

GEOCHEMISTRY OF RADIUM-226 AND RADIUM-228, AND RADON-222  
IN GROUND WATER IN THE CHICKIES QUARTZITE,  
SOUTHEASTERN PENNSYLVANIA

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ABSTRACT

Elevated radium activities in ground water of the Chickies Quartzite were detected in 1985. In 1986-88, the U.S. Geological Survey sampled 160 wells penetrating the Chickies Quartzite to determine the magnitude and distribution of radium and radon-222 activities in ground water and to characterize the geochemical environment associated with elevated radium.

The Chickies Quartzite is a Cambrian age basal conglomerate, quartzite, and slate that crops out in the Piedmont physiographic province of southeastern Pennsylvania. The formation is a low-yielding, fractured-rock, water-table aquifer recharged primarily by local precipitation.

Water-sample analyses included determination of dissolved radium-226, radium-228, radon-222, uranium, and major and minor ions. Activities of up to 41 pCi/L (picocuries per liter) for radium-226, 160 pCi/L for radium-228, and 32,280 pCi/L for radon-222 were measured. Nonparametric Spearman rho correlations show that dissolved radium activity relates negatively to pH and positively to dissolved organic carbon concentration. These factors may favor radium mobility by promoting a decrease in adsorption and an increase in solubility. Radon-222 activity does not correlate with activity of its parent, radium-226, in solution.

Radium activities were greatest in acidic ground water in the conglomerate and quartzite (median pH of 5.0 and 5.2, respectively) and least in more neutral water in the slate (median pH of 6.4). Radium-228 activity exceeds radium-226 activity in all water samples from the conglomerate and quartzite. Results of solid-phase analysis indicate that the conglomerate may contain more thorium and uranium than the quartzite. Median radon-222 activities in ground-water samples increase from the slate to the quartzite to the conglomerate. This suggests that the uranium content is lowest in the slate and highest in the conglomerate. Observed distributions of radium isotopes and radon-222 activities in ground water reflect geochemical controls on solubility and adsorption and variable distribution of parent thorium-232 and uranium-238 in the formation.

**KEY WORDS:** Radium radioisotopes, Radon-222, Ground-water, Geochemistry, Piedmont.

## INTRODUCTION

The Chickies Quartzite is a low-yielding, fractured-rock, water-table aquifer that crops out in southeastern Pennsylvania and serves as the sole source of water for thousands of domestic users. Following the discovery of radium (Ra) activities greater than the U.S. Environmental Protection Agency (USEPA) maximum contaminant level (MCL) of 5 pCi/L (picocuries per liter) (U.S. Environmental Protection Agency, 1986) in ground water from the Chickies Quartzite during routine sampling of public supply wells in 1985, the U.S. Geological Survey, in cooperation with the Pennsylvania Department of Environmental Resources, conducted a study of radium-226 (Ra-226), radium-228 (Ra-228), and radon-222 (Rn-222) in ground water from the Chickies Quartzite.

This paper describes the aquifer lithology and geochemical environment associated with elevated Ra in the ground water of the Chickies Quartzite, and presents data on the distribution and magnitude of Ra-226, Ra-228, and Rn-222 activities in ground water from 160 wells sampled in 1986-88.

Ra-226 and Ra-228 are the two most abundant and longest-lived naturally occurring isotopes of Ra. Ra-226 belongs to the uranium-238 (U-238) decay series, has a half-life of 1,600 years, and decays by alpha-particle emission to Rn-222. Rn-222, the longest-lived isotope of Rn, has a half-life of 3.825 days and decays by alpha-particle emission. Ra-228 belongs to the thorium-232 (Th-232) decay series, has a half-life of 5.75 years, and decays by beta-particle emission. Because of different decay rates, the mass of Ra-226 required to generate 1 pCi Ra-226 is about 275 times the mass of Ra-228 required to generate 1 pCi Ra-228. One gram of Ra-226 generates 1 Curie of Ra-226.

