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RELEASE OF RADIUM AND OTHER DECAY-SERIES ISOTOPES FROM FLORIDA PHOSPHATE ROCK

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FLORIDA INSTITUTE OF PHOSPHATE RESEARCH

RELEASE OF RADIUM AND OTHER DECAY-SERIES ISOTOPES FROM FLORIDA PHOSPHATE ROCK

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FINAL REPORT

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DISCLAIMER

PERSPECTIVE

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One of Florida's great natural resources is an abundance of natural phosphate rock. While especially rich deposits of the ore are found in central Florida in what is known as the "Bone Valley Formation," lower grade deposits are extensive throughout much of the state in the "Hawthorn Formation." It has been known for many years that phosphate ore contains 50 to 150 parts per million (ppm) of natural uranium, and hence its radioactive decay products, when compared to most other soils and rocks, which average 1 or 2 ppm. It is generally believed that uranium replaces the calcium in the apatite mineral. A fundamental question arises as to the nature of population exposure to natural radiation - primarily radium and its progeny within the uranium decay chain - and how that exposure is influenced by the presence and extraction of deposits of phosphate. To more completely understand exposure pathways, one must know something of how radium and its daughters are incorporated into phosphate rock, how they are released, and what factors affect their mobility.

It is generally conceded that the major environmental radiation exposure to the public is due to the short-lived decay products of radon gas, itself the daughter of radium. Just recently the state completed one of the largest surveys of indoor air pollution ever made - a survey of over 6,000 Florida homes for the presence of radon. Definite evidence of elevated radon potential was found in parts of some 18 counties, fairly closely matching the extent of the Bone Valley and Hawthorn geological formations. Earlier, concern had focused on relatively high levels of radium found in shallow drinking water wells in central and southwest Florida. Also, researchers at the University of South Florida and Florida State University had shown that polonium could be a radioisotope of concern in water supplies. There seems little question that the ultimate source of these nuclides is the uranium-enriched phosphatic strata common in Florida. On the other hand, many analyses of radionuclides in air and water even in central Florida have shown only low to moderate activities. These disparate findings suggest that it would be valuable to understand how and under what conditions uranium daughters become mobilized. If radioactive decay were the only determinant factor,. the daughters should occur in radioactive equilibrium. In reality, this almost never happens; daughter nuclides may be partitioned by chemical and physical means during natural weathering. Mining operations do not appreciably alter the natural pattern of radionuclides except in the pit and spoil areas themselves. The aquifers do not seem to be radiochemically disturbed. As a result of phosphate mining and processing, most radioelements are distributed in the waste clays, phosphate products, and by-product gypsum.

This present research at Florida State University addresses four questions:

(1) How are radionuclides incorporated into phosphate rock?

(2) Under what conditions are these radionuclides released to their surroundings?

(3) What transport paths do the isotopes take following their release?

(4) To what extent is polonium (Po-210) an isotope of concern in drinking waters of central Florida?

This work by Dr. Burnett and his associates found that weathered samples of phosphatic materials tend to have higher radionuclide activity than fresh samples, and that in weathered samples the activity appears concentrated in the very smallest and very largest particle size classes. Likely this is due to increased adsorption onto the greater surface area of small particles, and to the enhanced phosphate content generally found in "pebble" sized fractions. A surprising finding was a deficiency of polonium-210 with respect to its grandparent lead-210, indicating greater mobility of polonium than expected. This aspect deserves further study. These results also show that, unlike uranium and radium, any polonium that is leached from rock and put into solution is easily adsorbed back onto mineral surfaces.

Radon gas is very soluble in water and can migrate considerable distances in groundwater. Being a chemically inert gas, it is less likely than the other radionuclides to be adsorbed onto mineral surfaces. The presence of moisture was found in this study to enhance the escape of radon from rock materials, primarily by intercepting recoiling atoms before they could be adsorbed onto other surfaces.

Two environmental field investigations were included in this study. In one, the distribution of radium in the Suwannee River was examined. Radium concentrations were found to be fairly constant over a wide range of water flow conditions. Entry is largely via springs and to a lesser extent surface drainage; phosphate mining in the vicinity of the headwaters of the Suwannee apparently contributes very little radium to the river. In a second study, the investigators examined the surficial aquifer of west central Florida and found polonium levels in excess of public drinking water standards for total alpha activity in more than a fourth of wells tested. High polonium levels in water are associated with moderately high levels of dissolved radon gas, low pH, and the presence of sulfide. These correlations are in need of further study.

While this research has contributed to an understanding of chemical and physical properties affecting the uranium-series radionuclides in soils and water, unanswered questions remain, particularly regarding the chemistry of polonium. While polonium generally is associated with phosphatic strata, anomalous areas of low polonium in mineralized areas and enriched polonium found in non-mineralized areas have been documented, particularly in north Florida shallow groundwaters. Polonium is very "particle-reactive" and, on a national scale, high levels in groundwater are rarely found. Also puzzling is the finding that Po-210 is not supported by its grandparent, Pb-210. Polonium may be more mobile than expected, or the mobility may lie with its immediate parent bismuth-210, despite its rather short half-life. It may be that an observed polonium problem may be, in reality, a bismuth problem. Fortunately, the Institute has agreed to support financially a further two-year study of the polonium issue by the research team at FSU.

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Many people assisted us during the course of this research. We wish to especially acknowledge those people who helped in the field and in the laboratory. The collection of a representative series of weathered phosphate rocks was made possible through the assistance of James Cathcart (USGS), Henry Barwood (FIPR), and Stanley Riggs (East Carolina University). Sampling of springs which drain into the Suwannee River was accomplished with the help of James Cowart. Much of the sampling of the Suwannee River and estuary was made possible by use of the R/V BELLOWS of the Florida Institute of Oceanography. Captain W. Millander and his crew were extremely helpful on these cruises. The Suwannee River Water Management District also provided personnel and small boat support for sampling of the estuary.

Laboratory assistance at FSU was offered by Kee Hyun Kim, Sarah Eitzman, and Kathy Landing. Miriam Kastner and Anne Sturtz (Scripps Institution of Oceanography) made surface area measurements for us on several of these samples. Mineralogical characterization of the phosphatic samples was made at the FIPR laboratory by Henry Barwood and Debbie Herman. We were assisted in the interpretation of other XRD analyses performed at FSU by J.K. Osmond.

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EXECUTIVE SUMMARY

The purpose of this research project, initially funded by FIPR in August 1984, was to determine the conditions under which uranium decay-series isotopes are released from phosphate rock into the environment. We gave particular attention during our research to the behavior of radium, radon, and polonium. This emphasis was justified because of several documented cases citing elevated concentrations of these radio-elements occurring in Florida groundwaters. When it became clear that polonium was occasionally present at exceedingly high concentrations in shallow groundwaters, we expanded the scope of our project to include a study of the distribution of ^{210}Po in the surficial aquifer of west central Florida.

Our research plan took an integrated approach, combining both field and laboratory studies. The five main sections of our final report contain the results of these studies organized as five independent, yet related, projects. The first three chapters report our results of laboratory determinations and experiments concerning the concentration and release of uranium-series isotopes from phosphate rock. The last two chapters are field-oriented studies of the distribution of radium in Florida rivers and polonium in shallow groundwater from west central Florida. Together, these studies may represent one of the most thorough attempts thus far at recognizing the sources and transport paths of radionuclides released from the uranium-enriched phosphatic strata.

Radiochemical and geochemical studies of a series of phosphate rock samples representing various degrees of chemical weathering are the

subject of Chapter 1 of this report. Both bulk and size-fractioned samples were analyzed for several decay-series isotopes including: ^{238}U, ^{234}U, ^{230}Th, ^{226}Ra, ^{210}Pb, ^{210}Po, ^{232}Th, and ^{231}Pa. Our results showed that almost all uranium-series radionuclides display higher activities in weathered samples compared to fresh material. Most samples displayed a ^{210}Pb/^{226}Ra activity ratio less than secular equilibrium because of ^{222}Rn leakage. An unexpected result was the deficiency of ^{210}Po, relative to ^{210}Pb, in several weathered phosphate rock samples. When corrected back to the time of sampling, one sample had an apparent 50% deficiency in ^{210}Po. This result is significant because it implies that polonium, under certain conditions, may be more mobile than lead.

Our studies of individual size fractions separated from the bulk rocks showed that a significant portion (up to 60%) of the radioactivity within weathered phosphate rocks is located within the finest sized material. The activity of uranium and uranium daughters in fresh samples, however, tends to follow the predominant size of the phosphate particles. In general, the radionuclide distributions within phosphate rocks are governed by two processes which occur during intense weathering: (1) increased surface area with enhanced adsorption and thus higher concentrations in the finer material; and (2) transformation of the morphological form and size of the radionuclide-bearing material.

We utilized dried, homogenized splits of the same rock samples for a series of laboratory leaching experiments. The objective of these experiments, reported in Chapter 2, was to determine under which conditions uranium, radium, and polonium might become mobilized. Radon, being a noble gas, was considered a special case and treated separately. Our leaching experiments consisted of reacting powdered phosphate rock samples with a number of solutions chosen to mimic various ground water conditions. Results indicate that uranium is lost from phosphate rock during interaction with humic acid solutions, probably due to formation of uranium-organic complexes. Radium is leached from more highly weathered rock samples by several solutions, including deionized water, ammonium carbonate, ammonium chloride, and humic acids. Significantly, neither of these solutions, nor others which were tested, mobilized polonium beyond that which could be explained by simple dissolution of the sample. The release and transport of polonium, therefore, may be related to a different process than simple chemical leaching.

Experiments were also designed to evaluate the loss of ^{222}Rn from several bulk and size-fractioned samples of Florida phosphate rock as well as a few granite samples from New Hampshire. Results of these experiments, reported in Chapter 3, are given for both "dry" and "wet" conditions. Radon loss from dry phosphate samples, when taken as a percent of the 22 Ra activity, ranged from 1.1 to 25.3 %, averaging 12.4 %. Radon loss from the wet samples ranged from 18.1% to 66.1 %, averaging 32.4 %. On the average, wet experiments showed losses approximately 3 times that of the dry experiments. This illustrates the importance of groundwater for removal of radon from phosphatic strata. Our experiments showed that surface area and ^{226}Ra concentrations are the most important factors affecting radon loss from phosphate rock. In some cases, however, other factors, such as textural and mineralogical characteristics, must also play a significant role. Surprisingly, the granite samples, from an area characterized by extremely high radon in the groundwater, lost about the same relative amount under dry conditions as the phosphate rocks.

Chapter 4 reports our results for dissolved and particulate radium, measured in several dozen river, spring, and estuary water samples, in an effort to describe the transport mechanisms and pathways of ^{226}Ra. The mean concentration of ^{226}Ra in the Suwannee River (the river which was studied most intensively) during our study period was 11.8 pCi 100L^{-1}, 2-4 times higher than most other rivers. Radium in the Suwannee River appears to be controlled by two processes: (1) relative mixing of surface drainage (low radium) and groundwater input via springs (high radium); and (2) interaction between soluble radium and particulate matter in the suspended load of the river. Adsorption and ion exchange processes by suspended clays apparently maintain the soluble radium concentration within a fairly narrow range.

The annual discharge of dissolved ^{226}Ra from the Suwannee River and estuary to the Gulf of Mexico is approximately 1.5 x 10^{12} pCi yr^{-1}. This represents the highest radium flux from 11 Florida rivers which drain into the Gulf of Mexico but is approximately two orders of magnitude lower than the Mississippi River. Upon entrance into the Gulf, a portion of the particulate radium is released into solution, accounting for part of the high concentrations observed in the Suwannee River estuary as well as other portions of the west Florida shelf. This cannot account for all the excess radium in the estuary, however. The remainder must be contributed from another source, most likely the adjacent salt marshes or submarine springs.

The other main field component of our research concerned the distribution of polonium in the surficial aquifer of west central Florida. Our results, reported in Chapter 5, show that there are many wells in this region which contain high concentrations of ^{210}Po, a daughter of ^{222}Rn and the last radioactive member of the ^{238}U decay chain. Approximately one quarter of the 80 sites sampled and analyzed have ^{210}Po concentrations higher than the federally-mandated limit for "gross" alphas (15 pCi L^{-1}). These high activities are unexpected in view of the reactive nature of polonium. Measured ^{210}Po concentrations ranged from less than 1 to over 500 pCiL^{-1} in filtered (0.45 µm) samples and up to over 2500 pCi L^{-1} in the case of one unfiltered sample. Measurements of ^{222}Rn in many of the same wells showed a range from less than 100 to over 40,000 pCi L^{-1}. The longest-lived radon daughter, ^{210}Pb, intermediate between radon and polonium, showed relatively low concentrations -- always less than 10 pCi L^{-1}. Although the source of the polonium is undoubtedly from radon, it is not clear what mechanism is responsible for maintaining polonium in solution. Other characteristics which the high-polonium groundwaters have in common include low pH, presence of sulfide, and at least moderately high radon.

CHAPTER 1

DISTRIBUTION OF NATURAL DECAY-SERIES RADIONUCLIDES WITHIN A PHOSPHATE ROCK WEATHERING SEQUENCE IN FLORIDA

INTRODUCTION AND BACKGROUND

Uranium has three natural isotopes with half-lives sufficiently long that transport into natural water resources is possible. These isotopes are ^{238}U (99.27 % natural abundance, $t_{1/2} = 4.5 \times 10^9$ yrs); ^{235}U (0.72 % natural abundance, t1,2 = 7.1×10^8 yrs); and ^{234}U (0.006% natural abundance), $t_{1/2} = 2.5 \times 10^5$ yrs). All of these isotopes emit alpha radiation and produce a long decay series of progeny. These uranium isotopes are found in the earth's crust, in rocks and minerals such as granite, metamorphic rocks, lignites, monazite and phosphate deposits (CRPB, 1980).

Florida has one of the world's largest deposits of natural phosphate. In 1978, Florida supplied over 80 percent of the national output and more than 30 percent of the world's output. These phosphate ore deposits contain from about 50 to 500 ppm of uranium. It has been estimated that the Central and South Florida phosphate districts contain 3.7×10^5 metric tons of U_3O_8 (Sweeney and Windham, 1979). Consequently, the various radionuclides of the naturally-occurring uranium decay series would be expected to be present within this material in amounts predictable on the basis of secular equilibrium if the host rock remains a closed system. Chemical weathering of phosphate rock, however, may disrupt this equilibrium.

Intense public concern about the radioactivity contained in the Florida phosphate matrix began in September 1975 when the Environmental Protection Agency published its preliminary findings of unusually high ^{222}Rn levels in homes constructed on land reclaimed after phosphate mining (EPA, 1975). Irwin and Hutchinson (1976) conducted a reconnaissance water sampling in central and northern Florida and found that 19 percent of the water samples had ^{226}Ra activities equal to or in excess of 3 pCi L^{-1} (pCi L^{-1} = 2.22 dpm L^{-1}). The maximum ^{226}Ra activity observed in that study was 90 pCi L^{-1} in water from a shallow well in Polk County. Kaufmann and Bliss (1977) reported that many groundwater samples from Sarasota County contained ^{226}Ra in excess of the EPA Drinking Water Standard of 5 pCi L^{-1}. In 1982, scientists from the Geology Department at Florida State University found extremely high levels (up to thousands of pCi L^{-1}) of ^{210}Po in water samples from recharge wells in central Florida (Cowart, pers. comm.). Miller and Sutcliffe (1985) confirmed that water containing ^{226}Ra in excess of 5 pCi L^{-1} was obtained from the majority of wells sampled throughout Sarasota County. Lyman et al., (1985) reported an apparent association of cases of leukemia with elevated levels of ^{226}Ra in groundwater from central and southwest Florida. Recently, there has developed a nationwide concern that ^{222}Rn may be seeping into as many as 8 million homes in the United States, endangering the people who unsuspectingly inhabit them.

On the other hand, many analyses of uranium-series isotopes in ground and surface water of Florida display only moderate to low activities (Osmond, 1964; Kaufmann and Bliss, 1977; Fanning et al., 1982; Coffin, 1982; Deetae et al., 1983). It is clear that public concern is focused on a relatively few examples of significantly elevated activities which may pose health problems. The important environmental question is how and under what conditions do uranium daughters become mobilized in the environment so as to present a risk to human health.

Uranium in Phosphate Rock

It is clear that the ultimate source of most uranium-series radionuclides in groundwaters of Florida is from the uranium-enriched phosphatic strata. Menzel (1968) reviewed the uranium, radium and thorium contents of phosphate rock from many sources worldwide, including Florida. deMeijer and Braams (1973) reported the presence of uranium series radionuclides in phosphate slag. Bolch et al. (1976) reported that Florida's phosphate ore contains significant concentrations of uranium and its decay products. Roessler et al. (1979) documented that ^{238}U and ^{226}Ra are essentially in radioactive equilibrium in the phosphatic "matrix", but after chemical partitioning a disruption of this equilibrium occurs. Although it has been recognized that daughter nuclides may be partitioned by physical and chemical means during natural weathering and phosphate mining or processing, little detailed work on the release of uranium-series daughter nuclides from naturally-occurring phosphate minerals has been accomplished to date.

The Phosphate District of Florida offers the opportunity to investigate the partitioning of uranium-series isotopes from weathered products as well as from fresh phosphate rock. The upper part of the Bone Valley Formation has been leached and altered to aluminum phosphates as a result of lateritic weathering and groundwater alteration (Altschuler et al., 1956; Altschuler et al., 1958). Wavellite predominates at the top of a typical section, while calcium-aluminum phosphates (crandallite and millisite) are more common in the middle of the zone. Pebbles of leached carbonate fluorapatite often occur at the base of most weathered sections. Riggs (1979) has defined in detail a series of seven zones which constitute a complete weathering profile in the central Florida district. The work of Altschuler and his colleagues has shown that during lateritic or groundwater weathering, uranium may be leached from one zone while it accumulates in another. Uranium analysis of a series of slices through apatite pebbles sampled from the uranium phosphate zone showed significant depletion of uranium on the outside surface zone of each pebble compared to the inside, less weathered zone. Typical rock from the aluminum phosphate zone, however, shows about a two-fold enrichment over unaltered Bone Valley phosphorite. Within the aluminum phosphate zone, the distribution of uranium closely follows the distribution of calcium.

Wavellite, a pure aluminum phosphate, thus contains lesser amounts of uranium than the intermediate Ca-Al phosphates, crandallite and millisite (Altschuler et al., 1958).

Objectives of this Study

Although Altschuler's work is fundamental to our understanding of how uranium behaves in phosphatic strata during weathering, there was no attempt to describe how uranium daughters behaved. Altschuler's results indicate that there is considerable mobility of uranium during the weathering cycle. This study was intended to evaluate the extent of partitioning of uranium daughters as well as uranium isotopes themselves during weathering. The purpose of this study is thus twofold:

1. To describe the abundance of uranium and uranium-decay series daughters in both bulk and size-fractionated samples of a series of phosphate rock samples representing a transition from relatively fresh to very weathered material; and

2. To determine how uranium daughter nuclides are partitioned during the weathering process.

EXPERIMENTAL METHODS

Sampling and Sample Preparation

In order to get a reasonable range from fresh to very weathered material for the study, two field trips were arranged to six phosphate mines in central Florida in 1984 (Fig. 1). Eleven samples of phosphate rock were selected for this study, including samples of completely fresh phosphate ore from the Pungo River Formation in North Carolina and from a deep drill hole in north Florida (Table 1). For quality assurance, two phosphate rock standards (NBS 120b and NBS 694) were also run through most of our radiochemical and geochemical analyses.

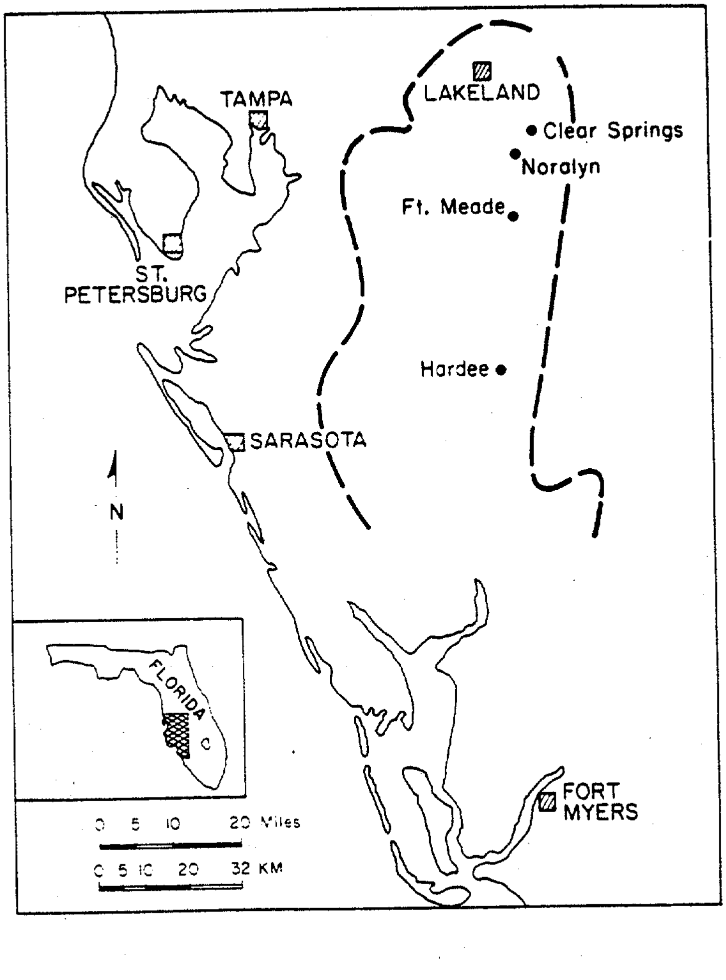

Figure 1. Locations of mines where samples were collected. The dotted line represents the approximate boundaries of the Central Florida Phosphate District.

Table 1. **Samples selected for complete uranium-series isotopic analysis on basis of degree of apparent weathering. Samples 120b and 694 are standards supplied by the National Bureau of Standards.**

Sample	Location	Date Collected	Field Description
NRM-3#	Noralyn Mine	10/16/84	Leached zone, highly weathered Bone Valley; wavellite, crandallite(?)
NRM-4#	Noralyn Mine	10/16/84	Soft white phosphate - crandallite zone
NRM-5#	Noralyn Mine	10/16/84	Apatite zone - top of matrix, below crandallite
NRM-10	Noralyn Mine	10/16/84	Consolidated highly weathered - millisite, crandallite (?)
FM-1	Fort Meade Mine	11/22/84	Partially consolidated, light yellow Al leached zone - reported to have high radioactivity
FM-3#	Fort Meade Mine	11/22/84	Relatively fresh, high grade ore
CSP-2.2	Clear Springs Mine	10/16/84	Consolidated, secondary apatite - below dark clay
CSP-4	Clear Springs Mine	10/16/84	Consolidated leached apatite pebbles
HM-1#	Hardee Mine	11/22/84	Fresh black apatite pellets in clean sand
HAW-1B	St. Augustine Basin	-	Fresh phosphate from Hawthorn Formation drilled from approx. 250' depth
PR-1#	Texas Gulf Mine, Aurora, N.C.	-	Unweathered phosphate from Unit-C of Pungo River Formation
120b	National Bureau of Standards	-	Phosphate concentrate, Bone Valley Fm.
694	National Bureau of Standards	-	Fresh phosphate rock, Dry Valley Ridge, Idaho

\# Unconsolidated samples sieved into standard size fractions for later analysis.

All of our phosphate rock samples were split into several portions, one of which was ground to a fine powder of approximately 200 mesh in a tungsten carbide automatic grinder and dried overnight at 100°C. Unconsolidated samples were sieved through standard mesh screens for later radiochemical analysis of individual size fractions. An archive portion of each sample was also retained for future microanalysis and other requirements.

Chemical and Mineralogical Analysis

Standard methods were used for characterization of the bulk samples in terms of general mineralogy and phosphatic phase chemistry. Fluoride was determined by an ion-specific electrode technique (Edmond, 1969) with a fluoride ion electrode, Orion Model 94-09, and a Metrohm-Brinkman Model 104 pH/mV meter. Total inorganic phosphate was measured from diluted aliquots of the same solution prepared for the fluoride measurements utilizing phosphomolybdate calorimetry (Murphy and Riley, 1962) with a Beckman DU Spectrophotometer. Mineralogy and structural-CO_2 were determined utilizing X-ray diffraction techniques with Ni-filtered Cu-Kα radiation (Gulbrandsen, 1970).

Size Fractionation

Six of the samples selected for detailed radiochemical study were unconsolidated samples which were separated into standard size divisions by first wet sieving with deionized water through a 63µm screen and then dry sieving through standard screens producing the following size intervals: <2,000µm; 1,000-2,000µm; 500-1,000µm; 250-500µm; 125-250µm; and 63-125µm. The <63µm fraction obtained during dry sieving was combined with the <63µm fraction obtained during the wet sieving process. In addition to sieving, one sample (designated NRM 4*) was chosen for a pipette analysis of the <63µm fraction for silt and clay distribution. All sieving followed standard procedures as outlined by Folk (1974). After size separation, all material was ground to a fine powder in the same manner as the bulk samples. In cases where the sample mass was very small, a small agate mortar was used.

Gamma-Rav Spectrometric Techniques

Analyses for ^{238}U, ^{226}Ra, and ^{210}Pb on bulk and size-fractionated samples were made by a non-destructive, high resolution gamma-ray spectrometric technique utilizing a well-type intrinsic germanium (IG) detector (Kim and Burnett, 7983). ^{238}U is measured via the photopeak of its direct daughter, ^{234}Th, at 63 and 93 KeV. ^{226}Ra is determined by taking the average activity obtained by utilizing three separate photo peaks of ^{226}Ra daughters, ^{214}Pb at 295 and 352 KeV and ^{214}Bi at 609 KeV. ^{210}Pb is measured directly from its peak at 46 KeV. The average precisions obtained for ^{238}U, ^{226}Ra, and ^{210}Pb are 1.8, 1.4, and 4.6 percent, respectively.

Radiochemical Separation and Alpha Spectroscopy

Determinations of ^{238}U, ^{234}U, ^{230}Th, ^{210}Po, ^{232}Th, and ^{231}Pa, were accomplished by isotope dilution alpha spectrometry utilizing a technique developed by the Institute of Nuclear Science (INS) in New Zealand (McCabe et al., 1979; Ditchburn and McCabe, 1984). A ^{232}U/^{228}Th spike in transient equilibrium and a ^{233}Pa solution were used for yield tracers. Briefly, the "INS" method involves combustion of a dried, powdered sample at 550°C for approximately 12 hours to destroy most organic materials. The cornbusted sample is then dissolved in a combination of HNO_3, $HClO_4$ and HF acids with later addition of boric acid to dissolve insoluble fluorides and convert to a fluoroborate matrix. The digested solution is used for direct electrodeposition of ^{210}Po onto a rotating stainless steel disc. The remaining solution is then loaded onto the main temperature-controlled cation exchange resin and the separation processes is accomplished by a series of elutions with tartaric acid and different strengths of HCl and H_2SO_4. The source preparation is based on electrodeposition utilizing a rotating disc unit with a temperature-controlled plating cell. The resulting sources, one each for uranium, thorium and protactinium, are mounted on highly-polished

2.54 cm diameter stainless steel discs. Counting is accomplished using surface barrier detectors routed to a Canberra Series 40 multichannel pulse height analyzer.

RESULTS AND DISCUSSION

Chemical and Mineral Characterization

Mineralogical and chemical characteristics of the 11 phosphate rock samples used for bulk analysis in this study are shown in Table 2. All samples analyzed contained apatite except FM-1 and NRM-3 which only contain 5.5 and 11.4 percent P_2O_5, respectively, the two lowest phosphate concentrations of all samples investigated. Although not all samples show a close correlation between uranium and phosphorus, the highly weathered samples FM-l, NRM-3, NRM-4, and NRM-10 plot along a trend line which is completely separate from the other, fresher materials (Fig. 2a). Furthermore, the weathered samples with a higher uranium content also tend to have better positive correlations when plotted against fluorine (Fig. 2b), Ap-CO_2 (Fig. 2c) and F/P205 (Fig. 2d). A regression of fluoride versus phosphorus (P_2O_5) for all 11 samples shows a very good positive correlation ($r = 0.96$, $P = 0.95$) with a slope of 0.110, characteristic of the F/P_2O_5 ratio of carbonate fluorapatite, the principal mineral phase of phosphate rock.

Mineralogical analyses by X-ray diffraction (XRD) (Table 2) confirmed that the major phase (>20%) of minerals in most samples is apatite. Most of the F/P_2O_5 weight ratios are higher than the stoichiometric ratio for theoretical fluorapatite (0.0898) and close to that (0.107) of typical sedimentary apatite from the Bone Valley Formation (Altschuler, et al., 1958). However, NRM-3, NRM-10, and FM-1 all have low F/P_2O_5 values, indicating significant contributions of phosphorus from other phases. Many of these samples also contain very low structural-CO_2 contents within the apatite lattice. This is especially true for samples NRM-3 and NRM-10 from the Noralyn Mine. These low values of structural-CO_2 are

Table 2. Mineralogical and chemical characteristics of 11 phosphate rock samples used for bulk radiochemical analysis. Minerals listed in approximate order of abundance.

Sample	X-ray Mineralogy[1]	^{238}U (ppm)	P_2O_5 (%)	F (%)	F/P_2O_5	Ap-CO_2 [2] (%)
NRM-3	Qtz, Cran, Mill, Kaol(?), MLC	295.1	11.43	0.60	0.052	bd
NRM-4	Ap, Qtz	756.8	24.65	2.31	0.094	3.1
NRM-5	Ap, Qtz, Smec	161.9	26.67	2.98	0.111	4.9
NRM-10	Qtz, Ap, Cran, Mill	572.3	17.89	1.18	0.066	1.5
FM-1	Qtz, Cran, Goethite Mill, Smec	151.5	5.50	0.14	0.025	bd
FM-3	Qtz, Ap, MLC	38.3	17.52	1.75	0.100	2.9
CSP-2.2	Ap, Wave(??)	100.0	36.87	3.38	0.092	1.7
CSP-4	Ap, Qtz,Kaol(?), Smec (?)	74.9	29.39	2.84	0.097	2.1
HM-1	Qtz, Ap, Smec	66.5	15.40	1.65	0.107	3.5
PR-1	Qtz, Ap, Cal, Ilit (?)	42.5	19.50	2.08	0.107	5.7
HAW-1B	Qtz, Ap, Smec	47.1	18.05	2.17	0.120	5.7
NBS 120b	--	126.9	34.57	3.84	0.111	-
NBS 694	--	143.1	30.24	3.20	0.106	-

[1] Abbreviation Used :

Ap = Apatite (carbonate fluorapatite)
Cal = Calcite
Cran = Crandallite
Ilit = Illite
Kaol = Kaolinite
Mill = Millisite
MLC = Mixed-layer clay
Qtz = Quartz
Smec = Smectite
Wave = Wavellite
bd = Below detection limit

[2] Structural carbonate determined by peak-pair method using XRD (Gulbrandsen, 1970)

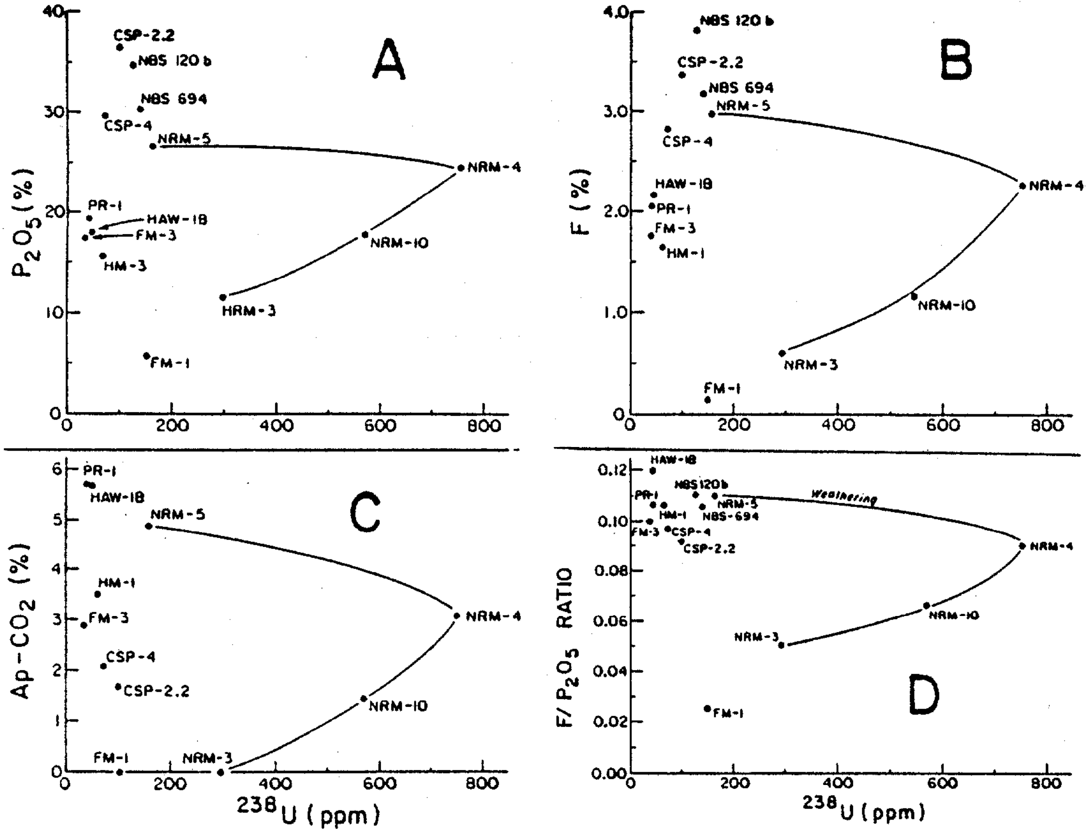

Figure 2. Relation of uranium to P_2O_5 (a), F (b), Ap-CO_2(c), and F/P_2O_5 ratio (d) in 11 bulk phosphate rock samples and two NBS standards. Connecting lines represent samples from the same locality.

most likely a reflection of selective carbonate loss during weathering (Lucas et al., 1980). The least weathered material in our sample set is probably PR-1 from North Carolina, which also contains the highest structural-CO_2 at 5.7 percent. Based upon the structural carbonate concentrations, F/P_2O_5 ratios, and the presence of secondary phosphate minerals, we attempted to group these samples into an approximate order of weathering (Table 3). There are clear compositional differences between the "fresh" and "weathered" samples, but the intermediate "leached" group is gradational. We designated a sample as "weathered" if secondary phosphate minerals were present. Samples termed "leached" still contained mostly apatite but with lowered carbonate concentrations.

Radionuclide Activities: Bulk Samples

Activities of ^{238}U, ^{234}U, ^{230}Th, ^{226}Ra, ^{210}Pb and ^{210}Po from the ^{238}U decay series as well as ^{232}Th and ^{231}Pa, have been determined in all 11 bulk samples of phosphate rock and the two NBS standards (Table 4). The activities vary considerably in this sample set. For example, the ^{238}U activities range from a low of 14.2 pCi g^{-1}(42.5 ppm) in the North Carolina sample (PR-1) to 252.5 pCi g^{-1} (756 ppm) in NRM-4 from the Noralyn Mine.

Activity ratios of several parent-daughter pairs (Table 5) show that, while in general the decay-series isotopes in these samples are close to secular equilibrium, there are some notable exceptions. Several samples, for example FM-1, FM-3, CSP-2.2, and NRM-3, have significant excess amounts of ^{234}U relative to ^{238}U. ^{230}Th is generally in isotopic equilibrium with its parent ^{234}U, but is depleted in NRM-4 and NRM-10 and is 33 percent enriched in NRM-3. Only NRM-4 seems to be significantly depleted in ^{226}Ra relative to ^{230}Th. Most samples show a $^{210}Pb/^{226}Ra$ activity ratio less than 1.0, an expected result because of radon leakage. The less than unity $^{210}Po/^{210}Pb$ activity ratios measured in a few of these samples are most surprising, however, in view of the short half-life of ^{210}Po.

Table 3. **Approximate order of weathering for the 11 phosphate rock samples analyzed in this study.**

Sample	Apatite[1]	Secondary Minerals[2]	Weathering Catagory
HAW-1B	present	none	very fresh
PR-1	∇	∇	∇
NRM-5	∇	∇	leached
HM-1	∇	∇	∇
FM-3	∇	∇	∇
CSP-4	∇	∇	∇
NRM-4	∇		∇
		∇	
CSP-2.2	∇	Wave (?)	weathered
NRM-10	∇	Cran, Mill	∇
NRM-3		Cran, Mill	∇
FM-1		Cran, Mill	∇

[1] From data in Table 2.

[2] Abbreviations as in Table 2.

Table 4. Activity of uranium-series nuclides in 11 bulk samples of phosphate rock and 2 phosphate rock standards. Samples arranged in approximate order of degree of weathering.

Sample	^{238}U	^{234}U	^{230}Th	^{226}Ra	^{210}Pb	^{210}Po	^{232}Th	^{231}Pa
				pCi g^{-1}				
				fresh				
HAW-1B	15.7	15.7	15.5	14.5	13.0	13.1	0.72	0.5
PR-1	14.2	14.4	13.6	13.3	13.4	11.3	0.72	0.68
				leached				
NRM-5	54.01	52.57	53.69	50.59	47.03	43.06	0.77	2.5
HM-1	22.2	22.4	22.6	21.9	21.9	20.1	0.5	0.86
FM-3	12.8	13.3	13.6	13.6	11.9	11.0	0.50	0.59
CSP-4	25.0	25.3	25.1	25.0	21.3	20.9	0.3	1.2
NRM-4	252.5	250.8	198.8	177.5	154.9	134.5	1.1	10.9
				weathered				
CSP-2.2	33.4	34.7	33.6	34.2	33.1	29.7	0.2	1.7
NRM-10	189.8	185.9	168.3	165.2	161.4	117.1	2.2	9.59
NRM-3	98.47	102.2	135.8	151.1	148.3	116.8	1.9	5.81
FM-1	50.54	53.83	55.41	55.32	53.06	44.8	1.2	2.6
				rock standards				
NBS 120b	42.3[1]	43.6	44.2	40.9	37.2	35.5	0.99	2.0
NBS 694	47.75[2]	47.52	46.98	43.6	40.8	40.5	0.2	1.6

[1] Certified activity = 42.9 pCi g^{-1}

[2] Certified activity = 47.25 pCi g^{-1}

Table 5. Disequilibrium relationships of uranium-series isotopes within 11 bulk samples of phosphate rock and 2 phosphate rock standards. All errors quoted are ±1σ based on counting statistics.

	ACTIVITY RATIOS					
Sample	$^{234}U/^{238}U$	$^{230}Th/^{234}U$	$^{226}Ra/^{230}Th$	$^{210}Pb/^{226}Ra$	$^{210}Po/^{210}Pb$	$^{231}Pa/^{235}U$
			fresh			
HAW-1B	0.994 ± 0.011	0.99 ± 0.02	0.94 ± 0.02	0.90 ± 0.02	1.02 ± 0.04	0.59 ± 0.06
PR-1	1.012 ± 0.017	0.94 ± 0.03	0.98 ± 0.02	1.01 ± 0.06	0.84 ± 0.06	1.03 ± 0.07
			leached			
NRM-5	0.973 ± 0.006	1.02 ± 0.02	0.94 ± 0.02	0.93 ± 0.03	0.92 ± 0.03	1.00 ± 0.03
HM-1	1.008 ± 0.008	1.01 ± 0.02	0.97 ± 0.02	1.12 ± 0.06	0.82 ± 0.05	0.84 ± 0.05
FM-3	1.043 ± 0.018	1.02 ± 0.02	1.01 ± 0.02	0.87 ± 0.05	0.92 ± 0.02	0.99 ± 0.07
CSP-4	1.011 ± 0.009	0.99 ± 0.02	0.99 ± 0.02	0.85 ± 0.05	0.98 ± 0.02	1.02 ± 0.04
NRM-4	0.993 ± 0.006	0.79 ± 0.02	0.89 ± 0.02	0.87 ± 0.02	0.87 ± 0.02	0.94 ± 0.03
			weathered			
CSP-2.2	1.040 ± 0.006	0.97 ± 0.01	1.02 ± 0.02	0.97 ± 0.04	0.90 ± 0.02	1.08 ± 0.03
NRM-10	0.979 ± 0.006	0.91 ± 0.02	0.98 ± 0.02	0.98 ± 0.02	0.73 ± 0.02	1.10 ± 0.07
NRM-3	1.038 ± 0.010	1.33 ± 0.03	1.11 ± 0.02	0.98 ± 0.03	0.79 ± 0.02	1.28 ± 0.07
FM-1	1.065 ± 0.010	1.03 ± 0.02	1.00 ± 0.02	0.96 ± 0.03	0.84 ± 0.02	1.10 ± 0.05
			Rock Standards			
NBS 120b	1.036 ± 0.010	1.02 ± 0.02	0.93 ± 0.03	0.88 ± 0.03	0.96 ± 0.04	1.02 ± 0.02
NBS 694	0.995 ± 0.008	1.00 ± 0.02	0.92 ± 0.03	0.94 ± 0.03	0.99 ± 0.04	0.74 ± 0.02

With a half-life of only 138 days, ^{210}Po will rise to within 3% of secular equilibrium with ^{210}Pb in approximately two years. Any loss of polonium, therefore, would quickly be compensated for by ingrowth from its parents. This implies that the process responsible for removal of ^{210}Po out of the rock must have been active either up to or just shortly before the sample was collected. Addition of ^{210}Pb, of course, could also result in a low $^{210}Po/^{210}Pb$ activity ratio. This seems unlikely, however, since the ^{210}Pb activities are all close to that of ^{226}Ra.

