compounds is paralleled by release of sulfate. No pattern can be discerned in the Floridan aquifer data.

Iron is a major metal commonly bound by natural organics. It has been shown to serve as a receptor for phosphate sorption on organics (Young and Comstock, 1986). Therefore, soluble organics may serve as vehicles for iron and phosphorus mobilization in ground water. Figure III-14 illustrates the relationship of iron to TOC. In the Surficial aquifer there is a noisy negative correlation between the two variables. Since the water samples were micropore filtered before metal analysis, large organic molecules and floccules that contain iron may have been removed from the sample. Thus, one could argue that high TOC waters may contain chelated iron that was removed by filtration and not detected. Furthermore, the pattern is consistent with other data in that iron can be released during oxidation of organics. Thus, loss of organics, and the chelating capacity they represent, leads to an increase in soluble iron.

Table III-1. - Means ($\bar{X}$) and standard deviations (σ) of raw data from monitor wells. See Chapter II for analytical procedures.

Variable	Surficial aquifer $\bar{X}$	Surficial aquifer σ	Floridan aquifer $\bar{X}$	Floridan aquifer σ
Temp. (°C)	24.2	0.7	24.4	1.2
Cond. (μmhos cm^{-1})	731.2	264.7	388.3	109.4
pH	5.3	0.8	7.3	0.2
Eh (mv)	-96.6	83.9	-139.1	64.1
D.O. (mg/l)	1.2	0.3	1.5	0.3
Alk. (mg/l)	68.7	69.9	183.6	13.0
Cl (mg/l)	26.7	14.8	8.9	1.6
F (mg/l)	0.1	0.1	0.7	0.1
HCO_3 (mg/l)	83.7	85.2	223.9	15.8
PO4 (mg/l)	0.3	0.2	0.1	0.1
SO_4 (mg/l)	243.2	177.0	8.3	15.0
SiO_2 (mg/l)	4.0	1.7	36.6	6.4
TOC (mg/l)	8.3	2.1	4.4	0.5
TDS (mg/l)	496.0	188.6	288.9	96.8
VDS (mg/l)	90.6	83.9	79.1	51.7
Al (μg/l)	71.5	81.7	0.0	0.0
Ca (mg/l)	26.3	23.8	35.2	3.8
Fe (μg/l)	5,414.0	3,218.5	12.6	16.5
K (mg/l)	0.4	0.1	1.2	1.1
Mg (mg/l)	14.2	7.7	17.6	4.3
Mn (μg/l)	10.7	4.8	0.7	0.2
Na (mg/l)	87.4	71.4	14.6	1.4
Pb (μg/l)	5.7	2.3	5.2	1.8
Sr (μg/l)	36.8	30.2	45.9	23.4
Pb-210 (pCi/l)	1.0	1.7	0.2	0.2
Po-210 (pCi/l)	18.8	21.2	0.8	0.9
Ra-226 (pCi/l)	1.6	1.1	1.0	1.0
U-234 (pCi/l)	0.3	0.1	0.1	0.2
U-238 (pCi/l)	0.1	0.0	0.1	0.1
A.R.	2.8	1.1	1.8	1.0
Gross Alpha (pCi/l)	38.3	40.5	5.8	2.6

Table III-2. - Means ($\bar{X}$) and standard deviations (σ) of raw data from recharge wells. See Chapter II for analytical procedures.

Variable	$\bar{X}$	σ
Temp. (°C)	22.8	5.2
Cond. (μmhos/cm)	193.4	168.8
pH	5.1	1.3
Eh (mv)	23.7	94.9
D.O. (mg/l)	3.4	1.9
Alk. (mg/l)	39.4	42.9
Cl (mg/l)	10.4	7.9
F (mg/l)	0.5	0.4
HCO_3 (mg/l)	48.0	52.3
PO4 (mg/l)	1.9	1.7
SO_4 (mg/l)	45.2	67.7
SiO_2 (mg/l)	5.9	3.2
TOC (mg/l)	6.4	3.7
TDS (mg/l)	174.7	128.1
VDS (mg/l)	62.9	49.8
Al (μg/l)	412.8	1283.3
Ca (mg/l)	13.6	8.4
Fe (μg/l)	1565.9	1814.3
K (mg/l)	0.6	0.5
Mg (mg/l)	6.7	5.0
Mn (μg/l)	12.1	15.3
Na (mg/l)	19.6	31.7
Pb (μg/l)	4.3	4.0
Sr (μg/l)	11.2	17.1
Pb-210 (pCi/l)	0.3	0.7
Po-210 (pCi/l)	3.9	5.1
Ra-226 (pCi/l)	1.2	2.0
U-234 (pCi/l)	0.2	0.2
U-238 (pCi/l)	0.1	0.2
A.R.	1.9	1.4
Gross Alpha (pCi/l)	8.4	7.9

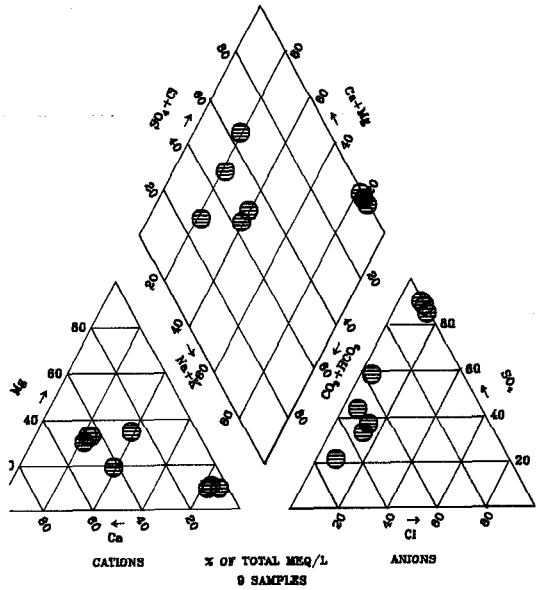
Table III-3. Activity ratios of aquifer water as compared to recharge well water. Ratios are calculated from mean values.

Isotope	Surficial aquifer Recharge wells	Floridan aquifer Recharge wells
Uranium-238	0.64	0.64
Uranium-234	1.19	0.52
Radium-226	1.31	0.83
Lead-210	2.85	0.50
Polonium-210	4.81	0.20
Gross-alpha activity	4.56	0.69

Table III-4. Average log-saturation indices of aquifer and recharge-well water with respect to selected mineral species.

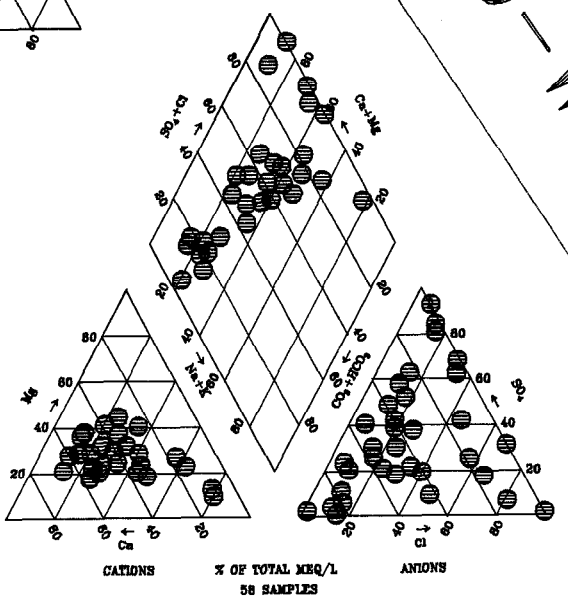
	Surfic. Aquifer		Recharge Wells		Floridan Aquifer	
Species	$\bar{X}$	σ	$\bar{X}$	σ	$\bar{X}$	σ
Calcite	-2.23	1.85	-3.42	0.91	-0.26	0.16
Dolomite	-4.40	3.58	-6.71	1.80	-0.81	0.96
$Fe(OH)_3$	-8.05	10.40	-7.86	2.36	-4.60	1.55
$Mn(OH)_3$	-24.65	2.27	-24.14	2.42	-19.67	1.82
$Al(OH)_3$	-2.16	1.85	-4.00	1.62	nd	nd
Boehmite	-1.04	1.12	-2.21	1.62	nd	nd
Diaspore	-0.02	0.82	-0.63	1.60	nd	nd

nd = no aluminum detected

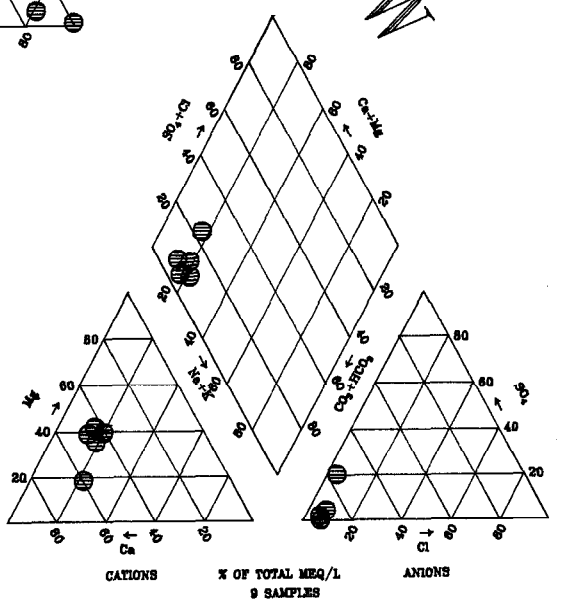


SURFICIAL AQUIFER

GROUND-WATER FLOW



RECHARGE WELLS



FLORIDAN AQUIFER

Figure III-1. Piper diagram showing major-element compositions of Surficial-aquifer, recharge well, and Floridan aquifer samples.

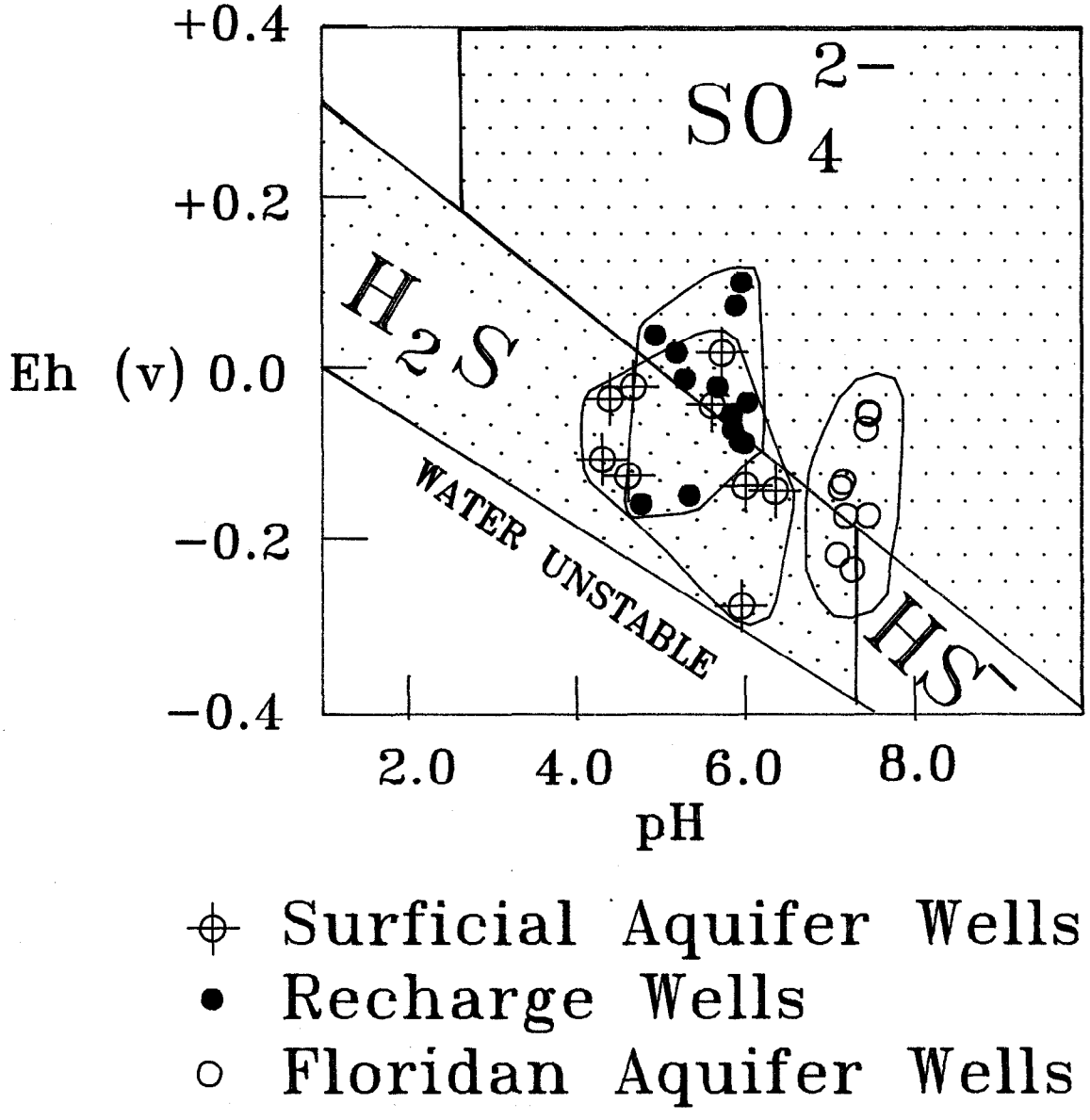


Figure III-2. Eh-pH diagram showing stability fields of major sulfur species.

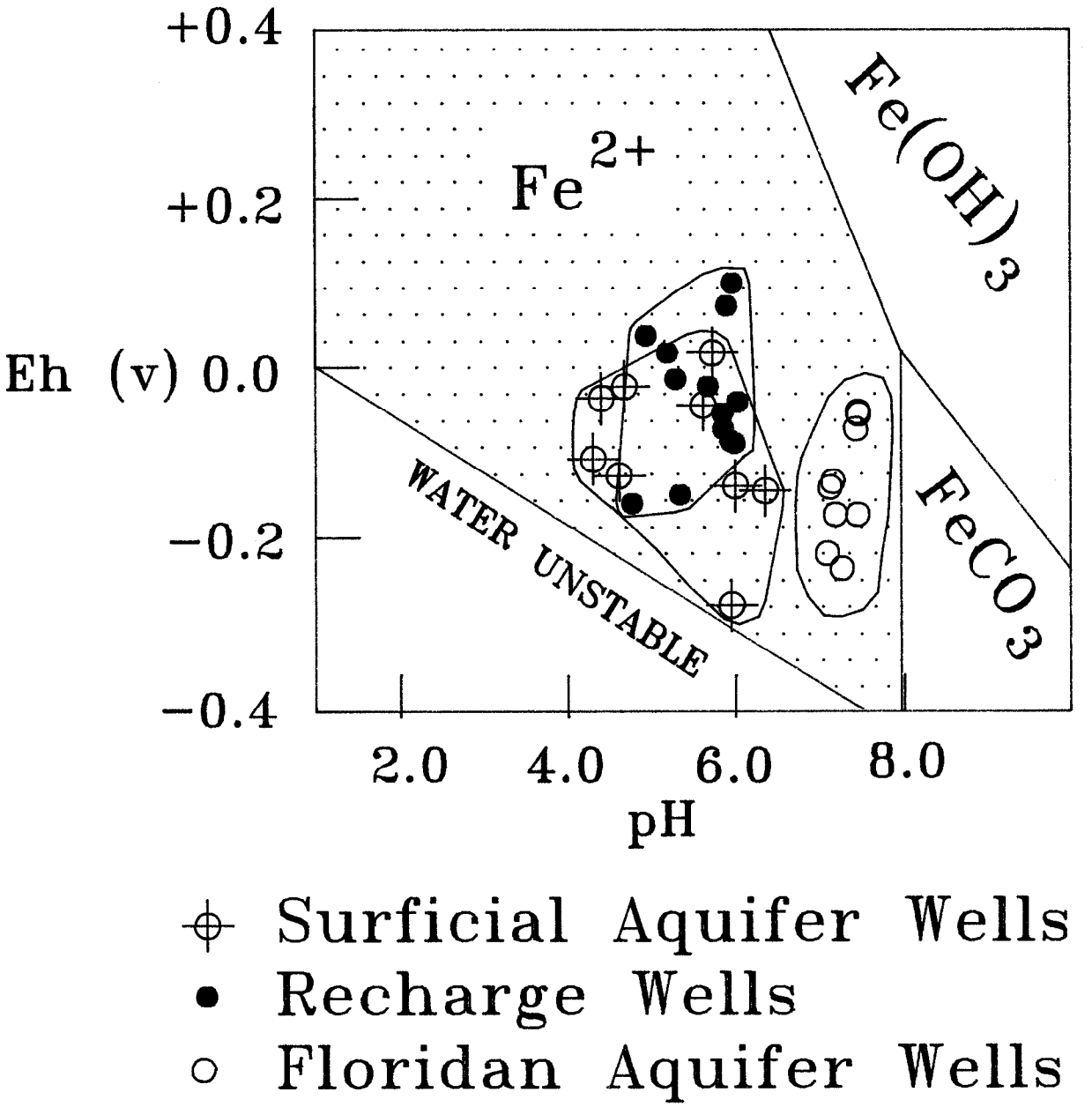


Figure III-3. Eh-pH diagram showing stability fields of major iron species.

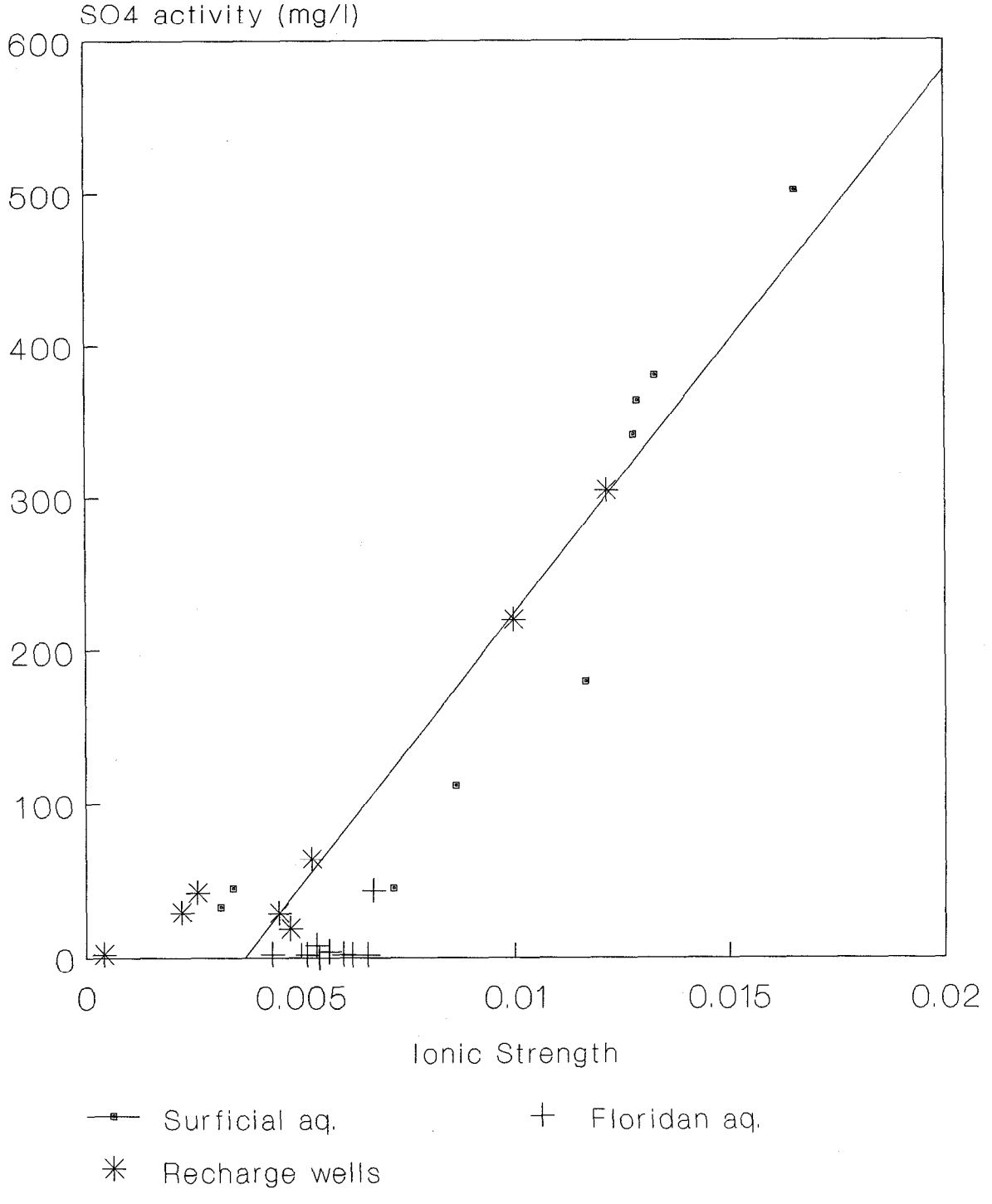


Figure III-4. Scatter diagram showing the relationship of calculated sulfate activity to ionic strength. Line is a linear regression on Surficial-aquifer samples.

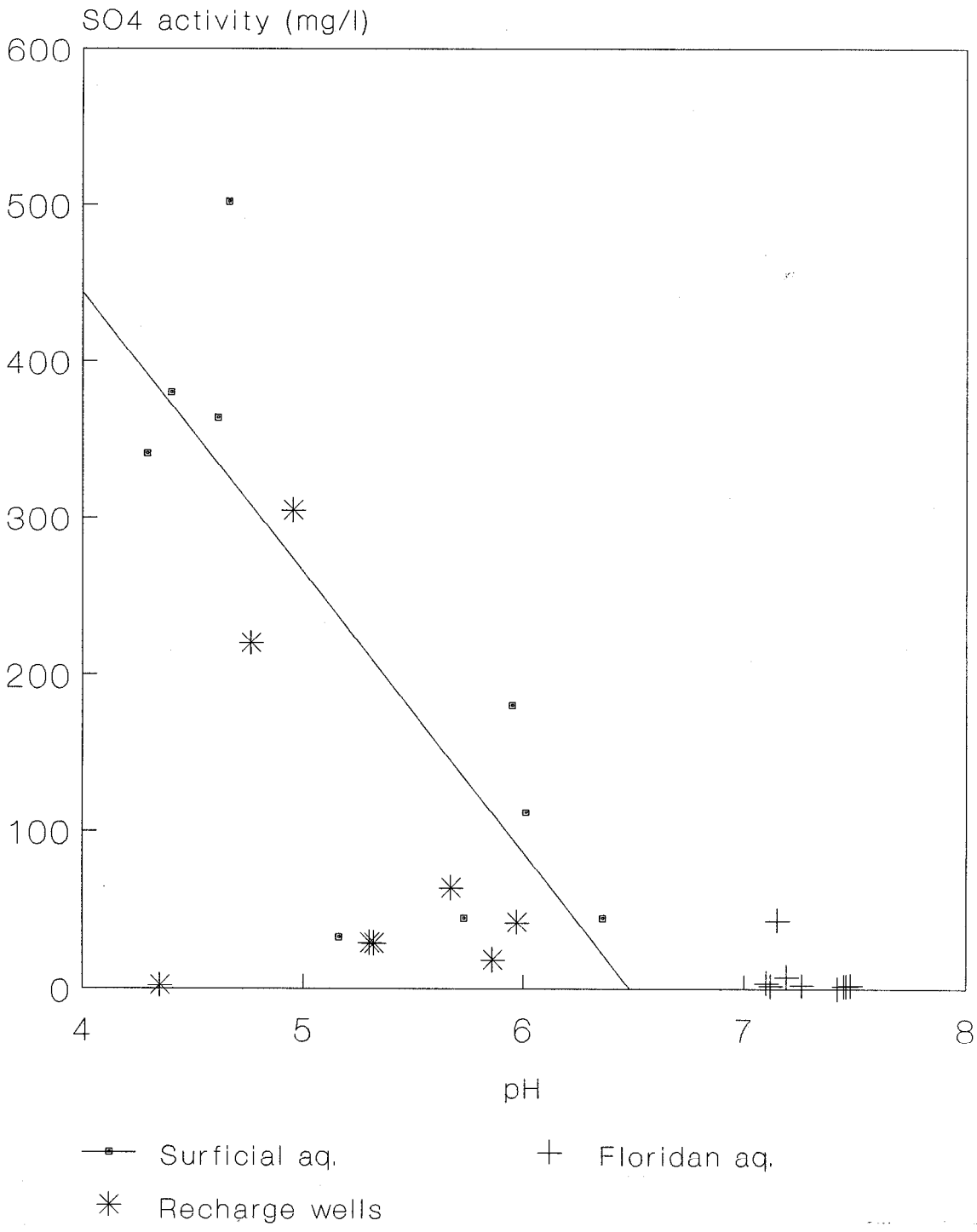


Figure III-5. Scatter diagram showing the relationship of calculated sulfate activity to pH. Line is a linear regression on Surficial aquifer data.

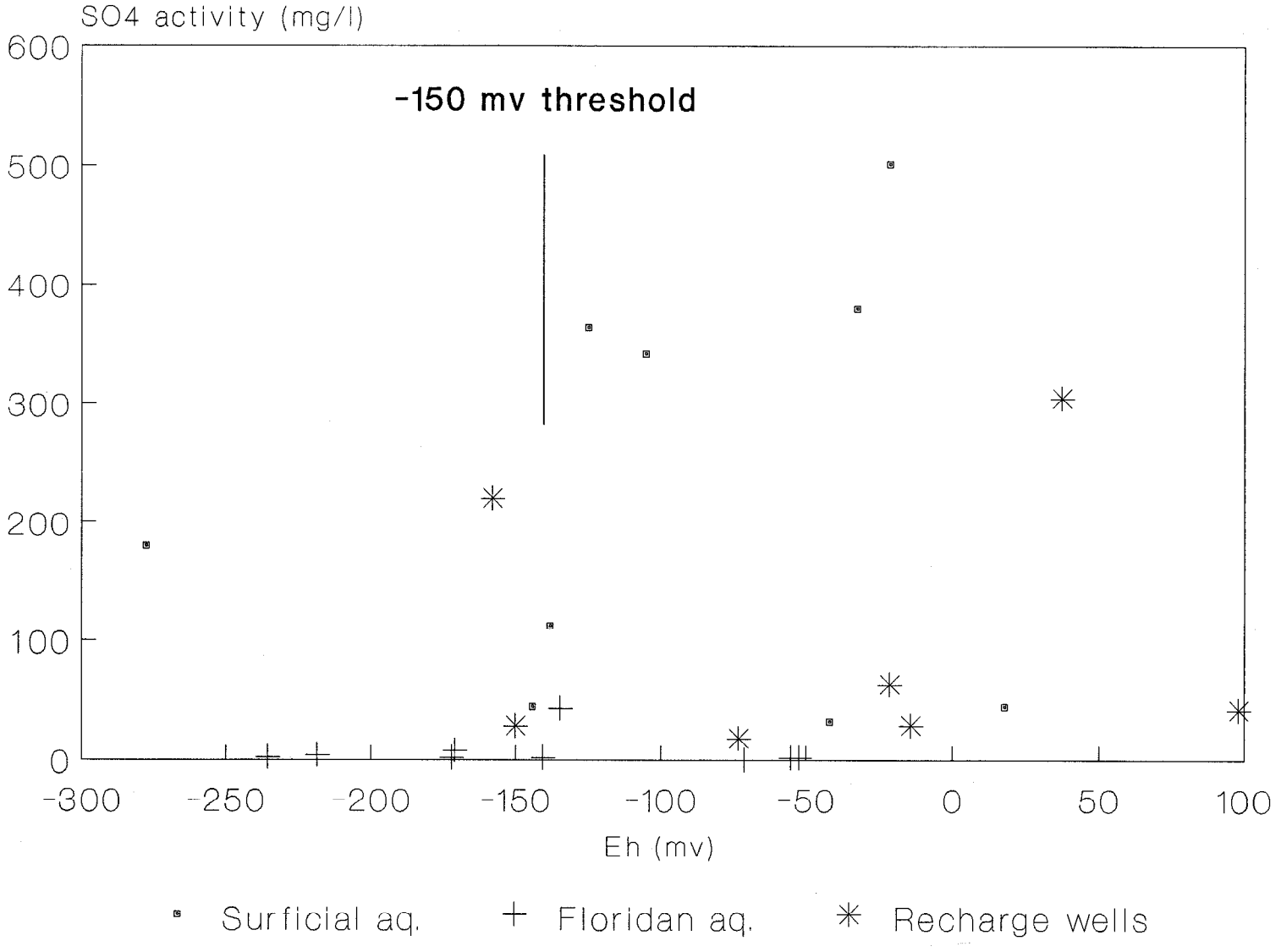


Figure III-6. Scatter diagram showing relationship of sulfate activity to redox potential (Eh). Note that, with the exception of two samples, all high sulfate samples occur at Eh's in excess of -150 mv.

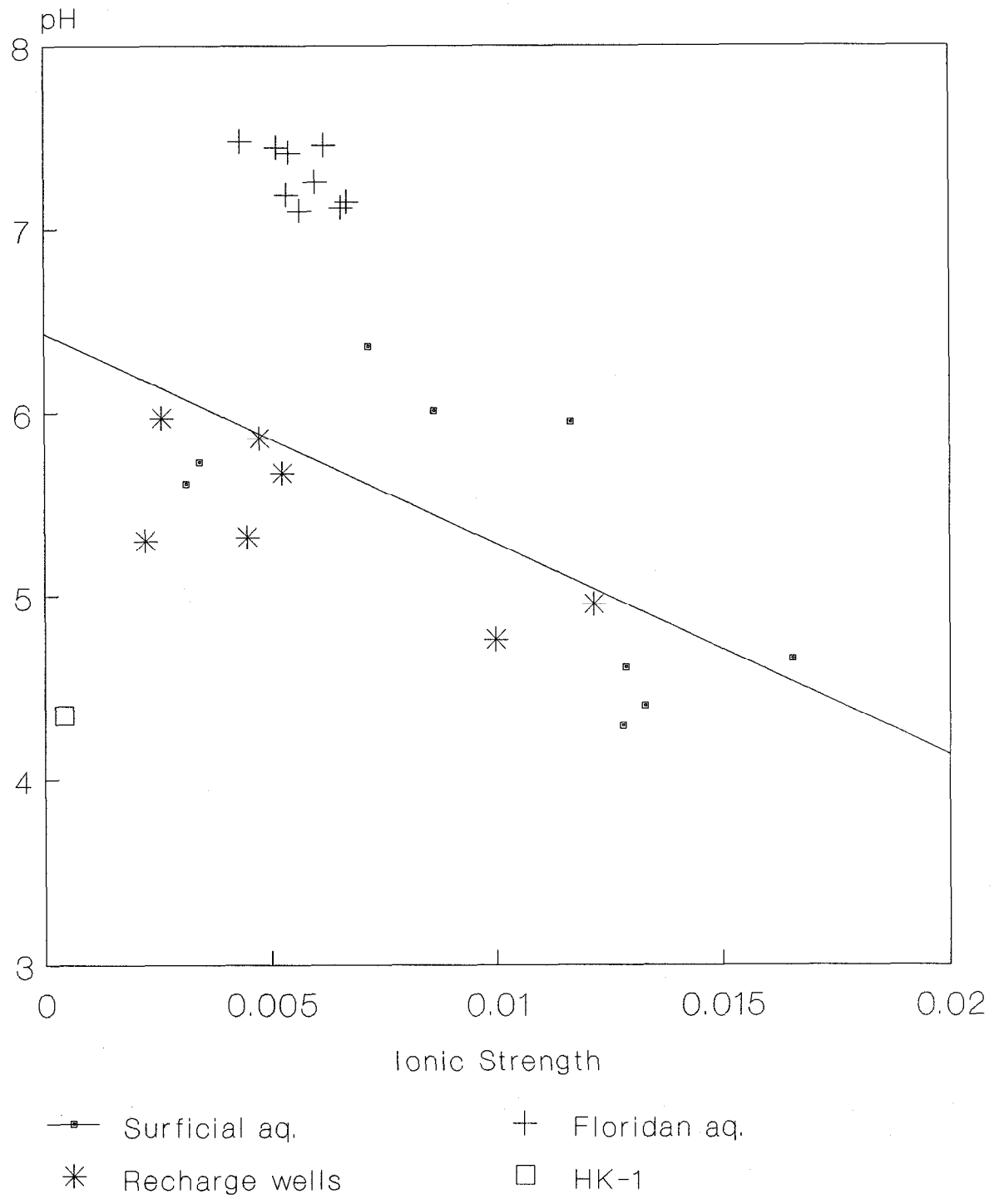


Figure III-7. Scatter diagram showing relationship of pH to ionic strength. Regression line is on Surficial aquifer samples.

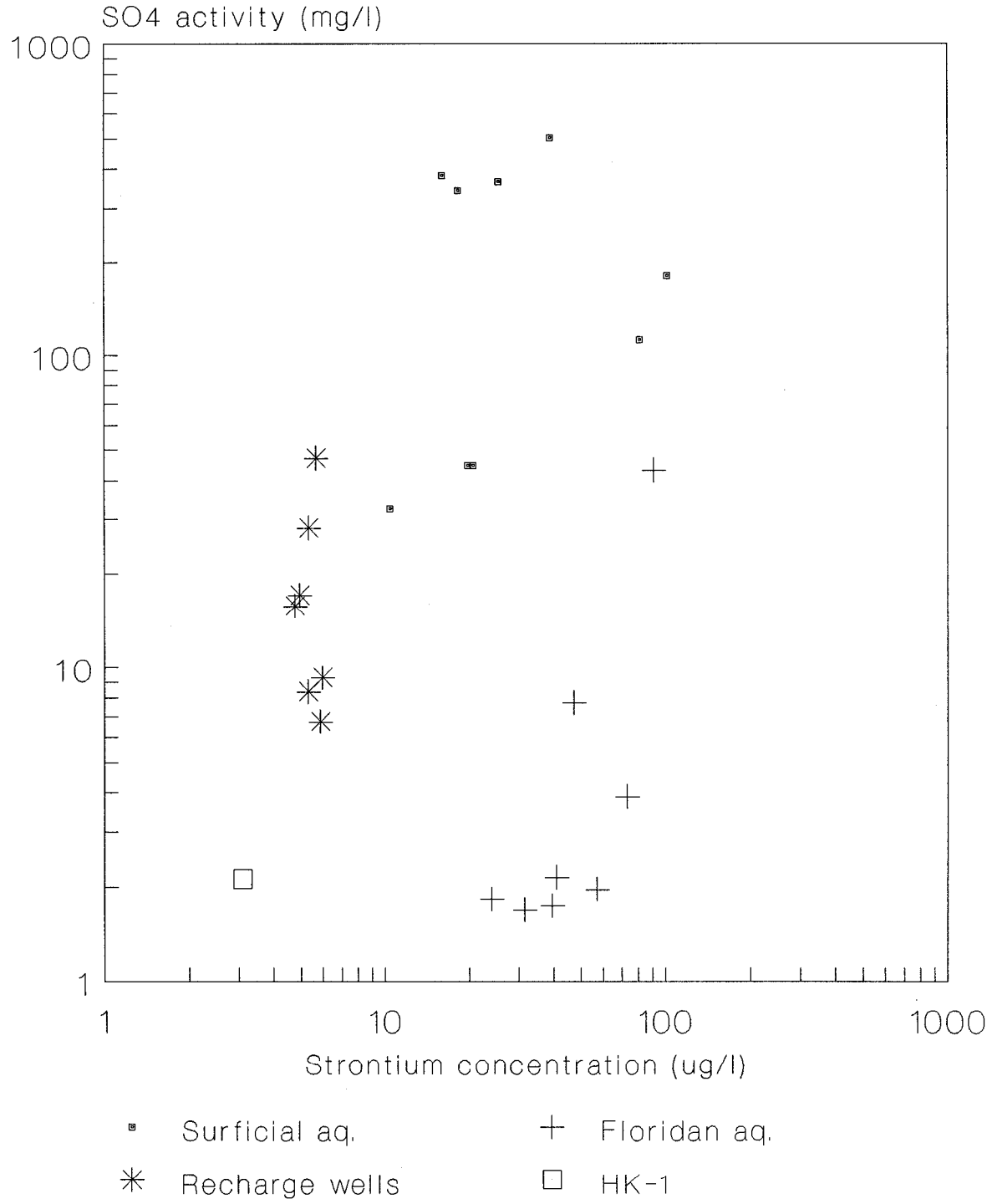


Figure III-8. Scatter diagram showing the relationship of strontium to log sulfate concentration. Note that there is no correlation within the data set.

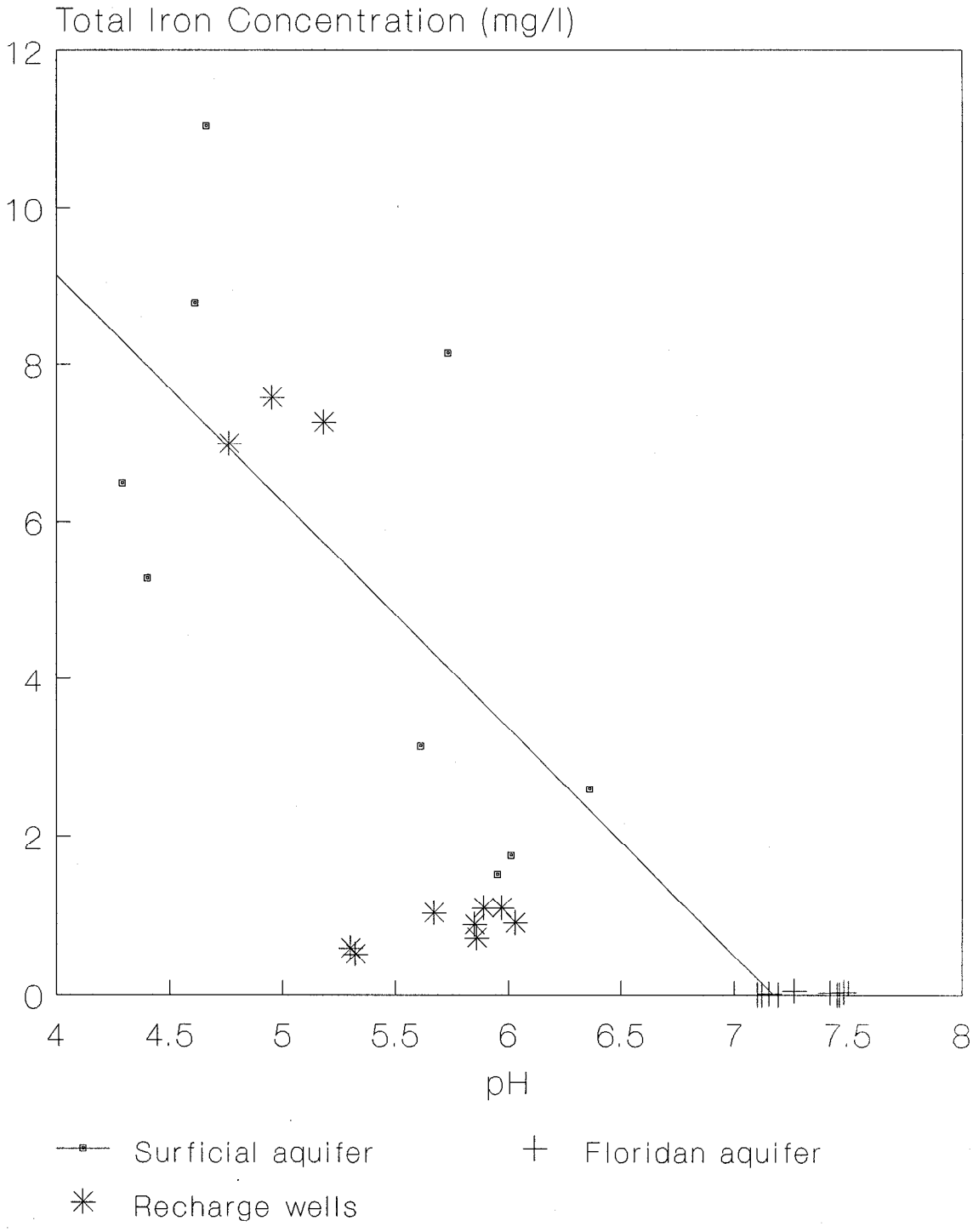


Figure III-9. Scatter diagram showing the relationship of total iron concentration to pH. Line is a linear regression on the Surficial aquifer data.