The presence of Ra and Rn in ground water implies the presence of U- and (or) Th-bearing minerals within the aquifer or within adjacent geologic units from which Ra has migrated. In addition to source mineral composition, lithologic controls on the distribution of Ra and Rn in ground water include ground-water chemistry and Rn emanation rates that reflect aquifer mineralogy, grain size, texture, porosity, and permeability. Ra-226 and Ra-228 have similar chemical behavior, but may become separated from the U and Th parents because of differences in chemical behavior of the elements in the U-238 and Th-232 decay series. Migration distances of radionuclides in ground water are further restricted by the half-life of each radionuclide and the ground-water flow rates. Thus, the relatively short-lived Rn-222 must be generated within a relatively short distance from its parent, Ra-226; relatively longer-lived Ra-226 and Ra-228 may be transported in ground water farther than Rn-222.

# GEOLOGY AND HYDROLOGY OF THE CHICKIES QUARTZITE

## Geology

The Chickies Quartzite is Early Cambrian in age and lies unconformably on older deformed and metamorphosed crystalline rocks in the Piedmont physiographic province. The Chickies Quartzite may be correlated with other basal conglomerates and quartzites that crop out in the Piedmont (Berg and others, 1986). The Lower Cambrian Harpers Phyllite and Antietam Quartzite, usually mapped as an undivided unit, conformably overlie the Chickies Quartzite.

The Chickies Quartzite crops out over an area of approximately 112 square miles in Pennsylvania. The formation has been folded and faulted repeatedly and is discontinuously exposed in fault slices and anticlinal or synclinal structures trending east-northeast for about 100 miles from Adams County, near the Maryland border, to Bucks County, near the New Jersey border (Fig. 1). The Chickies Quartzite is resistant to erosion and forms narrow ridges bordering uplands underlain by crystalline bedrock and valleys underlain by carbonate bedrock.

