

SOURCE OF GROSS-ALPHA RADIOACTIVITY ANOMALIES IN RECHARGE WELLS, CENTRAL FLORIDA PHOSPHATE DISTRICT



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IN RECHARGE WELLS, CENTRAL FLORIDA PHOSPHATE DISTRICT

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PERSPECTIVE

Gordon D. Nifong, Ph.D.
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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.

The state requires the monitoring of the quality of water recharging the Floridan aquifer; indeed that water is expected to conform to public drinking water standards. Recent monitoring of radiation parameters in recharge wells has cast doubt on the safety of the wells. State and federal regulations on radionuclides in potable water permit a maximum contaminant level of fifteen picocuries of gross (or total) alpha activity per liter of water (pCi/l), and a limit of five pCi/l of total radium. Past sampling has shown that, while most recharge wells conform to the radium standard, gross alpha radiation frequently exceeds standards. A high gross alpha level that could not be accounted for by the decay of radium has become known as the "gross alpha anomaly." This situation has resulted in a severe curtailment of the use of the recharge wells, much to the detriment of both the phosphate industry and the citizens of central Florida. This present study, conducted by Dr. S.B. Upchurch of the University of South Florida, working with the Southwest Florida Water Management District, had two goals:

- (1) To determine the radionuclide(s), if any, responsible for the gross alpha anomaly, and
- (2) To determine any effects methods of sampling and analysis had on the obtained results.

This work by Dr. Upchurch and his associates indicates that, of the decay products of uranium-238, polonium-210 is present in greatest quantities and most likely is the principle cause of the gross alpha anomaly. Apparently there is a build-up of radon in water during alpha decay, caused by recoil of the element from substrate to water. This results in an increase of water-borne radon decay products, including

polonium. Furthermore, measurements of polonium and of gross alpha are very sensitive to sampling procedures, sample preparation and analytical techniques. Both time of sample filtration and length of storage of the sample prior to analysis seem to affect polonium recovery. Also, the investigators found that sample fixation by acidification, and its timing, affected polonium recovery, and they suggest possible preservation with ammonium hydroxide. Dr. Upchurch points out that the current ASTM standard method for gross alpha includes several steps that render the method questionable for accurate polonium recovery, and he recommends several modifications in both collection and analysis. He concludes that polonium is very much sorbed on rock or soil surfaces in the well; and hence there appears to be little problem with transport of the element into the Floridan aquifer.

Dr. Upchurch's work suggests a need for further investigation of several topics, especially the stability of uranium and its daughters in Florida's waters. More information is needed on possible transformation that polonium might undergo in recharge wells. Finally, since polonium appears to be the major contributor of total alpha activity in many waters, the standard method for gross alpha should be critically received in the light of maximizing polonium recovery.

It bears repeating that use of recharge wells would be a very important procedure to add needed water to the Floridan aquifer for the eventual benefit of all, and provide a reasonable way for industry to dispose of unwanted surficial water. This cannot be done, however, at the expense of polluting the aquifer. Hopefully, this and future related research will provide the information that will allow such wells to be safely used.

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This study was first proposed by Ken Weber of the Southwest Florida Water Management District because of the need for standardization of radiological methods for evaluating recharge wells and of the problem of gross-alpha radiation that is unsupported by radium activities in recharge wells. We appreciate Ken's continued interest and support throughout the study.

The study was funded by a grant through the Southwest Florida Water Management District from the Florida Institute of Phosphate Research. We appreciate the Institute's support, especially in allowing us to change the scope of work of the project when we discovered the problems of polonium variability in recharge wells.

The International Minerals and Chemical Corporation allowed us access to their Kingsford property, provided us with background data, and drilled at their own expense four monitor wells and two cores at the recharge well we finally opted to study. Jay Allen and Jerry Tanner of IMCC were especially helpful in expediting these projects and providing us with industry viewpoints with respect to the recharge wells.

In order to complete this project we had to develop or modify several analytical procedures for which no standard methods exist. We want to express our deep gratitude to the researchers who have developed the commonly-accepted methods and whose work constitutes the pioneer efforts in radiation chemistry in natural waters. Dr. Willard Moore and Dr. Jacqueline Michel of the University of South Carolina were most patient with our questions and shared with us many of the "little tricks" that aren't in the literature. Dr. Claude Sill of EG&G IDAHO steered us through problems with polonium analysis. Dr. James Cowart of Florida State University offered considerable advice, drawing from his experience with analysis of Florida waters.

The Florida Department of Environmental Regulation furnished its well logger and provided geophysical logs of the recharge well and monitor wells.

Finally, we thank the seven companies and their staffs that participated in the study. These companies (International Minerals and Chemical, Gardinier, Mobil Chemical, Estech, Brewster Phosphate, W.R. Grace and AMAX) provided the most valuable information of the study.

CONCLUSIONS AND RECOMMENDATIONS

The central Florida phosphate industry utilizes recharge wells to mitigate withdrawals of water from the Floridan aquifer and to dewater the surficial aquifer prior to mining. From a water management point of view, these wells are efficient and serve a vital function. Recent monitoring of the radiation environment in these wells, however, casts doubts on the safety of the wells. While most of the wells conform to state and federal standards for radium, gross-alpha radiation frequently exceeds standards.

The purpose of this study was to determine the radionuclide(s) responsible for the high gross-alpha radiation and to identify a method for sampling of the recharge wells that would standardize data across the phosphate district. We found that there is, indeed, a radionuclide that causes the gross-alpha radiation to exceed standards and that sampling techniques, sample-preparation methods, and laboratory procedures grossly affect the results. This report constitutes our findings.

Conclusions

The gross-alpha anomaly, in the well studied, is primarily due to polonium-210. Polonium is present in activities greater than predicted by radium-226 activities because of alpha recoil of radon-222 from soil or rock grain surfaces into ground water and failure of the radon decay products, including polonium-210, to be completely sorbed on pore walls.

Polonium-210 and gross-alpha radioactivity measurements are extremely sensitive to sampling procedures, sample preparation techniques, and analytical procedures. Most thief-type samplers seem to secure adequate samples. Polonium decreases with depth in recharge wells, so sample depth influences the gross-alpha and polonium activities reported.

Clays (including silicates and ferric hydroxides), particulate organics, and dissolved organics can interfere with gross-alpha radioactivity measurements. Clays and particulate organics can sorb polonium and reduce the reported gross-alpha activity. Oxidation of organics can reduce the Eh of the water sample and produce volatile, divalent polonium compounds, which also reduce the gross-alpha activity. Time of filtration and length of storage of the sample before preparation for analysis affects polonium recovery. While gross-alpha analysis may detect refractory polonium, risks of loss exist.

The methods of radiation analysis and monitoring presently used by the phosphate industry introduce variability and reduce ability to detect, compare, and manage water-quality in the industry's recharge well system. A standard method is needed to remedy this problem. The recommended method is summarized below.

A high degree of sorption of, polonium on solids in the aquifer can be demonstrated. Therefore, there is little reason at this time for alarm that gross-alpha radiation exceeds the drinking-water quality standard of

15 pCi/l in some wells from time-to-time. Additional research, however, is needed to identify and evaluate the impact on aquifer use and human health of radionuclide-related reactions in the aquifer systems.

Recommendations

Based on this study, we recommend the following as a means of standardizing monitoring procedures on recharge wells. Note that the recommendation for fixation of the sample with acid, which follows standard methods now in effect, is an INTERIM recommendation. We plan to continue to evaluate the effects of different fixatives on polonium and gross-alpha radiation analyses and, if justified, make recommendations for changes in standard procedures to the American Society of Testing and Materials.

The recommended procedures are:

1. Samples should be collected with a closed, thief-type sampler.
2. Samples should be collected from the same horizon in all recharge wells. It is recommended that this horizon be either (a) just below standing water in the well or (b) at the bottom of the well casing where recharge water first comes in contact with the host aquifer rock,
3. Samples should be filtered immediately upon collection with a 0.45 micron filter.
4. Samples should be stored in plastic containers at all times.
5. Immediate fixation of the sample to prevent loss of polonium is necessary. If gross-alpha analysis is to be undertaken, sufficient nitric acid should be used to oxidize all soluble organics and minimize volatilization of polonium. If polonium is to be analyzed, we recommend an interim procedure of fixation with nitric acid as above to agree with standard methods now in use. However, immediate fixation with ammonium hydroxide increases our recovery of polonium.
6. The sample should be rushed to the analytical laboratory and placed in the queue for prompt analysis. Blind standards and replicate samples should be included frequently to insure quality control in the laboratory.

INTRODUCTION

Background

The Florida Public Drinking Water Systems Code (Chapter 17-22) sets the maximum gross-alpha radiation levels at 15 pCi/l (picocuries per liter) and radium (radium-226 plus radium-228) at 5 pCi/l. Section 17-22.104(1)(e) defines these maximum contaminant levels as follows:

- a. Radium is defined as radium-226, a daughter of uranium-238, plus radium-228, a daughter of thorium-232; and
- b. Gross-alpha radiation is defined as gross-alpha particle activity, including radium-226, but excluding radon and uranium.

Section 17-22.105(1)(e) sets the monitoring procedure. The annual compliance criteria shall be based on an annual composite of four, consecutive, quarterly samples or the average of analyses of four samples collected at quarterly intervals. A gross-alpha analysis can be substituted for the radium analysis provided that the gross-alpha activity does not exceed 5 pCi/l at a confidence level of 95%. If the gross-alpha activity exceeds 5 pCi/l, a radium-226 analysis is required. If the radium-226 activity exceeds 3 pCi/l, radium-228 analysis is required. In any condition where radium-228 is known to be present or can be expected to be present in drinking water, radium-226 and/or radium-228 will be analyzed if the gross-alpha radioactivity exceeds 2 pCi/l. The inherent assumption in these criteria is that radium is the important radionuclide in gross-alpha radioactivity.

Phosphate Industry Use of Recharge Wells

The Florida phosphate industry utilizes considerable amounts of water in mining and beneficiation of phosphate ore. As a means of mitigating water withdrawals from the Floridan aquifer, the industry has utilized recharge wells for well over a decade. These wells are screened through an interval in the surficial, quartz sand aquifer and drain that aquifer into the upper Floridan. By removing water from the surficial aquifer and transferring it into the Floridan, several benefits are derived. These include reduction in the impact of withdrawals on the Floridan aquifer and partial dewatering of land to be mined.

Recharge-well design includes intentional isolation of the phosphatic ore, which is known to contain uranium and its daughters, by casing out the Bone Valley and upper Hawthorn Formations. Regulatory agencies, including the Southwest Florida Water Management District, require monitoring of the quality of water recharging the Floridan in

these wells. Water being transported to the Floridan is expected to conform to Public Drinking Water standards. A chronic problem that has been detected in this monitoring program is the failure of water samples to meet gross-alpha radiation standards.

Problem Statement

Samples from many of the recharge wells in the phosphate district have been found to exceed the 15 pCi/l criterion for gross-alpha radiation. In many cases these samples are found to be within standards for radium and, thus, there appears to be alpha radiation that is not supported by decay of radium. The large difference between the radium and gross-alpha activities has become known as the "gross-alpha anomaly". In addition, it was found, after considerable sampling experience, that the radiation analyses show considerable variation from well to well and within a single well through time. The gross-alpha anomaly varies, therefore, spatially and with time.

Purpose of This Study

This study was funded by a grant from the Florida Institute of Phosphate Research (FIPR), through the Southwest Florida Water Management District (SWFWMD), to undertake the following tasks relative to the gross-alpha anomaly:

- a. Determine the radionuclide(s) responsible for the gross-alpha anomaly; and
- b. Determine the effects, if any, of sampling methodology and sample treatment on the reported analyses.

This report constitutes our findings relative to these two tasks.

PREVIOUS WORK

General Radiation Studies

It has been known for many years that the phosphate minerals of the Central Florida Phosphate District contain uranium and uranium daughters. There have been three episodes of research on uranium and its daughters in the District.

Initial studies in the 1950's of radionuclides in the District were directed to uranium as a resource. It was found that the phosphate minerals of the District contain uranium and its daughters (Altschuler et al., 1958.) It was also discovered that the uranium was conserved during weathering and concentrated in the weathering profile (the "leached zone") (Altschuler et al., 1956). There were many studies that dealt with the distribution of uranium as a resource (e.g., Cathcart, 1956, 1963, 1966). Uranium was recovered from phosphoric acid product during this period.

The second episode of interest was in part economically and in part environmentally motivated. During the late 1960's and early to middle 70's, there was a renewed interest in uranium recovery and a growing concern for environmental quality and radiation-health safety.

Several important studies dealt with the radionuclides in phosphatic ores, products, and wastes. Examples of these studies include Roessler, Smith, et al. (1979) and Roessler, Kautz, et al. (1980). The former describes the partitioning of radionuclides during chemical processing of phosphatic ores, the latter discusses the fate of radionuclides during mining and reclamation. Guimond (1977) discussed the radiation retained in phosphatic fertilizers and Guimond and Windham (1975) discussed the distributions of uranium, thorium, and daughters in ore, wastes, and products. Of importance to this study is the fact that these studies point out that uranium-238, the progenitor of radium-226, radon-222, and polonium-210, constitutes 99.3% (by mass) of the uranium present in the District. The remaining 0.7% is uranium-235. Thorium-232, the ancestor of radium-228, has an activity that is nearly two orders of magnitude less than that of uranium in the host rock. Thus, one can assume that, on the average, uranium-238 and its daughters constitute the primary sources of radiation in the District.

Environmental studies of importance with respect to ground water began at the same time. Several phosphate companies entered into new enterprises that required that major environmental impact studies be undertaken. Radiation analyses were required as part of these studies. Owing to pressures from the environmental movement, an area-wide study of the effect of the phosphate industry on the environment was also undertaken. A part of that study was an evaluation of radiation hazards (Texas Instruments, Inc., 1977). A major study by Kaufmann and Bliss (1977) investigated the impact of phosphate mining and mineralization on ground water. They concluded that most of the radium-226 found in central

Florida ground water is natural and not a result of industry activities. Radiation monitoring in ground water continues.

From the mid-1970's to the present, radiation studies have included a third emphasis -- studies of the causes of radiation in rock and water and mechanisms of radionuclide transport. Osmond and Cowart (1977); Cowart et al. (1978), and Osmond et al. (1983) have used uranium isotopic ratios to determine the origins of Floridan aquifer ground water. Humphreys (1984) and Osmond and Cowart (in press) discuss the migration of uranium and its daughters in the phosphate district, including recharge wells. Upchurch et al. (1981) studied the distribution of radium-226 in surface waters and biota in unmineralized, mineralized, mined, and reclaimed lands.

Radiation in Recharge Wells

There have been several radiation studies that dealt with recharge wells in particular. Upchurch et al. (1979a,b) undertook one of the first studies that allows evaluation of the effects of recharge wells on ground-water chemistry. They studied water from the surface, surficial aquifer, "Hawthorn-Bone Valley aquifer", and Floridan aquifer at the International Minerals and Chemical Corporation's (IMCC) Kingsford Mine. This is the same mine used in the present study and the well studied intensively in this study was included in the 1979 study. Their study included water from the top and from near the bottom of the recharge wells. They concluded that water in the recharge wells chemically reflects the surficial aquifer and that radium-226 in the recharge wells was within standards. They found no indication of contamination of the Floridan aquifer by radium-226 as a result of the recharge wells.

Kimrey and Fayard (1984) included 12 out of 140 recharge wells identified in the District in the early 1980's in their state-wide study of drainage wells. They found that:

- a. Turbidity exceeded standards in 10 samples, including 2 from one well;
- b. Total iron exceeded standards for 11 of the 12 wells;
- c. Six of the 12 wells exceeded gross-alpha radiation standards and one sample was within 0.2 pCi/l of the standard.

As mentioned earlier, Humphreys (1984) and Osmond and Cowart (in press) included recharge wells in their larger study. They concluded that, while mining disrupts uranium isotopic distributions and may be increasing the uranium concentrations in the surficial aquifer, there is little indication that mining has much effect on alpha activity in the aquifer system.