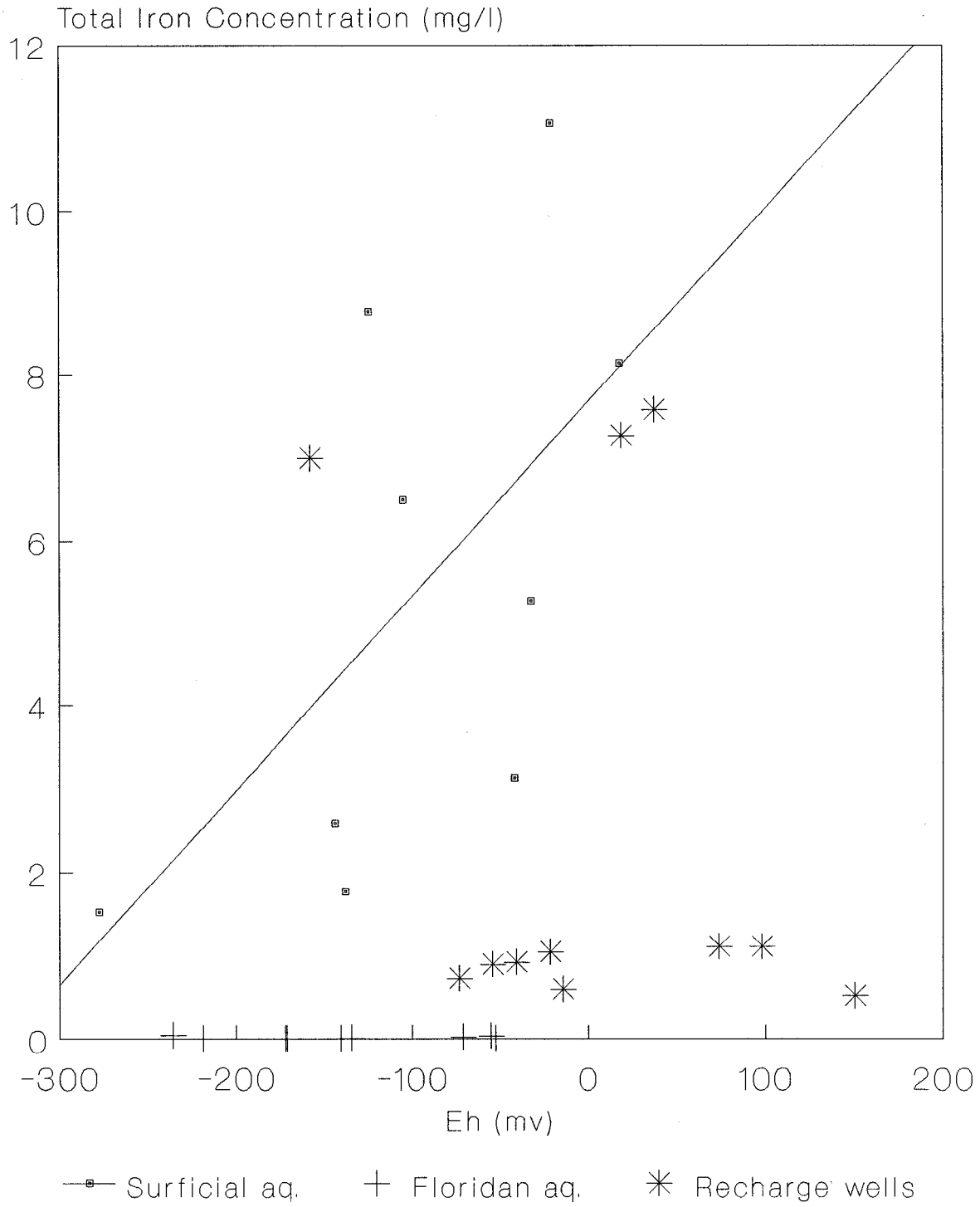


Figure III-10. Scatter diagram showing relationship of total iron concentration to redox potential (Eh). Note that, with the exception of one sample, all high iron concentrations occur at Eh's in excess of -150 mv. Regression line is for Surficial aquifer sample data. Compare with Figure III-6.

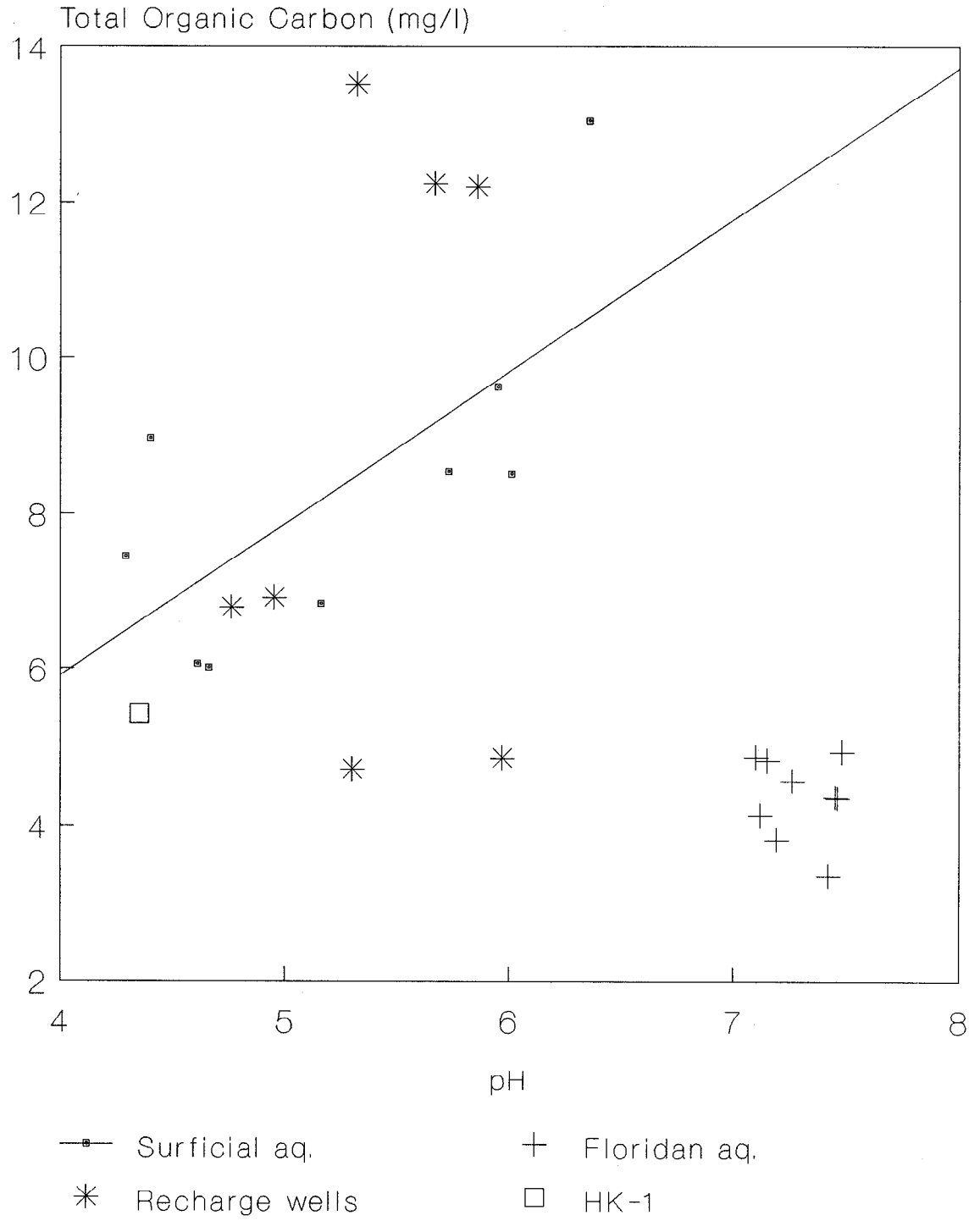


Figure III-11. Scatter diagram showing the relationship of total organic carbon (TOC) to pH. Weak correlation in the Surficial aquifer data is suggested by the linear regression.

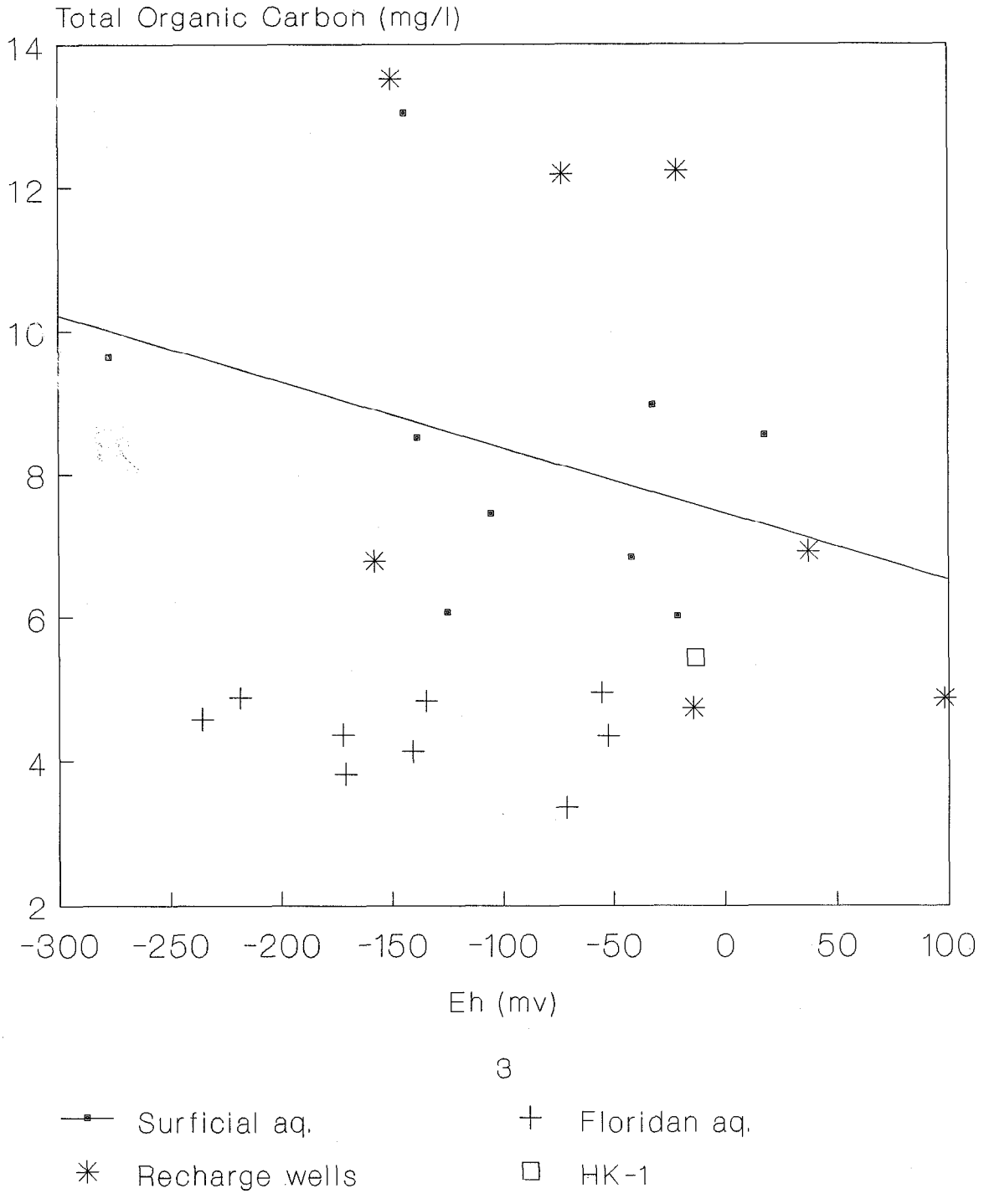


Figure III-12. Scatter diagram showing the relationship of total organic carbon (TOC) to redox potential (Eh). Regression line is based on Surficial aquifer data.

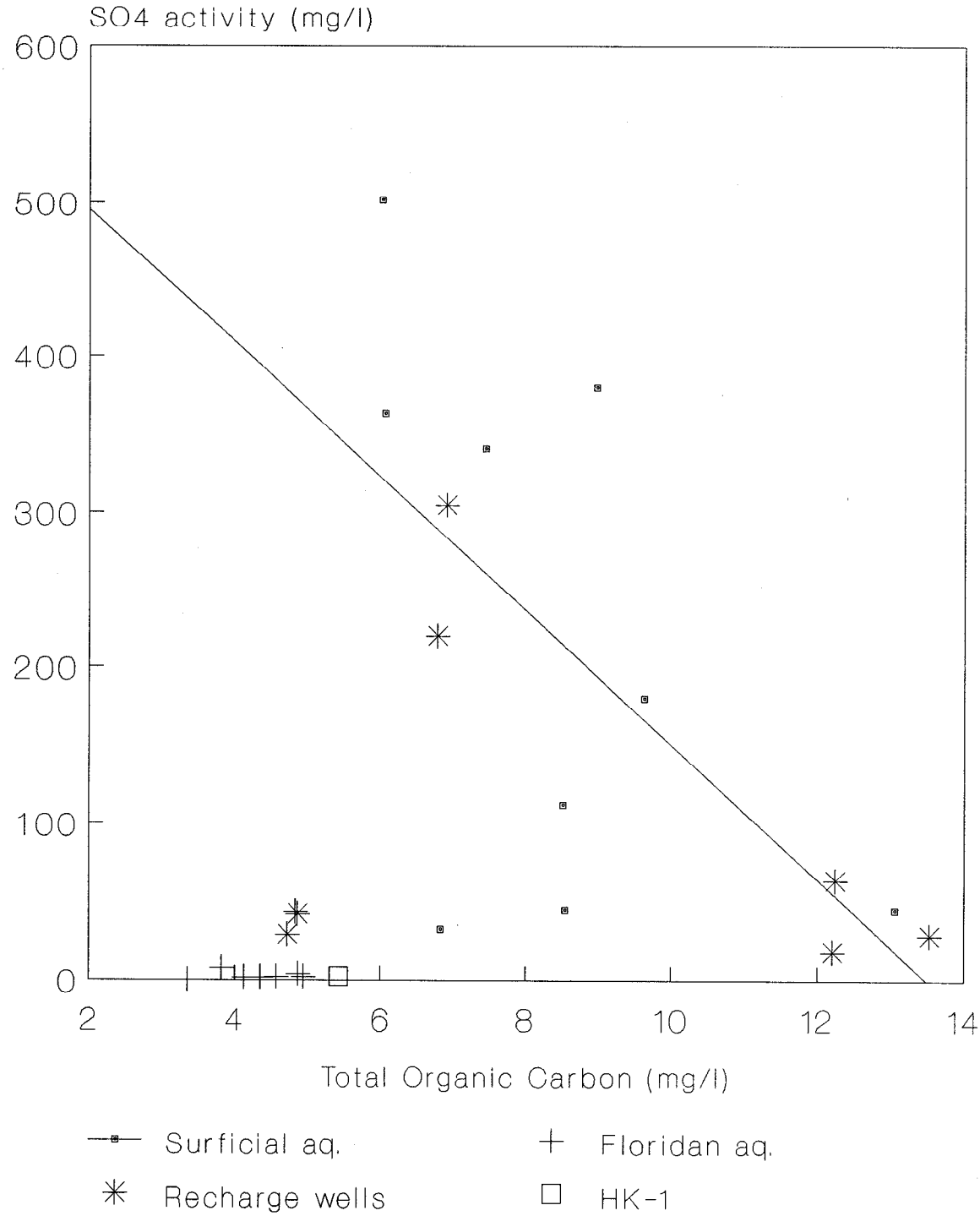


Figure III-13. Scatter diagram showing relationship of total organic carbon (TOC) to sulfate concentration. Regression line is on Surficial aquifer data.

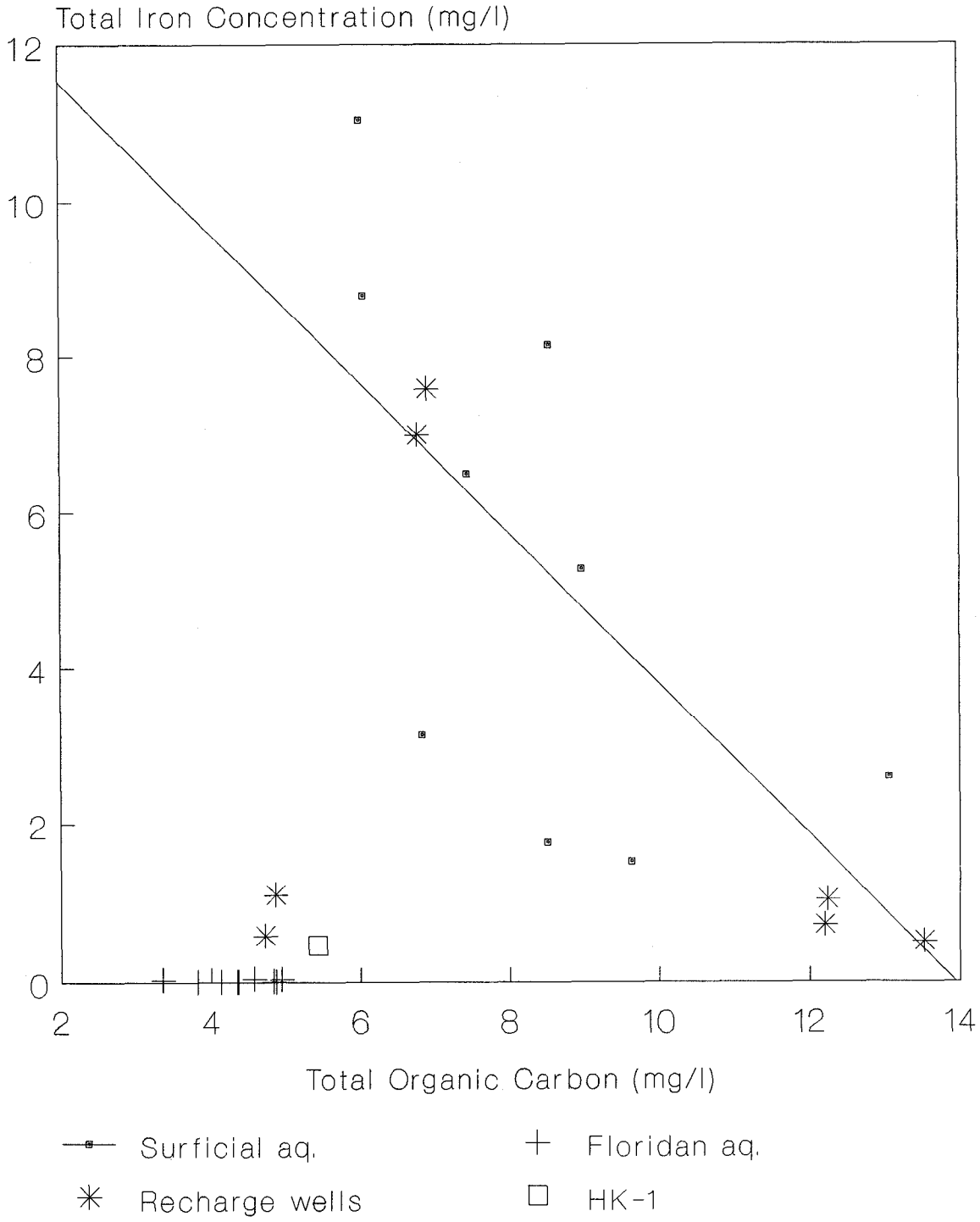


Figure III-14. Scatter diagram showing relationship of total organic carbon (TOC) to total iron concentration. Regression line suggests a weak correlation in the Surficial aquifer.

IV - RADIOCHEMICAL SYSTEMS

The purpose of this chapter is to explore the chemical fate of uranium daughters in recharge wells, the Surficial aquifer, and the Florida aquifer. Each major radioisotope is discussed in terms of the portions of the chemical system that cause mobilization and/or chemical fixation. Reference is made to the preceding chapters for basic chemical concepts and chemical conditions in the Surficial aquifer, recharge wells, and upper Floridan aquifer.

URANIUM SYSTEMS

Uranium Abundance

Uranium-238 and -234 respond in the recharge-well environment in a predictable manner. Uranium is most mobile as a uranyl complex in oxidizing waters. Since net oxidation is limited in the recharge-well environment to small-scale reactions in the cascading water, uranium mobilization is limited. Average activities in the recharge wells are 0.14 pCi/l ^{238}U (σ = 0.18) and 0.21 pCi/l ^{234}U (σ = 0.20). In the Floridan aquifer, average activities are 0.09 pCi/l ^{238}U (σ = 0.14) and 0.11 pCi/l ^{234}U (σ = 0.15), and they are 0.09 pCi/l ^{238}U (σ = 0.04) and 0.25 pCi/l ^{234}U (σ = 0.13) in the Surficial aquifer. As a result of immobilization in reducing environments, uranium does not appear to be a problem, nor has it ever been identified as a problem in recharge wells or natural aquifers in the study area.

The mean $^{234}U/^{238}U$ activity ratios are: Surficial aquifer = 2.82 (σ = 1.11), recharge wells = 1.87 (σ = 1.37), and Floridan aquifer = 1.77 (σ = 0.98). Ratios greater than 1 are interpreted in terms of "maturation", or aging, of aquifer water (Osmond and Cowart, 1976). Maturation is accompanied by in-growth of radioisotope daughters, and alpha recoil of the daughter uranium-234 into the water (Osmond and Cowart, 1976) causes the ratio to exceed 1. These ratios reflect a nearby source of uranium, such as the "leached zone". Uranium in the "leached zone" may account for the abundance of progeny in nearby aquifer systems.

Uranium Correlations

Correlation analysis indicates weak, but significant (α = 0.05) correlations with several chemical parameters (Table IV-1). For example, it is interesting to note that correlations with Eh are not significant. This is because the environment is sufficiently reducing to squelch solubility-Eh relationships.

Uranium-238 is only correlated with $Fe^{2+}_{aqueous}$ and $FeH_2PO_4^-$. Ferric iron is the reduced iron species, so a correlation with reduced uranium is not unexpected. The correlation with ferrous hypophosphate may suggest minor uranium mobilization as a phosphate complex.

Uranium-234 shows more significant, but weak, correlations than does uranium-238. This may be an artifact of the recoil mechanism or alpha decay in general. Recoil causes mechanical injection of an uranium-234 ion into the water from the surface of aquifer particles. Alpha decay within the body of an aquifer mineral, such as a phosphate grain, disrupts the crystal lattice, and may enhance solubility of the mineral and release of progeny. Under normal circumstances solubility relationships would dictate that the uranium remain largely in a particulate form. Recoil breaks the bonds of the atom with the particle and may allow chemical interactions with pore water. The correlations in Table IV-1, however, are probably spurious. For the most part, the correlations are with species involved with dissolution of carbonates (alkalinity, calcium, etc.), so the correlations are forced by the presence of the Floridan aquifer samples, which are lower in uranium-234 than are the Surficial aquifer samples.

The negative correlations with activity ratio are probably also spurious. However, the positive correlations with P_{CO_2} and H_2CO_3 suggest a possible leaching mechanism. If recoil injects uranium-234 into pore water and it then sorbs onto pore walls, acid leaching may temporarily remobilize the isotope into the pore water (Osmond and Cowart, 1976).

RADIUM SYSTEMS

Radium Abundance

While the Polk County Health Department, Office of Radiation Control (1983) study found that a modest percentage of the recharge wells tested exceeded the 5 pCi/l MCL for radium, the samples collected in this study indicate very few wells that violate the standard. None of the monitor-well samples violated the standard, and four recharge wells had activities as great as 8.5 pCi/l. Four other recharge well samples were within 0.25 pCi/l of the MCL. Mean radium-226 in the recharge wells was 1.24 pCi/l (σ = 1.99), while the Surficial-aquifer samples had a mean activity of 1.63 pCi/l (σ = 1.07) and Floridan-aquifer samples averaged 1.03 pCi/l (σ = 0.98).

Correlations With Radium

Table IV-2 gives the significant ($\alpha = 0.05$) correlations with radium-226. The correlations with TDS and ionic strength are a result of the fact that a dominant anion in the monitor-well data set is sulfate, which is correlated to radium activity. Figure IV-1 illustrates the relationship of radium-226 and ionic strength, and shows how weak these correlations are. The relationship with ionic strength exists, but the data are very noisy.

The correlation with gross-alpha activity reflects the ability of the gross-alpha method to "see" radium when the radon daughters are accounted for.

The correlations with the sulfate species, which are all aqueous complexes, strongly suggest that radium is mobilized as a complex with sulfate ($RaSO_{4_{aqueous}}$). Insufficient thermodynamic data exist to directly model the radium-sulfate complex, however. Figure IV-2 illustrates the relationship of radium-226 with sulfate activity. Surficial- and Floridan-aquifer samples form a continuum with respect to sulfate activity. Although the data are again noisy, the correlation is evident. One can conclude, therefore, that, until the water becomes saturated with respect to radium sulfate and precipitation occurs, radium complexing with sulfate as an aqueous species appears important and a major means of radium transport.

It has been suggested that the chemical behavior of strontium is similar to that of radium sulfate in water. The negative correlations with strontium ion and strontium bicarbonate (Table IV-2) reflect an inverse relationship where strontium appears to serve as a "catalyst" for nucleation of radium sulfate. Gilkeson et al. (1983) proposed that radium sulfate nucleation is encouraged if barium is present. The strontium data suggest the same phenomenon. Figure IV-3 illustrates the relationship of strontium and radium-226. Water with low strontium concentration generally contains the highest radium activities.

One cannot calculate radium species in the absence of good thermodynamic data, but one can calculate the maximum solubility of radium sulfate as a function of sulfate activity, which is determined by WATEQF. Sillen and Martell (1964) cite a solubility product constant (K_{sp}) for radium sulfate at 25°C of $10^{-10.4}$. The solubility reaction is

$$RaSO_4 \rightleftharpoons Ra^{2+} + SO_4^{2-}. \qquad \text{(IV.1)}$$

The solubility relationship is

$$K_{sp} = 10^{-10.4} = \frac{a_{Ra^{2+}} \cdot a_{SO_4^{2-}}}{a_{RaSO_4}}. \qquad \text{(IV.2)}$$

where $a_{Ra^{2+}}$, etc. indicate activities of the various species. A standard assumption in equilibrium calculations is that the activity of a solid that is present in excess quantities is 1. The maximum amount of radium that can exist in the water at any activity of sulfate is calculated by rearranging (IV.2) as follows

$$a_{Ra^{2+}} = \frac{10^{-10.4}}{a_{SO_4^{2-}}}. \qquad \text{(IV.3)}$$

Note that an initial assumption is the presence of excess radium sulfate, which is probably never the case in this system.

By use of the sulfate activities calculated for the data set, Figure IV-4 shows the maximum amount of radium, converted to picoCuries per liter, that can exist in the water as compared to the actual amount present. The water is clearly highly undersaturated with respect to radium sulfate. At high sulfate activities the degree of undersaturation is almost 6 orders of magnitude.

There is a persistent correlation reported in the literature of radium with total dissolved solids, ionic strength, conductivity, and other indicators of the total amount of soluble material in the water (i.e., Kaufmann and Bliss, 1977). Figure IV-5 shows the radium data and maximum radium activity as a function of ionic strength. Again, correlations exist (Table IV-2), but simple solubility is insufficient to explain the behavior of radium.

Two fallacies of the equilibrium approach are (1) that an excess of radium sulfate does not exist, so radium chemical activities are limited by radium availability, and (2) that the chemical activities of minute particles, which are colloidal in size and radioactive, probably far exceed 1. That is, the surface free energy of the colloid is in excess of the body free energy, and the tendency for radioactive decay disrupts any order within the body of the particle. This phenomenon has been investigated in other, non-radioactive, materials. For example, Chave and Schmalz (1966) examined the affects of particle size on calcite (rhombohedral $CaCO_3$ polymorph) activities. A grain 1 cm in diameter has an activity of 1, at 10^{-4} cm the activity is 1.02,

at $2x10^{-5}$ cm it is 1.15, and at 10^{-6} the activity is 8.9! Clearly, the smaller the particle the more reactive it is, and the higher the solubility of the compound, in this case radium sulfate. For comparison, at a sulfate activity of 10^{-4} m/l and assuming the activity of radium sulfate is 1, the equilibrium radium activity is $10^{-6.4}$ m/l. If one assumes that the radium sulfate is a radiocolloid with an activity of 8, the equilibrium radium activity increases to $10^{1.6}$! It seems unreasonable to assume that the radium sulfate particle has an activity of 1, or less, so saturation is probably never reached in the pore waters of the aquifer systems studied.

LEAD SYSTEMS

Lead-210 Abundance

Lead-210, the immediate ancestor of polonium-210 and a daughter of radon-222, is a beta emitter and is not considered a hazard to human health at the levels present in aquifer systems. However, as a source of polonium-210, it is important because of the high polonium-210 activities that have been discovered in the Surficial aquifer and in the recharge wells. Average lead-210 in the Surficial aquifer is 0.97 pCi/l (σ = 1.71 pCi/l), in recharge wells it is 0.34 (σ = 0.73), and in the Floridan aquifer it is 0.17 (σ = 0.22). One can conclude that lead-210 is slightly more mobile in the Surficial aquifer than in the Floridan, however, in neither aquifer are activities as high as reported for radium-226 or polonium-210. For comparison, activity ratios are given in Table IV-3. In all three environments there is less lead-210 activity than radium-226, even though radon-222 is a mobile intermediate step known to cause concentration of radon daughters in environments such as the Surficial aquifer. The polonium-210/lead-210 ratio greatly exceeds one, which also indicates an excess of polonium in the water as compared to lead. In both situations, the ratios indicate that lead-210 in water is out of equilibrium with parent and daughter. This is because lead is fixed by sorption and/or precipitation of mineral phases on the aquifer rock matrix.

Lead-210 Correlations

The correlation coefficients (Table IV-4) indicate mobility of lead-210 in acid, low alkalinity environments, such as the Surficial aquifer. In alkaline environments, such as the Floridan aquifer, the lead tends to precipitate as $PbCO_3$ (cerussite), which is very insoluble. Total lead concentrations from the Floridan aquifer samples indicate that the lead is near or at saturation with respect to cerussite. Figure IV-6 illustrates the

relationship of lead-210 to pH, and Figure IV-7 shows the relationship with sulfate, another indicator of acidity in this system. In both cases, lead activities are low in alkaline waters and high in acidic solutions.

The other set of significant correlations (Table IV-4) is with ionic strength indicators. These correlations reflect increased sulfate content and competition of cations for sorption sites as ionic strength increases. Figure IV-8 illustrates the variability of lead-210 with respect to ionic strength.

Lead-210 also correlates with polonium-210 (Table IV-4). Even though polonium-210 is present in the water in activities far in excess of those of the parent lead-210, the correlation indicates that the lead-210 parent is responding with the polonium to chemical conditions, and is nearby to serve as a source of polonium. In other words, the polonium-210 is being supplied by decay of lead-210 that is fixed in the aquifer matrix near the sample site. The polonium is not transported significant distances away from its parent.

It is interesting to note that lead-210 is not correlated with total lead (Table IV-4, Figure IV-9). Lead-210 is a minuscule portion of the total mass of lead available and is randomly related to it.

Lead Isotherms

A major question at the initiation of this study was whether the polonium is supported by lead-210. The analytical data clearly indicate that polonium-210 in solution <u>is not</u> supported by lead-210. In order to further predict lead mobility, a series of sorption isotherms was constructed using three different aquifer materials, limestone, ferruginous quartz sand, and clay (Table II.3).

Freundlich isotherms indicate that all three rock materials have significant abilities to fix lead (Figure IV-10). The clay sample has the highest capacity. At lowest concentration (1 mg/l), 96% of the lead was sorbed, and when in contact with the 20 mg/l solution 99.6% of the lead was sorbed. The sand and limestone samples have similar beginning and end points, but the sand is a somewhat better fixation medium than the limestone at intermediate lead concentrations. Both remove approximately 96% of the lead at the low concentration end of the graph, and 98% at the high concentration end. The quartz sand has a higher ability to fix lead than might be expected because of the ferric hydroxide grain coatings and particulate organics in the material.

Langmuir isotherms allow calculation of the adsorption "maximum" for each sample. The clay sample allows true, Langmuir adsorption on the clay surfaces. The calculated sorption maximum is 0.623 meq/100g. This maximum is low for a smectitic clay because many of the sorption sites are saturated with divalent cations, such as magnesium, and other cations. The sand and limestone samples do not follow the Langmuir adsorption isotherm and have negative slopes or sorption maxima. This phenomenon occurs when the sorption medium has a very low sorption capacity and the test solutions have initial concentrations that exceed the capacity of the medium for sorption. Instead, precipitation of new minerals takes place, and the isotherm reflects chemical equilibration between a precipitating phase and the supernatant. In the presence of limestone, the precipitating mineral is probably $PbCO_3$ (cerussite). In the sand the lead is probably also precipitating as cerussite or with ferric hydroxides. Comparison of the results with the data in Table II.3 suggests these trends. Note that the change in pH of the clay sample was towards increasing acidity, which indicates that lead was exchanged for hydrogen on adsorption sites. The final pH's of the sand and limestone samples increased, or became more alkaline, which suggests liberation of alkalinity and possible precipitation of cerussite.

Therefore, the isotherm data indicate that all materials tested can induce fixation of lead. The clay binds the lead by adsorption, so the lead can be exchanged back into the water if chemical conditions are altered. The lead precipitates as a mineral phase in the presence of sand and limestone. If the mineral is the lead carbonate, cerussite, the solubility is very low and lead release to the water is limited, given that no drastic changes in water chemistry occur.

POLONIUM SYSTEMS

Polonium-210 Abundance

It has been determined that polonium-210 is the major alpha-emitting isotope present in the recharge-well environment, and is the cause of the "gross-alpha anomaly" (Oural et al, 1986, 1989). Polonium-210 is most abundant in the Surficial aquifer, and appears to be unimportant in the Floridan aquifer. This is in agreement with the findings of Upchurch (1987), who described high polonium-210 activities in the Surficial aquifer and upper Hawthorn aquifers, and found no problem in the deeper Hawthorn or Floridan aquifers in Lee County.

Mean polonium-210 activity in the Surficial aquifer is 18.81 pCi/l (σ = 21.20). In the recharge-well data set, the mean

activity is 3.91 (σ = 5.11). Of the 9 monitor-well samples, 4 (all from KR-98B wells) exceeded the 15 pCi/l MCL for gross-alpha radiation, and only 1 of the recharge wells exceeded the MCL, although several were close. In the Floridan aquifer, the mean activity is 0.80 (σ = 0.89).

Table IV-3 illustrates the activity ratios of polonium-210 to its parent lead-210. In the Surficial aquifer and recharge wells, the activity ratio is greater than 10, which indicates that the polonium is not supported by soluble lead-210. In the Floridan aquifer, the ratio is reduced to 4, indicating that the polonium is nearer to equilibrium, but only because the activity of polonium is significantly reduced.

Correlations With Polonium-210

Correlation analysis supports a series of interpretations about polonium mobilization. In general, polonium-210 is correlated with indicators of acidity (pH, SO_4^{2-}, etc.) and ionic strength (sulfate is the dominant anion in many samples). Notable correlations include the correlation with Fe^{2+} and SO_4^{2-}. Negative correlations are with variables that represent alkalinity.

The positive correlation of polonium with sulfate is highly significant ($r = 0.92, r^2 = 84.6, \alpha = 0.05$). This is the opposite relationship to that suggested by Harada et al. (1989), who found a positive correlation with H_2S. They argued that sulfide oxidation in the presence of microbial activity is accompanied by conversion of soluble polonium to a filterable form. They did not measure redox potential, sulfate, or iron, so the explanation of this disagreement is not immediately clear. One possibility is that the polonium variability reported in this study is in response to a second factor, such as pH and oxyhydroxide formation. That is, in a iron-rich system such as described herein, polonium co-precipitates with ferric hydroxides as pH increases (see negative correlation with pH in Table IV-5), and both become more soluble as pH decreases. This reflects the iron-sulfide oxidation reactions given in equations III.3a and b. In their study, Harada et al. (1989) dealt with only one well and appear to have been working with a somewhat smaller range of pH and iron and sulfur-species concentrations than this study. Careful examination of their Figures 3 and 4 indicates that polonium activities increased slightly as pH declined in the pumped well.

The negative correlation with pH (Figure IV-11) suggests that polonium is mobilized in low pH solutions. In most samples in the data set, low pH solutions are sulfate rich, so polonium

shows a similar relationship to sulfate (Figure IV-12) and ionic strength (Figure IV-13). However, as will be noted below, low pH appears to be the first-order process associated with polonium mobilization, not sulfur reduction-oxidation.

While polonium has several valence states, the literature suggests that the +4 valence state is dominant. The correlation of polonium activity with Eh is not significant ($r = 0.37$), but examination of the distribution of the data suggests that a relationship other than valence change is related to Eh. Figure IV-14 shows the distribution of polonium-210 with Eh in the Surficial and Floridan aquifers. Polonium activities do not vary with Eh in the Floridan aquifer data set, which suggests a limitation in polonium availability rather than a solubility control. Polonium-210 in the Surficial aquifer, including recharge wells, is different. While most samples reflect low polonium at all Eh's, the KR-98B samples, which were the highest polonium-210 activities measured, consistently occur at Eh's greater than -150 mv. Recall that -150 mv is the threshold predicted by Connell and Patrick (1968) for the on-set of sulfate reduction. Therefore, the high polonium activities fall in the sulfate stability domain.

In previous chapters it was suggested that polonium hydroxide coprecipitates with ferric hydroxide. Examination of the correlation data (Table IV-5) shows a positive correlation with ferrous iron, but no correlation with ferric iron. Figure IV-15 shows the distribution of polonium with respect to total iron. Note that there is a rather poor positive correlation (suggested by the regression line) in the Surficial aquifer data. These data suggest that polonium can remain in solution with ferrous iron, but oxidation to ferric iron and precipitation as ferric hydroxides corresponds with low polonium activities.

It has also been suggested that polonium moves as an organic complex. This is apparently true in some cases, but there is no systematic behavior with TOC (Figure IV-16). The KR-98B samples show the highest polonium activities in waters of moderate TOC content, but high TOC waters do not show correspondingly high polonium.

The equilibrium approach discussed for radium can also be applied to polonium-210. The solubility constant for polonium hydroxide at 25°C is 10^{-37} (Ziv and Efros, 1959). The equation for the dissolution of polonium hydroxide is

$$Po(OH)_4 \rightleftharpoons Po^{4+} + 4(OH)^-. \qquad \text{(IV.4)}$$

The equilibrium equation is

$$K_{sp} = 10^{-37} = \frac{a_{Po^{4+}} \cdot a_{OH^-}^4}{a_{Po(OH)_4}}.$$

(IV.5)

Assuming that the activity of the solid phase is 1 and that it is present in excess quantities, the equilibrium activity of polonium for any hydroxyl activity is

$$a_{Po^{4+}} = \frac{10^{-37}}{a_{OH^-}^4}.$$

(IV.6)

Solving equation IV.6 for the hydroxyl activities calculated from the data set by WATEQF shows that the samples are below the maximum solubility of polonium, and the water is undersaturated with respect to polonium hydroxide. However, at the highest hydroxyl activities reported, the water samples are within 10^{-3} of saturation (Figure IV-17), and given the uncertainties in the equilibrium constant, assumptions of activities, and competing reactions, a "pseudo-equilibrium" may be achieved where colloidal polonium hydroxide forms. It is most likely, however, that these particles are chemically more like complexes than solids. One can conclude from the equilibrium relations that solubility and tendency to transport polonium is greater in acid waters and least in alkaline waters.