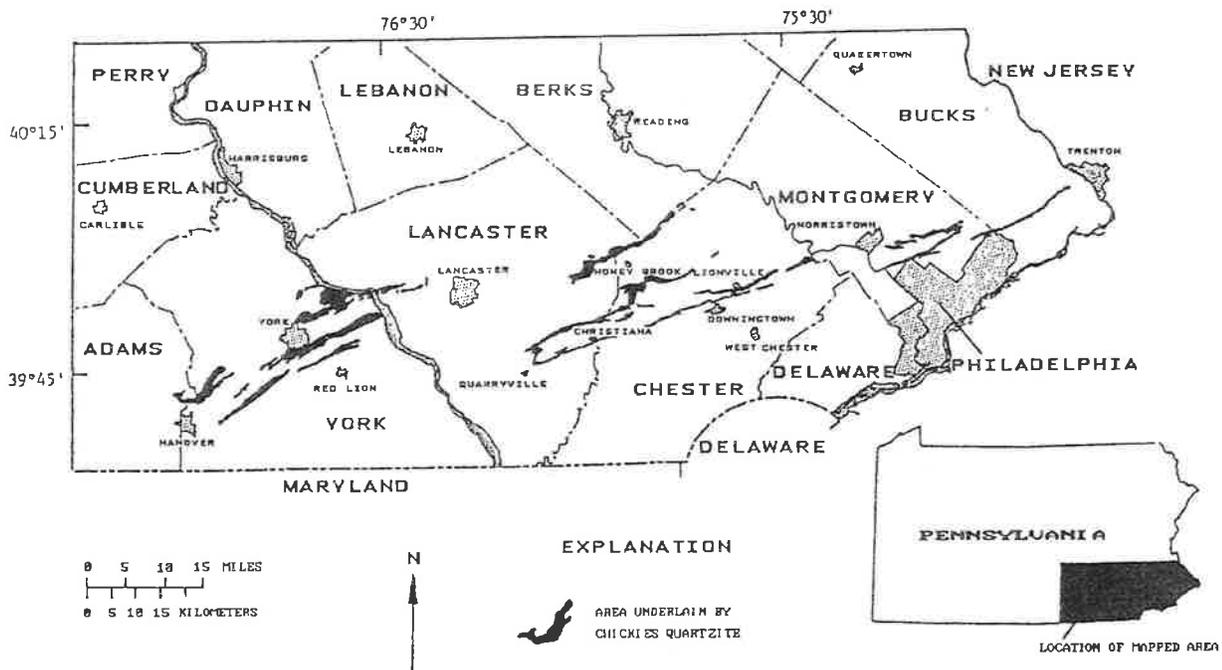


Figure 1. -- Chickies Quartzite in southeastern Pennsylvania.

The Chickies Quartzite is 430 to 1,300 feet thick and is composed of a basal conglomerate, quartzite, and slate (Lyttle and Epstein, 1987). These lithologies have been mapped in some areas as separate members or as units within members (Bascom and Stose, 1938; Knopf and Jonas, 1929; Stose and Stose, 1944). The oldest unit is the Hellam Member that consists of a coarse feldspar and quartz-pebble conglomerate grading into conglomeratic quartzite with a quartz and sericitic matrix and accessory magnetite, hematite, and zircon. It is about 200 to 500 feet thick. The Chickies Quartzite, above the Hellam Member, is a light gray to white, vitreous to granular quartzite and sericitic quartz schist, which are composed of quartz, sericite, some feldspar, and accessory zircon, rutile, apatite, monazite, limonite after pyrite, hematite, magnetite, nondetrital tourmaline, and unidentified opaque minerals. Interbeds of slate are reported within both the Hellam Member and Chickies Quartzite. In parts of York County, the Chickies Quartzite above the Hellam Member has been mapped as a slate unit that is up to 350 feet thick (Stose and Stose, 1944). It consists of interbedded slate, phyllite, and quartzite that are composed of quartz, feldspar, chlorite, muscovite, magnetite, pyrite, zircon, and tourmaline. The environments of deposition of the Chickies Quartzite have been interpreted as braided streams and intertidal and subtidal zones along a coastal margin (Adams and Goodwin, 1975).

In this paper, the terms conglomerate, slate, and quartzite refer to the three most important lithologies represented by the Hellam Member, the mapped area of slate in York County, and the rest of the Chickies Quartzite above the Hellam Member, respectively.

### Hydrology

The Chickies Quartzite is a low-yielding, fractured-rock, water-table aquifer recharged directly and primarily by local precipitation. Recharge occurs from infiltration through overlying shallow soil and weathered rock. Because the water-table is a subdued expression of topography and the Chickies Quartzite is in the highest topographic position, little or no inflow comes from adjacent units. Water levels are as much as 100 feet below ridge tops. Springs discharge on slopes and indicate shallow, local ground-water systems.

## METHODS OF DATA COLLECTION AND ANALYSIS

### Solid Phase

Samples of the Chickies Quartzite were collected from five quarries and from well cuttings of 14 recently drilled wells. Determination of U and Th concentrations in rock samples was performed by delayed neutron activation and long-lived analysis (INAA) at Nuclear Activation Services, Ann Arbor, Michigan<sup>1</sup>. Geophysical well logging, including

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<sup>1</sup> The use of firm, brand or trade names in this report is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.

natural gamma-ray and caliper logs, was conducted by the U.S. Geological Survey using a Mount Soprus model 2 logger.

### Ground Water

Samples of ground water were collected from 160 domestic and public water-supply wells completed in the Chickies Quartzite. Most sampling sites were privately owned domestic wells equipped with submersible pumps and drilled since 1960. Samples of untreated water for chemical and radiochemical analysis were collected from spigots nearest to the well head after wells were pumped at least 20 minutes or until temperature, pH, and specific conductance stabilized. Well-water temperature, pH, specific conductance, dissolved oxygen (DO), alkalinity, and platinum electrode potential (Eh) were measured in the field using established methods (Wood, 1976).