It is also possible that the low $^{210}Po/^{210}Pb$ activity ratios reported in Table 4 are actually artifacts caused by polonium loss during our analytical procedure. Polonium is known to be volatile under certain conditions and thus loss during sample combustion or acid digestion is possible. However, this is unlikely because: (1) analysis of two phosphate rock standards (NBS 120b and NBS 694) by the same procedure produced a $^{210}Po/^{210}Pb$ activity ratio within analytical error of secular equilibrium; and (2) ^{210}Po analyses of NRM-10 performed 164 and 260 days, respectively, after the first analysis produced activities exactly in line with the amount of ^{210}Po ingrowth expected from the deficiency originally measured (Fig. 3). Thus, these equilibrium relationships between ^{210}Pb and ^{210}Po appear to be real and may provide an important clue to the source of the anomalously high ^{210}Po in some Florida groundwaters.

Radionuclide Activities: Size Fractions

The specific activities of ^{238}U, ^{226}Ra, and ^{210}Pb, activity ratios, individual sample masses by size, and relative activities of ^{238}U, ^{226}Ra, and ^{210}Pb are given in Appendix 1. The maximum percent mass distribution in the unconsolidated samples occurs in size class 250-500µm, except NRM-4, a highly leached sample which contains significantly more fine-grained material (Fig. 4). Fresh samples, such as FM-3 and PR-1, on the other hand, have symmetrical mass distributions centering on the 250-500µm fraction. Fresh phosphate rock samples do

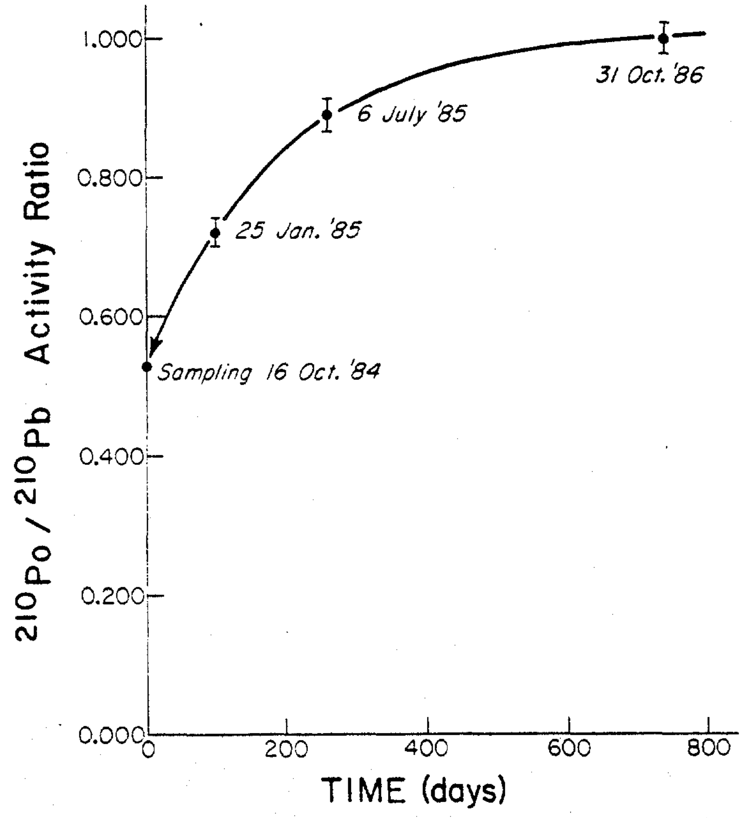

Figure 3. The theoretical development of the activity ratio ^{210}Po/^{210}Pb as a function of time together with analytical data points for sample NRM-10. Extrapolation to the date of sampling indicates that the activity ratio must have been about 0.53 at that time.

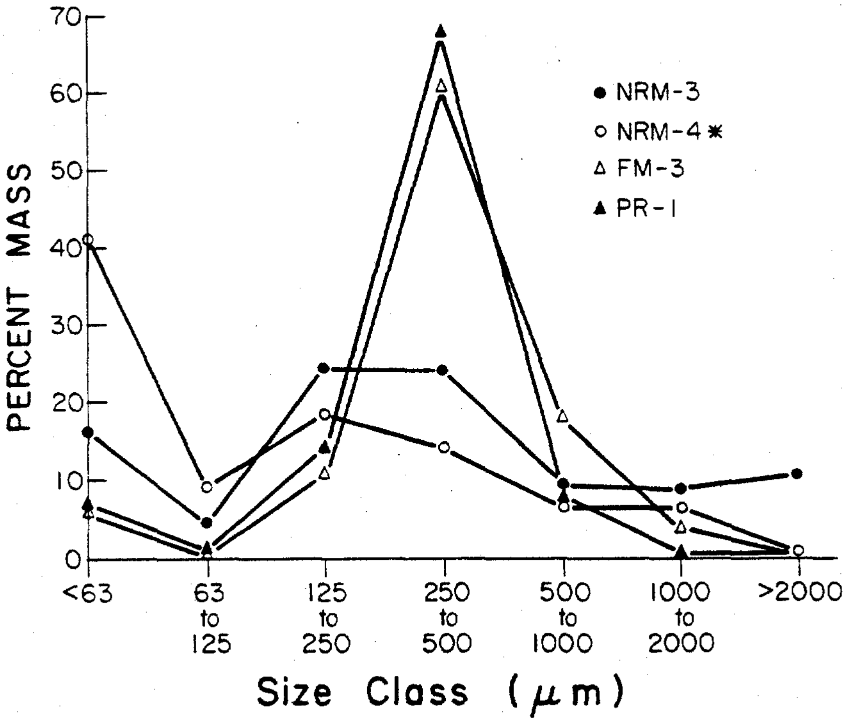

Figure 4. Percent mass distribution of 2 fresh (PR-1 and FM-3) and 2 weathered (NRM-3 and NRM-4*) phosphate rock samples.

not show a strong fractionation in radioactivity as a function of size (Fig. 5). Weathered samples, however, show the highest specific activities in the finest size fraction.

Normalizing the specific activity to the distribution of sample mass allows us to calculate the percent of the total activity that is contained within any one size class. This is a very useful way of considering the radionuclide distribution because it illustrates that uranium-decay series isotopes are strongly fractionated between different size classes during weathering. Highly weathered samples like NRM-3 and NRM-4 have a significant amount (44-60%) of their activity contained within the finest (<63μm) size class, while fresher samples (FM-3 and PR-1) tend to have the radioactivity concentrated within the same interval as sample mass (Fig. 6). The mass-normalized activities of ^{238}U, ^{226}Ra, and ^{210}Pb reflect this pattern. This is apparently one of the main effects of intense weathering on the distribution of uranium decay-series isotopes in phosphatic rocks; i.e., there is a "spreading out" of the activities into finer-sized material. This process may be very important to the ultimate release and/or transport of these nuclides to the environment.

It is apparent that all weathered samples have a similar pattern of maximum specific activities in the finest fraction and the minimum activities are found in the size classes 125-250μm and 250-500μm, probably the original positioning of much of the radioactivity.

Samples such as NRM-5; which contain phosphatic "pebbles", may have their activity concentrated in the coarsest size fraction (>2000μm). The activity ratios of ^{226}Ra/^{238}U and ^{210}Pb/^{226}Ra parent-daughter pairs (Appendix 1) show that there are some notable departures from secular equilibrium in each sample as well as across many different size fractions. NRM-3 has a significant excess amount of ^{226}Ra relative to ^{238}U in every size class. This is probably due to active adsorption of ^{226}Ra (as well as uranium) during weathering processes. However, the

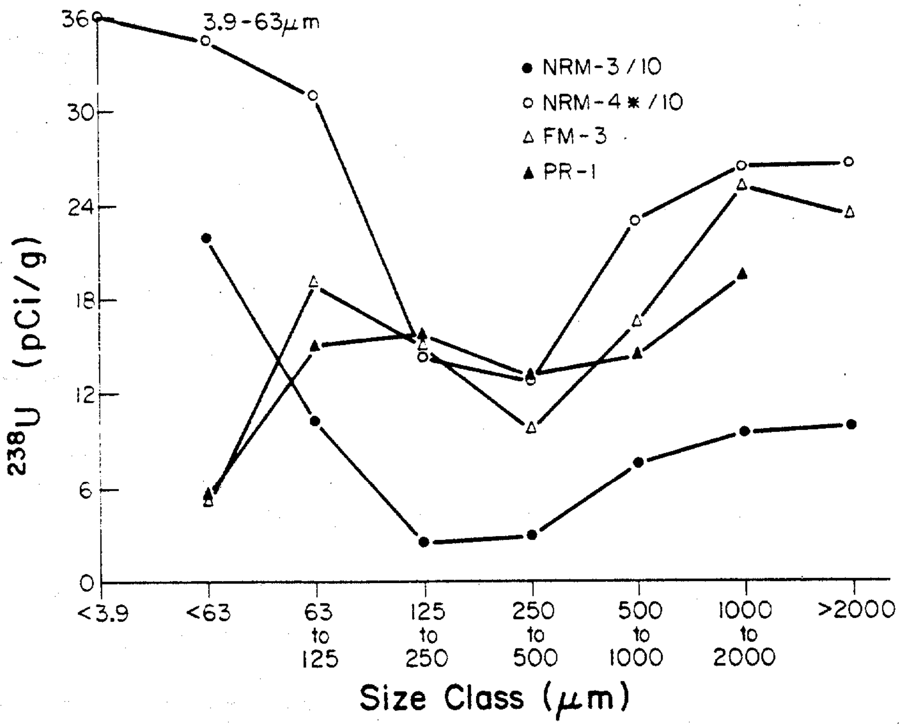

Figure 5. Specific activity of ^{238}U in various size classes of 2 fresh (PR-1 and FM-3) and 2 weathered (NRM-3 and NRM-4*) phosphate rock samples. Activities of NRM-3 and NRM-4* have been divided by 10 in order to display the data on the same scale.

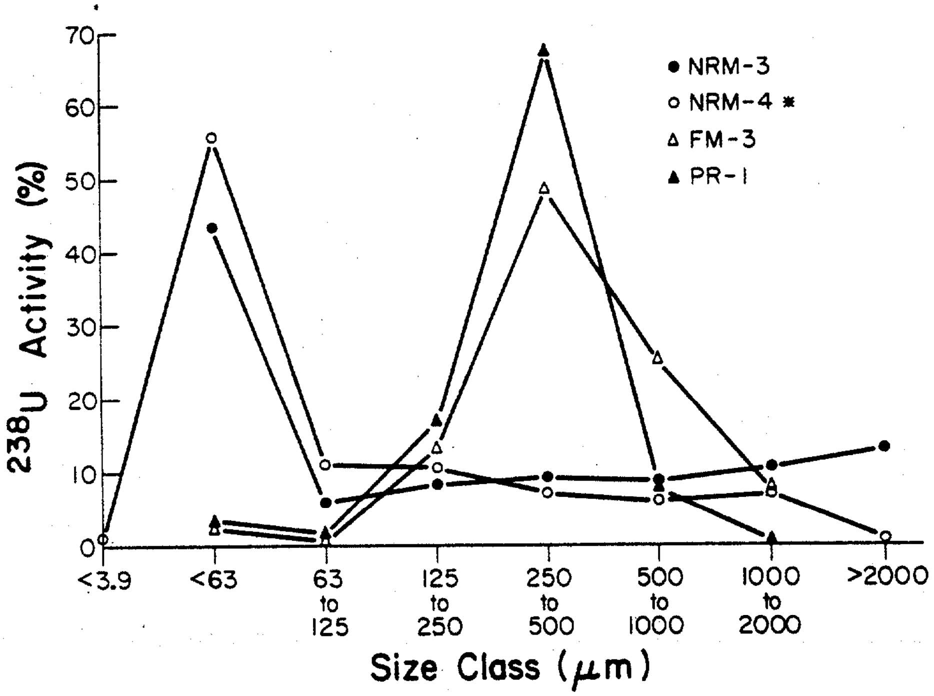

Figure 6. ^{238}U distribution expressed as a percent of the total activity in various size classes of 2 fresh (PR-1 and FM-3) and 2 weathered (NRM-3 and NRM-4*) phosphate rock samples.

same pattern (although more subdued) is also found in FM-3, a relatively fresh and high grade ore. The $^{226}Ra/^{238}U$ ratios of NRM-4 and NRM-5 show a deficiency of 10-40% of ^{226}Ra relative to ^{238}U.

It is interesting to note that, except for NRM-3, all weathered samples of Florida phosphatic rock in the fine size class showed an approximately 40% depletion of ^{226}Ra relative to ^{238}U, while the fresh sample, FM-1 showed a 14 percent excess of ^{226}Ra. The fresh phosphatic rock sample PR-1 has approximately 6 times excess ^{226}Ra relative to ^{238}U in the <63µm size fraction. Thus, it appears that there is a significant difference in the distribution of ^{226}Ra in the fine fraction of fresh and weathered phosphatic rock.

Most samples in size classes greater than 63_{um} showed a $^{210}Pb/^{226}Ra$ activity ratio less than 1.0, probably due to radon leakage as in the bulk samples. However, the fine size class ($<63_{um}$) of all samples except NRM-3 showed an activity ratio $^{210}Pb/^{226}Ra$ either in equilibrium or with some excess of ^{210}Pb relative to ^{226}Ra. Fresh samples (FM-3, PR-1) have significant excess amounts of ^{210}Pb (50-130%), while the ^{210}Pb of more weathered samples (NRM-3, NRM-4) is in equilibrium or slightly in excess relative to ^{226}Ra. The excess amounts of ^{210}Pb in the finest material are probably due to adsorption of particle-reactive ^{210}Pb onto the greater surface area present in the finer-sized particles.

After all the size fractions were analyzed from the six unconsolidated phosphatic rock samples, a mass balance calculation was attempted by summing all the mass-normalized size fraction results and comparing them to the analyses of the bulk solids. Ideally, the sum of the individually-determined size fractions after normalizing to the mass fraction should be equivalent to the activity measured for the bulk solid. In virtually every case, however, the sum of the activity of the size class data is less than that of the bulk analysis (Fig. 7). For at least two of the samples, FM-3 and PR-1, the differences are less than 10 percent

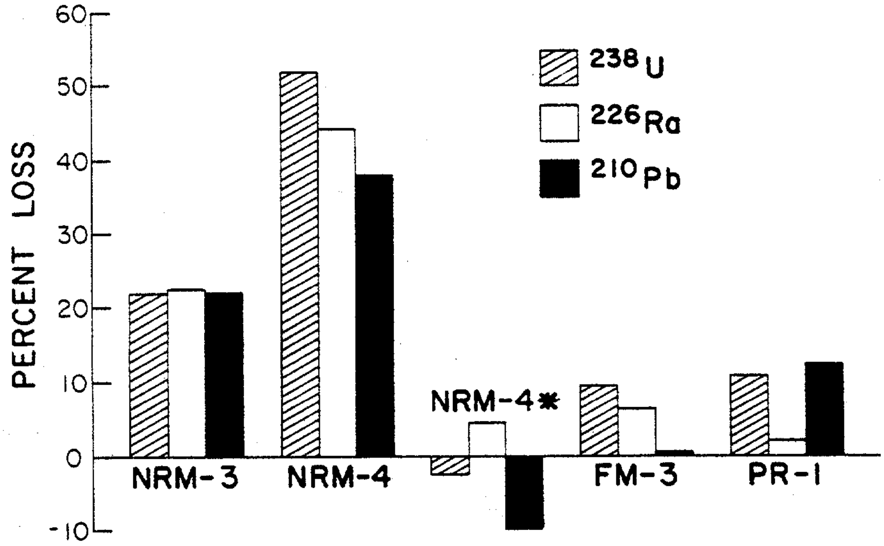

Figure 7. Comparison of the sum of the activities of ^{238}U, ^{226}Ra. and ^{210}Pb for individual size classes (Appendix 1) compared to the bulk analysis of the same sample (Table 4). NRM* refers to the 2nd wet seiving (under more controlled conditions) of sample NRM-4.

and probably are not significant. The two highly weathered samples (NRM-3 and NRM-4), however, display deficits in the sum of fractions compared to bulk measurement of about 22 and 45 percent, respectively. These deficiencies are clearly significant. The only possible explanation of this observation is that a loss of these isotopes occurred during the sieving process. This may represent an actual leaching of these radionuclides into the deionized water used for the wet sieving or, more likely, some particle loss of fine-grained, high activity solid material has occurred. It is possible that some very fine-grained material may have escaped from collection vessels when these samples were sieved.

To assess the cause of this discrepancy in our mass balance calculation, NRM-4 was, once again, sieved under more carefully controlled conditions. It was also separated into finer divisions by pipette analyses and all fractions analyzed radiochemically. This sample is referred to as NRM-4*. The new data set (Table 6) had a mass loss during the sieving process of only about 1 percent, and overall activities balance quite well (Fig. 7). In addition, we also analyzed the washed deionized water used during the wet sieving process for ^{226}Ra and ^{210}Po. We found total activities of about 2.3 pCi for each of these nuclides in the washing solution. This represents less than 1 percent of the initial activity found in the <63μm size fraction.

When activities of the various nuclides (as ^{238}U in Fig. 5) are plotted versus particle size, the weathered samples often display an interesting trend. For size class <3.9μm to 250-500μm, the specific activity increased as the particle size decreased, which implies a surface area effect. However, for the size classes larger than 250-500μm, it appeared that activity increased as the particle size increased, i.e., no positive correlation with increased surface area is apparent. We feel that this trend is due to the transformation of pellets into "pebble" material. This "pebble" material consists essentially of recrystalled phosphate pellets and is purer with respect to apatite and thus radionuclide abundance. These relationships imply that the mechanisms

Table 6. Specific activities and activity ratios of phosphate rock sample NRM-4* as a function of grain size.

	Size range (µm)							
	<3.9	3.9-63	63-125	125-250	250-500	500-1000	1000-2000	>2000
	Specific Activities (pCi g^{-1})							
^{238}U	336.7	289.1	145.6	55.77	66.98	186.9	215.7	NA#
^{234}U	313.0	277.7	142.9	55.45	67.39	186.8	211.8	NA
^{230}Th	285.9	238.7	133.1	46.94	56.49	151.8	165.4	NA
^{226}Ra	219.2	234.3	120.1	52.25	50.54	110.7	160.3	164.4
^{210}Pb	247.5	245.5	98.65	50.0	40.0	96.40	144.6	120.7
^{210}Po	234.6	205.9	136.1	42.8	43.4	124.2	130.7	NA
	Activity Ratios							
$^{234}U/^{238}U$	0.93	0.96	0.98	0.99	1.01	1.00	0.98	NA
$^{230}Th/^{234}U$	0.93	0.86	0.93	0.85	0.84	0.81	0.78	NA
$^{226}Ra/^{230}Th$	0.77	0.98	0.90	1.11	0.89	0.73	0.97	NA
$^{210}Pb/^{226}Ra$	1.13	1.05	0.82	0.96	0.79	0.87	0.90	0.73
$^{210}Po/^{210}Pb$	0.95	0.84	1.38	0.86	1.08	1.28	0.90	NA

Not analyzed because of insufficient material.

that cause "spreading out" of radionuclide activity through several size classes is not only due to simple adsorption, but includes mineral phase distribution in each size class as well.

CONCLUSIONS

1. Weathered samples have higher radionuclide activities than fresh samples by a factor of 1 to 10 depending upon the degree of weathering.

2. In general, the activity ratio of several parent-daughter pairs in bulk samples is close to secular equilibrium. However, fresh samples tend to have excess amounts of ^{234}U relative to ^{238}U. ^{230}Th is generally in isotopic equilibrium with its parent ^{234}U, but is depleted in highly weathered samples. Most samples showed a $^{210}Pb/^{226}Ra$ activity ratio less than 1.0 because of radon loss. The less than unity $^{210}Po/^{210}Pb$ activity ratios in some highly-weathered samples is apparently a reflection of the release of ^{210}Po into the environment.

3. Activity ratios of parent-daughter pairs in various size classes revealed notable departures from secular equilibrium in each sample and many different size fractions. Nearly all the fine size classes of the weathered samples showed an approximate 40 percent depletion of ^{226}Ra relative to ^{238}U, while fresh samples showed a 14 percent excess of ^{226}Ra. In the <63µm size class, fresh samples have a significant excess amount of ^{210}Pb (50-130%), while the excess ^{210}Pb in the fine material of the weathered samples is in equilibrium or slightly in excess relative to ^{226}Ra.

4. In highly weathered samples, a significant fraction (44-60%) of the activity is within the finest size class or, in some cases, in the coarser "pebble" fraction. In the fresher material, the activity tends to be contained within the same interval as the

mass distribution, i.e., the "pellet" size. This "spreading out" of the radionuclides may be caused by the processes of simple adsorption as well as recrystallization and "transformation" into purer phosphatic pebbles.

CHAPTER 2

LABORATORY LEACHING EXPERIMENTS OF FRESH AND WEATHERED FLORIDA PHOSPHATE ROCK

INTRODUCTION

The high concentrations of uranium and daughter isotopes contained in Florida phosphatic strata provide an opportunity for studying radionuclide migration in a natural environment. The release and transport of radioactive isotopes from the parent rock may be controlled by the chemical conditions that exist within the groundwaters and by the nature of the host material as well as the properties of the individual radionuclides. The purpose of this research project is to ascertain the conditions under which the uranium series nuclides ^{238}U, ^{226}Ra, ^{210}Po, and ^{210}Pb may be released from phosphate rock into groundwater. This was approached by designing a series of laboratory experiments on a collection of Florida phosphate rock samples that were selected to reasonably represent a range from fresh to very weathered material.

Most phosphate rocks are uraniferous and constitute a very large resource of uranium in Florida (Cathcart and Gulbrandsen, 1973). Because of the high concentration of uranium in this rock, the radioactive daughters that grow in from the parent uranium will also be present in amounts depending on the state of radioactive equilibrium. The natural radioisotopes, U, ^{226}Ra, and ^{222}Rn, are of greatest concern because of their relatively long half-lives and the associated health risks present in public drinking water.

Uranium-238 occurs as a common trace element in most rock types and has a natural abundance of 99.27% and a half-life of 4.7 x 10^9 years. Until recently, uranium has been considered by the U.S. Nuclear Regulatory Commission to be a toxic heavy metal with the standard for ingestion relating to its chemical toxicity (3 x 10^4 pCi L^{-1}). Note that it has no standard in water supplies as a radioactive element. However, Hess et al. (1985) have reported that elevated levels of this potentially dangerous alpha-emitting radionuclide are found in surface water, as well as in groundwater, throughout the United States.

Uranium occurs within the mineral carbonate fluorapatite, $Ca_{10}(PO_4,CO_3)_6(F,OH,Cl)_2$, the principal phosphatic phase of sedimentary phosphate rock. The structure of apatite is such that small quantities of CO_3, VO_4, AsO_4, and SO_4 may substitute for PO_4; and Na, U, Th, and the rare earth elements may substitute for Ca (Sweeney and Windham, 1979). Most workers agree that uranium as U(IV) replaces Ca in the apatite structure, or is in part adsorbed as the uranyl ion onto apatite crystal surfaces (Cathcart, 1978). However, there still persist some uncertainties with respect to the details of uranium substitution in apatite.

Uranium in phosphorite exists in the tetravalent (+4) and hexavalent (+6) oxidation states (Clarke and Altschuler, 1958; Altschuler et al., 1958; Kolodny and Kaplan, 1970; Burnett, 1974; and Burnett and Gomberg, 1977). The work of Altschuler et al. (1958) has shown that the U(IV)/U(VI) ratios are lowest in those samples which have clear indications of subaerial weathering. U(IV) is insoluble and must be oxidized in order to be transported in groundwater. The greater solubility of U(VI) is due in part to its tendency to form uranyl di- and tri-carbonate anions. Thus, U solubility is a function of not only the redox potential of water but also of the pH and the partial pressure of CO_2 in the system. In comparison to Ra, the stability of the uranyl complexes and their long half-life allow U to be transported long distances under oxidizing conditions. Uranium is removed from solution by sorption or reducing barriers (Hess et al., 1985).

Intensive weathering of the primary phosphate minerals, along with the associated clays, occurs in the Florida deposits as a result of groundwater percolation (Riggs, 1979). According to Altschuler (1973), only two lithologies (calcareous and argillaceous phosphates) need be considered. Also, the mineralogies and even the textures and morphologies of the weathered deposits are similar, under comparable degrees of weathering in chemically similar lithologies, whether igneous or sedimentary, insular or terrestrial, and regardless of the climate. In the Bone Valley Formation, the upper part has been leached and altered to aluminum phosphates as a result of lateritic weathering and groundwater percolation. Wavellite predominates at the top of a typical section while calcium-aluminum phosphates (crandallite and millisite) are most common in the middle of the zone. Pebbles of leached apatite occur at the base of most weathered sections.

The mere presence of a phosphate deposit does not necessarily result in significantly elevated concentrations of uranium-series nuclides in the surrounding environment. For example, the data in Chapter 4 of this report show that higher concentrations of soluble ^{226}Ra occur in downstream stations remote from phosphate mining operations on the Suwannee River than directly from the drainage of the phosphate district. Similar findings were also observed by Mitsch et al. (1984). They reported that both ^{226}Ra and ^{222}Rn concentrations recorded in wells located in the vicinity of the phosphate mining site in Aurora, N.C., were relatively low when compared to concentrations found elsewhere in the state.

The direct daughter of ^{226}Ra is ^{222}Rn, the inert gas whose leakage from phosphate rock samples will be the subject of Chapter 3. Radon-222 decays through a series of short-lived nuclides to ^{210}Pb ($t_{1/2}$ = 22 years) and ^{210}Po ($t_{1/2}$ = 138 days). Detectable activities of these daughters would be expected because of the relatively high concentration of ^{222}Rn present in many groundwaters. However, as Hess et al. (1985) discuss, the insolubility of these isotopes and their short-lived precursors in the aquifer is demonstrated by the fact that more than 99.9%

of the activity generated by radon decay in groundwater is removed within the 2 hours necessary for equilibrium to be established between ^{222}Rn and ^{214}Pb. Of the ^{210}Po and ^{210}Pb analyses presented by these authors throughout the United States, only one well in Louisiana had an anomalously high ^{210}Po value. These isotopes are generally not expected to occur in activities greater than 1.0 pCi L^{-1}.

In 1982, geologists from the Florida State University found extremely high levels (up to thousands of pCi L^{-1}) of ^{210}Po in water samples from recharge wells in central Florida (Cowart, pers. comm.). Approximately 80 wells from several counties in southwest Florida were sampled in response to these reports (Chapter 5, this report). Subsequent analyses indicated that ^{210}Po is often above the EPA drinking water standard of 15 pCi L^{-1} for total alphas. Activities of over 300 pCi L^{-1} were measured for many of the samples. These are shallow wells used for domestic consumption and therefore present an environmental problem.

EXPERIMENTAL METHODS

Phosphate Rock Samples

The phosphate rock samples which will be used in this study represent a reasonably complete weathering profile. All samples have been analyzed both radiochemically and geochemically as part of the characterization of isotopic equilibrium during weathering (Chapter 1). Nine of the samples were collected from the Central Florida Phosphate District. Two other samples, HAW-1, a drill sample from deep within the Hawthorn Formation of Northern Florida and PR-1 from Unit-C of the Pungo River Formation of North Carolina, were also included as fresh "end members".

Locations, field descriptions, X-ray mineralogy, P_2O_5, F, apatite structural-CO_2 results as well as the approximate order of weathering can be found in Chapter 1 of this report. This proposed order of weathering represents the transition from fresh to very weathered material and is based upon structural carbonate concentrations, F/P_2O_5 ratios, and the presence of secondary phosphate minerals.

Although laboratory leaching experiments have not been previously conducted on phosphate rock samples, other types of materials have been used by many other investigators. Crushed magmatic rocks were used by Szalay and Samsone (1970) with a 2% $NaHCO_3$ solution. Their results indicate that the concentrations of uranium in the water attain an equilibrium value within 4-5 hours. They replaced the leaching solution with fresh solution and obtained similar uranium concentrations on all the samples. Eyal and Fleischer (1985) reported U and Th isotope differences in leaching solutions (distilled water and bicarbonate) and concluded that preferential leaching is a function of the amount of radiation damage within particular uranium or thorium minerals. Yang and Edwards (1984) used KCl and $BaCl_2$ solutions on bottom sediments from river wastewater downstream from a U mine. The fact that most of the Ra and U were not displaced by K^+ or Ba^{2+} indicated that these nuclides were not absorbed on the particle surfaces but rather are associated with minerals of U ores or are partly trapped inside the colloidal hydroxides of Fe and Mn coated on the sediment. We might add that previous investigators have made no reference to sample dissolution--a complicating factor with phosphate samples.

In this study we will attempt to evaluate the leachability of U, Ra, Pb, and Po in a number of carefully selected solutions from Florida phosphate rock samples.

Experimental Design

The leaching experiments consisted of reacting powdered samples with a number of solutions carefully chosen to mimic various groundwater conditions. All rock samples, prior to leaching, were analyzed for ^{238}U , ^{234}U, ^{230}Th, ^{226}Ra, ^{210}Po, and ^{210}Pb from the ^{238}U decay chain, as well as ^{232}Th and ^{231}Pa. The solutions used in the leaching experiments were as follows:

(1) Double-deionized water;

(2) Humic acid in the form of either:

- Suwannee River water collected near Ellaville, Fla.; or
- Stock humic acid (Aldrich Labs)

(3) 2% NaOH;

(4) 5% $(NH4)_2CO_3$;

(5) 0.1M NH_4Cl;

(6) 0.1M Na_2S; and

(7) 1M $BaCl_2$

Double-deionized water and ammonium carbonate were used to simulate acidic rain conditions and natural weathering solutions in a carbonate terrain, respectively. Since humic acids are known for their ability as organic chelating agents and are very common in the environment, Suwannee River water was used, because its humic acid content is fairly high (> 15 mg L^{-1}). Stock humic acid solutions were also run for comparison. NH_4Cl and $BaCl_2$ solutions were used to evaluate which cations may be released by ion-exchange processes. Attack by the sodium carbonate solution is reasonably specific for dissolution of the non-crystalline silica and alumina fraction and will not dissolve minerals such as quartz, gibbsite, and well-crystallized clays. Treatment with NaOH is useful for removing humic and fulvic acids, as well as some amorphous aluminum (Airey, 1983). Na_2S solutions were prepared in a nitrogen atmosphere to evaluate whether the presence of sulfide would influence the mobility of polonium (see Chapter 5).

Sufficient dried sample was weighed out so that each reaction vessel (250 ml polycarbonate Erlenmeyer flasks) contained between 100-500 pg of ^{238}U. For many of the individual experiments, the ratio of the leaching solution to the sample mass was kept constant to allow for a direct comparison of the percent of sample mass lost from dissolution. The flasks were then placed onto a shaker table for agitation and run at room temperature for two weeks. A number of experiments were also run for 5 hours as a time comparison. After allowing one day to settle, the solid and solution phases were separated by decanting, centrifuging and filtering.

The procedure for evaluating the fraction of the radionuclides lost by leaching includes the following:

(1) Measurement of total sample mass both before and after leaching;

(2) Determination of ^{238}U, ^{226}Ra and ^{210}Pb by gamma spectroscopy in the solid phase after leaching; and

(3) Measurement of ^{210}Po in the solution after leaching.

The choice of analyzing the solid or solution phase for each radionuclide was based on convenience, i.e., ease of analysis for a particular isotope. We have computed a "percent leachable" factor to indicate preferential loss of an isotope to solution. It is defined as the percent of the original solid phase sample activity that is present in solution beyond that which would be present from simple sample dissolution. The correction made for sample dissolution assumes that the nuclide is distributed homogeneously throughout the sample. A positive value would therefore indicate preferential loss of an isotope to solution, while a negative value indicates preferential retention by the residual solid phases. Details of these computations are given in a later section.

Radiochemical Analyses

The radiochemical analyses included a non-destructive, high-resolution gamma spectrometric technique developed in our laboratory (Kim and Burnett, 1983) and isotope dilution alpha spectrometry, utilizing a separation scheme developed at the the Institute of Nuclear Sciences (INS) in New Zealand. Analyses for ^{226}Ra and ^{210}Pb, as well as ^{238}U (via

^{234}Th), were made by gamma spectroscopy. The INS separation process is accomplished by temperature-controlled ion exchange techniques. ^{210}Po is electroplated directly from the original sample solution before loading onto the ion exchange column. The source preparation is based on electrodeposition, utilizing a rotating disc electrodeposition unit with a temperature controlled electroplating cell. The sources are mounted on highly polished 1"-diameter stainless steel planchets and are ideally suited for low-level alpha particle spectroscopy. Chemical yields for ^{210}Po (determined by utilizing a ^{209}Po tracer) in residual solutions under 5% were not included in the final data set. For complete details of the method, see McCabe et al. (1979) and Ditchburn and McCabe (1984).

Because a few of the ^{210}Po source discs prepared by electrodepostion from the residual solutions were contaminated with uranium, a spontaneous deposition method was employed.

RESULTS AND DISCUSSION

Calculations and Mass Loss

Results of the leaching experiments for ^{238}U, ^{226}Ra, ^{210}Pb and ^{210}Po are provided in Tables 7, 8, 9, and 10, respectively. The data are grouped by leaching solutions in each of the tables. Within each of these sections the samples are listed in order of apparent weathering, according to the classification in Chapter 1, beginning with the freshest material at the top of the section. Duplicate experiments are indicated as a "#2" in the sample columns of the tables immediately below the first run. Within the humic acid section, solution strengths are given in the sample column in units of mg L^{-1}; "SRW" refers to Suwannee River water collected near Ellaville.

The amount of a particular nuclide leached from (or retained by) the sample beyond that which would be expected from sample dissolution is expressed as a percent of the initial sample activity of that particular nuclide. This "% leachable" is calculated by the following equation:

Table 7. Leaching data for ^{238}U in Suwannee River water and humic acid stock solutions at concentrations of 15 and 30 mg L^{-1}.

Sample	Leaching Solution	Mass Loss (%)	Bulk Activity (pCi g^{-1})	Initial Activity (pCi)	Residual Solid (pCi)	Solution Activity (pCi)	Dissolution Activity (pCi)	% Leachable
FM-3	SRW	0.28	12.8	193.	131	62.2	0.54	31.9
	HA,15	0.14	12.8	192.	164	28	0.27	14.2
	HA,30	0.79	12.8	193.	144	48.6	1.53	24.4
NRM-4	SRW	1.43	252.5	178.1	143	35	2.55	18.3
	HA,15	4.15	252.5	180.7	157	23	7.50	8.6
	HA,30	1.99	252.5	180.2	160	20	3.59	9.1

Table 8. Leaching data for ^{226}Ra in double-deionized water, humic acid, NaOH, $(NH_4)_2CO_3$, and NH_4Cl solutions. All experiments run for two weeks except where indicated (see text for details).

SAMPLE	Mass Loss (%)	Bulk Activity (pCi g^{-1})	Initial Activity (pCi)	Residual Solid (pCi)	Solution Activity (pCi)	Dissolution Activity (pCi)	% Leachable
Double-Deionized Water							
HAW-1B	3.05	14.5	152.	150.	2.2	4.64	-1.5
#2	4.33	14.5	37.5	36.9	.59	1.63	-2.6
5hr.	1.21	14.5	72.5	77.0	-4.95	0.87	-8.0
#2	3.15	14.5	36.0	36.1	-.09	1.14	-3.4
FM-3	0.49	13.6	207.	275.	-68.5	1.01	-33.7
CSP-4	0.85	25.0	170.	126.	44.2	1.45	25.1
NRM-4	6.97	177.5	117.1	92.3	24.4	8.162	13.9
5hr.	2.23	177.5	54.14	47.3	6.62	1.21	10.0
NRM-10	2.11	165.2	156.9	131.	25.5	3.30	14.1
NRM-3	1.55	151.1	259.9	224.	35.9	4.04	12.2
Humic Acid Solutions							
HAW-1B,15	0.85	14.5	139.	149	-10.3	1.18	-8.2
30	0.75	14.5	128.	128	0.34	0.97	-0.4
FM-3,SR	0.28	13.6	206.	191	13.9	0.58	6.5
15	0.14	13.6	205.	209	-3.30	0.29	-1.7
30	0.79	13.6	206.	164	41.3	1.63	19.2
NRM-4,SR	1.43	177.5	125.2	107	17.6	1.79	12.6
15	4.15	177.5	127.0	106	21.0	5.270	12.4
30	1.99	177.5	126.7	103	23.2	2.52	16.3
NRM-3,15	0.00	151.1	261.2	255	5.77	0.00	2.2
30	0.14	151.1	263.1	245	17.4	0.38	6.4
NaOH							
HAW-1B,5H	3.86	14.5	36.4	37.8	-1.4	1.41	-7.8
CSP-4	38.81	25.0	167.	105.	61.7	64.86	-1.8
NRM-4	28.57	177.5	124.2	90.1	34.3	35.50	-1.0
#2	31.53	177.5	61.85	37.6	24.2	19.50	7.7
5Hr	24.40	177.5	56.08	39.3	16.8	13.68	5.6
#2	28.40	177.5	53.15	35.1	18.1	15.10	5.6
NRM-10	44.44	165.2	148.6	115.	33.7	66.08	-21.8
NRM-3	35.29	151.1	256.9	199.	58.6	90.68	-12.6

Table 8. (Continued)

SAMPLE	Mass Loss (%)	Bulk Activity (pCi g^{-1})	Initial Activity (pCi)	Residual Solid (pCi)	Solution Activity (pCi)	Dissolution Activity (pCi)	% Leachable
				$(NH_4)_2CO_3$			
HAW-1B	2.10	14.5	151.	170	-19.2	3.17	-14.8
5hr.	1.01	14.5	72.5	86.0	-13.9	0.73	-20.2
#2	4.71	14.5	36.2	34.5	1.65	1.70	-0.1
FM-3	0.54	13.6	186.	230	-44.5	1.00	-24.4
CSP-4	34.33	25.0	167.	102	65.3	57.4	4.6
NRM-4	14.29	177.5	124.2	95.9	28.2	17.75	8.4
5hr.	3.77	177.5	53.6	45.0	8.51	2.02	12.1
NRM-10	11.11	165.2	148.6	130	18.6	16.52	1.4
NRM-3	5.88	151.1	256.9	218	38.4	15.11	9.1
				NH_4Cl			
HAW-1B	5.22	14.5	37.7	36.7	0.99	1.96	-2.6
CSP-4	6.91	25.0	42.3	40.0	2.31	2.92	-1.4
NRM-4	23.85	177.5	64.23	44.1	20.2	15.32	7.6
NRM-3	10.58	151.1	125.1	103.	22.5	13.24	7.4

Table 9. Leaching data for ^{210}Pb in double-deionized water, humic acid, $(NH_4)_2CO_3$, and NH_4Cl solutions. All experiments run for two weeks except where indicated (see text for details).

Sample	Mass Loss (%)	Bulk Activity (pCi g^{-1})	Initital Activity (pCi)	Residual Solid (pCi)	Solution Activity (pCi)	Dissolution Activity (pCi)	% Leachable
Double-Deionized Water							
HAW-1B	3.05	13.0	137.	167.	-34.3	4.18	-28.1
#2	4.33	13.0	33.9	28.8	5.05	1.46	10.7
5hr.	1.21	13.0	64.9	60.8	4.15	0.79	5.2
#2	3.15	13.0	32.4	26.4	5.99	1.02	15.3
FM-3	0.49	11.0	167.	141.	25.8	0.81	15.0
CSP-4	0.85	20.9	143.	149.	-5.99	1.21	-5.0
NRM-4	6.97	134.5	88.78	73.4	15.5	6.19	10.5
5hr.	2.23	134.5	41.0	40.0	0.99	0.91	0.2
NRM-10	2.11	117.1	111.2	138.	-26.9	2.34	-26.3
NRM-3	1.55	148.3	255.0	250.	5.68	3.96	0.7
Humic Acid Solutions							
HAW-1B,15	0.85	13.0	125.7	107.2	18.4	1.06	13.8
30	0.75	13.0	115.8	86.0	29.9	0.87	25.1
FM-3,SR	0.28	11.0	166.	153.	1.80	0.46	0.8
15	0.14	11.0	165.	203.	-37.7	0.23	-23.0
30	0.79	11.0	166.	118.	48.2	1.31	28.4
NRM-4,SR	1.43	134.5	94.86	100.	-5.77	1.36	-7.5
15	4.15	134.5	96.26	100.	-4.0	4.00	-8.3
30	1.99	134.5	96.08	91.0	4.77	1.91	3.0
NRM-3,15	0.00	148.3	256.3	229.	27.6	0.00	10.8
30	0.14	148.3	258.2	221.	37.2	0.37	14.3
NaOH							
HAW-1B,5H	3.86	13.0	32.8	15.0	32.8	1.27	96.1
CSP-4	38.81	20.9	140.	79.7	60.4	54.5	4.4
NRM-4	28.57	134.5	94.1	78.4	15.8	26.90	-11.8
#2	31.53	134.5	46.89	45.9	46.8	14.78	68.5
5Hr	24.40	134.5	42.50	29.3	42.5	10.37	75.6
#2	28.40	134.5	40.30	34.9	40.3	11.45	71.6
NRM-10	44.44	117.1	105.4	105.	-0.09	46.85	-44.5
NRM-3	35.29	148.3	252.1	185.	67.1	88.96	-8.6

Table 9. (Continued)

Sample	Mass Loss (%)	Bulk Activity (pCi g^{-1})	Initital Activity (pCi)	Residual Solid (pCi)	Solution Activity (pCi)	Dissolution Activity (pCi)	% Leachable
------ $(NH_4)_2CO_3$ ------							
HAW-1B	2.10	13.0	136.	183.8	-47.7	2.86	-37.3
5hr.	1.01	13.0	65.3	72.5	-7.2	0.66	-12.4
#2	4.71	13.0	32.6	27.6	4.95	1.53	10.4
FM-3	0.54	11.0	150.	163.	-12.7	0.80	-9.0
CSP-4	34.33	20.9	140.	72.1	68.0	47.7	14.1
NRM-4	14.29	134.5	94.14	95.9	-1.66	13.45	-16.1
5hr.	3.77	134.5	40.6	41.0	-0.35	1.53	-4.62
NRM-10	11.11	117.1	105.4	135.	-29.9	11.70	-39.5
NRM-3	5.88	148.3	252.1	230.	22.5	14.82	3.0
------ NH_4Cl ------							
HAW-1B	5.22	13.0	34.0	30.0	3.95	1.77	6.4
CSP-4	6.91	20.9	35.4	36.7	-1.32	2.44	-10.7
NRM-4	23.85	134.5	48.69	56.8	-8.28	11.60	-40.9
NRM-3	10.58	148.3	122.7	128.	-5.23	12.99	-14.8

Table 10. Leaching data for ^{210}Po in double-deionized water, humic acid, NaOH, Na_2S, $(NH_4)_2CO_3$, and NH_4Cl solutions. All experiments ran for two weeks except where indicated (see text for details).