The Polk County Health Department, Office of Radiation Control (1983) conducted a study of the radiation in 71 recharge wells. They used a variety of sampling techniques and modified generally-accepted techniques for radium-226, radium-228, and gross-alpha activity analyses. They found the following:

- a. 46 wells (65%) were within the 5 pCi/l limit for radium;
- b. 54 wells (76%) contained less than 1 pCi/l radium-228 and 99% (70 out of 71 wells) had less than 5 pCi/l;
- c. 35 wells (49%) had less than the 15 pCi/l limit for gross-alpha activity;
- d. There is a crude positive correlation between radium-226 and -228, with radium-226 activities normally at least 10 times -228 activities;
- e. There is (1) a fair positive correlation of gross-alpha radiation and (2) a good positive relationship of radium-226 with turbidity;
- f. There seems to be no correlation of gross-alpha or radium-226 activities with sample depth; and
- g. Inconsistencies in sampling vessels weakened comparisons between samples.

This is an important study because it gives credence to the concept that many recharge wells are in violation of drinking-water standards. It also indicates the need for a study in which sampling and analytical techniques are closely standardized.

Numerous other reports, including in-house studies by the phosphate industry and monitoring reports, exist. These consistently reflect the gross-alpha anomaly and indicate the need for standardized methodology in order to compare the results.

Because of the Polk County study and a contemporary study by King (1983), which showed that several water supplies in areas underlain by phosphatic terrane failed to meet radium standards, the Florida Department of Environmental Regulation was caused to order owners of cited wells to file for permits to operate those wells as Class V wells (Tschnikel, 1983). Pressure to abandon the wells has increased and many of the companies are removing or temporarily closing existing wells and few applications for permits to install new wells were received at SWFWMD in 1984.

METHODS

General Plan of Study

The initial methodology proposed was to have been a two-stage study. Task I was to take a single well and have the several companies sample it in order to hold regional variability constant and compare sampling methods. We then proposed (Task II) to make a regional study, holding the sampling method constant.

As the study progressed, we discovered that Task II was beyond the scope of the contract and that additional effort was required to characterize the behavior of the well singled out for Task I. With the concurrence of FIPR, the project was altered.

The first order of business was selection of the recharge well to be used for Task I, in which all of the companies would be invited to compare techniques. A meeting was held at the FIPR offices in Bartow on October 6, 1983. All mining companies, analytical laboratories, and regulatory agencies were invited to participate. At that meeting we explained our approach, solicited comments and criticisms, and asked for participation from each. The discussion centered around the cause of the gross-alpha anomalies and there seemed to be a consensus that sample collection, especially incorporation of particulates, was a major cause. At that meeting IMCC offered use of a recharge well that had a known history of gross-alpha anomalies and also offered to drill monitor wells so that undisturbed samples could be obtained. Seven companies agreed to participate.

A well was selected in cooperation with IMCC and the company initiated installation of the monitor wells. A complete description of the recharge well and monitor wells is included below. After installation, the Florida Department of Environmental Regulation's well logger provided geophysical logs of each.

We then began to sample and analyze the recharge and monitor wells in order to "fine tune" our techniques. We completed several experiments prior to the group sampling. In order to optimize the sample-handling procedure, we tested to determine the effects of samplers, the variation of radiation with depth, and the effects of filtering and sample preservation techniques.

Upon completion of the "fine-tuning" process, the sampling event in which all companies were invited to participate was scheduled. The seven companies that participated and the dates of their sampling are given in Table 1. We sampled at a fixed depth and with a standard sampler before and at the end of each day's sampling. The companies sampled the well according to their own practices. Their samples were split. Half was sent to a commercial laboratory that normally does their radiation work. The other half was analyzed by us using standardized procedures described in the following sections.

Table 1. - Companies participating in the group sampling exercise.

Company	Date of Sampling
AMAX Corp.	July 9, 1984
International Minerals and Chemicals.....	July 13, 1984
Gardiner, Inc.	July 16, 1984
Mobil Chemical Corp.	July 16, 1984
Estech, Inc.	July 16, 1984
Brewster Phosphate	July 20, 1984
W.R. Grace	July 20, 1984

Laboratory Equipment

The laboratory hardware used by us includes alpha- and gamma-detection systems linked to a Tracor Northern 1710 Multichannel Analyzer with a multiplexer/router for multiple acquisitions. An internal LSI-11-based computer is used for spectrum analysis. The alpha-detection system consists of two Tennelec TC-256 alpha spectrometers, each with low background, cleanable, 400 mm² surface-barrier detectors. The gamma-detection system consists of an EG&G Ortec high-purity, germanium semiconductor detector with low-background shield. The software developed for spectral analysis is described in Appendix A.

Chemical Procedures

Alpha spectroscopy is capable of directly identifying individual alpha emitters only under a restricted set of circumstances. In particular, the short range of alpha particles necessitates the use of chemical techniques to separate the alpha emitter from the bulk material of the sample. The chief aim of this separation process is to reduce the sample mass to the microgram range without significant loss of the alpha emitters under investigation.

In the search for a radioactive anomaly, a simple radionuclide budget was compiled by analysis of several of the relatively long-lived, suspect isotopes (Appendix B). The radionuclides chosen for analysis were the uranium isotopes, radium and thorium isotopes, and polonium-210. For a detailed discussion of the chemical techniques used see Appendix C.

Preconcentration and Purification of Uranium

Uranium is concentrated by coprecipitation with ferric hydroxide. The uranium is separated from thorium and radium isotopes by anion exchange and then scavenged by theonyltrifluoroacetone (TTA) in the presence of benzene. The benzene solution is then evaporated on a stainless-steel planchet for counting. This procedure is similar to that used by Cowart and Osmond (1980). Uranium-232 is used as an internal standard and allows evaluation of the efficiency of the recovery technique.

Separation of Polonium-210

Polonium is coprecipitated with ferric hydroxide in the same way as the uranium isotopes. After resolubilization, it is allowed to plate out on a polished silver disk for about 3 hrs at 85° C (Flynn, 1968). The silver disk is then counted by alpha spectroscopy. Polonium-209 is used as an internal standard.

Radium and Thorium Isotopes

Radium and thorium isotopes are quantitatively scavenged from ground-water samples by passing the water through manganese-impregnated acrylic fibers following the method of Moore (1975). The fiber is then ashed and packaged for analysis by gamma spectroscopy.

Field Methods

Field methods are not standardized and were a major object of this study. The methods investigated, including methods commonly in use by the phosphate industry, and our recommended procedures are given in the following sections.

In order to sample the wells, two different samplers were used. To sample the cascading water at the top of the well, an open bailer was used. The bailer is constructed of 4 in. PVC. To sample standing water below the potentiometric surface of the Floridan aquifer, a 4 in. PVC sampler with stoppers was constructed that could be closed to receive water from a specific depth. Appendix D gives the details of construction of both samplers.

After conducting tests to determine the variation in radioactivity with depth, it was decided that a standard depth of sampling of 75 ft. would be used. This is just below the standing water level and, while mixing is minimal at this depth, it is in the zone of initial mixing with Floridan water. By selecting this depth, we avoid problems with capturing water that has entered the screens at different horizons.

Field filtration is also extremely important. The final apparatus used is described in Appendix D. It consists of a plexiglass cylinder with a micropore filter. Positive pressure forces water through the filter at high volume and allows efficient micropore filtration in the field. Unless otherwise noted, filtration was on a 0.45 micron filter.

REGIONAL HYDROGEOLOGY

The Kingsford Mine area is characterized by three hydrostratigraphic horizons: (1) the surficial aquifer, (2) a complex of locally-confined aquifers and semipermeable layers of the "Hawthorn-Bone Valley" aquifer system and confining beds, and (3) the Floridan aquifer.

Surficial Aquifer

The surficial aquifer consists of clean quartz sand to clayey sand of eolian and marine origins. The age of the horizon varies from Plio-Pleistocene to Recent. Organic and ferruginous pans are locally present. Near the base of the aquifer phosphate grains may be reworked from the underlying Bone Valley Formation. The surficial aquifer at the study site is 47 ft. in thickness.

The sand 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.

At the study site, an extremely wet, non-cohesive layer was observed from 19 to 39 ft. below land surface. This horizon coincides with the slotted interval in the recharge well (see below) and constitutes the primary flow zone in the surficial aquifer at the study site.

Upchurch et al. (1979) collected water samples from wells in the surficial aquifer at the Kingsford Mine. Table 2 lists the mean chemical properties of the surficial aquifer in the study area. These data are for the entire Kingsford Mine, so they include samples from near the New Wales chemical plant, from unmined lands, from reclaimed lands, and from other land uses. Note that, in general, surficial aquifer waters are slightly 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. The chemical data from the study well, KR-98B (Table 3), are from waters that are cascading down the recharge well. These data reflect the surficial aquifer chemistry with the exception that equilibration with the atmosphere has modified pH, redox potential, iron valence, and other properties to some degree.

There are few good data on reduction/oxidation potentials in the surficial aquifer, yet the recharge wells are greatly affected by changes in the redox potential. LaMoreaux and Associates (1978) did a study on the behavior of soluble iron in recharge wells at Borden's Big Four Mine. The study was prompted because of problems common to recharge wells throughout the industry. Recharge wells suffer from clogging, which limits the flow of water out of the surficial aquifer. The clogging is caused by formation of iron oxyhydroxides and microbial populations on

Table 2. - Summary of mean chemical conditions at the Kingsford Mine by hydrostratigraphic horizon. Data are from Upchurch et al. (1979a,b).

	Horizon		
	Surficial Aquifer *	Hawthorn- Bone Valley System *	Floridan Aquifer
pH	7.2	7.8	7.6
Specific Conductivity (umhos/cm)	243.	258.	451.
Sulfate (mg/l)	5.3	7.3	97.6
Phosphate (mg/l)	.2	0.2	0.2
Fluoride (mg/l)	.04	.07	.06
Potassium (mg/l)	.7	.9	1.2
Sodium (mg/l)	6.7	13.8	8.3
Magnesium (mg/l)	13.5	12.6	17.3
Calcium (mg/l)	23.9	33.3	53.5
Radium-226	1.9	3.7	2.8

*Excludes water samples from recharge wells that are mixtures of surficial aquifer and upper Floridan aquifer water. Table 3 gives data for recharge wells.

the upper screens. The microbes are complex communities of iron- and sulfur-metabolizing organisms. The Borden study characterized 5 recharge wells. Shallow, surficial aquifer samples had the following average chemical conditions: pH = 5.6, Eh (mv) = 25¹, total iron (mg/l) = . The Eh (redox potential) average is misleading because the minimum potentials measured were -70 and -30 mv. All values were increasing as measured, which reflects equilibration with the atmosphere. It can be concluded from the Borden data that surficial aquifer water has negative Eh values and is strongly reducing before entering the recharge wells.

Hawthorn-Bone Valley System

The Mio-Pliocene Bone Valley Formation and the Miocene Hawthorn Formation constitute the Bone Valley-Hawthorn system. Both formations are phosphatic and are mined in the Central Florida Phosphate District. The Bone Valley is a sandy to clayey unit that contains rich beds of phosphorite. The upper part of the Hawthorn is also elastic in nature and contains phosphate, sand, and clay. It is generally somewhat more argillaceous than the Bone Valley. The lower Hawthorn contains extensive beds of dolostone and limestone that may be hydraulically connected to the underlying limestones.

The Bone Valley and upper Hawthorn Formations contain sufficient clay to serve as efficient aquitards to vertical flow of ground water. These beds constitute the upper unit that confines the underlying Floridan aquifer. Within the Bone Valley-Hawthorn confining unit complex there are numerous beds of coarse clastics that serve as local aquifers. These small aquifers may be confined and exhibit artesian flow. The carbonate beds of the lower Hawthorn are considered to be part of the Floridan aquifer.

Few wells are open to the localized, clastic aquifers within the Hawthorn-Bone valley, so it is difficult to evaluate the chemistry of the unit. The ground-water study by Upchurch et al. (1979a,b) discussed the quality of the Hawthorn-Bone Valley aquifer. Table 2 summarizes their results.

Floridan Aquifer

The Floridan aquifer is the principle aquifer of central Florida. It includes the carbonate beds of the lower Hawthorn and limestones of the Tampa Formation (Miocene), Suwannee Limestone (Oligocene), Ocala

1 Two Eh measurements were negative, two were positive. All were increasing as the sample equilibrated with the atmosphere. In situ, the water was clearly reducing.

Group (Eocene), Avon Park Limestone (Eocene), and, in some areas, lower Eocene and Paleocene strata. The Floridan is primarily a karst aquifer, although significant intergranular and moldic porosity exists. The aquifer is confined in the study area and the potentiometric surface rises as much as 100 ft. above the top of the aquifer. Recharge to the Floridan is through unconfined areas, such as the Green Swamp north of the phosphate district, local sinkholes and lineaments, and recharge wells.

Table 2 summarizes water quality in the Floridan aquifer at the Kingsford Mine. Floridan water is carbonate rich and alkaline. Sulfate increases with depth. LaMoreaux and Associates (1978) characterized Floridan water Eh and pH values. They found the Eh to be about -150 mv, pH of 8, and bicarbonate to be about 200 mg/l. Therefore, the Floridan can be thought to be strongly reducing and somewhat alkaline.

Recharge Wells

Recharge wells are advantageous to the phosphate industry because they allow dewatering of surficial sediments and mitigate withdrawals from the Floridan aquifer. Recharge wells operate by gravity. Surficial aquifer water flows into the well through screens placed above the base of the aquifer so as to avoid contamination by lower-quality waters of the Hawthorn-Bone valley. The water cascades downward to the Floridan aquifer potentiometric surface. This drop may be as much as 100 ft., although it is usually much less. Flow in the recharge wells ranges from 0 to over 200 gpm. The recharging water is received by the upper Floridan through karst conduits.

Recharge wells have been the target of several studies. Upchurch et al. (1979a,b) looked for evidence of contamination of the Floridan by recharge well operation at the Kingsford Mine. They found no evidence for contamination and, in fact, noted some evidence that sulfate concentrations in the Floridan might be diluted by the recharged waters. Monitoring programs have not found evidence of significant contamination directly attributable to recharge well operation either.

There are two major problems with recharge wells. The first, screen clogging, deals with efficiency of operation, rather than potential ground-water contamination. The ferric oxyhydroxide and microbe mats that form on the screen are a chronic problem and many of the wells require maintenance to keep them operating. The second problem, radiation, is not so simple to resolve. This problem is discussed throughout this report.

There are two studies that treat with the general chemistry of recharge wells. LaMoreaux and Associates (1978) compared the Eh and pH of waters cascading down 5 recharge wells. The cascading water, which reflects surficial aquifer water, is discussed above. The water found near the bottom of the recharge wells is a mixture of surficial and Floridan aquifer water. This water had average values as follows: pH = 6.3, Eh = +149 mv, and iron = 0.61 mg/l. Therefore, pH increases

Table 3. - Mean values of selected chemical constituents in recharge wells at the Kingsford Mine. Data are modified from Upchurch et al. (1979 a,b).

Variable	Approximate Depth (ft.)	
	100	150
pH	5.6	5.8
Temperature (deg. Celsius)	23.9	24.1
Specific Conductivity (mmhos/cm)	213	155
Sulfate (mg/l)	27.9	64.9
Phosphate (mg/l)	.8	1.3
Fluoride (mg/l)	.2	.05
Potassium (mg/l)	.4	.4
Sodium (mg/l)	11.4	15.7
Magnesium (mg/l)	6.6	5.2
Calcium (mg/l)	12.5	11.2
Radium-226 (pCi/l)	3.1	3.6

slightly, Eh increases dramatically, and iron decreases slightly with depth in recharge wells. These data suggest that several chemical reactions are taking place. First, oxidation through turbulent flow and contact with the atmosphere is taking place. Second, mixing with more alkaline Floridan waters occurs. These processes lead to precipitation of ferric oxyhydroxides and dilution, both of which may affect radionuclide concentrations.

Upchurch et al. (1979a,b) sampled at the top and bottom of several recharge wells at Kingsford. They found similar phenomena. First, mixing with Floridan waters reduces the concentrations of chemicals in the well water. Second, pH and temperature indicate that equilibration with the well atmosphere is extremely important. Table 3 gives the mean values for selected chemicals in Kingsford recharge wells as a function of depth. Comparison with Table 2 indicates that there are significant chemical changes that take place in recharge wells.