Separate laboratories were used for radiochemical and chemical analyses. Rn-222 was determined by the Physics Department, University of Maine, Orono, Maine. Dissolved concentrations or activities of constituents are reported for water samples filtered through a 0.45-micrometer filter in the field. Dissolved Ra-226, Ra-228, U, and gross alpha- and beta-particle activity were determined at Teledyne Isotopes, Westfield, New Jersey, and at U.S. Testing, Richmond, Washington. Ra-226 was determined by Rn emanation; Ra-228 by precipitation and beta counting of Actinium-228; and U by laser fluorometry and laser-induced phosphorimetry. Dissolved calcium (Ca), magnesium (Mg), sodium (Na), potassium (K), barium (Ba), iron (Fe), manganese (Mn), chloride (Cl), sulfate (SO<sub>4</sub>), nitrate (NO<sub>3</sub>), fluoride (F), silica (SiO<sub>2</sub>) total dissolved solids (TDS), as measured by residue on evaporation at 180 degrees Celsius, dissolved organic carbon (DOC), and total Fe were determined at the U.S. Geological Survey National Water Quality Laboratory, Arvada, Colorado.

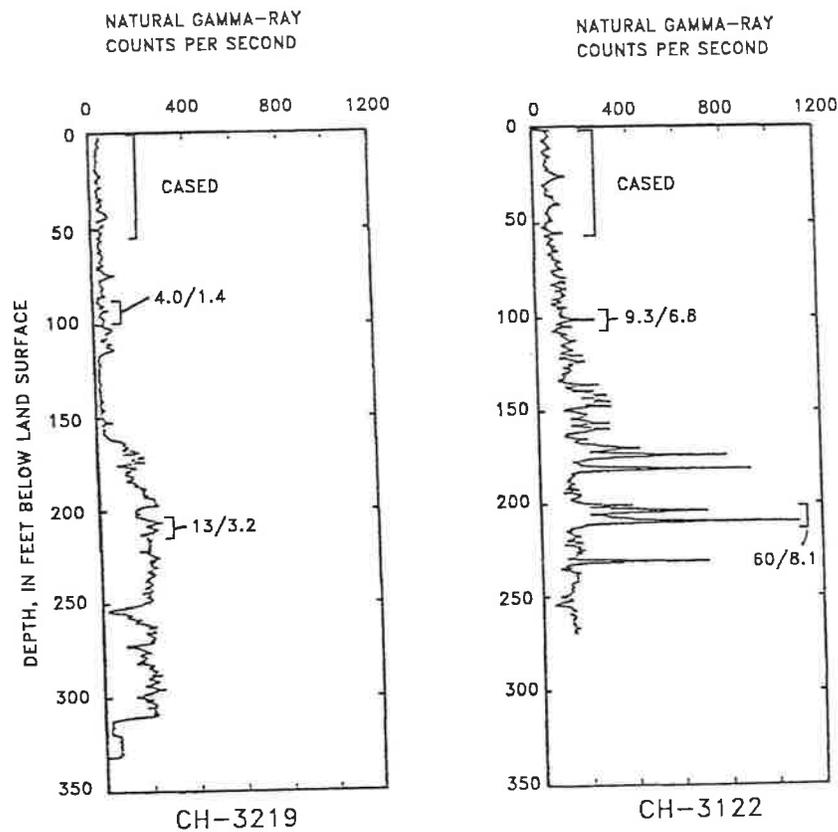
## GEOCHEMISTRY OF THE CHICKIES QUARTZITE