Sample	Mass Loss (%)	Bulk Activity (pCi g^{-1})	Initial Activity (pCi)	Dissolution Activity (pCi)	Solution Activity (pCi)	% Leachable
Double-Deionized Water						
HAW-1B	3.05	13.1	137.	4.20	0.01	-3.0
#2	4.33	13.1	34.0	1.47	0.06	-4.1
5hr.	1.21	13.1	65.3	0.79	0.01	-1.2
#2	3.15	13.1	32.5	1.02	0.01	-3.1
FM-3	0.49	11.0	117.	0.81	0.00	-0.5
CSP-4	0.85	20.9	143.	1.21	0.38	-0.6
NRM-4	6.97	134.5	88.8	6.19	4.35	-2.1
5hr.	2.23	134.5	41.05	0.91	0.06	-2.1
NRM-10	2.11	117.1	111.2	2.34	1.77	-1.4
NRM-3	1.55	116.8	200.9	3.12	1.62	-0.7
Humic Acid Solutions						
HAW-1B,15	0.85	13.1	126.	1.07	0.25	-0.7
30	0.75	13.1	116.	0.87	NA	NA
FM-3,SR	0.28	11.0	166.	0.46	0.20	-0.2
15	0.14	11.0	165.	0.23	0.00	-0.1
30	0.79	11.0	166.	1.31	0.00	-0.8
NRM-4,SR	1.43	134.5	94.86	1.36	0.08	-1.3
15	4.15	134.5	96.26	4.00	0.24	-3.9
30	1.99	134.5	95.99	1.91	1.91	0.0
NRM-3,15	0.00	116.8	201.9	0.00	0.68	0.3
30	0.14	116.8	203.3	0.29	1.05	0.4
NaOH						
HAW-1B,5H	3.86	13.1	32.9	1.27	0.02	-3.8
CSP-4	38.81	20.9	140.	54.5	1.14	-38.0
NRM-4	28.57	134.5	94.14	26.9	4.613	-23.7
#2	31.53	134.5	46.89	14.78	0.47	-30.5
5Hr	24.40	134.5	42.50	10.37	0.32	-23.7
#2	28.40	134.5	40.30	11.45	0.55	-27.0
NRM-10	44.44	117.1	105.4	46.84	6.995	-37.8
NRM-3	35.29	116.8	198.6	70.09	16.41	-27.0

Table 10. (Continued)

Sample	Mass Loss (%)	Bulk Activity (pCi g^{-1})	Initial Activity (pCi)	Dissolution Activity (pCi)	Solution Activity (pCi)	% Leachable
$(NH_4)_2CO_3$						
HAW-1B	2.10	13.1	136.	2.86	0.00	-2.1
5hr.	1.01	13.1	65.3	0.66	0.19	-0.7
#2	4.71	13.1	32.7	1.54	0.05	-4.5
FM-3	0.54	11.0	150.	0.81	0.09	-0.5
CSP-4	34.33	20.9	140.	48.2	NA	NA
NRM-4	14.29	134.5	94.14	13.45	6.284	-7.6
5hr.	3.77	134.5	40.64	1.53	2.45	2.3
NRM-10	11.11	117.1	105.4	11.71	3.84	-7.5
NRM-3	5.88	116.8	198.6	11.68	7.08	-2.3
NH_4Cl						
HAW-1B	5.22	13.1	34.1	1.78	0.05	-5.1
CSP-4	6.91	20.9	35.5	2.45	0.48	-5.6
NRM-4	23.85	134.5	48.69	11.61	0.42	-23.0
NRM-3	10.58	116.8	96.67	10.23	0.23	-10.3
Na_2S						
HAW-1A	6.60	13.1	28.9	1.91	0.25	-5.7
#2	7.83	13.1	28.9	2.26	0.00	-7.8
5hr.	2.74	13.1	28.9	0.79	0.00	-2.7
#2	3.86	13.1	29.9	1.15	0.12	-3.9
NRM-10	27.93	117.1	127.3	35.55	3.54	-27.9
#2	30.10	117.1	117.3	35.31	2.23	-30.1
5hr.	7.44	117.1	118.9	8.85	7.180	-1.4
#2	7.95	117.1	115.9	9.21	9.549	0.3
NRM-3	7.02	116.8	113.9	8.0	2.58	-4.8
#2	7.95	116.8	113.2	8.995	1.73	-6.4

% LEACHABLE = $[(S_A - D_A)/I_A] \times 100$; where:

S_A = solution activity, i.e., activity measured or calculated in the solution after leaching;

D_A = dissolution activity, i.e., activity that would be present in the leaching solution from simple dissolution of the solid sample (= I_A x mass loss %); and

I_A = initial activity, i.e., sample specific activity (pCi g^{-1}) x sample mass in experiment (g).

Since ^{238}U, ^{226}Ra and ^{210}Pb activities are measured by gamma spectroscopy in the residual solid, the solution activity is inferred as the difference between the initial activity and the activity measured in the residual material. An underlying assumption regarding calculation of the dissolution activity is that the radionuclides are homogeneously dispersed throughout the samples. In some cases, such as the weathered samples, this assumption would cause serious error. The mass losses for the two-week experiments were the greatest in NaOH and lowest in double-deionized water and the humic acid solutions. Sample mass losses within the individual solutions showed no apparent trends relating to the apparent degree of weathering. The 5-hour experiments consistently showed smaller or comparable mass losses for all the solutions.

Uranium

Because we are evaluating ^{238}U by counting the gamma emitting daughter, ^{234}Th ($t_{1/2}$ = 24.1 days), it is necessary to store the solid samples several months after the experiments to allow ^{234}Th to approach secular equilibrium. The results of our measurements are provided in Table 7. These results suggest that uranium is preferentially leached in both the synthetic humic acid solutions and in the Suwannee River water (Fig. 8).

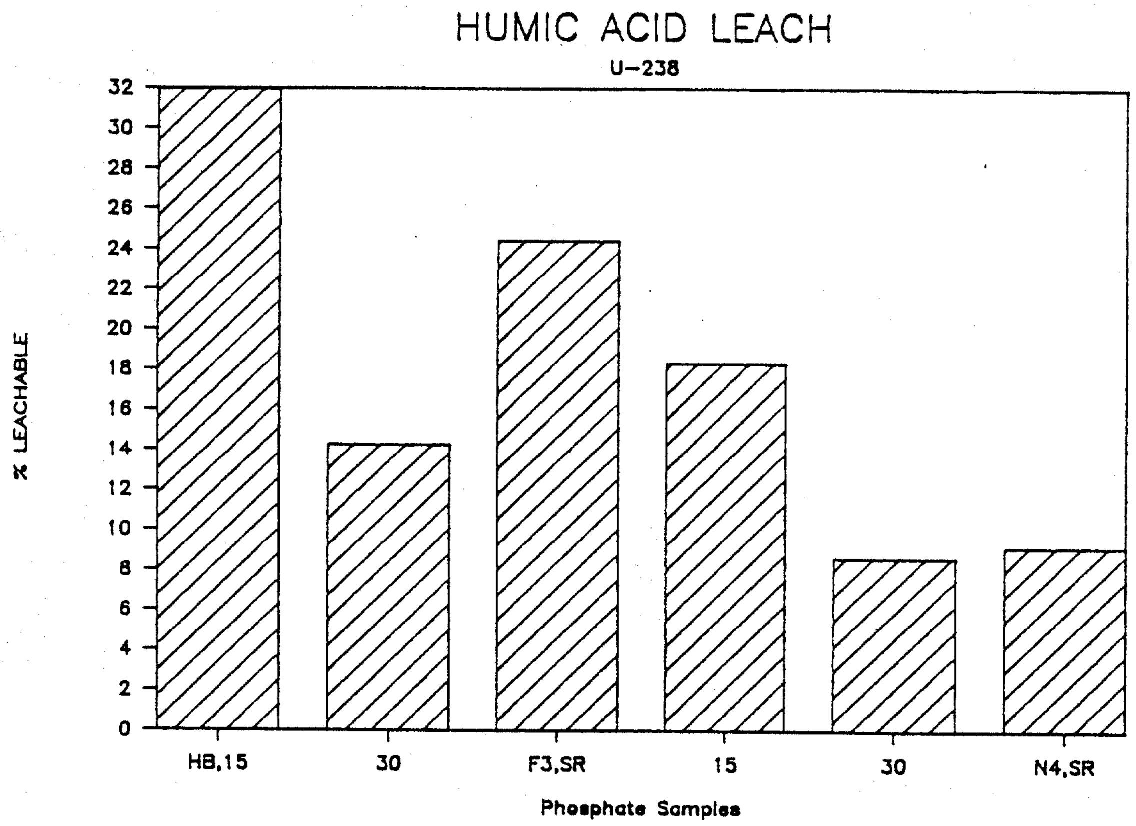

Figure 8. Calculated % ^{238}U leachable for powdered phosphate samples FM-3,(F3) and NRM-4 (N4), in Suwannee River Water (SRW) and humic acid solutions at concentrations of 15 and 30 mg L^{-1}. All experiments run for two weeks.

This is not surprising in view of the known affinity of uranium for organic complexes.

Radium

The ^{226}Ra data (Table 8) are quite interesting and are illustrated for each solution in Figs. 9 through 12. The % leachables in double-deionized water, $(NH_4)_2CO_3$, and NH_4Cl are greater for the more highly weathered samples. This trend is somewhat less striking in the humic acid solutions (Fig. 12) where ^{226}Ra is lost in almost every experiment.

Lead

As mentioned, gamma spectroscopy was employed for the determination of Ra and Pb (as well as U) activities. The counting errors associated with the ^{210}Pb peaks were very high (some greater than 10%), particularly for the lower activity samples (HAW-lB, FM-3, and CSP-4). Values of % leachable duplicates (Table 9) did not agree as well as our other duplicates. The apparent deviations within this data set make it essentially impossible to draw any substantive conclusions for the lead results.

Polonium

As is very apparent in Table 10, the % leachable calculated for the vast majority of all the samples is negative for Po. Notice that for individual samples high mass losses are always accompanied by highly negative % leachable factors. This indicates that in these solutions any polonium that may have been released by solution was subsequently adsorbed by the solid phase. It is also possible that polonium was not associated with the phases that were dissolved. This would result in an overestimate of the "dissolution activity" causing the negative leaching factors. In any event, polonium is not leached under any of the experimental conditions we have tested.

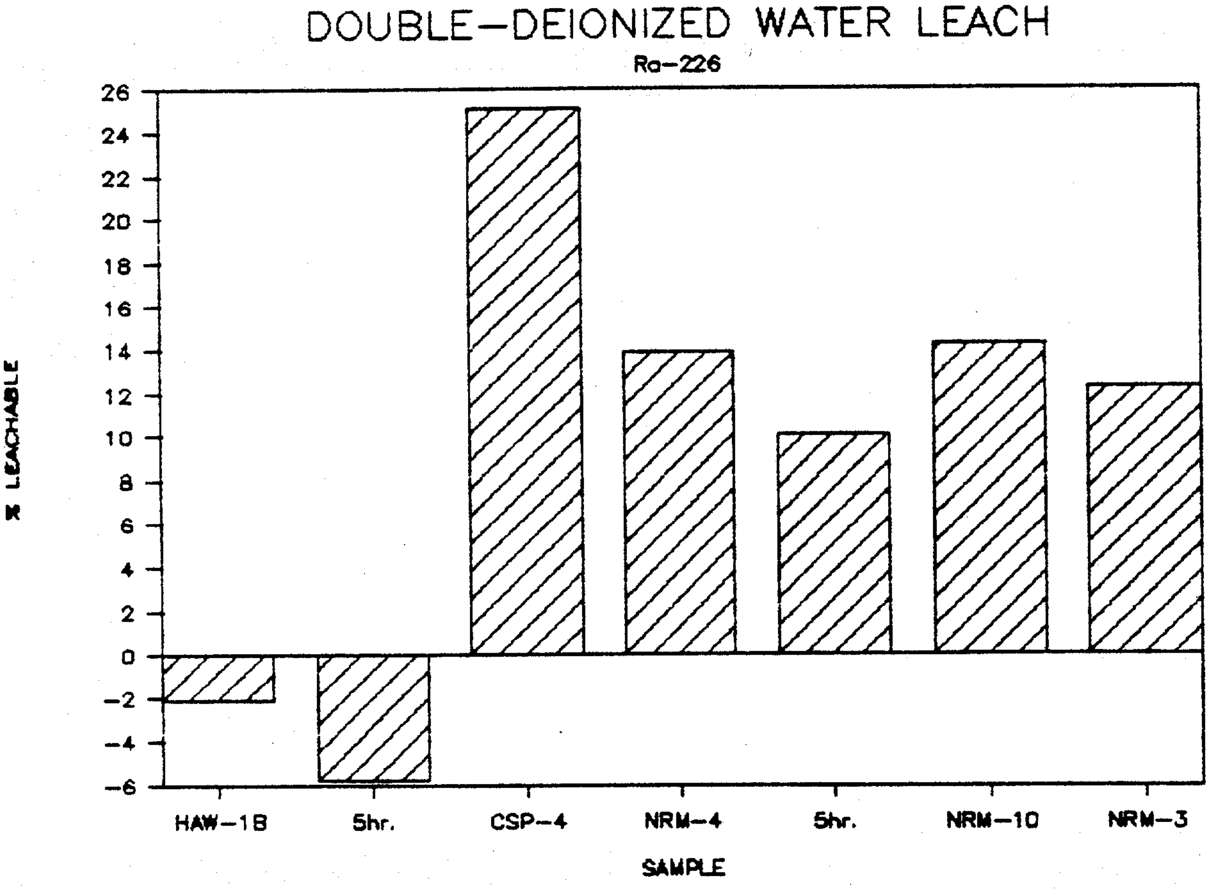

Figure 9. Calculated % ^{226}Ra leachable for powdered phosphate samples in double-deionized water. All experiments run for two weeks except where indicated.

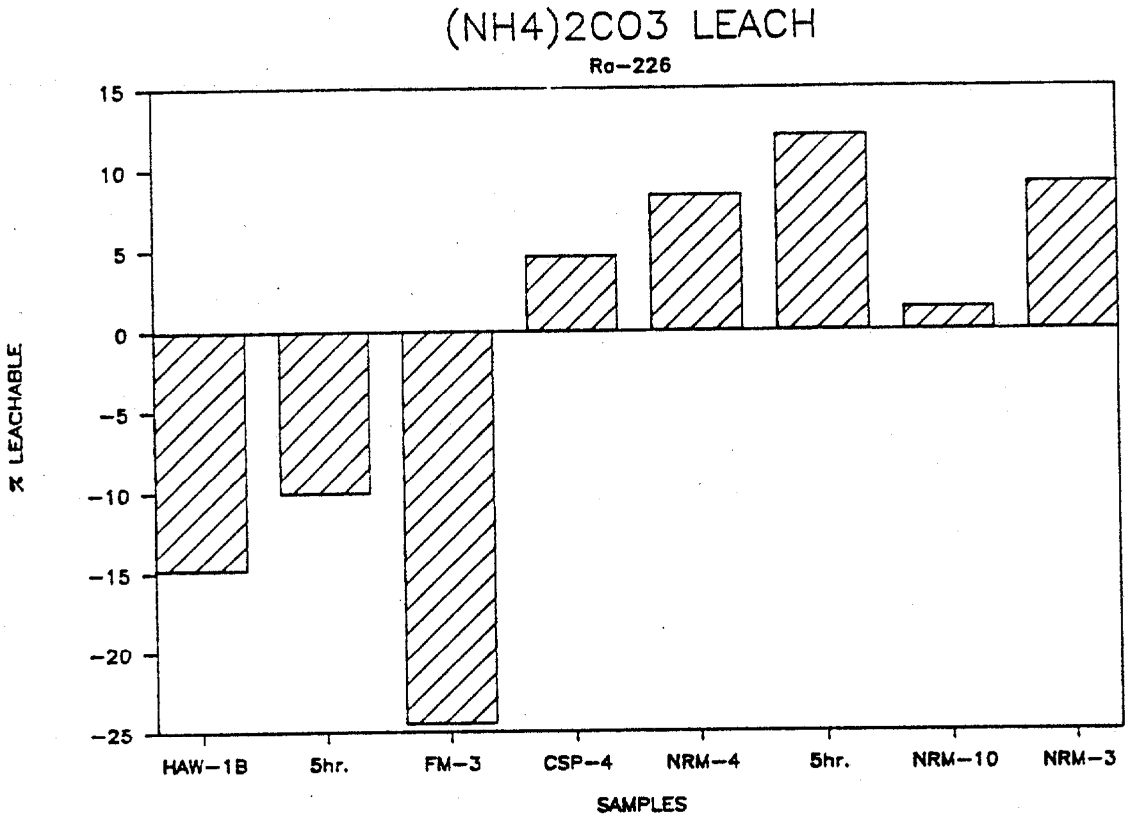

Figure 10. Calculated % ^{226}Ra leachable for powdered phosphate samples in 5% $(NH_4)_2CO_3$. All experiments run for two weeks except where indicated.

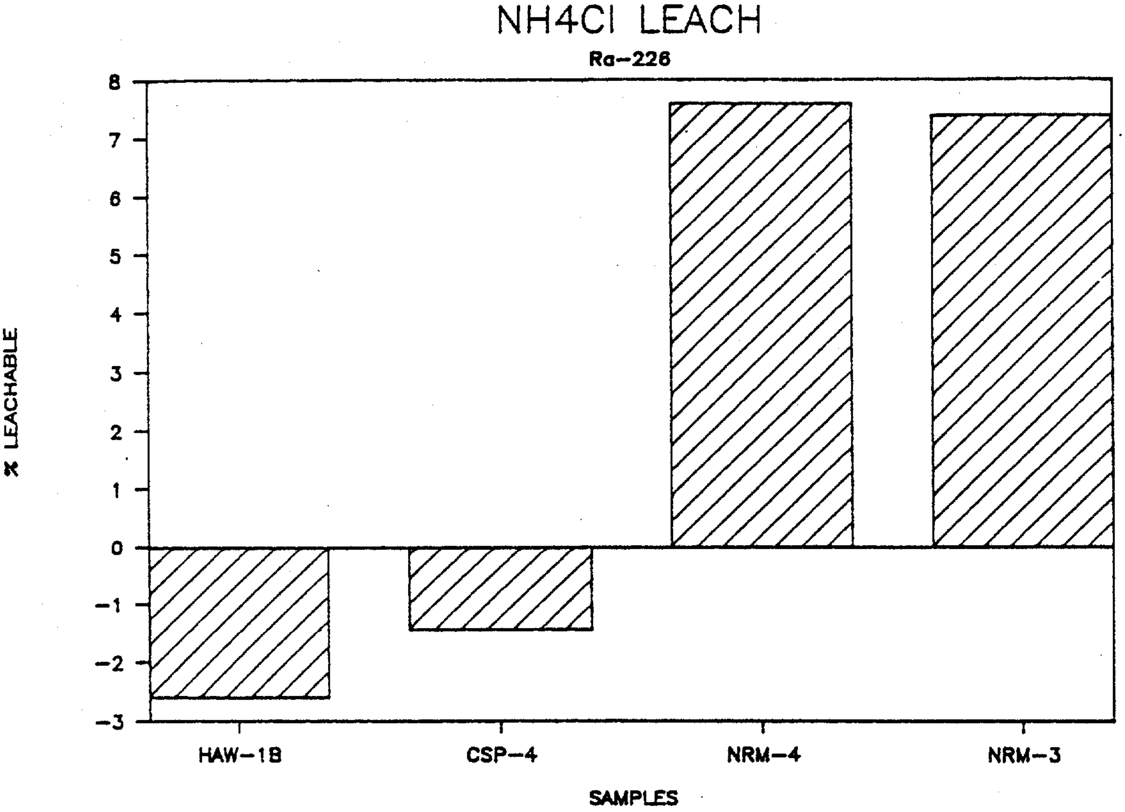

Figure 11. Calculated % ^{226}Ra leachable for powdered phosphate samples in 0.1M NH_4Cl. All experiments run for two weeks.

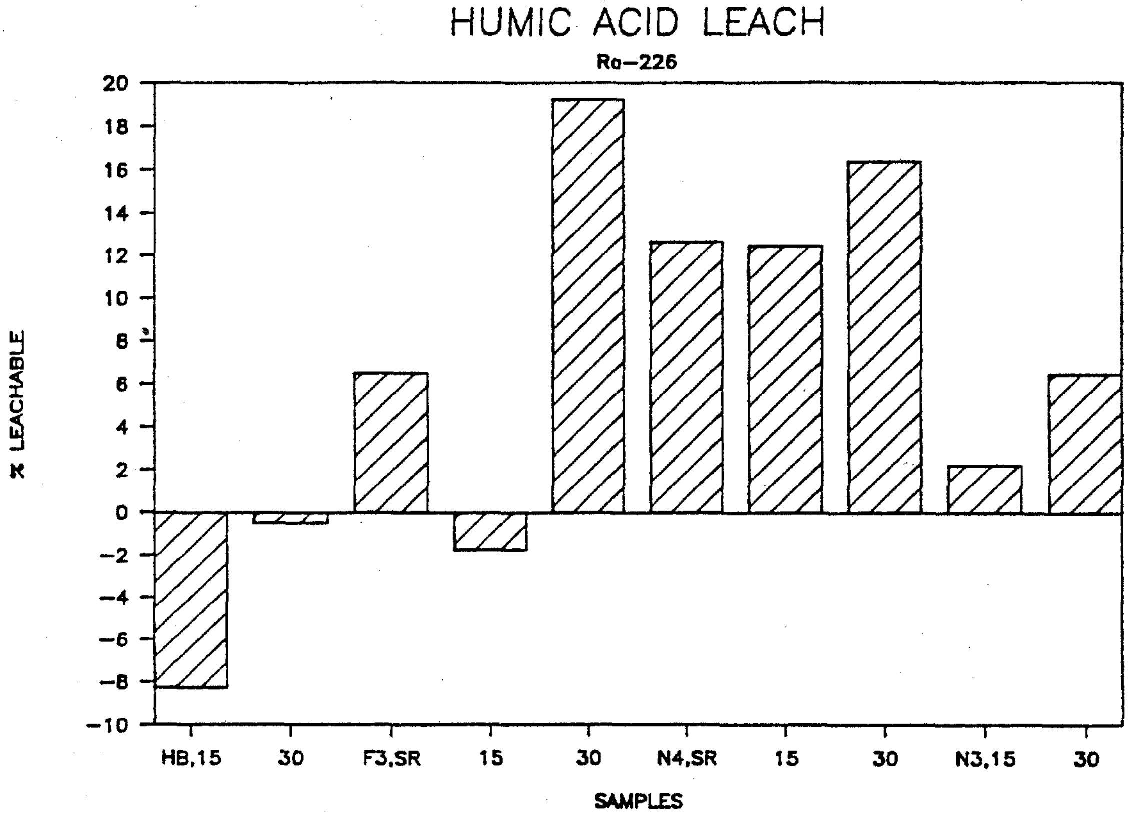

Figure 12. Calculated % ^{226}Ra leachable for powdered phosphate samples in Suwannee River Water (SRW) and humic acid solutions at concentrations of 15 and 30 mg L^{-1}. All experiments run for two weeks.

CONCLUSIONS

(1) Uranium is lost from phosphate rock during interaction with both synthetic and natural (Suwannee River water) humic acid solutions. This probably occurs as a result of formation of uranium-organic complexes.

(2) Our results indicate that inference of solution activities through measurement of nuclides in the residual solid (in particular ^{210}Pb, with associated high counting errors) reduces the precision of these types of experiments substantially.

(3) ^{226}Ra appears to be preferentially leached from more highly weathered phosphate samples by several solutions, including double-deionized water, ammonium carbonate, ammonium chloride, and humic acids.

(4) Experimental results indicate that all the solutions tested did not preferentially leach ^{210}Po from the phosphate rock samples. Rather, any ^{210}Po that may have been mobilized into solution by the dissolution of the sample appears to have been adsorbed back onto the solid phase materials.

CHAPTER 3

RADON LOSS EXPERIMENTS

INTRODUCTION

Radon occupies the last place in the group of noble gases in the Periodic Table and is essentially inert. The mobility of Rn isotopes is regarded as one of the main sources of disequilibrium in the U and Th decay series. Of the three naturally occurring isotopes of this gas, only ^{222}Rn (hereafter referred to as radon or Rn) of the ^{238}U decay chain will be considered in this chapter. It has a half life of 3.8 days and is the most abundant of these isotopes, particularly in phosphatic strata. Thoron (^{220}Rn) of the ^{232}Th decay chain and actinon (^{219}Rn) of the ^{235}U chain are not discussed in this report because of their short half lives and low abundance in phosphate rock samples.

Radon is very soluble in water (0.5 g L^{-1} at STP) and is often found in excess of its parent ^{226}Ra. Radon has been used in uranium exploration and as a tracer in the ocean to establish vertical mixing rates. High activities in air and water are associated with granitic rocks, U minerals, and tailings from phosphate fertilizer processing and uranium mines. Its occurrence is controlled by physical variables such as pressure, temperature, emissivity from rocks, as well as by time, and by the geochemistry of its parent ^{226}Ra.

^{222}Rn may be transported by water as well as air and can lead to public exposures by being ingested and exposing the digestive system as well as via indoor air pollution. Although there is currently no standard for Rn in water, Sasser and Watson (1978) recommended a maximum concentration of 10,000 pCi L^{-1}.

Groundwater Radon

Migration by transport in groundwater is a mechanism by which Rn can migrate over significant distances. Levinson et al. (1982) point out that the most common of the radioactive anomalies are the many mineral springs that are known to have extraordinarily high levels of radioactivity. In a typical aquifer, groundwater movement is slow, the amount of Rn removed by springs and wells is small, and the distance that Rn migrates is short.

Excess (^{226}Ra unsupported) radon measurements have been made on samples from shallow wells and springs in southwest Florida as part of our work on polonium (see Chapter 5). The radon levels were variable, but most often quite high, in the surficial aquifer with many above 10,000 pCi L^{-1} and some up to over 40,000 pCi L^{-1}. The extent of these instances of high activity, however, appears worldwide. As two noteworthy examples, Wathen and Hall (1986, unpublished report) reported radon levels ranging up to 145,000 pCi L^{-1} in wells drilled into two mica granites in Maine and New Hampshire and groundwater in the Helsinki area of Finland occasionally contains Rn as high as 888,000 pCi L^{-1} (Asikainen and Kahlos, 1979).

Indoor Radon

Outgassing creates levels of exposure to both radon and radon progeny. Radon produced from ^{226}Ra in the surficial soil and rock is released into houses from water, soil gas, fuel gas, construction materials, and outdoor air (Akerblom and Wilson, 1981). Once in the air, radon undergoes alpha decay to produce charged daughter ions. Of primary interest are the longer-lived daughters, namely ^{210}Pb, ^{210}Bi and ^{210}Po. These radon progeny are chemically reactive and soon become irreversibly associated with aerosol particles which are subsequently inhaled.

Unusually high ^{222}Rn levels in homes constructed on land reclaimed after phosphate mining were reported in an Environmental Protection Agency publication (EPA, 1975). Radon concentrations well over 10 pCi L^{-1} have been noted in buildings containing materials such as gypsum wall board derived from Florida phosphate residues or cinder-blocks made of fly ash or blast furnace slag (Hess et al., 1985). Here again the problem is not confined to one particular area or geology. Gunderson (1985) for example, recently reported high levels of radon in homes of the Reading Prong area of Pennsylvania and adjacent states.

Nero et al. (1986) reported distributions of radon concentrations in the air of single family homes from 38 U.S. areas. The resulting distribution of annual-average radon is characterized by an arithmetic mean of 1.5 pCi L^{-1} and a geometric mean of 0.9 pCi L^{-1}. They report that in the million homes with the highest concentrations, long-term occupants suffer an added lifetime lung cancer risk of at least 2%.

Radon Loss Mechanisms

Andrews and Wood (1972) examined the manner of release of radon from sedimentary rocks and identified four loss mechanisms:

1. Recoil of radon following the decay of ^{226}Ra at or near the surface of a particle;
2. Diffusion into water;
3. Recoil into grain boundaries; and
4. Release into porous secondary phases.

Since the effective range of alpha recoil is on the order of hundreds of angstroms (Tanner, 1964), radon loss from grains is inversely related to their size. For grains less than 149 µm, a maximum efficiency of 22%

was observed. Groundwater is generally drawn from pore openings in sand, gravel, and weathered rocks where the amounts of radon released by recoil from grain boundaries is negligible. Diffusion out of crystal lattices was also found to be small.

The presence of water in intergranular pores was found to increase the amount of radon escaping from the rock as water intercepted the recoiling atoms. Rama and Moore (1984) used electron microscopy to detect the presence of nanopores caused presumably by weathering into which radon could migrate and be available for interaction with the aquifer. These nanopores have large area to volume ratios compared to intergranular pores. Rama and Moore (1984) proposed that radon and other U-Th-series isotopes enter the nanopores by recoil in approximately equal quantities. Radon, being an inert gas, then may diffuse out of these nanopores while the other isotopes are adsorbed on the walls of these nanopores. Thus, levels of non-gaseous U-Th-series isotopes in the associated groundwater is three to five orders of magnitude lower than that of ^{222}Rn.

The main objectives of the experiments reported in this chapter were as follows:

(1) Measure the amount of radon gas emanating from different types of phosphate rock under both wet and dry experimental conditions and
(2) Relate this radon loss in each of the samples to other pertinent measurements and observations such as: ^{226}Ra activity, surface area, mineralogy and degree of weathering.

EXPERIMENTAL METHODS

Radon loss from the same bulk samples of phosphate rock discussed in Chapters 1 and 2, as well as 3 samples of New Hampshire granite sent to our lab was measured by the radon emanation method, a standard technique for the analysis of radon and radium in natural waters. This technique involves the collection of ^{222}Rn (direct daughter of ^{226}Ra) from a sealed container. The radon, together with helium carrier gas, is loaded into a "Lucas" cell and counted by alpha scintillation. The short half-life (3.8 days) of ^{222}Rn allows it to grow into secular equilibrium with its direct parent in only a few weeks.

Individual powdered samples of phosphate rock were dried in a 60°C oven and preweighed (0.5-2 grams, depending on the activity of ^{226}Ra in the sample). The samples were then transferred to acid-washed 125 ml. Erlenmeyer flasks which were subsequently sealed. The bulk phosphate samples were initially run under 3 different experimental conditions: dry, dry with agitation, and wet with agitation. Dry samples were simply left to sit in the flasks. For the "wet" experiments, we added 100 ml of double-deionized water (free of radium and radon) and placed the flasks on a shaker table for constant agitation.

Radon loss was also determined within individual size fractions from 2 phosphate samples, FM-3, a relatively fresh (leached) sample, and NRM-4, a weathered sample. These experiments were performed wet with agitation, as it had been previously determined that the loss was greater under these conditions. All samples were left for three weeks (over 5 half lives of ^{222}Rn) to insure a close equilibrium between radon and its parent radium in the solid material.

A homemade transfer line was used to quantatively sweep the gas from the sealed flasks to alpha scintillation (Lucas) cells. A bubbler was used to ensure that all radon dissolved in water was transferred together with the airborne radon. These cells were subsequently counted with either a Ludlum Model 2200 Scaler Ratemeter with a scintillation detector or a Randam Model SC-5 Counter. The entire system was calibrated using liquid NBS ^{226}Ra standards prepared in 125 ml Erlenmeyer flasks. In order to ascertain the % radon loss, that is, the percent of radon that decays from radium and is subsequently lost from the sample matrix, radium concentrations for each of the samples must also be determined. These concentrations were determined by gamma spectroscopy, the details of which have been discussed in Chapter 1.

Surface area measurements were made for us in M. Kastner's laboratory (Scripps Institution of Oceanography) by the Brunauer-Emmett-Teller (BET) method. Estimated precision of these determinations is about 3%.

In order to assess the precision of the experimental method, duplicate samples of HAW-1B were run both wet with agitation and dry (Table 11). The arithmetic mean calculated for the 3 samples run wet with agitation is 5.41 pCi g^{-1} with a relative standard deviation of 8.7%. The mean for the dry duplicates is 3.37 pCi g^{-1} with a relative standard deviation of 4.3 percent. Thus, apparent differences between experimental designs and between individual samples on the order of 10% or greater are clearly significant.

RESULTS AND DISCUSSION

Radon Loss from Bulk Samples

Results of the radon loss experiments for the bulk phosphate rock samples run dry, dry with agitation, and wet with agitation are provided in Table 12. In this table, as well as each of the data displays, the samples are arranged in the approximate order of degree of weathering (see Chapter 1 for additional details). Surface area (m^2 g^{-1} and ^{226}Ra activity (pCi g^{-1} for each of these samples are also provided in Table 12. Radon activities are expressed as activity per unit mass (pCi g^{-1} of sample, as a percent of the parent ^{226}Ra activity (%), and as activity normalized to surface area (pCi m^{-2}) . Results are shown as a series of bar graphs in Figs. 13 through 15. These graphs will assist the reader in recognizing differences in radon loss between samples and between the three experimental designs within individual samples.

The average radon loss for the phosphate samples run wet with agitation is 19.7 pCi g^{-1}, significantly higher than the average dry and dry with agitation experiments. The average percent radon loss for the wet run is calculated to be 32.9%. Hence, approximately 1/3 of the radon

Table 11. Radon loss data from replicate samples of HAW-IB. Samples run both wet with agitation and dry.

Sample No.	Rn Loss (pCi g^{-1})	Rn Loss (%)	Rn Loss (pCi m^{-2})
WET WITH AGITATION			
HAW-1B(#1)	5.09	35.1	0.22
HAW-1B(#2)	5.23	36.1	0.22
HAW-1B(#3)	5.95	41.1	0.24
MEAN	5.41	37.4	0.23
±%	0.46	3.2	0.01
DRY			
HAW-1B(#1)	3.5	23.9	0.14
HAW-1B(#2)	3.2	22.2	0.13
HAW-1B(#3)	3.5	24.0	0.14
MEAN	3.4	23.3	0.14
±%	0.17	4.3	0.01

Table 12. Radon loss data from 11 samples of bulk phosphate rock run wet with agitation and dry. Samples listed in approximate order of increasing degree of weathering.

Sample No.	Weathering Code*	Surface Area ($m^2\ g^{-1}$)	^{226}Ra ($pCi\ g^{-1}$)	-------- ^{222}Rn Loss -------- ($pCi\ g^{-1}$)	(%)	($pCi\ m^{-2}$)
----------------------- WET WITH AGITATION -----------------------						
HAW-1B	(1)	23.7	14.4	5.41	37.4	0.23
PR-1		30.1	13.3	4.73	35.5	0.16
NRM-5	(2)	13.10	50.59	9.86	19.5	0.75
HM-1		7.60	21.9	5.09	23.1	0.67
FM-3		9.90	13.6	2.5	18.1	0.25
CSP-4		16.80	25.0	11.8	47.2	0.70
NRM-4		33.05	177.5	57.52	32.4	1.74
CSP-2.2	(3)	14.90	34.2	22.7	66.1	1.52
NRM-10		12.80	165.2	39.8	24.1	3.11
NRM-3		11.75	151.1	38.1	25.2	3.24
FM-1		11.50	50.81	17.0	30.8	1.48
MEAN		16.84	65.63	19.5	32.7	1.26
>%		50.0	44.8	41.9	43.0	39.1
----------------------- DRY -----------------------						
HAW-1B	(1)	23.70	14.4	3.4	23.3	0.14
PR-1		30.10	13.3	3.2	24.4	0.11
NRM-5	(2)	13.10	50.59	3.0	5.9	0.23
HM-1		7.60	21.9	1.8	8.2	0.24
FM-3		9.90	13.6	1.4	9.9	0.14
CSP-4		16.80	25.0	0.3	1.1	0.02
NRM-4		33.05	177.5	33.3	18.8	1.01
CSP-2.2	(3)	14.90	34.2	3.6	10.4	0.24
NRM-10		12.80	165.2	13.4	8.1	1.05
NRM-3		11.75	151.1	16.8	11.1	1.43
FM-1		11.50	50.81	8.1	14.7	0.71
MEAN		16.84	65.63	8.02	12.6	0.48
>%		50.0	44.8	55.41	58.8	45.0

*Weathering Code: (1) fresh; (2) leached; and (3) highly weathered. See chapter 1 for additional information.

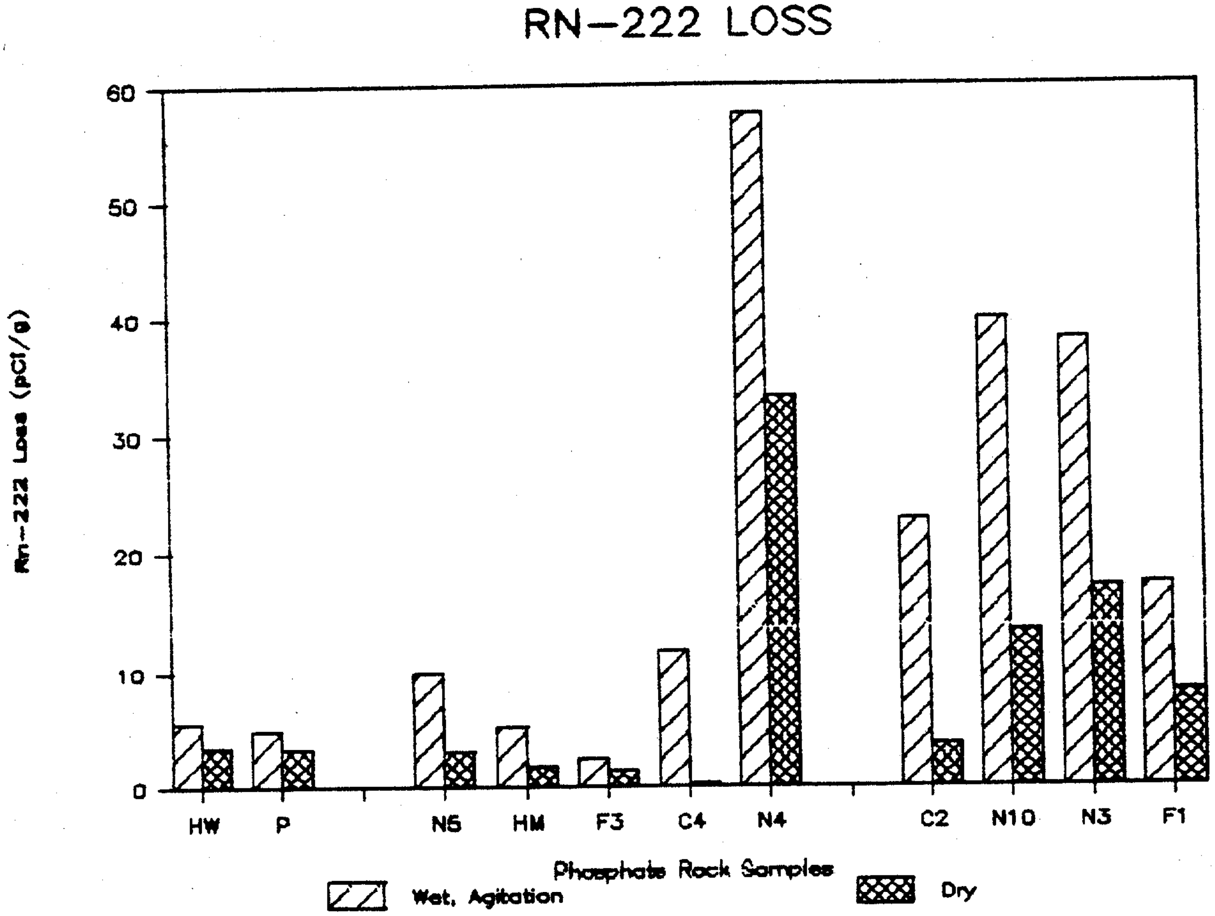

Figure 13. ^{222}Rn loss (pCi g^{-1}) from 11 powdered phosphate samples. All samples run both wet (with agitation) and dry in sealed flasks for a minimum of 3 weeks. Samples listed in approximate order of increasing degree of weathering from left to right.