The data collected by IMCC for the study well (Table 4) indicate these same phenomena and show that gross-alpha activity may be quite high in the surficial-aquifer water while radium-226 activity is low.

Therefore, a scenario for water-chemical changes in the vicinity of the recharge well can be constructed. Prior to contact with the recharge well, surficial aquifer water is reducing, acid, iron rich, low in radium activity and relatively high in gross-alpha activity. Upon entering the well, the water falls to the potentiometric surface of the Floridan. During the fall and subsequent flow out of the well, oxidation, mixing, and possible buffering occur. The pH and Eh increase with depth, temperature changes, and mixing alters the bulk chemistry. In this environment ferric hydroxide precipitates and microbial populations flourish. Once the water enters the Floridan many of these reactions appear to be reversed. The Eh begins to drop and net reduction occurs. With reduction, ferric hydroxides may dissolve. Buffering with the carbonates of the limestones and dolostones raises the pH and alkalinity.

STUDY WELL

Test Recharge Well

The recharge well selected was well KR-98B, which is located NW 1/4, s. 4, T31S, R23W on the Kingsford Mine of IMCC. The well is located near a clay-waste settling area and is in an unmined, open field. The well was installed June 21, 1976. It consists of 22 ft. of 10 in. PVC casing, 20 ft. of slotted casing in the surficial aquifer, 81 ft. of PVC casing to the top of the Floridan, and 427 ft. of open hole (Figure 1). The well was grouted with 30 bags of cement. Two different company measurements of flow in 1978 indicated 220 and 122 gpm at a depth of 85 ft. In 1984 the well was found to have silted up to a depth of 205 ft. and flow was reduced to as little as 16 gpm.

The well is regularly monitored by IMCC and Table 4 shows the results of this surveillance. IMCC's sampling method is to capture cascading water with a metal bailer. Based on the Office of Radiation Studies, Polk County Health Department (1983) study, well KR-98B seems typical of recharge wells in the District.

Cores

Cores were taken with a rotary drilling rig by the Leonard Burnett Drilling Company, IMCC's usual driller. The cores were taken with a sharpened 4 in. casing length and recovery was excellent. The cores were logged as collected. Appendix E gives the detailed core logs. The northeast core was located 109.3 ft. N75E of the recharge well and the southwest core was 80.7 ft. S45.5W of the recharge well.

Monitor Wells

Four 4 in. monitor wells were installed around KR-98B. The site design included a pair of shallow and deep wells up and down gradient of the recharge well. The monitor wells were installed at the same time as cores were taken and by the same driller. Standard rotary-drilling practices were used in installation.

The shallow monitor wells are intended for monitoring of water entering the recharge well from the surficial aquifer. The shallow monitor wells were set with a 20 ft. length of PVC casing and a 20 ft. length of slotted PVC for a screen. One foot of casing was left above ground level, so the slotted interval is from 19 to 39 ft. below ground surface. The slotted interval, therefore, corresponds with the slotted interval on the recharge well and the flow zone noted in the aquifer. The shallow wells are within the cone of depression of the recharge well. The north well is 26.4 ft. N34E of the recharge well and the south well is 24.8 ft. S31E.

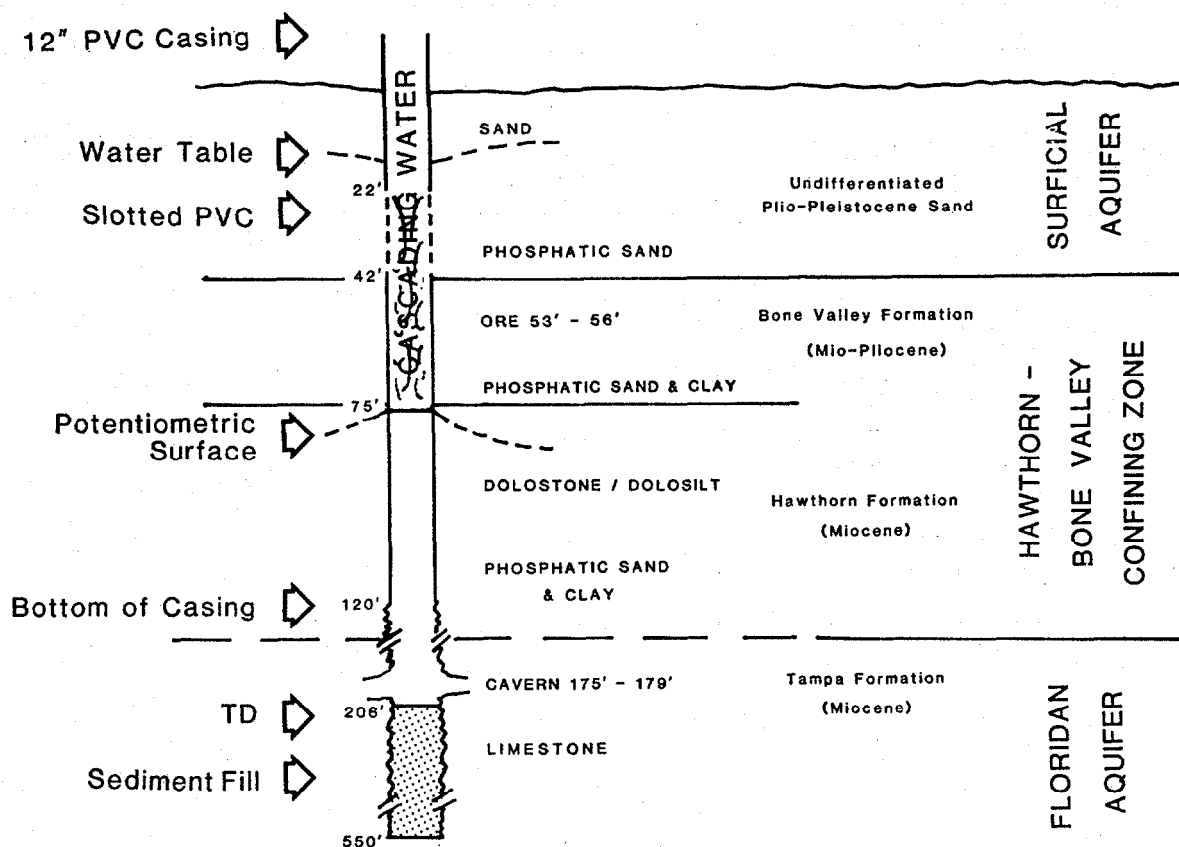


Figure 1

Diagram showing the design of recharge well KR-98B and the hydrostratigraphy of a typical recharge well in the central Florida Phosphate District.

Comparison of the gamma logs of all wells and the cores indicates that the shallow monitor wells and the recharge well are screened in an interval of elevated radioactivity (Figure 2). The cores show a minor increase in phosphate grains in this interval and absorption of radionuclides on other grain surfaces probably contributes to the gamma activity in the interval.

The deep monitor wells consist of 4 in. PVC, as well. One hundred twenty feet of casing was set with complete cement grout. The hole was then extended to a total depth of 207 ft. (south well) and 209 ft. (north well). The open hole section of the monitor wells corresponds with that portion of the recharge well remaining open (Figure 2). The north deep monitor wells is located N32 1/2E 107.9 ft. from the recharge well and the south well is 532W 77.1 ft.

Comparison with the lithologic logs (Appendix E) indicates that the deep monitor well casings are set in the dolomitic section of the upper Hawthorn Formation. This zone is generally considered the top of the "upper Floridan" aquifer in the District. Gamma-radiation logs (Figure 2) indicate that the top of the limestone of the Floridan is at 168 ft. below land surface. It is not possible to identify the formation present without cuttings, but it is certainly either Tampa Formation (Miocene) or Suwannee Limestone (Oligocene). The low gamma activity suggests the latter.

Table 4. - Chemical characteristics of well KR-98B. Data furnished by IMCC. Samples were taken with a bailer from cascading water.

Constituent	Mean	Maximum	Minimum
Flow (gpm)	60.	220	16
pH	6.0	5.3	7.3
Total Dissolved Solids (mg/l)	144.	225.	49.
Specific Conductance (mho/cm)	183.	440.	29.7
Suspended Solids (mg/l)	9.8	38.8	2.
Turbidity (n.t.u.)	10.4	41.	1.7
Sulfates (mg/l)	43.98	90.20	12.35
Fluorides (mg/l)	.19	.41	.14
Orthophosphate as P (mg/l)	.78	1.13	.22
Total Phosphate as P (mg/l)	.79	1.24	.04
Ferrous Iron (mg/l)			
Filtered	1.88	3.16	.1
Unfiltered	2.92	10.0	.1
Ferric Iron (mg/l)			
Filtered	1.21	2.51	.3
Unfiltered	2.93	4.93	1.36
Gross-alpha activity (pCi/l)	22.6	122.0	6.77
Radium-226 (pCi/l)	2.2	7.6	.1
Dates of analyses	April 1978 to September 1984 (quarterly)		

Site plan and logs of the deep wells at site KR-98B.

CAUSES OF THE GROSS-ALPHA ANOMALY

The first goal of this project was to identify the cause of the gross-alpha anomaly. As established earlier, uranium-238 and its daughters are expected to be the most abundant radionuclides present based on analyses of parent isotopes in phosphate rock (Guimond and Windham, 1975). Within the uranium-238 decay series (Appendix B), radium-226 and polonium-210 are alpha emitters that could contribute to the gross-alpha problem.

An initial group of tests was designed to determine the relative magnitudes of the dissolved radionuclide activities in ground water at KR-98B. The results of these tests were used to target radionuclides for additional study.

Table 5 indicates that, within the uranium-238 decay series, polonium-210 is present in greatest quantities and is most likely to contribute to the gross-alpha anomaly. Polonium-210 had an activity of 18 pCi/l, which equals or exceeds the gross-alpha activity reported at the well on several occasions. Therefore, it was concluded that polonium-210 is the principle cause of the anomaly.

The uranium-238 decay series can reach secular equilibrium within a few hundred thousand years. Should this happen, the activities of all daughters should be equal to the decay of uranium-238. If radium is separated from its parent, equilibrium with its daughters in a closed system would occur in about 200 years. Radon-222, the immediate daughter of radium-226, is an inert gas. Given the opportunity, the gas can move independently of water flow or chemical diffusion.

During alpha decay, there is a possibility that the radionuclide under decay may recoil from its site in a given substrate into any adjacent void space. The recoil event introduces the daughter isotope into the atmosphere or water adjacent to the substrate that contains the decaying isotope. Krishnaswami et al. (1982) and Rama and Moore (1984) have discussed this recoil mechanism and used it to explain why radon accumulates in ground water while parent and daughter isotopes do not. Krishnaswami et al. (1982) argued that alpha recoil has the potential to introduce any isotope that undergoes alpha decay on a soil or rock grain surface into adjacent void space. They argued that radon accumulates because it is a noble gas and not subject to sorption reactions, while the other isotopes are reactive and, therefore, readily resorbed on nearby grain surfaces. Rama and Moore (1984) refined this argument by showing that much of the radon introduced into pore space is in the exceedingly small "nanopores" within mineral grains. The high surface area to volume ratio of these nanopores assures sorption of reactive isotopes, while radon has a chance of diffusing into adjacent megapores. Thus, there is a natural buildup of radon gas in ground water and there is no reason to expect that the radon is supported by radium or other predecessor isotopes in the water mass. Radon gas may further migrate and

Table 5. - Radionuclide activities in water from recharge well KR-98B. Isotopes are ranked in order of decreasing alpha activity. Samples were collected by open bailer at standing-water level (approx. 75 ft.).

Isotope	Sample No.	Activity (pCi/l)*
Polonium-210	R98B-1	18.12 +/- 1.34
Radium-226	R98B-5	1.92 +/- 0.10
	R98B-16 **	4.21 +/- 0.24
	R98B-21	3.42 +/- 0.20
Uranium-238	R98B-2	0.13 +/- 0.04
	R98B-15 **	0.59 +/- 0.04
Uranium-234	R98B-2	0.18 +/- 0.06
	R98B-15 **	0.49 +/- 0.04
Radium-228	R98B-5	0.27 +/- 0.10
	R98B-16 **	0.35 +/- 0.24
	R98B-21	0.44 +/- 0.28

All samples were filtered on Whatman #1 paper approximately 3 hrs. after collection and acidified with 1% HCl immediately after filtration.

* Error limits are counting errors +/- 2 standard deviations.

** These samples were collected with the closed thief sampler at 150 ft. depth,

accumulate when it evolves in the presence of a pressure gradient, such as (1) near the water table, (2) near pumping or flowing wells, or (3) near advective water flow. Radon and radon daughters are present, therefore, in excess of radium (Table 5). Sorption of the daughter isotopes on rock or soil minerals and organic particulates controls the amount of radon daughters remaining in the water.

It should also be noted that uranium-238 and -234 are in approximate equilibrium in the ground water (Table 5). Radium-226 is not quite in equilibrium with its predecessors because of the chemistry of the surficial aquifer. Uranium is most soluble in oxidizing, neutral to slightly alkaline solutions (Langmuir, 1977). Radium, on the other hand is somewhat more soluble in acid than in basic waters. Thus, the surficial aquifer tends to promote slight enhanced mobility of radium.

Finally, note that radium-228, a product of the thorium-232 decay series, is present in the water in minor activities compared with radium-226 and polonium-210.

SAMPLE PREPARATION

Effects of Sample Preparation

Once polonium was confirmed to be the major cause of the gross-alpha anomaly, we proceeded to determine if the variation in gross-alpha results reported is due to sample preparation. Our initial presumption was that polonium, like other metals, can sorb onto container walls and particulates. This sorption decreases the available metal and biases the analytical result. Since polonium analysis uses a polonium spike (Appendix C), adsorption can be tracked to some degree. We used addition of acid (Appendix C) to retard sorption on container walls. This is a standard practice in the phosphate district and is required in metals treatment by E.P.A.

Gross-alpha radiation is commonly run by laboratories distant to the sample collection site. At the time of collection the sample may or may not be fixed with acid and/or filtered. Furthermore, the sample may sit in the lab or in transit for an unspecified time. All of these procedures were thought to affect the analysis results.

To test the impact of preparation we chose to filter and acidify a set of samples at differing times. The sample water was collected at one time from a depth of 150 ft. with the closed thief sampler. The water was thoroughly mixed and homogenized, then split into different samples. Table 6 gives the conditions of each sample treatment and the resulting polonium activity.

Note in Table 6 that time of filtration is most important. The water samples lost up to 70% of the polonium-210 activity to suspended particulates in a 3 hr. period and 83% within 24 hrs. The 3 hr. interval included time to drive the samples back to USF for analysis, so they were agitated, heated, and possibly oxidized during the 3 hrs. Sorption is, therefore, very rapid and the final activity is highly dependent on turbidity of the sample and length of time before filtration. The test results clearly indicate the need for immediate filtration.

We also tested the use of different filter pore sizes. Filtration pore size has less impact than time of filtration. Micropore (0.45 micron pore size) filtration reduced the reported polonium activity by about 25%. For example, samples R98B-3 and -4 were collected to test the effects of filtration. The samples were collected at a depth of 70 ft. Radium-226 in these samples was 2.05 ± 0.10 pCi/l. Polonium varied with filtration medium. R98B-3 was filtered through Whatman #4 filter paper and then acidified. It had a polonium-210 activity of 25.25 ± 0.64 pCi/l. R98B-4 was filtered through Whatman #4 paper and then through 0.45 micron Millipore paper. Acidification followed filtration. The polonium-210 activity was 19.20 ± 0.64 pCi/l. Therefore, some of the polonium-210 is fixed on micron-sized, filterable solids.

In order to conform to U.S. Environmental Protection Agency and Florida Department of Environmental Regulation definitions of particulate

and dissolved materials, it is recommended that 0.45 micron micropore filter paper be used for filtration.

Sample R98B-14 (Table 6) is anomalously high, presumably because of ferric hydroxide formed during the 2 week interval. Ferric hydroxide is most successful at sorbing polonium-210 and is used to collect the isotope for analysis (Appendix C). Ferric hydroxide precipitates from recharge-well water samples as the water warms and equilibrates with the atmosphere. The ferric hydroxide-polonium complex retains polonium in a form that can be recovered as the hydroxide is dissolved.