### Th and U in the Solid Phase

Natural gamma-ray logs of wells penetrating the Chickies Quartzite suggest that the conglomerate contains more gamma-emitting material than the quartzite. The natural gamma-ray logs for CH-3122, a well drilled through the conglomerate into the underlying crystalline basement rock, and well CH-3219, located up section of CH-3122 and drilled into the quartzite, are shown in Figure 2. Wells CH-3122 and CH-3219 are located about 3 miles south of Honey Brook (Fig. 1). Well cuttings from the depth intervals indicated on the logs were analyzed for Th and U content. Well cuttings collected from the depth interval with highest gamma-ray counts per second (cps) from well CH-3122 contained 60 ppm (parts per million) Th and 8.1 ppm U. Well cuttings from a depth interval of low gamma-ray cps from well of CH-3219 contained only 4.0 ppm Th and 1.4 ppm U.

Host minerals for Th and U include monazite and zircon that occur with other heavy minerals in the Chickies Quartzite and in other basal conglomerates of the Piedmont. Variation in gamma-ray activity shown by logs probably corresponds to the variable distribution of Th- and U-bearing minerals in the aquifer and reflects variable distribution of heavy minerals in the original environment of deposition.

Thirty-five samples of cuttings were collected from 14 wells at depths of both high and low gamma-ray activity with a bias toward samples with high activity; they do not represent average values for the formation. The range and median concentrations of Th and U and the mass and activity ratios of Th/U in well cuttings from the conglomerate and quartzite lithologies are given in Table 1. The concentration of Th and U in quartzite samples from quarries and average concentrations of Th and U for bulk crustal composition, sandstones, and shales also are listed in Table 1. The Th/U activity ratios of samples of Chickies Quartzite are close to average values for the earth's crust and shales, with some Th enrichment within the conglomerate, which has Th/U activity ratios that are similar to the average for sandstones.



**Figure 2.** -- Natural gamma-ray logs of wells CH-3122 and CH-3219. Annotated values on plots are Th/U content, in parts per million, of well cuttings from indicated depth intervals.

Table 1.-- Thorium and uranium content of well cuttings and quarry rock samples from the conglomerate and quartzite of the Chickies Quartzite.

Sample source	Number of samples	Th (ppm) Range Median	U (ppm) Range Median	Th/U Mass ratio Range Median	Th/U Activity ratio <sup>1</sup> Range Median
Well cuttings Quartzite	15	2.2 - 16 11	0.8 - 4.5 3.2	2.7 - 4.1 3.1	0.9 - 1.4 1.0
Conglomerate	20	4.9 - 60 10	1.7 - 8.1 2.8	1.0 - 7.7 3.9	.3 - 2.6 1.3
Quarry rocks Quartzite	6	3.1 - 8.2 5.8	1.6 - 3.1 2.7	1.9 - 3.3 2.4	.6 - 1.1 .8
All samples	41	2.2 - 60 10	0.8 - 8.1 3.1	1.0 - 7.7 3.1	.3 - 2.6 1.1
Average abundance of Th and U for various rocks (Durrance, 1986, p. 31); mass and activity ratios calculated from average values					
Earth's crust		8.5	2.7	3.2	1.1
Shale		12	3.7	3.2	1.1
Sandstone		1.7	.45	3.8	1.3

<sup>1</sup> Activity ratio calculated using the approximation that 9 ppm Th and 3 ppm U are each equivalent to 1 picocurie per gram.

### Ground-Water Quality

The ground water of the Chickies Quartzite is commonly soft, acidic, and low in TDS. Detectable amounts of DO and DOC and variable amounts of dissolved Mn and Fe are present. Table 2 shows the range and median of chemical and radiochemical constituents analyzed and the range and median of measured properties for well-water samples. In the pH range of the water samples, bicarbonate is assumed to be the measured component of alkalinity determined by titration to pH 4.5.