Co-precipitation With Iron Hydroxides

The data presented above suggest that polonium behaves in a sympathetic manner with iron. In order to determine the best model for formation of the polonium-hydroxide, which appears to behave as a radiocolloid, a comparison was made of polonium activity with several soluble complexes of iron and hydroxyl.

Figure IV-18 compares polonium-210 activity with uncomplexed ferrous iron ($Fe^{2+}_{aqueous}$). Note that most of the iron in the system is in the ferrous valence state, and the absence of a relationship between the two variables suggests that soluble, ferrous iron has no affect on polonium mobility. The same is true for ferric iron ($Fe^{3+}_{aqueous}$) (Figure IV-19), which is present at activities orders of magnitude smaller than ferrous iron.

Good negative correlations exist between polonium-210 activity and iron hydroxide complexes (Figures IV-20, -21, -22, -23). Comparison with two ferrous hydroxide complexes ($(Fe^{2+}(OH))^+_{aqueous}$ and $(Fe^{2+}(OH)_2)^0_{aqueous}$) suggests that the strongest

relationship is with $(Fe^{2+}(OH)_2)^0_{aqueous}$ (Figure IV-21). The pattern with $(Fe^{3+}(OH)_2)^+_{aqueous}$ is also relatively strong (Figure IV-22), while that with $(Fe^{3+}(OH)_4)^-_{aqueous}$ is weak (Figure IV-23).

A moderately good pattern is indicated when aqueous ferric hydroxide complex ($(Fe^{3+}(OH)_3)^0_{aqueous}$) is compared with polonium activity (Figure IV-24). The pattern is noisy, but indicates that a negative correlation exists. A comparison with the saturation index of ferric hydroxide ($Fe^{3+}(OH)_{3_{amorphous}}$) with polonium activity (Figure IV-25) also suggests that polonium solubility is related to iron-hydroxide complexes. Extrapolation of the slope of a line fit through the highest polonium activities at each saturation index number intersects the minimum polonium activity at saturation with respect to the solid.

Therefore, the data suggest that polonium behaves as a filterable radiocolloid. Iron hydroxide formation is a function of pH. As soluble iron hydroxide complexes, especially those with several hydroxyls coordinated with the iron, form with increasing pH, polonium hydroxide complexes also form. Polonium is most mobile, therefore, in waters in which iron-hydroxide and polonium-hydroxide complexes are minimized.

GROSS-ALPHA RADIATION

Analytical Methods

As Oural et al. (1987, 1989) indicate, analytical method is very critical with respect to gross-alpha analysis. Historical data examined as part of the time-series analysis (Chapter V) contain numerous "spikes" where gross-alpha radioactivity shows an extremely high value for one month. Preceding and subsequent months are at "background". These peaks are a apparently a result of counting water samples that have been recently collected and still have considerable radon and/or radon progeny (Oural et al., 1989). The background samples were evidently analyzed sufficiently long after collection that the radon and progeny had decayed to lead-210. Gross-alpha analyses given in this report were analyzed after the radon/radon progeny had decayed to lead-210.

Gross-Alpha Radioactivity Distribution

Gross-alpha radioactivity from monitor wells in the Surficial aquifer averages 38.3 pCi/l (σ = 40.5 pCi/l). However,

this number is misleading because, of the 9 samples analyzed from 4 monitor wells, only 4 samples from the KR-98B complex exceeded the 15 pCi/l MCL. The data are, therefore, highly skewed. Maximum gross-alpha radioactivity in the Surficial aquifer was 135.1 pCi/l.

Gross-alpha radioactivity in the Floridan aquifer monitor wells averaged 5.8 pCi/l (σ = 1.0 pCi/l), with no samples in excess of the MCl and only one from KR-98B over 10 pCi/l.

Of the 57 samples taken from recharge wells throughout the district, average gross-alpha radioactivity was 8.4 pCi/l (σ = 7.9 pCi/l). Eight wells exceeded the 15 pCi/l MCL, and the highest gross-alpha activity reported was 39.0 pCi/l.

Source of Gross-Alpha Radioactivity

Comparison with the other radionuclide data indicates that polonium-210 is the major alpha emitter present, and it is responsible for most of the gross-alpha activity. Figure IV-26 compares gross-alpha activity with radium-226, polonium-210, and radium-226 plus polonium-210 activities. On each graph the 1:1 ratio line indicates a situation where all gross-alpha activity results from the radioisotopes indicated. Note that radium-226 (Figure IV-26a) shows little correspondence with gross alpha. Polonium-210 (Figure IV-26b) shows a better correlation with gross-alpha radioactivity, and the sum of the two isotopes (Figure IV-26c) shows even better correspondence. The scales of the graphs are logarithmic, so correspondence is weak. This indicates the weaknesses in the gross-alpha method due to radon progeny and other alpha sources, and self absorption in high ionic strength solutions (Oural et al., 1989).

Table IV-1. Significant Pearson product-moment correlations of chemical variables with uranium. All correlations are significant at an $\alpha = 0.05$. AR = activity ratio.

Variable	^{238}U	^{234}U	AR
P_{CO2}	----	----	0.63
CO_2 (tot.)	----	----	0.48
Tot. alkalinity	----	-0.53	----
Carb. alkalinity	----	-0.53	----
Ca^{+2}	----	-0.50	----
Mg^{+2}	----	-0.49	----
K^{+}	----	-0.58	----
H_2CO_3	----	----	0.66
$MgOH^{+1}$	----	----	-0.55
$MgCO_3$	----	----	-0.59
MgF^{+}	----	----	-0.53
$CaSO_4$	----	----	0.49
$CaHCO_3^{+}$	----	-0.52	----
CaF^{+}	----	-0.50	----
Fe^{+2}	0.55	0.62	----
$FeH_2PO_4^{-}$	0.60	----	----
$Al(OH)_{4\ aq}$	----	----	0.88
$CaHPO_4$	----	-0.50	----
$NaHPO_4^{-}$	----	-0.51	----
^{234}U	0.77	1.00	----

Table IV-2. Significant Pearson product-moment correlations of chemical variables with radium-226.

Variable	Correlation coefficient
Ionic strength	0.51
Total Dissolv. Solids	0.50
Na^{+}	0.49
Cl^{-}	0.51
SO_4^{-2}	0.61
$NaSO_4^{-}$	0.62
$NaCl_{aq}$	0.48
$KSO4^{-2}$	0.60
Fe^{+2}	0.56
FeH_2PO4^{-1}	0.66
$FeSO_4$	0.82
Sr^{+2}	-0.55
$SrHCO_3^{+}$	-0.64
Gross-alpha activity	0.58

Table IV-3. Average activity ratios for radium-226, lead-210, and polonium-210 by environment.

Environment	Lead-210 / Radium-226	Polonium-210 / Lead-210
Surficial aquifer	0.60	19.39
Recharge wells	0.27	11.50
Floridan aquifer	0.17	4.71

Table IV-4. Significant (α = 0.05) Pearson product-moment correlations with respect to lead-210.

Variable	Correlation Coefficient
pH	-0.83
log P_{CO2}	-0.68
Ionic strength	0.92
Total dissolved solids	0.90
Total alkalinity	-0.85
Carbonate alkalinity	-0.85
Ca^{+2}	-0.77
Na^{+}	0.99
H^{+}	0.95
Cl^{-}	0.97
SO_4^{-2}	0.96
HCO_3^{-}	-0.76
$MgSO_{4\_aq}$	0.85
$NaSO_4^{-}$	0.98
NaCl	0.99
KSO_4^{-}	0.85
HSO_4^{-}	0.98
$FeH_2PO_4^{+1}$	0.98
$FeH_2PO_4^{+2}$	0.90
$FeCl_3$	0.80
$FeSO_4$	0.84
MnOH	-0.74
$MnSO_4$	0.84
$MnCl^{+1}$	0.75
$MnCl_2$	0.90
$MnCl_3$	0.93
$Al(OH)_4^{-1}$	-1.00
$H_2PO_4^{-1}$	0.96
$MgH_2PO_4^{+1}$	0.89
^{210}Po	0.99
Gross-alpha activity	0.88

Table IV-5. Significant Pearson product-moment correlations (α = 0.05) of monitor-well data with polonium-210.

Variable	Correlation Coefficient
pH	-0.80
log P_{CO2}	-0.70
$CO_{2\ tot}$	-0.63
Ionic strength	0.84
Total dissolved solids	0.82
Total alkalinity	-0.85
Carbonate alkalinity	-0.84
Ca^{+2}	-0.70
Mg^{+2}	-0.49
Na^{+}	0.97
K^{+}	-0.49
H^{+}	0.91
Cl^{-}	0.92
SO_4^{-2}	0.92
HCO_3^{-}	-0.78
OH^{-}	-0.48
F^{-}	-0.57
$MgSO_4$	0.65
$MgHCO_3^{+}$	-0.62
MgF^{+}	-0.56
$CaHCO_3^{+}$	-0.67
CaF^{+}	-0.61
$NaSO_4^{-}$	0.97
$NaHCO_3$	-0.60
NaCl	0.96
KSO_4^{-}	0.78
HSO_4^{-}	0.95
$H_3SiO_4^{-}$	-0.47
Fe^{+2}	0.62
$FeHPO_4^{+1}$	0.59
$FeH_2PO_4+^{1}$	0.91
$FeH_2PO_4+^{2}$	0.72
$FeCl_3$	0.80
$FeSO_4$	0.85
$H_2PO_4^{-}$	0.94
$MgH_2PO_4^{+}$	0.78
^{210}Pb	0.99
Gross-alpha activity	0.86

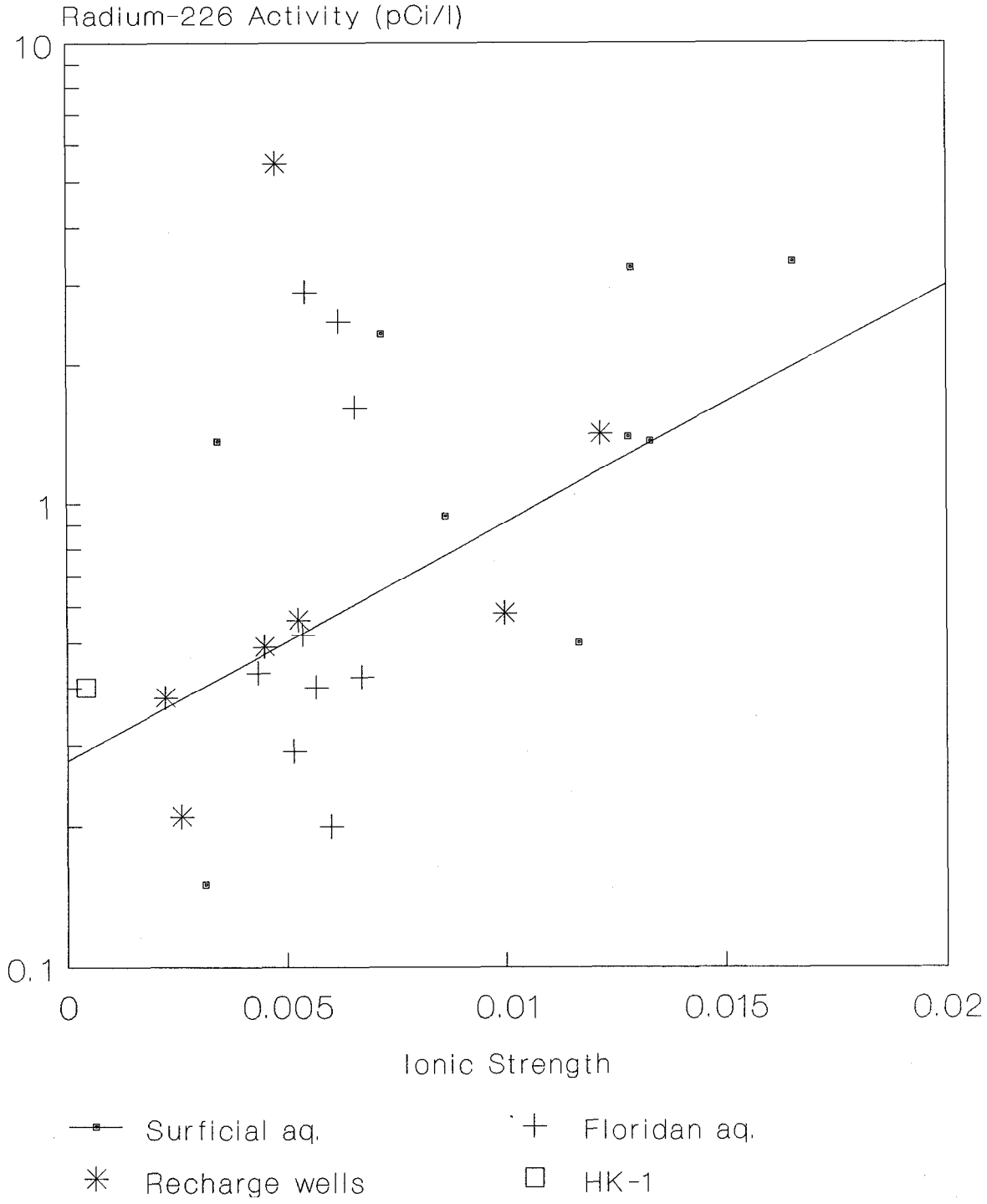


Figure IV-1. Scatter diagram showing relationship of radium-226 activity to ionic strength. Regression line is on surficial aquifer data.

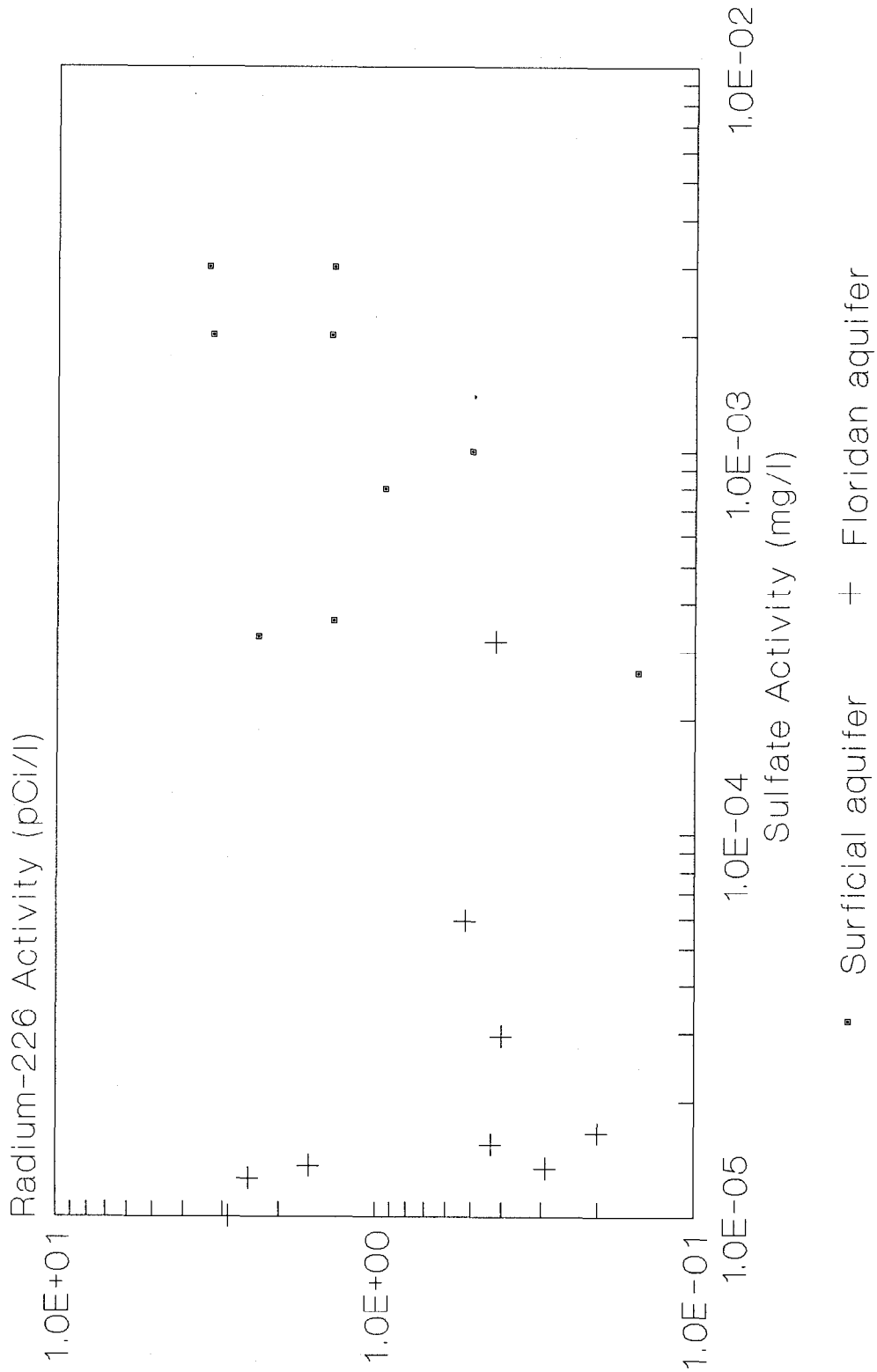


Figure IV-2. Scatter diagram showing relationship of radium-226 activity to calculated sulfate activity.

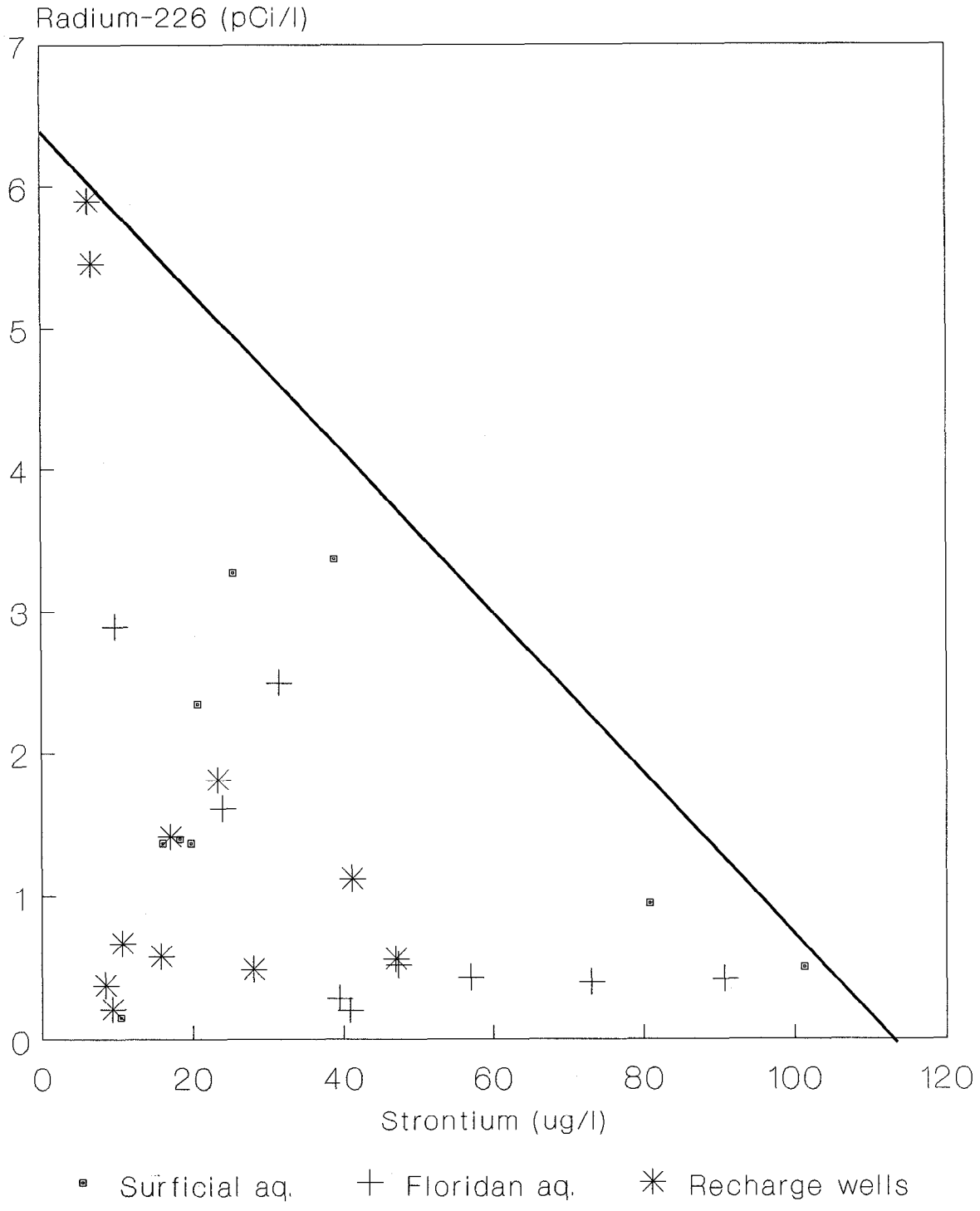


Figure IV-3. Scatter diagram showing relationship of radium-226 activity to strontium concentration. Heavy line is a fence to emphasize crude negative relationship of strontium to radium.

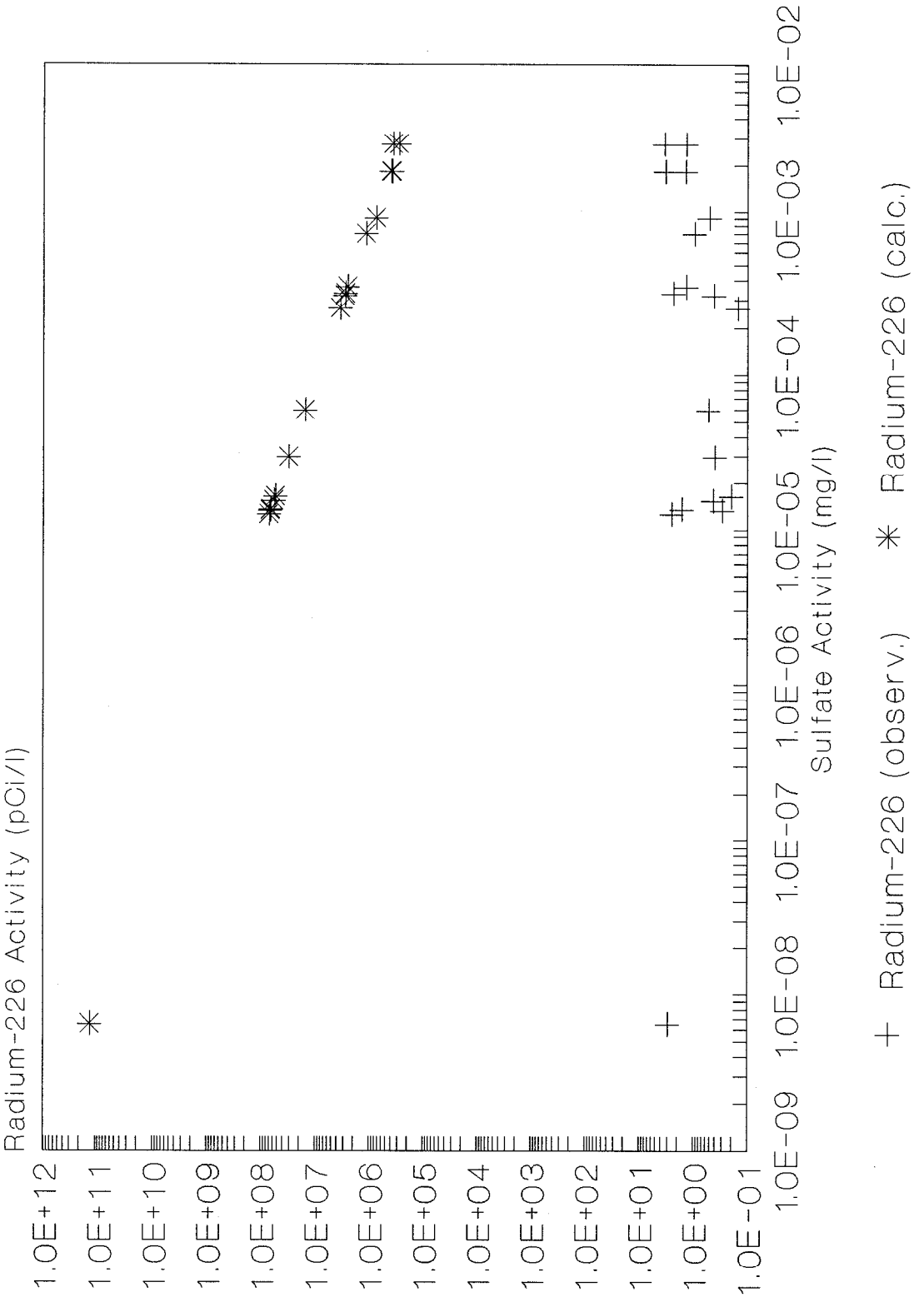


Figure IV-4. Scatter diagram comparing calculated maximum radium activity, based on saturation with respect to radium sulfate, and measured radium activity to sulfate activity.

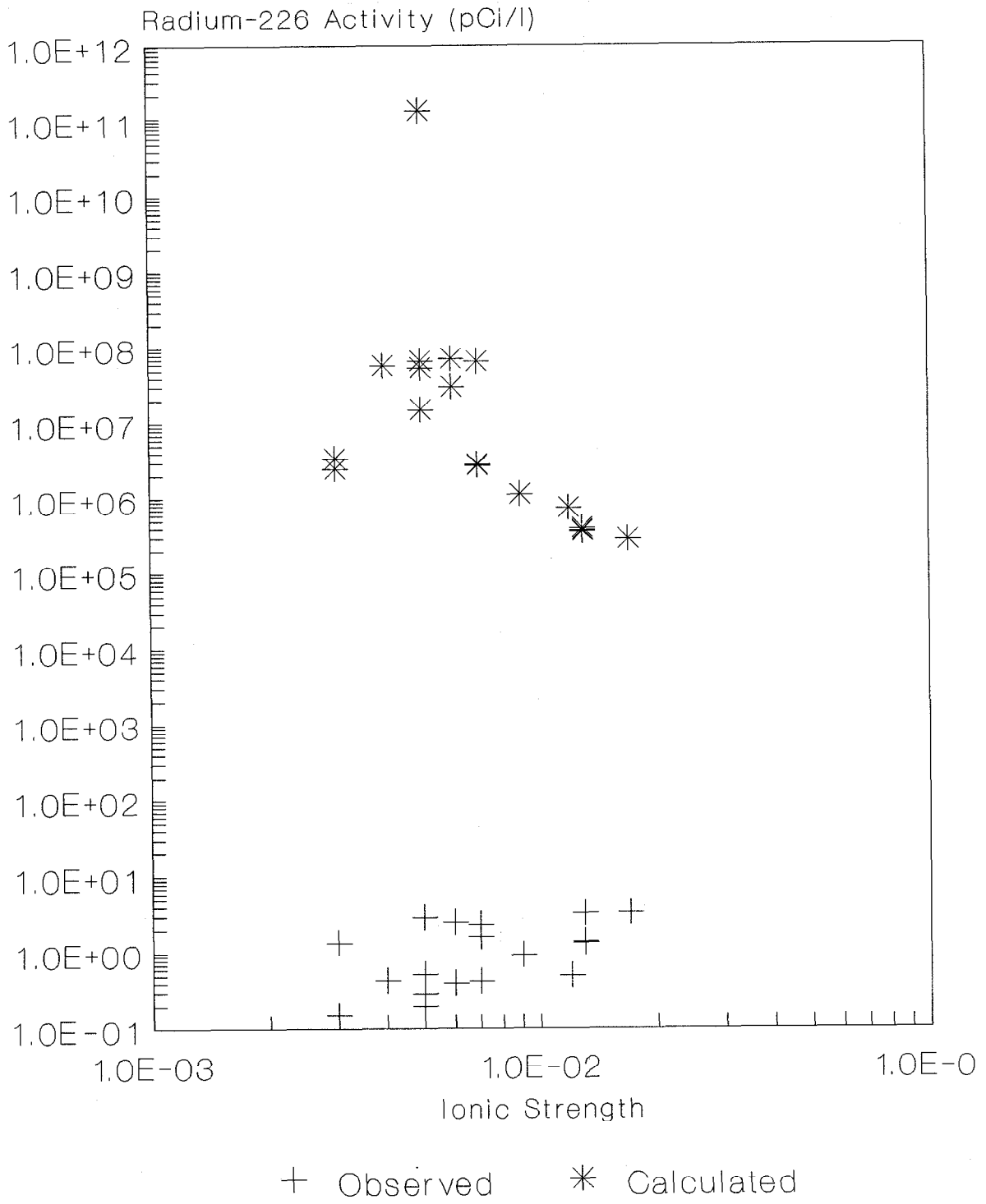


Figure IV-5. Scatter diagram comparing calculated maximum radium activity, based on saturation with respect to radium sulfate, and measured radium activity to ionic strength.

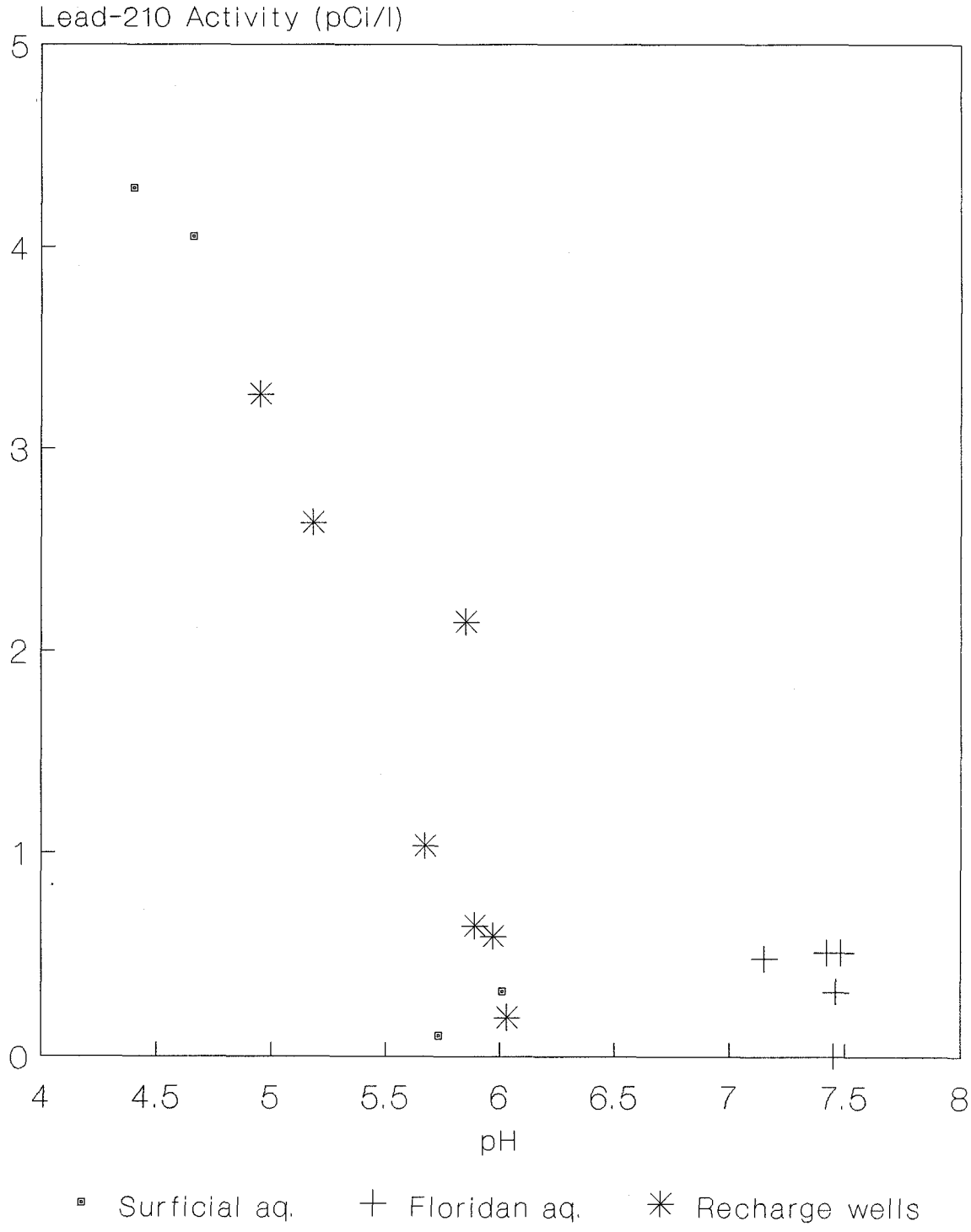


Figure IV-6. Scatter diagram illustrating the relationship of lead-210 activity to pH.

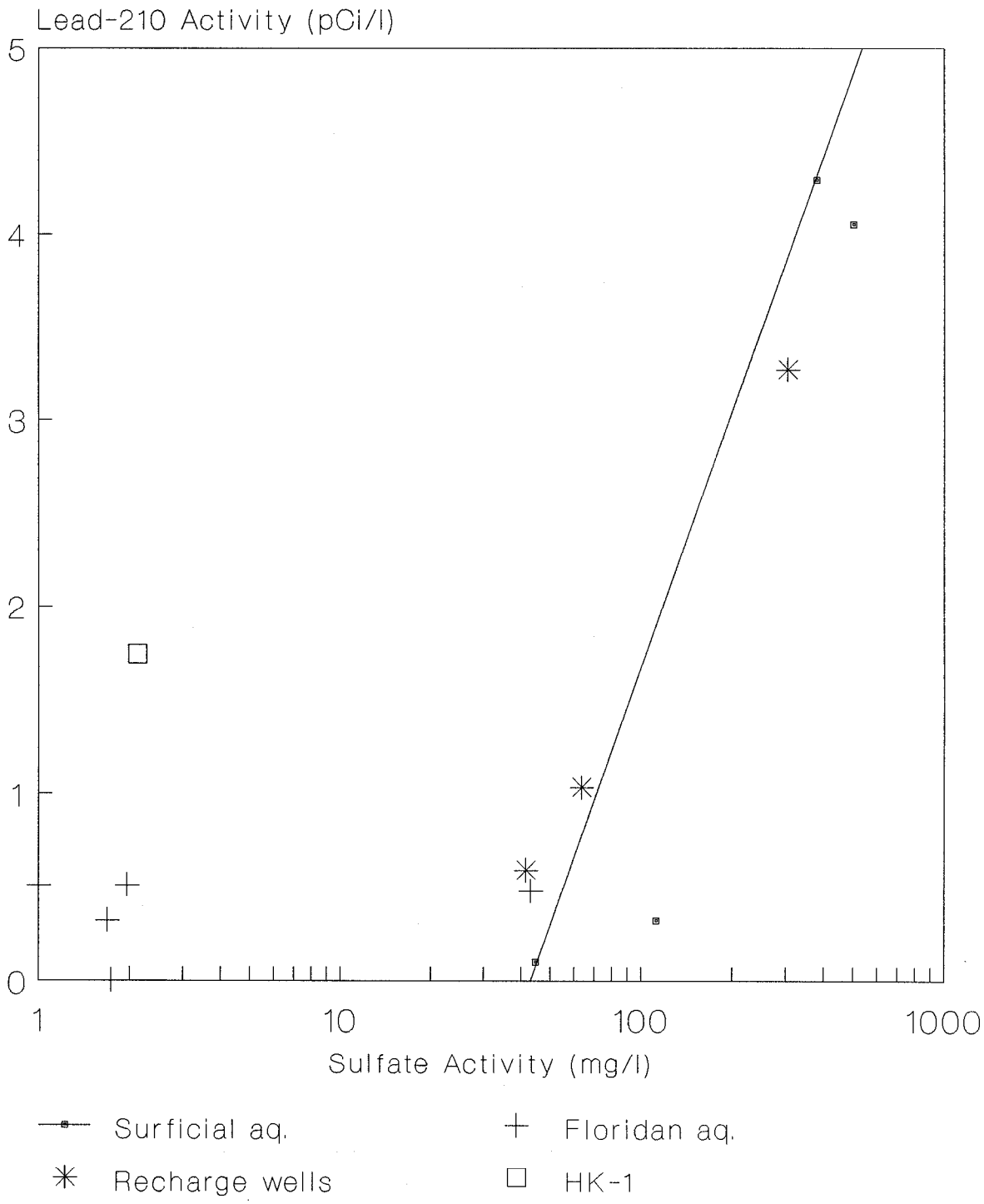


Figure IV-7. Scatter diagram showing the relationship of lead-210 activity to calculated sulfate activity. Regression line is on Surficial aquifer data.

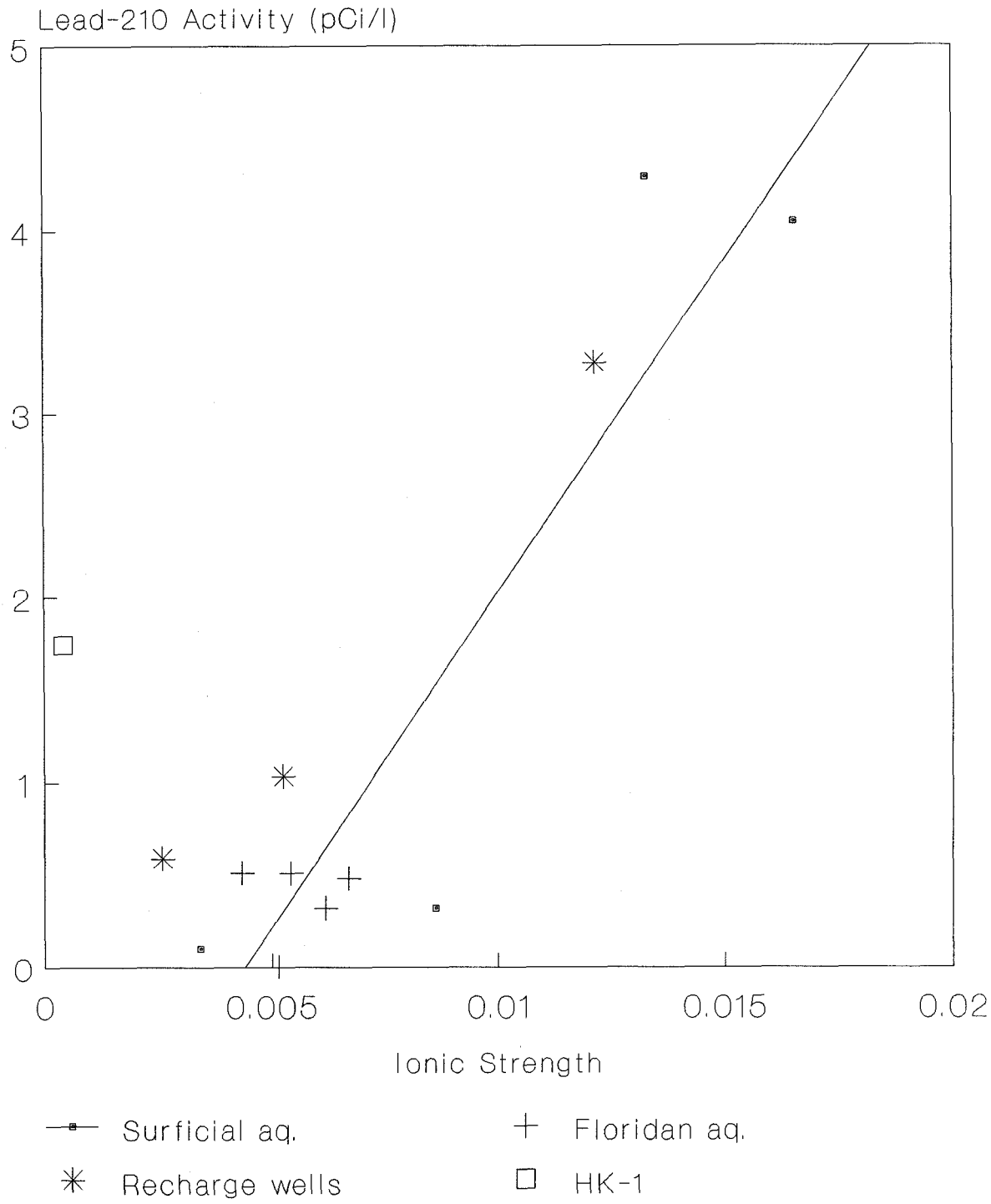


Figure IV-8. Scatter diagram showing the relationship of lead-210 to ionic strength. Line is a linear regression on the surficial aquifer data.