Refrigeration seems much less important as a sample-preservation technique than rapid filtration, but additional studies of the effects of refrigeration are indicated. Note that refrigeration of the sample stored for 2 weeks inhibited the precipitation of ferric hydroxide and the resulting polonium activity is the lowest of the sample set. Therefore, it appears that refrigeration has a negative impact on polonium analysis and until such time as further tests can be made, refrigeration is not recommended.

Acidification Studies

Late in the study we conducted a test to determine if the time of acidification affected the analytical results. The results were disturbing and unexpected by ourselves and all of the other polonium analysts whom we questioned. The resolution of the problem described below is beyond the scope of this study and must be addressed before reliance in the validity of gross-alpha or polonium analyses can be assured.

Two tests of the impact of time of acidification were run (Tables 7 and 8). Both tests gave repeatable results. It was discovered that, while the amount of spike recovered remained constant, the amount of polonium-210 detected increased with the time between collection and acidification.

In light of the experience with sample R98B-14 (Table 6), it was decided to try using a base to encourage initial fixation of the polonium with ferric hydroxide. We chose to preserve the sample with ammonium hydroxide because it is used in the laboratory procedure to coprecipitate ferric hydroxide and polonium (Appendix C) and it has the added advantage that ammonia has the strongest exchange capacity of the common cations and is used to wash exchangeable cations from clays. Thus, the ammonia may serve to saturate the sample container walls and prevent sorption of polonium.

The results of the tests with ammonium hydroxide are given in Tables 7 and 8. We cannot state that this is the optimal method for polonium recovery, but the preliminary tests do indicate that fixation with ammonium hydroxide increases the recovery of polonium in water samples when the

Table 6. - Sorption of polonium-210 as a function of filtration and acidification time. All activities are in pCi/l at the 95% confidence level. Confidence limits are due to counting error alone.

Sample No.	Treatment ¹	Polonium-210 (pCi/l)
R98B-9	Filtered upon collection	14.86 +/- 0.30
R98B-10	Filtered after 3 hours	4.90 +/- 0.18
R98B-13	Filtered after 24 hours	2.59 +/- 0.14
R98B-14	Filtered after 2 weeks	8.78 +/- 0.34
R98B-11	Refrigerated upon collection, filtered after 24 hours	3.33 +/- 0.14
R98B-12	Refrigerated upon collection, filtered after 2 weeks	1.43 +/- 0.08

¹ Samples were collected at 150 ft. depth with a closed thief sampler, mixed thoroughly, then split. Acidification was with nitric acid (Appendix C) after filtration.

Table 7. Effects of time of acidification on polonium recovery. Activities are at the 95% confidence level. Confidence limits are due to counting error alone. R98B-47 is a single water sample split 6 ways and filtered on a 0.45 micron filter in the field.

Sample No.	Treatment	Polonium-210 (pCi/l)
R98B-47-A1	1. Acidify sample bottle 2. Add water to bottle	13.30 +/- 0.34
R98B-47-A2	1. Acidify sample bottle 2. Add water to bottle	13.34 +/- 0.34
R98B-47-B1	1. Add water to bottle 2. Acidify in lab after 3 hrs.	15.70 +/- 0.38
R98B-47-B2	1. Add water to bottle 2. Acidify in lab after 3 hrs.	16.02 +/- 0.38
R98B-47-B3	1. Add water to bottle 2. Acidify in lab after 3 days	18.00 +/- 0.50
R98B-47-C	1. Add ammonium hydro- xide to sample bottle 2. Add water to bottle 3. Acidify in lab after 3 hrs.	21.17 +/- 0.48

samples are analyzed by spontaneous deposition of polonium on silver. The causes of the differences in recovery of the polonium-210 with time of acidification and/or the nature of the fixative are poorly known and need additional investigation. Polonium occurs in four valence states, of which the +4 and +2 states are most stable (Bagnall, 1957). Bernabee and Sill (undated) have examined the reactions that control recovery of polonium for alpha spectroscopy. They found that the valence state of the polonium is critical to polonium recovery. The best recovery is accomplished when the polonium is kept in the tetravalent state. They found the following:

- a. Both hydrochloric and nitric acid can be used as carriers for polonium;
- b. Divalent polonium is highly volatile and should not be allowed to form in the sample;
- c. Organics in the sample can reduce the polonium and enhance losses by volatilization. Nitric acid is used to oxidize organics and prevent reduction of the polonium; and
- d. Polonium dioxide is refractory and is not recovered on the silver disks used in alpha spectroscopy.

Divalent halides are volatile, so fixation with hydrochloric acid includes the risk of formation of the volatile dichloride. In the presence of ammonium hydroxide, polonium forms polonium tetrahydroxide, which is stable and recoverable. In nitric acid it forms polonium nitrate.

Thus, it appears that the acidification problem is complex. If the sample is stored without fixation, one of two processes can occur. First, in the presence of organics, which are abundant in the surficial aquifer waters and in the microbially-dominated recharge wells, recovery of polonium may not be representative because of loss through volatilization. Second, warming of the sample drives the water towards oxygen saturation. In the aquifer, the water is cool and what little dissolved oxygen is present is well below the maximum that can be dissolved at that temperature. The water is undersaturated with respect to oxygen. As the water warms during pumping and in the sample container, that small amount of oxygen remains constant, but the total capacity of the water to hold oxygen decreases and oxygen saturation is approached. Ferric hydroxide forms and should fix polonium in an available state. If, however, polonium dioxide forms, the polonium analysis yields an activity less than the true polonium activity.

In the case of the experiment shown in Table 7, it appears that polonium dioxide is destroyed in the interval prior to acidification. The spike, which is in the form of polonium-209 nitrate, is not affected and recovery (or analytical efficiency) remains constant while the sample polonium-210 in a recoverable form increases. Thus, it appears that polonium hydroxide coprecipitated with the ferric hydroxide and either formation of polonium dioxide or volatilization was inhibited.

Table 8. Effects of fixation with acid and base on recovery of polonium. Samples were homogenized and split. All samples were filtered on 0.45 micron paper. Activities are at the 95% confidence level, based on counting error alone.

Sample No.	Treatment	Polonium-210 (pCi/l)
R98B-48A	1. Acidify bottle 2. Add water sample 3. Spike in field	7.44 +/- 0.24
R98B-48B	1. Acidify bottle 2. Add water sample 3. Spike in lab after 3 hrs.	7.88 +/- 0.22
R98B-48C	1. Place water in bottle 2. Add spike in field 3. Acidify in lab after 3 hrs.	11.00 +/- 0.32
R98B-48D	1. Add ammonium hydroxide in field 2. Add water sample 3. Add spike in field 4. Acidify in lab after 3 hrs	18.40 +/- 0.36
R98B-48E	1. Add ammonium hydroxide in field 2. Add water sample 3. Add spike in field 4. Acidify in lab after 10 days	31.13 +/- 1.30
R98B-48F	1. Add ammonium hydroxide in field 2. Add water sample 3. Add spike in lab after 3 hrs. 4. Acidify in lab after 10 days	26.42 +/- 0.68

There is a problem with use of the spike that is not completely resolved. In order for the polonium-209 nitrate spike to accurately represent the polonium-210, including refractory polonium dioxide, in the sample, equilibration of the spike and polonium-210 must occur. That is, there must be equivalent proportions of polonium-209 and -210 in all polonium-bearing phases in the sample. Our data suggest that equilibration is not necessarily complete, which results in failure to account for some of the refractory or volatile polonium-210.

Fixation with nitric acid, therefore, is inadequate as it is now used. It either inhibits formation of the hydroxides, so that polonium dioxide can form and reduce recovery or it does not adequately oxidize the organics and volatilization after reduction results. Additional nitric acid fixative might resolve the latter problem.

Addition of ammonium hydroxide encourages the formation of polonium hydroxide ($\text{Po}(\text{OH})_4$), which is the form of the coprecipitate with ferric hydroxide. This polonium hydroxide preserves the polonium in the +4 state and makes it available for recovery by the prescribed methods.

Impact on Standard Methods

The acidification and volatilization problems with polonium cast doubt on the gross-alpha radiation analytical method. This method (American Society of Testing and Materials, 1981) involves several steps that render polonium recovery questionable. Recall that Florida Statute 17-22.104(1)(e) excludes radon gas and uranium from gross-alpha analysis, but does not exclude polonium. The steps that render the method questionable are:

- a. Plastic or glass containers are allowed. Bernabee and Sill (undated) found polonium sorption on glass to be a problem;
- b. Filtration through a 0.45 micron filter is required, but no time of filtration is specified. Immediate filtration is necessary;
- c. Preservation is with 0.5N nitric acid, but no amount of preservative is specified;
- d. A shelf life of up to 1 yr. is allowed. Formation of polonium dioxide, volatilization, and sorption problems necessitate shorter holding times; and
- e. The liquid sample is evaporated on a planchet for counting. Evaporation, especially by heat application, can enhance polonium volatilization.

Therefore, the gross-alpha radiation analytical procedure probably does not reflect the actual polonium activity in the water. In order to standardize sample collection procedures and preservation methods, it is

necessary to make interim recommendations, but these recommendations are made with the understanding that there are flaws in the procedures. The recommendations will serve only to eliminate differences in reported radiation results caused by differing sampling methods.

Final Sample Preservation Procedure

Because of the high rate of polonium adsorption on particulates, the final sample preparation procedure for gross-alpha radiation analysis includes immediate filtration at the time of collection. Removal of the suspended solids is accomplished by passing the sample through a 0.45 micron filter. The filtration apparatus we used is described in Appendix D. It uses positive pressure and a large filter area, which renders the filtration process efficient. It is recommended that an apparatus, such as the one described in Appendix D, be used.

Filtered samples for the analysis of polonium are immediately preserved with 1 to 2%, by volume, nitric acid. Choice of immediate preservation with nitric acid will standardize the results and conform with the recommended method (which suggests use of hydrochloric acid) for polonium analysis (Rushing, 1966; Work Group 5 on Chemical and Physical Quality of Water, 1982). Samples for uranium and radium analysis are immediately preserved with 1% hydrochloric acid. Samples for gross-alpha radiation analysis should be treated with nitric acid in the same fashion as if polonium is the target radionuclide. Standard gross-alpha analysis should have no problem in detecting polonium dioxide, so volatilization and sorption are the major concerns.

The sample should be analyzed as soon as possible. If gross-alpha radiation analysis is to be undertaken, care should be exercised to prevent chemical reduction or volatilization of polonium through heating of the sample.

It must be noted that THESE RECOMMENDATIONS ARE INTERIM PROCEDURES ONLY. Fixation with ammonium hydroxide or other procedures may be recommended upon further examination of the problem. Gross-alpha radiation results should be considered as minima, because of the unknown loss of polonium.

Behavior of Polonium in Aquifers

These data indicate that polonium is the major source of gross-alpha radiation in ground water. They also point out several important trends and the necessity for additional work on the stability of uranium and its daughters in Florida's aquifers.

First, based on the filtration studies, polonium is clearly sorbed on soil and/or rock minerals. This is in agreement with the findings of many authors (e.g., Hansen and Watters, 1971; Krishnaswami et al., 1982; Rama and Moore, 1984). The rate of sorption, preference for different

minerals, and chemical conditions necessary for ion exchange should be investigated, but there appears to be little problem with transport in the aquifer. Both the Floridan and the surficial aquifer are reducing and Po^{+2} should be the stable form. While volatile in atmospheric conditions, divalent polonium should strongly sorb to rock or soil minerals and not be a hazard to users of the aquifer.

Second, there is a probability that the polonium undergoes several transformations in recharge wells. The microbial communities in the wells may well be able to sorb polonium, especially if it is in the divalent state. Polonium is known to be strongly sorbed or metabolized by organisms (e.g., Teplykh, 1973; Shannon, 1973; Heyraud and Cherry, 1979). The partial oxidation of water during and after its fall in the well can cause coprecipitation as polonium hydroxide. Thus, changes in Eh and pH in the well may enhance short-term mobility of the radionuclide. These processes should also be studied.

SAMPLING METHODS

Introduction

Industry personnel use many different methods and devices to collect samples from recharge wells and they sample from several different depths in the wells. At the October 6, 1983 meeting there was much discussion about the impacts of these different devices and methods on the radiation results. In order to identify these variations, we undertook two sets of experiments. The first was to sample well KR-98B at different depths to determine if there is any stratification of polonium in the well. The second was to invite interested companies to come to KR-98B and sample it using their own procedures. By comparison of their results with our own, we can evaluate the different methods.

Polonium Stratigraphy in Well KR-98B

In order to determine if there is any stratification of polonium in the well, we collected 5 samples with depth. The open bailer was used to sample the cascading water and the closed thief was used for all other samples. Samples were taken from depths of 50 ft. (cascading water), 75 ft. (standing water at the top of the Floridan potentiometric surface), 100, 150, and 200 ft. These results were filtered on the 0.45 micron filter, and immediately acidified with 1 to 2% nitric acid by volume. Table 9 gives the results of the analysis.

Note in Table 9 that there is a dramatic decline in polonium-210 activity with depth in the well. The polonium activity is 77% lower at the bottom of the well than it is in the cascading water (Figure 3).

This reduction in polonium activity may be caused by any of three different processes. First, simple mixing of recharge surficial aquifer water with the Floridan water can dilute the polonium. The chemical data of Upchurch et al. (1979) (Table 3) indicate that several of the major elements in recharge wells vary with depth, which supports the hypothesis that mixing is a major cause of reduction in polonium with depth. Second, turbidity increases with depth in KR-98B. The sorption data indicate that clays and organics can sorb polonium, so the reduction may be in part due to the increase in turbidity. Finally, the bulk chemistry of the well, including Eh and pH, changes with depth, so it is possible that the valence state and form of the polonium changes as well. This could cause a change in the ability to detect the polonium and, thus, the reported activities.

Industrial Sampling and Analytical Methods

The individual phosphate companies are responsible for regular

Table 9. - Stratification of polonium-210 in well KR-98B. Ninety-five percent confidence limits are based on counting error alone.

Sample No.	Sampling Depth (feet)	Polonium-210 (pCi/l)
R98B-41	50 (cascading water)	11.26 +/- 1.20
R98B-42	75 (top of pot. surface)	7.11 +/- 0.70
R98B-43	100	5.84 +/- 0.22
R98B-44	150	6.64 +/- 0.22
R98B-45	200 (bottom of well)	2.62 +/- 0.18

R98B-41 was collected with an open bailer. All other samples were collected with the closed thief. All samples were filtered in the field on the 0.45 micron filter.