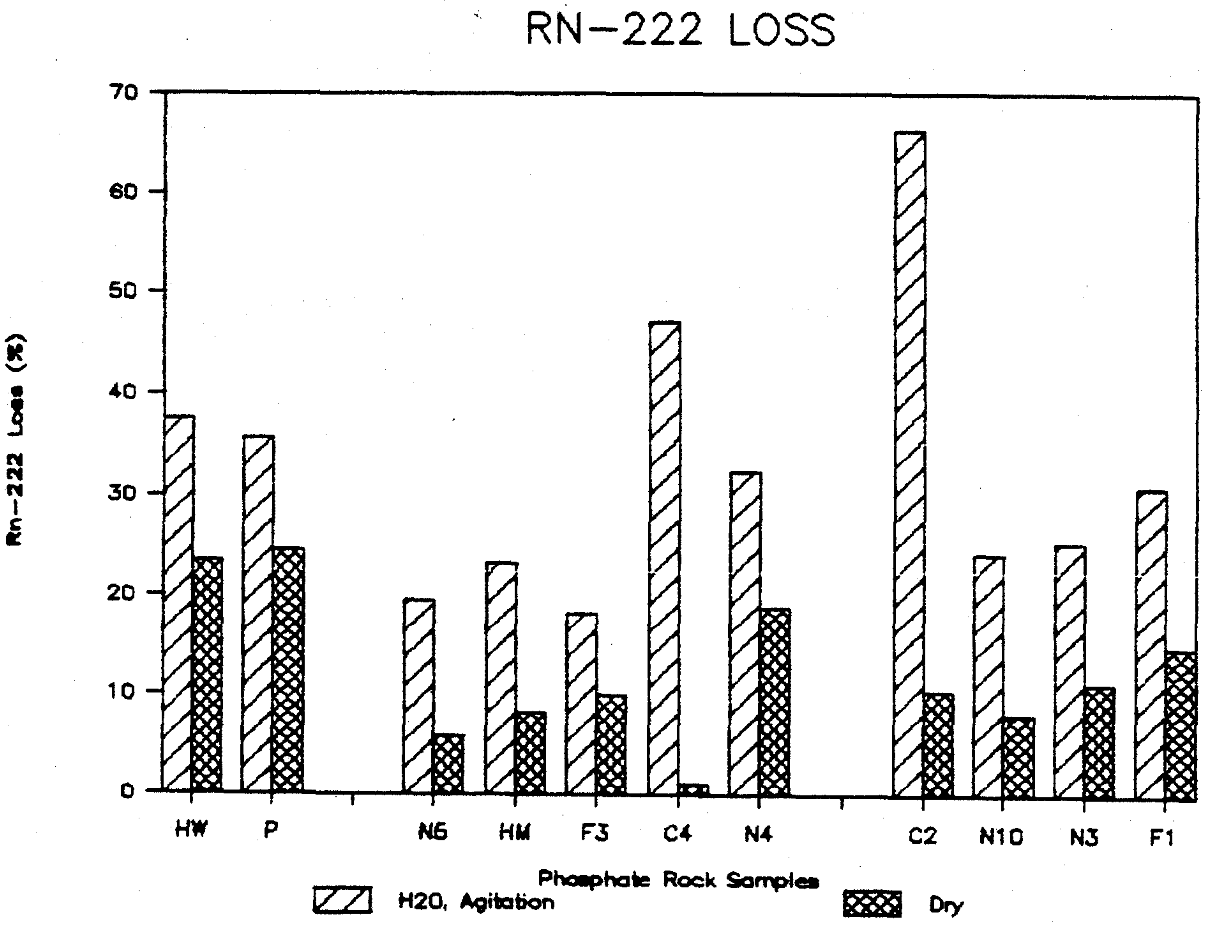

Figure 14. Percent ^{222}Rn loss from 11 powdered phosphate samples. All samples run both wet (with agitation) and dry in sealed flasks for a minimum of 3 weeks. Samples listed in approximate order of increasing degree of weathering from left to right.

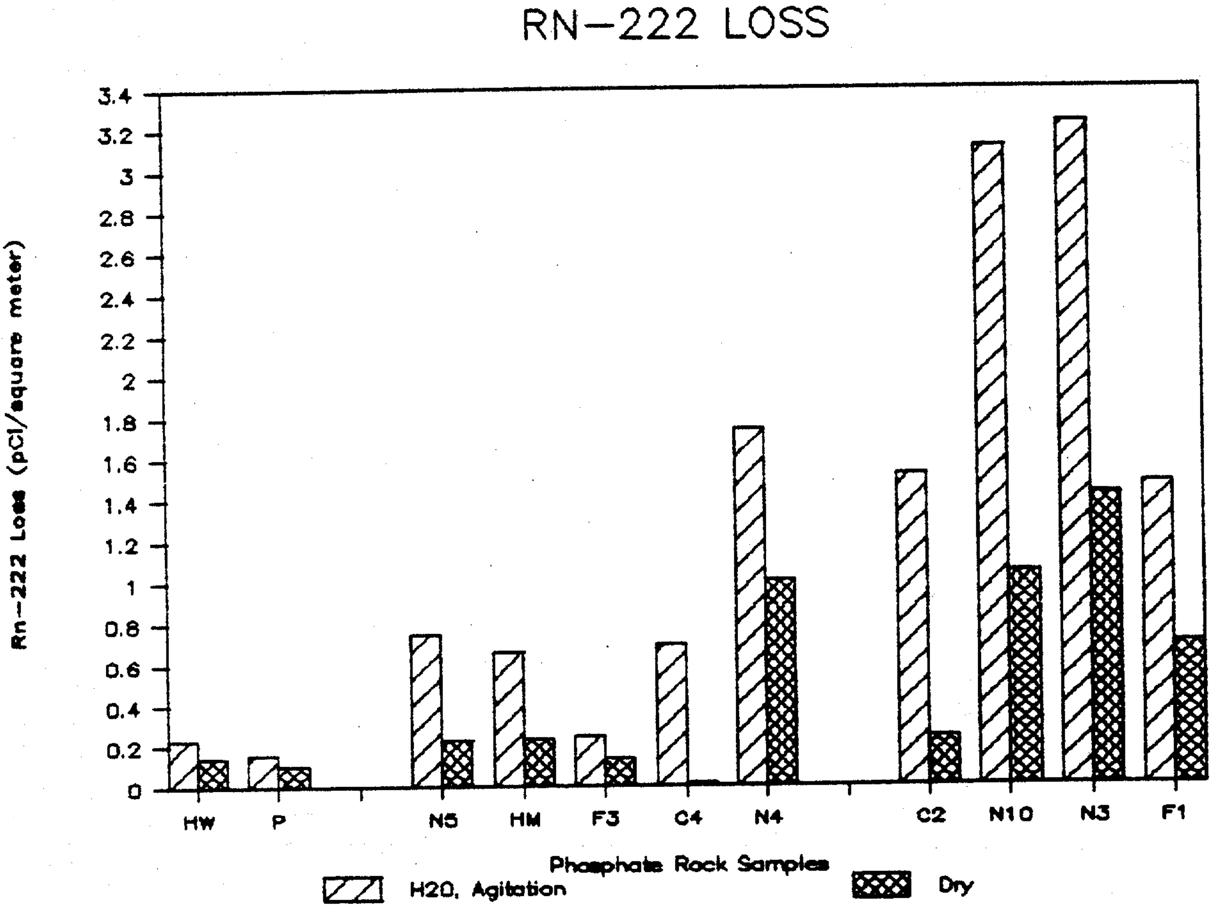

Figure 15. ^{222}Rn loss (pCi m^{-2}) normalized to surface area. All samples run both wet (with agitation) and dry in sealed flasks for a minimum of 3 weeks. Samples listed in approximate order of increasing degree of weathering from left to right.

produced from decay of ^{226}Ra is lost from the bulk samples under these experimental conditions. This percent loss ranges from 18.1% in FM-3 (which happens to have the lowest Ra activity of all the samples) to 66.1% in CSP-2.2. No striking differences in percent loss between the weathered and unweathered samples is observed (Fig. 14). When the data are normalized to surface area (Fig. 15), there is a clear indication of higher radon losses in the more weathered materials (as NRM-3 and NRM-10) compared to the fresh samples (as PR-1 and HAW-1B).

The average radon loss for the "dry" experiments is 8.02 pCi g^{-1}, about 2.5 times lower than the average loss of the wet with agitation experiment. The average percent loss is only 12.1%, ranging from a very low 1.1% in CSP-4 to 24.4% in PR-1. Note that for the "dry" experiments, the percent loss is highest in the two unweathered samples, HAW-1B and PR-1. This is clearly different from the "wet" experiment and indicates a significant difference in the interaction of water with fresh versus weathered phosphate rock. The percent loss of these two samples after normalization to surface area, on the other hand, appears lower than the more highly weathered samples. This indicates that surface area may explain the higher percent leakage of Rn from phosphate rock, at least under dry conditions.

To further clarify what factors are important in controlling the loss of radon from phosphate rock, we have plotted (Fig. 16) the radon loss from the "wet" experiment normalized to surface area (pCi m^{-2}) versus the "potential" radon concentration, expressed as the concentration of ^{226}Ra in pCi g^{-1}. Assuming that the only two factors which affect radon loss in our experiment are: (1) surface area; and (2) concentration, then all results should lie on the same trend. Most samples do, in fact, lie along a fairly well-defined trend with NRM-4 being the only notable exception. NRM-4 has lost less radon than would be predicted based on its radium concentration and surface area. Thus, other factors besides concentration and surface area must play a role in at least some cases. These other factors may be related to textural and/or mineralogical characteristics.

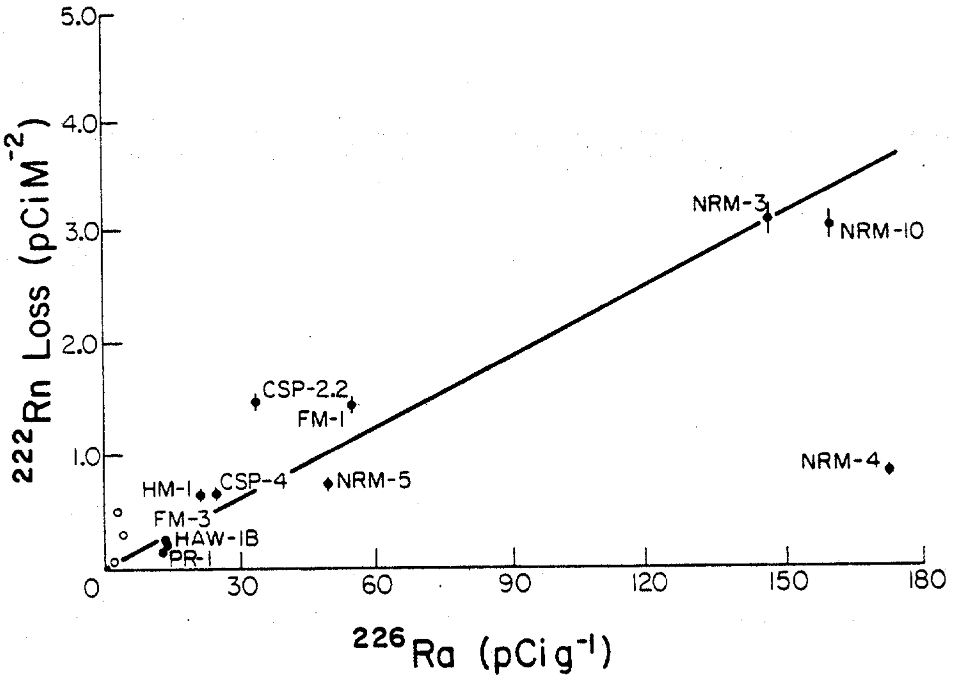

Figure 16. Radon loss normalized to surface area plotted against ^{226}Ra concentration for 11 phosphate rock samples and 3 granite samples for the wet experiment.

A plot of the percent difference of radon loss between the "dry" and "wet" experiments (Fig. 17) shows the differences are fairly constant within the data set (about 10 to 15 percent) except for the two samples from the Clear Springs Mine (CSP-4 and CSP-2.2). Both of these samples show greatly enhanced radon loss under "wet" conditions. Preliminary measurements of the samples run dry with agitation reveal that the activities fall between those calculated for the dry and wet with agitation runs. Apparently, both the presence of water and agitation enhances the loss of radon from phosphate rock.

Radon Loss from Size Fractionated Samples

The radon-loss data measured from size fractions of two phosphate rock samples, FM-3 and NRM-4, are included in Tables 13 and 14, respectively. These samples were run wet, as this should more closely resemble the natural environment. Plots of the activity (pCi g^{-1}) and percent radon lost in both samples (Figs. 18 and 19) show that the smallest size fraction (<63 μm) loses the most Rn, with all remaining size fractions losing approximately equal amounts. It is interesting that while the finest size class of FM-3 does not have the highest concentration of radium nor the highest radon loss on an activity basis, it does display the highest radon loss as a fraction of the total available. Thus, the surface area effect-seemed to dominate in this case.

Radon Loss from New Hampshire Granite Samples

The results of the radon loss measurements for three New Hampshire granite samples run dry have been provided in Table 15. The average percent radon loss of these samples (12.7%) is similar to the average percent loss of the phosphate rock samples run dry (12.4%). Because of the low concentrations of radium and associated low activities of radon, background corrections become significantly large and lead to greater uncertainties in the measurements compared to those of the phosphate rock samples.

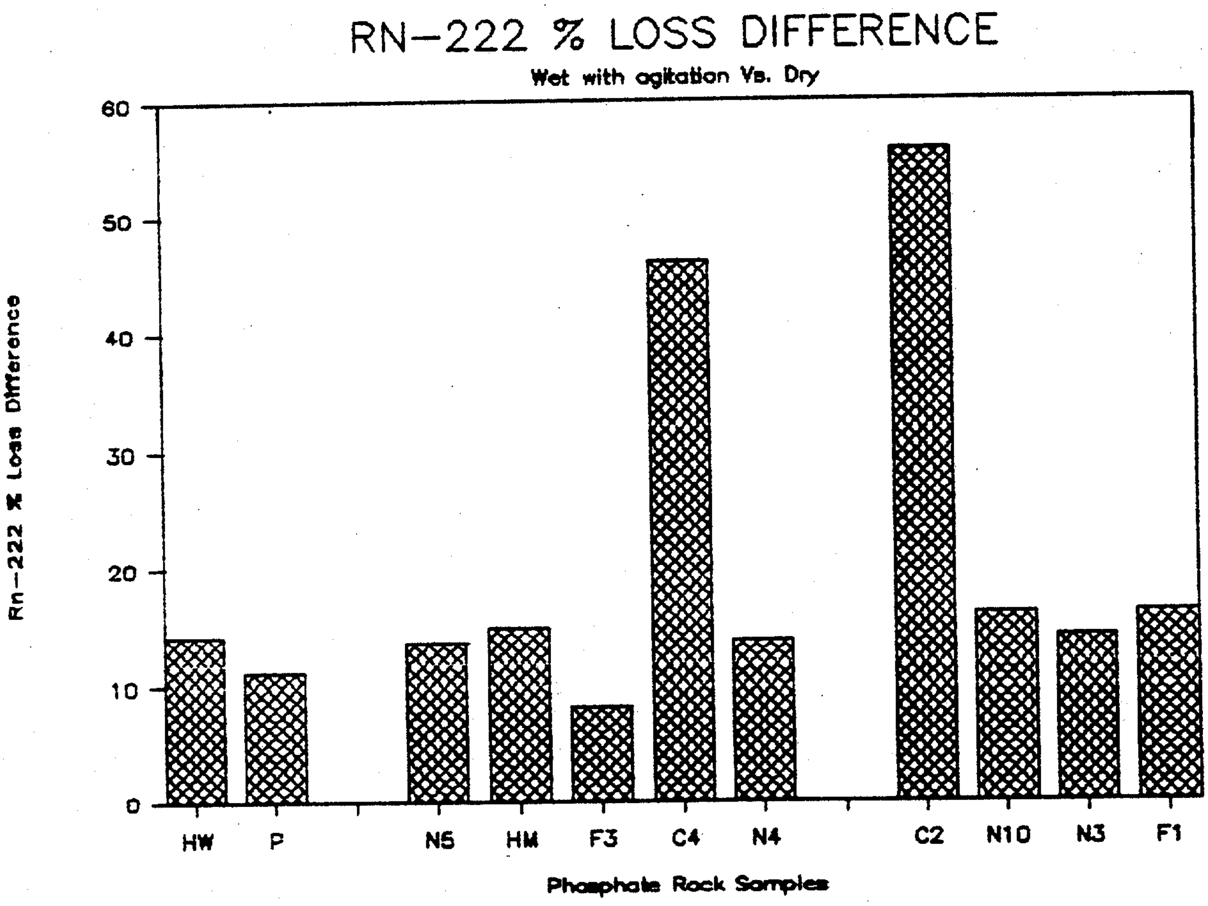

Figure 17. Percent difference of radon loss between "dry" and "wet" experiments.

Table 13. Radon loss in size fractions of leached phosphate rock sample, FM-3. Experiment run wet with agitation.

Size Fraction (μm)	226Ra (pCi g^{-1})	----- Rn Loss	------
		(pCi g^{-1})	(%)
<63	5.54	3.0	54.4
63-125	19.4	5.90	30.5
125-250	16.0	4.86	30.5
250-500	10.3	2.3	21.9
500-1000	18.2	4.68	25.8
>1000	25.4	8.20	32.4

Table 14. Radon loss data from size fractions of weathered phosphate rock sample, NRM-4. Experiment run wet with agitation.

Size Fraction (um)	^{226}Ra (pCi g^{-1})	------ Rn Loss ------ (pCi g^{-1})	(%)
<63	235.5	100.7	42.8
63-125	189.4	32.5	17.2
125-250	85.09	31.2	36.6
250-500	87.34	19.3	22.1
500-1000	159.1	97.0	27.5
1000-2000	177.1	62.7	35.4
>2000	178.6	56.62	31.7

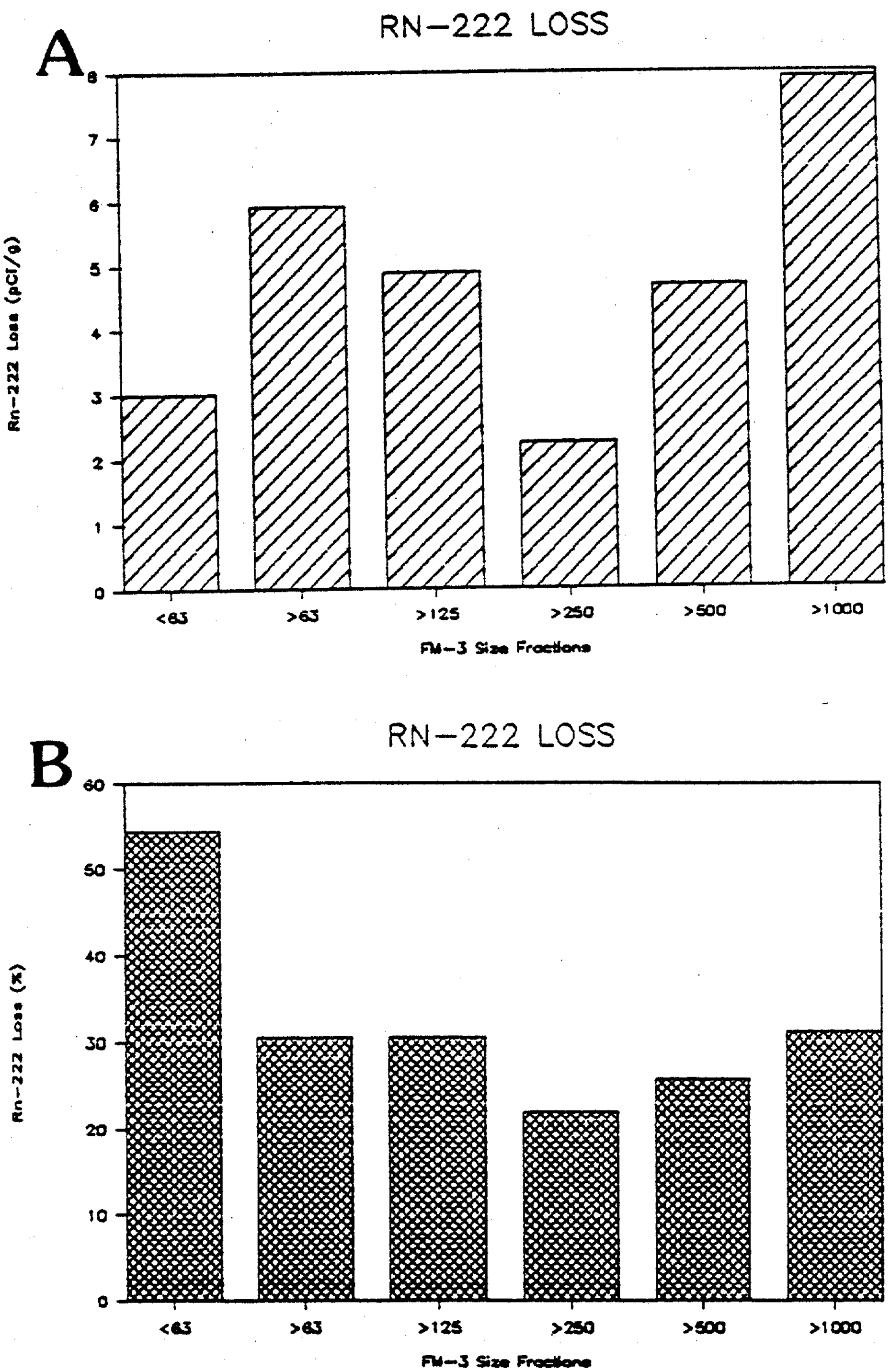

Figure 18. (A) ^{222}Rn loss (pCi g^{-1}) from individual size fractions of a relatively fresh phosphate sample, FM-3. All individual fractions run wet (with agitation) for a minimum of three weeks.

(B) Percent ^{222}Rn loss from individual size fractions of FM-3.

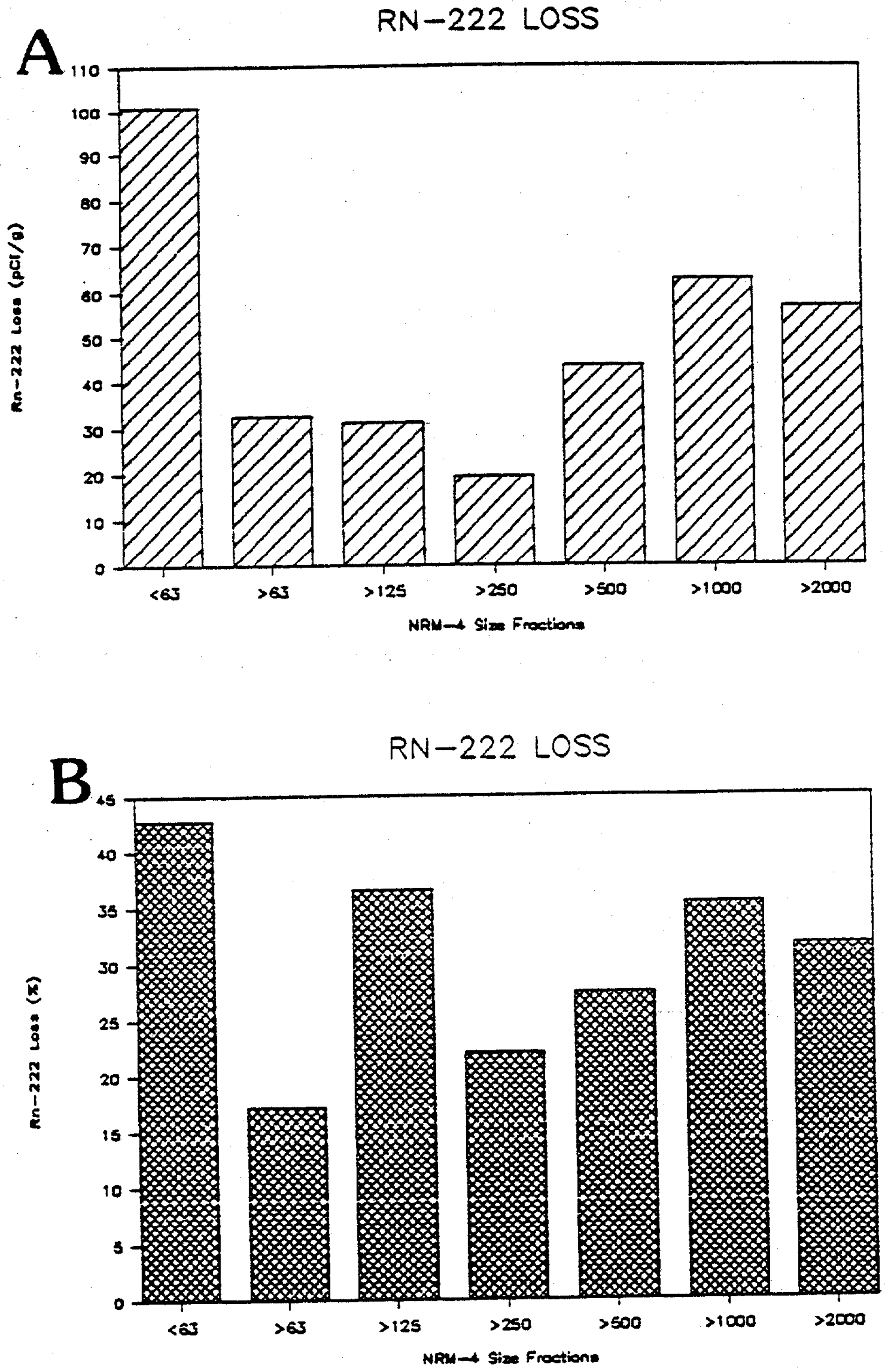

Figure 19. (A) ^{222}Rn loss (pCi g^{-1}) from individual size fractions of weathered phosphate sample, NRM-4. All individual fractions run wet (with agitation) for a minimum of three weeks.
(B) Percent ^{222}Rn loss from individual size fractions of NRM-4.

Table 15. Radon loss data from 3 New Hampshire granite samples. Experiment run dry.

Sample #	Surface Area (m^2 g^{-1})	^{226}Ra (pCi g^{-1})	Rn Loss (pCi g^{-1})	Rn Loss (%)	Rn Loss (pCi m^{-2})
FW-1	1.9	2.13	0.23	10.83	.12
SP-10	2.1	1.27	0.24	19.00	.11
SO-3	2.8	2.49	0.20	8.21	.07
MEAN	2.3	1.96	0.23	12.68	.10

CONCLUSIONS

(1) Experimental results indicate that the presence of both water and added agitation increases the amount of radon lost from powdered phosphate rock. Within individual samples the difference in percent Rn lost between "dry" and "wet" conditions appears to be fairly constant.

(2) The percent radon loss from size fractions of two of the phosphate samples does show the effects, occasionally in opposite directions, of surface area and concentration.

(3) Other factors, such as texture and mineralogy of constituent grains, must also be important in controlled radon retention in some types of materials.

(4) The average percent radon loss from powdered New Hampshire granite is similar to the average loss from powdered Florida phosphate rock.

CHAPTER 4

RADIUM IN THE SUWANNEE RIVER-ESTUARY AND OTHER FLORIDA RIVERS

INTRODUCTION

Radioactive disequilibrium within the uranium isotope series in the aquatic environment is of major importance in terms of geochronological studies and understanding the geochemical mass balance of these radionuclides in the oceanic system. Broecker and Peng (1982) pointed out that information concerning pathways of "reactive" metals is mainly derived from radioisotope study. Furthermore, natural radioactive decay can serve as a powerful tool in the effort to understand chemical "scavenging" processes that control ocean chemistry, dynamics of material transport, ocean boundary effects on chemical distribution, and fluxes in the ocean interior (Bacon, 1984).

The principal delivery pathways of uranium-series radionuclides into the oceans are: atmospheric deposition, river runoff, and in situ production in ocean water. Among these pathways, river runoff and in situ production are the major sources (Krishnaswami and Lal, 1982). During the transportation process via river runoff, radionuclides encounter a complex and dynamic environment, an estuary. From a geochemical point of view, an estuary is a reaction vessel where the mixing of fresh and saline waters takes place and through which the fluvial flux of continentally-weathered materials must pass to enter the marine environment. The various radionuclides of the naturally-occurring uranium decay-series are present in Florida phosphate rock at higher concentrations than most areas of the earth's crust. The uranium-series daughter products are partitioned by physical and chemical means during natural weathering (Chapter 1), as well as by phosphate mining and subsequent processes (Roessler et al., 1979). Radium, the subject of this investigation, has three natural isotopes, i.e., ^{226}Ra. ^{228}Ra, and ^{224}Ra which have half-lives long enough to be of environmental interest.

Scope of this Study

The unique characteristics of the Suwannee River, as well as concern over potential release of radium from adjacent phosphate mining operations into the river, led to this systematic study of radium in the Suwannee. The study embraces the major components of the Suwannee hydrologic system - the river water, spring water from the major springs, and the estuary.

The purpose of the present investigation was threefold:

1. To determine the temporal and spatial distribution of ^{226}Ra in the Suwannee River and evaluate whether there is any detectable impact from the phosphate mining operations at Swift Creek.

2. To determine the behavior of ^{226}Ra during the mixing of spring and river water, which may provide clues to the transport pathways of radium upon entry into aquatic systems.

3. To determine the behavior of radium in the Suwannee Estuary, both in dissolved and particulate form. This is important in order to evaluate the actual contribution to the radium budget of the Gulf of Mexico.

The Suwannee River and Estuary System

The Suwannee River is the second largest river in Florida (Fig. 20) with an average flow of about 311 $m^3\ s^{-1}$ to the Gulf of Mexico (Kenner et al., 1975). This river has been designated an Outstanding Florida Water (OFW), according to the water quality standards of the State of Florida and because of the river's exceptional ecological and recreational

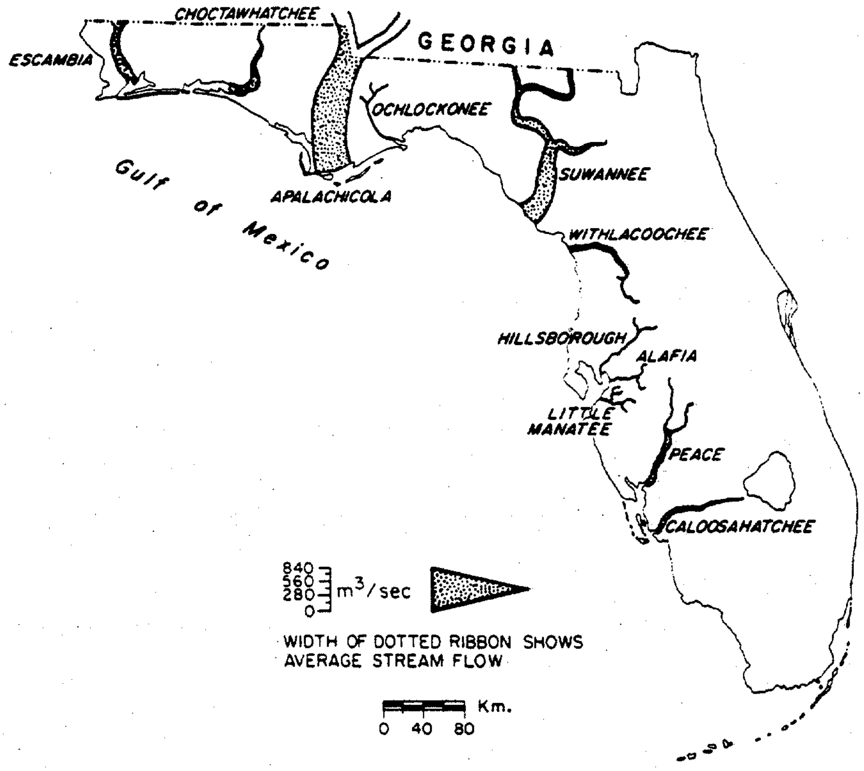

Figure 20. Major Florida rivers entering the Gulf of Mexico. Most of these rivers were sampled for ^{226}Ra measurements during this study.

significance. The Suwannee is one of the few free-flowing river-estuary systems in the southeastern United States and is relatively unspoiled at the present time due to the generally undeveloped nature of the basin. The Suwannee River originates in the second largest swamp in the United States, the Okefenokee Swamp in southern Georgia, and flows southward to the Gulf of Mexico with a river length of about 380 km. The portion of the river within the state of Florida to the river mouth is about 257 km. The primary economy of the, drainage area is agriculture. However, a large portion of the work force is Involved in construction, mining, manufacturing, and agribusiness. The major tributaries to the river are the Alapaha, Withlacoochee, and Santa Fe rivers. There are also at least 50 springs in the 8 counties adjacent to the Suwannee River that contribute to the flow of the Suwannee and its tributary system (Fig. 21). Among these, 9 first magnitude springs, having an average discharge greater than 2.8 $m^3 s^{-1}$ (100 cubic feet per second), flow into the river. These springs act as a direct connection between the Suwannee River and the underground aquifers (Rosenau et al., 1977). By the time the waters of the Suwannee reach the Gulf of Mexico, a very significant fraction of the water has been contributed via springs.

The Suwannee River basin drains approximately 28,600 km^2 of the coastal plains region in- southern Georgia and north central Florida (Leadon, 1980). Below a sill at Mixon Ferry, south of the Okefenokee Swamp, the river water is acidic, soft, and tea-colored as it flows southward through a broad flood plain. Upstream from White Springs, Florida, the river is superimposed on thick (up to 100 m) Miocene deposits. of sandy clay, clayey sand, sandstone and limestone. The flow for this portion of the river is essentially derived from surface runoff. Beginning at White Springs, the river channel deepens, its bank becomes steeper and higher; the river cuts into the Suwannee Limestone of the Floridan aquifer and bends abruptly to the northwest until it reaches Ellaville where it resumes its southward flow to the Gulf. From White Springs, the Alapaha and Withlacoochee rivers contribute about 15 and 24 percent, respectively, to the average flow at Ellaville (Leadon, 1980). From this point downstream, the Suwannee River receives significant amounts of spring

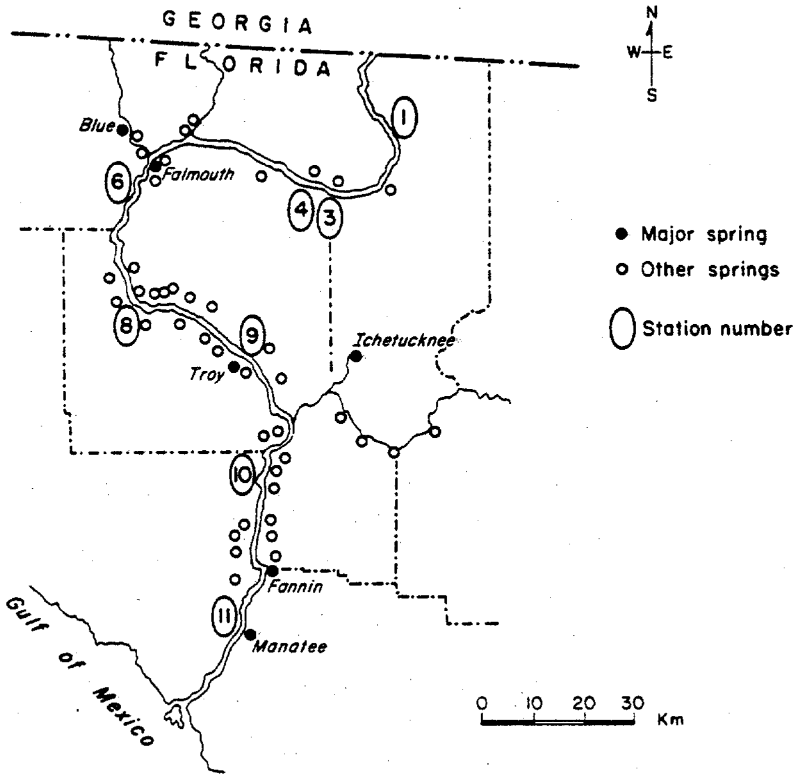

Figure 21. Locations of where water samples were collected monthly during 1982-1983. Station numbers from the Suwannee River study of the Florida Department of Environmental Regulation. Locations of springs which drain into the Suwannee River are also shown.

water from over 50 springs. During lower river stages, groundwater discharge to the river supplements runoff, but during high river stages the surface water may provide direct recharge to the Floridan aquifer. Below Ellaville, the river enters a region of thin sandy soil overlying the Ocala Limestone of the Floridan aquifer. This region is characterized by low relief, few tributaries and increasingly numerous springs that significantly change the flow and quality of the river water. Near Branford, the river channel broadens between low, marshy banks, which is typical of the lower coastal plain counties. Approximately 16 km below Branford, the third major tributary, the Santa Fe River, enters the Suwannee River. The Santa Fe drains about 109,000 km^2 and contributes roughly 15 percent of the Suwannee River flow at Wilcox (FDER, 1985). At a distance of about 37 km from the river mouth, the last first magnitude spring, Manatee Springs, contributes about 5 $m^3 s^{-1}$ of crystal clear water to the Suwannee River. Finally, at its mouth, the river separates into two main channels around Hog Island as East Pass and West Pass and the river water exits to the Gulf of Mexico through these channels and numerous tidal creeks.

General Character and Geochemistry of Radium

Radium is a radioactive element that occurs in nature in extremely small amounts as a daughter of uranium. It is a member of the alkaline-earth group of metals, appearing as an analog to barium. Discovered in 1898 by M. and Mme. Curie in pitchblende samples from North Bohemia, there is about 1 gram of radium in 7 tons of pitchblende. At present, 16 isotopes are known, of which, ^{223}Ra, ^{224}Ra, ^{226}Ra, and ^{228}Ra are naturally occurring members of the uranium-thorium decay series. The body metabolizes radium in a manner similar to that of calcium. If radium is introduced into the blood stream, it is ultimately fixed in the bone along with calcium and can cause cancer. The maximum permissible burden in the total body for ^{226}Ra is 0.2 µCi.

Radium generally occurs in uranium-containing minerals, i.e., uraninite, torbernite, autunite and zircon. However, radium can be found in non-uranium minerals such as calcite, barite, pyromorphite, limonite and pyrolusite (Vdovenko and Dubasov, 1975). Radium is an electropositive element, tends to form strong ionic bonds, and can form insoluble salts, particularly radium sulfate and carbonate.

The presence of ^{226}Ra and ^{228}Ra in natural waters is a function of the content of their parents, ^{238}U and ^{232}Th, in the host matrix, the geochemistry of the parent and the half-lives of the radium isotopes. After the host matrix is weathered and leached by groundwater, uranium and ^{226}Ra can be readily solubilized, transported, and deposited quite far away from the host material matrix. Unsupported ^{226}Ra decays more than 90% after 5,000 years, and the only significant radium left will be that continually produced by uranium decay. Due to the chemical and crystallophysical properties of ^{226}Ra, supported ^{226}Ra does not occupy regular lattice positions within uranium-bearing minerals. Therefore, ^{226}Ra enters groundwater more readily than uranium and may migrate a considerable distance because of its long half-life (1622 years).

The mechanisms that cause radium to enter groundwater are: (i) dissolution of aquifer solids; (ii) direct alpha recoil across the liquid-solid boundaries during its formation by radioactive decay of its parents in the solid; and (iii) by desorption from particle surfaces. The alpha recoil process is a prime factor in the higher solubility of progeny isotopes compared with their parents (Hess et al. 1985). King et al. (1982) reported that in spite of the much longer half-life of ^{226}Ra, the distance of radium transport in groundwater was less than that of ^{222}Rn (with a half-life of 3.8 days) and suggested that this was due to continual adsorption of radium onto aquifer solids. Krishnaswami et al. (1982) calculated adsorption and desorption rate constants for radium in Connecticut aquifers and reported that radium removal rates were rapid, as short as a few minutes. They also suggested that equilibrium between adsorption and desorption is also quickly established. Additionally, these authors concluded that the partition coefficient for radium under these conditions strongly favors the solid phase; almost all radium introduced into groundwater resides on particle surfaces in the adsorbed state, and the extent of sorption is controlled by the geochemical reactivity of the aquifer materials.

Groundwater generally has radium concentrations an order of magnitude higher than that of surface water and oceanic water (Kaufmann and Bliss, 1977). In central and north Florida, Irwin and Hutchinson (1976) reported that ^{226}Ra in groundwater was found in a range from 0.05 to 90 pCi L^{-1}. Kaufmann and Bliss (1977) analyzed ^{226}Ra in Florida groundwater and reported that the geometric mean in areas outside the central Florida land pebble phosphate district is about 0.9 pCi L^{-1}, several times higher than the U.S. national geometric mean of 0.1 pCi L^{-1}. ^{226}Ra in groundwater within the phosphate area is higher yet, with a range from 1.5 to 15 pCi L^{-1}. Humphreys (1984) concluded that the high activity of ^{226}Ra in central Florida is due to secondary accumulation of uranium within aquifer materials and is also related to higher total dissolved solids in waters of the aquifer. Relatively few data concerning ^{226}Ra in river water are available (Rona and Urry, 1952; Moore, 1967; Bhat and Krishnaswami, 1969). Scott (1982) compiled previous published data on radium in world rivers, including those rivers that discharge into the Gulf of Mexico. Generally, concentrations of ^{226}Ra in river water are less than 0.05 pCi L^{-1} but for rivers draining arid areas such as Rio Grande and Pecos, and those that traverse uranium matrix strata (South Texas rivers) and phosphate deposits (Suwannee River), concentrations of ^{226}Ra were found to be 2 to 3 times the world average.

EXPERIMENTAL METHODS

Sampling Location and Methods

Station number, locations and time period during which monthly samples were analyzed for radium and other parameters along the Suwannee River are summarized in Table 16 and plotted on Fig. 21. In the river portion of this study, water samples were collected at various times just under the surface at fixed station locations. For estuarine samples, the samples were collected on the basis of the prevailing salinity gradient. A hand

Table 16. Station numbers, locations, and time periods of sampling for this study.

Station	Location	Time Period	Distance from river mouth (km)
	River		
1	400 m upstream of Hunter Creek	Jan. '82 - Jan. '84	312
3a	350 m upstream of Swift Creek	Jan. '82 - Jan. '84	269
3b	duplication of station 3a	Jan. '82 - Jan. '84	
4a	300 m downstream of Swift Creek	Jan. '82 - Jan. '84	268
4b	duplication of station 4a	Jan. '82 - Jan. '84	
6	1 km downstream of Withlacoochee River; approx. 300 m upstream of Florida Power's intake canal	Jan. '82 - Jan. '84	205
8	2.5 km upstream from Florida Rt. 51 bridge near Luraville	Feb. '82 - May, '82	164
9	5 km upstream U.S. Highway 27 bridge near Branford	Jan. '82 - Jan. '84	127
10	700 m upstream of Florida Rt. 340 bridge near Rock Bluff	Aug. '82 - Jan. '84	92
11	6 km downstream of New Pine Landing adjacent to Manatee Spring State Park	Sept. '82 - Jan. '84	40
	Estuary		
ES-1	Suwannee River Estuary by small boat	December 20, 1982	--
ES-2	Suwannee River Estuary by small boat	March 3, 1983	--
ES-3	Suwannee River Estuary by small boat	June 22, 1983	--
BL-1	Suwannee River Estuary Bellows Cruise I	October 6-9, 1983	--
OLN-1	Ochlockonee River Estuary by small boat	January 4, 1984	--
BL-2	Suwannee River Estuary Bellows Cruise II	July 10-12, 1984	--
BL-3	Suwannee River Estuary Bellows Cruise III	July 12-13, 1985	--

refractometer and a portable inductive salinometer were used to measure the salinity in the field. More precise analyses of salinity were performed later in the laboratory. The laboratory data are reported here.