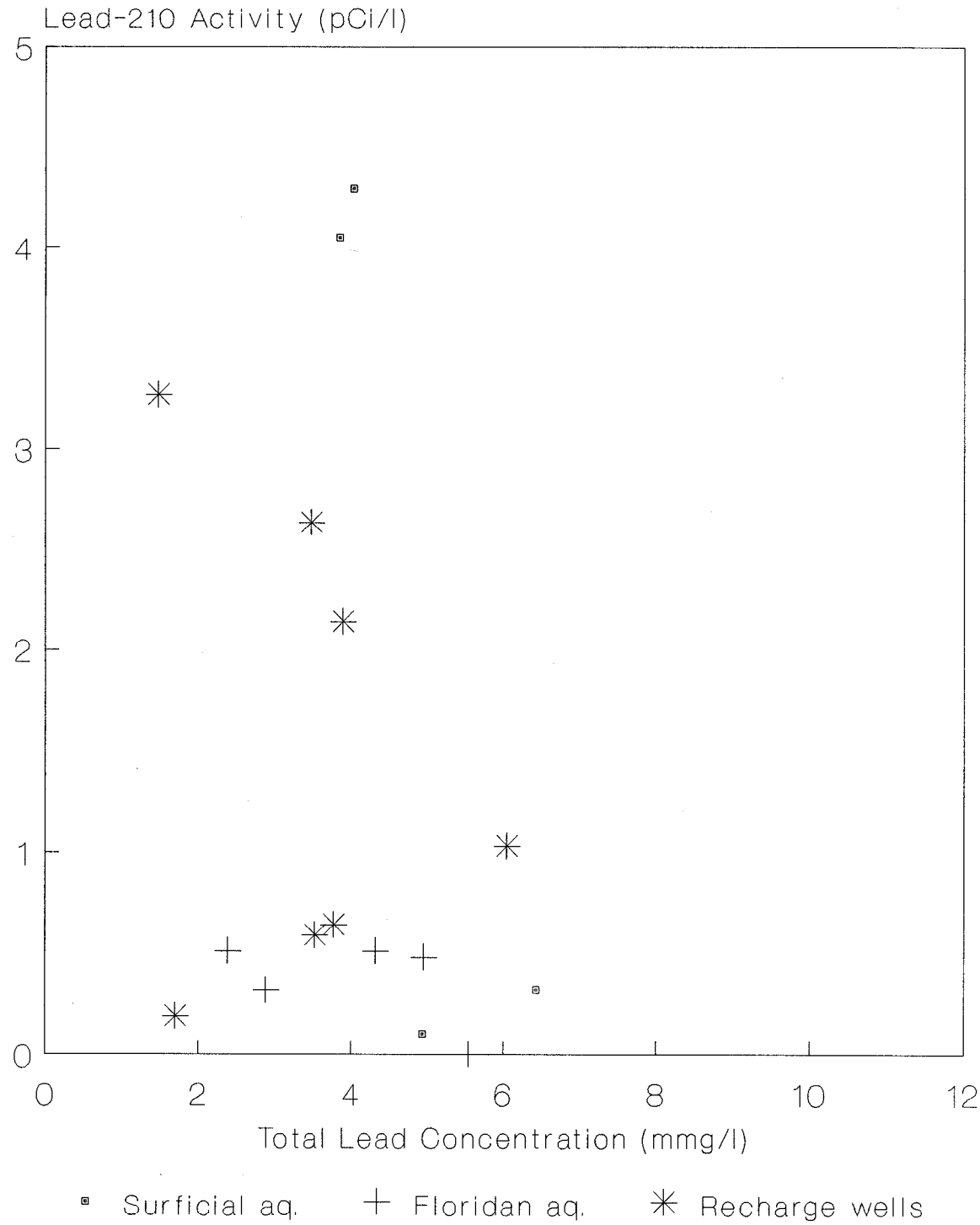


Figure IV-9. Scatter diagram illustrating the relationship of lead-210 to total lead concentration.

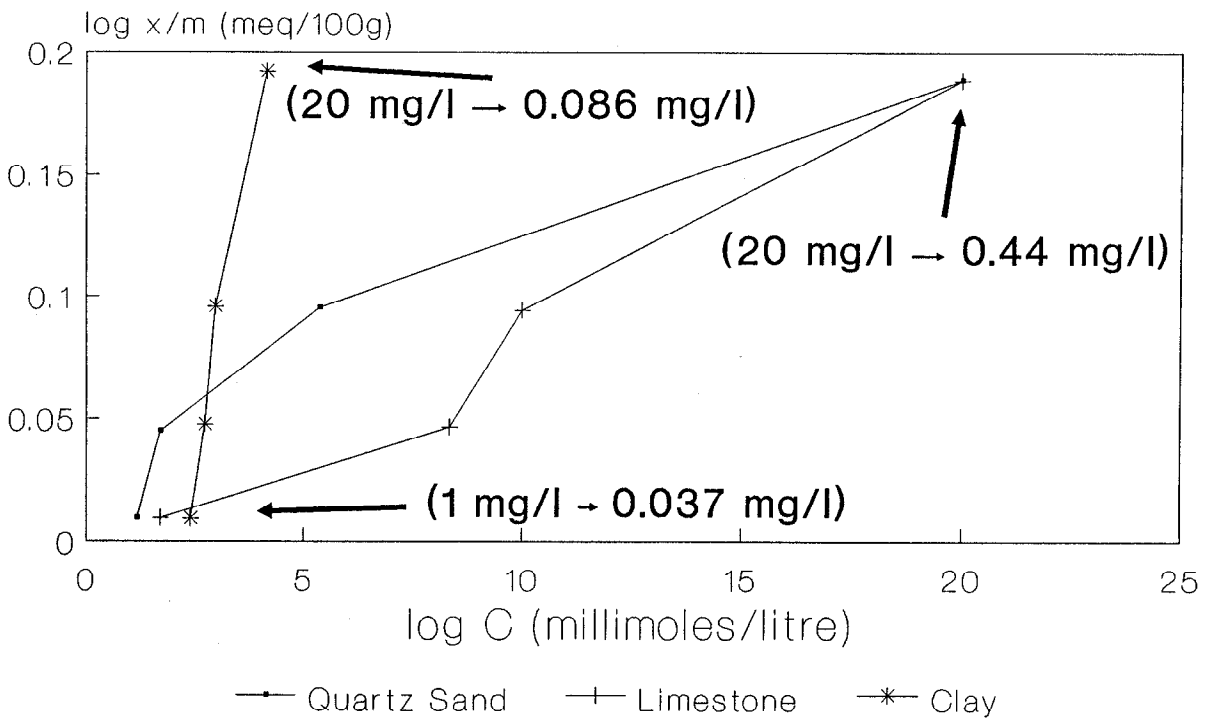


Figure IV-10. Freundlich isotherms for the three aquifer materials. Bold numbers indicate average beginning and end concentrations of lead solutions.

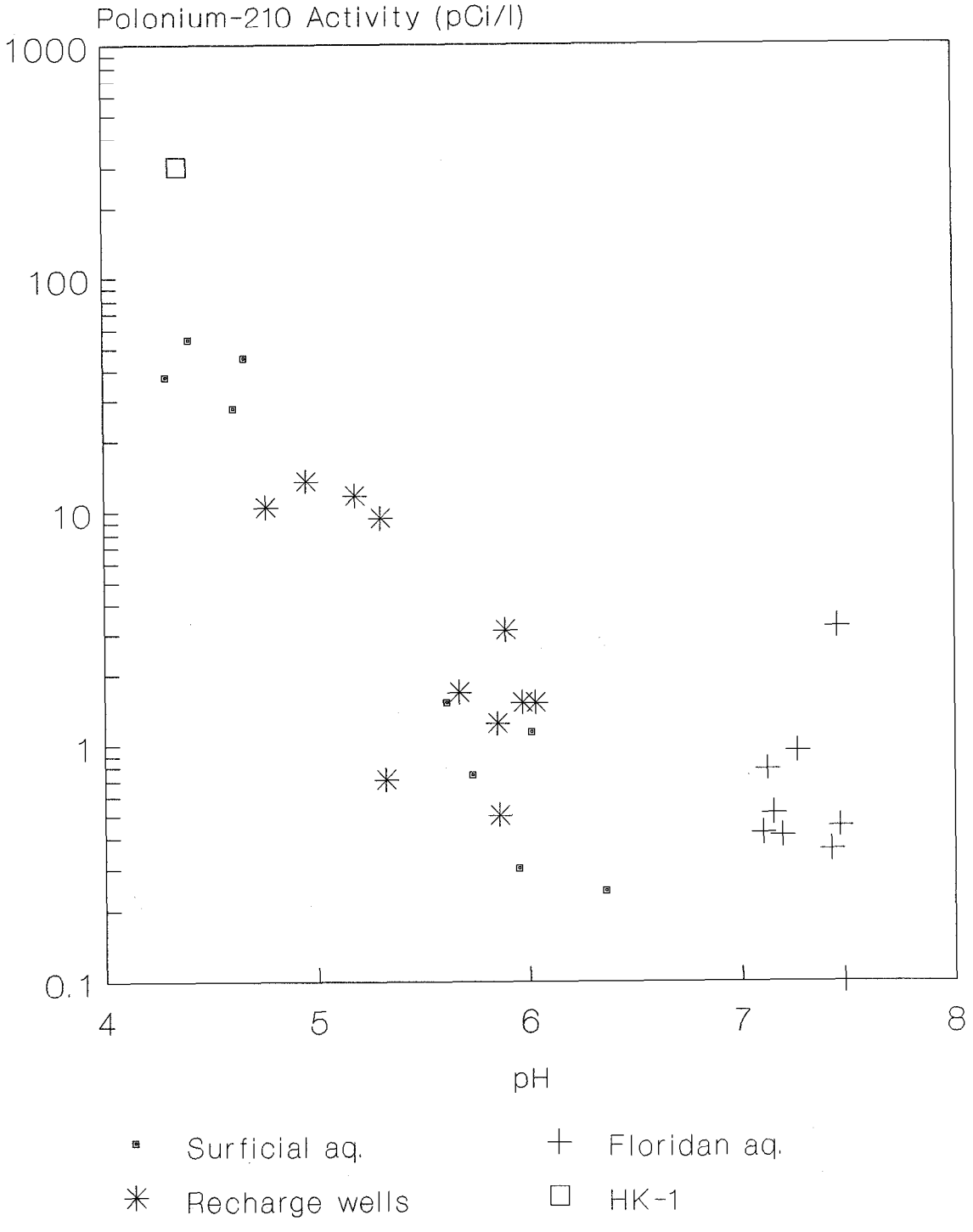


Figure IV-11. Scatter diagram showing the relationship of polonium-210 activity to pH.

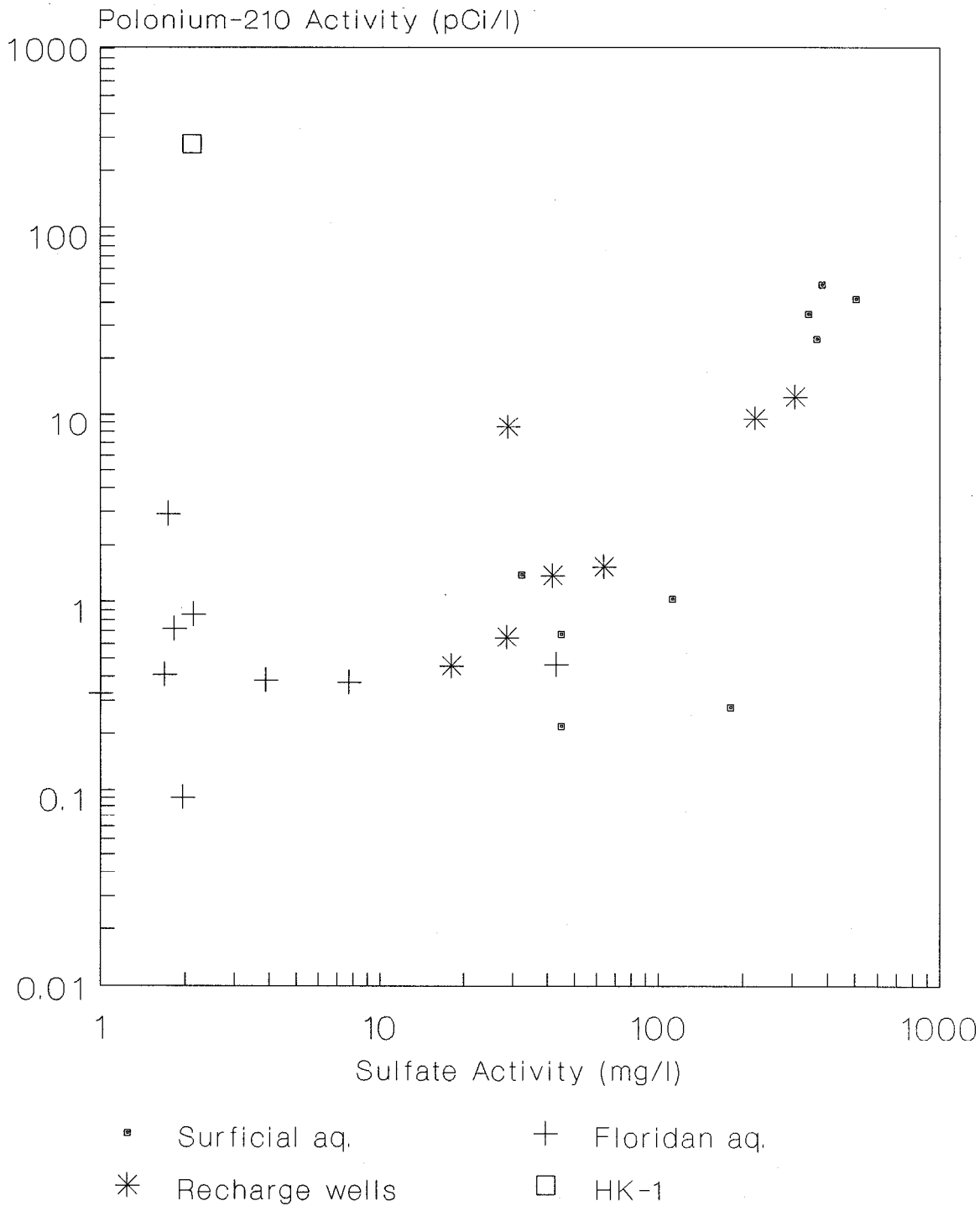


Figure IV-12. Scatter diagram illustrating the relationship of polonium-210 to sulfate activity.

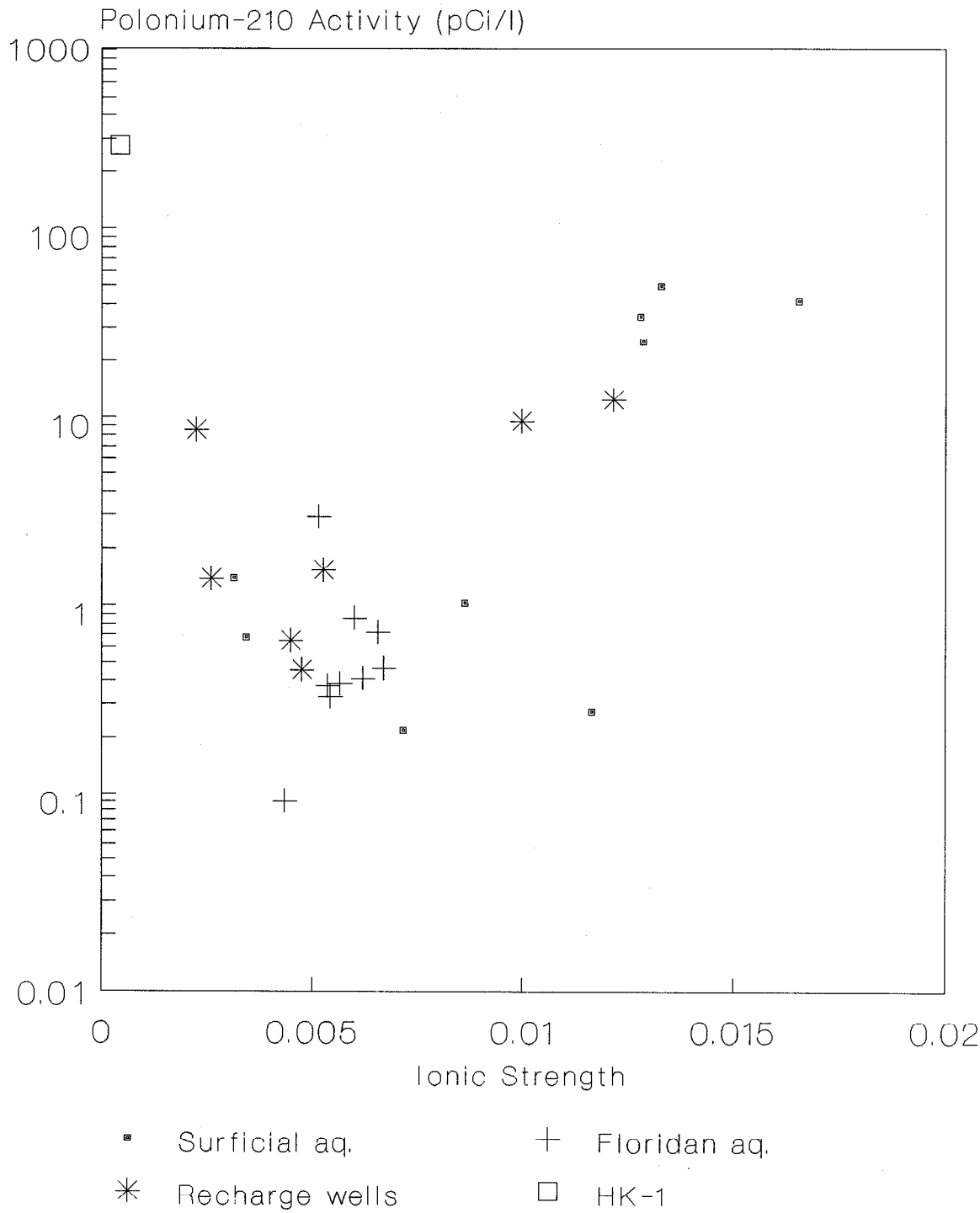


Figure IV-13. Scatter diagram illustrating the relationship of polonium-210 to ionic strength.

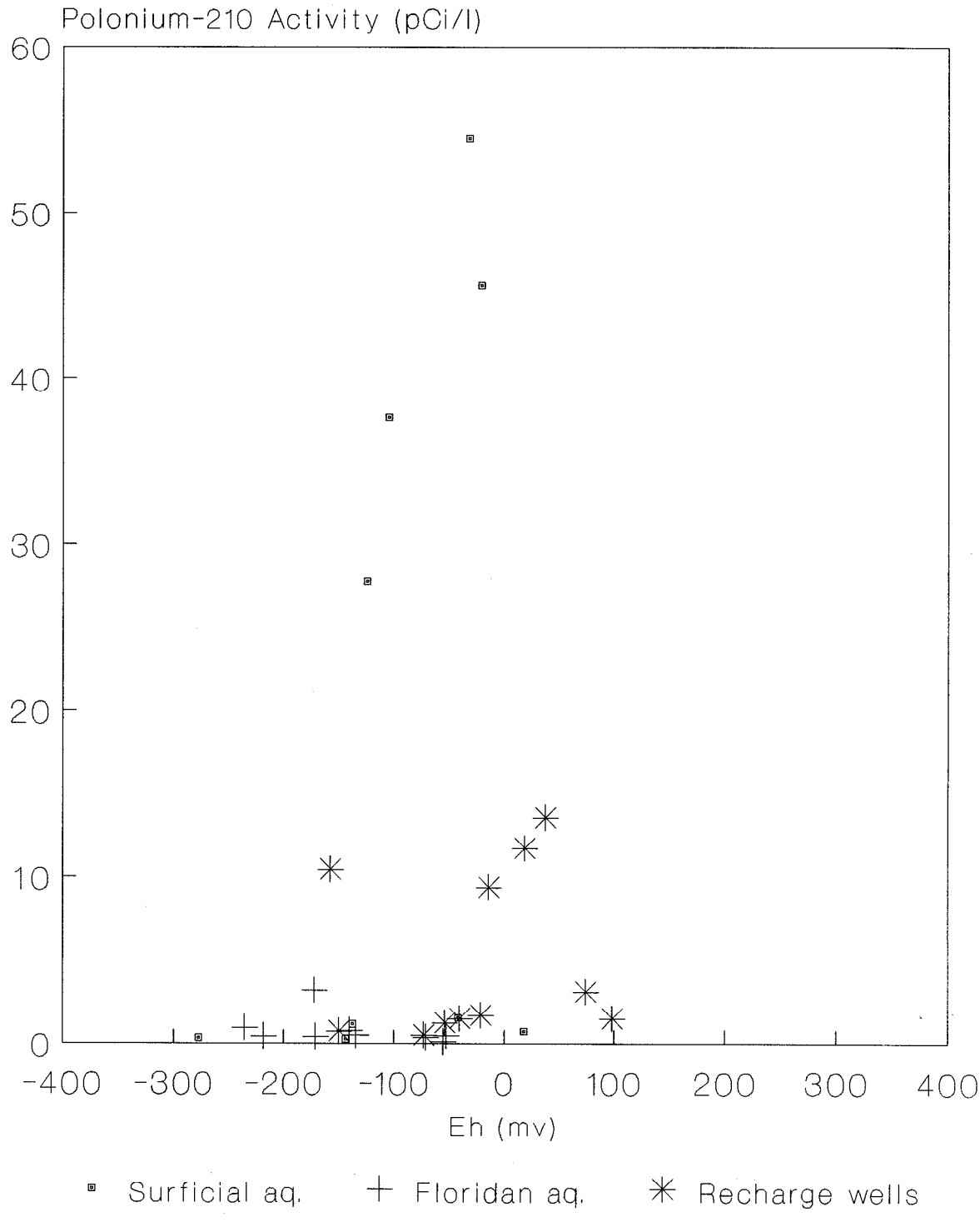


Figure IV-14. Scatter diagram showing the relationship of polonium-210 to redox potential (Eh).

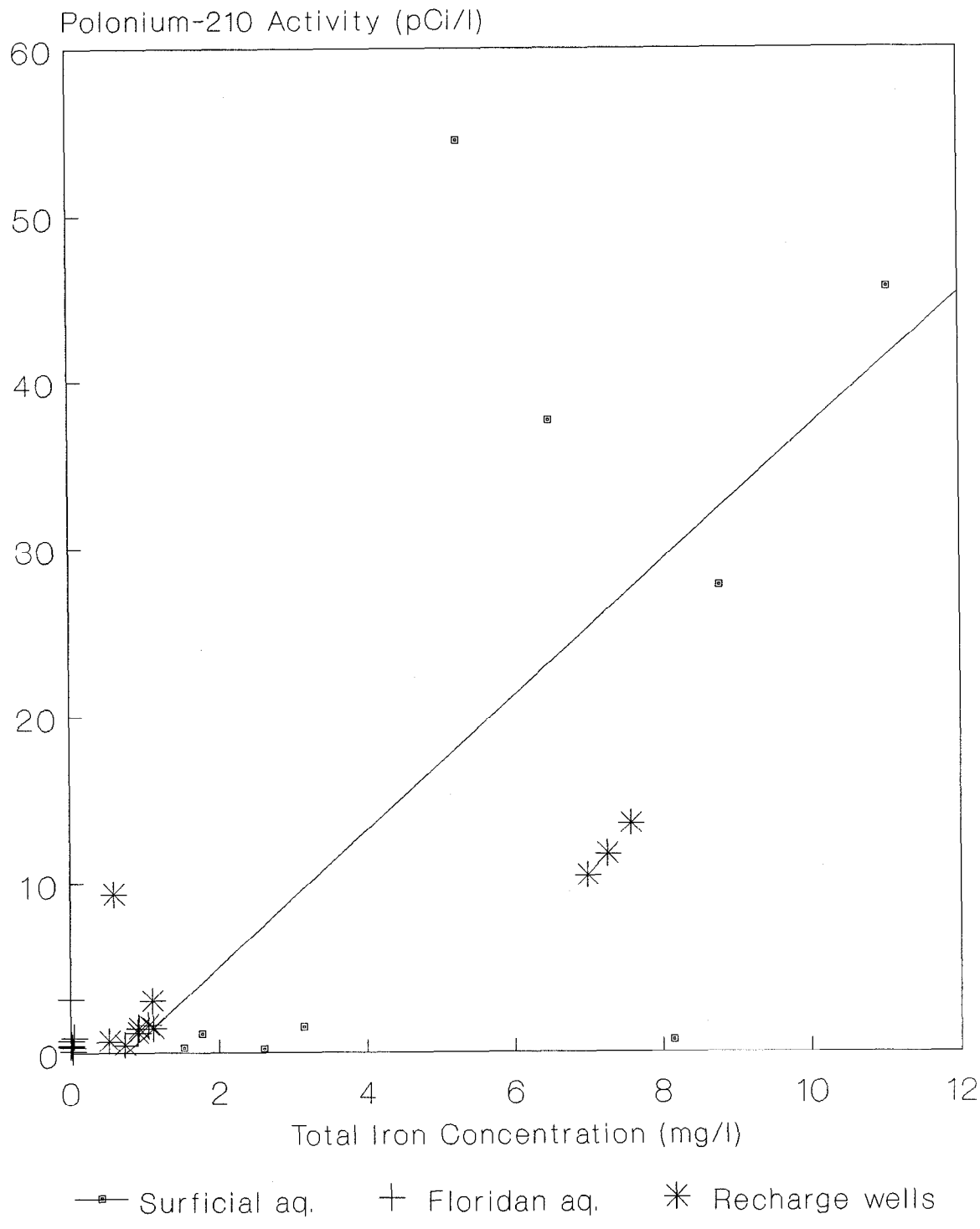


Figure IV-15. Scatter diagram showing the relationship of polonium-210 to total iron concentration. Regression line is on the Surficial aquifer data.

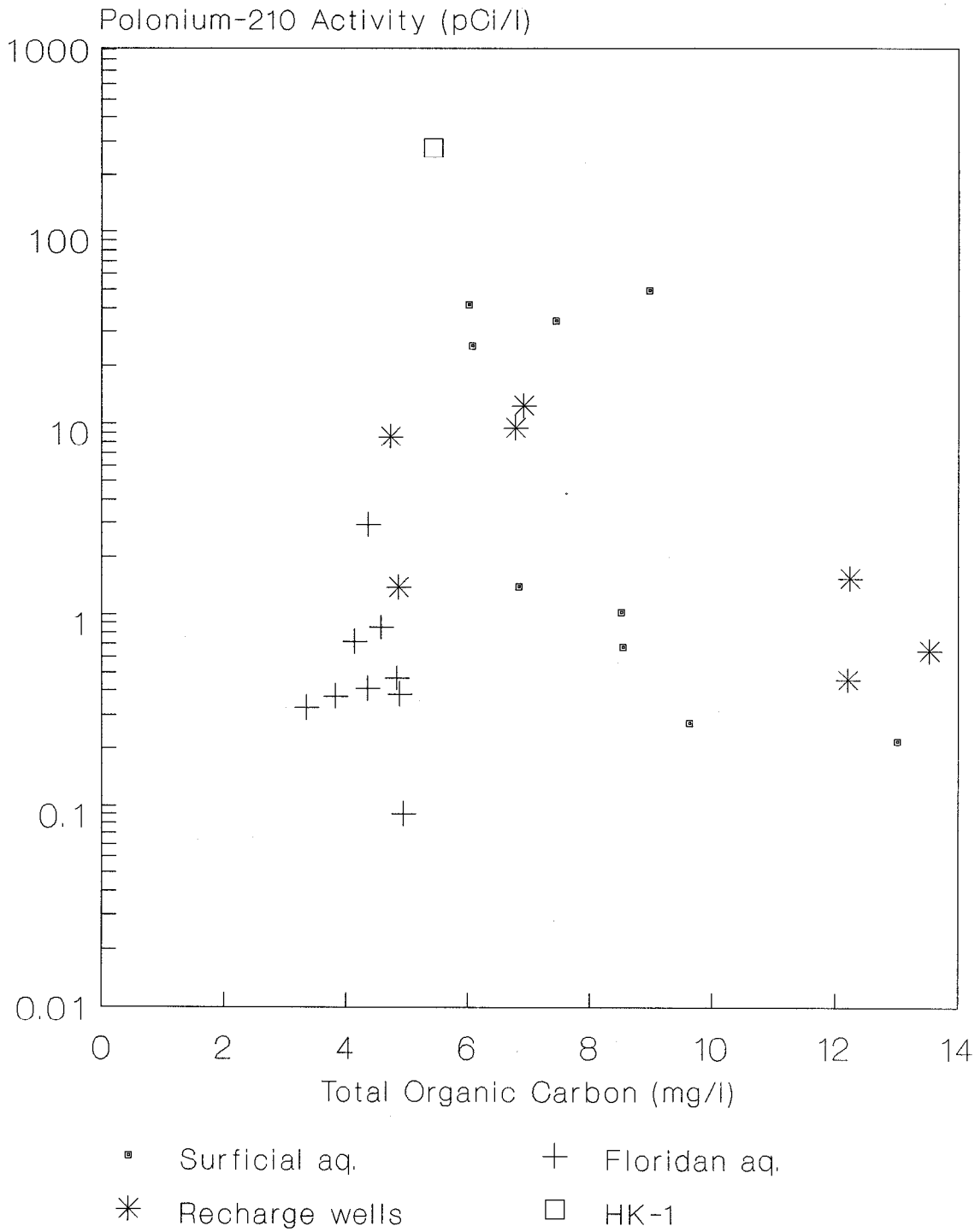


Figure IV-16. Scatter diagram showing the relationship of polonium-210 to total organic carbon (TOC).

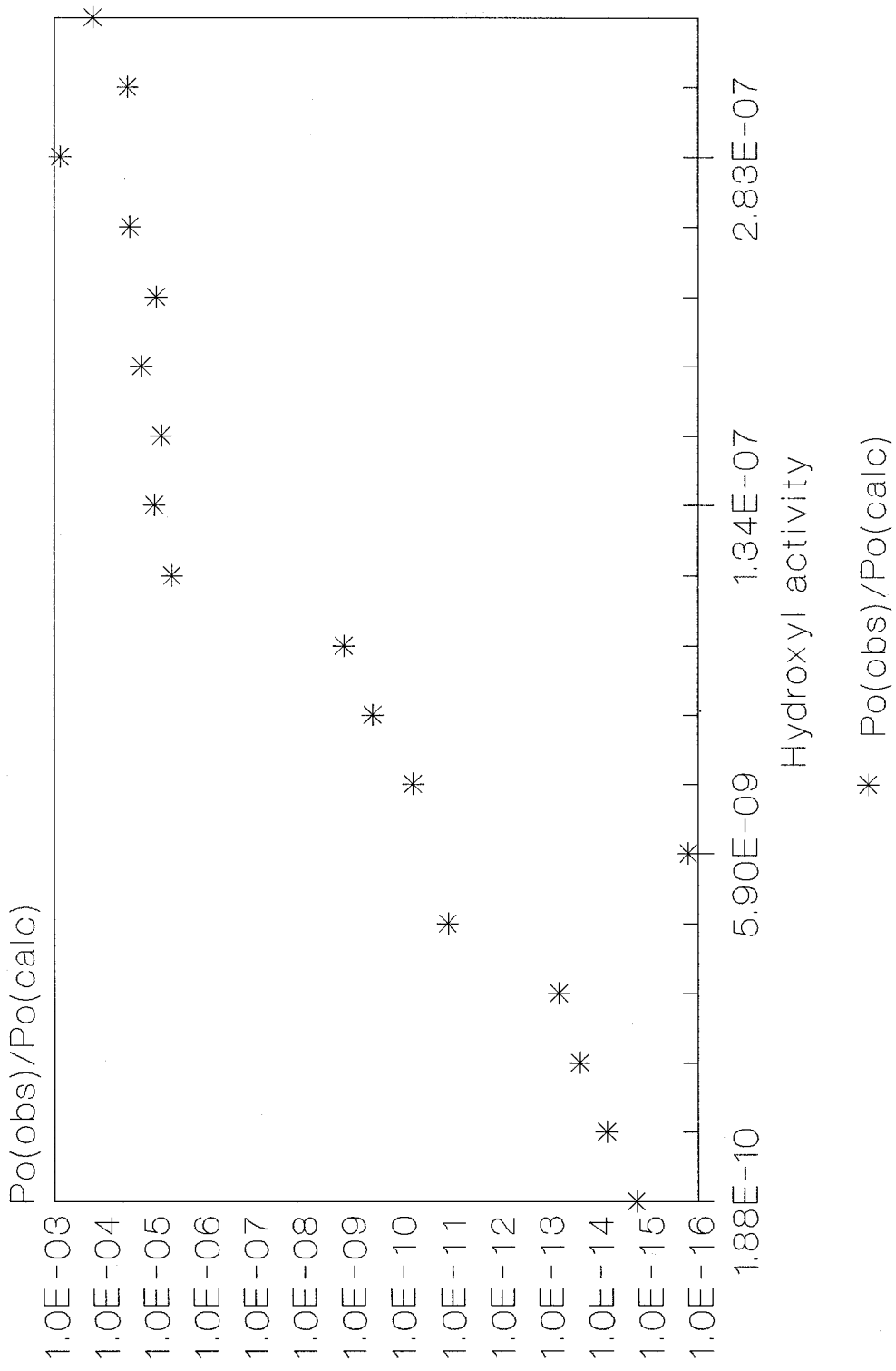


Figure IV-17. Scatter diagram showing the ratio of actual polonium-210 activity to the maximum polonium activity possible assuming equilibrium with polonium hydroxide as a function of calculated hydroxyl activity.

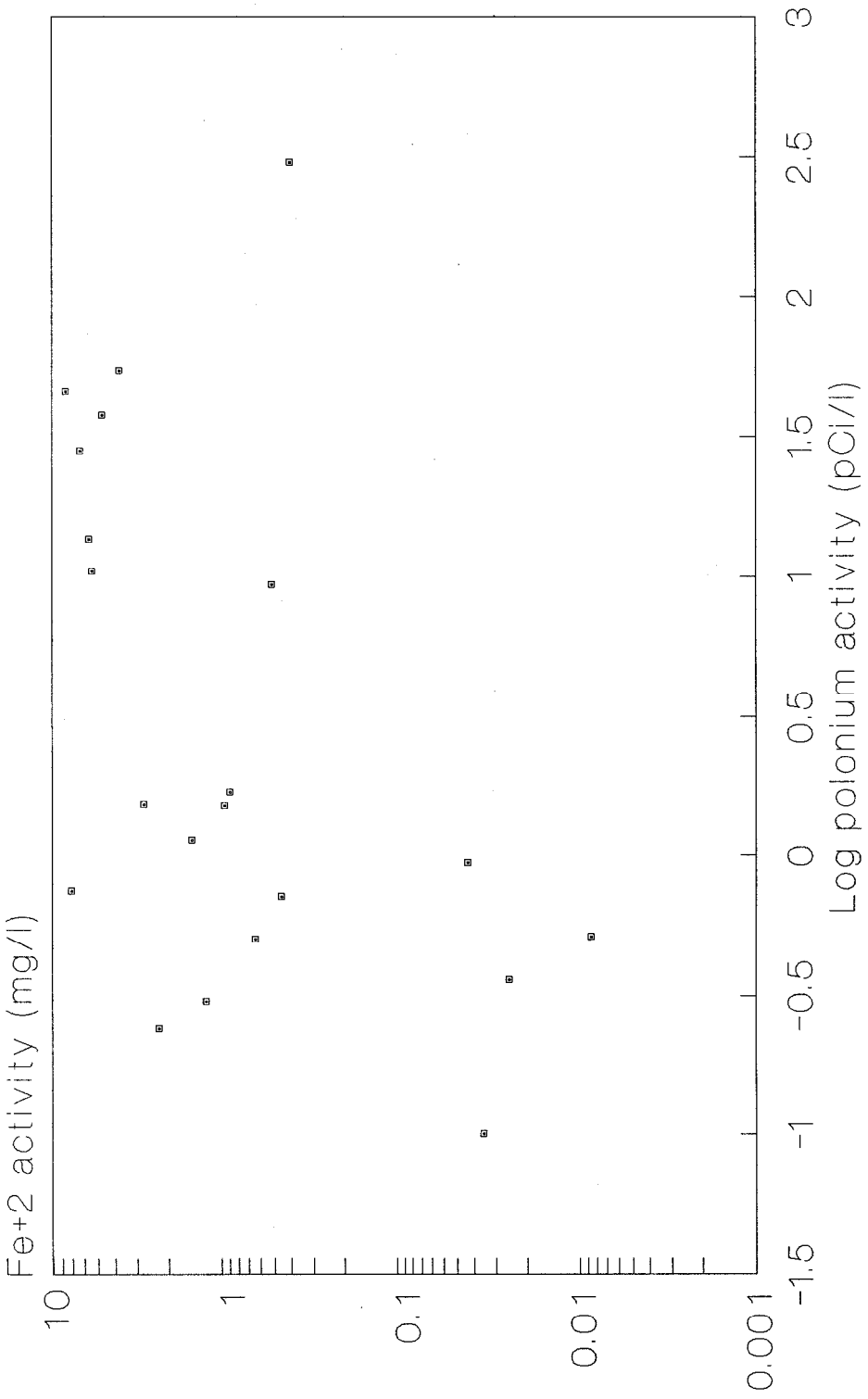


Figure IV-18. Scatter diagram showing the relationship of ferrous iron (Fe^{+2}) activity to polonium-210 radioactivity.

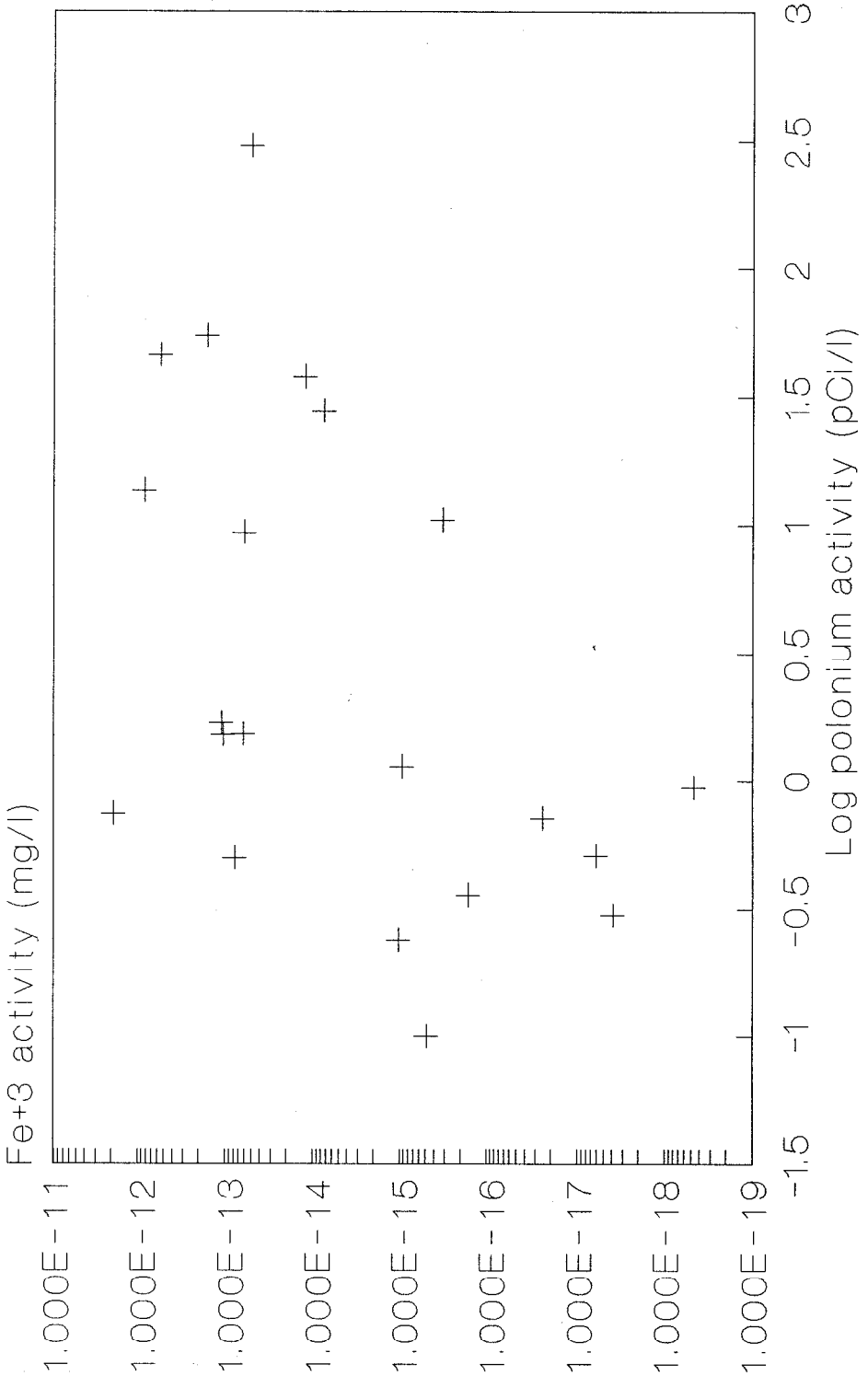


Figure IV-19. Scatter diagram showing the relationship of ferric iron (Fe^{+3}) activity to polonium-210 radioactivity.