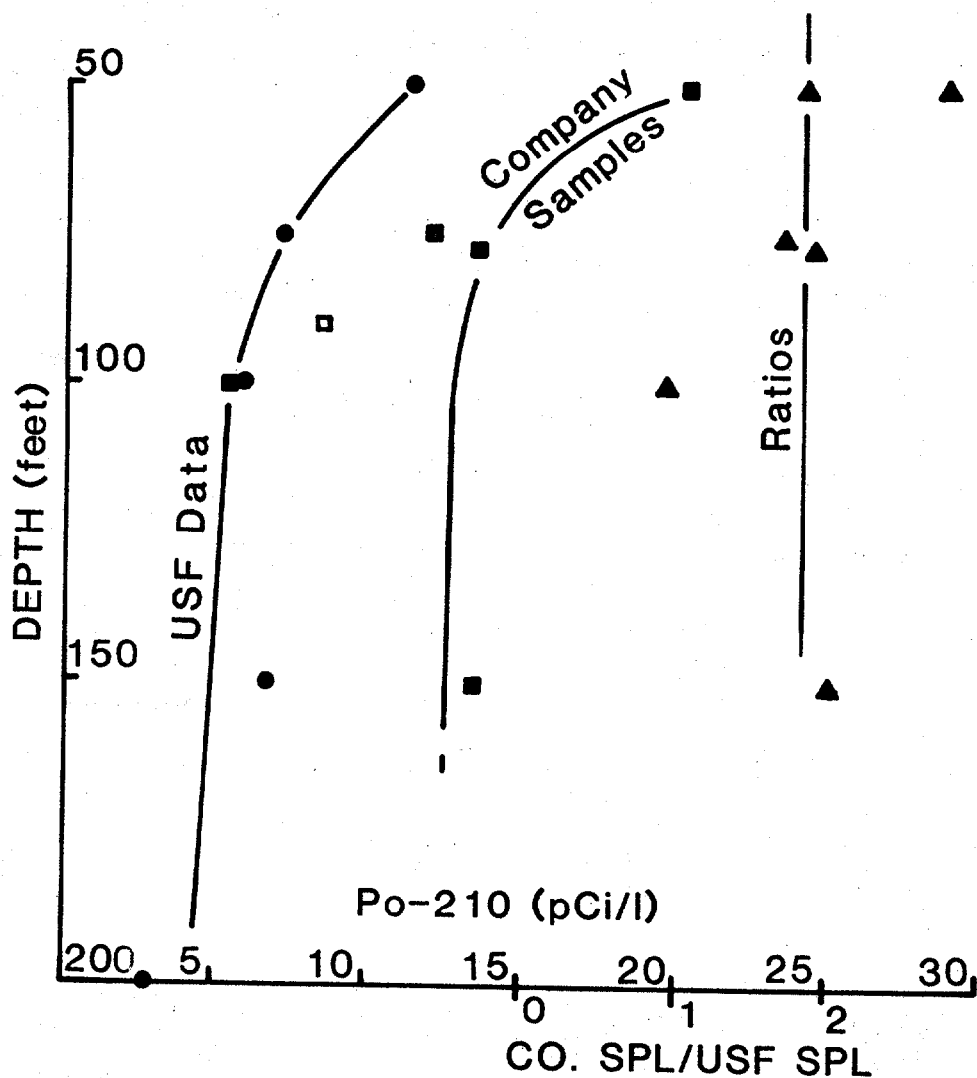


Figure 3

Polonium-210 activities in well KR-98B as a function of depth. Circles are USF samples filtered with 0.45 micron paper. Squares are company samples analyzed by USF. The open square represents a lab-filtered sample, all others were field filtered. Co. Spl/USF Spl represents the ratio of polonium activity measured in the company sample to that measured in the USF-collected sample.

monitoring of their recharge wells. They use radically different sampling methods, different sample-preparation techniques, and different analytical laboratories. In order to determine whether these factors are at least partly responsible for the gross-alpha anomaly, a series of tests was performed on KR-98B with company participation.

Each of the seven participating companies (Table 1) came to KR-98B and sampled it according to their usual sampling method and sample preparation technique. We sampled the well at a standard depth (75 ft.) with the open bailer before and after the company sampling. In this way we could detect any changes in polonium in the well with time or due to the sampling. The company sample was split. Both halves were sampled according to the company's method. One half was analyzed by us for polonium-210. The other half was sent to the company's usual radiation laboratory for radium-226 and gross-alpha radiation analyses.

By this technique, we were able to control water quality and determine the differences in technique. Water samples taken before and after the company sampling provide control on changes in actual polonium activity. The samples taken by the company method and analyzed by us allow identification of differences in sampling and sample preparation technique, while the samples sent to the commercial laboratories allow identification of variations in analytical procedures.

Temporal Variations

The samples taken by us at the beginning and end of each company sampling day indicate that there was little variation in polonium activity with time (Table 10, Figure 4A). These data also show the consistency in the results of our analyses, provided that sample preparation was held constant.

Three samples, R98B-20 B, R98B-23 E and R98B-27 E, were filtered approximately 3 hrs. after collection, upon return to the laboratory. Some of the polonium-210 was lost through sorption on suspended solids or formation of polonium dioxide. All other samples were filtered in the field. The difference in activities from beginning to the end of the sampling day reflects the difference in time of acidification, which was in the laboratory 3 hrs. after collection. The samples that were allowed to set for several hours longer (the beginning samples), therefore, showed somewhat higher polonium activities.

Company Sampling Results

The data from the companies varied significantly, but we were able to reconcile much of the variability. The companies used a number of different techniques for sampling. These are summarized in Table 11. Two companies used "home made" open bailers to sample cascading water. The other companies used entirely different methods, including (1) a Lab-Line

Table 10. - Polonium-210 activities in the control samples taken at the beginning and end of each company sampling day. Error estimates are 95% confidence limits, based on counting error alone. B = beginning sample, E = end sample.

Sample Day	Sample No.	Polonium-210 (pCi/l)
1	R98B-20 B *	18.11 +/- 0.38
	R98B-23 E *	9.75 +/- 0.26
2	R98B-24 B	21.91 +/- 0.52
	R98B-27 E *	13.45 +/- 0.36
3	R98B-30 B	21.71 +/- 0.40
	R98B-34 E	18.03 +/- 0.74
4	R98B-36 B	21.25 +/- 0.36
	R98B-39 E	17.02 +/- 0.36

Samples were filtered upon collection and acidified approximately 3 hrs. after collection.

* These samples were filtered in the laboratory approximately 3 hours after collection.

bailer, (2) a geophysical logger, (3) a flow-through, check-ball thief sampler, (4) an ISCO bladder pump, and (5) a "home-made" air-lift system. Descriptions of these systems are on file at the Geology Department at the University of South Florida, at the Southwest Florida Water Management District, and at the Florida Institute of Phosphate Research. Since specific designs are not relevant, as it turns out, the details of most designs are not discussed herein.

Two companies sampled cascading water. They argued that this is the most likely place to detect water-quality problems. One company sampled just below standing water and the remainder sampled at varying depths to 150 ft.

Comparison of Sampling Techniques

The results of our analyses of polonium-210 in the sample splits are given in Table 12. First examination of the data indicates that these samples reflect a great deal of variation. Figure 4B shows these data plotted against the USF beginning sample for the day of collection. This figure clearly shows that the variability is not due to changes in water chemistry, but is due to the sampling.

This variation is in part due to sampling method and in part due to depth. Figure 3 shows these data plotted as a function of depth. Three samples (companies 1, 5, and 6) fall off of the curve. The other samples fall on a curve that parallels the curve for our data. The difference in position of these two curves (the USF-collected and the company-collected samples) is due to the differences in filtration method and problems in acidification mentioned above. The ratio of the data points at a given depth is also plotted on Figure 3 and indicates that, with the exception of the three samples mentioned above, the ratio is constant. Therefore, one can conclude that most of the variation in the samples is due to sampling at differing depths.

The three samples that do not conform to the depth curve indicate some of the problems with sampling. One sample (the 31.06 pCi/l sample collected by company 1) was taken with a metal bailer. Bailers have two obvious problems. First, unless the water pouring into the well is homogeneous, there is a chance of collecting a non-representative sample. Second, if the sampler scrapes the casing wall, microbes, clays and scale can be incorporated into the sample. Rapid filtration should account for these particulates, but chemical changes, such as reduction and/or flocculation of hydroxides, could prejudice the results. The 5.45 pCi/l sample from 100 ft. collected by company 6 is also anomalous. This sample was collected by airlift, which certainly oxidized the iron and polonium. The sample was not filtered in the field. By the time it was filtered, in the lab, the polonium had been removed in the ferric hydroxide. The third sample, the 8.40 pCi/l sample taken from 90 feet by company 5 (the open box in Figure 3), is probably reduced because of our procedures. The sample was filtered in the laboratory with Whatman paper, rather than in the field. Removal of the coprecipitated polonium hydroxide during filtration may have reduced the polonium available for recovery and analysis.

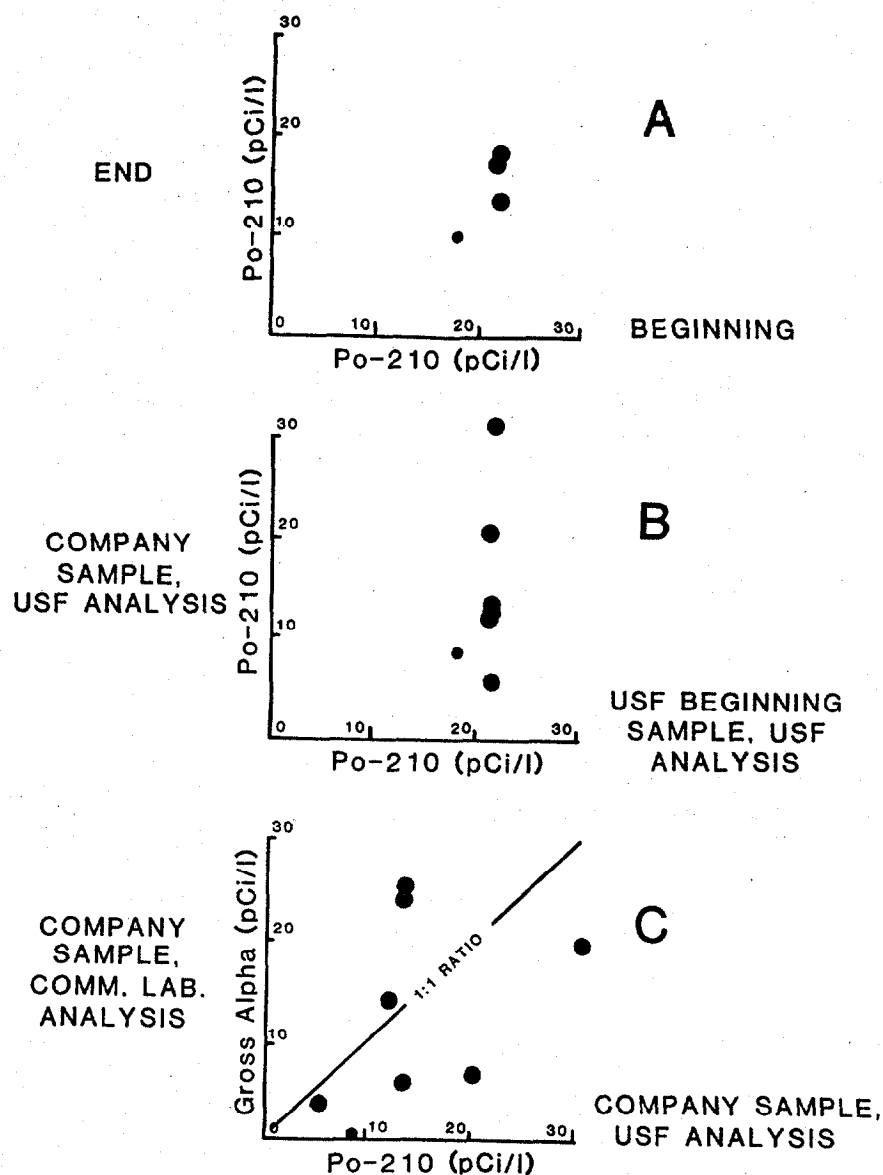


Figure 4

A - Comparison of polonium-210 activities at beginning and end of each day of sampling. B - Comparison of polonium activities in company-collected samples and USF sample collected at the beginning of each sampling day. C - Comparison of polonium activity and gross-alpha radiation in company-collected samples. The small dot represents the sample filtered in the laboratory. See text for explanation.

Table 11. - Sampling devices and depths used by each participating company.

Company	Depth of Sample (feet)	Sampling Device	Sample Preparation and Analytical Laboratory
1	50 (cascading water)	Metal bailer	Micropore filtration; Lab No. 1
2	50 (cascading water)	Metal bailer	No preparation; Lab No. 2
3	75 (standing water)	LAB-LINE bailer	Refrigerate in field; Lab No. 2
4	78 (standing water)	Flow-through, check ball thief	Micropore filtration on 1 of 2 samples; Lab No. 3
5	90	ISCO bladder pump	Refrigerate in field; Lab No. 4
6	100	Air-lift sampler*	Refrigerate in field; Lab No. 4
7	150	Stainless steel geophysical logger	No preparation; Lab No. 5

* This sampler consists of a length of 1 in. PVC pipe that extends to sample depth. An air hose is used to blow compressed air and water up the pipe. The water is highly aerated as it leaves the pipe.

Table 12. - Polonium-210 activities (pCi/l) in samples taken by phosphate-company representatives. Samples analyzed at USF. Uncertainties are based on the 95% confidence limit for counting alone.

Company	Depth (feet)	Polonium-210 (pCi/l)
1	50	31.06 +/- 0.58 *
2	50	20.34 +/- 0.48
3	75	12.00 +/- 0.38
4	78	13.53 +/- 0.40 *
5	90	8.40 +/- 0.24
6	100	5.45 +/- 0.18
7	150	13.45 +/- 0.34

* Samples filtered in field with a 0.45 micron filter, all others filtered in field with Whatman #1 paper.

Table 13. Laboratories used by the participating phosphate companies for radium-226 and gross-alpha radiation analysis. Note that the, order of listing hoes not correspond with the numbers assigned to the laboratories in Table 14.

-
- a. One company used its own laboratory
 - b. P.E. LaMoreaux & Associates
 - c. Thornton Laboratories, Inc.
 - d. Pembroke Laboratory
 - e. KNL Laboratory Services
-

Commercial Laboratory Analyses

The companies were asked to submit their splits of the samples they collected to the normal analytical laboratories for radium-226 and gross-alpha analysis. Five laboratories were used (Table 13). Only one laboratory filtered the sample prior to analysis. The lag times between sample receipt and analysis are not indicated on the laboratory reports. All participating laboratories are certified to do these analyses by the Florida Department of Health and Rehabilitative Services.

Table 14 gives the results of these analyses. Comparison of these data with the polonium data taken on the USF split of each sample indicates that the depth relationship is not clearly represented. Lab 4, in particular, seems to report low results.

In order to evaluate these laboratory results, two comparisons can be made. First, if gross-alpha radiation reflects radium-226 and its kin, then one would expect a crude linear relationship between the two variables. Figure 5 illustrates the relationship for these data. Note that there is no correlation in the data at all. This lack of a systematic relationship could be the result of one of the uranium daughters, such as radon, radium, or polonium, breaking the equilibrium chain or it could be due to sampling and/or analytical error.

A simple test of analytical validity can be made by comparing the reported gross-alpha radiation with polonium activity, which we have determined to be the major cause of the gross-alpha anomaly. Figure 4C illustrates this comparison. Note that the 1:1 ratio line indicates equal activities of the two variables. Clearly, if recovery of all radionuclides is efficient, the gross-alpha activity must be greater than the polonium activity, which constitutes part of the gross-alpha radiation. Therefore, only those samples that fall above the 1:1 ratio (gross-alpha greater than polonium activity) are realistic. Those samples that fall below the line have low gross-alpha activities compared to the polonium we report.

One cannot say that these inconsistencies are a result of the analytical laboratories alone. Samples from four different laboratories fall below the line. One laboratory, which reported analyses for two different companies, had a sample on each side of the 1:1 ratio line. One laboratory, which did work for two different companies, had both samples below the line and these samples were also inconsistent with the depth relationship in polonium (Figure 3), so sampling and sample preparation are questionable. In this latter case, however, the sampling method produced small reductions in recoverable polonium activity compared to the gross-alpha activities reported.