Samples were returned to the laboratory the same day and each sample was filtered through three in-line filters consisting of a Whatman glass microfiber (934-AH), GF/F, and Millipore AA (0.45 µm), respectively. Results for radium reported here are thus considered "dissolved" unless stated otherwise.

Samples in the estuary were collected on board a small boat and the R.V. BELLOWS. Filtering of the estuarine samples was performed immediately. Large volume samples, on the order of a few hundred to about one thousand liters of surface water, were also occasionally processed, for ^{228}Ra analysis. This was achieved by using a gasoline pump and two water-purification cartridges, one packed with un-coated and the other packed with Mn-coated acrylic fibers (Moore, 1981). These acted as a pre-filter and extracting medium, respectively. The water volume circulated through this system was measured by a flow meter coupled at the final outlet. Pumping time for these samples ranged from 40 minutes to a few hours.

Spring water and a series of samples representing various mixtures of river and spring water were also collected and analyzed during this study. We used the unique optical characteristics of the crystal-clear spring water and the dark-brown color of the highly organic Suwannee River water to evaluate the extent of the mixing. The absorbance of the filtered river-spring water at 400 nm in a 10 cm path length was found to be an excellent indicator of percent spring water in the mixed samples. Known-mixtures of the filtered river and spring water "end members" served as standards (Fig. 22). In the field, pure spring water (sampled directly from the discharge vent) and river water (sampled a few hundred meters upstream of spring discharge) were collected and filtered to construct a preliminary field calibration curve. Then, samples were collected on the basis of visual color, filtered and measured for absorbance on board the

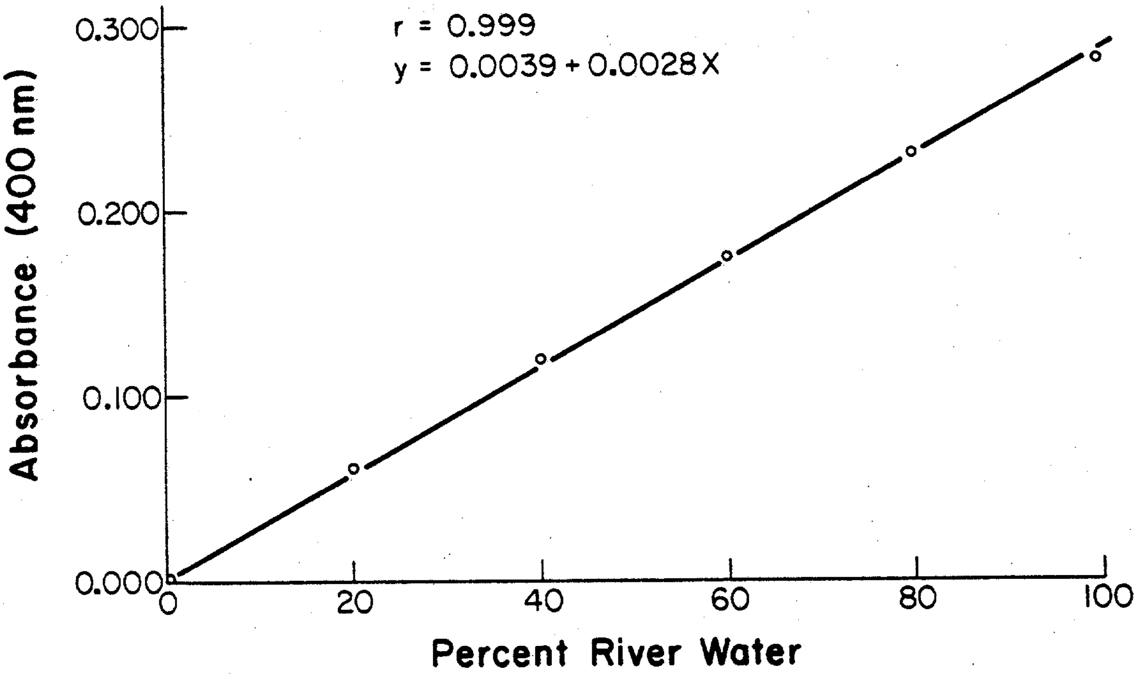

Figure 22. Calibration curve for the artificial mixtures of Suwannee River water and Manatee Springs water. After calibration, the percent river water may be determined by measuring the absorbance at 400 nm.

ship. By using the field calibration curve, the required range of spring river mixed water was sampled. The absorbances and standardization were later repeated under more controlled conditions in the laboratory.

All of the particulate data in this, study were derived from the combined amount of particulate material remaining on all filters used during the filtering process. After filtering, the filters were partially dried at room temperature, then dried at 60°C overnight. The dry filters were cut into small pieces in a glass container and processed for analysis. In a few cases, hundreds of liters of river water were collected and centrifuged to obtain a larger sample of the particulate fraction.

Radiochemical Analyses

^{226}Ra was determined in two different ways, both of them based on the quantitative extraction of radium from natural water by Mn-impregnated acrylic fiber. For samples from the- January-May 1982 sampling period, a modified method based on gamma-counting peaks of ^{226}Ra daughters from a $BaSO_4$ precipitate was utilized (Michel et al., 1981; Kim and Burnett, 1983). Briefly, the filtered water sample (15-20 L) was passed through a small column of 0.5 M $KMnO_4$-treated acrylic fiber (Mn-fiber) which has a dry weight of about 5-8 g. The water is processed at a rate of 200-300 ml min^{-1}. Radium, quantitatively adsorbed onto the Mn-fiber at these flow rates (Reid et al., 1979), is subsequently leached with hot 6 M HCl and precipitated with BaC12 and sulfuric acid as $BaSO_4$. The $Ba(Ra)SO_4$ precipitate is collected by centrifuging into 2.5 ml polyethylene vials, sealed with epoxy resin to prevent radon escape, and aged at least three weeks to allow ^{226}Ra daughters to grow into secular equilibrium. The sample is then counted with a well-type intrinsic germanium (IG) detector with a rated resolution (FWHM) of 1.95 KeV and peak to Compton ratio of 36.7 at 1332 KeV. ^{226}Ra is determined by averaging the activities obtained by three separate photopeaks: ^{214}Pb at 295 and 352 KeV, and ^{214}Bi at 609KeV. Data from the IG detector is collected by use of 4,000 channels of a Canberra Series 80 multichannel analyzer. To calibrate the

IG detector for ^{226}Ra daughters, an ^{226}Ra standard solution (NBS-4958) is diluted and ^{226}Ra precipitated with $BaSO_4$, exactly in the same manner as our samples. After counting in the IG system to establish an absolute full energy efficiency curve, final activities (corrected for background and geometry effects) are calculated using a computer program written in our laboratory. Two EPA radioactivity standards and four NBS standards not used in our detector calibration were analyzed as "unknowns". In every case, our results agreed with the certified activities within 1 standard deviation, based on counting statistics (Kim and Burnett, 1983).

In order to reduce processing time, ^{226}Ra samples collected after May 1982 were determined by the radon emanation method (Lucas, 1964). This method is a standard technique for the analysis of radium in natural waters, and involves the collection of ^{222}Rn (direct daughter of ^{226}Ra) from the water after sufficient time is allowed for ingrowth of ^{222}Rn by radioactive decay. The ^{222}Rn is evacuated from a sealed sample container by carrier gas and is loaded into a "Lucas" cell and counted by alpha scintillation. Following the method of Moore (1981), water samples for ^{226}Ra analyses were concentrated on Mn-fiber as previously described. Instead of leaching ^{226}Ra from the Mn-fiber with acid, the partially wet Mn-fiber is kept in sealed 125 ml glass containers for a period of three weeks, and then ^{222}Rn is evacuated directly into a Lucas cell and counted by alpha scintillation. The final ^{226}Ra activity is calculated from factors which consider ingrowth, decay factors and Lucas cell efficiencies. These efficiencies were derived from passing known amounts of NBS-4958 ^{226}Ra standard solution to the Mn-fiber and processing exactly in the same manner as our samples. Due to the non-destructive nature of the emanation technique, each sample was analyzed at least twice or until the results agreed to better than 10 percent. In most cases, the precision was considerably better than that.

A "whole bottle" emanation technique was also utilized to compare radium concentrations derived by the Mn-fiber technique. For "whole bottle" analysis, approximately 20 liters of water were sealed in large-volume, glass, wine-making bottles and purged with helium gas for at least two hours. After 3 weeks for ^{222}Rn ingrowth, the radon gas was again emanated and measured in the same manner as the Mn-fiber emanation procedure.

^{224}Ra and ^{228}Ra were also analyzed in some samples during this study. These two radium isotopes were determined by utilizing gamma-ray spectroscopy techniques to measure activity ratios of radium collected by processing large-volume water samples. The specific activity of ^{226}Ra in the same samples was measured by standard emanation techniques. Details of ^{224}Ra and ^{228}Ra analyses can be found in Elsinger et al. (1982) and Michel et al. (1981), respectively. In this study, water samples on the order of few hundred to one thousand liters were processed to extract enough radium for these measurements. The first cartridge in our pumping system was packed with untreated acrylic fiber and acted as a prefilter for particulate matter, while the second one was packed with loose Mn-fiber and was used as a radium extraction medium. In the laboratory, the Mn-fibers from the large volume water sampling were washed with deionized water to clean off particulate matter and were leached with 6 M HCl. Radium from the leached solution was precipitated as $BaSO_4$, loaded in counting vials for gamma spectroscopy and counted for ^{224}Ra first (Elsinger et al. 1982). After three weeks, ^{226}Ra and ^{228}Ra were counted as mentioned above.

RESULTS AND DISCUSSION

Radium in the Suwannee River: Soluble and Total Radium

Complete data tabulation for the 2-year sampling for soluble ^{226}Ra in the Suwannee River has been given by Burnett and Deetae (1984). Summarized statistics of radium and discharge for this period are shown in Table 17. Discharge values used are from the closest U.S.G.S. gauging station to each of the sampling stations.

Table 17. Summarized statistics of dissolved ^{226}Ra and discharge in the Suwannee River during the 2-year study period.

		Stations								
		1	3a	3b	4a	4b	6	9	10	11
<u>1982</u>	N	12	11	10	11	10	12	9	5	4
	Range	2.7-29.3	2.7-23.1	6.2-16.2	4.5-15.1	4.6-15.8	8.1-16.6	1.8-15.1	5.0-19.2	7.7-15.9
^{226}Ra	Mean	10.5	11.4	11.9	8.2	8.4	12.7	11.1	12.7	11.4
(pCi 100L^{-1})	S.D.	7.39	4.77	3.0	4.1	3.9	3.2	4.5	6.35	4.1
	N	12	12	12	12	12	12	12	12	12
	Range	0.1-5.1	0.3-6.5	0.3-6.5	0.1-0.4	0.1-0.4	4.4-14.4	7.3-26.4	2.0-7.9	15.0-41.6
Discharge	Mean	1.9	2.7	2.7	2.9	2.9	4.5	15.3	4.1	24.9
(m^3 s^{-1})*	S.D.	1.6	2.1	2.1	2.1	2.1	4.5	6.5	1.7	8.0
<u>1983</u>										
	N	12	12	12	12	12	12	12	12	12
	Range	2.5- 8.3	3.2-12.1	3.0-12.5	5.4-9.97	4.77-10.9	8.87-16.1	5.13-14.5	6.5-18.6	5.04-15.8
^{226}Ra	Mean	5.3	7.9	7.9	7.5	7.2	12.0	9.7	12.3	11.8
(pCi 100L^{-1})	S.D.	1.5	2.5	2.9	1.5	1.8	2.7	2.9	3.6	3.3
	N	12	12	12	12	12	12	12	12	12
	Range	0.5-27.4	1.2-25.8	1.2-25.8	0.1-0.9	0.1-0.9	0.5-50.6	8.3-11.9	3.0-8.9	17.2-84.1
Discharge	Mean	7.2	7.4	7.4	0.3	0.3	9.1	27.4	5.2	39.3
(m^3 s^{-1})*	S.D.	7.9	7.8	7.8	0.2	0.2	14.0	20.1	1.5	20.7

*Data divided by 10.

These long-term results show that there is little significant variation in radium concentration between stations. We could detect no significant difference in the radium concentration downstream from the mining activities. In fact, the Z-year mean radium activity at station 4 was slightly lower than the upstream station. The overall mean ^{226}Ra activity for the 25-month period was equal to 10.1 ± 3.8 pCi $100L^{-1}$ Stations closer to the head waters (stations 1, 3, and 4) are somewhat more variable in radium content, as shown by the higher standard deviation.

It is interesting that radium concentrations remain within relatively narrow limits during conditions of extreme fluctuations of flow. Station 6, for example, has a maximum range in ^{226}Ra from 6.26 to 16.8 pCi $100L^{-1}$, or less than a 3-fold variation. Discharge at the same station, however, displays a range from 1 to 51 m^3s^{-1}. This represents over an order of magnitude variation in the flow of the river at this point. Although there is some tendency for radium concentration to be lower during periods of high discharge (Fig. 23), simple dilution does not appear to be a dominant mechanism. Since the total flow of the Suwannee River is a combination of surface and spring input, the relatively low radium concentrations during periods of high flow may indicate a relatively higher proportion of surface water input with corresponding low radium contents during those times. Radium analyses of some of the first-magnitude springs which flow into the Suwannee River were made during this study. All of these springs contain relatively high ^{226}Ra (Table 18). It is interesting to note that ^{226}Ra concentrations in these springs increased downstream progressively (southward) as deeper aquifers become more important in supplying water to the river.

Although the data are too few to be convincing, there is a suggestion of a seasonal trend in some of our radium results. These trends are more evident in the downstream stations, i.e., stations 6-11, than those further upstream (stations 1-4). The radium results for station 6, for example, show a distinct cycle with a frequency of approximately 6-7 months (Fig. 24). High radium occurs in the early winter and summer,

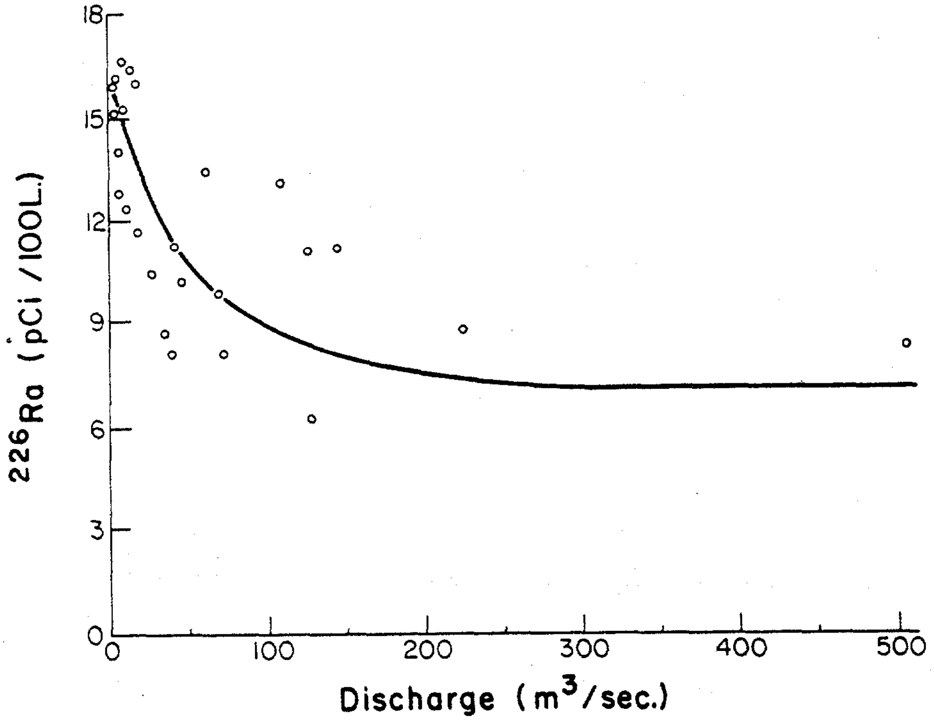

Figure 23. Dissolved (Mn-fiber) 226Ra versus discharge at Suwannee River station 6. Samples were collected monthly over the period January, 1982-January, 1984.

Table 18. Concentration of ^{226}Ra and discharge to the Suwannee River in some first magnitude springs measured during this study.

Spring	Location	Flow $m^3\ s^{-1}$	226Ra pci $100L^{-1}$	226Ra Discharge 1010 pCi yr^{-1}
Blue	Lat 30° 28' 49" N. Long 83° 14' 40" W.	3.3	6.98 ± 0.3	0.72
Falmouth	Lat 30° 21' 40" N. Long 83° 08' 07" W.	4.5	15.7 ± 0.5	2.22
Troy	Lat 30° 00' 21" N. Long 82° 59' 51" W.	4.7	15.7 ± 0.4	2.32
Ichetucknee	Lat 29° 59' 02' N. Long 82° 45' 43" W.	10.2	13.5 ± 0.4	4.34
Fannin	Lat 29° 35' 15" N. Long 82° 56' 08" W.	2.9	24.3 ± 0.6	2.23
Manatee	Lat 29° 29' 22" N. Long 82° 58' 37" W.	5.1	41.3 ± 0.7	6.67
			Total	18.50

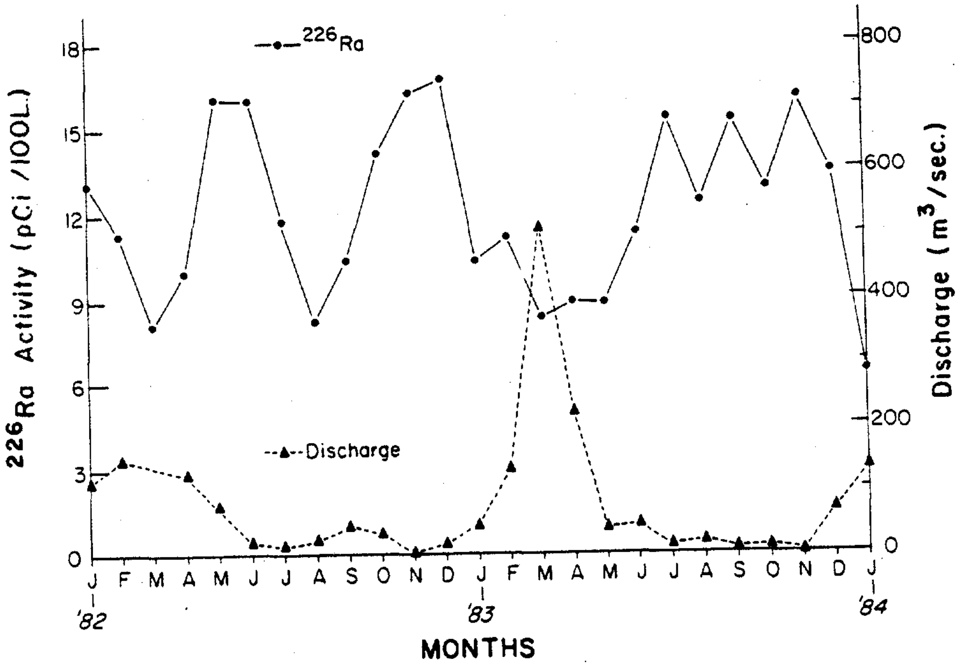

Figure 24. Time-series plot of dissolved ^{226}Ra (pCi 100L^{-1}) and discharge (m^{3}s^{-1}) at station 6. The apparent seasonal cycle in the radium data is discernable but more subdued in the discharge data.

while low values appear in the early spring and fall. It is possible that this is a reflection of a productivity cycle, with soluble radium being depleted during periods of relatively high productivity. It is known that certain types of plankton, such as some species of diatoms, concentrate radium (Koide et al., 1976).

Since the concentration of radium does not change nearly as much as discharge, there must be an additional control on radium concentration within these waters. One possibility would be an interaction between the soluble radium and suspended particles in the river water. To evaluate this effect, one complete month's sample set (June, 1983) was analyzed for particulate as well as dissolved radium. The results (Table 19) of this analysis proved to be very interesting. In spite of a range in the concentration of suspended sediment among all seven stations from 0.3 to 17.5 mg L^{-1}, the maximum range of percent particulate radium is only from 25 to 48 percent. In fact, with the exception of station 6, all other stations have a range of particulate radium of only between 25-35 percent. This narrow range can only be maintained by an extreme variation in the specific activity of ^{226}Ra within the suspended sediment itself. In this sample set, the ^{226}Ra activity ranged from 2.7 to 156 pCi g^{-1}. Thus, the distribution of radium between the soluble and particulate phases in the river is maintained at a constant level by increasing the specific activity of radium in the solid phase fraction (Fig. 25). It is likely that the principal carrier phase of particulate radium is a clay mineral with ion exchange properties. We attempted to identify this fine-grained material filtered from a downstream station by an X-ray diffraction (XRD) techniques. Although we could not positively identify the mineral because of a diffuse X-ray pattern, it appeared to be a smectite-like clay, perhaps similar to the high-activity mixed-layer clay material found in some of the weathered phosphate deposits discussed in Chapter 1.

In an effort to further clarify the form of radium in the Suwannee River, as well as to investigate any possible relation to dissolved organic carbon (DOC), field sampling was arranged in February, 1985 to

Table 19. Soluble, particulate and total ^{226}Ra in Suwannee River water samples collected in June, 1983. Radium in suspended sediment measured by leaching with 6 M HCl and subsequent analysis by radon emanation.

Station	Load mg L^{-1}	Susp. ^{226}Ra pCi g^{-1}	^{226}Ra (pCi 100L^{-1}) Dissol.	Susp.	Total*	Percent Dissol.	Percent Susp.
1	3.1	6.3	5.7	1.9	7.6	75	25
3a	6.7	4.1	6.2	2.8	9.0	69	31
3b	6.8	4.2	5.8	2.5	8.3	70	30
4a	13.7	2.7	7.1	3.7	10.8	66	34
4b	11.7	3.1	6.7	3.6	10.4	65	35
6	17.5	4.6	8.7	8.1	16.8	52	48
9	2.6	16.4	9.6	4.2	13.9	69	31
10	2.5	14.2	9.7	3.6	13.3	73	27
11	0.3	156.0	11.9	5.1	17.1	70	30

*Sum of dissolved and suspended radium.

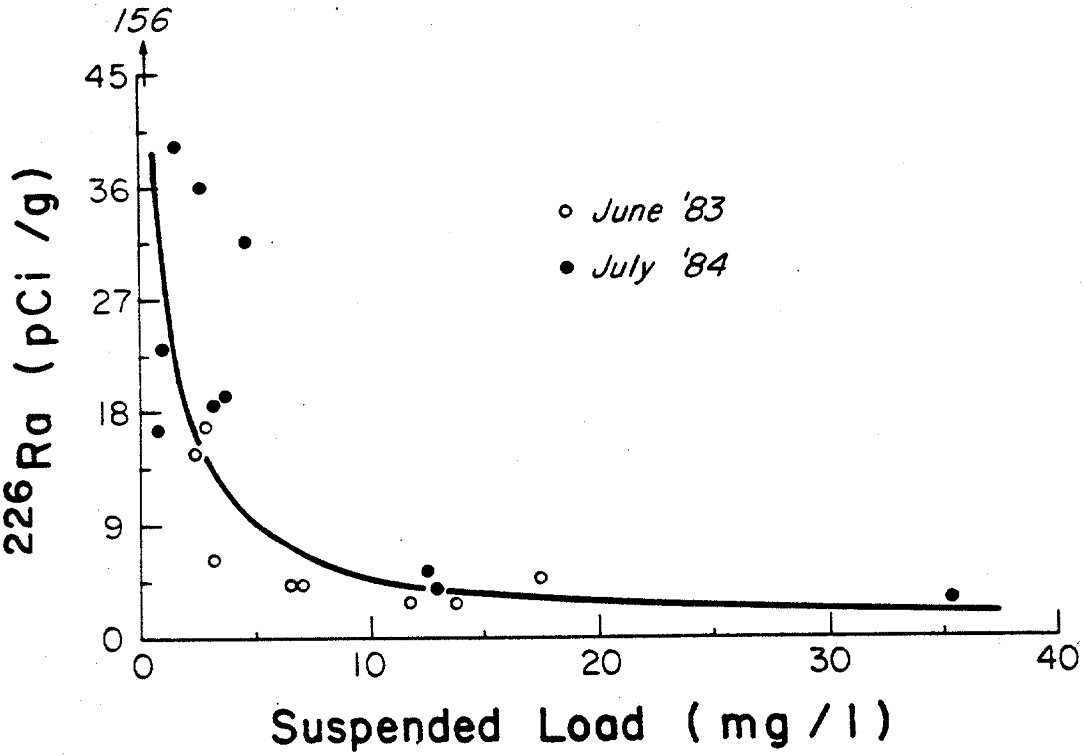

Figure 25. ^{226}Ra (pCi g-l) in the particulate load versus the concentration of suspended sediment (mg L^{-1}) in the Suwannee River. The data point for station 11 is offscale at 156 pCi g^{-1}.

collect water samples in the upper Suwannee River between Pecker Road (station 1) and Branford (station 9). River water samples were collected from six stations which were known to have markedly different contents of DOC from high values (40 mg L^{-1}) in the northern upstream to relatively low (5 mg L^{-1}) in the area further downstream around Branford. Water was collected from six stations with duplicates collected at the upper and lower end of the profile for ^{226}Ra analysis of both filtered and unfiltered water. All samples were analyzed for ^{226}Ra by both "whole-bottle" and Mn-fiber extraction, as well as determinations of the total amount of suspended particulate matter. All ^{226}Ra determinations were performed in our laboratory and thus tied to the same NBS radium standard. Any difference, therefore, between the technique employed cannot be due to calibration errors.

Results from these samples confirm that ^{226}Ra, determined by the "whole bottle" radon emanation technique, is consistently higher than that by Mn-fiber extraction, followed by radon emanation in unfiltered Suwannee River samples (Table 20). This effect had been noted earlier during an intercomparison between our group and investigators at the University of South Florida (USF). Their results at one downstream station in the Suwannee River were considerably higher than those reported here (Fanning et al., 1982). The USF team had theorized that organically-bound radium may pass through Mn fibers and thus remain undetected. Our results do not, however, support a relationship between DOC and the quantity of "missing radium'. In fact, the filtered "whole bottle" measurements are not significantly different from the Mn-fiber unfiltered results. This implies that the difference noted between these two techniques may simply be a function of particulate radium by-passing the Mn-fiber extraction. If we assume that the "whole bottle" measurement represents "total" radium (soluble and radium present on particulate surfaces), then the differences between that measurement and the Mn-fiber value should be roughly equivalent to the particulate ^{226}Ra. Based on the previous measurements of both soluble and particulate radium in the Suwannee River (Table 19), it was shown that the particulate burden is usually about 25-30 percent of the total. These results do not rule out the possibility of organic

Table 20. Comparison of ^{226}Ra activities measured in six Suwannee River water samples by "whole bottle" radon emanation and Mn-fiber extraction followed. by radon emanation. Samples collected on February 15, 1985. Dissolved organic carbon (DOC) and suspended load are also given for these stations.

Station	Location	DOC* mg L^{-1}	Susp. Load mg L^{-1}	Whole Bottle pCi $100L^{-1}$	Mn-fiber pCi $100L^{-1}$	Difference (%)
9	Branford					
	Unfiltered	5	-	13.6	12.8	5.9
	Filtered		13.20	12.1	-	-
6	Ellaville	10	9.96	21.6	15.0	30.6
	Suwannee Sprs.	25	3.47	13.2	7.6	42.
4	I-75	35	6.93	8.7	7.0	20.
3	White Sprs.	40	8.98	7.7	6.1	21.
1	Pecker Rd.					
	Unfiltered	40	-	4.1	3.5	15.
	Filtered		3.62	3.7	-	-

*Approx. values from SRWMD results in December 1984.

complexes with radium, but suggest that the differences between the two techniques may be explained by consideration of particulate as well as soluble radium.

Concentrations of ^{226}Ra in the Suwannee as well as other major Florida rivers, are shown in Table 21. It is obvious that rivers in northwest Florida (Escambia, Choctawhatchee, Apalachicola, and Ochlockonee) have low concentrations of radium compared to those found in central and southwest Florida. This is not surprising, because most central Florida rivers are spring fed and drain an area of high grade phosphate materials. It is significant to note that the "whole bottle" (unfiltered) and Mn-fiber (filtered) radium results agree very well for this sample set. This suggests that Mn-fibers apparently retain their full efficiency for extracting radium, even in organic-rich rivers. If organo-radium complexes do exist in these waters, they apparently do not interfere with analysis of radium via Mn-fibers.

Estimates of the radium discharge to the Gulf of Mexico via the Suwannee and other Florida rivers show that the Suwannee has the highest discharge of the rivers investigated, accounting for about 25 percent of the total flux of radium from all of these rivers. The estimated total discharge of radium by these rivers to the Gulf of Mexico, 6.85×10^{12} pCi yr^{-1} is very low compared to that of the Mississippi, recently estimated to be 1.40×10^{14} pCi yr^{-1} (Moore and Scott, 1986).

Entry of Radium into the Suwannee River: The Manatee Springs Profile

Results of the analysis of the water collected in the Manatee Springs-Suwannee River mixing profile show that about 95 percent of ^{226}Ra in the spring water is in dissolved form, while in the Suwannee River end member, dissolved radium is only about 77 percent of the total (Table 22). A plot of total (whole bottle) and dissolved (Mn-fiber) radium versus percent river water indicates that when spring water is mixed with river water, the total ^{226}Ra behaves "conservatively", i.e., the amount of total radium in the water parcel is a result of simple

Table 21. ^{226}Ra in major Florida rivers and their contribution of ^{226}Ra into the Gulf of Mexico. Samples collected in May, 1986.

River	Km[1]	Cond.	Susp. load	Av. Flow[2]	Unfilt. Whole Bottle	Filt. Mn-Fiber	Leached Susp.	Susp. Radium pCi g^{-1}	Calculated Total pCi 100L^{-1}	^{226}Ra Discharge 10^{12} pCi yr^{-1}
		mMHOS cm^{-1}	(mg L^{-1})	(m^3 s^{-1})	<------------	pCi 100L^{-1}	------------>			
Escambia	8	130	8.01	175.2	7.3 ± 0.2	NA NA	1.8 ± 0.1	2.3 ± 0.2	NA	0.40
Choctawhatchee	40	109	13.86	192.8	3.9 ± 0.1	NA NA	3.4 ± 0.3	2.4 ± 0.2	NA	0.24
Apalachicola	96	125	29.71	718.5	5.9 ± 0.4	2.5 ± 0.3	5.2 ± 0.2	1.9 ± 0.1	7.7	1.33
Ochlockonee	10	NA	36.15	48.5	NA ± NA	4.6 ± 0.6	7.8 ± 0.4	2.2 ± 0.1	12.4	0.07[3]
Suwannee	16	155	0.85	311.1	18.1 ± 0.5	18.0 ± 1.1	1.4 ± 0.1	16.7 ± 1.5	19.4	1.77
Withlacoochee	10	195	1.41	56.9	12.7 ± 0.5	12.2 ± 0.7	NA NA	NA NA	NA	0.23
Hillsborough	80	700	1.90	18.8	22.1 ± 0.2	19.5 ± 1.1	0.3 ± 0.04	1.6 ± 0.3	19.8	0.13
Alafia[4]	65	290	0.17	12.1	24.5 ± 1.6	26.7 ± 1.3	0.1 ± 0.0	5.5 ± 0.5	26.8	0.09
Alafia (5 ppt)	48	8300	5.70	12.1	NA ± NA	72.1 ± 1.0	10.0 ± 0.3	17.6 ± 0.6	82.1	0.273
Peace	65	400	2.77	61.3	52.1 ± 2.7	49.0 ± 3.4	1.2 ± 0.1	4.2 ± 0.5	50.2	1.01
Little Manatee[4]	112	350	1.35	7.5	96.1 ± 3.4	93.4 ± 3.6	2.5 ± 0.2	18.4 ± 1.3	95.9	0.23
Caloosahatchee	80	350	2.78	48.2	89.6 ± 3.9	94.5 ± 2.3	5.8 ± 0.3	20.9 ± 1.0	100.3	1.36
									Total	6.85

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[1] Approximate distance from river mouth.

[2] From Kenner, W.E., Hampton, E.R., and Conover, C.S. 1975.

[3] Calculated from Mn-fiber + leached suspended radium.

[4] Data from 1983 annual discharge.

Table 22. ^{226}Ra in a profile representing mixing of water from Manatee Springs (A) into the Suwannee River (J). An additional 2 river samples given for comparison, 1 upstream from Manatee Springs (K) and another down river at the junction of the East and West Pass (L) of the river.

Sample ID	Absorb. 400 nm	River %	Load mg L1-1	^{226}Ra Total[1]	(pCi 100L^{-1}) Dissol.[2]	Susp.[3] ^{226}Ra pCi g^{-1}	- Percent - Dissol.	Susp.
A	0.000	0.0	1.05	47.3	43.2	2.4	94.7	5.3
C	0.016	4.3	35.59	48.8	31.1	11.4	73.2	26.8
B	0.022	6.5	13.04	51.2	46.7	5.1	90.2	9.8
D	0.054	17.9	3.37	43.4	31.6	6.4	83.3	16.7
E	0.123	42.5	12.56	39.9	32.2	6.5	83.2	16.8
F	0.150	52.1	NA	29.5	24.6	NA	NA	NA
G	0.182	63.6	1.55	34.8	29.1	6.2	82.6	17.4
H	0.216	75.7	3.51	28.9	23.6	6.3	79.0	21.0
I	0.255	89.6	3.60	29.5	23.3	6.8	77.4	22.6
J	0.280	100	NA	25.5	18.6	NA	NA	NA
K	0.280	100	2.74	22.5	18.9	9.8	65.8	34.2
L	NA	100	4.70	20.7	15.7	15.0	51.2	48.8

[1] Total ^{226}Ra from whole bottle measurement

[2] Dissolved ^{226}Ra from Mn-fiber measurement

[3] Leached from filter with 6N HCl.

mixing of ^{226}Ra from each end member (Fig. 26). However, an interesting phenomenon is observed in the case of dissolved radium. Although not all points plot below the ideal mixing line, there is a definite suggestion of non-conservative behavior of dissolved radium. This may imply removal of radium during the mixing process. High concentrations of dissolved radium from spring water may thus be transformed into particulate radium when mixed with Suwannee River water. This removal process, presumably adsorption, helps maintain the proportion of dissolved and particulate radium in the Suwannee River in a fairly constant ratio. This supports the concept of radium control by particle interaction, resulting in a uniform distribution of radium between phases in the river. The sorption process may provide an explanation for the observation that the activity of suspended radium tends to increase downstream, while the concentration of total suspended material is decreasing. Results presented here have shown that the specific activity of ^{226}Ra in particles is usually highest between station 11 and the river mouth (Table 19).

The suspended radium in the Suwannee River-Manatee Springs profile was also analyzed (Table 23), both by direct radon emanation and after leaching with 6 M HCl. The suspended ^{226}Ra varies from 3-36 pCi g^{-1} and varies inversely with the concentration of suspended particles as observed earlier (Table 19; Fig. 25). The significantly greater recoveries of particulate radium by HCl leaching relative to simple degassing of the particles implies that a significant amount of the radium is tightly bound. Perhaps the radium measured by direct radon emanation represents adsorbed radium, while the HCl leached radium represents radium in ion-exchange sites.

Particulate Radium Concentrations

The highest particulate activities are found downstream in the vicinity of station 11, a part of the river which normally has very low concentrations of total suspended matter. Furthermore, most suspended radium samples from the river end members collected during the estuarine sampling (see next section) invariably show concentrations of radium

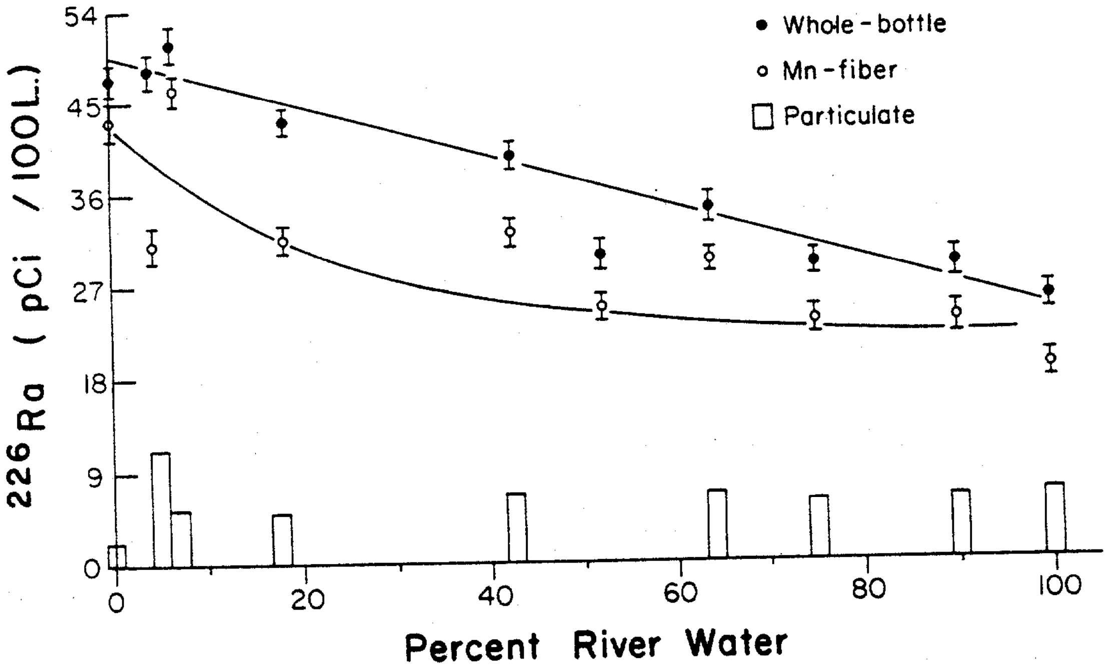

Figure 26. Whole bottle, M-fiber, and particulate ^{226}Ra (pCi $100L^{-1}$) in a series of samples which represent a natural mixing series between pure Manatee Springs water and Suwannee River water.

Table 23. Suspended ^{226}Ra in a profile representing mixing of water from Manatee Springs (A) into the Suwannee River (J).

Sample ID	River %	Load mg L^{-1}	Particulate ^{226}Ra (pCi g^{-1}) HCl	De-Em*	Ratio HCl/De-Em
A	0.0	1.1	22.9	7.3	3.15
C	4.3	35.6	2.9	1.2	2.37
B	6.5	13.0	3.9	0.5	9.05
D	17.9	3.4	18.8	4.5	4.18
E	42.5	12.6	5.2	1.3	3.98
F	52.1	NA	NA	NA	NA
G	63.6	1.6	29.7	13.4	2.96
H	75.7	3.5	17.9	3.6	5.05
I	89.6	3.6	18.9	3.4	5.49
J	100	NA	NA	NA	NA
K	100	2.7	35.8	12.6	2.83
L	100	4.7	31.8	5.9	5.34

*Measured directly from suspended matter without HCl leaching.

comparable to that observed in the river below Manatee Springs (station 11). Unfortunately, the high suspended ^{226}Ra in the downstream samples was always associated with very low suspended loads and detailed study of the particulates was thus hampered by insufficient sample size. In an attempt to resolve this weight problem, approximately 100 liters of water were collected from each of 3 sites in this area and centrifuged at about 5000 rpm in order to collect enough particulate material for more detailed analysis. Eventually, sufficient material was recovered for analysis by non-destructive gamma-ray analysis (Table 24). Although the specific activities of radium were not as high as anticipated, there was a significantly higher concentration of both excess ^{226}Ra and ^{210}Pb below Manatee Springs relative to the upstream station. This may be due to additional input from the spring and subsequent uptake by the particles. It was observed that a considerable amount of very fine-grained particles were not brought down as suspended matter during the centrifugation process, and there was some loss of the finest particles during decantation from the centrifuge tube. This may explain why even higher activities were not observed.

Visual examination of a sample of the sandy bottom taken at the junction of the East and West Passes showed that some very small, dark brown particles were present. The sample was separated into standard size fractions and analyzed by gamma spectroscopy in the same way as the phosphate rock samples reported in Chapter 1. Results (Table 25; Fig. 27) show that although the fine fraction constitutes a very small amount (0.06 %) of the total sediment, it is very enriched in ^{226}Ra and ^{210}Pb -- many times the equilibrium activity of ^{238}U .This finding of relatively high ^{226}Ra (20.3 pCi g^{-1}) in the <63 µm size fraction of the Suwannee River bottom sediment confirms the suspicion that fine-grained particles are a major transport path of radium to the estuary. Suspended ^{226}Ra in the Suwannee River is consistently above 4.5 pCi g^{-1}, and often higher, while particles in the Mississippi River are only about 1.5 pCi g^{-1} (Moore and Scott, 1986) and in the Amazon River range from about 0.77 to 1.2 pCi g^{-1} (Dion, 1983; Key et al., 1985). It is obvious that suspended ^{226}Ra in the Suwannee River is often 3-6 times higher, and

Table 24. Particulate ^{238}U, ^{226}Ra, and ^{210}Pb in the Suwannee River. Samples collected by centrifugation of large-volume water samples and measured by gamma spectroscopy.