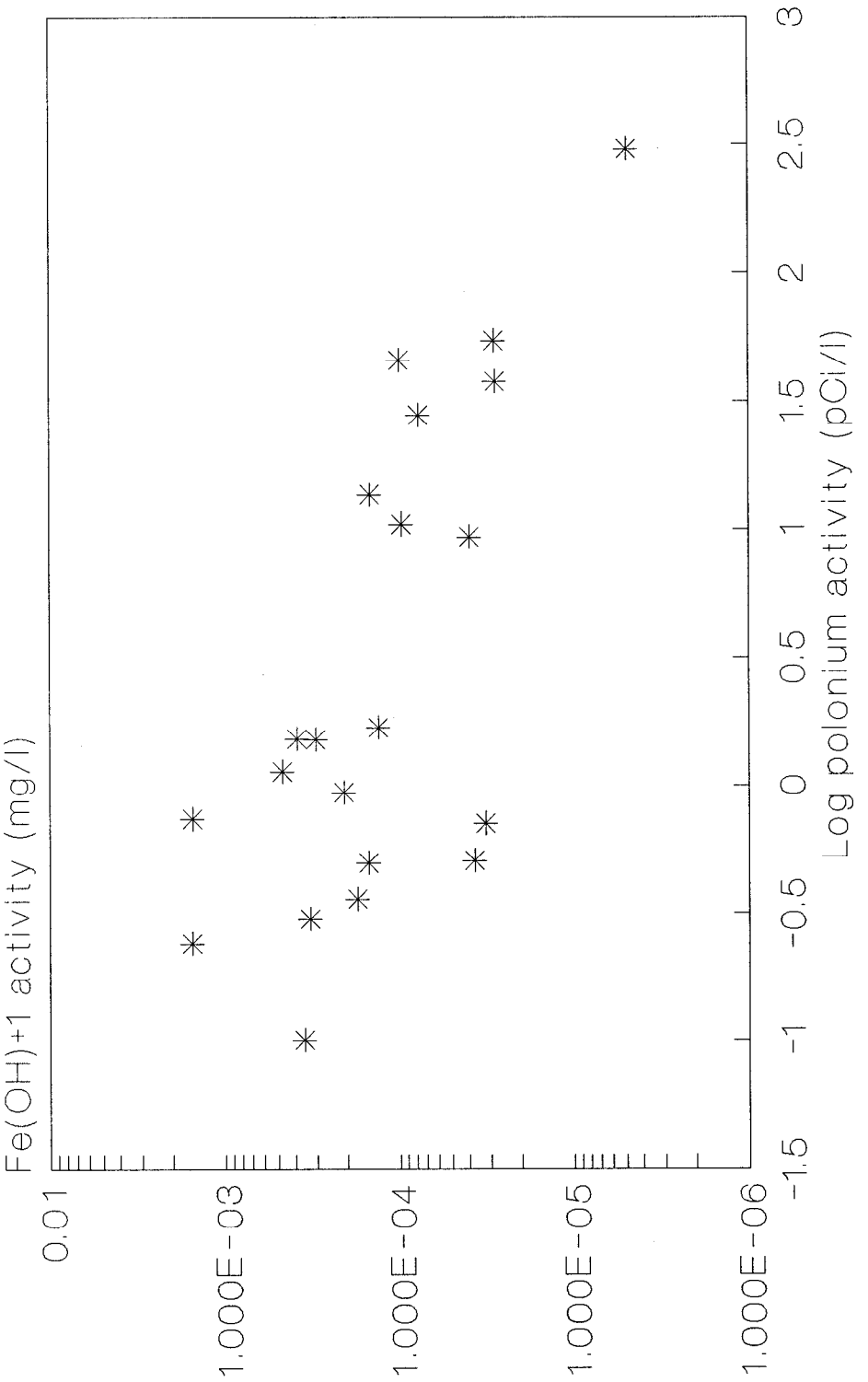


Figure IV-20. Scatter diagram comparing polonium-210 activity with $Fe(OH)^{+1}$ activity.

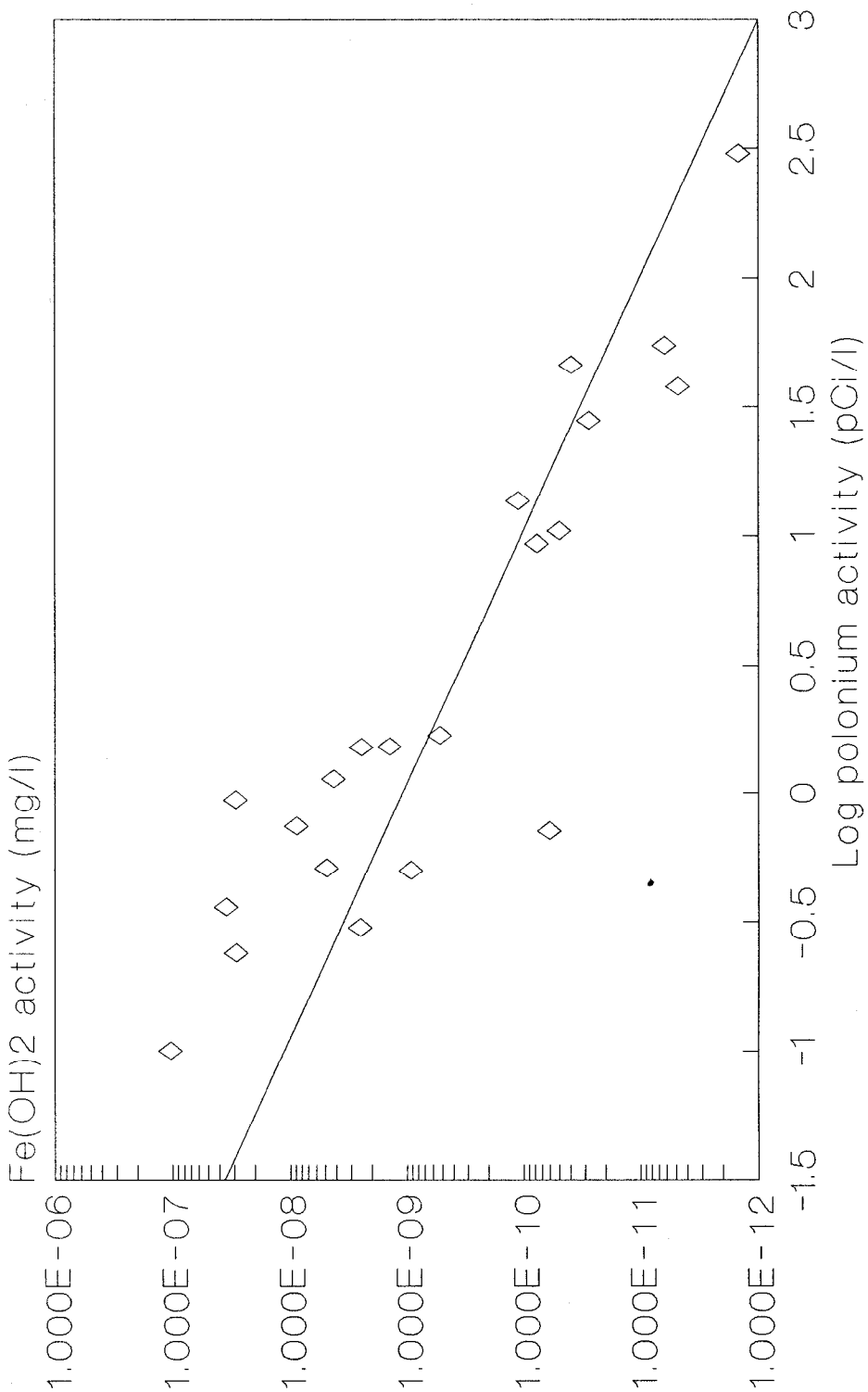


Figure IV-21. Scatter diagram showing the relationship of polonium-210 activity to $Fe(OH)_2$ activity.

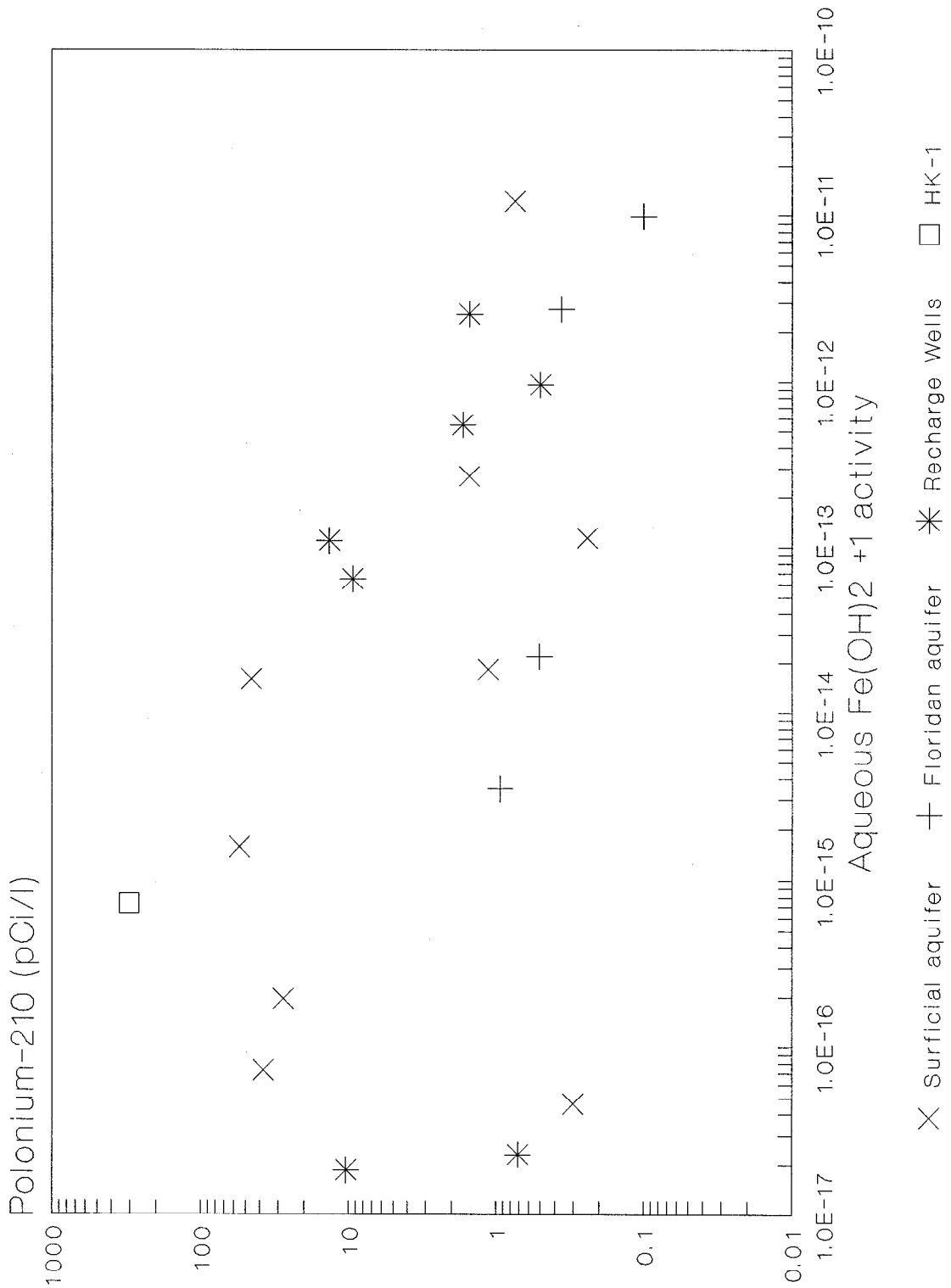


Figure IV-22. Scatter diagram showing relationship of polonium-210 radioactivity to $Fe(OH)_2^+$ activity.

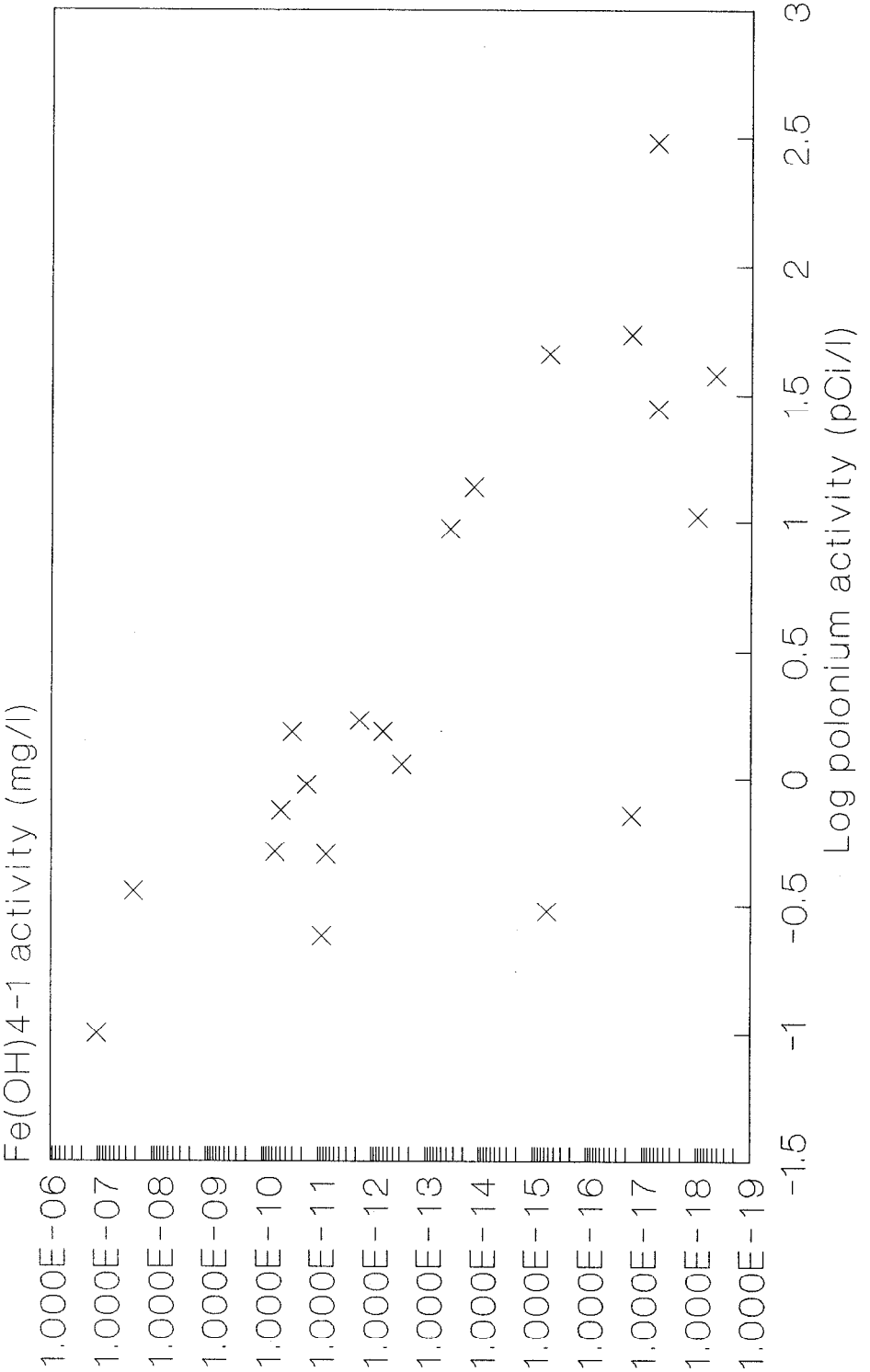


Figure IV-23. Scatter diagram showing relationship of polonium-210 radioactivity to $Fe(OH)_4^{-1}$ activity.

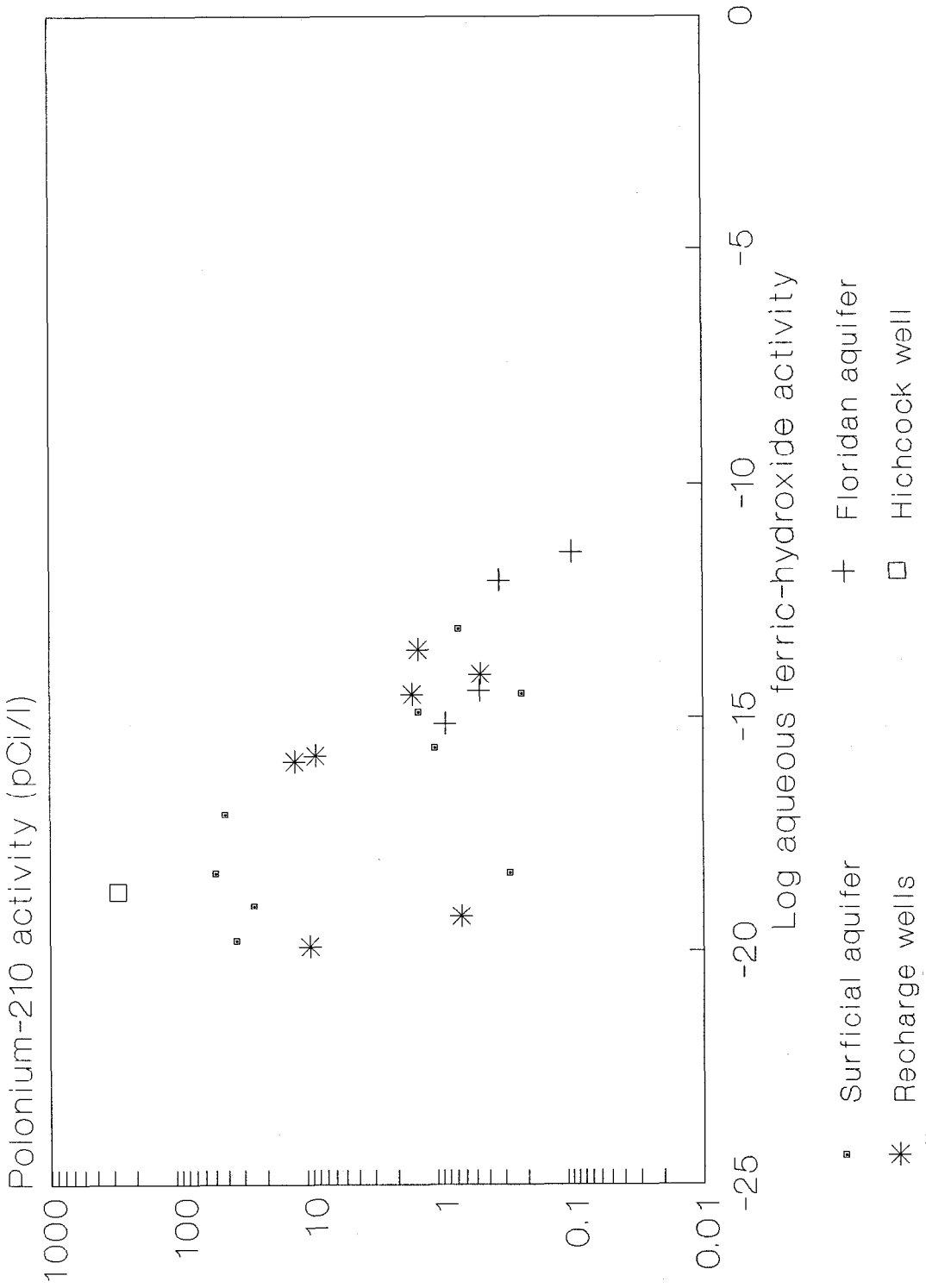


Figure IV-24. Scatter diagram showing the relationship of polonium-210 radioactivity to aqueous ferric hydroxide ($Fe(OH)_3$) activity.

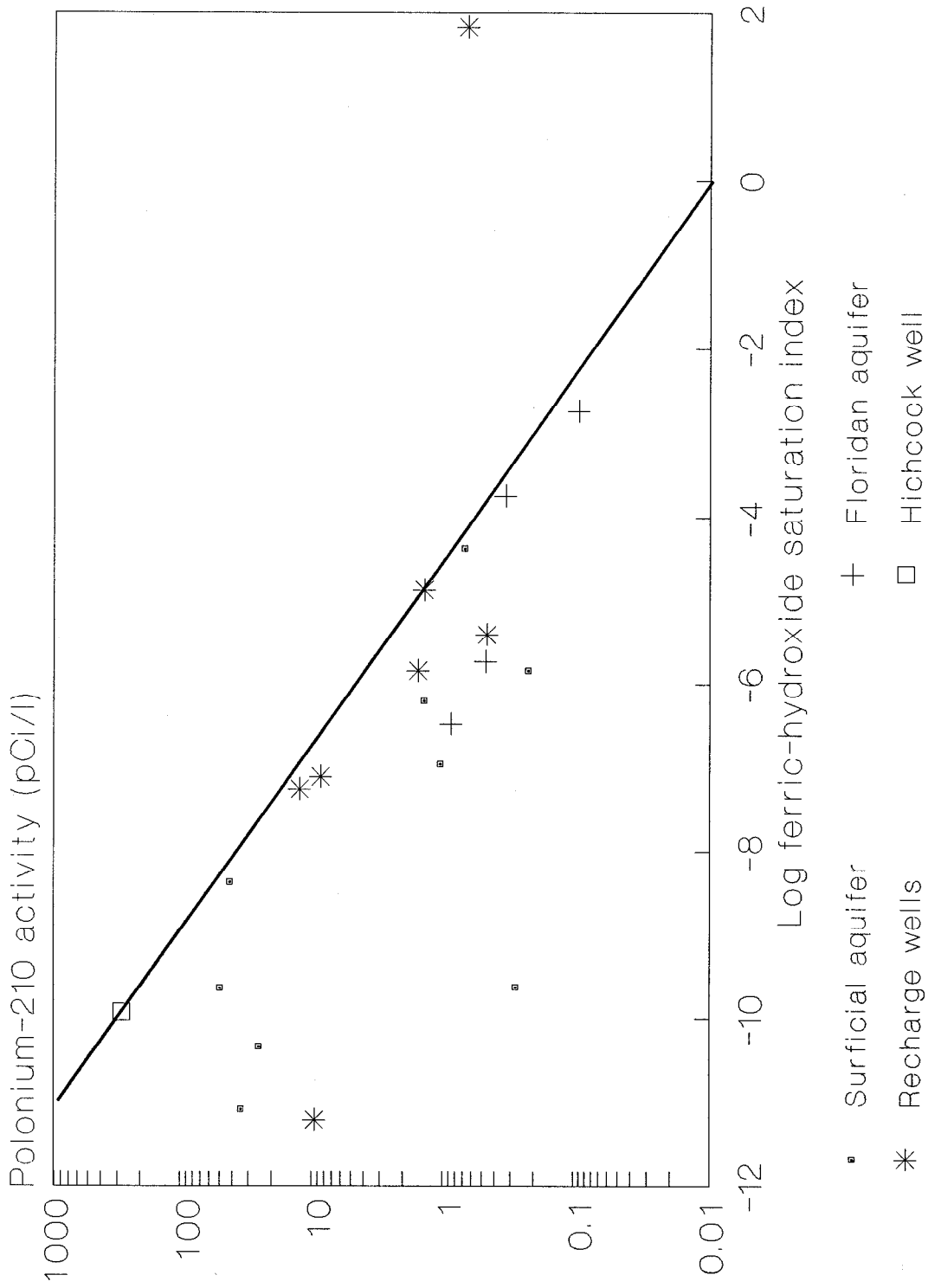


Figure IV-25. Scatter diagram showing relationship of polonium-210 radioactivity to ferric hydroxide ($Fe(OH)_{3\ amorph}$) saturation index. A value of 0 indicates saturation. Line is fit through maximum polonium activities at various saturation indices.

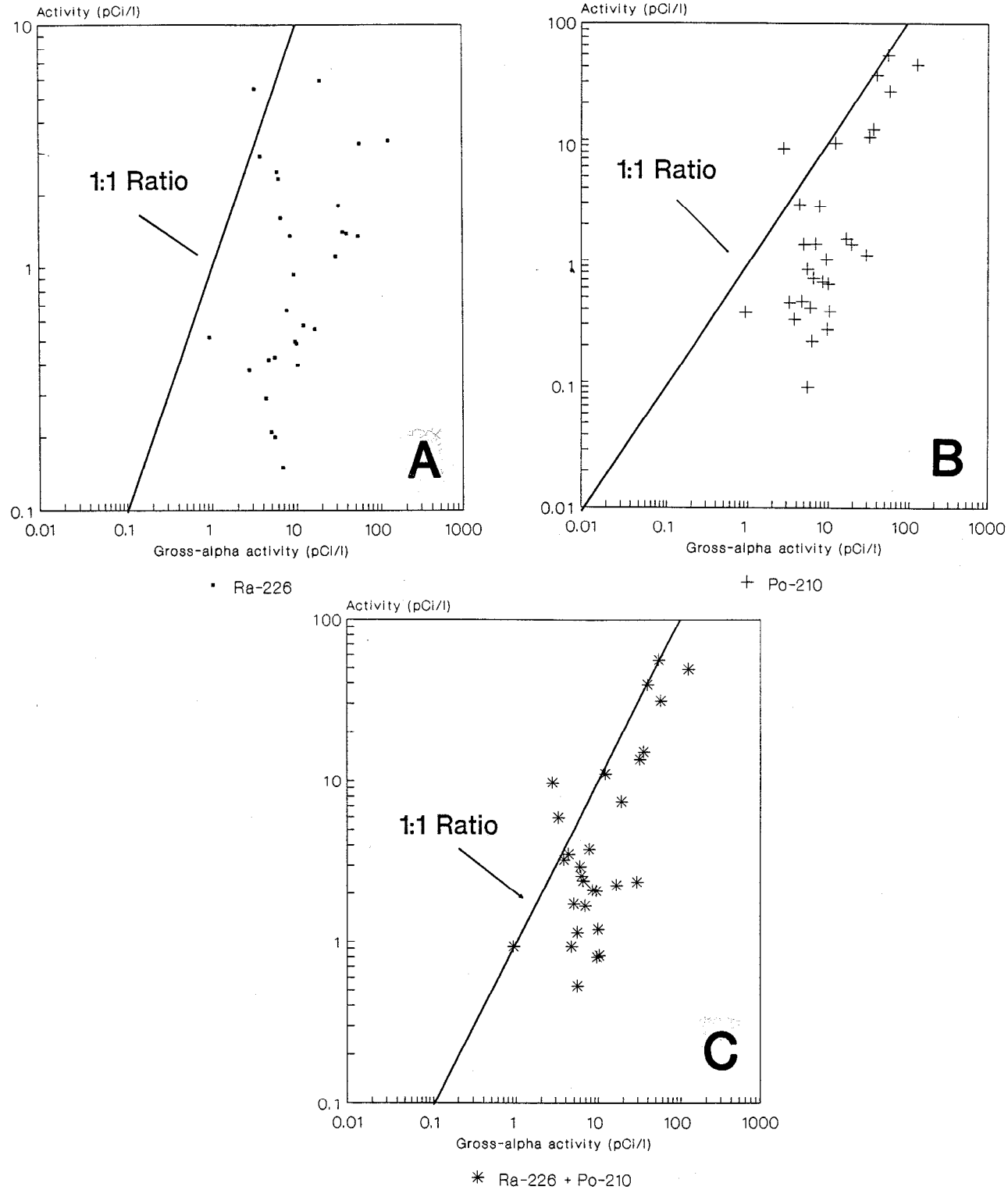


Figure IV-26. Relationship of gross-alpha radioactivity to radium-226 and polonium-210. 1:1 line indicates that all gross-alpha radioactivity can be accounted for by the isotope of interest. A. Relationship to radium-226. B. Relationship to polonium-210. C. Relationship to the sum of radium-226 and polonium-210 activities.

V. SEQUENTIAL-DATA ANALYSIS

SPATIAL ANALYSIS

Distribution of Wells That Exceed the MCL

Spatial analysis of the data from the Keysville Quadrangle is important because it shows that there are areas where recharge wells can be located that are unlikely to have gross-alpha radiation problems. Table V-1 characterizes the gross-alpha radioactivity data from the 270 recharge wells reported to SWFWMD. Figure V-1 shows the locations of all known recharge wells in the Keysville Quadrangle. Size of the dots indicates the amount of time that data from the well exceeded the 15 pCi/l MCL for gross-alpha radiation. Comparisons of the photolinear features identified by Upchurch and Kaufmann (1979b) and Culbreth (1983) with data on number of times the 15 pCi/l gross-alpha radiation MCL was exceeded at each well (Figure V-1) indicate that there is a relationship between the two. That is, the wells that consistently exceed the MCL seem to be near photolinear features.

Nearest-Neighbor Analysis

To further clarify this relationship, the shortest distance from each well with at least 10 months of record to the nearest photolinear feature was measured. These data (Figure V-2) show a clear pattern. While many wells do not exceed the MCL, all of the wells that exceed the MCL a significant amount (over 5%) of time are located within 0.3 km of a photolinear. Banwell and Parizek (1988) found a similar half-width for helium emanation from fracture traces in Pennsylvania. The half-width coincides with the predicted half-width of medium-sized fracture traces according to Parizek (1976). The three wells that do not fit this pattern appear to be near photolinears that were not identified by the sources used.

Discussion of Spatial Analysis Data

It appears that, within 0.3 km of the axis of a fracture trace, hydrogeochemical conditions exist that encourage some wells to have high polonium-210, or other alpha emitter, activities. This is a strong pattern, and, accounting for abnormally high alpha activities in the data sets that resulted from analysis of short-lived radon daughters (Oural et al., 1987, 1989), it seems clear that a water-management strategy can be developed to minimize risk of locating a well where it will consistently fail the MCL criterion. The strategy is simply **locate recharge wells no closer to fracture traces that 0.3km.**

The fact that wells located near fracture traces may exhibit high gross-alpha activities reflects at least two phenomena. First, Cathcart (1956, 1963, 1966) has indicated that enhanced uranium concentrations in the "leached zone" occur near many of the linear features attributed by us to fracture traces. These features include straight stream segments and alignments of depressions and wetlands. The photolinear features may have formed by dissolution of carbonates in the underlying strata by downward-moving water. This same water may have been responsible for weathering the phosphatic Hawthorn Group and concentrating uranium and uranium daughters in the thickened weathering profile. Thus, the thicker "leached zone" may serve as a reservoir of radionuclides which, upon mobilization, may adversely affect recharge wells. Second, those areas with wells that exceed the MCL are located in portions of a photolinear that appear to serve hydrologically as recharge conduits to lower aquifer systems (Upchurch and Kaufmann, 1979b). If this is the case, then dynamic flow of water with radionuclides, i.e., radon, toward the fractures may provide the gross-alpha activity.

It is not surprising that all wells within 0.3 km of a photolinear do not show high rates of violation of the MCL. Some of the photolinears may not be fracture traces. Even along fracture traces, the fracture is not a continuous, open, vertical crack. The clays, silts, and pasty carbonates through which the fractures penetrate are somewhat plastic, so many stretches of the fractures are probably plugged. The nature of ground-water flow is such that scattered, localized, high-permeability sites, such as at fracture intersections, generally take most of the water flow. Thus, a map of a fracture trace with "hot spots" of radioactivity, or vertical flow, highlighted should look more like a "string of pearls" than a straight line.

TIME-SERIES ANALYSIS

Data Trends

The 10 wells with high quality, monthly gross-alpha analyses were subjected to time-series analysis. Figures V-3 and V-4 show time trends of data from 7 of the wells on the Keysville Quadrangle. Note that there is variability at two scales. There are small, short-term peaks that persist for less than 3 months and seem to repeat from year to year, and there are broad, long-term peaks that extend for more than 3 months and do not repeat from year to year. Repetition of peaks from year-to-year and/or broad peaks that extend for three months or more are taken to indicate real variations as opposed to analytical problems (Oural et al., 1987, 1989). Variations in gross-alpha radiation at both time scales seem to be related to water-table position as

indicated by precipitation data from the New Wales chemical plant.

The wells in operation from 1980-1982 (Figure V-3) show no long-term trend, and gross-alpha data coincide. This is an important observation because the data come from two different companies and two different mines. Thus, the patterns can be interpreted as being real, rather than an artifact of sampling or analysis. In general, gross-alpha radiation was at background (approx. 2 pCi/l) in 1980 and 1982. In 1981, all 3 wells showed peaks that extended over at least 6 months. Precipitation in 1980-1982 followed extreme ranges (Figure V-5), with dry spring seasons and wet summer seasons. The wells that have data for the period 1983-1985 (Figure V-4) show a declining trend with time which corresponds to a period of transition from minimum seasonal variation in precipitation to maximum variation (Figure V-5).

Short-Term Variations - To determine if short-term, gross-alpha peaks that are less than 3 months in duration result from fluctuations of the water-table, two tests were run.

First, long-term trends can be removed from the radiation data by calculation of residuals from a linear, least-squares regression of the trends (Davis, 1973). By plotting the time series for gross-alpha residuals after subtracting the linear trend versus residuals for precipitation, the month-to-month correspondence between precipitation and radiation is apparent. Figure V-6 shows a typical graph of these residuals. Note that troughs in the precipitation residuals represent peaks in the raw precipitation data and peaks in the gross-alpha residuals represent lows in the raw radioactivity data.

Second, cross-correlation of gross-alpha and precipitation residuals shows the same relationship (Figure V-7). When the data are synchronous, there is a statistically significant negative correlation between precipitation and gross-alpha radiation ($r = -0.76$, $\alpha = 0.05$). There is a 12-month cycle to the negative correlation (Figure V-7), indicating that the short-term response of the gross-alpha radioactivity to precipitation (water-table) fluctuations is annual. Thus, on a month-to-month basis there is an inverse relationship between precipitation and radiation. Gross-alpha radiation is highest during periods of low precipitation and vice versa. This is clearly a dilution and discharge phenomenon.

Long-Term Variations - The short-term variations are superimposed on longer term trends during which gross-alpha activity may remain stable for several years and then show a peak that extends

over at least six months. Figures V-3 and V-4 illustrate examples of these peaks. Note that the peaks last for several months and that they occur in wells distributed over a large area and mines owned by several companies.

The long-term variation of gross-alpha radiation with precipitation is best depicted by plotting alpha radioactivity versus precipitation. Graphs showing the relation of raw gross-alpha activity data to precipitation data are difficult to interpret because there is considerable noise on a month-to-month basis. The noise is a combination of short-term variability and analytical error, including failure to account for short-lived radon daughters (Oural et al., 1987, 1989). By smoothing the data, short-term and analytical variability is minimized. Care must be taken in interpreting the smoothed data because a peak of 1-month duration is averaged over 5 months and becomes a loop instead of a peak.

In the 1980-1983 data set, which shows no long-term trend (Figure V-3), there is a minor peak of approximately 4.5 pCi/l above background. During 1980 and 1982, precipitation was highly seasonal (Figure V-5) and gross-alpha radiation variations were minimal. The gross-alpha peak in 1981 occurred late in the year in the three MOB wells and corresponds with high precipitation during the rainy season. Examination of the sequence of development of the peaks as shown by the arrows on the smoothed data (Figure V-3) indicates that the peak developed as precipitation was initiated in the rainy season and, presumably, the water table began to rise. Thus, this peak is opposite to the short-term, inverse relationship between gross-alpha radiation and precipitation that has been attributed to dilution. The data from the AMX-14 well show a large peak that corresponds with a period of very low precipitation at the gauge approximately 10 km to the north (Figure V-1). This is the only data set that shows this pattern and, considering the distance of the well from the gauge, there may be a relationship with the water table that cannot be characterized by the precipitation data.

In the 1983-85 data set (Figure V-4), which shows a long-term decline in alpha activity and a peak that is approximately 7 pCi/l above background, there is a negative correlation between gross alpha and precipitation (Figure V-4) in 1983, early 1984, and late 1985. This relationship, which results in the upper-left to lower-right trend in the graphs of precipitation versus gross- alpha activity using smoothed data (Figure V-4), corresponds with the dilution relationship noted in the short-term data analysis. The peak exhibited by IMC-97 in late 1984 and the peaks exhibited by the other wells in early 1983 are similar to the peaks in the MOB wells shown in Figure V-3. These peaks develop with a rising water table (increasing precipitation) and, in the case of IMC-97, start during a "dry"

season in which precipitation was relatively high (Figure V-5) and the water table probably did not drop as much as in previous years.

Discussion of Time-Series Data

Several important conclusions can be derived from the time-series data. First, there is a short-term inverse relationship between precipitation and gross-alpha activity. This relationship suggests that there is a dilution/concentration effect on the scale of a few months. Shortly after a period of heavy rainfall and recharge to the Surficial aquifer, there is increased, short-term discharge into the wells and dilution results. This relationship suggests that polonium-210 is present in a soluble form that can be diluted under high water-table conditions. As Oural et al. (1986, 1987, 1989) indicate, the polonium may be bound on dissolved humic substances, so dilution represents flushing of organics from the Surficial aquifer. It is also possible, as indicated in previous chapters, that decomposition of sulfate-rich soil particles, such as organics, or oxidation of sulfide minerals may reduce the pH of soil moisture and mobilize polonium-210 during periods of normal discharge. This soluble polonium can be temporarily stored in meteoric water, so that during periods of high discharge it can be diluted and flushed into the wells. It is also possible that, during periods of high discharge into the recharge wells, the chemical system becomes less reducing and/or less acid, which reduces mobilization of polonium through formation of radiocolloids, polonium hydroxide, or polonium sorbed on soil particles. Reduction in the amount of soluble polonium combined with an increase in discharge to the recharge wells would greatly exaggerate the apparent dilution phenomenon.

On the time scale of 6 months or longer, there is a different relationship of gross-alpha radiation with precipitation and Surficial-aquifer hydraulics. It appears that major gross-alpha activity peaks are related to episodes in which the water table remains high and there is a relatively thick phreatic zone. This condition exists when there has been a relatively wet "dry" season. Conversely, during years in which there is a pronounced dry season and a thick vadose zone develops, the water table is likely to have fluctuated greatly from wet to dry season and gross-alpha activity remains at low levels.

Based on the known chemical behavior of polonium, a model for the relationship of gross-alpha radiation to water-table behavior can be proposed. The key to the model is the mobilization of polonium by

(1) a reduction of ground-water pH,
(2) an increase in sulfur- and phosphorus-based acids, and/or
(3) an increase in dissolved organics in ground water.