Therefore, the analytical procedures used contribute to the uncertainties in determining radiation in recharge wells. With the

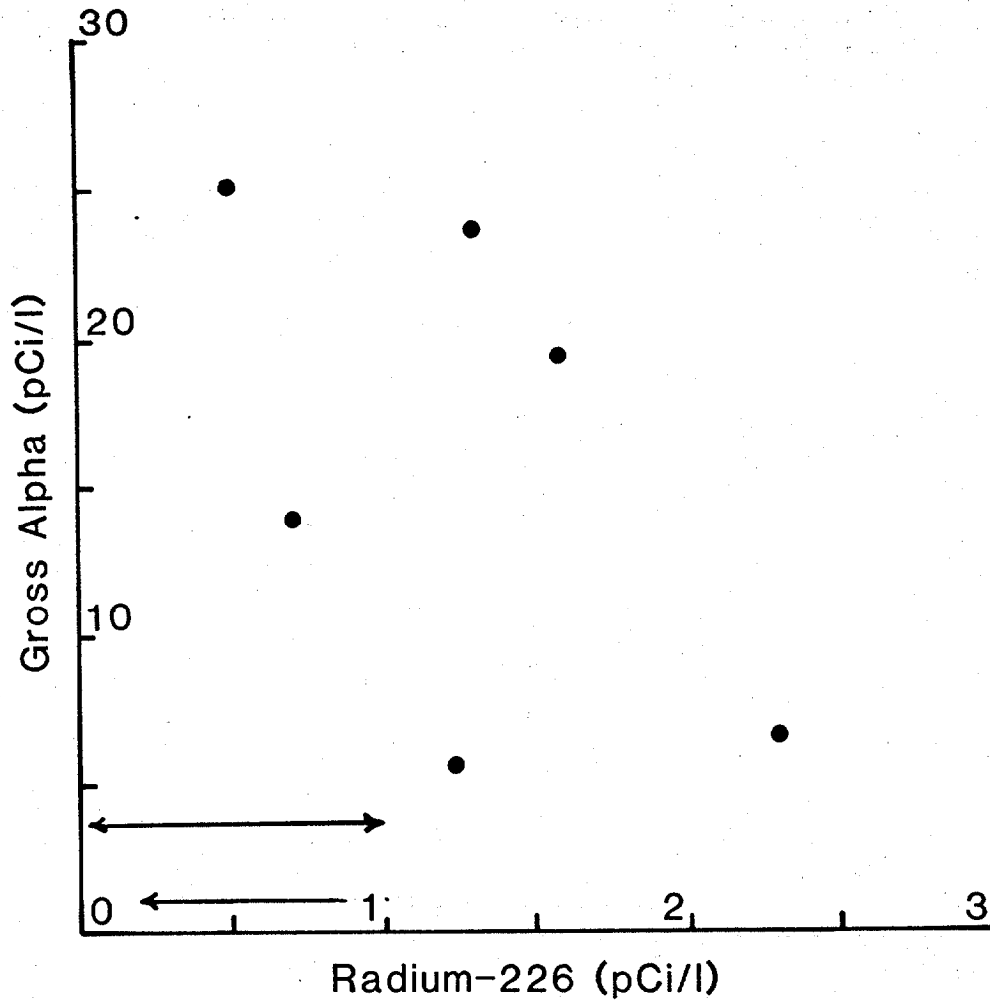


Figure 5

Relationship of gross-alpha and radium-226 activities in company-collected and commercial laboratory-processed samples. The lines represent "less than" activities (e.g., less than 1 pCi/l, etc.).

Table 14. - Results of the commercial laboratory analyses of radium-226 and gross-alpha radiation. See Table 11 for details of sample preparation.

Comp. No.	Lab. No.	Depth (feet)	Gross-alpha radiation (pCi/l)	Radium-226 (pCi/l)
1	1	50	19.3 +/- 2.5 *	1.58 +/- 0.25 *
2	2	50	6.5 +/- 1.9	2.3 +/- 0.2
3	2	75	13.9 +/- 2.3	0.7 +/- 0.1
4	3	78	25.0 +/- 1.6 * 23.6 +/- 1.6 **	0.5 +/- 0.8 * 1.3 +/- 0.1 **
5	4	90	less than 1	less than 1
6	4	100	3.7 +/- 1.1	less than 1
7	5	150	5.6 +/- ???	1.22 +/- ???

* Reported as filtered upon collection. See Table 11.

** Reported as non-filtered.

exception of the results of one laboratory (Lab. No. 4), it appears that these uncertainties are less than those introduced by sampling.

Comparison of Gross-Alpha, Radium, and Polonium Data

We are quite confident of our data. Use of replicates (in which the results were within the limits of the counting statistics), spikes of known activity (which serve as internal calibration and recovery tracers), and well accepted methods insure this confidence. Thus, comparisons can be made with gross-alpha and radium data submitted by the companies' laboratories.

Radium and uranium activities remained consistently low when compared to polonium-210 activity. For identical field procedures, our average activity for total uranium was 0.36 pCi/l; for radium-226 it was 3.29 pCi/l; and for polonium-210 it was 19.98 pCi/l. Since all other alpha activity is much lower than the above, a close approximation of gross-alpha activity can be obtained by the summation of radium-226 and polonium-210 activities.

Summary of Industry Procedures

Sampler - It appears that, with the exception of two sampling devices, all of the samplers produce reliable results. The air-lift system used by company 6 clearly does not provide a representative sample. Use of a bailer is less clearly incorrect. The variability introduced by use of a bailer appears to be a result of accumulation of debris from the sides of the well or from sampling stratified water in the cascading zone. In order to avoid these uncertainties, a closed sampler should be used.

Sample Depth - Depth of sample collection introduces the greatest systematic variation in the samples. Polonium-210, and therefore gross-alpha radiation, decreases with depth in the well. In order to compare well data and impose uniform criteria, it is necessary that a standardized depth of sampling be adopted.

There are arguments to be made for sampling at a number of different depths. The object of these sampling strategies is to sample the recharging water before contact is made with the receiving water in order to protect the receiving-water aquifer. These strategies are summarized below:

1. Monitor wells - For water quality management, the optimal procedure would be to establish monitor wells in the surficial aquifer within the cone of depression of the

recharge well. Several wells would be required and the cost of installation and monitoring is unrealistic.

2. Sample at standing water - The first horizon in the well where well-mixed water, which closely reflects the surficial-aquifer water cascading into the well, can be sampled is just below the top of the potentiometric surface -- just below standing water. This position in the well allows minimum mixing with Floridan water. The disadvantage of sampling in this position is that it does not allow identification of any chemical reactions that occur in the recharge well with depth. Sampling at this horizon is recommended as alternative 1.
3. Sample at bottom of casing - Sampling at the bottom of the casing has the advantage of providing a measurement of the quality of water where it first comes in contact with the Floridan aquifer. Because there appear to be some chemical reactions in the recharge well, this is a horizon sensitive to the ultimate quality of water in the Floridan. Sampling at this horizon has the additional advantage of providing industry with a zone in which water-quality improvements can be demonstrated. In effect, it provides a mixing/reaction zone outside of contact with the rock of the Floridan aquifer. Sampling at this horizon is recommended as alternative 2.

Sampling depth should be closely coordinated, so that the data from different companies can be compared. Sampling of cascading water, while conceptually the best way to evaluate the water being introduced to the Floridan, is fraught with uncertainties and should be discontinued.

Sample Preparation

Sample preparation has been previously discussed. All samples should be treated in the same fashion. Immediate filtration on a 0.45 micron micropore filter, and then fixation with 2%, by volume, nitric acid was recommended as in interim procedure. Additional tests must be undertaken to determine if this is sufficient to prevent volatilization of polonium through reduction. These interim procedures conform with present standard methods.

Laboratory Analysis

If the samples are prepared properly, there should be no loss of polonium by volatilization and gross-alpha-analysis should be adequate for evaluation of the radiation environment of the wells. It is clear that some of the laboratories used in this study report unusually low or inconsistent activities, even accounting for the variability introduced

by sampling. Blind standard samples, such as E.P.A. check samples, with known gross-alpha and radium-226 activities and replicate samples of recharge well water should be submitted to all labs as a matter of routine. If the replicates do not overlap or if the blind standards are not correctly analyzed within counting error, then laboratory procedures must be investigated and, possibly, a change in analytical services undertaken.

ORIGIN OF THE GROSS-ALPHA ANOMALY

Disequilibrium in Uranium Daughters

As has been demonstrated, the gross-alpha anomaly is due to the disequilibrium between polonium-210 and its predecessors in the uranium-238 decay series. The cause of this disequilibrium is discussed in this section.

For any particular daughter 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 next daughter. A condition of equilibrium is achieved if the entire series is contained in a chemically and physically closed system over a long period of time. This decay equilibrium is maintained only if the system remains undisturbed.

In aqueous systems (e.g., ground-water systems) chemical reactions, such as ion exchange, chemical complexing, and equilibration reactions with minerals, 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).

Uranium Chemistry and Migration

In general, uranium, which is polyvalent, is most soluble in oxidizing waters where the hexavalent uranyl ion can form (Langmuir, 1977). Uranyl complexes with fluoride, phosphate, sulfate, and carbonate form under these conditions. In the reduced tetravalent state, uranium is relatively insoluble and ion exchange and mineral precipitation occur.

Radium Chemistry and Migration

Radium enters ground water through ion exchange, recoil, and mineral dissolution in acid environments. Changes in ionic strength and competition for sorption sites encourages release of sorbed radium into ground waters.

Radon Chemistry and Migration

Because radon is a noble element incapable of sorption or equilibration with mineral phases, considerably greater disequilibrium occurs with respect to its precursors and its daughters. Radon-222 is an inert, radioactive gas with a half life of 3.8 days. It is the sixth

decay product in the uranium-238 series and occurs in ground water in widely varying concentrations. Radon can migrate through porous media by diffusion and by the flow of fluids. Activities of radon in ground-water systems vary from a few picoCuries per liter to well over ten thousand.

There are numerous factors that affect the emanation of radon into ground water and soil atmospheres. At the rock or soil pore-space scale, radon in the pore water may be approximately equal to that 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 in these studies 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 (Rama and Moore, 1984).

Rama and Moore (1984) attempted to understand the mechanism of release of radon and other uranium- and thorium-series isotopes into ground water. Their experiments show 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) radon must be coming out of the mineral phase in other ways. Rama and Moore (1984) 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. Migration of radon-222 and its progeny through nano-, micro-, and macropores is not well understood. The process, however, allows the isotopes to accumulate in pores in relatively high concentrations.

Radon can migrate from pore to pore under certain conditions and additional accumulation may result. Several workers (Tanner, 1964; King, 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).

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 the radon distribution in springs and found that about 40% of the radon is lost within 4 ft. of the spring emergence. Belin (1959) related radon solubility to pH and residence time in contact with rock sources. Andrews (1972) has related radon in ground water to rainfall. He suggested that soil moisture dissolves radon, which is then transported in the direction of flow.

Radon can diffuse upward through porous strata. The presence of fractures or other pathways of increased porosity and/or permeability encourages migration. Radon detection has, therefore, been used to locate faults and fractures (Stothart, 1948; Israel and Bjornsson, 1966, Chiang, 1977). Israel and Bjornsson (1966) suggested that, in the vadose zone, diffusion controls radon migration. Diffusion coefficients may be as great as $1 \times 10^{-2} \text{ cm}^2/\text{sec}$, depending on porosity, permeability, and soil moisture. They argued that in phreatic environments the diffusion coefficient is less than a $1 \times 10^{-5} \text{ cm}^2/\text{sec}$., therefore radon would decay through many half lives before it traveled 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. The impact of flow in systems influenced by wells is unknown. Recharge wells may encourage some accumulation of radon gas.

Therefore, there is good evidence that radon gas can migrate in ground-water systems. There should be a radon concentration gradient in the surficial aquifer. Well use may or may not alter the distribution of radon in the surficial aquifer, but there are several possible consequences 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, areas of the aquifer. Second, production of a cone of depression in the surficial aquifer by artificial recharge alters a portion of the aquifer from phreatic to vadose. This change in regolith pore filling (water to atmosphere) may have an impact on the radon distribution and on the distribution of sorbed, reactive parents and daughters of radon.

Polonium Chemistry and Migration

Little is known about the chemistry and migration of polonium and lead in ground-water systems. Decay proceeds rapidly from radon-222 to lead-210 (half life = 22 yrs.). Thus, lead is made available for transport by radon release and it may exist in solution in pores or sorbed on pore walls. This lead essentially controls the fate of its granddaughter, polonium-210. Lead is strongly sorbed on silicate clays, carbonate mineral grain surfaces, and on organics. As discussed above, polonium is also easily sorbed, but reduction of the polonium may volatilize it and formation of chemical complexes may mobilize it. Either process can cause the polonium to enter the water column.

Given the ground-water system chemistry of Florida's phosphate industry recharge wells, it appears that lead-210 and polonium-210 should be sorbed in a restricted space around the recharge well. Thus, there is little reason to suspect that recharge wells are impairing the quality of Floridan aquifer water with respect to radiation. We will propose, as a continuation of this study, to track the fate of lead-210 and polonium-210 in the Floridan aquifer and to construct chemical models to

predict the sorption and equilibrium reactions that govern transport of these and the other uranium-daughter isotopes.

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Appendix A

SPECTRUM ANALYSIS SOFTWARE

Gamma Spectroscopy Program Description

Tracor Northern's Automatic Isotope Analysis (AIA) program is designed to locate peaks in a gamma-ray spectrum, to identify those radionuclides that are present, and to calculate the activity in picoCuries associated with each identified nuclide (Tracor Northern, 1980). The program actually consists of three individual FLEXTRAN programs which are executed in sequence to perform the complete analysis. These programs are called the Control Calculation program.

The function of the Control program is to initialize parameters required for the subsequent data analysis.

The Peak Search program automatically locates and measures positions and intensities of photopeaks in a gamma-ray spectrum. Peaks are located by passing a digital filter through the spectrum channel-by-channel. The effect of the filter is to reduce the background portion of the spectrum to a level near zero but leave the peak. The program uses a non-linear least-squares fitting procedure to obtain peak parameters from the background-corrected data points of a located peak.

The Activity Calculation program makes use of a previously established isotope table to match known gamma-ray energies of the radionuclides of interest with observed photopeak energies found during the peak search. When a match occurs, the activity of the radionuclide is calculated by the equation:

$$pCi = \frac{N}{2.22 \cdot \epsilon \cdot I_{\gamma} \cdot t \cdot V} \quad (1)$$

where pCi = activity in picocuries

N = net counts in the photopeak

2.22 = conversion factor from dpm to picocuries

ϵ = detector efficiency

I_{γ} = % gamma-rays per disintegration

V = sample volume

t = acquisition live time.

In order to obtain the activity for an isotope that has more than one associated photopeak in the spectrum, a least-squares analysis is performed on the experimental data. Equation 1 is written in form:

$$(N/\epsilon)_i = k(I_\gamma)_i \quad (2)$$

where i denotes the i^{th} identified gamma-ray of the radionuclide, and

$$k = \text{pCi} \cdot 2.22 \cdot t \cdot V \quad (3)$$

The value of k is constant and is determined from:

$$k = \frac{\sum_{i=1}^n \frac{1}{\sigma_i^2} (N/\epsilon)_i (I_\gamma)_i}{\sum_{i=1}^n \frac{1}{\sigma_i^2} (I_\gamma)_i^2} \quad (4)$$

where σ_i = counting error of $(N/\epsilon)_i$

and n = the number of transitions identified for the nuclide.

The weighting factor is:

$$\text{WT} = \frac{1}{\sigma_i^2} (I_\gamma)_i \quad (5)$$

and an estimate of the error is then:

$$\sigma_k^2 = \frac{1}{\sum_{i=1}^n \frac{1}{\sigma_i^2} (I_\gamma)_i^2} \quad (6)$$

The activity, in pCi, is calculated from equation 3 by using k evaluated from equation 4. The statistical error in the activity is calculated from the propagation of error in equation 3.

Alpha Spectroscopy Program Description

Evaluation of spectral lines in complex alpha spectra is made difficult by sample-to-sample variations in peak-position and peak-shape. Good chemical separation and sample deposition techniques help minimize effects of noise, interferences, peak shifting and broadening. It is

difficult to design a program that deals in general with all possible sample variations. For this reason we developed a program designed specifically for the analysis of uranium and polonium isotopes.

Alpha Spectrum Analysis - Uranium - Our Alpha Spectrum Analysis (ASA) program for uranium is designed to locate peaks due to U-238, U-235, U-234 and U-232, to define peak limits, subtract that portion due to interference and background, and determine the activities of the uranium isotopes by comparison with a known amount of radioisotope spike; U-232. The program is user interactive so that the peak limits can be adjusted to accommodate for inter-sample variability in peak parameters. A five-point average is calculated for the base line at both the high and low energy ends of the peak, and background is determined by summing the counts below the line joining these points. Peak widths are generally between 50 to 60 keV full-width at half-maximum. Evaluation of the U-232 is a bit more complicated.

Uranium-232 is a radioisotope that does not occur naturally. It decays by alpha emission to thorium-228 and progeny which are members of the naturally-occurring thorium decay series (Appendix B). Chemical separation techniques are not effective in entirely removing the thorium-228 and daughters and they may appear in the spectrum. The complication arises because U-232 and Th-228 have decay energies of 5.28 and 5.34 MeV respectively and the peaks cannot be sufficiently resolved.