Total dissolved Ra that exceeds the USEPA MCL for drinking water of 5 pCi/L was found in water from 47 percent (75) of the 160 wells sampled. The sum of Ra-226 and Ra-228 activities is reported as total Ra. Total Ra activities greater than 5 pCi/L were measured in water samples collected from wells penetrating the Chickies Quartzite along the entire outcrop (Fig. 1). Ra-228 activity commonly was greater than Ra-226 activity. The median Ra-228/Ra-226 activity ratio is 2.7, and 95 percent of the ratios are greater than 0.9. The Ra-228/Ra-226 activity ratio is reported only for samples in which both Ra-228 and Ra-226 activities are above the lowest limits of detection.

Table 2.-- Range and median values of chemical radiochemical constituents and properties for 160 well-water samples from the Chickies Quartzite.

Constituent or property	Number of samples	Range	Median
<b>Dissolved chemical constituents</b>			
Ca (mg/L)	159	< 0.10 - 33	3.4
Mg (mg/L)	159	.20 - 14	2.9
Na (mg/L)	159	.70 - 59	4.0
K (mg/L)	159	.30 - 11	1.8
Ba (mg/L)	159	< 2.0 - 380	63
B (mg/L)	58	<10 - 290	10
Fe (mg/L)	159	< 3.0 - 27,000	20
Mn (mg/L)	159	< 1.0 - 870	36
Cl (mg/L)	160	.30 - 100	7.3
SO <sub>4</sub> (mg/L)	160	< .20 - 62	5.7
F (mg/L)	160	< .10 - .50	.1
SiO <sub>2</sub> (mg/L)	160	3.40 - 28	8.3
NO <sub>3</sub> (mg/L as N)	57	< .10 - 16	1.1
NH (mg/L as N)	57	< .01 - 1.4	.01
PO <sub>4</sub> (mg/L)	58	< .001 - .052	.001
DOC (mg/L)	147	.30 - 10.0	.80
<b>Total chemical constituent</b>			
Fe (mg/L)	159	< .01 - 440.0	.180
TDS (mg/L)	159	7 - 229	51
<b>Chemical properties measured in the field</b>			
pH	160	4.3 - 6.9	5.12
Alkalinity (mg/L as CaCO <sub>3</sub> )	156	.0 - 130	6.0
Specific Conductance (mS/cm)	160	10 - 633	85
DO (mg/L)	154	.0 - 12.1	7.55
Temperature (°C)	159	9.0 - 16.0	12.0
Eh (mV)	111	139 - 890	550
<b>Radiochemical constituents</b>			
Ra-226 (pCi/L)	160	< .2 - 41	1.2
Ra-228 (pCi/L)	160	< 1.0 - 160	2.55
Alpha (pCi/L)	160	< .1 - 171	4.5
Beta (pCi/L as Cs-137)	160	1.0 - 230	6.95
Rn-222 (pCi/L)	160	114 - 32,280	2,385
U (mg/L)	160	< .05 - 6.6	.09
<b>Calculated values</b>			
Ra-226 + Ra-228 (pCi/L)	160	< 1.2 - 172	4.19
Ra-228/Ra-226 <sup>1</sup> (pCi/L/pCi/L)	100	0.37 - 30	2.37

<sup>1</sup> Activity ratio calculated only where both Ra-226 and Ra-228 activities are above lowest limit of detection.