The data presented in Chapters IV and V indicate that a reduction of pH can dissolve $Po(OH)_4$, which probably co-precipitates with ferric oxyhydroxides in the Surficial aquifer. Lowering of pH is a result of increases in sulfate, as sulfuric acid complex, which may be a product of microbial oxidation of soil organics, or inorganic oxidation of pyrite and other trace sulfides. Therefore, conditions (1) and (2) are related.

Condition (3), mobilization with organics, is also related to changes in pH. Dissolved organics in recharge-well waters range from trace quantities that are below detection limits to almost 20 mg/l total organic carbon. Therefore, there is considerable dissolved organic matter in Surficial aquifer water in the study area, and a widespread reservoir exists in the organic "hardpans" prevalent in the region. Soil organics can be crudely classified on the basis of solubility in acids and bases. Particulate soil organics can be leached by treatment with sodium hydroxide solution. Readjustment of the pH of the leachate with acid causes a fraction of the organics to precipitate. Therefore, two fractions can be separated. The fulvic-acid fraction is base and acid soluble, the humic acid fraction is base soluble, acid insoluble (Hem, 1970). Black and Christman (1963) characterized fulvic acids and found that they included polyhydroxy aromatic methoxy carboxylic acids. Most of the material was filterable, with diameters between 4.8 and 10 μm. Note that the organic fraction reported in this report was filtered prior to analysis, so TOC reflects soluble organics, not filterable. Many such organic compounds are strong chelating agents.

There are problems with extracting organics and maintaining sorbed polonium, but it appears that polonium-210 is partitioned into the fulvic-acid fraction. A sample from KR-98B, for example, had 3.5 $\pm$0.1 pCi/l polonium-210 in the digested humic-acid fraction, and 27 $\pm$0.3 pCi/l in the digested fulvic-acid fraction (Oural et al., 1987). Thus, a significant portion of polonium may be transported as organic complexes. Since the polonium appears to be associated with the organic fraction and the organics, especially the humic-acid fraction, vary in solubility with pH, slight changes in pH of aquifer waters probably affect solubility of the organics and mobilization of any complexed polonium.

Therefore, if there is a thick vadose zone for a portion of the year, oxidation (especially in the lower B and organic pan horizons) results in (1) microbial and inorganic decomposition of organics with release of sulfates and oxidation of sulfides to

sulfates, (2) a reduction in the availability of soluble organic acids, and (3) net precipitation of mineral oxyhydroxides. For example, a bacterially mediated reaction for oxidation of pyrite (ferrous sulfide) can be written as

$$2FeS_2 + 5H_2O + 7.5O_2 \rightleftharpoons 2FeO(OH) + 4SO_4^{2-} + 8H^+. \quad (V.1)$$

This reaction characterizes destruction of mineral sulfides, with production of ferric oxyhydroxide, acidity, and sulfate. Thus, precipitation of ferric oxyhydroxides and acidity represent a buffered reaction in which polonium could be mobilized by the sulfuric acid or sequestered with the ferric oxyhydroxides. Given the excess of ferric hydroxide in soil B zones and low H_2SO_4 activities detected in the Surficial aquifer water (Chapters III and IV), sequestering is predicted. Therefore, in vadose environments, polonium is oxidized and co-precipitates with ferric hydroxides as polonium hydroxide, so it is fixed and cannot be easily transported. Lack of flux of meteoric waters appears to also restrict mobility, except during short-term, precipitation-related hydrologic events.

Conversely, if the phreatic environment prevails and water-table elevations remain relatively high, short-term, dilution-related gross-alpha and polonium peaks are minimized, and polonium is mobilized by other mechanisms. In water-saturated environments, organics are destroyed by bacterially mediated sulfate reduction. An example reaction can be written as follows

$$SO_4^{2+} + 2CH_2O \rightleftharpoons S^{2-} + 2CO_2 + 2H_2O. \quad (V.2)$$

CH_2O is a simple carbohydrate used as an example of an organic hydrogen donor. Sulfate is abundant in the phreatic zone (see Chapters III and IV) as are particulate and soluble organics. Sulfide is a strong base, so it readily reacts with carbon dioxide in the water according to the reaction

$$S^{2-} + 2CO_2 + 2H_2O \rightleftharpoons 2HCO_3^- + H_2S, \quad (V.3)$$

Which results in hydrogen sulfide generation and production of alkalinity. Trace quantities of hydrogen sulfide are present in many wells, and Burnett et al. (1987) and Cowart et al. (1987) have associated high polonium with the odor of hydrogen sulfide in shallow aquifer waters. Harada et al. (1989) documented the correlation with H_2S. Also, microbial decomposition of organics

is a step-wise series of reactions in which large, high molecular weight, chemically complex, particulate and dissolved organics go through a series of degradation steps in which less complicated, fragmentary organics are produced. These degradation products (fulvic and humic acids) constitute the soluble fractions that color water, that contain chemically unsatisfied functional groups capable of complexing inorganic ions, and that have been shown to be associated with polonium.

If organic acid production and net reduction in a phreatic environment is encouraged by a high water table, polonium may be reduced to the +2 valence state, which would encourage complexing with soluble organics. The chemical data presented in this report indicate that Surficial aquifer waters remain within the stability field of sulfate, and that bicarbonate alkalinity is minimal in some cases. Therefore, hydrogen sulfide and bicarbonate production may not be dominant processes, and acidity and sulfate may prevail. This suggests that microbial reduction of sulfate is inhibited. The inverse relationship of polonium-210 with hydroxyl and pH, and the positive relationship with sulfate activity strongly indicate that acidity (organic or sulfuric acid) plays a significant role in mobilization in phreatic environments.

CAUSES OF SPATIAL AND TEMPORAL VARIABILITY

High gross-alpha radiation reports from the Surficial aquifer in central Florida are, in part, a result of two causes. Extremely high, single-event activities appear to be a result of counting short half-life radon daughters (Oural 1987, 1989). When these anomalously-high activities are present in a data set, all correlation with environmental conditions fails and the gross-alpha peaks behave as random events. Some of the high alpha activities reported in historical data from recharge wells are real, and result from polonium-210 activity that is in excess of radium-226 (Oural et al., 1986, 1989). Time-series and spatial analysis of monthly data that contain a minimum of noise indicate that the high gross-alpha activities can be explained by environmental conditions in the Surficial aquifer.

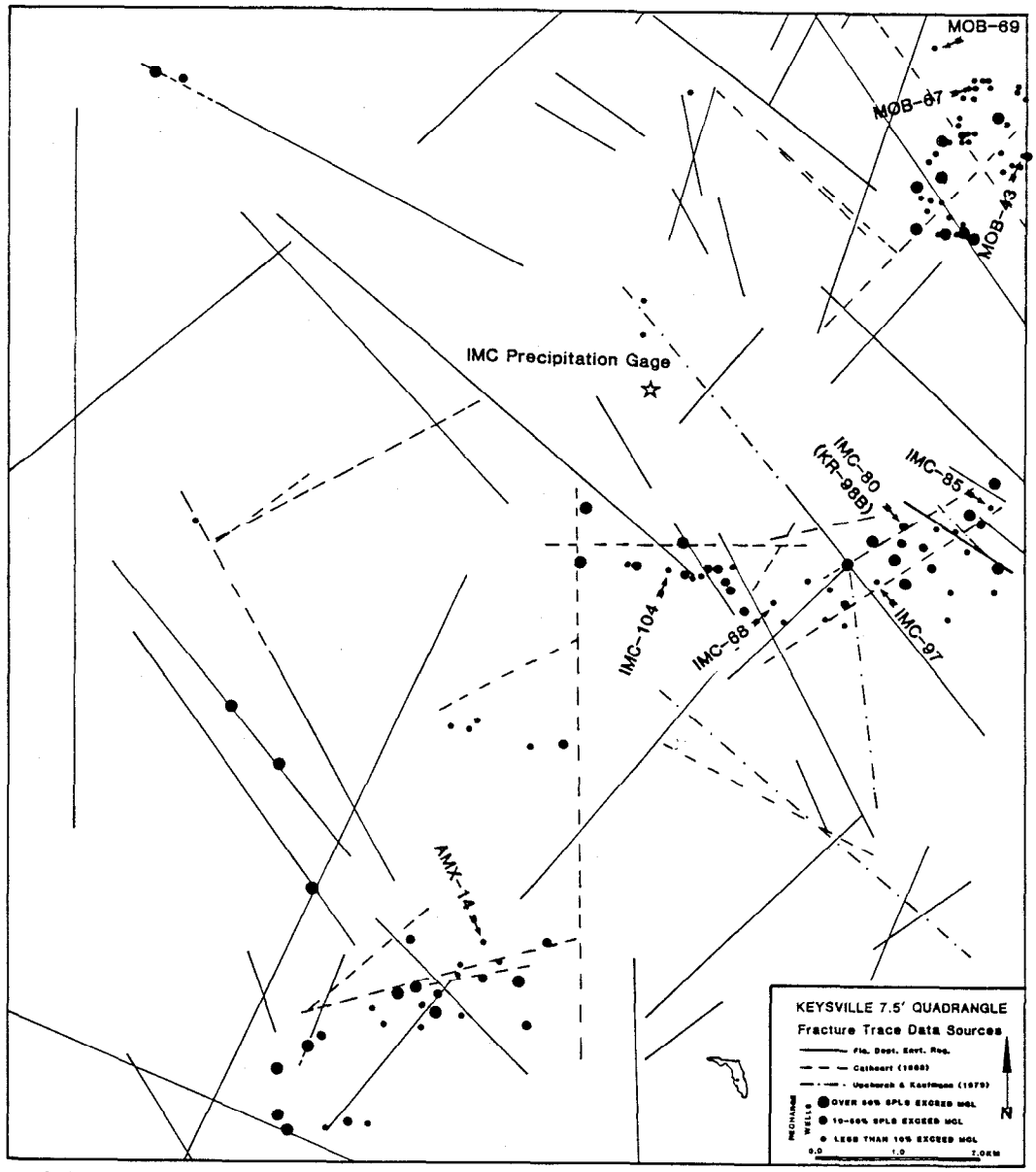
Spatially, it appears that high gross-alpha activities are most likely in water that is within 0.3 km of the axis of a fracture trace. These high activities are a result of radon and radon-daughter migration towards discharge sites in the aquifer or storage of residual radioactivity in the thickened "leached zone" associated with many fracture traces. Thus, given proper chemical conditions, there is increased probability of mobilized polonium in areas where the reservoir of uranium daughters (especially radon daughters) is greatest. Should this pattern hold in other areas, there is every indication that proper well

location to avoid fracture traces can minimize risks of high gross-alpha activities as a result of polonium.

Temporally, there are two scales of behavior that indicate the nature of gross-alpha (polonium) mobilization mechanisms. On the short term (scale of months), gross-alpha radiation is inversely related to precipitation and, therefore, water-table position. During wet months, gross alpha declines, most likely due to increased discharge and dilution. During dry months, gross-alpha activity increases.

On the long term (scale of a year) two patterns are present. The short-term, inverse relationship with water-table position is represented. However, the most important relationship reflects the magnitude of the dry season and vadose-zone development. The data sets include a number of years in which there was a relatively dry interval. If there was a dry period, which resulted in a relatively thick vadose environment, then gross-alpha activity remained low all year. If the "dry" season was relatively wet and the vadose zone was minimized, then there was a peak in gross-alpha activity. During years when water-table fluctuations were maximal, that is monthly precipitation values showed maximum ranges and dry seasons were quite dry, gross-alpha activity did not reach a peak and the alpha activity reflects the long-term changes in water-table elevation. During years when the water table remained relatively high and constant in position, that is monthly precipitation values show a minimum range and the dry season was relatively wet, gross-alpha radiation peaked. Individual months with high precipitation result in a dilution of gross alpha, but only in years when gross precipitation was high.

An interpretation of the behavior of the time-series data based on the chemistry of polonium requires a change in reduction-oxidation potential and microchemistry as a result of water-table behavior. During periods of maximum annual water-table fluctuation and a pronounced dry season, the vadose zone is thickest and tetravalent polonium hydroxide coprecipitates with ferric oxyhydroxides in the soil zone. These precipitates are relatively insoluble and most of the polonium remains fixed. If, however, the water table does not fluctuate greatly, a proportion of the aquifer that otherwise would have been unsaturated remains saturated and reducing. It is likely that organic and sulfuric acids, which form and migrate in the aquifer under saturated soil conditions, mobilize sorbed or precipitated divalent polonium.



LOCATIONS OF LINEAMENTS AND INTERAQUIFER CONNECTOR WELLS - KEYSVILLE QUADRANGLE, FLORIDA

Figure V-1. Fracture-trace map of the Keysville Quadrangle showing locations of recharge wells and the precipitation gage at the New Wales chemical plant. Size of well-location dots reflects the percentage of the samples that exceeded the 15 pCi/l MCL for gross-alpha radiation.

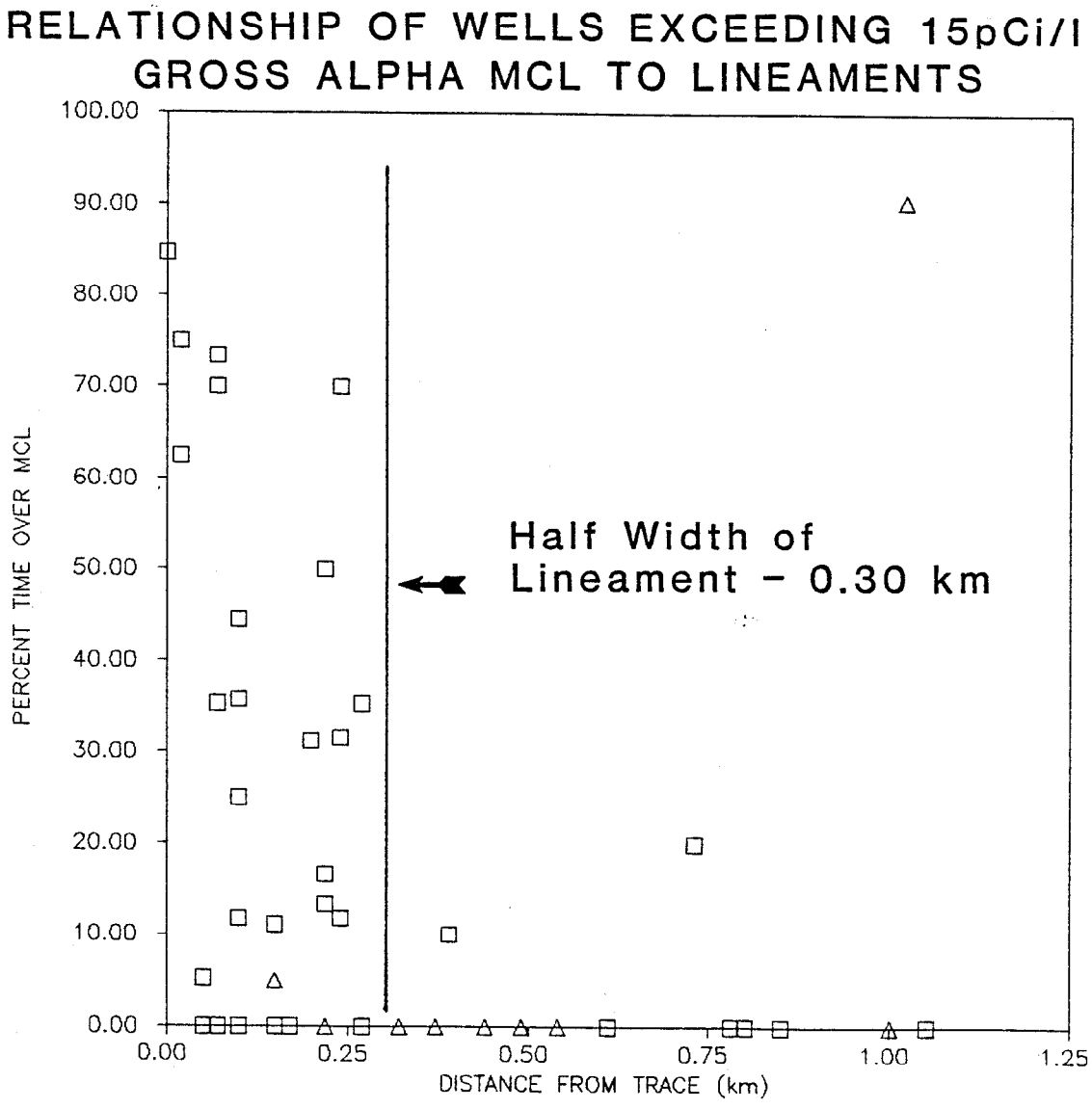


Figure V-2. Scatter diagram showing the percentage of samples that exceeded the 15 pCi/l MCL for gross-alpha radiation as a function of distance from the nearest fracture trace.

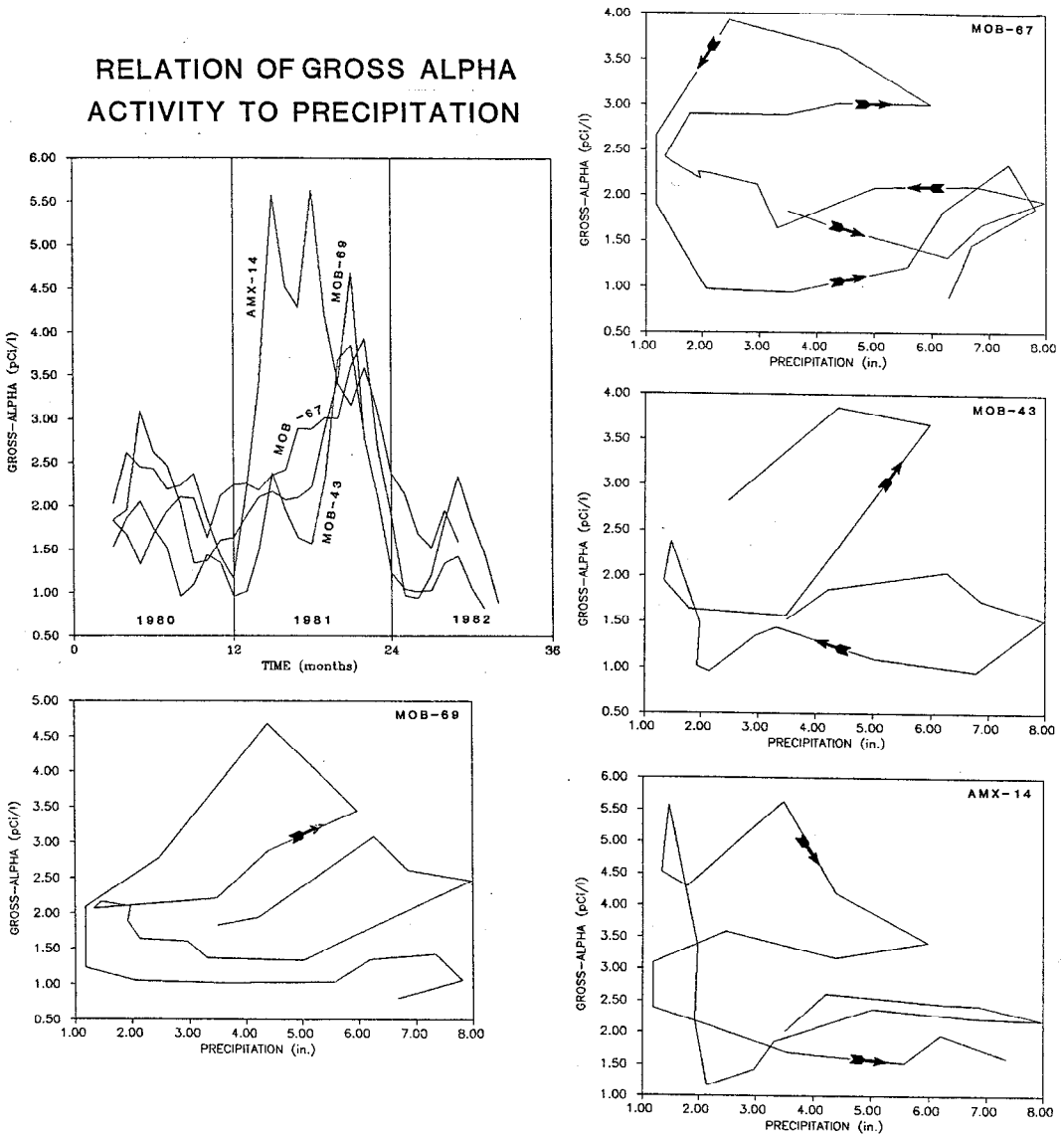


Figure V-3. Time-series diagrams showing the temporal variation and progressions of gross-alpha radiation as a function of precipitation for 4 selected recharge wells in 1980-1982.

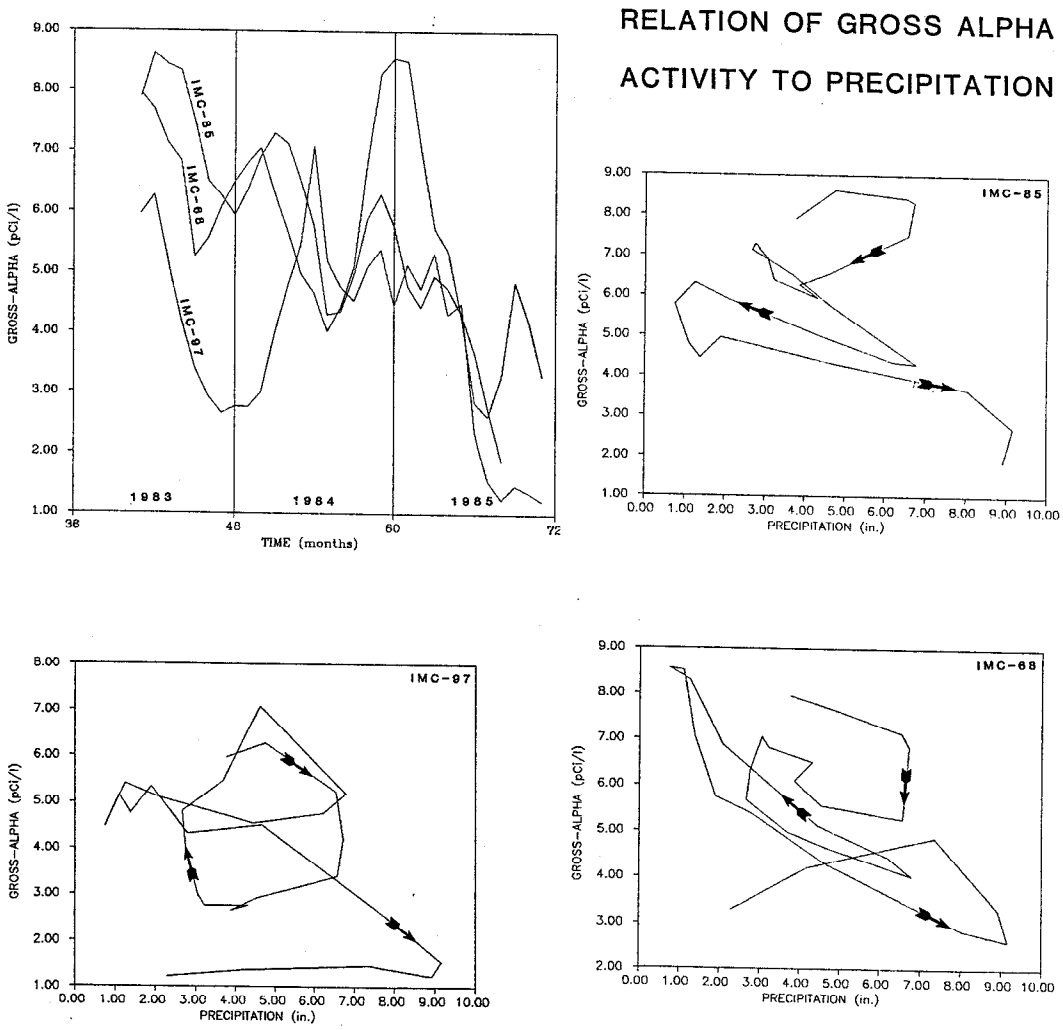


Figure V-4. Time-series diagrams showing the temporal variation and progressions of gross-alpha radiation as a function of precipitation for 3 selected recharge wells in 1983-1985.

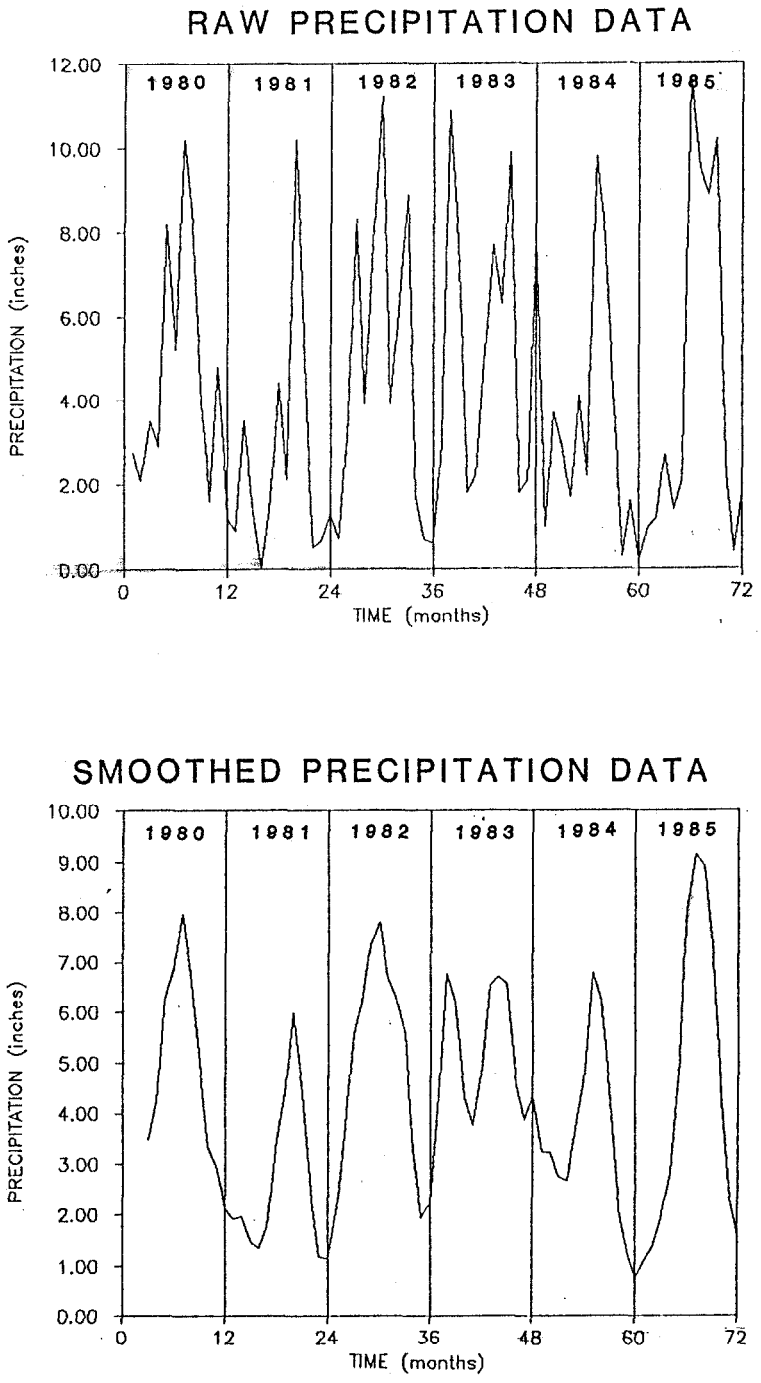


Figure V-5. Temporal variation of monthly precipitation during the period of study at the New Wales chemical plant, Keysville Quadrangle.

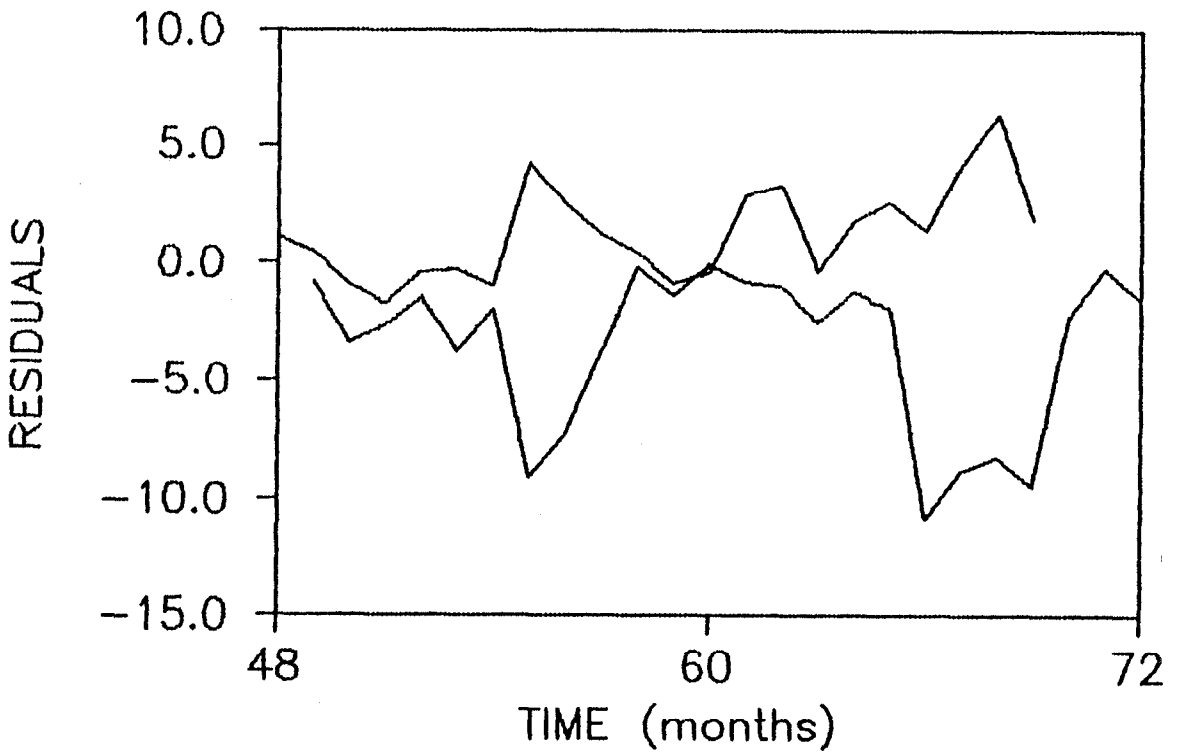


Figure V-6. Time-series response of residuals from linear regressions on gross-alpha radiation and precipitation. Negative residuals on lower line indicate peak monthly precipitation. The upper curve is gross-alpha radioactivity, where peaks correspond with declines in gross-alpha radioactivity.

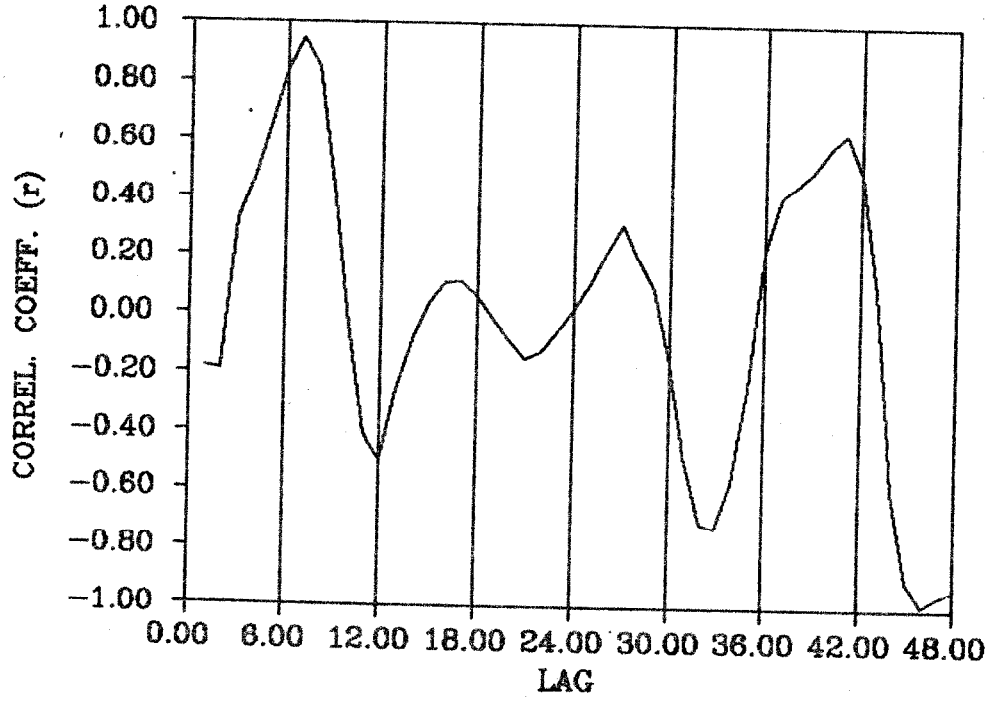


Figure V-7. Correlogram showing the cross-correlation of gross-alpha radiation and precipitation of a typical recharge well. Negative correlations at 12-month intervals indicate an inverse relationship between the two variables.

VI. - SUMMARY AND CONCLUSIONS

Chemical analysis of water from interaquifer connector wells ("recharge wells") and associated monitor wells in the Central Florida Phosphate District has provided a basis for understanding the chemistry of the Surficial and upper Floridan aquifers and of recharge wells. The data suggest chemical controls on the mobility of uranium and uranium progeny. Time-series and nearest-neighbor analyses of historical data suggest hydrologic conditions that cause mobilization of iron, sulfur, and radionuclides in ground water and provide a basis for recharge-well location and management to minimize risks of failure of water-quality criteria for gross-alpha radioactivity, iron, and color.

Twenty three recharge wells were sampled. A total of 51 water samples from these recharge wells were analyzed for 31 chemical variables, including redox potential, pH, major elements, iron, manganese, aluminum, uranium-238, uranium-234, radium-226, lead-210, and polonium-210.

Monitor wells were installed around three recharge wells in order to provide undisturbed samples of Surficial and Floridan aquifer waters. The Surficial aquifer monitor wells were placed within the cone of depression and were screened at the same elevation as the recharge wells . The Floridan aquifer monitor wells were located down flow and within the cone of impression of the recharge wells. The Floridan monitors were completed in the cavernous zones that appear to receive most of the recharging water, and one well was demonstrated to be in the same cavern as the recharge well water. Eighteen samples were analyzed from the monitor wells.

The Surficial aquifer is acid, reducing, and organic rich. Eh-pH data show that the aquifer water is near the hydrogen sulfide-sulfate stability boundary. While many samples are within the sulfide stability field, the redox potential and pH's may not be conducive for microbial sulfate reduction to rapidly occur. Ferrous iron is the stable iron species, and precipitation of ferric hydroxides is inhibited within the saturated zone. Polonium and, to some degree, radium may be present in activities sufficient to be of concern. Polonium is the major radionuclide that causes high gross-alpha radioactivity in the Surficial aquifer.

Floridan aquifer water is neutral to slightly alkaline and generally slightly reducing. Both sulfate and sulfide are present, and microbial sulfate reduction may be taking place. Ferrous iron is the most abundant, aqueous iron species. Activities of radionuclides are low in the Floridan aquifer where sampled, although radium has been shown to be a problem in other

studies.

Surficial aquifer water varies from predominantly a sodium-sulfate water to a calcium-sodium-bicarbonate-sulfate water, while the upper Floridan aquifer water is a calcium-bicarbonate solution.

In recharge wells, iron may be oxidized to the ferric state if sufficient oxygen is introduced into the water by cavitation. Most of the ferric hydroxides encountered appear to have formed on well casings and screens above standing water, not in the turbulent flow of the well water. In general, recharge-well water closely reflects the chemistry of Surficial-aquifer water, from which it is derived, and there is little change in the chemistry of the water in the well bore. The most dramatice changes in water quality come with buffering and dilution in the carbonate-rich Floridan aquifer.

Iron, bacteria, and turbidity have been chronic water-quality concerns in recharge wells. It is clear that most of this material is derived by scraping the casing during sampling and is not in the undisturbed water. Sampling trials indicate that much of the ferric hydroxide and biomat can be avoided by sampling with a tripod to prevent contact of the sampling vessel with the walls of the well. Combined with the sampling recommendations made by Oural et al. (1986, 1989), many of the water-quality problems that are artifacts of sampling can, therefore, be avoided.

Gross-alpha radioactivity measurement techniques are not reliable measurements of true alpha activity because of short-lived radon daughters that may be present in the sample. Gross-alpha radioactivity should only be used as a screening technique to determine if there is a potential for radiation problems.

Uranium activity was low in all samples and is not a problem. Uranium is mobilized as uranyl ion in oxidizing conditions.

Radium was not a problem in most samples. Four recharge wells had samples in excess of the 5 pCi/l standard. Radium appears to be mobilized as an aqueous sulfate complex. Strontium, and perhaps barium, appears to enhance nucleation of radiocolloids of radium sulfate. All samples were well below chemical equilibrium with respect to particulate radium sulfate.

Lead-210 is present in all systems in minor quantities. Soluble lead-210 does not support its daughter polonium-210, so the polonium is derived from lead sorbed or precipitated on aquifer materials. Isotherms indicate that lead is strongly adsorbed on clays and is precipitated in contact with ferruginous quartz sand and limestone. Lead is slightly mobile in the

Surficial aquifer owing to the low pH of the water. In the Floridan aquifer it appears to be controlled by precipitation of cerussite. Lead-210 activity is not correlated to total lead concentration.

Polonium-210 is most abundant in the Surficial aquifer where it constitutes most of the gross-alpha radioactivity. Sulfate reduction is initiated at reduction-oxidation (redox) potentials less than -150 mv. Polonium activities are low in water less than -150 mv, and it appears that polonium is mobilized when sulfate is formed and pH is thereby reduced. Polonium mobility is controlled by solubility of the radiocolloids and/or ion-pair complexes formed by association of polonium with hydroxyl. In acid, low OH^{-1} water, polonium is mobilized, while in alkaline, high OH^{-1} waters it forms radiocolloid-like hydroxyl complexes. The polonium-hydroxide co-exists and co-precipitates with iron-hydroxy complexes. Movement of the radiocolloid and iron-hydroxy colloids is mechanically inhibited in aquifer systems.

High gross-alpha radioactivity is spatially related to fracture traces. Fracture traces are characterized by enhanced vertical leakance, thickened "leached zone", and extreme temporal variability in saturated-zone thickness. Recharge wells within 0.3 km of the axis of a fracture trace are considered to be within a fracture trace. Wells outside of these fracture traces do not significantly exceed the gross-alpha activity MCL. It appears that careful selection of well locations can be used to minimize exposure to these gross-alpha activities that are in violation of the 15 pCi/l MCL for gross-alpha radioactivity. Therefore, placement of recharge wells over 0.3 km from fractures should be a management strategy required for recharge-well permitting.

Gross-alpha (polonium) radioactivity in recharge wells is seasonally related to water-table fluctuations (as reflected in precipitation data at a nearby gauge). High recharge and water-table conditions lead to dilution of the radioactivity on the scale of weeks to a month. On the longer term, it appears that years with maximum unsaturated zone development (low water table elevations or wide variations in water-table elevation) have low gross-alpha radioactivity in recharge wells. This is because the polonium-hydroxide complexes (and other metal-iron-oxyhydroxide complexes) are stable and not transported. In wet years, when the saturated zone is thick (high water table, little variation in water-table elevation), acid conditions develop that break up the hydroxy-complexes and polonium is mobilized to produce high gross-alpha radiation in the wells.

In summary, it appears that recharge wells can be utilized in the Central Florida Phosphate District if simple precautions are taken. First, they should be located to avoid fracture traces or other locations where the "leached zone" is thick and water-

table conditions favor acid water. Second, sampling protocols should be carefully designed, in conjunction with regulatory agencies, to avoid contamination from casing slimes. Finally, recharge wells should not be located in areas influenced by phosphochemical plants.

Chemical modeling and raw data clearly indicate that conditions for transport of polonium and lead exist in the Surficial aquifer, but not in the Floridan aquifer. Therefore, it appears that, with respect to the parameters measured, the quality of receiving Floridan aquifer waters is not jeopardized by the practice of interaquifer connector (recharge) wells.