Location	^{238}U (pCi g^{-1})	^{226}Ra (pCi g^{-1})	Excess ^{210}Pb (pCi g^{-1})
Above Manatee Sprs.	bd*	3.5 ± 0.2	13.6 ± 2.5
Below Manatee Sprs.	bd	4.8 ± 0.4	22.1 ± 5.9
East-West junction	bd	5.2 ± 0.2	7.3 ± 2.5

*bd = below detection.

Table 25. Percent mass distribution, specific activities and activity ratios of a Suwannee River sandy bottom sediment (BL3) collected at the junction of the East and West Passes.

	Size range (µm)					
	<63	63-125	125-250	250-500	500-1000	1000-2000
Mass (%)	0.1	0.1	2.8	23.1	67.6	6.3
Activities (pCi g^{-1})						
^{238}U	1.6	1.2	0.1	bd*	bd	bd
^{226}Ra	20.3	6.2	0.7	0.5	0.3	0.3
^{210}Pb	30.4	7.7	0.7	0.2	bd	bd
Activity ratio						
$^{226}Ra/^{238}U$	11.49	4.99	10.53	-	-	-
$^{210}Pb/^{226}Ra$	1.68	1.25	0.94	0.45	-	-

* bd = Below detection.

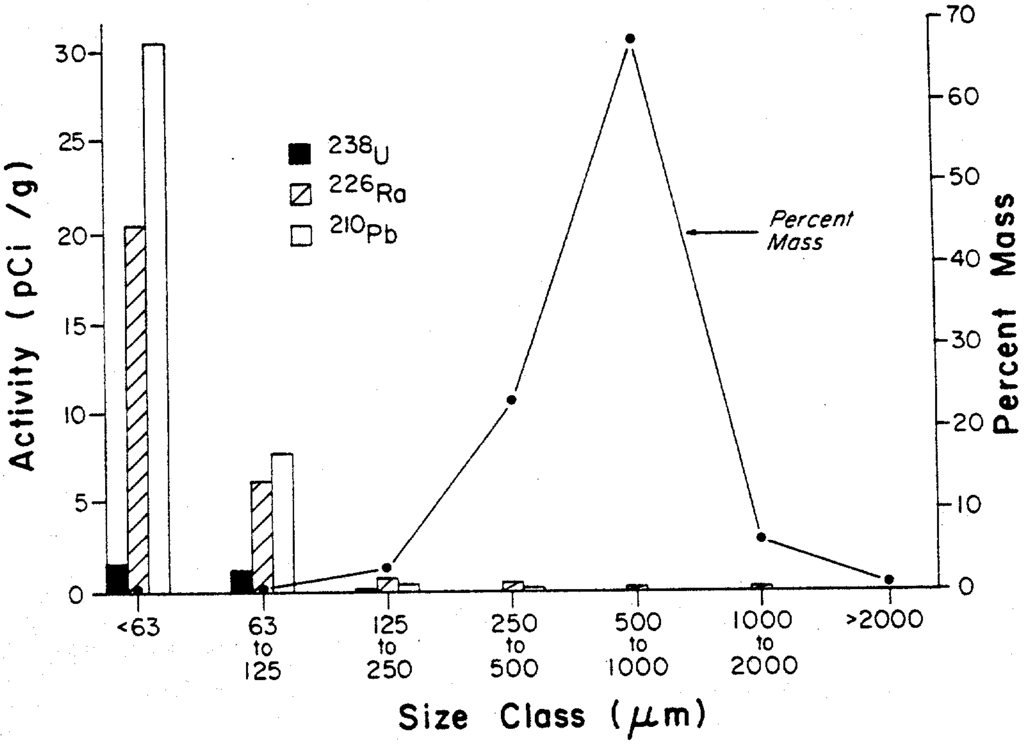

Figure 27. Specific activity (pCi g^{-1}) of ^{238}U, ^{226}Ra, and ^{210}Pb as well as percent mass distribution in different size fractions of Suwannee River sediment BL3. Note high activities and disequilibrium in finest size classes.

occasionally orders of magnitude higher, than reported suspended ^{226}Ra from other rivers. The fraction of the total radium which is particulate is high in the Suwannee compared to those in central and southwest Florida (Table 21). Rivers such as the Peace, Little Manatee, and Caloosahatchee have much higher dissolved radium concentrations and lower percent particulate values than the Suwannee. It may be that the character of the particulate matter in these streams does not have as high an adsorptive or exchange capacity compared to Suwannee particulates.

Radium in the Suwannee River Estuary

Because of compensating changes in concentration, discharge does not have a significant effect on the rate of supply of dissolved radium to the Gulf of Mexico. The suspended load tends to be much higher during high flow periods than during low flow periods. When discharge is low, however, the specific activity of radium within the suspended matter is significantly higher than that present during high flow.

Plots of ^{226}Ra concentration versus salinity show similar increases of ^{226}Ra from the river end member (20 °/oo to a maximum value around a salinity of 20 °/oo), followed by a decrease to the ocean end member (Fig. 28). The concentration of dissolved ^{226}Ra in the Suwannee River Estuary mixing zone ranged from approximately 13.5 to 56.3 pCi 100L^{-1} during this study (Appendix 2). The mean of the maximum value found around 20 °/oo salinity is about 40.5 pCi 100L^{-1}. This maximum is significantly higher than other reported values for ^{226}Ra in estuaries studied thus far. The concentration of dissolved ^{226}Ra in the river end member remained rather constant around 13.5 pCi 100L^{-1} throughout this study period. This is in contrast to the marked fluctuations of ^{226}Ra observed during different flow conditions in the Mississippi River (Moore and Scott, 1986).

Results from the sampling in March and June, 1983 seem to indicate simple linear mixing of radium between the river and Gulf at those times. During the March, 1983 sampling, the entire range of salinity was not

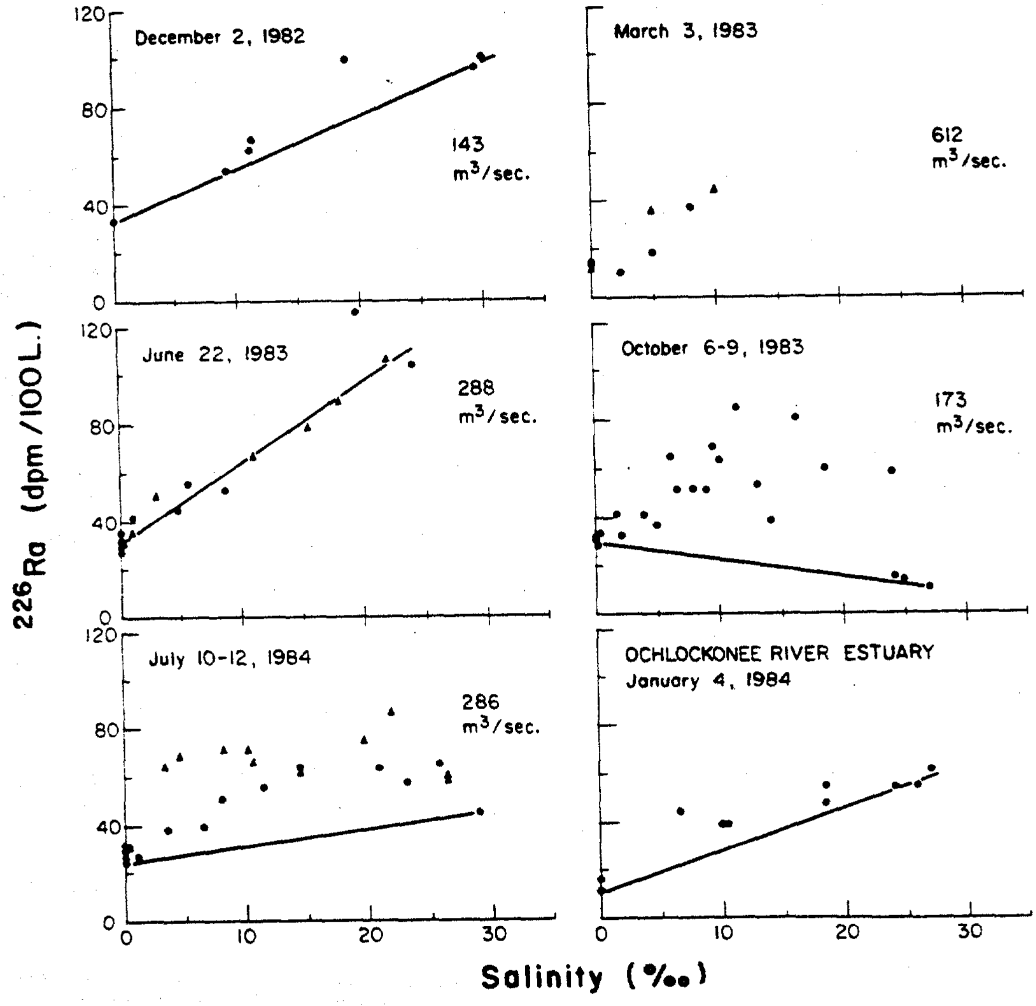

Figure 28. Plots of dissolved ^{226}Ra versus salinity in the Suwannee Estuary for 5 different sampling trips. Discharge values measured for each day also shown. The line connects the river end member to the most saline sample collected on each trip. One profile from the Ochlockonee River Estuary is presented for comparison.

covered because of very bad weather. Moreover, during these two periods, there was very high discharge in the river. Conservative-shaped radium mixing curves were also observed in the Pee Dee River-Estuary study during a period of high discharge (Elsinger and Hoore, 1980). It may be that during high discharge, the river sediments are carried out of the river channel so fast that a significant amount of ^{226}Ra desorption may occur in shelf waters rather than in the estuary. In general, the desorption curves of ^{226}Ra in the Suwannee River Estuary are similar to those found in the Pee Dee, Hudson and Amazon rivers but different from those of the particle-rich Mississippi River. The Mississippi has its maximum ^{226}Ra concentration at a low salinity of about 5 °/oo. Moore and Scott (1986) suggested that the 5 °/oo maximum is caused by the unique characteristics of the particulate matter in this river.

These results suggest that ^{226}Ra in the Suwannee River is kept at a relatively modest concentration by adsorption and/or ion exchange onto clay mineral surfaces and is subsequently released from these surfaces upon entering the high ionic strength water of the Gulf of Mexico. Once entering the marine water with high concentrations of divalent cations such as calcium, magnesium, and strontium, radium may exchange thus enriching the coastal waters with desorbed ^{226}Ra from the river-borne sediment. The net effect is a decrease in the particulate radium (Fig. 29) and an increase in the dissolved radium within the estuary. Although the specific activity of ^{226}Ra in the particulate matter of the Suwannee River is quite high, the suspended load of the river is very low compared to that of such rivers as the Mississippi or Amazon. In fact, the distribution of suspended matter in the Suwannee River Estuary has an opposite trend compared to many rivers. The suspended load in the Suwannee River Estuary tends to increase as the salinity increases showing that the Suwannee is not a significant source of particulates to the Gulf. Furthermore, the river-end member suspended load is only about 4 mg L^{-1} compared to approximately 100 mg L^{-1} in the Amazon (Key et al., 1985), and about 500 mg L^{-1} in the Mississippi River (Moore and Scott, 1986).

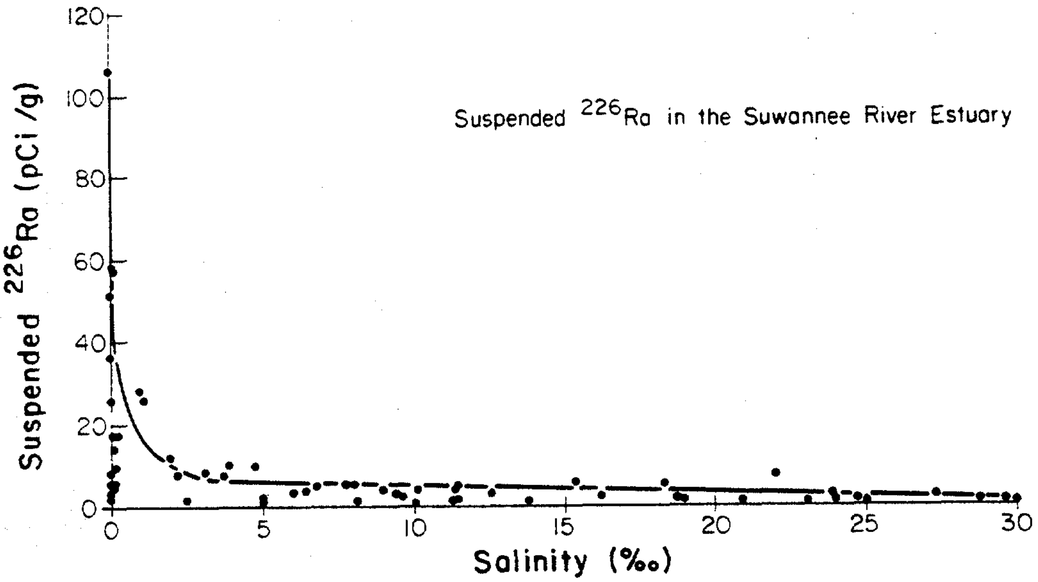

Figure 29. ^{226}Ra concentrations (pCi g^{-1}) within particles collected from various salinities within the Suwannee River Estuary.

Measurements of ^{224}Ra and ^{228}Ra, as well as ^{228}Ra/^{226}Ra ratios were measured for some of the sampling trips in the Suwannee River Estuary. A plot (Fig. 30) of the absolute concentration of ^{224}Ra and ^{228}Ra against salinity shows that both ^{224}Ra and ^{228}Ra show a non-conservative increase from the river end-member to higher salinity as did ^{226}Ra. The desorption curves generally mimic that of ^{226}Ra, not surprising because of their identical chemistries. However, the maximum concentration of ^{224}Ra occurs at about 5 °/oo, while the peaks in the ^{228}Ra and ^{226}Ra profiles are observed around 10-12 °/oo salinity. ^{224}Ra concentrations are related to ^{228}Th, which is particle reactive. ^{228}Th produced in the water column from ^{228}Ra decay should be quickly removed by particles and trapped in the turbidity maxima of the estuary (Elsinger and Moore, 1983). Consequently, ^{224}Ra generated from decay of ^{228}Th will be released to the water and generate higher activities of ^{224}Ra in the water parcel in the area of high particulate concentration. In the Suwannee Estuary, the maximum ^{224}Ra coincides with the area where there is the most sudden increase in particulate concentrations. Furthermore, if the suspended load has a longer residence time at any position in the estuary than the water, it may scavenge more ^{228}Th and thus release more ^{224}Ra. Since the calculated average residence time (based on flow and estimated volume) of water in the estuary is approximately 4 days, and the half-life of ^{224}Ra is roughly the same (3.7 days), significant decay of ^{224}Ra will have already occurred for parts of the estuary far from the radium source. In the salinity range of 5 to 29 °/oo, ^{224}Ra shows a conservative mixing trend with the seawater end member. This suggests that the source of ^{224}Ra must be somewhere close to the river mouth, such as the salt marsh area, as has been suggested by Elsinger and Moore (1983) for Winyah Bay and Delaware Bay and by Bollinger and Moore (1984) for Bly Creek, South Carolina.

The absolute concentration of ^{228}Ra in the Suwannee River Estuary is always less than that of ^{226}Ra and hence produces ^{228}Ra/^{226}Ra activity ratios from about 0.2 in the river to approximately 0.5 at the high salinity end. ^{228}Ra/^{226}Ra activity ratios in the high salinity end of the estuary are comparable to those of 0.47 to 0.58 found in the surface water of the Gulf of Mexico (Reid et al., 1979). ^{228}Ra/^{226}Ra activity

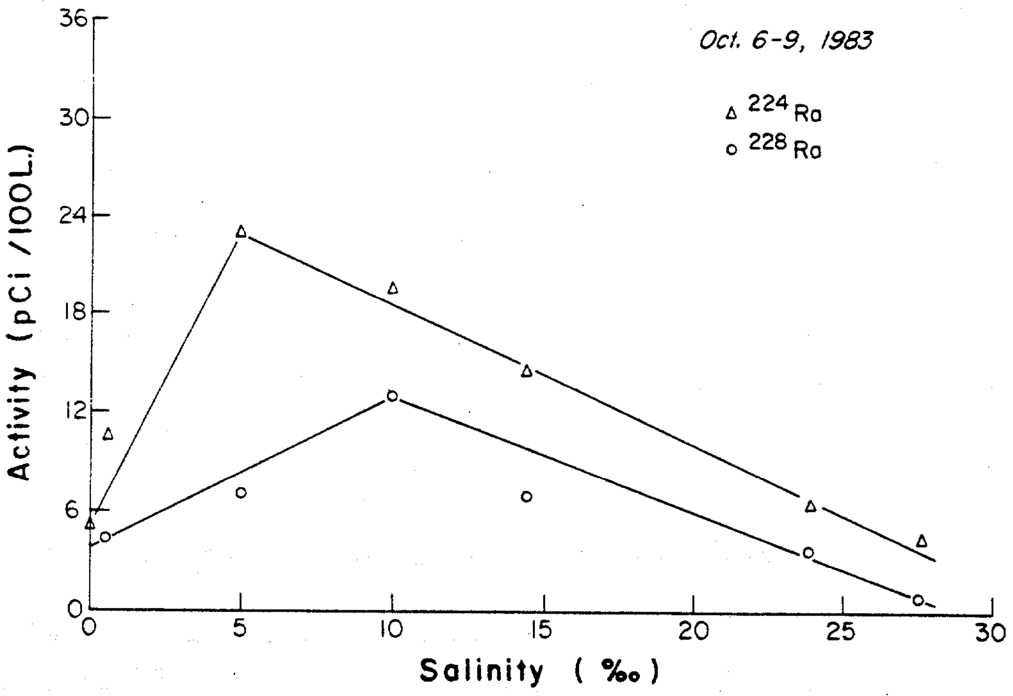

Figure 30. Plot of dissolved ^{224}Ra and ^{228}Ra (pCi 100L^{-1}) in the Suwannee River Estuary for the October, 1983 sampling trip.

ratios less than 1.0 in this river-estuary system represents an opposite pattern to that found in Winyah Bay, Delaware and the Yangtze River, China where the activity ratio of ^{228}Ra/^{226}Ra was consistently greater than 1.00 (Elsinger and Moore, 1984). Recent data from the Amazon River also show ^{228}Ra/^{226}Ra activity ratios greater than 1.00 (Key et al., 1985). This difference may be attributed to the fact that the Suwannee River has a much smaller suspended load compared to those estuaries and the dissolved ^{226}Ra is about 2-3 times higher.

Contribution of Radium from the Suwannee River to the Gulf of Mexico

Li and his co-workers have developed a method for calculation of the annual contribution of radium from the Hudson River estuary to the ocean (Li et al., 1977; Li and Chan, 1979). This method was also employed by Key et al. (1985) to calculate the flux of ^{226}Ra and ^{228}Ra from the Amazon River Estuary and the same approach was used by Moore and Scott (1986) to calculate the total yearly contribution of ^{226}Ra from the Mississippi to the ocean. This method involves determination of radium from 2 sources of the river-estuary system: (1) the river output; and (2) the river-estuary output.

The "river output" is calculated by adding the annual dissolved radium output from the initial river water to the annual desorbed radium from the river suspended sediment. The initial radium river output is obtained by multiplying dissolved radium in the river end-member by the total annual river discharge. The desorbed radium is estimated by multiplying the annual river discharge by an estimate of the amount of radium desorbed from suspended matter. Key et al. (1985) suggested that the best method to obtain this estimate is to perform desorption experiments on samples of total suspended solids taken from river water upstream of the estuary in a manner similar to that of Li and Chan (1979). This approach needs to assume that the collected sample of suspended matter is representative of the river-borne sediment and that estuarine conditions causing desorption can be duplicated in the laboratory. Because of the very low concentrations of suspended matter in the Suwannee, it was decided to use an alternative method. This method estimates desorbed radium by considering the decrease in total ^{226}Ra measured on suspended solids in the river end member compared to the seawater end member (Key et al., 1985; Moore and Scott, 1986).

The "total river-estuary output" of ^{226}Ra is estimated by a linear regression from the plot of dissolved radium versus salinity in the estuary (Fig. 28). A straight line is drawn along the linear portion of the desorption curve between the radium maximum and the shelf water end-member. The line is extrapolated to intercept 0 $^{0}/_{00}$ salinity to estimate an "apparent" radium concentration in the river end member. This extrapolation shows that the "apparent total river-estuary" concentration for the October, 1982 sampling is 45.5 ± 17 pCi $100L^{-1}$ while in July, 1984, the apparent concentration was 67.6 ± 36 pCi $100L^{-1}$. Based on these estimates, an average of 56.8 ± 20 pCi $100L^{-1}$ was used for flux calculations. By multiplying this apparent concentration by the annual river discharge, an "apparent total river-estuary flux" is calculated. The apparent radium flux is a composite flux from 4 possible sources: (1) initial dissolved radium in the river water; (2) dissolved radium in sea water; (3) desorbed radium from suspended matter supplied to the estuary by the river; and (4) net addition of radium resulting from the diffusional flux from the sediment.

For our mass balance calculation, the annual discharge of the Suwannee River at the U.S.G.S. discharge station at Wilcox was used because it is the nearest station to the Gulf. For comparative purposes, we estimated the radium mass balance from each sampling trip and then the overall result was estimated by using the mean results from all sampling periods (Table 26). For the individual trips, the mean of all parameters for river water found in salinities less than 1 $^{o}/_{oo}$ was used as a value for the river end member. The discharge of each sampling date was used as a basis for estimating the annual river discharge for that particular sampling period. For the overall value, the long term (30 year) average

Table 26. Results and parameters used in calculation of radium flux from the Suwannee River to the Gulf of Mexico.

Parameters	Units	Sampling Date Dec.20,'82	June 22,'83	Oct 6-9,'83	July 10-12,'84	Overall Average
Flow rate						
Sampling day	$(m^3\ s^{-1})$	142.7	288.2	172.5	286.0	331.1
Suspended Load	$(mg\ L^{-1})$	0.97	2.60	1.50	2.30	1.84
Dissolved ^{226}Ra	$(pCi\ 100L^{-1})$					
River end		14.9	14.5	14.2	14.0	14.4
Max. Sal. end		44.5	46.8	5.0	20.0	29.1
Suspended ^{226}Ra	$(pCi\ g^{-1})$					
River end		51.4	22.7	46.4	17.7	34.5
Max. Sal. end		0.5	10.2	2.3	0.7	3.4
Desorbed		50.8	12.5	44.0	17.0	31.1
Dissolved ^{228}Ra	$(pCi\ 100L^{-1})$					
River end		3.1	NA	3.7	NA	3.5
Max. Sal. end		27.3	NA	2.1	NA	14.7
Dissolved ^{224}Ra	$(pCi\ 100L^{-1})$					
River end		NA	NA	8.6	NA	8.6
Max. Sal. end		NA	NA	4.6	NA	4.6
Apparent Riv-Est	$(pCi\ 100L^{-1})$					
^{226}Ra		51.8	NA	45.5	67.6	56.8
^{224}Ra		NA	NA	27.9	NA	27.9
^{228}Ra		NA	NA	20.3	NA	20.3
Yearly Discharge						
Dissolved River	$(10^{12}\ pCi\ yr^{-1})$					
^{226}Ra		0.7	1.3	0.8	1.3	1.5
^{224}Ra		NA	NA	0.4	NA	0.4
^{228}Ra		0.1	NA	0.2	NA	0.2
Desorbed River	$(10^{12}\ pCi\ yr^{-1})$					
^{226}Ra		0.2	0.3	0.4	0.4	0.6
Total River	$(10^{12}\ pCi\ yr^{-1})$					
^{226}Ra		0.9	1.6	1.1	1.6	2.1
^{224}Ra		NA	NA	1.3	NA	1.3
^{228}Ra		NA	NA	0.9	NA	0.9
Apparent Riv-Est	$(10^{12}\ pCi\ yr^{-1})$					
^{226}Ra		NA	NA	2.5	6.1	5.9
^{224}Ra		NA	NA	1.3	NA	1.3
^{228}Ra		NA	NA	0.9	NA	0.9

river flow was utilized in the calculation.

Our calculations indicate that the Suwannee River carried approximately 1.3 x 10 pCi yr^{-1} of total radium into the Gulf of Mexico during our study period. A long-term average is estimated to be approximately 2.1 x 1012 pCi yr^{-1} (Table 26). Major Florida rivers, combined, discharge approximately 6.8 x 10^{12} pCi yr^{-1} of total ^{226}Ra to the Gulf of Mexico (Table 21). This is about an order of magnitude less than that calculated for the Mississippi River (Moore and Scott, 1986).

Calculation of the overall estimated river-estuary flux results in a radium flux of approximately 5.9 x 10^{12} pCi yr^{-1}. Since this flux is so much larger than the total river flux of 2.1 x 10^{12} pCi yr^{-1} the supply of ^{226}Ra by diffusion from estuarine and adjacent shelf sediments or some other source is apparently about 2 times more important than the dissolved and desorbed flux from the Suwannee River discharge. The river appears to contribute about 23% in the form of dissolved radium and about 8% as desorbed radium to the estuary. Desorption from river-borne sediment, therefore, cannot account for all the excess ^{226}Ra found in the estuary. A few sediment samples from the estuary were measured for radium and found to be quite low. Thus, diffusion from bottom sediment is probably not a significant source of the high radium. Another possible source might be submarine springs with high radium activity or seepage of high-radium groundwater into the coastal and estuarine water as suggested earlier by Fanning et al. (1982). Presumably, radium in spring waters discharging directly into the high ionic strength waters of the estuary would remain in solution and not interact with particles as in the river.

CONCLUSIONS

(1) Experimental results confirm that Mn-fiber will quantitatively extract dissolved radium from natural waters, including organic-rich river water.

(2) Any discrepancies in measuring radium by the "whole bottle" and "Mn-fiber" techniques may be attributed to radium contained in suspended matter which is not retained by the Mn-fibers.

(3) The overall mean concentration of dissolved ^{226}Ra in the Suwannee River over a 2-year period was equal to 10.1 ± 0.8 pCi $100L^{-1}$.

(4) No increase was detected In radium measured directly downstream from Swift Creek which drains the phosphate mining operations at White Springs, Florida.

(5) Radium in the Suwannee River is influenced by the relative mixing of surface drainage (low radium) and groundwater entry via springs (high radium). As a consequence, radium in the river is generally low during periods of high flow, reflecting dilution of ground and surface water.

(6) The distribution of radium between the dissolved and suspended fractions in the river is very constant with the suspended radium constituting 25-35 percent of the total. Although the exact mechanisms are not understood, it is suspected that this distribution is the result of adsorption and/or ion exchange onto fine-grained particulate phases present in the suspended matter.

(7) Soluble radium concentrations increase dramatically in the more saline parts of the Suwannee River Estuary, suggesting an additional source of radium. Comparison of the total river flux to the "apparent total river-estuary" flux of radium indicates that desorption cannot account for all the excess radium in the estuary. Other possible sources include submarine springs, offshore seepage of high radium groundwater, and the adjacent salt marshes.

(8) All major Florida rivers contribute approximately 6.8×10^{12} pCi yr^{-1} of total radium to the Gulf of Mexico, about an order of magnitude less than that contributed by the Mississippi River.

CHAPTER 5

POLONIUM IN THE SURFICIAL AQUIFER OF WEST CENTRAL FLORIDA

INTRODUCTION

^{222}Rn and ^{210}Po are radiogenic, alpha-emitting daughters of the natural ^{238}U decay series (Fig. 31) with half-lives of 3.8 and 138.38 days, respectively. An intermediate daughter product, ^{210}Pb, is a beta-emitting nuclide with a much longer half-life, 22.3 years. ^{210}Po is the only natural polonium isotope with a half-life longer than a few hours.

EPA maximium contaminant levels for radiation in groundwaters are 5 pCi L^{-1} for ^{226}Ra and 15 pCi L^{-1} for total or "gross" alphas. The EPA limit for ^{222}Rn in the air is 4 pCi L^{-1}. The danger arising from ingestion or inhalation of radioactivity is from the bioaccumulation of these radionuclides in the body. Clinical experiments show radium to be preferentially concentrated in bones and organs, while polonium and radon are absorbed by soft organs and tissues (Bagnall, 1966). It may be that the radiotoxicity attributed to ^{222}Rn is actually caused by its progeny, including the short-lived polonium daughters (National Academy of Sciences, 1980). The physical effects expected from ingestion or inhalation of alpha particles include genetic alterations resulting in mutation or formation of cancerous cells. Both ^{210}Po and ^{222}Rn are classified as being carcinogenic (Lyman et al., 1985, Hess et al., 1983 and Martell, 1975). In the case of ^{210}Po, its high specific activity (0.222 Ci mg^{-1}) results in a radiotoxicity 4 to 5 orders of magnitude greater than either plutonium or radium (Fink, 1950).

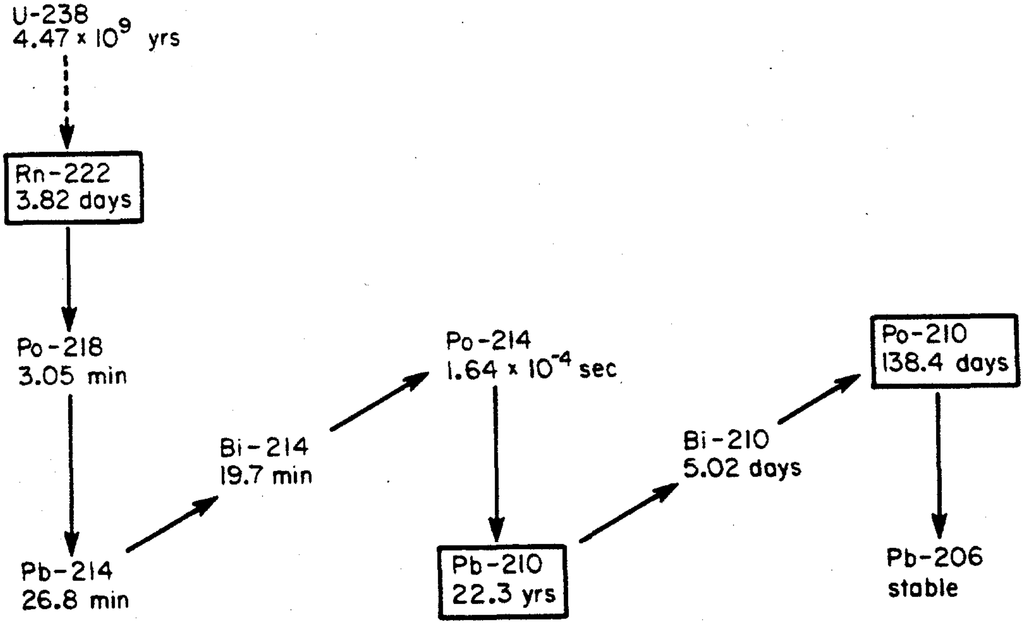

Figure 31. Abbreviated ^{238}U decay scheme with half-lives of all isotopes from ^{222}Rn through ^{210}Po. There are several intermediate daughters not shown between ^{238}U and ^{222}Rn.

Disequilibria in the natural ^{238}U-series within uranium-rich minerals are caused by internal processes like recoil and diffusion, while external processes, such as weathering and leaching, also contribute to the release of radionuclides into the environment in particulate, dissolved and gaseous forms.

Since much of west central Florida is underlain by the Hawthorn and Bone Valley formations which contain phosphate orebodies containing substantial amounts of uranium, there is a very large potential source of ^{238}U-series daughter products. The phosphatic horizons in Florida are normally overlain by a sand sheet on the order of 10 m thick. A study conducted by Hinton and Whicker (1985) showed that for a reclaimed uranium mill tailing deposit covered by 1.5 m of vegetation or 0.3 m of bare overburden, the ^{222}Rn flux was reduced to background levels (1.01± 0.36 pCi m^{-2} s^{-1}. However, an increase in moisture content by precipitation would result in a 25 to 30% increase in the flux rate.

Estimates for how long it would take a ^{222}Rn atom to tranverse several meters of bedrock can be approached by comparison to estimates for the equivalent time for radon migration in air or water. On the average, it will take 13 days for a radon atom to diffuse through 5 m of air or 5 cm of water (W.H.O., 1977); ignoring convection, it takes approximately 52 days to migrate through 20 m of air or 5200 days to migrate through 20 m of water. This is time enough for complete decay of both ^{222}Rn and ^{210}Po, if unsupported. Since consistently high radionuclide concentrations have been measured in some groundwaters from west central Florida, active escape of radon from the Hawthorn Formation must be taking place. In general, high radioactivity of short-lived daughters in groundwater must necessarily arise from one of the following scenarios: (1) a highly radioactive point source of continuous emission; (2) a persistent flux of these radionuclides emanating from the pathway walls; or (3) emission from particulates carried by the groundwater.

The purpose of this paper is to report our observations of anomalously-high ^{210}Po in some groundwaters from the surficial aquifer in west central Florida. Although it is still unclear why polonium occasionally exists at such high levels, simultaneous measurements of other ^{238}U-series nuclides as well as several chemical parameters have provided some important clues.

EXPERIMENTAL METHODS

(1) Measurement of Polonium-210

The procedure we utilized for the analysis of ^{210}Po is modified from that of Oural et al. (1986). Two 900 ml water samples are collected from each station. One sample is immediately filtered through a 0.45 µm Millipore filter for analysis of "dissolved" activity and the other sample is collected unfiltered and represents the "total" activity within a sample. Each sample is then immediately fixed by addition of concentrated nitric acid (2% by volume) and spiked with a known activity of yield tracer, ^{209}Po. Samples are left to equilibrate in the laboratory for at least 24 hours after which time approximately 20 mg of iron carrier solution is added. Solutions are left to equilibrate for a further 48 hours, then the polonium is coprecipitated with iron hydroxide by addition of concentrated ammonium hydroxide. Samples are well mixed, and the precipitate allowed to settle for approximately 48 hours. The liquor is decanted from the precipitate and discarded. The precipitate is centifuged and supernate discarded. The precipitate is then dissolved in 6M HCl and transferred to a plating cell.

A modified version of Flynn's (1968) procedure is used for the spontaneous plating of ^{210}Po onto silver disks. The changes we have incorporated include: (1) the plating solution is adjusted to approximately 0.5N HCl; and (2) the addition of 100 mg of ascorbic acid. Yields from simple ^{209}Po-spiked deionized water solutions are typically 80 to 95%, while natural groundwater samples are invariably lower, with a range from as low as a few percent to over 60%. The prepared discs are then counted by alpha spectrometry. Our yield tracer, ^{209}Po, has been standardized against the reported ^{210}Pb activity of EPA standard "Climax Sand Tailings".

(2) Measurement of Radon-222

Excess ^{222}Rn is measured by liquid scintillation counting, using the procedure of Prichard and Gesell (1977) on sample volumes of 10 mls. The analyses are all done in triplicate. All results are corrected for decay to time of sampling. Standards have been prepared from NBS Standard Reference Material 4958, radium solution. Standards prepared ranged from 100-100,000 pCi L^{-1}.

(3) Lead-210 Measurements

We used a modified procedure for analysis for ^{210}Pb modified from the method of Thomson and Turekian (1976) and Koide et al. (1972). All sample bottles are precleaned with 6N HCl, rinsed several times with distilled water, followed by a final rinse with double deionized water. A 1.9 liter water sample is collected in the field after rinsing the bottle several times with some of the sample water. The sample is immediately fixed by addition of 10 ml of concentrated HCl, so the resultant pH during storage is 1.2. On arrival back at the laboratory, 2 ml of Fe^{3+} carrier (10 mg Fe/ml as $FeCl_3$) and 2 ml of Pb^{2+} carrier (30 mg Pb/ml as $Pb(N0_3)_2$ are added. The bottles are shaken and then left to equilibrate for at least several days. Samples are then neutralized and Fe(OH)3 precipitate containing scavenged lead is formed upon addition of 20 ml of ammonia solution. The precipitate is separated from the liquor by filtering the sample through a 47-mm diameter, 0.45 µm Millipore HA filter paper. The precipitate is dissolved off the filters with a jet of 8N HCl and a small amount of double deionized water. The final HCl concentration is 8N in a volume of 25 ml (acidified with concentrated HCl). The solution is ultrasonicated and left to equilibrate overnight.

The next day, the sample is loaded onto a Biorad AG 1x8, 100-200 mesh anion exchange Column (12 cm x 1 cm) for removal of Fe (and any U). Two successive 40-ml aliquots of 8N HCl are used to rinse the column. All the effluents from the column are collected in a 200 ml teflon PFA beaker and evaporated to dryness overnight in a steambath. The residue is dissolved in 10 ml of 6N HCl, ultrasonicated, followed by the addition of 30 ml of double deionized water, making the final solution 1.5N HCl. The solution is gently heated on a hotplate and then ultrasonicated. The sample is then loaded onto a similar ion exchange column as that used for the Fe separation for the separation of Pb. The column is washed twice with 30 ml of 1.5N HCl, and the Pb is finally eluted with two 40-ml aliquots of double deionized water. The solution is left to equilibrate overnight. $PbSO_4$ is precipitated from the eluate at pH 2 by addition of 30 ml of saturated sodium sulfate. The precipitate mixture is ultrasonicated and left overnight. $PbSO_4$ is filtered through a predried and preweighed 0.45 µm HA 47.mm diameter Millipore filter. The filter is dried at 60°C overnight and then weighed for a gravimetric Pb yield. The edges of the filter are burnt with a hot glass rod to prevent flare-ups and then combusted in a muffle furnace, with temperature rising slowly from 0 to 200°C. This procedure promotes a slow moving burn rather than a spontaneous combustion. The ash as $PbSO_4$ is weighed again and then loaded into vials for counting of the 46.5 KeV photopeak of ^{210}Pb by an intrinsic germanium well-type detector. Standardization of the efficiency and geometry effects were obtained by analyzing standard ^{210}Pb solutions in the same manner.

(4) Chemical and Physical Parameters

Measurements of temperature, pH, conductivity, turbidity, absorbance (color), fluoride, and sulfide were all made on subsamples collected at the same time as the samples for radiochemical analysis. Sample storage and analysis was accomplished using recommended techniques (EPA, 1983).

RESULTS AND DISCUSSION

Regional Results

The distribution of our sample collection sites is shown in Fig. 32.

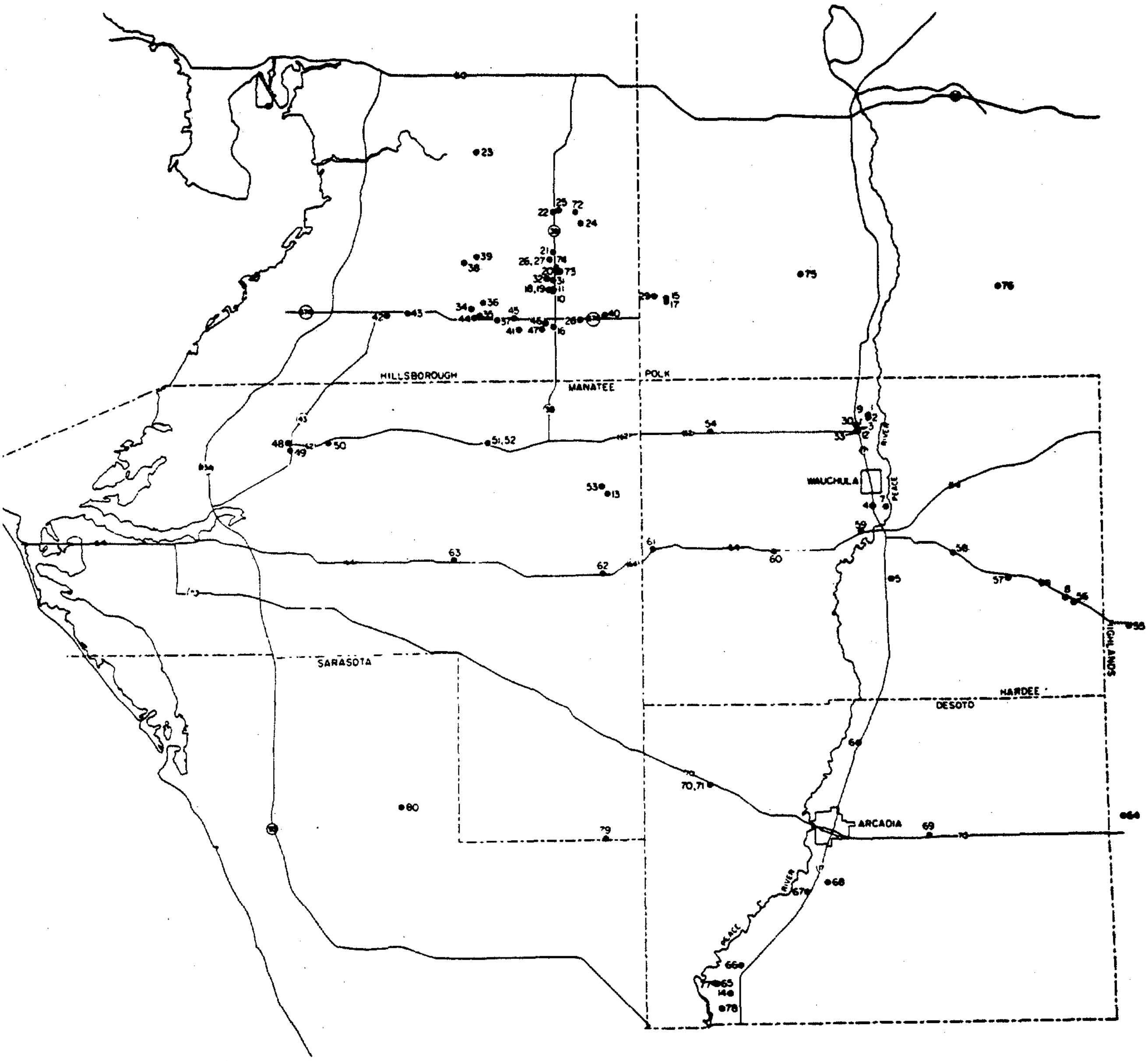

Figure 32. Index map of southwest Florida showing locations of sampling sites. Most of these sites are private wells drawing water from the surficial aquifer.