Rather than use a very complicated deconvolution algorithm in order to determine the counts in the uranium-232 peak attributed to the thorium, the nature of the thorium-228 decay is exploited. At secular equilibrium the thorium daughters must decay at the same rate as their parent, Th-228. A spectrum will, therefore, contain the same number of counts in the higher energy, thorium-228 daughter peaks as are in the unresolvable U-232 - Th-228 spectral line. The Th-228 daughter chosen for this analysis is polonium-216 at 6.78 MeV. This is a clean, high-energy spectral line with no interferences. Secular equilibrium with thorium-228 is achieved after approximately 36 days based on the cumulative half-lives of the thorium daughters to Po-216. The U-232 - Th-228 peak is evaluated as described and the gross counts in the Po-216 line are included as background and subtracted from the U-232 - Th-228 peak. The net counts calculated for the U-238, U-235 and U-234 peaks are compared to that of the U-232 peak and the activities are derived. The standard deviation associated with the quoted activities is due to counting statistics alone and is given by:

$$\sigma_{(U-234,235,238)} = A_s \sqrt{\frac{C_n^2 (SC_g + SC_b)}{SC_n^4} + \frac{(C_g + C_b)}{SC_n^2}} \quad (7)$$

where C_g , C_b , C_n = gross, background and net counts for U-234, U-235 and U-238;

SCg, SCb, SCn = gross, background and net counts for
spike, U-232; and

As = spike activity in pCi/l.

Alpha Spectrum Analysis - Polonium - The Alpha Spectrum Analysis program for polonium is designed to operate in the same way as for uranium. The polonium isotope used for comparison is polonium-209. The advantage of using this isotope over the more commonly used polonium-208 is that the energy at which Po-209 decays is sufficiently low to be completely resolved from the Po-210 being measured. Errors are calculated from equations similar to equation 7.

Appendix B

DECAY SERIES DATA FOR URANIUM-238

THORIUM-232 AND URANIUM-235

THE URANIUM SERIES

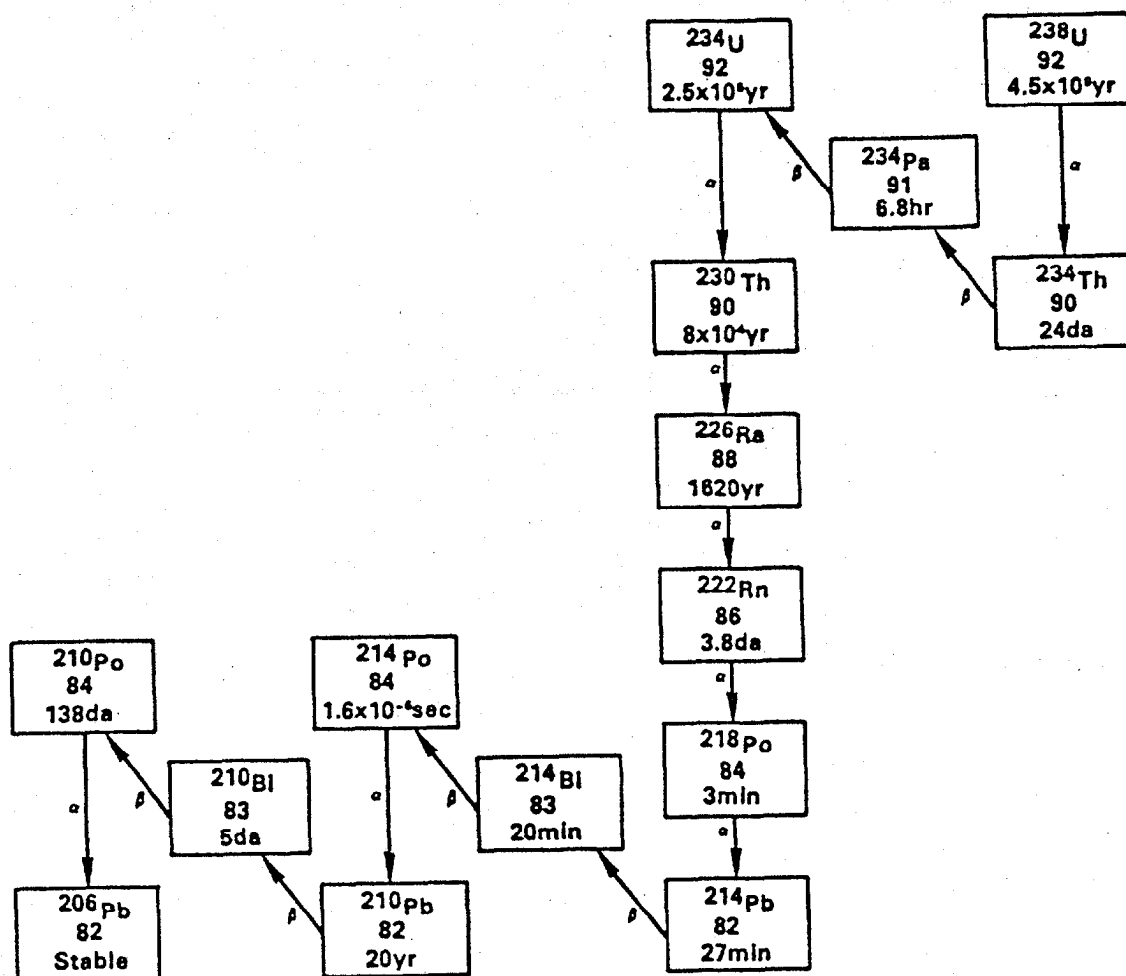


Figure 6A

Decay series data for uranium-238.

THE THORIUM SERIES

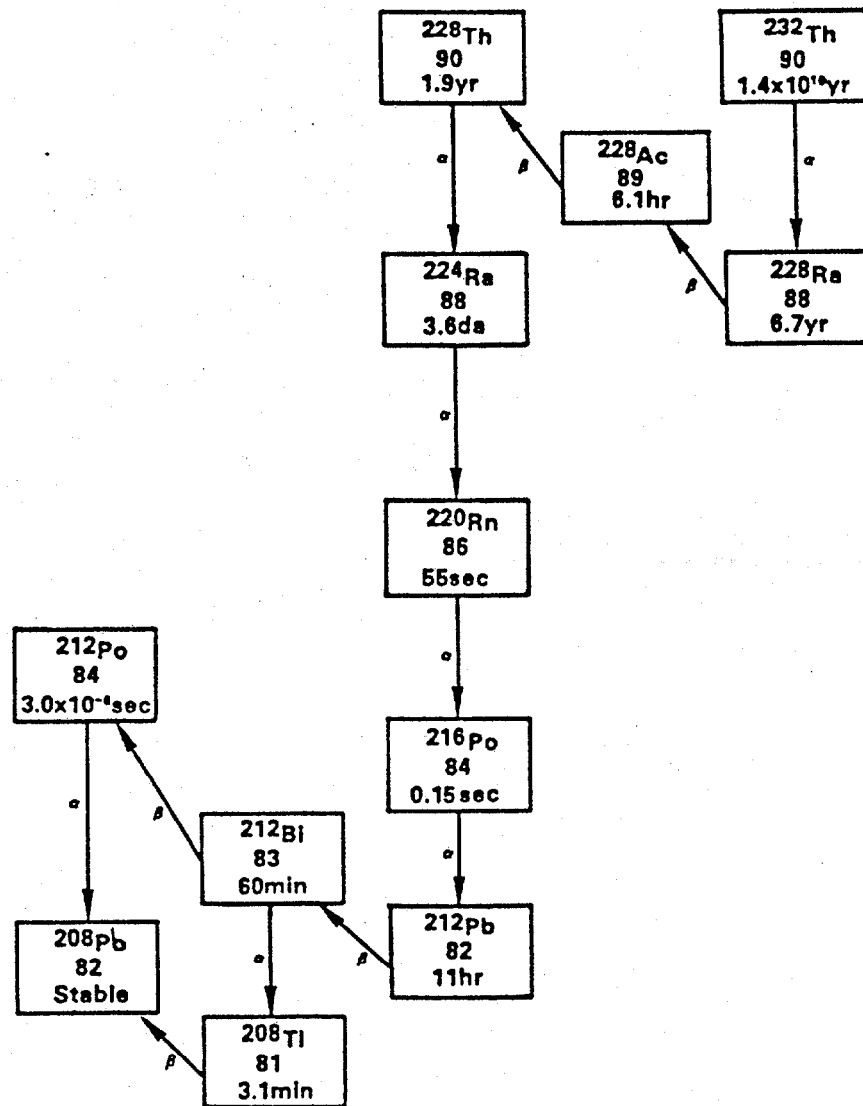


Figure 6B

Decay series data for thorium-232.

THE ACTINIUM SERIES

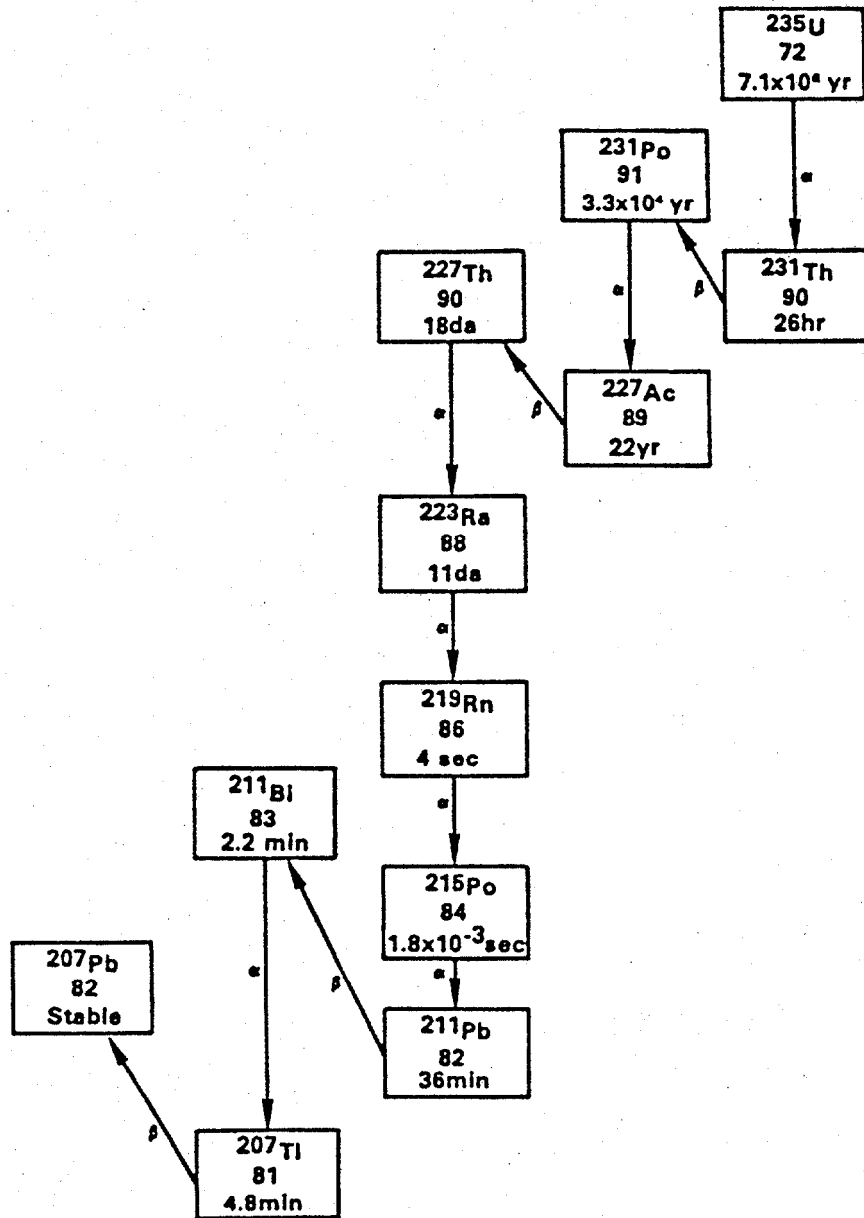


Figure 6C

Decay series data for uranium-235.

Appendix C

CHEMICAL PROCEDURES

Preconcentration and Purification of Uranium

Approximately ten liters of sample volume are needed for the chemical analysis of uranium. The sample is acidified with hydrochloric acid sufficient to yield a pH of at least one. The sample is spiked in the laboratory with 10 pCi U-232 (1 pCi/l) and 2 ml/l iron carrier is added in the form of ferric chloride (concentration: 12.5 mg/l). After equilibration for a minimum of ten days, the pH is brought to ten by adding concentrated ammonium hydroxide. With the change in pH, a gelatinous, ferric-hydroxide precipitate forms which quantitatively scavenges the dissolved uranium. After 24 hours, the sample is passed through two Whatman #4 filters where the precipitant is trapped. It is then dissolved and transferred into a 600 ml beaker from the paper by a jet of 1N HCl. The acid solution is boiled to 5 ml, then brought up to 50 ml with 8N HCl.

Ion Exchange Procedure - The separation of iron and uranium from the bulk of the other elements commonly occurring in water is made possible by the fact that these elements are able to form anionic complexes in strong hydrochloric acid, so that they are adsorbed in an anion exchange column. Alkalis, alkaline-earths, thorium, and other elements pass through the column (Veselsky, 1973). In very dilute hydrochloric acid solutions, however, the complex ions UO_2Cl_4^- and FeCl_4^- are not stable and uranium and iron can be eluted from the column with HCl of appropriate concentration.

Dowex AG 1-X8 anion exchange resin, 50-100 mesh, chloride form, purified and sized by Biorad Laboratories, Richmond, California, is used. The ion exchange columns contain a bed of resin 1 cm by 15 cm, capped with a 50 ml reservoir and plugged at the bottom with glass wool. The column is equilibrated with four volumes of 8N HCl and the sample is passed through. The iron and uranium remain on the column, and much of the thorium and radium can be made to pass by flushing with four volumes of 8N HCl. The iron and uranium are eluted with four volumes of 0.4N HCl.

Solvent Extraction - The iron and uranium fraction is boiled to near dryness, then brought to a volume of 5 ml with 8N HCl. The iron is extracted with isopropyl ether by combining 3 ml ether with the acid solution. The solution is mixed, then centrifuged, and the bottom, colorless layer is extracted. The ether extraction may be repeated if the iron is not completely removed.

The solution is boiled to dryness and 3 ml AlNO_3 saturated in 4N HNO_3 is added with 3 ml ethyl acetate. This is mixed and centrifuged and the bottom layer is discarded. This aids in removing salts which would increase the thickness of the final source. To the ethyl acetate and uranium solution is added 7 ml distilled/deionized water, the solution is mixed and centrifuged and the uranium and water are removed. The pH is adjusted to 3.5.

Thenoyltrifluoroacetone (TTA) reacts with uranium to form a chelate which can be extracted from aqueous solutions of pH 3 or higher. The extractant used is 0.5 M TTA dissolved in benzene. The uranium is extracted by adding 3 ml TTA/benzene, mixing and centrifuging. The top layer is mounted by slowly dripping the solution on a stainless steel planchet at approximately 200°C. The planchet is then flamed to just under red in order to burn off residues, and is then ready for counting.

Separation of Polonium-210

One to two liters of sample volume is needed for the chemical analysis of polonium. The sample is acidified with 1.5 percent by volume nitric acid, is spiked in the laboratory with 203.0 pCi Po-209 and the ferric chloride carrier is added. The sample is left to equilibrate for at least ten days. After this period, the polonium is coprecipitated with ferric hydroxide. The precipitate is caught on Whatman #4 filter paper and then dissolved and transferred into a 600 ml Teflon beaker with a jet of 1N HCl. The sample is brought to 200 ml with 1N HCl, and 100 mg hydroxylamine hydrochloride along with 100 mg ascorbic acid is added. The hydroxylamine hydrochloride eliminates interference from oxidants and the ascorbic acid is found to facilitate plating. The solution is stirred with a Teflon paddle and heated to 85°C. After 15 minutes a polished silver disk, 7/8 inches in diameter, is placed into the solution. The plating involves the spontaneous deposition of both Po-209 and Po-210 onto the silver. Plating continues for 1.5 hours at which time the disk is removed and rinsed with distilled/deionized water and methanol, labeled and counted.