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APPENDIX A

LITHOLOGIC LOGS OF CORES ASSOCIATED WITH MONITOR WELLS

Lithologic Log of Core KR-83-D, IMCC Kingsford Mine, Polk Co., Florida

Date: January 24, 1985
Logged by: Daniel Foss, Department of Geology, University of South Florida, Tampa, Florida 33620
Location: Approx. 9 m (30 feet) from recharge well KR-83 (s.5,T31S, R23W), International Minerals and Chemical Corp., Kingsford Mine, Polk/Hillsborough Counties, Florida.
Driller: Florida Department of Environmental Regulation (Bill Davis, driller)
Nature of core: Core taken by rotary drilling while installing deep monitor well. Well cased with 4 in. ID PVC casing 0-118 ft.; 4 in. ID stainless steel casing 118-128 ft.; total depth is 265 ft. BLS. Hole diameter 8.5 in. Field log and subject to revision.

Depth (ft.)	Field description
	Plio-Pleistocene Undifferentiated
0.00-1.25	SAND, quartz, fine, loose, light gray.
1.25-4.25	SAND, quartz, fine, sl. cohesive, lt. red-brown.
4.25-7.5	SAND, quartz, fine, clayey, cohesive, mottled, gray-tan to purple-red.
7.5-9.25	SAND, quartz, fine, sl. clayey, mod. cohesive, sl. mottled, gray-tan to gray-yellow.
9.25-14	SAND, quartz, medium to fine, sl. clayey, pale tan-gray.
14-19.6	MISSING, no sample recovered.
19.6-25.5	SAND, quartz, medium to fine, clean, loose, sl. phosphatic, pale tan.
25.5-45	MISSING, no sample recovered.
45-50	SAND, quartz, medium, phosphatic.
	Peace River Formation, Bone Valley Member (Hawthorn Group)
50-55	SAND, medium to granule, 50% fine to pebble phosphate, cream color.
55-60	MISSING, no samples recovered.
60-62	SAND, quartz, medium to granule, sl. clayey, 25% fine to granule phosphate, blue-gray.
62-80	MISSING, no sample recovered
	Peace River Formation (undifferentiated).
80-82	SAND, quartz, fine to medium, clayey, 10% fine

to	granule phosphate, blue-gray.
82-90	MISSING, no sample recovered.
90-91.5	CLAY, sandy, 8% fine to coarse phosphate, green-gray.
91.5-92	MISSING, no sample recovered.
	Arcadia Formation (Hawthorn Group)
92-95	DOLOSTONE, sandy, 7% fine to coarse phosphate, mod. hard, tan-cream color.
95-95.75	SAND, quartz, fine, dolomitic, 5% fine to coarse phosphate, mod. hard, gray-brown.
95.75-99.75	DOLOSILT, sandy, 3% fine phosphate, cohesive, light gray.
99.75-104.8	DOLOSILT, sandy, 4% phosphate, mottled, med. gray-brown.
104.8-105.75	DOLOSILT, sl. sandy, 6% phosphate, mod. cohesive, lt. gray.
105.75-108.25	SAND, quartz, dolomitic, 8% phosphate, occ. fossils, soft to cohesive, gray-white.
108.25-110.5	DOLOSTONE, fine, sandy, 7% phosphate, sl. clayey, dk. gray-brown.
110.5-110.75	CLAY, sandy, dolomitic, 3% phosphate, mottled, dk. gray.
110.75-115	DOLOSTONE, fine grained, sl. sandy, 5% fine phosphate, freq. fossil molds, soft to hard, lt. gray-white.
115-115.5	SAND, quartz, fine to medium, 8% phosphate, clayey, dk. gray-brown.
115.5-116.8	DOLOSTONE, fine grained, sandy, 5% fine phosphate, occ. fossil molds, hard, lt. gray-tan.
116.8-117.25	SAND, quartz, dolomitic, clayey, 10% phosphate, sl. cohesive, mottled, dk. gray.
117.25-120	SAND, quartz, fine, dolomitic, clayey, 20% phosphate, med. gray.
120-123.5	MISSING, no sample recovered.
123.5-123.9	SAND, quartz, clayey, sl. dolomitic, 4% phosphate, sl. cohesive, med. tan.
123.9-126	DOLOSTONE, fossiliferous, fine grained, 3% phosphate, porous, hard, mottled, lt. gray-cream.
126-133.25	MISSING, no sample recovered.
133.25-134.4	SAND, quartz, fine, clayey, sl. dolomitic, 3% phosphate, med. gray.
134.4-137.5	DOLOSTONE, fine, sandy, sl. clayey, 2% phosphate, soft to hard, cream-gray.
137.5-145.3	SAND, quartz, fine to coarse, clayey, 4% phosphate, soft to hard, dolomitic, clay and dolosilt content increasing toward contact with underlying unit, dk. gray-blue to gray-cream.
145.3-150	SAND, quartz, fine, clayey, 2% phosphate,

	cohesive, dk. gray-blue.
150-165	DOLOSTONE, fine, fossiliferous, porous, 5% phosphate, occ. gray clay stringers and phosphatized bones, mod. soft to hard, cream to tan.
165-167	DOLOSILT, v. sl. sandy, 3% phosphate, lt. gray.
167-169	DOLOSTONE, fine, dense, hard, 3% phosphate, lt. gray.
169-174.35	DOLOSTONE, fine, sl. sandy, fossiliferous in thin zones, 5% phosphate, mod. hard to hard, lt. tan.
174.35-174.45	CLAY, sl. sandy, sl. blocky, soft, dk. gray-green.
174.45-177.65	DOLOSTONE, fossiliferous, med. gray chert stringers, porous, 2% phosphate, voids filled with green-brown clay, cream-tan.
	Tampa Member, Arcadia Formation
177.65-214.55	LIMESTONE, fine, sandy, occ. pelecypod mold, soft to mod. hard, lt. tan to cream.
214.55-215.2	CHERT, glassy, hard, dr. gray, cont. pockets of sandy, cream-colored limestone.
215.2-218	LIMESTONE, fine, sandy, numerous voids filled with lt. green clayey sand, white.
218-220.3	LIMESTONE, sandy, fossiliferous, porous, hard, mottled, tan to lt. brown.
220.3-245	LIMESTONE, v. sandy, friable, tan.
245-252.9	CLAY, soft, blocky, cont. clasts of white, fine-gr. limestone, dr. green.
252.9-253	CHERT, glassy, hard, fossil molds present, dk. gray.
253-255	CAVITY, no sample.
	Suwannee Limestone
255-265	LIMESTONE, sandy, fossiliferous, porous, chalky, mod. hard, lt. tan to bone white.
	TD. at 265 ft. BLS

Caliper log of recharge well KR-83 furnished by IMCC and taken by P.E. LaMoreaux & Assoc., Inc. on Jan. 20, 1978 indicates well screens at 15-20 ft. BLS. Bottom of casing is at 120 ft. BLS, and cavernous zones are located at 178-187 ft. and 212-230 ft. BLS.

Lithologic Log of Core KR-127-D, IMCC Kingsford Mine, Polk Co., Florida

Date: January 10, 1985
Logged by: Daniel Foss, Department of Geology, University of South Florida, Tampa, Florida 33620
Location: Approx. 30 feet from recharge well KR-127 (s.6, T31S,R23W), International Minerals and Chemical Corp., Kingsford Mine, Polk/Hillsborough Counties, Florida.
Driller: Florida Department of Environmental Regulation (Bill Davis, driller)
Nature of core: Core taken by rotary drilling while installing deep monitor well. Well cased with 4 in. ID PVC casing 0-163 ft.; 4 in. ID stainless steel casing 163-173 ft.; total depth is 271.75 ft. BLS. Hole diameter 8.5 in. 0-173 ft.; 4 in. 173-223 ft.; 2 3/7 in. 223-271.75 ft. Field log and subject to revision.

Depth (ft.)	Field description
	Plio-Pleistocene Undifferentiated
0.00-15	SAND, fine to co. grained, quartz; sl. phosphatic, approx. 3% med. to coarse, sand-sized phosphate; high organics; iron stained; red-brown.
15-25 sand-	SAND, quartz; sl. phosphatic, approx. 2% fine sized phosph.; sl. iron stained; gray tan.
25-30	SAND, quartz; clayey; sl. phosph., approx. 1% fine sand-sized phosph.; tan-gray.
30-32	SAND, quartz; clayey; dolomitic; soft; lt. brown.
32-33	SAND, quartz; calcareous; clayey; sl. phosphatic, approx. 3% v. fine sand-sized phosph.;lt. gray.
33-40	SAND, quartz; dolomitic; clayey; v. weakly cemented; tan-lt. brown.
40-50	SAND, quartz; clayey; phosphatic, approx. 15% v. fine sand- to pebble-sized phosph.; med. gray.
	Bone Valley Member, Peace River Formation (Hawthorn Group)
50-55	CLAY, v. sandy, approx. 35% quartz sand; phosph., approx. 15% v. fine sand- to pebble-sized phosph.; blue gray.
55-60	SAND, quartz; phosphatic, approx. 50% co. sand- to

	pebble-sized phosph., blue gray.
60-63	SAND, phosphatic, clayey; 50% fine sand to pebble-sized phosphate; green-gray.
	Peace River Formation (undifferentiated)
63-65	CLAY, phosphatic, sandy; approx. 45% fine sand to pebble sized phosphate, approx. 10% fine to medium quartz sand; mottled, yellow green-gray.
65-70	CLAY, phosphatic, sandy; approx. 35% v. fine sand to pebble sized phosphate, dolomitic, approx. 15% fine to med. quartz sand; soft; gray-green.
70-79	CLAY, phosphatic, sandy; approx. 35% fine sand to pebble sized phosphate, approx. 15% fine to med. quartz sand; soft, lt. gray.
	Arcadia Formation (Hawthorn Group)
79-85	DOLOSTONE, phosphatic; hard; v. fine grained; approx. 22% med. sand sized phosphate, approx. 5% med. quartz sand; tan-brown.
85-105	DOLOSTONE, fossiliferous, cont. mollusc molds; sl. phosphatic, approx. 4% fine to co. sand sized phosphate, approx. 2% fine to med. quartz sand; v. soft to hard; pale tan-gray.
105-129	DOLOSILT, sandy, phosphatic; approx. 3% phosphate; soft; lt. gray.
129-145	DOLOSTONE, v. fn. grained; sl. sandy; dense; sucrosic; 2% phosphate; pale gray.
145-153	DOLOSTONE, v. fn. grained; sl. sandy; dense; sucrosic; 2% phosphate; lt. tan.
153-155	SAND, clayey, dolomitic; 4% phosphate; soft; gray-blue.
155-159	DOLOSTONE, fine grained; sl. sandy; 2% phosphate; sucrosic; lt. tan.
159-160	DOLOSILT, sandy; 2% phosphate; soft; pale tan to white.
160-171	DOLOSTONE, fn. grained; soft; sl. sandy; 3% phosphate; cream-white.
171-175	DOLOSTONE, fn. grained; sl. sandy; 2% phosphate; v. hard; lt. gray to tan-gray.
175-180	LIMESTONE, dolomitic; sandy; 2% phosphate; soft; cream-white.
	Tampa Member, Arcadia Formation
180-185	LIMESTONE, sandy; fn. grained; mod. hard; green, flaky clay present.
185-221.5	LIMESTONE, sandy, fn. grained; soft; white; lowest 5 ft. contains stringers of dense, glassy,

	honey-yellow chert.
221-5-226.25	LIMESTONE, cherty; fn. grained; sandy; cont. numerous stringers of honey-yellow to dk. gray, hard, glassy chert; soft; tan.
226.25-231.9	LIMESTONE, sandy; mod. fossiliferous; friable to mod.hard; grades into underlying calcareous sand; lt. tan.
231.9-238	SAND; quartz; fn grained; calcareous; weakly cemented; cream colored.
238-253.25	LIMESTONE, sandy; fn. grained; cont. minor shell frags; rubbly; numerous clasts of dk. green clay, clay increases toward base of unit; mottled; tan.
253.25-254	CLAY, calcareous; blocky; greasy; cont. clasts of lt. gray, fn. grained, hard limestone; dk gray green to dk green.
254-263	CLAY; blocky; numerous lg. clasts of hard, fine-grained limestone; stingers of fossiliferous, hard, fn. grained limestone part. repl. by dk. gray, glassy chert present near lower contact; dk. green.
	Suwannee Limestone
263-271.75	LIMESTONE; fine grained; fossiliferous; mod. hard to hard; pale gray.
	TD at 271.75 ft.

Caliper log of KR-127, furnished by IMCC and taken by P.E. LaMoreaux & Assoc. on 1/24/78 indicates that the recharge well is cased to 73 ft. BLS. Minor cavernous porosity or a caved zone is indicated at 122 ft. BLS.

Lithologic Log of Core KR-98B-SW, IMCC Kingsford Mine, Polk Co., Florida

Date: January 25, 1984
Logged by: Sam B. Upchurch, Department of Geology, University of South Florida, Tampa, Florida 33620
Location: Approx. 87 feet S49W of recharge well 98B (NW, s.4, T31S, R23W), International Minerals and Chemical Corp., Kingsford Mine, Polk/Hillsborough Counties, Florida.
Driller: Leonard Burnett Drilling Co.
Nature of core: 4 inch core taken by rotary drilling with sharpened casing section as core tube. Log is field log and subject to revision. SW-1 @ 5', etc. indicate sample numbers. (See Oural et al. (1986) for additional details)

Depth (ft.)	Field description
	Plio-Pleistocene Undifferentiated
5-6	SAND, light brown, sl. argillaceous, cohesive; SW-1 @ 5'.
6-11	SAND, light reddish brown, wet and non-cohesive, sloughs; SW-2 @ 9'.
11-11.5	SAND, argillaceous, blocky, mottled; SW-3 @ 11.5'.
11.5-12	SAND, argillaceous, hard.
12-16	SAND, low clay content, sloughs, wet; SW-4 @ 13'.
16-19	SAND, medium grained, clean, dries to blocky, coarser than above; SW-5 @ 19'.
19-39	SAND, clean, fine to medium grained, wet, sloughs, appears to be a major flow zone; SW-6 @ 20, SW-7 @ 25, SW-8 @ 33, SW-9 @ 39'.
39-42	SAND, argillaceous, cohesive, wet, some portions of core slough slightly on sitting, approx. 1% phos.; SW-10 @ 41.
42-45	SAND, very fine grained, sl. argillaceous, sloughs slightly, approx. 1% phos. near top incr. to approx. 3% near lower foot; SW-11 @ 42.5, SW-12 @ 44'.
45-47	SAND, as above, clay stringers 0.5' above base, much compaction from 44-48'.
	Bone Valley Member, Peace River Formation (Hawthorn Group)
47-47.5	CLAY, dense, cohesive, plastic, bright green, montmorillonitic acc. R.N. Strom (XRD); SW-13 @ 47'.
47.5-48	SAND, fine grained, slightly argillaceous,

	cohesive, approx. 1% phos., clay laminae and balls; SW-14 @ 47.5'.
48-53	SAND, argillaceous, dark gray, cohesive, approx. 3% phos.; SW-15 @ 50'.
53-56	SAND, phosphatic, dark gray, approx. 50% phos., argillaceous, mine geologist says this the ORE matrix; SW-16 @ 53'.
	Peace River Formation (undifferentiated) (?)
56-57.5	CLAY, blue-green and brown mottled, cohesive, approx. 50% phos.; SW-17 @ 56, SW-18 @ 57'.
	Arcadia Formation (Hawthorn Group)
57.5-59	DOLOSILT, phosphatic (approx. 50%), clay stringers, yellowish; SW-19 @ 58.5'.
59-62	DOLOSILT, less phosphate, otherwise as above, gradational to unit below; SW-20 @ 60, SW-21 @ 61.5'.
62-72	CLAY, sandy, dark gray, approx. 30% phos., mottled in some areas, laminated, few coarse phos. zones, clasts of underlying dolomite at 72'; SW-22 @ 62.5, SW-23 @ 64, SW-24 @ 70, SW-25 @ 72'.
72-72.5	DOLOSTONE, light gray, soft; SW-26 @ 72.5'.
72.5-73	CLAY, sandy, phosphatic, as 62-72; SW-27 @ 73'.
73-75	SAND, rubbly, clay-rich, dark gray, coarse phos. pebbles; SW-28 @ 74, SW-29 @ contact (75').
75-78	CLAY, sandy, rubbly, phosphate rich, light gray; SW-30 @ 77'.
78-88.5	DOLOSTONE, fossiliferous (pelecypods, etc.), 3' washed casing; SW-31.
88.5-89	DOLOSILT, pasty, wet; SW-32 @ 88.5'.
89-91	DOLOSTONE, fossiliferous, rel. soft; SW-33.
91-91.5	DOLOSILT, gray, sandy.
91.5-93	CLAY, sandy, dark gray, phosphatic; SW-34 @ 92'.
93-97	SAND, well sorted, clay-rich, minor phos.; SW-35 @ 96'.
97-100	SAND, as above, light gray; SW-36 @ 98'.
100-103	DOLOSILT, approx. 5% phos., light gray; SW-37 @ 101'.
103-104.5	SAND, clayey, phosphatic; SW-38 @ 105'.
104.5-115	DOLOSTONE, soft at top, fossiliferous, large pelecypod internal mold at 111', well-developed opaline chert nodule in dolomite at 112'; SW-39 @ 111, SW-40 @ 112'.
115-117	DOLOSTONE/DOLOSILT, soft, sandy, becomes more sand rich with depth; SW-41 @ 116'.
117-119	SAND, argillaceous, phosphatic; SW-42 @ 119'.

TD at 119' -- driller reports hard rock.

Lithologic Log of Core 98B-NE, IMCC Kingsford Mine, Polk Co., Florida

Date: January 23-24, 1984
Logged by: Sam B. Upchurch, Department of Geology, University of South Florida, Tampa, Florida 33620
Location: Approx. 112 feet N47E of recharge well 98B (NW, s.4, T31S, R23W), International Minerals and Chemical Corp., Kingsford Mine, Polk/Hillsborough Counties, Florida.
Driller: Leonard Burnett Drilling Co.
Nature of core: 4 inch core taken by rotary drilling with sharpened casing section as core tube. Log is field log and subject to revision. NE-1 @ 7', etc. refer to samples (see Oural et al., 1986, for additional details)

Depth (ft.)	Field description
	Plio-Pleistocene Undifferentiated
5-6	SAND, fine grained, iron stained, wet.
6-9	SAND, fine grained, argill., mottled, dry; NE-1 @ 7'.
9-10	SAND, fine grained, slightly argillaceous, sloughs; NE-2 @ 9'.
10-12.5	SAND, fine grained, slightly argillaceous, clean, dry; NE-3 @ 12'.
12.5-13	SAND, as above, wet, sloughs.
13-14	SAND, as above, dark gray, cohesive; NE-4 @ 14'.
14-15	SAND, very white, clean, sloughs; NE-5 @ 14'.
15-16	SAND, dark, brownish color, slightly argillaceous, stiff; NE-6 @ 16'.
16-17	SAND, fine grained, gray and brown laminated and mottled, organic fragments; NE-7 @ 17'.
17-18	SAND, light gray, not cohesive.
18-20	SAND, medium brown, fine to medium grained, slightly cohesive.
20-23	SAND, as above, wet, not cohesive; NE-8 @ 22'.
23-23.5	SAND, coarse, brown.
23.5-26	SAND, medium to coarse grained, wet, gray; NE-9 @ 25'.
26-27	SAND, fine to medium grained, very wet, white.
27-28	SAND, moderately fine grained, sloughs.
28-33	SAND, as above, more cohesive, gray; NE-10 @ 30'.
33-36	SAND, medium grained, drains well, less than 1% phos. at top, phos. incr. to approx 1% at bottom; NE-11 @ 33, NE-12 @ 34'.
36-37	SAND, light gray, sloughs, approx. 2% phos.
37-41	SAND, as above, up to 3-5% phos. granules and and;

	NE-13 @ 38.5'.
41-45	SAND, as above, less phos.; NE-14 @ 43'.
45-46.5	SAND, as above, clay balls and stringers at 46', few phos. granules, much phos. fine sand; NE-15 @ 46'.
	Bone Valley Member, Peace River Formation (Hawthorn Group)
46.5-47	CLAY, dark green, cohesive; NE-15a @ 46.5'.
47-52.5	SAND, medium grained, phos. var. from 2 to approx. 10% with depth, cohesive; NE-16 @ 47'.
52.5-56	SAND, argillaceous, phos. pebbles and sand, 30-50% phos., mine geologist says this is ore matrix, clay balls and blebs; NE-17 @ 53.5'.
56-61	SAND, finer than above, more clay, approx. 40% phos., cohesive, brown; NE-18 @ 58'.
61-69	SAND, very clay rich, approx. 30% fine phos.; NE-19 @ 62.5'.
69-71	SAND, slightly argillaceous, phos. pebbles to sand approx. 50%; NE-20 @ 68, NE-21 @ 69'.
	Peace River Formation (undifferentiated)
	Absent (?)
	Arcadia Formation (Hawthorn Group)
71-72.5	DOLOSILT, with fine sand, minor phos., light gray; NE-22 @ 71.5'.
72.5-74.5	SAND, much clay, approx. 40% phos. granules and sand; NE-23 @ 73'.
74.5-77	SAND, rubbly, phos. granules and sand; NE-24 @ 75.5'.
77	MICROSPHORITE SURFACE, aphanitic, bored, on dolostone, driller reports 5' washed casing; NE-25 @ 77'.
77-77.5	DOLOSTONE, phosphatic, moldic with Pecten, Chione, etc.; NE-26 @ 77.5'.
77.5-79	SAND, clayey, approx. 6% phos., cohesive.
79-80.5	CLAY, very sandy, approx. 3% phos., cohesive; NE-27 @ 80'.
80.5-82	DOLOSTONE, rubbly, pebbles, Pecten, gray; driller reports 2' washed casing; NE-28 @ 81'.
82-84	CLAY, dark gray to black, slightly sandy, organic rich(?); NE-29 @ 82'.
84-86	DOLOSTONE, interbedded sandy, clayey, phos. dolostone and fossiliferous dolostone; driller reports 4' washed casing.
86-91	CLAY, sandy, dark gray to black, hackly fracture, cohesive; NE-30 @ 89'.
91-94	CLAY, slightly sandy, phos. specks, dark gray;

	NE-31 @ 93.5'.
94-95	CLAY, very sandy, as above, to SAND, very argillaceous; NE-32 @ 94'.
95-100	CLAY, sandy, medium gray, phos. specks; NE-33 @ 96, NE-34 @ 100'.
	TD at 100'

APPENDIX B

RAW CHEMICAL DATA

1. Surficial Aquifer Monitor Wells

Well Number	Sample Number	Date Sampled	Approx. Sample Depth (ft. BLS)	Temp-erature (deg. C)	Cond-uctivity (umhos/cm)	pH	Redox Potent. (mv)	Dissol. Oxygen (mg/l)	Alkalinity (mg/l as CaCO3)
KR-83S	KR-83-2S	07-14-87	30	26.00	251.00	5.73	17.60	0.85	68.02
	KR-83-3S	10-15-87	30	23.80	830.00	5.61	-42.10	0.85	61.03
KR-98B-US	KR-98B-2US	07-28-87	36	24.20	1025.00	4.66	-21.50	1.28	3.86
	KR-98B-3US	10-11-87	36	24.20	920.00	4.61	-125.00	1.60	4.04
KR-98B-DS	KR-98B-2DS	07-28-87	37	24.20	980.00	4.40	-32.60	1.32	0.00
	KR-98B-3DS	10-17-87	36	24.30	890.00	4.29	-105.40	1.45	0.00
KR-127S	KR-127-3S	02-17-87	33	23.00	403.00	6.36	-144.30	0.80	182.07
	KR-127-4S	08-19-87	32	24.00	472.00	6.01	-138.20	0.92	158.65
	KR-127-5S	10-20-87	33	24.00	810.00	5.95	-277.60	1.75	140.45
		AVERAGE	34	24.19	731.22	5.29	-96.57	1.20	68.68
		STD. DEV.	3	0.74	264.69	0.75	83.93	0.34	69.90
		MINIMUM	30	23.00	251.00	4.29	-277.60	0.80	0.00
		MAXIMUM	37	26.00	1025.00	6.36	17.60	1.75	182.07

Well Number	Sample Number	Chloride (mg/l)	Fluoride (mg/l)	Bicar-bonate (mg/l)	Ortho-phosphate (mg/l)	Silica (mg/l)	Sulfate (mg/l)	Total Organic Carbon (mg/l C)	Total Dissolved Solids (mg/l)
KR-83S	KR-83-2S	12.58	0.05	82.93	.00	2.17	48.00	8.54	382.00
	KR-83-3S	9.62	0.05	74.41	0.04	3.35	34.70	6.83	220.00
KR-98B-US	KR-98B-2US	39.83	0.13	4.71	0.43	6.45	540.00	6.01	754.00
	KR-98B-3US	43.20	0.20	4.93	0.48	5.10	390.00	6.06	672.00
KR-98B-DS	KR-98B-2DS	40.13	0.09	0.00	0.62	6.25	404.00	8.97	532.00
	KR-98B-3DS	48.53	0.21	0.00	0.42	5.04	367.60	7.44	754.00
KR-127S	KR-127-3S	15.60	0.13	221.98	0.22	3.10	52.20	13.05	250.00
	KR-127-4S	14.00	0.10	193.43	0.14	2.17	131.50	8.51	432.00
	KR-127-5S	17.18	0.21	171.24	0.13	2.20	220.50	9.63	468.00
		26.74	0.13	83.74	0.28	3.98	243.17	8.34	496.00
		14.79	0.06	85.22	0.20	1.65	177.02	2.06	188.55
		9.62	0.05	0.00	.00	2.17	34.70	6.01	220.00
		48.53	0.21	221.98	0.62	6.45	540.00	13.05	754.00

Well Number	Sample Number	Volatile Dissolved Solids (mg/l)	Aluminum (ug/l)	Calcium (mg/l)	Iron (ug/l)	Potassium (mg/l)	Magnesium (mg/l)	Manganese (ug/l)	Sodium (mg/l)
KR-83S	KR-83-2S	68.00	22.80	14.90	8136.94	0.26	4.06	21.92	15.58
	KR-83-3S	40.00	0.00	10.79	3132.11	0.25	8.67	7.12	18.35
KR-98B-US	KR-98B-2US	50.00	74.69	13.18	11041.44	0.54	12.04	15.30	180.79
	KR-98B-3US	106.00	162.29	10.97	8774.42	0.40	10.49	11.95	149.58
KR-98B-DS	KR-98B-2DS	0.00	198.03	5.25	5274.24	0.30	10.20	7.70	172.10
	KR-98B-3DS	72.00	185.68	8.36	6492.01	0.26	13.29	8.43	163.89
KR-127S	KR-127-3S	16.00	0.00	44.24	2596.00	0.26	19.78	9.68	24.10
	KR-127-4S	184.00	0.00	52.18	1760.15	0.43	21.05	7.04	27.77
	KR-127-5S	279.00	0.00	76.81	1518.78	0.58	31.00	6.92	34.43
		90.56	71.50	26.30	5414.01	0.36	14.51	10.67	87.40
		83.86	81.73	23.77	3218.49	0.12	7.66	4.76	71.42
		0.00	0.00	5.25	1518.78	0.25	4.06	6.92	15.58
		279.00	198.03	76.81	11041.44	0.58	31.00	21.92	180.79

Well Number	Sample Number	Lead (ug/l)	Strontium (ug/l)	Lead-210 (pCi/l)	Po-210 (pCi/l)	Radium-226 (pCi/l)	U-234 (pCi/l)	U-238 (pCi/l)	Activity Ratio (234/238)
KR-83S	KR-83-2S	4.93	19.75	0.10	0.74	1.36	0.45	0.12	3.68
	KR-83-3S	6.04	10.39	NA	1.52	0.15	0.42	0.11	4.02
KR-98B-US	KR-98B-2US	3.84	38.81	4.05	45.62	3.37	0.17	0.09	1.90
	KR-98B-3US	6.82	25.36	NA	27.73	3.27	0.14	0.08	1.66
KR-98B-DS	KR-98B-2DS	4.02	15.99	4.29	54.43	1.36	0.31	0.16	1.97
	KR-98B-3DS	9.25	18.22	NA	37.62	1.39	0.35	0.13	2.69
KR-127S	KR-127-3S	1.38	20.64	NA	0.24	2.34	0.05	0.04	1.26
	KR-127-4S	6.42	80.66	0.32	1.13	0.94	0.22	0.06	3.66
	KR-127-5S	8.24	101.19	NA	0.30	0.50	0.14	0.03	4.52
		5.66	36.78	0.97	18.81	1.63	0.25	0.09	2.82
		2.27	30.24	1.71	21.20	1.07	0.13	0.04	1.11
		1.38	10.39	0.00	0.24	0.15	0.05	0.03	1.26
		9.25	101.19	4.29	54.43	3.37	0.45	0.16	4.52

Well Number	Sample Number	Gross-Alpha (pCi/l)	Total anionic epm's (1)	Total cationic epm's (2)	Electrical neutrality (2)-(1)
KR-83S	KR-83-2S	9.26	2.72	2.06	-0.66
	KR-83-3S	7.51	2.22	2.17	-0.05
KR-98B-US	KR-98B-2US	135.14	12.46	9.93	-2.53
	KR-98B-3US	62.31	9.45	8.26	-1.18
KR-98B-DS	KR-98B-2DS	59.31	9.57	8.81	-0.76
	KR-98B-3DS	43.54	9.05	8.90	-0.15
KR-127S	KR-127-3S	6.76	5.18	4.98	-0.20
	KR-127-4S	10.26	6.31	5.62	-0.69
	KR-127-5S	10.51	7.90	7.95	0.06
		38.29	7.21	6.52	-0.69
		40.51	3.20	2.78	0.76
		6.76	2.22	2.06	-2.53
		135.14	12.46	9.93	0.06

2. Floridan Aquifer Monitor Wells

Company	Well Number	Well Number	Sample Number	Date Sampled	Approx. Sample Depth (ft. BLS)	Temp-erature (deg. C)	Cond-uctivity (umhos/cm)	pH
I.M.C.C.	KR-83D	KR-83D	KR-83-2D	07-14-87	128	25.00	321.00	7.48
			KR-83-3D	10-18-87	125	24.80	560.00	7.19
	KR-98B-UD	KR-98B-UD	KR-98B-2UD	07-24-87	205	25.90	352.00	7.46
			KR-98B-3UD	10-17-87	110	25.00	476.00	7.12
	KR-98B-DD	KR-98B-DD	KR-98B-2DD	08-03-87	120	24.50	348.00	7.15
			KR-98B-3DD	10-18-87	120	25.00	570.00	7.10
	KR-127D	KR-127D	KR-127-3D	02-18-87	175	22.20	300.00	7.42
			KR-127-4D	08-19-87	170	24.80	301.00	7.45
			KR-127-5D	11-20-87	125	22.20	267.00	7.26
				AVERAGE	142	24.38	388.33	7.29
				STD. DEV.	31	1.22	109.44	0.15
				MINIMUM	110	22.20	267.00	7.10
				MAXIMUM	205	25.90	570.00	7.48

Company	Well Number	Redox Potent. (mv)	Dissol. Oxygen (mg/l)	Alkalinity (mg/l as CaCO3)	Chloride (mg/l)	Fluoride (mg/l)	Bicar-bonate (mg/l)	Ortho-phosphate (mg/l)	Silica (mg/l)
I.M.C.C.	KR-83D	-55.30	0.87	170.87	9.75	0.65	208.45	0.02	29.20
		-171.20	1.60	170.97	9.90	0.80	208.45	0.07	31.70
	KR-98B-UD	-52.50	1.81	202.22	10.23	0.56	246.55	0.17	28.90
		-140.60	1.95	196.34	10.00	0.61	239.38	0.02	30.16
	KR-98B-DD	-134.70	1.30	196.52	5.88	0.56	239.61	0.02	40.75
		-218.60	1.30	196.71	6.33	0.72	239.83	0.17	46.33
	KR-127D	-71.20	1.32	176.12	9.10	0.70	214.73	0.09	38.50
		-172.20	1.12	171.71	9.30	0.74	209.35	0.02	39.40
		-235.70	1.80	171.34	9.90	0.61	208.90	0.10	44.50
		-139.11	1.45	183.64	8.93	0.66	223.92	0.08	36.60
		64.06	0.34	12.98	1.55	0.08	15.82	0.06	6.37
		-235.70	0.87	170.87	5.88	0.56	208.45	0.02	28.90
		-52.50	1.95	202.22	10.23	0.80	246.55	0.17	46.33

Company	Well Number	Sulfate (mg/l)	Total Organic Carbon (mg/l C)	Total Dissolved Solids (mg/l)	Volatile Dissolved Solids (mg/l)	Aluminum (ug/l)	Calcium (mg/l)	Iron (ug/l)	Potassium (mg/l)
I.M.C.C.	KR-83D	2.20	4.94	464.00	134.00	0.00	33.47	35.37	1.33
		8.93	3.82	346.00	36.00	0.00	35.42	0.00	1.13
	KR-98B-UD	2.00	4.35	152.00	24.00	0.00	41.80	0.00	1.23
		2.15	4.13	288.00	94.00	0.00	35.82	0.00	1.31
	KR-98B-DD	50.00	4.83	304.00	52.00	0.00	40.28	8.95	1.26
		4.50	4.87	330.00	86.00	0.00	33.68	0.00	1.26
	KR-127D	0.00	3.35	230.00	0.00	0.00	35.79	25.30	0.94
		2.00	4.36	348.00	162.00	0.00	31.05	0.00	0.94
		2.45	4.57	138.00	124.00	0.00	29.21	43.48	1.06
		8.25	4.36	288.89	79.11	0.00	35.17	12.57	1.16
		14.95	0.50	96.79	51.70	0.00	3.78	16.47	0.14
		0.00	3.35	138.00	0.00	0.00	29.21	0.00	0.94
		50.00	4.94	464.00	162.00	0.00	41.80	43.48	1.33

Company	Well Number	Magnesium (mg/l)	Manganese (ug/l)	Sodium (mg/l)	Lead (ug/l)	Strontium (ug/l)	Lead-210 (pCi/l)	Po-210 (pCi/l)	Radium-226 (pCi/l)
I.M.C.C.	KR-83D	6.41	0.62	13.39	4.32	56.98	0.51	0.10	0.43
		16.17	0.72	15.41	6.92	47.30	NA	0.41	0.52
	KR-98B-UD	21.34	0.91	12.78	2.88	31.50	0.32	0.45	2.49
		21.34	0.85	13.21	4.53	23.96	NA	0.79	1.61
	KR-98B-DD	19.82	0.70	15.96	4.95	90.68	0.48	0.51	0.42
		19.41	0.58	15.24	7.56	73.00	NA	0.42	0.40
	KR-127D	18.79	0.94	12.67	2.38	9.79	0.51	0.36	2.89
		17.36	0.59	16.27	5.54	39.42	0.00	3.22	0.29
		17.76	0.14	16.09	7.43	40.86	NA	0.94	0.20
		17.60	0.67	14.56	5.17	45.94	0.20	0.80	1.03
		4.28	0.23	1.43	1.77	23.39	0.23	0.89	0.98
		6.41	0.14	12.67	2.38	9.79	0.00	0.10	0.20
		21.34	0.94	16.27	7.56	90.68	0.51	3.22	2.89

Company	Well Number	U-234 (pCi/l)	U-238 (pCi/l)	Activity Ratio (234/238)	Gross-Alpha (pCi/l)	Total anionic epm's (1)	Total cationic epm's (2)	Electrical neutrality (2)-(1)
I.M.C.C.	KR-83D	0.08	0.02	4.15	6.01	3.77	2.82	-0.96
		0.07	0.07	1.01	1.02	3.93	3.80	-0.13
	KR-98B-UD	0.05	0.05	0.98	6.51	4.41	4.43	0.02
		0.03	0.02	1.33	7.13	4.28	4.15	-0.13
	KR-98B-DD	0.04	0.02	2.50	5.11	5.16	4.37	-0.79
		0.04	0.02	2.17	11.26	4.25	3.97	-0.27
	KR-127D	0.05	0.04	1.31	4.13	3.82	3.91	0.09
		0.52	0.48	1.08	4.76	3.77	3.71	-0.06
		0.13	0.09	1.37	6.01	3.79	3.65	-0.14
		0.11	0.09	1.77	5.77	4.13	3.87	-0.26
		0.15	0.14	0.98	2.57	0.43	0.45	0.34
		0.03	0.02	0.98	1.02	3.77	2.82	-0.96
		0.52	0.48	4.15	11.26	5.16	4.43	0.09

Company	Well Number	Comments	Na/Cl	Na/Cl Deviation from Seawater
I.M.C.C.	KR-83D		1.37	2.49
			1.56	2.82
	KR-98B-UD		1.25	2.26
			1.32	2.39
	KR-98B-DD		2.71	4.91
			2.41	4.36
	KR-127D		1.39	2.52
			1.75	3.17
			1.63	2.94
			1.63	2.95
			0.92	1.67
			2.15	3.90
			1.59	2.88

3. Monitored Recharge Wells

Company	Well Number	Sample Number	Sample Number	Date Sampled	Approx. Sample Depth (ft. BLS)	Temp-erature (deg. C)	Cond-uctivity (umhos/cm)	pH
	KR-83	KR-83-1	KR-83-1	10-07-86	52	23.80	151.00	5.96
		KR-83-2	KR-83-2	07-13-87	80	23.40	150.00	5.97
		KR-83-2BH	KR-83-2BH	07-14-87	175	23.80	149.00	5.89
		KR-83-3	KR-83-3	10-15-87	92	24.80	432.00	5.30
	KR-98B	KR-98B-1	KR-98B-1	09-29-86	* NA	25.80	65.00	4.60
		KR-98B-2	KR-98B-2	07-24-87	84	23.80	830.00	4.95
		KR-98B-2BH	KR-98B-2BH	07-24-87	190	24.00	800.00	5.18
		KR-98B-3	KR-98B-3	10-11-87	110	24.20	800.00	4.76
	KR-127	KR-127-1	KR-127-1	12-15-86	102	23.50	275.00	5.98
		KR-127-2	KR-127-2	02-11-87	81	23.40	278.00	5.94
		KR-127-3	KR-127-3	02-17-87	81	23.40	271.00	5.86
		KR-127-3BH	KR-127-3BH	02-18-87	200	23.20	278.00	6.03
		KR-127-4	KR-127-4	08-18-87	96	23.40	262.00	5.67
		KR-127-4BH	KR-127-4BH	08-19-87	200	23.30	259.00	5.85
		KR-127-5	KR-127-5	11-20-87	140	24.00	266.00	5.32
				MEAN	112.20	23.85	351.07	5.55
				STD. DEV.	55.95	0.66	243.40	0.47
				MINIMUM	0.00	23.20	65.00	4.60
				MAXIMUM	200.00	25.80	830.00	6.03

Company	Well Number	Sample Number	Redox Potent. (mv)	Dissol. Oxygen (mg/l)	Alkalinity (mg/l as CaCO3)	Chloride (mg/l)	Fluoride (mg/l)	Bicar-bonate (mg/l)	Ortho-phosphate (mg/l)
	KR-83	KR-83-1	NA	3.55	34.49	10.45	0.16	42.05	1.06
		KR-83-2	97.90	3.75	30.33	11.17	0.23	36.98	0.82
		KR-83-2BH	74.00	6.10	29.41	10.57	0.22	35.86	0.71
		KR-83-3	-14.30	3.20	27.58	10.44	0.31	33.62	1.33
	KR-98B	KR-98B-1	NA	3.61	13.62	7.91	0.30	16.61	2.19
		KR-98B-2	37.30	6.30	11.95	39.18	0.37	14.57	2.28
		KR-98B-2BH	18.60	5.45	12.87	39.18	0.37	15.69	1.94
		KR-98B-3	-158.10	1.70	11.21	41.28	0.43	13.67	2.44
	KR-127	KR-127-1	-87.70	1.65	122.39	11.40	0.54	149.22	1.09
		KR-127-2	-85.60	2.40	120.41	10.60	0.51	146.81	1.20
		KR-127-3	-73.30	1.22	122.80	12.90	0.55	149.72	1.07
		KR-127-3BH	-40.80	2.95	127.22	9.55	0.54	155.11	1.09
		KR-127-4	-21.60	2.90	98.17	10.49	0.45	119.69	0.92
		KR-127-4BH	-54.20	3.38	104.24	10.73	0.43	127.09	0.86
		KR-127-5	-150.20	2.10	100.74	10.00	0.43	122.83	0.80
			-30.53	3.35	64.50	16.39	0.39	78.63	1.32
			71.20	1.50	47.16	11.80	0.12	57.49	0.57
			-158.10	1.22	11.21	7.91	0.16	13.67	0.71
			97.90	6.30	127.22	41.28	0.55	155.11	2.44