Tabulated results of filtered and unfiltered ^{210}Po from all these sites are given in Appendix 3. Although the results are "spotty", there is a rather wide distribution of samples with elevated levels of ^{210}Po, normally a very particle-reactive element. In most of our samples, the concentrations of ^{210}PO commonly range from <0.1 to 10's pCi L^{-1}, activities of 100's pCi L^{-1} are found in a few cases and more than 2,000 pCi L^{-1} was found in one unfiltered sample.

Thus far, we have found ^{210}Po values greater than the EPA limit of 15 pCi L^{-1} in wells from every county we have sampled, i.e., Hillsborough, Polk, Manatee, Hardee, De Soto and Highlands counties. Of the 80 sites analyzed so far, 25 have ^{210}Po activities which are greater than 15 pCi L^{-1} (Fig. 33). Almost all of these wells are shallow, usually on the order of 10 m deep. Some of the wells in southern De Soto County, however, are much deeper (at about 85 m), yet contain levels of ^{210}Po up to over 90 pCi L^{-1} in the unfiltered water. Anomalously high polonium levels are thus not restricted to the surficial aquifer, nor to the immediate vicinity of phosphate mining areas.

Only two other cases are known to us where polonium has been detected in concentrations comparable to what we have measured (up to hundreds of pCi L^{-1}) in groundwaters. One well is located in Louisiana in an area of extensive faulting and is believed to overlie a uranium ore deposit (Mullin, 1982). The other well is located in central Florida and serves as a recharge well for a phosphate mine (Oural et al., 1986).

An analysis of our ^{222}Rn data collected thus far (Appendix 4), shows that the concentrations tend to be high and extremely variable in the shallow aquifer. The mean value of all stations is 8,440 pCi L^{-1}. Almost all samples contain greater than 2,000 pCi L^{-1}, with about 20% of our samples having concentrations above 20,000 pCi L^{-1}. A few samples are much higher. The station with the highest ^{222}Rn concentration, station 45, is close to the station with the highest ^{210}Po concentration, station 18. Although these radon levels are not as spectacular as the >100,000 pCi L^{-1} levels reported in the granitic

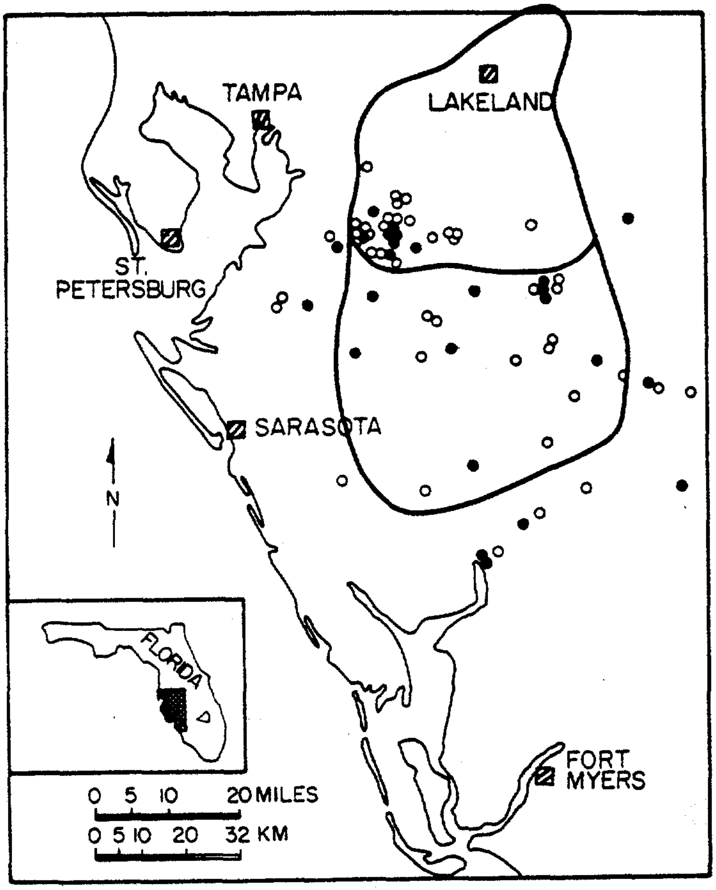

Figure 33. Distribution of ^{210}Po in the surficial aquifer of SW Florida. Solid circles refer to concentrations above 15 pCi L^{-1}. The solid line indicates the approximate outline of the Central Florida Phosphate District and its extension to the south.

areas of New England and Finland, the levels in the surficial aquifer are significantly elevated compared to "normal" groundwater.

^{222}Rn will emanate more easily from a medium relative to other members of the uranium series because it is an inert gas, so reports of high ^{222}Rn concentrations in the water are not uncommon (Brutsaert et al., 1981; Asikainen, 1981) and the mechanism responsible is by recoil and diffusion (Rama and Moore, 1984):

In a few cases, we have relatively complete analyses of well water for several members of the ^{238}U decay chain (Table 27). Apparently, subsurface leaching and transport by groundwaters have led to marked disequilibria between members of the ^{238}U-series. The concentrations of 238U in all wells measured were in the ppb range, while the ^{234}U/^{238}U ratio is greater than unity in almost all cases. There is an inverse correlation between the uranium activity ratio and concentration, a situation which has been previously observed by Osmond and Cowart (1976). The ^{234}U/^{238}U activity ratios indicate that significant leaching of the bedrock has taken place, releasing recoil ^{234}U preferentially to ^{238}U.

A comparison of our polonium and radon results (Appendix 4) shows that wells possessing high polonium activities also have high excess radon. However, low polonium wells also occur in cases where we have low or high radon activities. When there is high ^{222}Rn and low ^{210}Po in the water, all the ^{210}Pb and ^{210}Po are apparently strongly adsorbed onto particle surfaces. Analyses for the intermediate daughter, ^{210}Pb, have ranged from below detection to 10 pCi L^{-1}. The anomalously high ^{210}Po, therefore, appears to be largely unsupported.

Most of our work has been concentrated at the site of the highest ^{210}Po values, station 18, in an effort to identify the unique characteristics of this environment in terms of why it has such high levels of radioactivity in its water compared to groundwaters from other, apparently similar, environments.

Table 27. ^{238}U-series radionuclides in unfiltered groundwater samples from west central Florida.

Station No.	U (ppb)	^{234}U/^{238}U A.R.	^{226}Ra (pCi L^{-1})	^{222}Rn (pCi L^{-1})	^{210}Pb[1] (pCi L^{-1})	^{210}Po (pCi L^{-1})
8	0.141	9.96	1.0	NA[2]	NA	17
9	0.020	2.01	NA	NA	NA	145
10	0.014	4.67	2.8	2590-3470	NA	27.4-178
12	0.013	3.59	1.1	24800	2.75	92-142
14	0.486	1.07	NA	7160-8260	NA	83-260
15	2.310	0.97	NA	NA	NA	3.62
16	0.020	2.71	NA	NA	NA	4.21
17	0.756	2.03	NA	NA	NA	9.20
18	0.008	2.91	0.73-1.1	16100-19000	2.0-4.4	260-2570
23	0.916	0.67	NA	244	NA	0.59
26	0.025	2.55	NA	NA	NA	NA
37	NA	NA	8.5-9.5	26500	NA	0.26
56	NA	NA	NA	7030	2.43	6.19
62	NA	NA	NA	6730	7.70	0.95

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[1] ^{210}Pb in filtered water samples.
[2] NA = not analyzed.

Station #18 Results

Replicate samples of water collected on October 24, 1986 from 1 large water sample from station #18 were analyzed for ^{210}Po (Table 28). The filtered samples were filtered sequentially from the bulk sample in the order of A to E without replacing the Millipore filter. Both filtered and unfiltered ^{210}Po activities lie within a two standard deviation counting error of the average activities and most are within one standard deviation counting error. These results imply that the average filtered and unfiltered activities are significantly different. Filtering in the field, however, has occasionally resulted in higher filtered versus unfiltered concentrations.

Different pretreatment (oxidizing) conditions for unfiltered samples from station #18 show a wide variation in ^{210}Po results, from 323-805 pCi L^{-1}. The types of oxidizing treatment, timing of addition of acids, etc., and ^{210}Po results are given in Table 29. Assuming that the higher values are more correct, it may be preferable to fix the sample with either a mixture of acids or ammonium hydroxide. If acid fixation is used, a digestion procedure is required, which is not the case for the ammonia treated sample. Acid fixation followed by digestion or ammonium fixation give similar results, which are higher for ^{210}Po than just following a HNO_3 fixation followed by iron coprecipitation. These results are consistent with those reported earlier by Oural et al. (1986).

Results from sequential analyses of a large, filtered water sample from station #18 collected on August 1, 1986, are given in Table 30. These results show that the ^{210}Po activity has decreased over time since the collection date of the bulk sample and the half-life of the decay curve of this sample (Fig. 34) are approximately 141 days, close to the half-life of ^{210}Po. This implies that polonium is largely unsupported in concurrence with our direct measurements for ^{210}Pb.

Table 28. Replicate analyses of samples from a homogeneous bulk sample collected from station #18 on October 24, 1986. Errors quoted are ±1σ based on counting statistics.

Sample	^{210}Po Filtered[1]	^{210}Po Unfiltered
	--- pCi L^{-1} ---	
A	430 ± 20	513 ± 22
B	340 ± 23	578 ± 23
C	436 ± 20	512 ± 20
D	437 ± 34	564 ± 36
E	487 ± 21	557 ± 33
Mean[2]	447 ± 27	545 ± 31

---

[1] Samples were filtered in sequential order from A to E.

[2] This is the mean and standard deviation of 4 replicate analyses. The filtered sample B was considered an outlier and excluded from the calculation.

Table 29. Results of various pretreatments of unfiltered water from station #18. All samples collected on June 21, 1986.

Notes	Experimental Treatment	^{210}Po (pCi L^{-1})
(1)	1 ml $HClO_4$ + 1 ml HNO_3	805 ± 5
	1 ml $HClO_4$ + 1 ml HNO_3	700 ± 6
	1 ml HCl + 1 ml HNO_3	665 ± 20
	1 ml $HClO_4$ + 1 ml HNO_3 + 1 ml H_2O_2	697 ± 18
	1 ml H_2SO_4 + 1 ml HNO_3	679 ± 25
(2)	1 ml $HClO_4$ + 5 ml HNO_3 + 3 ml H_2SO_4 + 3g Na_2SO_4	687 ± 23
(3)	18 ml HNO_3	323 ± 13
(4)	18 ml NH_4OH	651 ± 27

(1) 100 ml of sample was fixed in the field and ^{209}Po tracer added. On return to the laboratory the acids were added and the sample fumed to approximately 5 mls in teflon beakers. Acids were added a second time and fumed to 1 ml. The sample was then prepared for spontaneous plating.

(2) 100 ml of sample was fixed in the field and ^{209}Po added. On return to the laboratory the acids were added and the sample fumed to a Na_2SO_4 cake in a teflon beaker. Acids were added again and fumed to a Na_2SO_4 cake a second time. Sample was diluted to a HCl molarity of 0.1 M and prepared for spontaneous plating.

(3) 900 ml of sample was collected in the field and ^{209}Po added. Upon return to the laboratory, Fe^{3+} was added and polonium was co-precipitated by addition of Na_4OH. The sample was then prepared for spontaneous plating.

(4) Procedure same as that in note 3.

Table 30. Results of long-term experiment to determine if ^{210}Po is supported by successive measurements from one large-volume sample, collected August 1, 1986. Activities in pCi L^{-1}.

Date Measured	HNO_3-Fixed	NH_4OH-Fixed
Aug. 1, 1986[1]	320.4	-
Aug. 26, 1986	289.4 ±.4	295 + 11
Sept. 24, 1986	-	303.6 + 6.5
Sept. 26, 1986	257.9 ±.8	-
Oct. 19, 1986	229.6 ±.1	-
Oct. 20, 1986	-	271.0 + 7.2
Oct. 21, 1986[2]	231.5 ±.7	-
Oct. 22, 1986[3]	240.6 ±.3	-
Oct. 30, 1986[4]	198.8 ±.0	230.3 + 3.9
Dec. 5, 1986	194.6 ±.9	235.9 + 8.9

1 Values are calculated assuming ^{210}Po is unsupported based on extrapolated value from Fig. 34.

2 This sample represents a separate aliquot taken on August 1, 1986, precipitated and processed just before counting.

3 Separate aliquot also taken on August 1, 1986, precipitated and processed just before counting.

4 Recount of ^{210}Po planchet from Aug. 26, 1986.

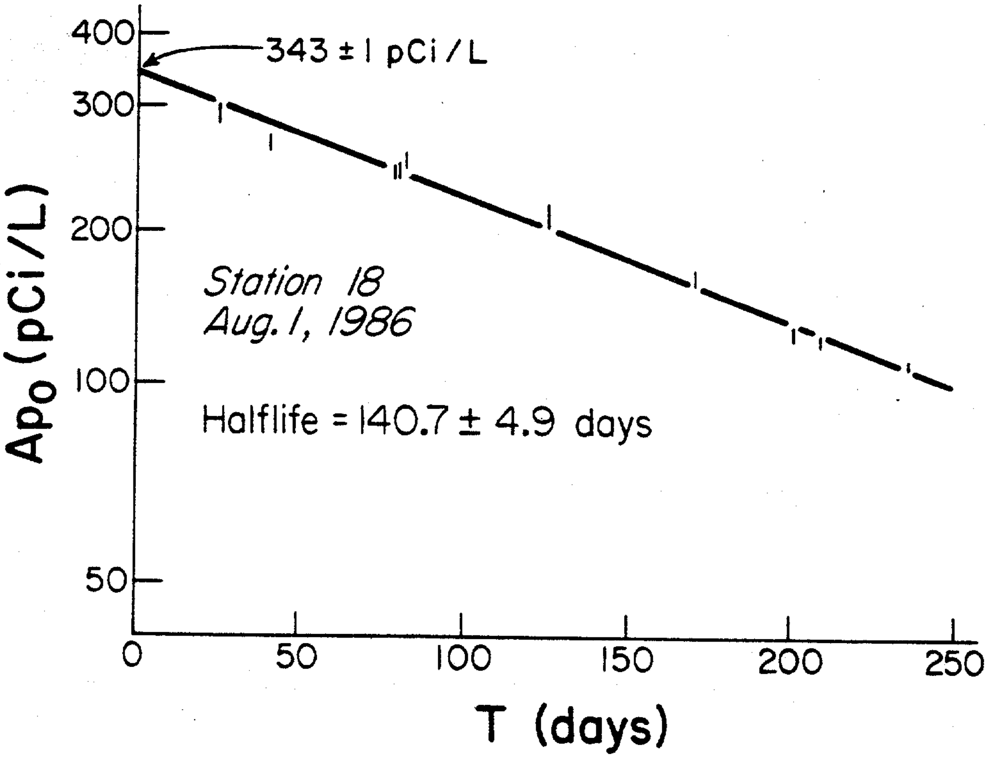

Figure 34. ^{210}Po activity measured at various times from one large, filtered and acidified water sample. The slope of this curve indicates an apparent half-life of about 141 days, close to the expected half-life for ^{210}Po (138.4 days).

A short time-series analysis over an interval of approximately 2 hours was performed at station #18 to evaluate short-term fluctuations (Fig. 35). In fact, there were several significant changes noted during this time. The maximium ^{210}Po activity occurred during the first 15 minutes after the water valve was opened. This time may represent the flushing time required to draw fresh water from the well into the tank. The decrease in ^{210}Po activity after this time may be due to water being cycled in the tank and ^{210}Po being adsorbed onto the tank walls immediately, or the activity is declining to some real base value representative of the shallow groundwater. The ^{222}Rn behaves more-or-less as expected with an initial rise as the tank is flushed, then a levelling off at a fairly constant level.

Activities of ^{238}U radionuclides in station #18 water samples show extreme disequilibrium between all parent-daughter pairs measured (Fig. 36). The disruption of equilibrium in the radon-lead-polonium chain may occur by: (1) adsorption of dissolved lead onto particles or surfaces such as the bedrock of the reservoir; or (2) the authigenic precipitation of lead from the dissolved phase as a lead sulfide. Either of these removal mechanisms must then be followed by a partial release of polonium into the water or removal of lead while leaving significant amounts of polonium in solution. The latter mechanism is possible under these conditions. A study by Jean and Bancroft (1986) showed a pH of at least 6 is required before adsorption takes place upon a sulphide mineral surface; the pH we find at station #18 has ranged from 3.8 to 5.19 during the course of this study (Appendix 4). In addition, sulfide concentrations are always significant in all the groundwaters containing elevated polonium. We have also noted that, upon addition of Pb^{2+} as $PbNO_3$, precipitation of lead sulfide occurs immediately, implying that these waters are saturated with respect to PbS. Ingrowth of ^{210}Po occurs into the ^{210}Pb and a significant fraction may be subsequently released into the aqueous media by diffusion and perhaps other processes.

Analysis for activities in a scale sample from the inside of the pressure tank at station #18 showed a marked disequilibria pattern similar

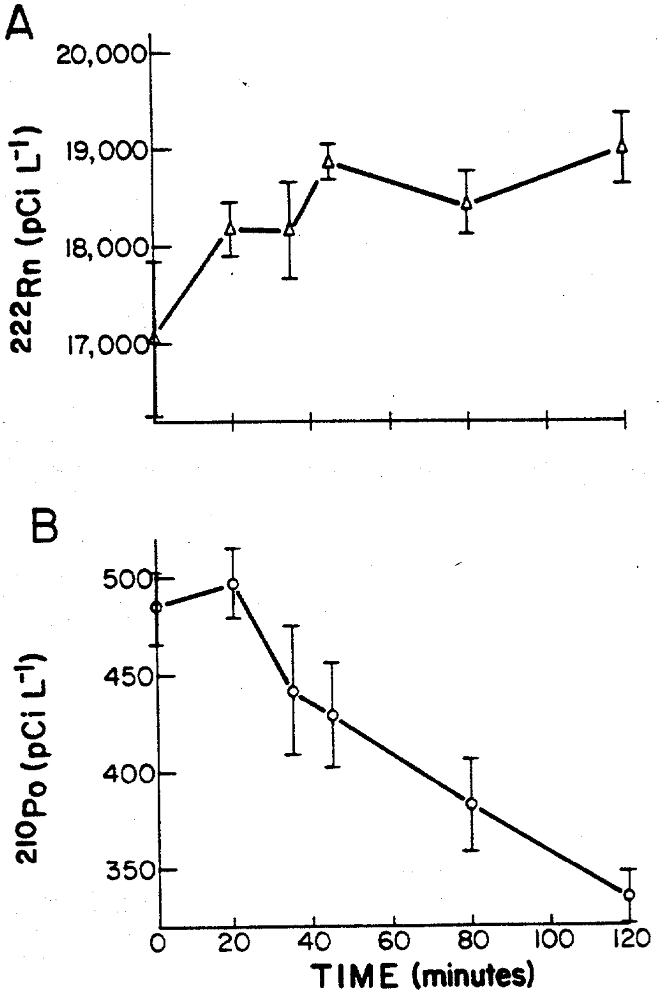

Figure 35. (A) ^{222}Rn activity at station 18 measured in discrete samples collected over about 2 hours with the water tap running.
(B) ^{210}Po analyses for the same samples as in (A).

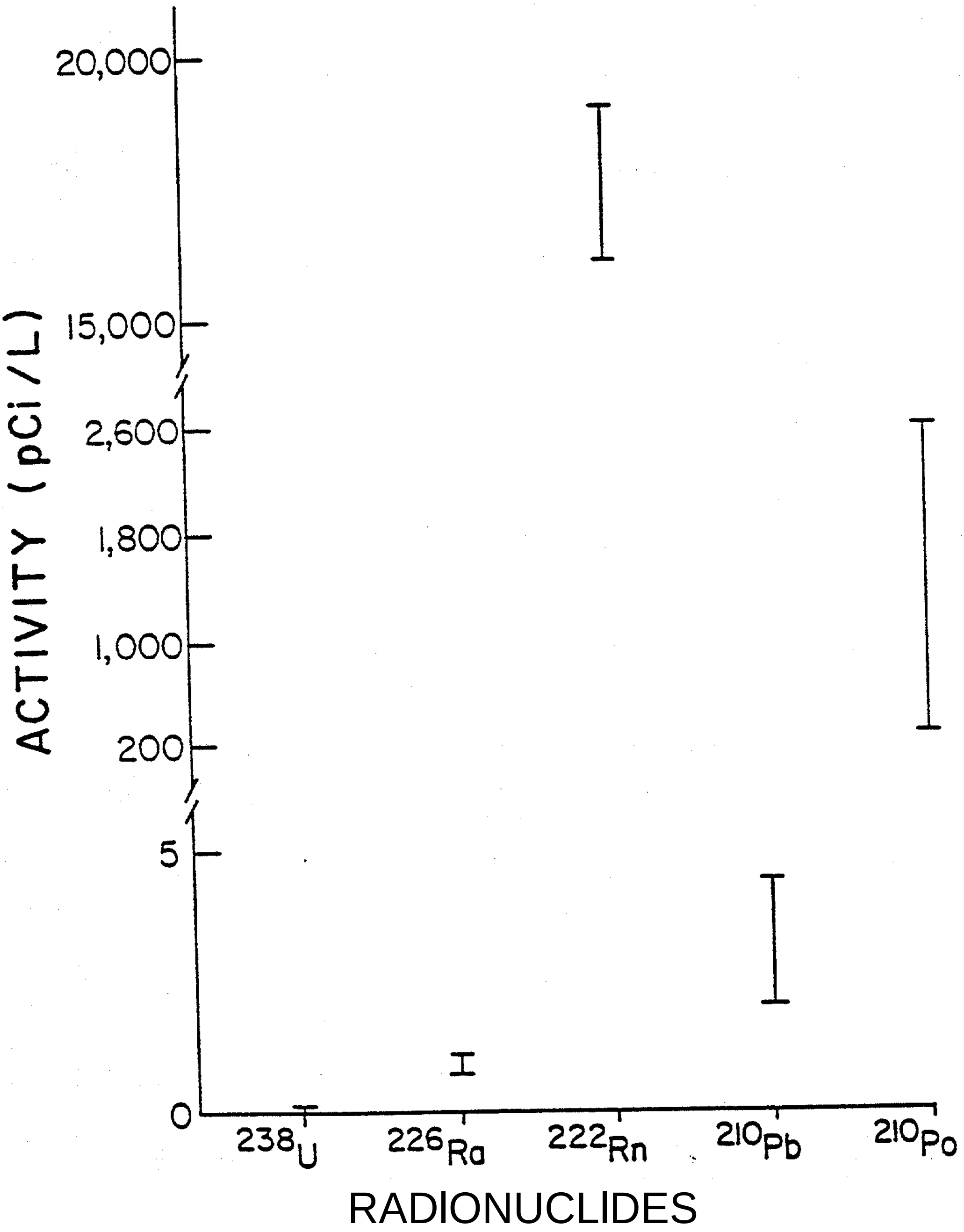

Figure 36. Concentration ranges of ^{238}U, ^{226}Ra, ^{222}Rn, ^{210}Pb, and ^{210}Po in station 18 water samples. Note two changes in scale.

to that found in the water (Fig. 37). Although the absolute activities of the radionuclides in the scale were considerably higher than that in the water, the ratios are similar. The scale thus serves as a useful monitor of the conditions within the groundwater. Although lead and polonium are particle reactive under the conditions of low pH, high sulfide and low Eh found in this environment, significant amounts of ^{210}Po are still available in solution.

Water Chemistry

Analysis of the water chemistry of the groundwaters from the same stations (Appendix 4) implies that three types of groundwater are present. The first type has low ^{210}Po activity and is characterized by variable pH and sulfide concentrations. The second category has variable ^{210}Po activity, variable pH and sulfide concentrations. The third type of groundwater has high ^{210}Po activity, low pH and sulfide always present. All of the groundwaters with high ^{210}Po also have at least moderately high ^{222}Rn. The results indicate that low pH is a necessary, though not sufficient, condition for high ^{210}Po activity in groundwater. It is unequivocal that the ultimate source of radiation in groundwaters is migration of activity from an underlying natural uranium-containing bedrock. The primary source of this in west central Florida is most likely related to the release of radon with subsequent decay or direct leaching of the phosphate ore. Our results indicate that high ^{210}Po, low ^{210}Pb and high ^{222}Rn activities can occur when the groundwater has a low pH and fairly high sulfide concentrations.

Radioactivity in New Hampshire Groundwater

Three groundwater samples from New Hampshire with ^{222}Rn activities ranging from 5,000 to 122,000 pCi L^{-1}, were provided to us by colleagues from the University of New Hampshire (UNH) for analysis of other decay-series isotopes. The ^{210}Po activities in these samples ranged from 0.2 to 8.0 pCi L^{-1} (Table 31). Thus, even though these waters contain extraordinary amounts of ^{222}Rn, their ^{210}Po levels were reasonably low. No

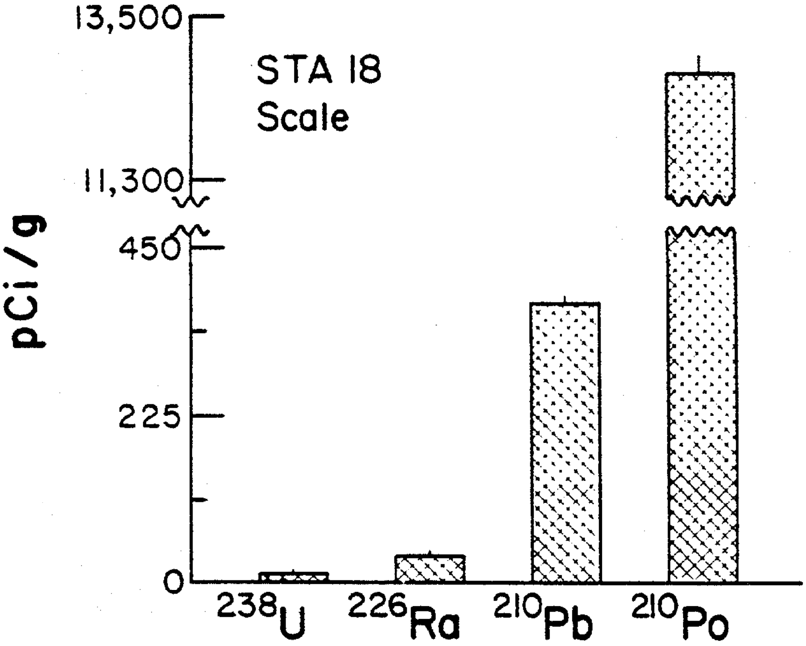

Figure 37. Radiochemical results of an analysis of solid scale removed from the inside of a water storage tank. Activities given in pCi g^{-1}. Note change in scale.

Table 31. ^{238}U-series radionuclides in unfiltered, radon-rich groundwater from New Hampshire. The ^{222}Rn concentrations were measured at the University of New Hampshire. Note that the units for ^{222}Rn are in nanocuries per liter, while all other parameters are in picocuries per liter.

Sample	^{238}U	^{234}U	^{226}Ra	^{222}Rn	^{210}Po	^{231}Pa	^{232}Th	^{230}Th
	---- pCi L^{-1} ----			(nCi L^{-1})	-------- pCi L^{-1} -------			
D1	9.44	9.70	6.74	122	7.33	BD*	0.01	0.04
D19	NA	NA	BD	5	0.22	NA	NA	NA
D21	NA	NA	0.17	118	4.77	NA	NA	NA

*BD = Below Detection. Approximate detection limits as follows: ^{231}Pa = 0.003 pCi L^{-1}; and ^{226}Ra = 0.01 pCi L^{-1}.

chemical parameters were measured in these waters but we noted the absence of any sulfur smell. We propose that these samples from New Hampshire represent a case of high excess ^{222}Rn and low ^{210}Po in a system with fast moving groundwater associated with relatively low activities of ^{210}Pb and ^{210}Po on particulates.

CONCLUSIONS

(1) Some groundwater in the surficial aquifer of west central Florida contains significantly elevated levels of ^{210}Po, a daughter of ^{222}Rn.

(2) High values of ^{210}Po exist in both filtered and unfiltered samples although filtered samples are significantly lower in some cases.

(3) The waters with anomalously high values of ^{210}Po are characterized by moderately high ^{222}Rn, low pH, and the presence of sulfide.

(4) Waters from a granitic terrain with exceedingly high ^{222}Rn have low ^{210}Po, supporting the interpretation that the presence of high ^{222}Rn alone will not necessarily lead to high polonium in groundwater.

REFERENCES

Airey, P.L., 1983. Radionuclide migration around uranium ore bodies -analogue of radioactive waste repositories. AAEC/ C34, Quarterly Report No. 5, 12 p.

Akerblom, G.V. and Wilson, V., 1981. Radon gas--A radiation hazard from radioactive bedrock and building materials. Bull. Int. Assoc. Engin. Geology, 23:51.

Altschuler, Z.S., 1973. The weathering of phosphate deposits: geochemical and environmental aspects. In E.J. Griffin, A. Beeton, J.M. Spencer, and D.J. Mitchell (Editors), Environmental Phosphorus Handbook: New York, John Wiley and Sons, p. 33-96.

Altschuler, Z.S., Clark, R.S., and Young, E.Y., 1958. Geochemistry of uranium in apatite and phosphorite Geol. Surv. Prof. Paper 314D, 87 p.

Altschuler, Z.S., Jaffee E.B., and Cuttitta, F., 1956. The aluminium phosphate zone of the Bone Valley Formation, Florida, and its uranium deposits. In: U.S. Geol. Surv. Prof. Paper 300 (Stocking and Smith, eds.), p. 495-504.

Andrews, J.N. and Wood, D.F., 1972. Mechanism of radon release in rock matrices and entry into groundwaters. Applied Earth Sci., 81: 198-201.

Asikainen, M., 1981. State of disequilibrium between ^{238}U, ^{234}U, ^{226}Ra and ^{222}Rn in groundwater from bedrock. Geochim. Cosmochim. Acta 45:201-206.

Afikainen, M. and Kahlos, H., 1979. Anomalously high concentrations of uranium, radium and radon in water from drilled wells in the Helsinki region. Geochim. Cosmochim. Acta 43:1681-1686.

Bacon, M.P., 1984. Radionuclide Fluxes in the Ocean Interior: in Global Ocean Flux Study. Proceeding of a workshop. September 10-14, 1984. National Academy of Sciences. National Academy Press. Washington D.C. p. 181-205.

Bagnall, K.W., 1966. The Chemistry of Selenium, Tellurium and Polonium. Topics in Inorganic and General Chemistry. Vol. 7. Elsevier, Amsterdam 1966.

Bhat, S.G. and Krishnaswami, S., 1969. Isostopes of uranium and radium in Indian Rivers. Proc. Ind. Acad. Sci. 69:1-17:

Belch, W.E., Whitney, E.D., Chhatre, R.M., and Roessler, C.E., 1976. Uranium and Radium Concentration in Florida Phosphate by GeLi Spectrometry. Paper presented at Health Physics Society Tenth Midyear Topical Symposium "Natural Radioactivity in Man's Environment." Saratoga Springs, New York, October 11-13, 1976, 8 p.

Bollinger, M.S. and Moore, W.S., 1984. Radium fluxes from a salt marsh. Nature, 309:444-446.

Broecker, W.S. and Peng, T.H., 1982. Tracers in the Sea. Lamont-Doherty Geological Observeratory, Columbia Univ., Palisades; N.Y. 690 p.

Brutsaert, W.F., Norton, S.A., Hess, C.T. and Williams, J.S. 1981. Geologic and hydrologic factors controlling Radon-222 in groundwater in Maine. Ground Water, 19:407-417.

Burnett, W.C., 1974. Phosphorite deposits from the sea floor off Peru and Chile: Radiochemical and geochemical investigations concerning their origin. Hawaii Inst. Geophys. Rep. 74-3, 164 p.

Burnett, W.C. and Deetae, S., 1984. Radium in the Suwannee River. Report to Florida Department of Environmental Regulation. Contract No. LR-48, 48 p.

Burnett, W.C. and Gomberg, D.N., 1977. Uranium oxidation and probable subaerial weathering of phosphatized limestone from the Pourtales Terrace. Sedimentology, 24:291-302.

Canadian Radiation Protection Bureau, 1980. Section on Uranium from Canadian Radiation Protection Bureau Guidelines for Canadian Drinking Water Quality 1978. (1980 Support Documentation, Health and Welfare, Ottawa, Canada), 79 p.

Cathcart, J.B., 1978. Uranium in phosphate rock. United States Geol. Survey Prof. Paper 988, A1-A6.

Cathcart, J.B. and Gulbrandsen, R.A., 1973. United States Mineral Resources, Phosphate Deposits. Geol. Prof. Paper 820: 515-525.

Clarke, R.S. and Altschuler, Z.S., 1958. Determination of the oxidation state of uranium in apatite and phosphorite deposits. Geochim. Cosmochim. Acta, 13:127-142.

Coffin, J.E., 1982. Quality of surface water at selected sites in the Suwannee River Basin, Florida, 1980. U.S. Geol. Surv. Open-File Report 82-103, 107 p.

Deetae, S., Moriconi, L.M., and Burnett, W.C., 1983. Radium in the Suwannee River and Estuary (abs.). Florida American Chemical Society Meeting, Jacksonville, Florida, 1 p.

deMeijer, R.J. and Braams, R.; 1973. The Natural Radioactivity of Phosphorus Slags and Its Danger as Construction Material. Fysisch Laboratorium Pyhsumiriestect Utrecht, The Netherlands.

Dion, E.P., 1983. Trace elements and radionuclides in the Connecticut and Amazon river estuary. Ph.D. thesis, Yale Univ., New Haven, Conn., 233 p.

Ditchburn, R.G. and McCabe, W.J., 1984. An improved method for the purification and electrodeposition of protactinium for application to the INS uranium-series dating project. Institute of Nuclear Sciences (NZ) Report INS-R-325, 10 p.

Edmond, C.R., 1969. Direct determination of fluoride in phosphate rock samples using the specific ion electrode. Anal. Chem., 41:1327-1328.

Elsinger, R.J., King, P.T., and Moore, W.S., 1982. ^{224}Ra in natural waters measured by gamma-ray spectrometry. Anal. Chem. Acta., 144:277-281.

Elsinger, R.J. and Moore, W.S., 1980. Ra-226 behavior in the Pee Dee River-Winyah Bay Estuary. Earth Planet. Sci. Lett., 48:239-249.

Elsinger, R.J. and Moore, W.S., 1983. ^{224}Ra, ^{228}Ra, and ^{226}Ra in Winyah Bay and Delaware Bay. Earth Planet. Sci. Lett., 64:430-436.

Elsinger, R.J. and Moore, W.S., 1984. ^{226}Ra and ^{228}Ra in the Mixing zone of the Pee Dee River-Winyah Bay, Yangtze River and Delaware Bay Estuary. Estuarine, Coastal and Shelf Sci., 18:601-613.

Environmental Protection Agency, 1975. Preliminary Findings, Radon Daughter Levels in Structures Constructed on Reclaimed Florida Phosphate Land. ORP/CSD-75-4, 23 p.

Environmental Protection Agency, 1983. Methods for Chemical Analysis of Water and Wastes. EPA-600/4-79-020, 490.

Eyal, Y. and Fleischer, R.L., 1985. Preferential leaching and the age of radiation damage from alpha decay in minerals. Geochim. Cosmochim. Acta, 49:1155-1164.

Fanning, K.A., Bruland II, J.A., and Byrne, R.H., 1982. Radium-226 and Radon-222 in the coastal water of West Florida: High concentration and atmospheric degassing. Science, 215:667-670.

Fink, R.M., 1950. Biological Studies With Polonium, Radium, and Plutonium. McGraw-Hill Book Company, New York.

Florida Department of Environmental Regulation, State of Florida, 1985. Limnology of the Suwannee River, Florida. Tallahassee, Florida, 267 p.

Flynn, W.W., 1968. The determination of low levels of ^{210}Po in environmental materials. Anal. Chim. Acta, 43:221-227.

Folk, R.L., 1974. Petrology of Sedimentary Rocks. Hemphil Publ. Co., Austin, Texas, 185 p.

Gulbrandsen, R.A., 1970. Relation of carbon dioxide content of apatite of the Phosphoria Formation to regional facies. U.S. Geol. Soc. Prof. Paper, 700-B: B9-B13.

Gunderson, L.C., 1985. Geologic and geophysical exploration for uranium in the Reading Prong and its application in defining areas of high radon risk. U.S. Geological Survey Draft Report, Branch of Energy Minerals, Denver, CO.

Hess, C.T., Weiffenbach, C.V. and Norton, S.A. 1983. Environmental Radon and cancer correlations in Maine. Health Physics, 45:339-348.

Hess, C.T., Michel, J., Horton, T.R., Prichard, H.M., and Coniglio, W.A., 1985. The occurrence of radioactivity in public water supplies in the United States. Health Physics, 48:553-586.

Hinton, T.G. and Whicker: F.W. 1985. A field experiment of Rn flux from reclaimed uranium mill tailings. Health Physics, 48:421-427.

Humphreys, C.L., 1984. Uranium and radium isotopic distributions in groundwaters and sediments of the Land-Pebble Phosphate District and surrounding areas of west-central Florida. M.S. Thesis, Fla. State Univ., Tallahassee, 141 p.

Irwin, G.A. and Hutchinson, C.B., 1976. Reconnaissance water sampling for Ra-226 in central and northern Florida, December 1974-March 1976. U.S. Geol. Surv. Water Resource Investigation, 76-103, 16 p.

Jean, G.E. and Bancroft, G.M., 1986. Heavy metal adsorption by sulphide mineral surfaces. Geochim. Cosmochim. Acta, 50:1455-1463.

Kaufmann, R.F. and Bliss, J.D., 1977. Effect of phosphate mineralization and the phosphate industry on Ra-226 in groundwater of central Florida. EPA Publ. 520-6-77-010, 114 p.

Kenner, W.E., Hampton, E.R., and Conover, C.S., 1975. Average flow of major streams in Florida. U.S.G.S. Map Series No. 34, Updated.

Key, R.M., Stallard, R.F., Moore W.S and Sarmiento, J.L., 1985. Distribution and flux of ^{226}Ra and ^{228}Ra in the Amazon River Estuary. J. Geophys. Res., 90:6995-7004.

Kim, K.H. and Burnett, W.C., 1983. Gamma-ray spectrometric determination of uranium series nuclides in marine phosphorite. Anal. Chem., 55: 1796-1800.

King, P.T., Michel, J., and Moore, W.S., 1982. Groundwater geochemistry of Ra-228, Ra-226, and Rn-222. Geochim. Cosmochim. Acta, 46:1173-1182.

Koide, M., Bruland, K., and Goldberg, E.D., 1976. Ra-226 chronology of coastal marine sediments. Earth Planet Sci. Lett., 33:31-36.

Koide, M., Soutar, A. and Goldberg, E.D., 1972. Marine geochronology with ^{210}Pb. Earth Planet. Sci. Lett., 14:442-446.

Kolodny, Y. and Kaplan, I.R., 1970. Uranium isotopes in sea-floor phosphorites. Geochim. Cosmochim. Acta., 34:3-24.

Krishnaswami, S., Graunstein, W.C., Turekian, K.K., and Dowd, J.F., 1982. Radium, thorium, and radioactive lead isotopes in groundwater: application to the in situ determination of adsorption-desorption rate constants and retardation factors. J. Water Resources Res., 18: 1633-1675.

Krishnaswami, S. and Lal, D., 1982. Deep-sea sedimentation and chronology. In: Nuclear and Chemical Dating Techniques Interpreting the Environmental Record, Currie, L.A., (ed.), ACS Symposium Series 176, p. 363-388.

Leadon, C., 1980. The Upper Suwannee River, an outstanding national water. Suwannee River Water Management District., Staff Rept. 80-1, 25 p.

Levinson, A.A., Bland, C.J., and Lively, R.S., 1982. Exploration for uranium ore deposits. In: Uranium Series Disequilibrium: Application to Environmental Problems, Ivanovich, M. and Harmon, R.S. (eds.), Clarendon Press, Oxford, p. 351-381.

Li, Y.H. and Chan, L.H., 1979. Desorption of Ba and Ra-226 from river-borne sediments in the Hudson Estuary. Earth Planet. Sci. Lett., 43:343-350.

Li, Y.H., Mathieu, G., Biscaye, P., and Simpson, H.T., 1977. The flux of ^{226}Ra from estuarine and continental shelf sediments. Earth Planet. Sci. Lett., 37:237-241.

Lucas, J., Flicoteaux, R., Nathan, Y., Prevot, L., and Shahar, Y., 1980. Different aspects of phosphorite weathering. SEPM Special Publication 29:45-51.

Lyman, G.H., Lyman, C.G., and Johnson, W., 1985. Association of leukemia with radium ground water contamination. JAMA 454:621-626.

Martell, E.A., 1975. Tobacco radioactivity and cancer in smokers. Am. Scientist, 63:404-412.

McCabe, W.J., Ditchburn, R.G., and Whitehead, N.E., 1979. The quantitative separation, electrodeposition and alpha-spectrometry of uranium, thorium and protactinium in silicates and carbornates. Institute of Nuclear Sciences (NZ) Report INS-R-262, 29 p.

Menzel, R.G., 1968. Uranium, radium and thorium content in phosphate rocks and their possible radiation harzard. J. Agri. Food Chem., 16:231-237.

Michel, J., Moore, W.S., and King, P.T., 1981. Gamma-ray spectrometry for determination of radium-228 and radium-226 in natural waters. Anal. Chem., 53:1885-1889.

Miller, R.L. and Sutcliff, H., Jr., 1985. Occurrence of natural Ra-226 radioactivity in groundwater of Sarasota County Florida. U.S. Geol. Surv. Water Resources Inv. Rep., 84-4237, 34 p.

Mitsch, B.F., Watson, J.E., and Hayes, J.A., 1984. A study of radium-226 and radon-222 concentrations in groundwater near a phosphate mining and manufacturing facility with emphasis on the hydrogeologic characteristics of the area. U.S. Dept. of Interior Report No. 216, 69 p.