## Geochemical Environment Associated with Elevated Radium Activity in Ground Water of the Chickies Quartzite

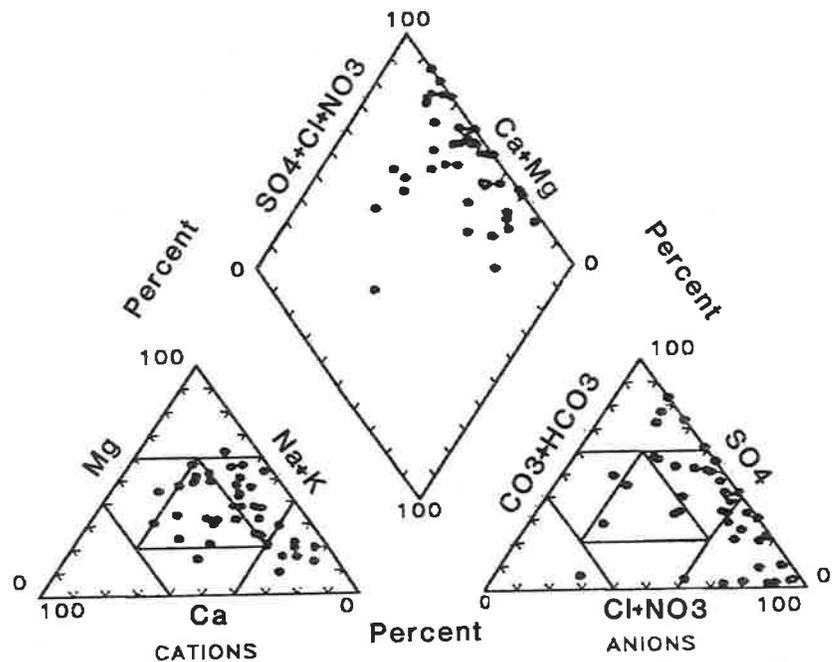
The general chemical characteristics of ground water from the Chickies Quartzite that contains or is likely to contain Ra exceeding the USEPA MCL was determined graphically and statistically. A comparison of piper diagrams showing relative concentrations of major cations and anions in milliequivalent percents for well-water samples that contain total Ra activities greater than or equal to 5 pCi/L (Fig. 3a) and less than 5 pCi/L (Fig. 3b) indicate that elevated Ra activities are associated with relatively higher Mg, SO<sub>4</sub>, and Cl concentrations, and lower Ca and bicarbonate concentrations.

The nonparametric Spearman's rho correlation coefficient ( $r_s$ ) test that indicates monotonic change between two variables was used to determine the chemical constituents and properties that correlate with Ra-226, Ra-228, and Rn-222 in ground water. Correlations are between ranks of activities of Ra-226, Ra-228, and Rn-222, and ranks of corresponding concentrations of chemical constituents and magnitudes of chemical properties in ground water. Results of the two-tailed Spearman's rho correlation test significant at the 95-percent confidence interval for Ra-226 and Ra-228 activity in ground water are shown in Table 3. The following discussion of Ra correlations applies to both Ra-226 and Ra-228, unless otherwise specified, because Ra-226 and Ra-228 correlate with the same constituents and properties.

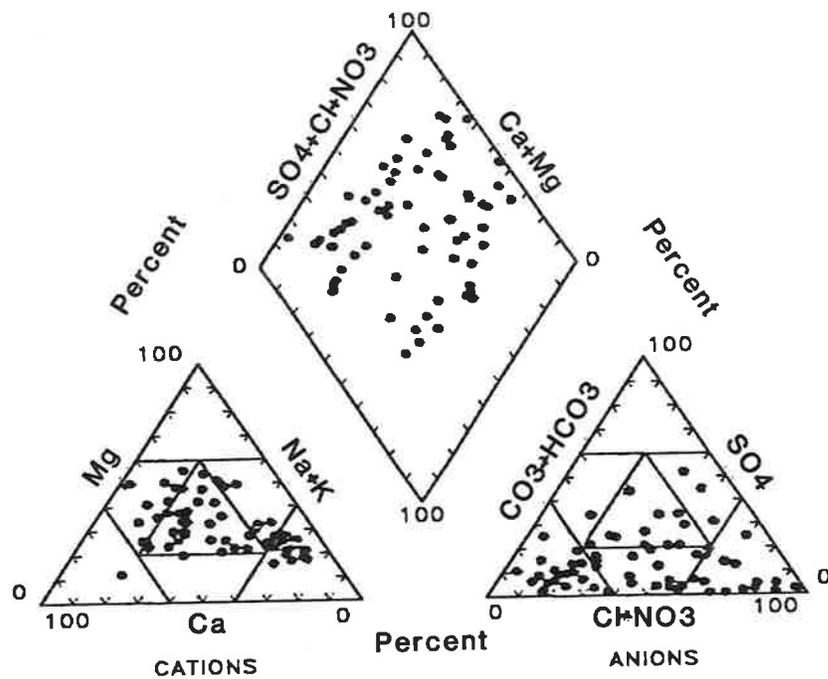
The correlation analysis indicates that increasing Ra-226 and Ra-228 activities are most strongly associated with decreasing pH, alkalinity, and SiO<sub>2</sub> and increasing DOC, Ba, SO<sub>4</sub>, Mn, and specific conductance. Weaker, but significant, positive correlations between Ra and Cl, NO<sub>3</sub>, Na, Mg, K, U, TDS, and Eh suggest that geochemical controls on these other constituents and properties differ in some ways from controls on Ra.