Company	Well Number	Sample Number	Silica (mg/l)	Sulfate (mg/l)	Total Organic Carbon (mg/l C)	Total Dissolved Solids (mg/l)	Volatile Dissolved Solids (mg/l)	Aluminum (ug/l)	Calcium (mg/l)
	KR-83	KR-83-1	3.81	36.00	5.40	76.00	4.00	16.94	11.70
		KR-83-2	6.25	44.00	4.86	312.00	98.00	63.42	10.51
		KR-83-2BH	6.08	51.00	4.81	300.00	34.00	21.56	10.58
		KR-83-3	4.95	30.50	4.72	270.00	40.00	0.00	9.10
	KR-98B	KR-98B-1	4.90	218.00	7.55	480.00	52.00	71.82	12.76
		KR-98B-2	9.35	336.00	6.91	476.00	0.00	196.06	17.20
		KR-98B-2BH	8.82	304.00	7.14	476.00	16.00	123.54	18.12
		KR-98B-3	7.40	240.00	6.78	454.00	96.00	241.55	17.25
	KR-127	KR-127-1	6.59	7.15	12.90	274.00	66.00	34.23	25.13
		KR-127-2	6.20	28.20	19.65	274.00	94.00	35.76	25.66
		KR-127-3	4.92	20.50	12.20	176.00	70.00	18.80	24.80
		KR-127-3BH	6.74	39.30	14.05	268.00	216.00	55.27	25.35
		KR-127-4	3.30	71.00	12.24	330.00	166.00	0.00	26.32
		KR-127-4BH	3.30	78.30	12.81	278.00	48.00	0.00	29.95
		KR-127-5	1.80	32.00	13.52	64.00	56.00	0.00	21.58
			5.63	102.40	9.70	300.53	70.40	58.60	19.07
			2.01	107.99	4.35	127.57	56.54	71.34	6.71
			1.80	7.15	4.72	64.00	0.00	0.00	9.10
			9.35	336.00	19.65	480.00	216.00	241.55	29.95

Company	Well Number	Sample Number	Iron (ug/l)	Potassium (mg/l)	Magnesium (mg/l)	Manganese (ug/l)	Sodium (mg/l)	Lead (ug/l)	Strontium (ug/l)
	KR-83	KR-83-1	742.40	0.39	6.52	8.59	13.70	0.00	0.30
		KR-83-2	1103.78	0.35	5.41	5.11	13.20	3.52	9.29
		KR-83-2BH	1100.01	0.38	5.45	6.14	13.09	3.77	10.61
		KR-83-3	591.03	0.36	5.40	3.16	14.04	5.96	8.38
	KR-98B	KR-98B-1	6353.50	0.84	8.28	13.31	110.10	22.47	2.35
		KR-98B-2	7577.30	0.86	11.01	17.15	147.12	1.47	17.08
		KR-98B-2BH	7262.61	0.93	11.24	17.29	146.37	3.47	23.28
		KR-98B-3	6992.38	0.81	11.07	16.03	136.03	5.51	15.75
	KR-127	KR-127-1	796.70	1.12	14.32	7.83	21.29	2.01	8.18
		KR-127-2	857.35	2.72	14.53	10.64	20.58	2.14	7.93
		KR-127-3	721.00	1.13	14.17	10.69	20.70	1.38	6.72
		KR-127-3BH	911.60	1.63	14.90	11.39	20.30	1.70	6.26
		KR-127-4	1040.94	1.04	16.45	12.84	19.10	6.04	46.93
		KR-127-4BH	889.54	1.25	16.84	15.15	19.47	3.89	41.09
		KR-127-5	513.74	1.09	16.07	13.40	18.39	11.30	28.04
			2496.93	0.99	11.44	11.25	48.90	4.98	15.48
			2757.90	0.58	4.13	4.24	52.51	5.37	13.30
			513.74	0.35	5.40	3.16	13.09	0.00	0.30
			7577.30	2.72	16.84	17.29	147.12	22.47	46.93

Company	Well Number	Sample Number	Lead-210 (pCi/l)	Po-210 (pCi/l)	Radium-226 (pCi/l)	U-234 (pCi/l)	U-238 (pCi/l)	Activity Ratio	Gross-Alpha (pCi/l)
	KR-83	KR-83-1	NA	10.18	0.36	0.26	0.07	3.57	3.97
		KR-83-2	0.59	1.512	0.21	0.17	0.07	2.30	5.44
		KR-83-2BH	0.64	3.11	0.67	0.15	0.03	6.08	8.41
		KR-83-3	NA	9.36	0.38	0.18	0.05	3.89	3.00
	KR-98B	KR-98B-1	NA	11.30	8.46	0.23	0.14	1.64	6.98
		KR-98B-2	3.27	13.54	1.41	0.21	0.13	1.56	39.04
		KR-98B-2BH	2.63	11.70	1.81	0.19	0.23	0.82	34.91
		KR-98B-3	NA	10.42	0.58	0.20	0.17	1.13	13.26
	KR-127	KR-127-1	NA	0.53	4.83	0.24	0.15	1.63	5.61
		KR-127-2	NA	0.50	4.87	0.15	0.12	1.25	NA
		KR-127-3	NA	0.50	5.46	0.15	0.12	1.25	3.55
		KR-127-3BH	0.19	1.51	5.90	0.31	0.20	1.52	21.02
		KR-127-4	1.03	1.68	0.56	0.36	0.16	2.25	18.02
		KR-127-4BH	2.14	1.23	1.12	0.30	0.19	1.59	32.28
		KR-127-5	NA	0.71	0.49	0.32	0.14	2.34	10.89
			0.70	5.09	2.47	0.23	0.13	2.19	13.76
			1.05	5.02	2.58	0.07	0.06	1.33	12.18
			0.00	0.00	0.21	0.15	0.03	0.82	0.00
			3.27	13.54	8.46	0.36	0.23	6.08	39.04

Company	Well Number	Sample Number	Total anionic epm's (1)	Total cationic epm's (2)	Electrical neutrality (2)-(1)	Comments
	KR-83	KR-83-1	ERR	1.75	ERR	
		KR-83-2	1.88	1.60	-0.28	
		KR-83-2BH	1.98	1.60	-0.38	
		KR-83-3	1.54	1.54	.00	
	KR-98B	KR-98B-1	ERR	6.36	ERR	
		KR-98B-2	8.43	8.48	0.05	Alk. is lab determination
		KR-98B-2BH	7.77	8.49	0.72	
		KR-98B-3	6.49	7.99	1.50	
	KR-127	KR-127-1	ERR	3.42	ERR	
		KR-127-2	3.36	3.48	0.12	
		KR-127-3	3.31	3.36	0.05	
		KR-127-3BH	3.69	3.45	-0.24	
		KR-127-4	3.79	3.56	-0.23	
		KR-127-4BH	4.07	3.79	-0.27	
		KR-127-5	3.01	3.25	0.24	
			ERR	4.14	ERR	
			ERR	2.40	ERR	
			ERR	1.54	ERR	
			ERR	8.49	ERR	

4. Other Recharge Wells

Company	Well Number	Sample Number	Date Sampled	Approx. Sample Depth (ft. BLS)	Temp-erature (deg. C)	Cond-uctivity (umhos/cm)	pH	Redox Potent. (mv)	Dissol. Oxygen (mg/l)	Alkalinity (mg/l as CaCO3)
MOBIL (old AMAX)	PRW-2	APRW-2-1	11-04-86	* NA	24.00	198.00	5.35	NA	3.70	7.74
		APRW-2-2	10-28-87	96	23.30	215.00	4.71	274.30	3.10	4.23
	PRW-6	APRW-6-1	10-21-87	60	27.60	124.00	5.65	78.10	6.05	19.67
	PRW-9	APRW-9-1	11-05-86	15	25.00	73.00	4.55	NA	6.32	1.84
		APRW-9-2	10-21-87	40	24.10	172.00	4.56	-124.30	2.35	0.55
	PRW-10	APRW-10-1	11-07-86	45	24.40	44.00	5.46	NA	5.55	9.07
		APRW-10-2	10-09-87	90	25.20	43.00	5.41	193.20	3.17	6.99
	TRW-17	ATRW-17-1	10-28-86	* NA	23.90	59.00	5.43	NA	3.10	10.42
		ATRW-17-1 (rep)			NA	NA	NA	NA	NA	NA
		ATRW-17-2	10-09-87	95	25.50	75.00	5.22	-30.52	2.50	20.96
		ATRW-17-2 (ufl)			NA	NA	NA	NA	NA	NA
	TRW-28	ATRW-28-1	11-10-86	50	24.50	203.00	5.95	NA	3.50	114.95
		ATRW-28-2	10-28-87	86	24.90	237.00	5.36	17.40	2.80	100.38
	TRW-29	ATRW-29-1	11-05-86	60	24.80	73.00	5.66	NA	4.60	12.44
		ATRW-29-2	09-23-87	74	24.20	72.00	5.75	139.40	9.00	15.26
	TRW-30	ATRW-30-1	11-07-86	60	24.10	69.00	5.80	NA	8.50	13.60
		ATRW-30-2	09-25-87	85	24.70	72.00	5.39	186.00	8.30	15.26
W.R. GRACE	RK-01	WRG-01	10-03-86	60	24.00	41.00	4.92	NA	0.95	2.30
		WRG-01 (rep)			NA	NA	NA	NA	NA	NA
	RK-02	WRG-02	10-06-86	60	23.90	39.00	4.79	NA	0.80	1.95
I.M.C.C.	KR-22	KR-22-1	12-15-86	63	24.00	322.00	5.95	-56.50	2.18	60.43
		KR-22-2	08-04-87	75	24.00	350.00	5.76	-57.60	4.45	57.73
	KR-80	KR-80	11-25-86	* NA	24.10	147.00	5.95	71.80	5.02	22.59
	KR-83	KR-83-1	10-07-86	52	23.80	151.00	5.96	NA	3.55	34.49
		KR-83-2	07-13-87	80	23.40	150.00	5.97	97.90	3.75	30.33
		KR-83-2BH	07-14-87	175	23.80	149.00	5.89	74.00	6.10	29.41
		KR-83-3	10-15-87	92	24.80	432.00	5.30	-14.30	3.20	27.58
	KR-86 (KR-18)	KR-86 (KR-18)	12-16-86	90	23.00	142.00	5.68	46.10	1.78	33.39
	KR-87A	KR-87A-1	12-16-86	87	23.30	192.00	5.75	44.20	2.24	41.36
		KR-87A-2	06-15-87	75	22.70	198.00	5.76	23.30	2.30	44.67
	KR-95	KR-95	10-01-86	* NA	25.00	207.00	5.60	NA	2.90	46.33
	KR-98B	KR-98B-1	09-29-86	* NA	25.80	65.00	4.60	NA	3.61	13.62
		KR-98B-2	07-24-87	84	23.80	830.00	4.95	37.30	6.30	11.95
		KR-98B-2BH	07-24-87	190	24.00	800.00	5.18	18.60	5.45	12.87
		KR-98B-3	10-11-87	110	24.20	800.00	4.76	-158.10	1.70	11.21
	KR-117	KR-117-1	12-05-86	90	23.80	196.00	5.54	31.80	3.16	22.70
		KR-117-1 (dup)	12-05-86	90	23.80	196.00	5.54	31.80	3.16	22.48
		KR-117-2	06-12-87	90	23.50	252.00	5.62	41.60	4.20	29.60
	KR-118	KR-118-1	11-24-86	72	23.80	153.00	5.87	0.80	2.30	42.84
		KR-118-2	06-14-87	75	23.00	220.00	5.94	-3.28	3.95	37.87
	KR-120	KR-120-1	11-24-86	72	24.70	155.00	5.90	-19.50	2.15	52.95
		KR-120-2	06-14-87	54?	23.00	196.00	5.87	-32.20	2.18	47.98
	KR-122	KR-122-1	11-25-86	90	24.20	230.00	5.95	8.10	1.48	95.60
		KR-122-2	06-15-87	90	23.90	237.00	5.97	-3.28	1.50	94.49

Company	Well Number	Sample Number	Chloride (mg/l)	Fluoride (mg/l)	Bicar-bonate (mg/l)	Ortho-phosphate (mg/l)	Silica (mg/l)	Sulfate (mg/l)	Total Organic Carbon (mg/l C)	Total Dissolved Solids (mg/l)
MOBIL (old AMAX)	PRW-2	APRW-2-1	20.17	0.61	9.44	0.62	1.54	25.00	3.35	186.00
		APRW-2-2	20.21	0.73	5.16	0.50	4.05	2.45	2.78	131.00
	PRW-6	APRW-6-1	5.59	0.36	23.98	0.17	5.10	11.10	2.04	9.00
	PRW-9	APRW-9-1	8.30	0.12	2.24	0.12	2.03	20.40	3.90	26.00
		APRW-9-2	12.23	0.41	0.67	0.32	3.05	35.80	4.00	18.00
	PRW-10	APRW-10-1	6.15	0.13	11.06	0.89	2.63	4.04	3.60	12.00
		APRW-10-2	5.44	0.23	8.52	1.27	2.85	1.38	2.99	84.00
	TRW-17	ATRW-17-1	7.08	0.17	12.70	1.07	3.70	2.00	5.50	20.00
		ATRW-17-1 (rep)	NA	NA	NA	NA	NA	NA	NA	NA
		ATRW-17-2	6.16	0.24	25.55	0.86	4.77	7.85	5.26	7.00
		ATRW-17-2 (ufl)	NA	NA	NA	NA	NA	NA	NA	NA
	TRW-28	ATRW-28-1	13.84	1.04	140.15	2.63	13.48	1.03	9.05	180.00
		ATRW-28-2	13.35	1.37	122.38	3.56	14.10	0.00	10.20	244.00
	TRW-29	ATRW-29-1	7.00	0.43	15.16	3.24	4.60	13.20	3.35	32.00
		ATRW-29-2	6.66	0.41	18.60	2.19	4.85	13.25	4.92	72.00
	TRW-30	ATRW-30-1	7.60	0.45	16.58	2.83	4.34	6.50	3.50	56.00
		ATRW-30-2	6.16	0.50	18.60	3.64	5.80	10.45	3.41	184.00
W.R. GRACE	RK-01	WRG-01	5.18	0.31	2.80	1.90	3.08	3.10	4.90	64.00
		WRG-01 (rep)	NA	NA	NA	NA	NA	NA	NA	NA
	RK-02	WRG-02	5.75	0.00	2.38	2.40	2.10	2.00	3.70	48.00
I.M.C.C.	KR-22	KR-22-1	15.22	0.95	73.67	2.44	10.76	108.75	8.75	192.00
		KR-22-2	15.70	0.93	70.38	2.21	5.18	111.00	7.48	314.00
	KR-80	KR-80	8.46	0.91	27.54	2.84	5.35	34.50	5.95	138.00
	KR-83	KR-83-1	10.45	0.16	42.05	1.06	3.81	36.00	5.40	76.00
		KR-83-2	11.17	0.23	36.98	0.82	6.25	44.00	4.86	312.00
		KR-83-2BH	10.57	0.22	35.86	0.71	6.08	51.00	4.81	300.00
		KR-83-3	10.44	0.31	33.62	1.33	4.95	30.50	4.72	270.00
	KR-86 (KR-18)	KR-86 (KR-18)	13.84	0.99	40.71	6.94	12.75	11.20	2.95	144.00
	KR-87A	KR-87A-1	8.30	0.45	50.43	2.68	5.31	22.60	8.00	168.00
		KR-87A-2	9.88	0.25	54.47	5.45	3.68	53.84	9.92	246.00
	KR-95	KR-95	14.15	0.23	56.49	1.29	6.68	39.50	9.75	160.00
	KR-98B	KR-98B-1	31.64	0.30	16.61	2.19	4.90	218.00	7.55	480.00
		KR-98B-2	39.18	0.37	14.57	2.28	9.35	336.00	6.91	476.00
		KR-98B-2BH	39.18	0.37	15.69	1.94	8.82	304.00	7.14	476.00
		KR-98B-3	41.28	0.43	13.67	2.44	7.40	240.00	6.78	454.00
	KR-117	KR-117-1	9.15	0.63	27.68	5.58	8.52	59.40	5.75	178.00
		KR-117-1 (dup)	11.60	0.57	27.41	5.42	8.19	60.80	5.95	168.00
		KR-117-2	12.82	0.62	36.09	5.06	10.55	70.35	9.75	234.00
	KR-118	KR-118-1	13.20	0.34	52.23	1.88	4.26	46.80	7.50	160.00
		KR-118-2	13.45	0.40	46.17	2.56	7.35	65.00	8.20	220.00
	KR-120	KR-120-1	11.70	0.53	64.56	3.77	6.59	23.20	5.13	156.00
		KR-120-2	12.10	0.53	58.50	4.72	10.05	38.50	7.34	224.00
	KR-122	KR-122-1	9.58	0.96	116.56	4.49	10.59	13.00	6.30	200.00
		KR-122-2	9.95	1.00	115.21	5.21	11.00	24.80	8.85	234.00

Company	Well Number	Sample Number	Volatile Dissolved Solids (mg/l)	Aluminum (ug/l)	Calcium (mg/l)	Iron (ug/l)	Potassium (mg/l)	Magnesium (mg/l)	Manganese (ug/l)	Sodium (mg/l)
MOBIL (old AMAX)	PRW-2	APRW-2-1	144.00	376.35	21.80	128.80	0.35	9.49	20.05	5.33
		APRW-2-2	129.00	540.22	18.55	24.12	0.49	8.95	12.49	5.31
	PRW-6	APRW-6-1	8.00	0.00	7.29	96.67	0.22	2.93	3.68	3.53
	PRW-9	APRW-9-1	14.00	1111.57	3.08	477.30	0.17	3.23	2.20	4.95
		APRW-9-2	13.00	1949.02	6.57	906.24	0.23	5.53	2.53	7.61
	PRW-10	APRW-10-1	0.00	23.15	3.08	146.50	0.48	1.31	1.46	3.94
		APRW-10-2	60.00	76.41	2.44	109.65	0.04	1.15	1.57	3.51
	TRW-17	ATRW-17-1	16.00	144.73	4.04	536.60	0.20	1.95	2.04	4.36
		ATRW-17-1 (rep)	NA	105.88	NA	NA	NA	NA	NA	NA
		ATRW-17-2	6.00	14.99	8.74	263.06	0.10	1.70	1.85	4.31
		ATRW-17-2 (ufl)	NA	225.83	8.59	485.79	0.119	1.66	1.86	4.34
	TRW-28	ATRW-28-1	166.00	22.51	31.60	912.90	0.37	9.63	18.77	10.28
		ATRW-28-2	82.00	39.75	24.20	1819.06	0.38	9.08	16.25	11.04
	TRW-29	ATRW-29-1	24.00	70.00	8.13	250.00	0.14	1.77	4.12	4.63
		ATRW-29-2	48.00	0.00	8.73	76.28	0.14	1.58	3.05	4.46
	TRW-30	ATRW-30-1	14.00	43.26	7.53	30.30	0.13	1.80	3.97	4.27
		ATRW-30-2	168.00	0.00	7.59	227.39	0.23	1.80	2.75	3.89
W.R. GRACE	RK-01	WRG-01	44.00	631.35	2.22	315.00	0.20	0.90	1.24	3.18
		WRG-01 (rep)	NA	610.23	NA	NA	NA	NA	NA	NA
	RK-02	WRG-02	16.00	356.96	0.84	255.05	0.15	0.81	0.00	3.21
I.M.C.C.	KR-22	KR-22-1	142.00	18.54	25.28	2064.40	1.19	9.29	14.55	43.23
		KR-22-2	50.00	0.00	27.01	1733.99	1.07	10.73	12.00	42.18
	KR-80	KR-80	108.00	0.00	11.87	441.90	0.41	4.27	80.81	10.59
	KR-83	KR-83-1	4.00	16.94	11.70	742.40	0.39	6.52	8.59	13.70
		KR-83-2	98.00	63.42	10.51	1103.78	0.35	5.41	5.11	13.20
		KR-83-2BH	34.00	21.56	10.58	1100.01	0.38	5.45	6.14	13.09
		KR-83-3	40.00	0.00	9.10	591.03	0.36	5.40	3.16	14.04
	KR-86 (KR-18)	KR-86 (KR-18)	76.00	0.72	15.91	2550.50	0.72	3.82	27.45	7.15
	KR-87A	KR-87A-1	90.00	41.56	15.25	2520.20	0.34	11.01	14.04	11.14
		KR-87A-2	120.00	5.15	12.95	1762.40	0.35	11.40	14.99	11.40
	KR-95	KR-95	72.00	69.28	13.97	1766.40	0.87	8.52	6.65	18.59
	KR-98B	KR-98B-1	52.00	71.82	12.76	6353.50	0.84	8.28	13.31	110.10
		KR-98B-2	0.00	196.06	17.20	7577.30	0.86	11.01	17.15	147.12
		KR-98B-2BH	16.00	123.54	18.12	7262.61	0.93	11.24	17.29	146.37
		KR-98B-3	96.00	241.55	17.25	6992.38	0.81	11.07	16.03	136.03
	KR-117	KR-117-1	76.00	58.82	13.87	3361.10	0.51	4.37	13.82	21.16
		KR-117-1 (dup)	36.00	54.06	14.34	3310.60	0.50	4.39	10.86	21.26
		KR-117-2	86.00	33.93	13.79	2492.50	1.15	4.36	92.11	20.58
	KR-118	KR-118-1	34.00	33.45	14.12	2555.60	0.33	7.22	14.44	20.99
		KR-118-2	92.00	12.52	14.17	1978.21	0.36	6.61	14.32	18.36
	KR-120	KR-120-1	66.00	24.34	14.12	2830.80	0.72	6.36	13.13	15.13
		KR-120-2	98.00	57.16	15.61	2222.73	0.79	6.37	14.34	13.97
	KR-122	KR-122-1	78.00	5.80	23.94	1056.80	0.76	9.90	15.51	15.15
		KR-122-2	90.00	46.36	20.62	1210.83	0.74	9.67	13.24	16.13

Company	Well Number	Sample Number	Lead (ug/l)	Strontium (ug/l)	Lead-210 (pCi/l)	Po-210 (pCi/l)	Radium-226 (pCi/l)	U-234 (pCi/l)	U-238 (pCi/l)	Activity Ratio
MOBIL	PRW-2	APRW-2-1	2.26	2.83	NA	1.48	8.52	0.36	0.13	2.68
(old AMAX)		APRW-2-2	10.04	21.86	NA	1.39	4.83	0.50	0.28	1.77
	PRW-6	APRW-6-1	8.69	6.11	NA	0.55	0.20	0.07	0.03	2.34
	PRW-9	APRW-9-1	3.24	4.34	NA	9.23	1.80	0.18	0.06	2.92
		APRW-9-2	7.66	15.39	NA	8.32	0.90	0.06	0.01	7.75
	PRW-10	APRW-10-1	1.26	6.01	NA	1.37	0.39	0.08	0.04	2.19
		APRW-10-2	4.58	6.40	NA	0.95	0.17	0.12	0.05	2.46
	TRW-17	ATRW-17-1	0.00	1.41	NA	1.53	0.32	0.11	0.03	3.83
		ATRW-17-1 (rep)	NA	NA	NA	NA	NA	NA	NA	NA
		ATRW-17-2	5.10	4.14	NA	0.98	0.22	0.16	0.04	3.61
		ATRW-17-2 (ufl)	7.06	12.46	NA	1.637	0.12	0.21	0.07	2.96
	TRW-28	ATRW-28-1	2.14	3.16	NA	7.61	0.16	0.06	0.05	1.28
		ATRW-28-2	5.96	12.43	NA	3.41	0.14	0.14	0.04	3.34
	TRW-29	ATRW-29-1	1.13	1.87	NA	4.57	0.26	0.07	0.04	1.66
		ATRW-29-2	4.58	11.58	0.40	3.65	0.15	0.03	0.02	1.24
	TRW-30	ATRW-30-1	1.26	0.00	NA	7.76	0.27	0.03	0.02	1.48
		ATRW-30-2	4.70	8.59	2.19	7.25	0.12	NA	NA	NA
W.R. GRACE	RK-01	WRG-01	0.00	0.00	NA	1.35	0.20	0.02	0.04	0.42
		WRG-01 (rep)	NA	NA	NA		NA	NA	NA	NA
	RK-02	WRG-02	0.00	1.87	NA	5.69	0.16	0.07	0.03	1.97
I.M.C.C.	KR-22	KR-22-1	3.01	4.29	NA	0.54	0.62	0.25	0.25	0.98
		KR-22-2	4.63	26.50	0.63	0.52	1.43	1.01	0.87	1.16
	KR-80	KR-80	2.89	0.00	NA	1.97	0.22	0.07	0.08	0.78
	KR-83	KR-83-1	0.00	0.30	NA	10.18	0.36	0.26	0.07	3.57
		KR-83-2	3.52	9.29	0.59	1.512	0.21	0.17	0.07	2.30
		KR-83-2BH	3.77	10.61	0.64	3.11	0.67	0.15	0.03	6.08
		KR-83-3	5.96	8.38	NA	9.36	0.38	0.18	0.05	3.89
	KR-86 (KR-18)	KR-86 (KR-18)	1.88	0.00	NA	0.41	0.26	0.06	0.05	1.08
	KR-87A	KR-87A-1	1.00	2.83	NA	0.78	0.21	0.31	0.19	1.63
		KR-87A-2	2.83	25.13	1.12	0.72	3.68	0.38	0.13	2.83
	KR-95	KR-95	0.00	1.20	NA	3.47	0.53	0.35	0.26	1.34
	KR-98B	KR-98B-1	22.47	2.35	NA	11.30	8.46	0.23	0.14	1.64
		KR-98B-2	1.47	17.08	3.27	13.54	1.41	0.21	0.13	1.56
		KR-98B-2BH	3.47	23.28	2.63	11.70	1.81	0.19	0.23	0.82
		KR-98B-3	5.51	15.75	NA	10.42	0.58	0.20	0.17	1.13
	KR-117	KR-117-1	2.14	6.72	NA	2.99	0.26	0.12	0.13	0.96
		KR-117-1 (dup)	3.93	0.94	NA	NA	NA	NA	NA	NA
		KR-117-2	1.21	3.92	0.63	1.57	0.19	0.08	0.10	0.85
	KR-118	KR-118-1	2.52	3.33	NA	2.44	1.12	0.58	0.40	1.44
		KR-118-2	2.02	12.17	0.43	1.52	0.31	0.32	0.26	1.22
	KR-120	KR-120-1	3.60	0.30	NA	0.69	1.39	0.32	0.33	0.98
		KR-120-2	0.69	121.59	1.19	0.62	4.82	0.20	0.16	1.26
	KR-122	KR-122-1	2.26	1.70	NA	2.06	1.20	0.82	0.91	0.90
		KR-122-2	3.64	13.43	0.95	1.28	0.08	0.87	0.81	1.07

Company	Well Number	Sample Number	Gross-Alpha (pCi/l)
MOBIL (old AMAX)	PRW-2	APRW-2-1	14.49
		APRW-2-2	16.14
	PRW-6	APRW-6-1	5.26
	PRW-9	APRW-9-1	9.61
		APRW-9-2	11.26
	PRW-10	APRW-10-1	2.10
		APRW-10-2	3.75
	TRW-17	ATRW-17-1	5.61
		ATRW-17-1 (rep)	NA
		ATRW-17-2	7.26
		ATRW-17-2 (ufl)	NA
	TRW-28	ATRW-28-1	2.48
		ATRW-28-2	4.13
	TRW-29	ATRW-29-1	5.36
		ATRW-29-2	7.01
	TRW-30	ATRW-30-1	6.76
		ATRW-30-2	6.76
W.R. GRACE	RK-01	WRG-01	3.60
		WRG-01 (rep)	NA
	RK-02	WRG-02	0.85
I.M.C.C.	KR-22	KR-22-1	3.35
		KR-22-2	11.51
	KR-80	KR-80	3.85
	KR-83	KR-83-1	3.97
		KR-83-2	5.44
		KR-83-2BH	8.41
		KR-83-3	3.00
	KR-86 (KR-18)	KR-86 (KR-18)	9.61
	KR-87A	KR-87A-1	2.67
		KR-87A-2	8.63
	KR-95	KR-95	18.62
	KR-98B	KR-98B-1	6.98
		KR-98B-2	39.04
		KR-98B-2BH	34.91
		KR-98B-3	13.26
	KR-117	KR-117-1	11.71
		KR-117-1 (dup)	NA
		KR-117-2	6.26
	KR-118	KR-118-1	4.07
		KR-118-2	6.51
	KR-120	KR-120-1	5.71
		KR-120-2	4.51
	KR-122	KR-122-1	2.10
		KR-122-2	3.75

Company	Well Number	Sample Number	Date Sampled	Approx. Sample Depth (ft. BLS)	Temp-erature (deg. C)	Cond-uctivity (umhos/cm)	pH	Redox Potent. (mv)	Dissol. Oxygen (mg/l)	Alkalinity (mg/l as CaCO3)
	KR-127	KR-127-1	12-15-86	102	23.50	275.00	5.98	-87.70	1.65	122.39
		KR-127-2	02-11-87	81	23.40	278.00	5.94	-85.60	2.40	120.41
		KR-127-3	02-17-87	81	23.40	271.00	5.86	-73.30	1.22	122.80
		KR-127-3BH	02-18-87	200	23.20	278.00	6.03	-40.80	2.95	127.22
		KR-127-4	08-18-87	96	23.40	262.00	5.67	-21.60	2.90	98.17
		KR-127-4BH	08-19-87	200	23.30	259.00	5.85	-54.20	3.38	104.24
		KR-127-5	11-20-87	140	24.00	266.00	5.32	-150.20	2.10	100.74
	KR-135	KR-135-1	10-09-86	87	24.40	248.00	6.33	NA	1.45	141.43
		KR-135-2	06-12-87	80	24.00	319.00	6.22	6.66	5.10	157.73
	NR-2	NR-2-1	11-11-87	148	23.00	27.00	4.42	79.80	3.95	0.00
	NR-3	NR-3-1	08-05-87	45	23.00	171.00	4.03	76.00	5.40	0.00
		NR-3-2	10-24-87	80	22.80	216.00	3.86	17.80	2.00	0.00
	NR-4	NR-4-1	11-11-87	90	23.00	137.00	3.96	296.50	3.35	0.00
	NR-5	NR-5-1	11-11-87	115	21.20	192.00	3.74	380.40	3.40	0.00
	NR-6	NR-6-1	10-24-87	158	26.20	67.00	5.80	89.50	6.05	27.58
	NR-7	NR-7-1	10-24-87	162	25.30	40.00	4.99	-95.90	2.50	11.40
	NR-8	NR-8-1	11-12-87	168	21.40	41.00	4.10	48.60	3.10	0.00
	NR-9	NR-9-1	11-12-87	168	23.20	63.00	5.01	164.20	2.90	23.90
MEAN				83.81	22.79	193.37	5.13	23.65	3.37	39.36
STD. DEV.				49.97	5.23	168.79	1.31	94.86	1.93	42.90
MINIMUM				0.00	0.00	0.00	0.00	-158.10	0.00	0.00
MAXIMUM				200.00	27.60	830.00	6.33	380.40	9.00	157.73

Company	Well Number	Sample Number	Chloride (mg/l)	Fluoride (mg/l)	Bicar-bonate (mg/l)	Ortho-phosphate (mg/l)	Silica (mg/l)	Sulfate (mg/l)	Total Organic Carbon (mg/l C)	Total Dissolved Solids (mg/l)
	KR-127	KR-127-1	11.40	0.54	149.22	1.09	6.59	7.15	12.90	274.00
		KR-127-2	10.60	0.51	146.81	1.20	6.20	28.20	19.65	274.00
		KR-127-3	12.90	0.55	149.72	1.07	4.92	20.50	12.20	176.00
		KR-127-3BH	9.55	0.54	155.11	1.09	6.74	39.30	14.05	268.00
		KR-127-4	10.49	0.45	119.69	0.92	3.30	71.00	12.24	330.00
		KR-127-4BH	10.73	0.43	127.09	0.86	3.30	78.30	12.81	278.00
		KR-127-5	10.00	0.43	122.83	0.80	1.80	32.00	13.52	64.00
	KR-135	KR-135-1	1.92	2.07	172.43	0.67	7.45	4.04	4.40	148.00
		KR-135-2	10.42	1.95	192.31	0.42	6.35	21.45	11.24	268.00
	NR-2	NR-2-1	3.62	0.05	0.00	1.08	5.04	2.15	3.02	208.00
	NR-3	NR-3-1	5.77	0.15	0.00	0.09	4.48	48.50	5.33	214.00
		NR-3-2	6.08	0.26	0.00	0.17	5.35	107.90	5.90	348.00
	NR-4	NR-4-1	4.23	0.11	0.00	0.15	5.35	58.75	2.96	58.00
	NR-5	NR-5-1	6.16	0.13	0.00	0.01	5.80	75.00	2.99	11.00
	NR-6	NR-6-1	3.75	0.17	33.62	0.07	10.07	2.14	2.97	2.00
	NR-7	NR-7-1	4.16	0.10	13.90	0.48	6.75	4.50	4.90	272.00
	NR-8	NR-8-1	5.22	0.21	0.00	2.48	5.80	0.00	9.29	280.00
	NR-9	NR-9-1	3.82	0.10	29.14	0.47	11.40	0.00	5.44	2.00
MEAN			10.44	0.47	47.98	1.88	5.92	45.21	6.42	174.65
STD. DEV.			7.88	0.41	52.31	1.69	3.18	67.67	3.73	128.09
MINIMUM			0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
MAXIMUM			41.28	2.07	192.31	6.94	14.10	336.00	19.65	480.00

Company	Well Number	Sample Number	Volatile Dissolved Solids (mg/l)	Aluminum (ug/l)	Calcium (mg/l)	Iron (ug/l)	Potassium (mg/l)	Magnesium (mg/l)	Manganese (ug/l)	Sodium (mg/l)
	KR-127	KR-127-1	66.00	34.23	25.13	796.70	1.12	14.32	7.83	21.29
		KR-127-2	94.00	35.76	25.66	857.35	2.72	14.53	10.64	20.58
		KR-127-3	70.00	18.80	24.80	721.00	1.13	14.17	10.69	20.70
		KR-127-3BH	216.00	55.27	25.35	911.60	1.63	14.90	11.39	20.30
		KR-127-4	166.00	0.00	26.32	1040.94	1.04	16.45	12.84	19.10
		KR-127-4BH	48.00	0.00	29.95	889.54	1.25	16.84	15.15	19.47
		KR-127-5	56.00	0.00	21.58	513.74	1.09	16.07	13.40	18.39
	KR-135	KR-135-1	40.00	11.20	25.05	1870.00	0.49	19.07	21.70	17.74
		KR-135-2	52.00	21.56	23.59	1327.44	0.91	16.67	24.64	17.01
	NR-2	NR-2-1	106.00	63.45	0.61	270.50	0.14	0.56	0.55	2.87
	NR-3	NR-3-1	62.00	5143.53	8.80	4915.07	0.41	4.13	5.45	13.32
		NR-3-2	108.00	8542.31	10.00	4063.29	0.34	5.18	6.64	13.92
	NR-4	NR-4-1	56.00	1909.69	14.24	788.45	0.32	2.70	16.70	3.04
	NR-5	NR-5-1	1.00	1647.77	17.60	3607.70	0.29	4.76	23.68	3.59
	NR-6	NR-6-1	1.00	0.00	6.12	303.58	0.34	2.89	2.51	3.07
	NR-7	NR-7-1	52.00	0.00	2.66	1266.78	0.20	1.31	1.10	2.43
	NR-8	NR-8-1	102.00	500.13	1.85	203.63	0.56	0.91	1.07	2.89
	NR-9	NR-9-1	0.00	71.38	6.02	96.51	0.40	3.00	3.52	2.12
MEAN			62.94	412.80	13.62	1565.91	0.55	6.72	12.07	19.59
STD. DEV.			49.76	1283.25	8.36	1814.34	0.46	5.02	15.30	31.74
MINIMUM			0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
MAXIMUM			216.00	8542.31	31.60	7577.30	2.72	19.07	92.11	147.12

Company	Well Number	Sample Number	Lead (ug/l)	Strontium (ug/l)	Lead-210 (pCi/l)	Po-210 (pCi/l)	Radium-226 (pCi/l)	U-234 (pCi/l)	U-238 (pCi/l)	Activity Ratio
	KR-127	KR-127-1	2.01	8.18	NA	0.53	4.83	0.24	0.15	1.63
		KR-127-2	2.14	7.93	NA	0.50	4.87	0.15	0.12	1.25
		KR-127-3	1.38	6.72	NA	0.50	5.46	0.15	0.12	1.25
		KR-127-3BH	1.70	6.26	0.19	1.51	5.90	0.31	0.20	1.52
		KR-127-4	6.04	46.93	1.03	1.68	0.56	0.36	0.16	2.25
		KR-127-4BH	3.89	41.09	2.14	1.23	1.12	0.30	0.19	1.59
		KR-127-5	11.30	28.04	NA	0.71	0.49	0.32	0.14	2.34
	KR-135	KR-135-1	0.00	7.20	NA	2.50	0.17	0.20	0.14	1.44
		KR-135-2	1.21	20.79	1.06	1.57	0.53	0.12	0.19	0.64
	NR-2	NR-2-1	10.09	4.50	NA	2.32	0.28	0.12	0.04	2.93
	NR-3	NR-3-1	4.34	11.56	NA	11.22	1.27	0.10	0.09	1.13
		NR-3-2	8.54	20.26	2.52	8.23	1.51	0.08	0.03	2.86
	NR-4	NR-4-1	10.06	19.20	NA	0.64	0.21	0.25	0.12	2.08
	NR-5	NR-5-1	11.00	5.49	NA	0.40	0.13	0.39	0.13	3.14
	NR-6	NR-6-1	9.80	7.46	NA	1.52	0.22	0.03	0.03	1.23
	NR-7	NR-7-1	10.21	6.57	NA	31.07	0.15	0.05	0.02	3.47
	NR-8	NR-8-1	6.87	5.71	NA	11.00	0.14	0.21	0.07	3.03
	NR-9	NR-9-1	11.82	7.96	NA	1.47	0.19	0.12	0.05	2.28
MEAN			4.30	11.18	0.34	3.91	1.24	0.21	0.14	1.87
STD. DEV.			4.04	17.08	0.73	5.11	1.99	0.20	0.18	1.37
MINIMUM			0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
MAXIMUM			22.47	121.59	3.27	31.07	8.52	1.01	0.91	7.75

Company	Well Number	Sample Number	Gross-Alpha (pCi/l)
	KR-127	KR-127-1	5.61
		KR-127-2	NA
		KR-127-3	3.55
		KR-127-3BH	21.02
		KR-127-4	18.02
		KR-127-4BH	32.28
		KR-127-5	10.89
	KR-135	KR-135-1	6.23
		KR-135-2	13.14
	NR-2	NR-2-1	3.00
	NR-3	NR-3-1	21.77
		NR-3-2	7.51
	NR-4	NR-4-1	10.51
	NR-5	NR-5-1	8.76
	NR-6	NR-6-1	4.25
	NR-7	NR-7-1	11.26
	NR-8	NR-8-1	8.45
	NR-9	NR-9-1	3.50
MEAN			8.39
STD. DEV.			7.91
MINIMUM			0.00
MAXIMUM			39.04