Moore, W.S., 1967. Amazon and Mississippi river concentration of uranium, thorium, and radium isotopes. Earth Planet. Sci. Lett., 2:231-234.

Moore, W.S., 1981. Radium isotopes in the Chesapeake Bay. Estuarine, Coastal Shelf Sci., 12:713-723.

Moore, D.G. and Scott, M.R., 1986. Behavior of Ra-226 in the Mississippi River Mixing Zone. J. Geophys. Res. (ocean), 19:14317-14329

Mullin, A., 1982. Abnormally high alpha activity in a Louisiana drinking water supply. Paper presented at 27th Annual Meeting, Health Physics Society, 27 June-1 July, 1982, Las Vegas, NV.

Murphy, J. and Riley, J.P., 1962. A modified single solution method for determination of phosphate in natural waters. Anal. Chim. Acta, 27: 31-36.

National Academy of Sciences. 1980. The Effects on Populations of Exposure to Low Levels of Ionizing Radiation. Committee on the Biological Effects of Ionizing Radiation, Division of Medical Sciences, Assembly of Life Sciences, National Research Council, Washington DC, National Academy Press.

Nero, A.V., Schwehr, M.B., Nazaroff, W.W., and Revzan, K.L., 1986. Distribution of airborne Radon-222 concentrations in U.S. homes. Science, 234:992-997.

Osmond, J.K., 1964. The distribution of the heavy radioelements in the rocks and waters of Florida. In: The Natural Radiation Environment, Adams, J.A.S., and Lowder, W.M. (eds.), University of Chicago Press, p. 153-159.

Osmond, J.K. and Cowart, J.B., 1976. The theory and uses of natural uranium isotopic variations in hydrology. Atomic Energy Review, 14:621-679.

Oural, C.R., Brooker, H.R. and Upchurch, S.B., 1986. Source of Gross-Alpha Radioactivity Anomalies in Recharge Wells, Central Florida Phosphate District. Florida Institute of Phosphate Research, Publication No. 05-014-034.

Prichard, H.M. and Gesell, T.F., 1977. Rapid measurements of ^{222}Rn concentrations in water with a commercial liquid scintillation counter. Health Physics, 33:577-581.

Rama and Moore, W.S., 1984. Mechanism of transport of U-Th series radioisotopes from solids into groundwater. Geochim. Cosmochim. Acta, 48:395-399.

Reid, D.F., Key, R.M., and Schink, D.R., 1979. Radium, thorium, and actinium extraction from sea water using an improved manganese-oxide-coated fiber. Earth Planet. Sci. Lett., 43:223-226.

Riggs, S.R., 1979. Petrology of the Tertiary phosphorite system of Florida. Econ. Geol., 74: 195-220.

Roessler, C.E., Smith, Z.A., Bolch, W.E., and Prince, R.J., 1979. Uranium and radium-226 in Florida phosphate material. Health Physics, 37: 269-277.

Rona, E. and Urry, W.D., 1952. Radioactivity of ocean sediments. VIII. Radium and uranium content of ocean and river water. Am. J. Sci., 250:242-262.

Rosenau, J.C., Faulkner, G.L., Hendry, C.W., Jr., and Hull, R.W., 1977. Springs of Florida. Geol. Bull. No. 31 (revised). U.S. Geol. Surv. in cooperation with Florida Department of Natural Resources, Bureau of Geology, Tallahassee, Florida, 461 p.

Sasser, M. K. and Watson, J.E., 1978. An evaluation of the radon concentrations in North Carolina ground water supplies. Health Physics, 34:667-671.

Scott, M.R., 1982. The Chemistry of U and Th-series nuclides in rivers. In: Uranium Series Disequilibrium: Applications to Environmental Problems, Ivanovich, M. and Harmon, R.S. (eds.), Clarendon Press, Oxford, p.181-201.

Sweeney, J.W. and Windham, S.R., 1979. Florida: The New Uranium Producer. Bureau of Geology, Division of Resource Management, Florida Department of Natural Resources. Special Publication No. 22, 13 p.

Szalay, A. and Samsoni, Z., 1970. Investigations on the leaching of uranium from crushed magmatic rocks. In: Hydrogeochemistry, Proceedings of a Symposium, Tokyo, Japan, Clarke Co., Washington D.C.

Tanner, A.B., 1964. Radon migration in the ground: A review. In: The Natural Radiation Environment, Adams, J.A.S. and Lowder, W.M. (eds.), University of Chicago Press, p. 161-190.

Thomson, J. and Turekian, K.K., 1976. ^{210}Po and ^{210}Pb distributions in ocean water profiles from the eastern South Pacific. Earth Planet. Sci. Lett., 32:297-303.

Vdevenko, V.M. and Dubasov, Y.V., 1975. Analytical Chemistry of Radium. Translated by IPST staff. Malamet, D. (ed.). John Wiley & Sons, New York, 198 p.

Wathen, J.B. and Hall, F.R., 1986. Factors affecting levels of Rn-222 in wells drilled into two mica granites in Maine and New Hampshire. Unpublished Report, 32 p.

World Health Organization, 1977. Environmental Health Criteria No. 25: Selected Radionuclides-Radon. United Nations Environment Programme and the World Health Organization, Geneva.

Yang, I.C. and Edwards, K.W., 1984. Releases of radium and uranium into Ralston Creek and Reservoir, Colorado, from uranium mining. American Chemical Society.

Appendix 1. Distribution of the specific activities of ^{238}U, ^{226}Ra and ^{210}Pb, activity ratios of ^{226}Ra/^{236}U and ^{210}Pb/^{226}Ra, distribution of mass and fractions of ^{238}U, ^{226}Ra, and ^{210}Pb as a function of particle size in unconsolidated phosphate rock samples.

	Size Range (µm)							
Sample	<3.9	<63	63-125	125-250	250-500	500-1000	1000-2000	>2000
^{238}U (pCi/g)								
NRM-3	NA	219.6	101.9	25.4	31.3	73.6	92.3	95.9
NRM-4	NA	311.4	145.6	55.8	67.0	186.9	215.7	NA
NRM-4*	362.5	350.1#	311.5	142.6	127.2	226.3	262.8	265.9
NRM-5	NA	50.5	33.3	16.5	15.2	40.5	52.2	58.6
HM-1	NA	87.5	NA	9.7	9.7	23.4	43.0	NA
FM-3	NA	4.9	19.0	14.9	9.3	16.4	25.0	23.2
PR-1	NA	5.1	14.9	15.5	12.6	14.1	19.3	NA
^{226}Ra (pCi/g)								
NRM-3	NA	306.4	165.8	50.3	52.6	113.9	142.7	143.7
NRM-4	NA	241.4	120.1	52.3	50.5	110.7	160.3	164.4
NRM-4*	219.2	234.3#	189.4	53.5	87.3	159.1	177.1	178.6
NRM-5	NA	31.5	23.8	14.7	14.2	37.8	49.5	57.3
HM-1	NA	52.6	NA	10.9	10.1	24.5	43.6	NA
FM-3	NA	5.5	19.4	16.0	10.3	18.2	26.5	25.4
PR-1	NA	30.7	16.1	13.8	11.0	12.2	15.6	NA
^{210}Pb (pCi/g)								
NRM-3	NA	291.2	163.4	51.7	56.3	116.1	136.5	138.6
NRM-4	NA	241.8	98.5	50.1	40.0	96.4	144.5	120.6
NRM-4*	247.5	245.5#	179.1	84.5	83.1	146.3	162.2	172.4
NRM-5	NA	36.4	26.4	13.2	15.2	36.5	43.5	48.8
HM-1	NA	96.2	NA	11.1	9.2	19.0	36.7	NA
FM-3	NA	12.7	19.1	12.9	9.8	15.0	22.2	24.3
PR-1	NA	45.9	26.6	14.1	8.3	5.9	12.8	NA
^{226}Ra/^{238}U								
NRM-3	NA	1.40	1.63	1.98	1.68	1.55	1.54	1.50
NRM-4	NA	0.98	0.82	0.94	0.75	0.59	0.74	0.71
NRM-4*	0.60	0.87#	0.61	0.60	0.69	0.70	0.67	0.67
NRM-5	NA	0.62	0.71	0.89	0.94	0.93	0.95	0.98
HM-1	NA	0.60	NA	1.13	1.04	1.05	1.01	NA
FM-3	NA	1.14	1.02	1.09	1.11	1.11	1.06	1.10
PR-1	NA	5.97	1.08	0.89	0.87	0.86	0.81	NA
^{210}Pb/^{226}Ra								
NRM-3	NA	0.95	0.99	1.03	1.07	1.02	0.96	0.96
NRM-4	NA	1.00	0.82	0.96	0.79	0.87	0.90	0.73
NRM-4*	1.13	1.05#	0.95	0.99	0.95	0.92	0.92	0.97
NRM-5	NA	1.15	1.11	0.90	1.07	0.97	0.88	0.85
HM-1	NA	1.83	NA	1.01	0.91	0.77	0.84	NA
FM-3	NA	2.30	0.99	0.80	0.95	0.83	0.84	0.96
PR-1	NA	1.49	1.65	1.03	0.76	0.48	0.82	NA

Appendix 1. Continued.

	Size Range (µm)							
Sample	<3.9	<63	63-125	125-250	250-500	500-1000	1000-2000	>2000
Percent mass								
NRM-3	NA	16.32	4.87	24.60	24.43	9.95	9.02	10.82
NRM-4	NA	23.35	2.93	15.22	30.98	9.42	10.21	7.90
NRM-4*	1.01	41.39#	9.37	18.60	14.78	6.80	6.60	1.46
NRM-5	NA	13.66	0.89	4.28	16.68	6.59	16.49	41.41
HM-1	NA	1.99	0.09	2.38	38.94	51.62	4.98	NA
FM-3	NA	5.43	1.05	10.36	60.84	17.82	3.68	0.82
PR-1	NA	7.02	1.70	13.95	67.91	7.90	1.27	0.26
Percent ^{238}U								
NRM-3	NA	44.41	6.15	7.74	9.46	9.07	10.31	12.85
NRM-4	NA	46.03	2.43	6.23	12.73	8.38	13.20	11.00
NRM-4*	1.41	55.81#	11.24	10.21	7.24	5.92	6.68	1.49
NRM-5	NA	15.00	0.64	1.53	5.50	5.82	18.71	52.79
HM-1	NA	8.71	NA	1.15	18.96	60.47	10.70	NA
FM-3	NA	2.25	1.71	13.02	48.51	24.97	7.91	1.64
PR-1	NA	2.84	2.00	17.03	67.42	8.79	1.92	NA
Percent ^{226}Ra								
NRM-3	NA	40.65	6.56	10.06	10.43	9.21	10.45	12.63
NRM-4	NA	45.73	2.85	6.45	12.70	8.46	13.28	10.53
NRM-4*	1.30	56.79#	10.39	9.27	7.56	6.33	6.84	1.53
NRM-5	NA	10.28	0.50	1.50	5.66	5.94	19.50	56.61
HM-1	NA	5.22	NA	1.30	19.64	63.03	10.80	NA
FM-3	NA	2.34	1.58	12.90	48.73	25.23	7.60	1.63
PR-1	NA	16.62	2.12	14.84	57.49	7.40	1.53	NA
Percent ^{210}Pb								
NRM-3	NA	39.34	6.59	10.53	11.38	9.56	10.19	12.41
NRM-4	NA	50.08	2.56	6.77	10.99	8.06	13.09	8.45
NRM-4*	1.45	59.06#	9.75	9.14	7.13	5.78	6.22	1.46
NRM-5	NA	13.04	0.61	1.49	6.66	6.31	18.83	53.06
HM-1	NA	11.02	NA	1.53	20.60	56.36	10.50	NA
FM-3	NA	5.82	1.68	11.21	50.15	22.57	6.88	1.69
PR-1	NA	26.98	3.80	16.55	47.42	3.90	1.36	NA

\# Size range is 3.9-63 µm for this sample.

Appendix 2. Radium and silica in the Suwannee River Estuary.

Sample ID	Sal. (ppt)	Silica (µM)	Susp. Load (mg L^{-1})	^{226}Ra Total*	Dissol.	Susp.	^{226}Ra Leached (pCi g^{-1})	Ratio ^{226}Ra Diss./Total
				<——(pCi	100L^{-1})	——>		
December 20, 1982								
ES1-0	0.02	116.1	0.97	19.9	14.9	5.0	51.4	0.749
ES1-5	9.62	84.7	8.76	26.8	24.3	1.8	2.0	0.931
ES1-9	11.45	79.0	12.21	30.1	28.1	2.0	1.6	0.934
ES1-0A	11.46	76.9	6.76	33.0	30.5	2.5	3.7	0.924
ES1-15	19.12	51.3	8.34	45.4	44.7	0.6	0.8	0.986
ES1-1	29.85	4.6	22.46	45.3	42.8	2.5	1.1	0.946
ES1-2	30.13	3.2	27.59	45.9	44.5	1.4	0.5	0.968
March 3, 1983								
ES2-0E	0.00	NA	2.83	6.0	5.6	0.5	1.5	0.927
ES2-5E	5.00	NA	18.29	16.2	15.9	0.3	0.2	0.981
ES2-10E	10.00	NA	21.58	19.7	19.5	0.3	0.1	0.984
ES2-0W	0.00	NA	6.65	10.1	6.1	4.1	6.1	0.601
ES2-0WA	0.00	NA	7.00	8.5	6.6	1.9	2.7	0.779
ES2-2.5W	2.50	NA	14.77	6.8	4.9	1.7	1.1	0.743
ES2-5W	5.00	NA	15.55	11.0	8.7	2.3	1.5	0.792
ES2-8W	8.00	NA	13.34	18.6	16.6	2.0	1.5	0.893
June 22, 1983								
ES3-0W5A	0.00	104.0	3.23	18.6	15.8	2.8	8.6	0.851
ES3-0W8A	0.03	104.3	2.22	18.2	14.2	4.0	17.8	0.783
ES3-0WCA	0.03	104.0	4.19	16.4	12.5	3.9	9.2	0.764
ES3-0W	0.08	104.0	0.77	19.7	15.5	4.2	55.2	0.784
ES3-1W4A	1.04	101.8	1.45	22.2	18.9	3.3	22.8	0.850
ES3-3W	4.84	93.6	2.23	22.7	20.4	2.3	10.2	0.900
ES3-4W	5.71	89.7	2.96	NA	24.8	NA	NA	NA
ES3-6W	8.81	85.5	3.22	NA	23.6	NA	NA	NA
ES3-20W	19.53	28.8	12.85	NA	56.3	NA	NA	NA
ES3-26W	23.54	9.6	7.18	NA	46.5	NA	NA	NA
ES3-28W	24.31	2.9	7.02	NA	46.8	NA	NA	NA
ES3-FAN	0.05	88.7	NA	NA	24.3	NA	NA	NA
ES3-MAN	0.00	84.7	NA	NA	41.3	NA	NA	NA
ES3-RAMP	0.06	103.3	1.59	16.8	16.1	0.7	4.5	0.958
ES3-EWJ	0.03	103.3	1.78	16.0	15.2	0.8	4.5	0.950
ES3-0E	1.12	104.3	2.21	19.3	16.2	3.1	14.1	0.839
ES3-5E	3.06	89.7	3.02	25.6	23.0	2.7	8.7	0.897
ES3-10E	11.40	71.6	4.53	32.7	30.5	2.3	5.0	0.931
ES3-15E	15.49	64.4	2.72	36.8	35.3	1.6	5.8	0.957
ES3-20E	18.32	53.8	3.53	42.2	40.5	1.8	5.0	0.958
ES3-25E	22.15	34.2	2.27	49.8	48.0	1.8	7.8	0.964

* Sum of dissolved and suspended radium.

Appendix 2. Continued.

Sample ID	Sal. (ppt)	Silica (µM)	Susp. Load (mg L^{-1})	^{226}Ra Total*	^{226}Ra Dissol.	^{226}Ra Susp.	^{226}Ra Leached (pCi g^{-1})	Ratio ^{226}Ra Diss./Total
				<—— (pCi 100L^{-1})		——>		
October 6-9, 1983 (BELLOWS CRUISE I)								
ALL-20	0.02	87.2	NA	NA	16.5	NA	NA	NA
ALL-22	0.01	84.7	NA	NA	36.8	NA	NA	NA
ALL-21	0.01	115.0	1.06	18.1	14.3	3.8	36.1	0.787
ALL-19	0.01	116.1	0.03	16.9	13.7	3.2	106.0	0.809
ALL-18	0.01	113.2	1.39	18.6	14.9	3.6	26.1	0.804
ALL-8	0.20	114.7	0.89	17.8	12.7	5.1	57.0	0.715
ALL-28	0.63	109.7	4.14	18.4	11.2	2.7	6.7	0.851
ALL-17	1.92	106.5	1.93	21.5	19.2	2.3	11.9	0.893
ALL-15	2.26	106.1	3.31	17.5	15.0	2.6	7.7	0.854
ALL-16	3.94	97.6	3.99	22.5	18.4	4.1	10.2	0.820
ALL-27	5.17	90.4	11.95	NA	16.6	NA	NA	NA
ALL-7	6.10	87.9	5.61	31.3	29.5	1.8	3.2	0.942
ALL-13	6.44	87.2	5.59	25.3	22.9	2.4	4.2	0.906
ALL-14	7.78	97.2	7.29	27.1	23.2	4.0	5.5	0.853
ALL-12	9.03	73.7	7.11	26.0	23.3	2.7	3.8	0.896
ALL-6	9.41	74.1	8.95	33.8	30.8	3.09	3.4	0.911
ALL-26	10.06	68.7	12.02	33.0	28.5	4.5	3.8	0.863
ALL-4	12.92	62.3	9.32	26.1	24.1	2.1	2.2	0.921
ALL-23	14.34	88.7	72.70	NA	17.1	NA	NA	NA
ALL-2	16.24	50.6	16.38	39.7	36.5	3.2	2.0	0.919
ALL-3	18.63	38.8	26.61	30.4	26.7	3.7	1.4	0.877
ALL-25	23.93	1.8	16.33	10.4	7.2	3.3	2.0	0.686
ALL-1	24.04	1.4	16.47	28.2	26.7	1.5	0.9	0.947
ALL-11	24.75	0.4	23.63	9.9	6.8	3.2	1.4	0.681
ALL-24	27.46	0.4	25.85	11.1	5.0	6.1	2.3	0.453
January 4, 1984 (Ochlockonee River Estuary)								
OLN-1	0.02	99.3	36.15	12.3	4.6	7.5	2.2	0.373
OLN-2	0.05	95.8	8.93	13.1	7.4	5.7	6.4	0.564
OLN-12	6.50	66.6	7.21	23.4	20.0	3.4	4.7	0.856
OLN-11	9.81	60.2	8.02	20.9	17.4	3.5	4.3	0.835
OLN-10	10.20	59.5	7.43	21.4	17.4	3.9	5.3	0.817
OLN-9	12.62	50.6	7.71	27.7	19.1	4.1	8.8	0.821
OLN-6	18.72	33.5	9.14	28.6	24.1	4.5	5.0	0.842
OLN-7	18.98	34.5	8.62	25.5	20.6	4.9	5.6	0.809
OLN-5	20.41	30.3	4.89	19.1	14.7	4.4	8.9	0.772
OLN-8	23.96	19.2	4.91	29.6	24.7	5.0	10.1	0.832
OLN-3	25.88	16.0	16.19	26.4	24.9	1.6	0.9	0.941
OLN-4	27.22	11.8	17.12	28.8	27.5	1.3	0.8	0.956

* Sum of dissolved and suspended radium.

Appendix 2. Continued.

Sample ID	Sal. (ppt)	Silica (µM)	Susp. Load (mg L^{-1})	^{226}Ra Total*	^{226}Ra Dissol.	^{226}Ra Susp.	^{226}Ra Leached (pCi g^{-1})	Ratio ^{226}Ra Diss./Total
				<— (pCi $100L^{-1}$)		—>		
July 10-12, 1984 (BELLOWS II)								
BL2-W11	0.03	111.8	2.27	18.0	14.0	4.0	17.7	0.777
BL2-W9	1.12	111.4	3.06	16.1	12.4	3.8	22.1	0.767
BL2-W10	3.68	99.7	6.28	21.7	17.2	4.5	7.2	0.792
BL2-W6	6.73	83.3	14.30	25.0	17.9	7.2	5.0	0.714
BL2-W8	7.95	74.1	14.72	31.0	22.7	8.2	5.6	0.734
BL2-W1	11.29	65.2	21.72	30.1	24.8	5.3	2.4	0.825
BL2-W7	14.30	53.4	21.26	29.8	27.8	2.0	0.9	0.932
BL2-W2	21.06	24.9	31.27	30.6	28.2	2.4	0.8	0.921
BL2-W5	23.22	25.3	14.44	27.1	25.9	1.2	0.8	0.956
BL2-W3	25.78	20.3	25.67	30.6	29.1	1.6	0.6	0.949
BL2-W4	29.09	8.9	16.82	21.1	20.0	1.1	0.7	0.946
BL2-E11	0.13	113.6	3.42	NA	14.7	NA	NA	NA
BL2-E10	3.39	99.7	8.13	NA	29.5	NA	NA	NA
BL2-E9	4.67	99.7	8.44	NA	31.5	NA	NA	NA
BL2-E7	8.38	81.9	19.13	NA	32.8	NA	NA	NA
BL2-E5	10.23	74.4	16.80	NA	31.9	NA	NA	NA
BL2-E6	10.64	76.2	17.88	NA	29.3	NA	NA	NA
BL2-E8	14.34	57.0	22.58	NA	27.8	NA	NA	NA
BL2-E3	19.32	43.1	26.77	NA	33.3	NA	NA	NA
BL2-E3	21.92	35.3	31.18	NA	39.2	NA	NA	NA
BL2-E2	26.49	13.5	27.16	NA	25.9	NA	NA	NA
BL2-E1	26.50	20.3	19.55	NA	26.9	NA	NA	NA

* Sum of dissolved and suspended radium.

Appendix 3. Locations, names, county, station numbers and filtered and unfiltered ^{210}Po concentrations from all stations. Replicate analyses of many stations, special treatments and miscellaneous samples also reported.

Well name or location	County[1]	Station No.	^{210}Po Filt pCi L^{-1}	Unfilt pCi L^{-1}
**** JUNE 16-17, 1985 ****				
RALPH GIBSON	HARD	1	0.6	1.6
ANCHONDO	HARD	2	0.1	0.2
J. ZAJICEK	HARD	3	1.4	2.4
J.D. ALBRITTON	HARD	4	0.3	1.3
C. HOWZE	HARD	5	0.9	1.3
A.R. LARSON	DESO	6	0.2	3.0
COMMUNITY WELL - SE WACHULLA	HARD	7	0.3	0.3
G. SMITH	HARD	8	17.3	17.0
ROGER'S MARKET	HARD	9	109.1	145.2
**** AUGUST 29-30, 1985 ****				
C.B. HISCOCK, Rt #1	HILLS	10	29.0	112.7
R. HISCOCK	HILLS	11	145.6	189.2
HILL (BEFORE WATER SOFTENER)	HARD	12	74.1	92.2
HILL (AFTER WATER SOFTENER)	HARD	12*[2]	NA[3]	3.9
DUETTE ROAD	MANA	13	0.8	1.4
J. WORLEY	DESO	14	62.9	114.8
WHEELER	POLK	15	1.2	3.6
SARBAUGH	HILLS	16	1.2	4.2
CHICORA RD.	POLK	17	0.8	9.2
**** NOV 14-15, 1985 ****				
J. HARDY	HILLS	18	338.3	NA
C. HISCOCK	HILLS	19	23.5	NA
WALKER	HILLS	20	5.0	NA
T. HOLLAND - BEFORE PURIFIER	HILLS	21	2.5	NA
" "AFTER PERMANGANATE PURIFIER	HILLS	21*	3.2	NA
W. SHIVER - AFTER SOFTENER	HILLS	22	2.6	NA
LITHIA SPRINGS	HILLS	23	31.0	NA
S. FORK ALAFIA RIVER	HILLS	24	9.4	0.6
SULLIVAN	HILLS	25	0.6	NA
SWEATT	HILLS	26	0.5	NA
MORGAN	HILLS	27	.0	NA
STANALAND	HILLS	28	20.4	31.1
SHEFFIELD	POLK	29	6.5	4.3
BLAS CRUZ	HARD	30	47.3	NA

Appendix 3. Continued.

Well name or location	County	Station No.	Filt pCi L^{-1}	Unfilt pCi L^{-1}
**** JAN. 30-31, 1986 ****				
ALLEN SAWMILL	HILLS	31	NA	86.9
DOYEN	HILLS	32	NA	8.0
LAMBERT	HILLS	33	NA	5.1
**** MAY 1-2, 1986 ****				
T. BUTTS	HILLS	34	0.7	0.3
UNNAMED SPRING	HILLS	35	1.1	0.4
ORANGE GROVE - STATE RD #674	HILLS	36	1.0	0.5
E. RICHARDS	HILLS	37	0.4	0.3
H.HAGEN	HILLS	38	2.8	2.7
N.JAMESON	HILLS	39	21.9	0.3
E.REYNOLDS	HILLS	40	0.7	0.6
R.R. COLDING	HILLS	41	12.9	20.7
**** MAY 23-24, 1986 ****				
WEST LAKE AUTO/BEFORE FILTER	HILLS	42	NA	27.5
WEST LAKE AUTO/AFTER FILTER	HILLS	42*	3.6	5.1
FRED'S CORNER 6TH ST & RT 674	HILLS	43	1.5	2.6
J. BUTTS	HILLS	44	37.2	50.6
A. HOLMAN	HILLS	45	0.7	1.5
H. McCABE	HILLS	46	3.7	2.7
M. GONZALEZ	HILLS	47	1.1	0.8
CORNER 1st & 1st, PARRISH	MANA	48	2.4	0.2
G. COOLEY	MANA	49	1.1	2.1
HATCHER	MANA	50	1.1	55.4
GROVER MEAT MARKET, SHALLOW	MANA	51	20.0	38.3
GROVER MEAT MARKET, DEEP	MANA	52	2.2	BD
M. CHANCEY	MANA	53	3.1	10.5
D. CHANCEY	HARD	54	58.2	57.9
**** JUNE 20-21, 1986 ****				
P. LANDIS	HIGH	55	6.3	1.3
O. McGEE	HARD	56	9.0	6.2
W. BEATTY	HARD	57	0.7	0.9
G. COLLINS	HARD	58	2.6	20.7
RICKELLS	HARD	59	4.0	3.1
A. MARTINEZ	HARD	60	9.3	6.4
F. CURRIE BEFORE SOFT.	HARD	61	16.5	18.3
F. CURRIE AFTER SOFT.	HARD	61*	NA	16.2
BAUKNIGHT	MANA	62	19.1	1.0
R. RICH	MANA	63	15.7	24.1

Appendix 3. Continued.

Well name or location	County	Station No.	Filt pCi L^{-1}	Unfilt pCi L^{-1}
*** JULY 31-AUG 1, 1986 ***				
BLUE HEAD RANCH	HIGH	64	19.1	21.8
R. CRAWFORD	DESO	65	8.5	92.9
S. HAYDEN	DESO	66	8.5	9.2
DYE	DESO	67	7.4	67.3
N. WORLEY	DESO	68	1.2	3.2
L.H. AVANT Jr.	DESO	69	9.3	1.6
M. E. FLOYD	DESO	70	2.2	17.8
M. E. FLOYD	DESO	71	0.9	21.7
*** AUG 28-29, 1986 ***				
S. CUNDIFF	HILLS	72	9.4	0.4
AUSBURN	HILLS	73	1.6	2.6
B.J. SANDIFER	HILLS	74	0.6	0.5
P. ALBRITTON	POLK	75	12.0	0.7
R. SANDLER	POLK	76	1.3	18.2
*** OCT 23-24,1986 ***				
SCHAFFER	DESO	77	4.0	2.0
SHORES	DESO	78	3.5	2.2
J BAR C RANCH	MANA	79	0.4	3.0
MYAKKA R. ST. PK.	SARA	80	1.8	8.2

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****REPLICATES & SPECIAL TREATMENTS****

####AUGUST 29-30, 1985 ####				
ZAJICEK Rt 1 - OTHER HOUSE	HARD	38	1.5	17.0
ROGER'S MARKET	HARD	9	143.1	173.3
####NOV 14-15, 1985 ####				
C.B HISCOCK, Rt #1	HILLS	10	14.6	178.3
R. HISCOCK	HILLS	11	205.2	272.4

Appendix 3. Continued.

Well name or location	County	Station No.	Filt pCi L^{-1}	Unfilt pCi L^{-1}
####JAN. 30-31, 1986 ####				
C.B. HISCOCK, Rt #1	HILLS	10	93.8	114.5
R. HISCOCK	HILLS	11	281.0	244.1
HILL BEFORE WATER SOFTENER	HARD	12	74.1	104.3
HILL AFTER WATER SOFTENER	HARD	12*	NA	19.2
JOHN HARDY	HILLS	18/1	298.5	259.9
JOHN HARDY	HILLS	18/2	282.4	463.6
C. HISCOCK	HILLS	19	29.5	NA
LITHIA SPRINGS	HILLS	23	1.3	0.6
BLAS CRUZ	HARD	30	68.8	24.8
####MAY 1-2, 1986 ####				
C.B. HISCOCK, Rt #1	HILLS	10	36.5	27.4
R. HISCOCK	HILLS	11	60.7	99.0
JOHN HARDY	HILLS	18	181.8	282.5
####MAY 23-24, 1986####				
R. HISCOCK	HILLS	11	87.4	340.9
HILL BEFORE SOFTENER	HARD	12	378.7	141.6
JOHN HARDY - 0.45 um	HILLS	18	456.0	2569.4
JOHN HARDY - 10.0 um	HILLS	18	334.7	NA
JOHN HARDY - GEOTECH A	HILLS	18	401.9	NA
JOHN HARDY - GEOTECH B	HILLS	18	401.0	NA
#### JUNE 20-21, 1986 ####				
JOHN HARDY-TIME SERIES	HILLS	18-1	446.0	468.3
JOHN HARDY-TIME SERIES	HILLS	18-2	461.5	481.9
JOHN HARDY-TIME SERIES	HILLS	18-3	480.7	424.4
JOHN HARDY-TIME SERIES	HILLS	18-4	433.3	416.0
JOHN HARDY-TIME SERIES	HILLS	18-5	384.0	369.6
JOHN HARDY-TIME SERIES	HILLS	18-6	380.0	323.4
JOHN HARDY-TIME SERIES	HILLS	18-6	NA	651.1
### JULY 31- AUG 1, 1986 ###				
JERE WORLEY	DESO	14	244.3	257.4
JOHN HARDY-HNO_3	HILLS	18	289.4	358.6
JOHN HARDY-NH_3	HILLS	18	295.3	413.3

Appendix 3. Continued.

Well name or location	County	Station No.	Filt pCi L^{-1}	Unfilt pCi L^{-1}
### AUG 28-29, 1986 ###				
C.B. HISCOCK	HILLS	10	141.4	177.2
J. HARDY	HILLS	18	566.8	538.6
C. HISCOCK	HILLS	19	4.0	2.3
WALKER	HILLS	20	2.1	24.7
T. HOLLAND	HILLS	21	1.3	4.2
W. SHIVER	HILLS	22	10.1	2.7
SULLIVIAN	HILLS	25	2.4	0.6
A. SAWMILL	HILLS	31	35.5	33.2
DOYEN	HILLS	32	6.2	18.4
###OCT 23-24, 1986###				
J. WORLEY	DESO	14	63.7	83.3
J. HARDY - diff. treatments	HILLS	18a	383.1	456.8
J. HARDY " "	HILLS	18b	303.1	515.4
J. HARDY " "	HILLS	18c	377.1	444.8
J. HARDY " "	HILLS	18d	379.4	487.9
J. HARDY " "	HILLS	18e	416.8	476.7
R. CRAWFORD	DESO	65	34.5	23.9
+++				
****MISCELLANEOUS - SPRINGS, RIVERS, ETC. ****				
TLH TAP H_2O 7-25-85		NA	NA	2.1
MIAMI WELL H_2O SEPT'85		NA	NA	0.1
MANATEE SPRS 11-3-85		NA	NA	0.3
CRYSTAL RIVER 11-18-85		NA	0.9	NA
HOMOSASSA SPRS 11-18-85		NA	14.7	NA
WEEKIWATCHEE SPRS 11-18-85		NA	1.6	NA
GOODWOOD WELL,TLH 12-2-85		NA	NA	2.1
A. WATKINS, MELBOURNE 4-9-86		NA	NA	2.8
*** JULY 15, 1986 ***				
CAMPISANO UNH	NEW HAMPS	D1	NA	7.5
CAMPISANO UNH	NEW HAMPS	D19	NA	0.2
CAMPISANO UNH	NEW HAMPS	D21	NA	4.5

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[1] Abbreviations used: HARD = Hardee; HILLS = Hillsborough; MANA = Manatee; DESO = De Soto; and SARA = Sarasota.

[2] Station numbers with "*" suffix refer to stations where water purification apparatus was installed and samples retrieved both before and after purifier.

[3] NA = Not Analyzed

Appendix 4. Chemical and physical characteristics, ^{222}Rn, and filtered and unfiltered ^{210}Po in water samples from wells in west central Florida where all parameters were measured.

Station No.	Temp (°C)	pH	Conductivity (µmhos)	Turbidity (NTU's)	Absorbance @ 400 nm	Fluoride (ppm)	Sulphide (µM)	^{222}Rn^{1} (pCi L^{-1})		^{210}Po Filtered (pCi L^{-1})	^{210}Po Unfiltered (pCi L^{-1})
****MAY 1-2, 1986*****											
10	24.5	4.26	169	1.70	0.210	NA^{2}	NA	3470	± 114	36.5	27.4
11	24.5	4.64	239	3.30	0.045	NA	NA	10690	± 320	60.7	99.0
18	23.0	4.80	43	0.50	0.061	NA	NA	16100	± 1008	181.8	282.5
34	26.5	5.34	62	1.10	0.095	NA	NA	7064	± 88	0.7	0.3
35	24.0	6.54	223	0.35	0.061	NA	NA	2840	± 112	1.1	0.4
36	24.0	5.13	90	4.40	0.109	NA	NA	2263	± 35	1.0	0.5
37	23.5	6.45	291	0.30	0.012	NA	NA	26480	± 254	0.4	0.3
38	23.5	4.56	43	0.40	NA	NA	NA	13500	± 254	2.8	2.7
39	23.0	4.93	294	0.40	0.018	NA	NA	10110	± 581	21.9	0.3
40	23.0	4.76	550	0.28	0.017	NA	NA	19190	± 262	0.7	0.6
41	24.0	4.85	44	1.10	0.030	NA	NA	21550	± 459	12.9	20.7
****MAY 23-24, 1986*****											
11	24.5	5.15	173	0.89	0.020	NA	NA	10570	± 224	87.4	340.9
12	23.0	4.60	52	2.90	0.012	NA	NA	24810	± 344	378.7	141.6
18	23.3	3.80	40	1.50	0.048	NA	NA	16480	± 663	456.0	2569.4
42	23.0	4.43	93	1.60	0.147	NA	NA	6435	± 95	NA	27.5
42*	24.3	NA	190	0.82	0.152	NA	NA	6008	± 41	3.6	5.1
43	25.0	4.69	88	0.34	0.091	NA	NA	1273	± 24	1.5	2.6
44	24.5	4.52	45	9.20	0.066	NA	NA	22910	± 308	37.2	50.6
45	24.0	4.95	55	0.24	0.001	NA	NA	41440	± 925	0.7	1.5
46	26.0	5.03	38	11.00	0.017	NA	NA	17340	± 327	3.7	2.7
47	24.0	4.70	90	2.50	0.019	NA	NA	8500	± 514	1.1	0.8
48	NA	5.86	148	5.90	0.088	NA	NA	NA	NA	2.4	0.2
49	25.5	5.86	102	6.20	0.001	NA	NA	2552	± 39	1.1	2.1
50	24.0	7.05	315	3.80	0.074	NA	NA	3457	± 44	1.2	55.4
51	23.0	4.26	48	15.00	0.097	NA	NA	1195	± 26	20.0	38.3
52	29.5	7.15	312	0.72	0.032	NA	NA	3064	± 61	2.2	BD^{3}
53	23.5	4.76	65	0.23	0.010	NA	NA	3810	± 138	3.1	10.5
54	23.9	4.23	134	0.60	0.007	NA	NA	13730	± 299	58.2	57.9
****JUNE 20-21, 1986****											
18-1	26.1	5.13	40	0.46	0.060	0.09	38	17070	± 799	446.0	468.3
18-2	24.0	5.19	40	0.35	0.055	0.10	35	18170	± 285	461.5	481.9
18-3	24.0	4.99	40	0.75	0.055	0.09	38	18160	± 500	480.7	424.4
18-4	24.0	5.08	40	0.49	0.060	0.07	40	18870	± 173	433.3	416.0
18-5	24.0	5.00	40	0.49	0.066	0.08	41	18450	± 318	384.1	369.6
18-6	23.6	5.06	40	0.60	0.050	0.16	34	19020	± 372	380.0	323.4
18-6	23.6	5.06	40	0.60	NA	0.16	34	NA	NA	NA	651.1
18-7	NA	NA	NA	NA	NA	NA	NA	18520	± 371	NA	NA
55	26.0	5.20	44	0.51	0.235	0.12	6	120	± 26	6.3	1.3
56	24.1	5.24	33	0.47	0.140	BD	BD	7030	± 29	9.0	6.2
57	24.0	7.47	132	0.22	0.008	0.28	BD	2560	± 377	0.7	0.9
58	23.9	5.77	150	7.75	0.085	0.04	BD	4580	± 105	2.6	20.7
59	22.9	5.14	72	0.74	0.005	0.07	15	636	± 20	4.0	3.1

Appendix 4. Continued.

Station No.	Temp (°C)	pH	Conductivity (µmhos)	Turbidity (NTU's)	Absorbance @ 400 nm	Fluoride (ppm)	Sulphide (µM)	^{222}Rn (pCi L^{-1})			^{210}Po Filtered (pCi L^{-1})	^{210}Po Unfilt (pCi L^{-1})
60	24.0	5.69	142	10.00	0.065	0.94	BD	28320	±	550	9.3	6.4
61	24.3	5.01	30	0.34	0.090	0.05	22	5352	±	3	16.5	18.3
62	24.0	5.04	62	1.51	0.055	BD	BD	6730	±	563	19.1	1.0
63	24.5	4.92	58	8.10	0.045	BD	25	1095	±	37	15.7	24.1
				****JULY 31- AUG 1, 1986****								
14	25.3	5.28	67	3.50	0.364	0.66	40	7157		37	244.3	257.4
18	28.0	4.61	48	0.45	0.054	0.67	46	16160	±	371	289.4	358.6
64	28.0	7.05	473	12.00	0.108	0.68	NA	59	±	27	19.1	21.8
65	25.5	7.19	790	2.50	0.026	0.62	214	2555	±	24	8.5	92.9
66	28.0	7.35	1000	2.00	0.039	0.60	229	1088	±	56	8.5	9.2
67	24.8	7.10	720	2.50	0.064	0.68	90	9180	±	275	7.4	67.3
68	26.0	4.59	710	0.60	0.014	0.66	4	4750	±	216	1.4	3.2
69	28.0	4.68	780	0.80	0.011	0.64	BD	4420	±	156	10.1	1.6
70	28.2	5.22	447	16.00	0.021	0.72	BD	35000	±	1713	2.7	17.8
71	27.1	7.12	360	13.00	0.055	0.67	4	2476	±	80	0.9	21.7
				****AUGUST 28-29, 1986****								
10	26.0	4.58	140	2.00	0.065	0.06	43	2590	±	109	141.4	177.2
18	26.8	4.80	46	0.65	0.050	0.06	35	15140	±	472	566.8	538.6
19	26.5	5.75	312	6.00	0.025	0.24	BD	7120	±	367	4.0	2.3
20	28.0	6.12	310	4.50	0.015	0.30	BD	3900	±	221	2.1	24.7
21	28.5	4.95	219	0.50	0.015	0.19	BD	3410	±	258	1.3	4.2
22	26.0	6.43	400	3.00	0.025	0.43	BD	8380	±	333	10.1	2.7
25	24.5	6.05	365	1.25	0.015	0.20	BD	4127	±	58	2.4	0.6
31	26.0	3.85	40	4.50	0.030	0.02	BD	13960	±	388	35.5	33.2
32	24.0	6.12	230	6.75	0.025	0.16	BD	3180	±	100	6.2	18.4
72	25.0	6.00	193	9.50	0.045	0.16	BD	2780	±	244	9.4	0.4
73	26.0	6.25	300	10.00	0.015	0.34	BD	4690	±	473	1.6	2.6
74	25.0	6.45	183	0.70	0.015	0.43	BD	2346	±	65	0.6	0.5
75	25.0	6.40	312	5.00	0.015	0.22	BD	10780	±	286	12.0	0.7
76	26.5	6.13	301	2.00	0.065	0.16	BD	5000	±	225	1.3	18.2
				****OCT 23-24, 1986****								
14	26.1	5.11	97	1.70	0.437	0.37	22	8260	±	65	63.7	83.3
18	25.4	5.00	52	0.45	0.108	0.07	20	17290	±	354	425.9	544.7
65	26.0	7.30	830	3.25	0.029	1.45	230	3119	±	23	34.5	23.9
77	25.5	7.21	940	6.50	0.215	1.39	220	3171	±	40	4.0	2.0
78	25.9	7.20	600	0.60	0.034	0.83	NA	NA		NA	3.5	2.2
79	25.0	7.22	1200	1.50	0.339	1.77	149	1441	±	60	0.4	3.0
80	24.9	6.82	1100	0.55	0.056	1.27	163	2210	±	118	1.8	8.2

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[1] Standard deviation of ^{222}Rn concentrations based on triplicate measurements.

[2] BD = Below detection.

[3] NA = Not analyzed.