Radium and Thorium Isotopes

Radium and thorium isotopes are quantitatively scavenged from ground water by passing the water through manganese-impregnated acrylic fibers following the method of Moore (1975). The fiber is made by placing approximately 5 grams of Monsanto (ACRILAN, 3.0 denier, type B-16) acrylic fiber in one fiber volume of 0.5 M potassium permanganate solution at 75°C. The solution partially oxidizes the fiber and deposits manganese dioxide on it. The reaction is stopped after 10 minutes by removing the fiber and washing it in distilled/deionized water that has been cleaned of radium and thorium isotopes by this process.

No less than ten liters of sample volume are usually required for this analysis. Since the water is preserved with acid in the field, the pH must be adjusted to approximately seven (6 to 7.5) just prior to

processing. The fiber is placed in a 50 ml cartridge and stoppered. At each end, the cartridge is designed with openings which are connected to Tygon tubing that allows the water to pass. The water is transferred to a Nalgene carboy with spigot connected to the Tygon tubing and cartridge, and the water is allowed to flow at a rate of less than 100 millileters per minute pass the fiber. We have found this method to be greater than 99% efficient in removing radium from ground water. The fiber is removed from the cartridge and allowed to dry in air for approximately 24 hours.

The dry fiber is ashed in a muffle furnace at 500°C for 5 to 7 hours. The ash is sandwiched in a small metal contained in order to achieve as fine a lamina as possible. This insures a constant geometry by eliminating any effects of spacial distribution of the radioisotopes on the fiber and maximizes the detector efficiency by placing the source as close to the detector's sensitive region as possible.

The analysis of radium-226 by gamma spectroscopy requires special attention. Although Ra-226 has a gamma decay, the energy at which it decays is very nearly that of a U-235 gamma decay. Detector resolution is not sufficient to distinguish the peaks. In order to analyze Ra-226, secular equilibrium with its immediate daughters is achieved (Appendix B) by sealing the fiber in a container for 30 days to allow for ingrowth of radon-222 gas. A metal container is used to prevent diffusion and loss of the radon through the container walls.

Standards Employed

The uranium-232 solution was obtained from Isotope Products Laboratories, Burbank, California, and calibrated against a standard uranium-238 solution obtained from the Quality Assurance Division, Environmental Monitoring Systems Laboratory, U.S. Environmental Protection Agency; Las Vegas, Nevada.

The polonium-209 solution was obtained from the Nuclear Division, Oak Ridge National Laboratories. The standardization was done by the supplier.

The radium procedure was calibrated using a standard radium-226 solution also obtained from the Las Vegas Office of the U.S. Environmental Protection Agency.

Prevention of Recoil Contamination of Solid State Alpha Detectors

When an alpha particle is ejected from the nucleus of an atom, the residue recoils in the opposite direction as a positively-charged ion of the daughter element. If unimpeded, these recoil atoms strike the detector with the same geometry as the alpha particles and are retained quantitatively within the detector (Sill, 1983, p. 45). The recoil products produce alpha spectra that can severely interfere with the measurement of the radionuclides of interest. Use of uranium-232 as an isotopic tracer, for example, can cause a great deal of interference in

polonium-210 spectra by depositing its decay-recoil product, thorium-228 (1.91 years) and daughters, on the detector.

It should be possible to exploit the physical properties of alpha particles and recoil atoms and to select an absorber sufficiently thin to permit alphas to pass, yet significantly reduce the number of recoil atoms reaching the detector. Most commercial films are so thick that the alpha spectra are degraded untenably. In contrast, any desired thickness of absorber can be easily and conveniently obtained by merely adjusting the air pressure inside the spectrometer chamber (Sill and Olson, 1970). Figure 7, and Table 15 from Sill and Olson (1970), show the effect of various thicknesses of air on the resolution and peak position of a Po-210 source.

Air pressure alone is not sufficient to reduce recoil contamination on detectors. The air pressure is necessary to absorb the recoil energy and bring the atoms to rest but the residual atoms are positively charged and are attracted toward the detector because of the charge existing on the detector use. Only a slight negative potential is required to attract the positive ions back to the original plate (Sill and Olson, 1970).

Air pressure is easily controlled by using a Cartesian diver (Gilmont instruments, Inc., Great Neck, N.Y., catalog no. C2100), which was installed in our vacuum line to automatically limit the evacuation of the chamber to about 45 mm Hg. With a source to detector distance of 0.5 cm, our air thickness is about $37 \mu\text{g}/\text{cm}^2$. An absolute pressure gauge reading from 0 to 150 mm of mercury is also installed to monitor the pressure of the system. The negative potential is supplied by a 5.6-volt mercury battery (Duracell No. PX23B) installed on a brass source holder and connected to ground by contact with the aluminum rack which holds the source holder in the vacuum changer (Figure 8). The negative pole is in contact with a fitted source plate, insulated from the source holder by a coat of epoxy. The stainless steel planchets are placed in the source plate which supplies the negative potential which attracts the positive recoil ions.

Table 15. Effect of air pressure on resolution, counting rate, and apparent energy of polonium-210. (From Sill and Olson, 1970)

Air pressure mm Hg	Air thickness $\mu\text{g}/\text{cm}^2$	FWHM keV	Total Cnts. ($\times 10^4$)	Apparent energy MeV
0.1	0.3	18	3.25	5.305
0.5	...	...	...	...
1.0	...	19	3.27	5.305
2.0	...	...	...	...
3.0	...	...	...	...
4.0	...	...	...	...
5.0	...	...	...	...
6.0	...	...	...	...
7.0	...	...	...	...
10	30	21	3.25	5.296
20	60	24	3.29	5.278
50	150	31	3.25	5.224
100	300	47	3.26	5.116
150	450	61	3.24	5.008
200	600	73	3.25	4.927
250	750	90	3.23	4.828

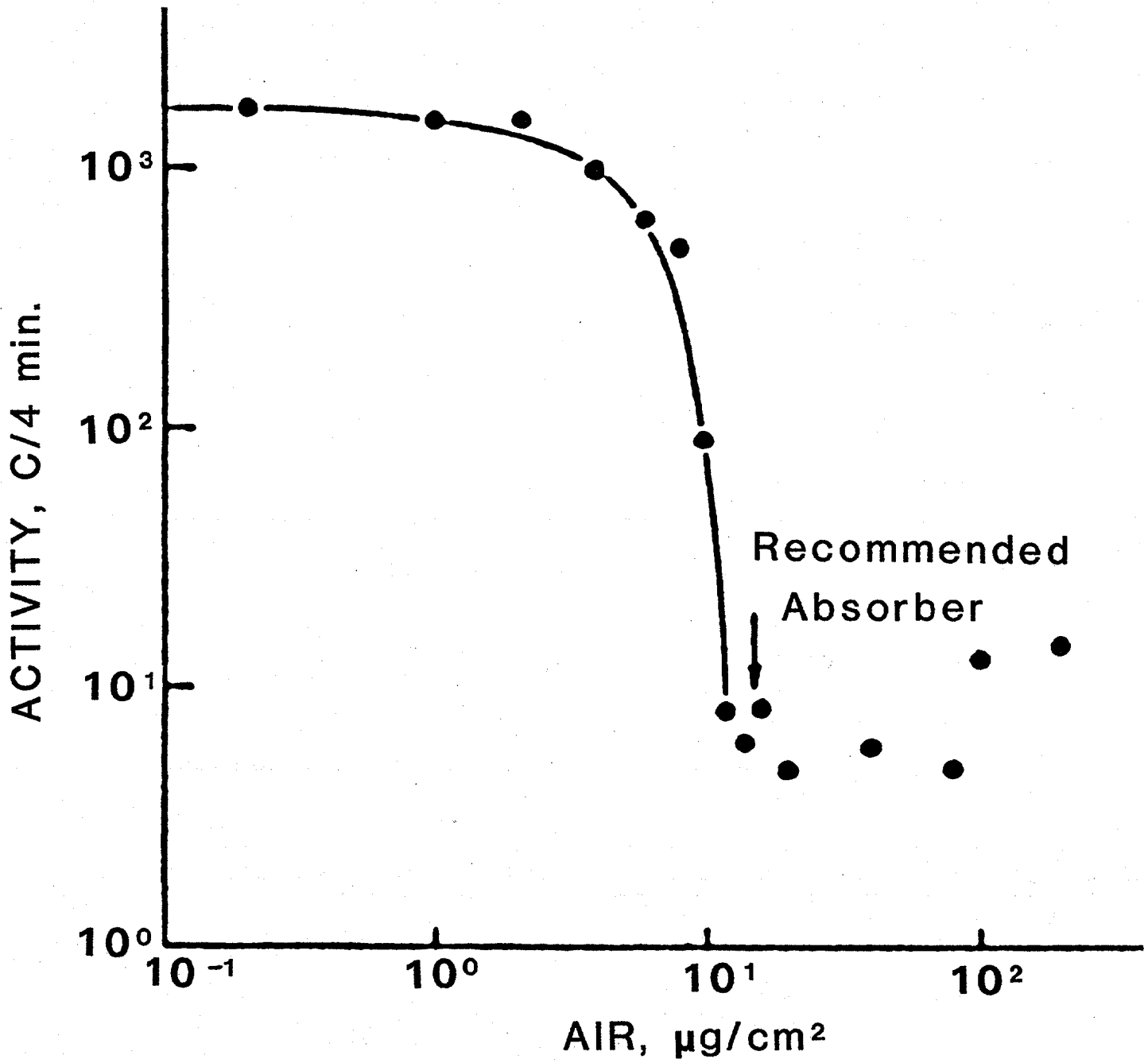


Figure 7

Decrease in recoil contamination of FR-221 with increasing air pressure. (From Sill and Olson, 1970).

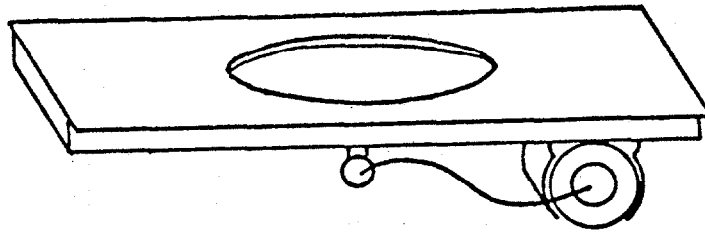


Figure 8

Source holder for prevention of alpha recoil contamination.

Appendix D

FIELD EQUIPMENT

Millipore Filtration Apparatus

A 2.4 liter commercial filtration unit was purchased from Geofilter; Leonard Mold and Die Works, Inc.; Denver, Colorado. This portable, plastic, pressure-filtration unit greatly facilitates rapid micropore membrane field filtration of up to several liters of water. Vacuum filtration is neither efficient nor practical when the operation must be accomplished in the field. This pressure filter can be more easily operated in the field and is much more effective.

The filter unit (Figure 9) consists of two separable sections: a bottom flange and filter support (A) and sample reservoir (B). The filter assembly consists of a prefilter (1), O-ring (2), 0.45 μm membrane filter (3), filter support screen (4), and polycarbonate center support (5).

Sampling Devices

Two well samplers were constructed in order to retrieve water from various horizons within the well. Both are formed of 4" i.d. PVC pipe. The open bailer (Figure 10) is designed to collect water which enters through the well screens and cascades to standing water. The closed thief (Figure 11) is designed to capture water at a specific depth. This sampler remains open throughout its journey down the well, allowing water to pass through and flush the open pipe. At the desired depth the sampler is closed, capturing water from that horizon, by pulling the rope and lifting the thief to the surface.

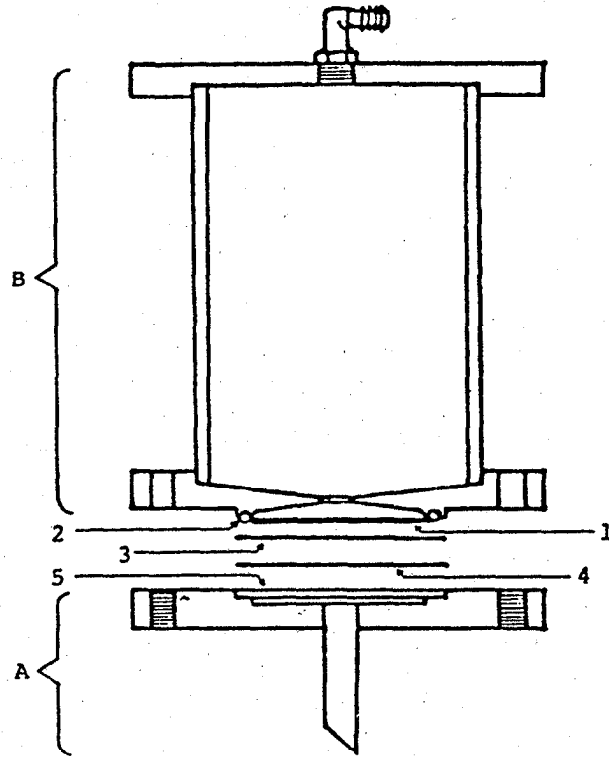


Figure 9

Pressure filtration unit.

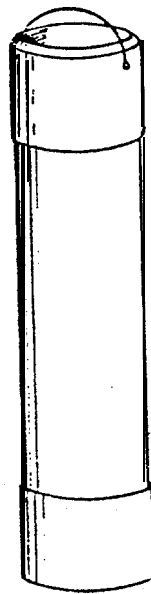


Figure 10

Open bailer for capturing cascading water.

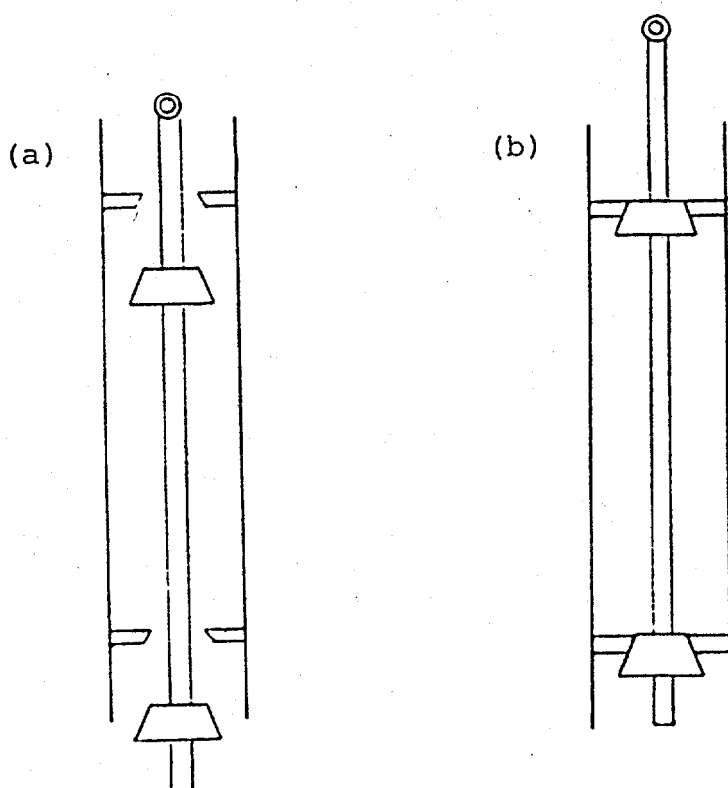


Figure 11

Cross section of closed thief sampler. Illustrations (a) and (b) represent the opened and closed configurations of the sampler, respectively.

Appendix E

LITHOLOGIC LOGS OF WELL 98B CORES

Lithologic Log Of Core 98-SW, IMCC Kingsford Mine

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.

Depth (ft.)	Field description (SW-# = sediment sample number)
<u>Plio-Pleistocene Undifferentiated</u>	
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 Formation (Pliocene)

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 is the ORE matrix; Sw-16 @ 53'.
- 56-57.5 CLAY, blue-green and brown mottled, cohesive, approx. 50% phos.; SW-17 @ 56, SW-18 @ 57'.
- 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'.

Hawthorn Formation (Miocene)

- 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

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.

Depth Field description (NE-# = sediment sample number)
(ft.)

Plio-Pleistocene Undifferentiated

5-6	SAND, fine grained, iron stained, wet.
6-9	SAND, fine grained, argillaceous, 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 sand; 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 Formation (Pliocene)

- 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'.

Hawthorn Formation (Miocene)

- 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, hackley 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'	