The negative correlation of Ra with pH is expected and was reported by Cecil and others (1987) for ground water from the Chickies Quartzite. All ground-water samples from the Chickies Quartzite with pH less than 4.7 contain combined activities of Ra-226 and Ra-228 greater than 5 pCi/L. Low pH decreases adsorption of Ra and other ions by silica, kaolinite (Riese, 1982), and other mineral surfaces, such as Fe and Mn hydroxides. Negative correlations are expected between Ra and constituents that correlate positively with pH. For example, Ra correlates negatively with alkalinity and SiO<sub>2</sub>, both of which correlate positively with pH ( $r_s = 0.89$  and  $0.55$ , respectively). The weathering of silicate and/or carbonate minerals consumes hydrogen ions and increases alkalinity and SiO<sub>2</sub> concentrations.

Positive correlations are expected between Ra and constituents that correlate negatively with pH. Increasing DOC, like Ra, also correlates ( $r_s = -0.51$ ) with decreasing pH; this relation may indicate decreased adsorption and slow degradation of DOC in acidic ground water (Thurman, 1985) or recharge from low pH, DOC-rich waters of meteoric origin. However, increasing DOC appears to be associated with increasing Ra-226 and



a) Total radium activity  $\geq$  5 picocuries per liter



b) Total radium activity  $<$  5 picocuries per liter

**Figure 3.** -- Chemistry of ground-water samples from the Chickies Quartzite. Percentages of ions are in milliequivalents.

Table 3.-- Correlations between activities of Ra-226 and Ra-228, and chemical constituents and properties, significant at the 95 percent confidence interval. [pCi/L, picocuries per liter;  $r_s$ , Spearman rho correlation coefficient].

Ra226 (pCi/L)		Ra228 (pCi/L)	
Chemical constituent or property	$r_s$	Chemical constituent or property	$r_s$
Correlation coefficient p-values less than 0.0001			
Total Ra <sup>1</sup>	0.93	Total Ra <sup>1</sup>	0.97
Alpha	.91	Beta	.88
Ra228	.85	Alpha	.87
Beta	.85	Ra226	.85
pH	-.68	pH	-.67
Ba	.62	DOC	.67
DOC	.60	Ba	.60
Alkalinity	-.60	Alkalinity	-.59
SiO <sub>2</sub>	-.51	SiO <sub>2</sub>	-.54
Mn <sup>2</sup>	.49	SO <sub>4</sub>	.43
SO <sub>4</sub>	.37	Mn <sup>4</sup>	.42
Specific Conductance	.33	Specific Conductance	.34
Correlation coefficient p-values greater than or equal to 0.0001; p-value in parenthesis ( ) following coefficient			
NO <sub>3</sub>	0.39(0.0034)	NO <sub>3</sub>	0.30(0.0272)
Eh <sup>3</sup>	.32 (.0008)	Cl <sup>3</sup>	.29 (.0003)
Cl	.29 (.0003)	Eh	.28 (.0036)
TDS	.28 (.0006)	TDS	.28 (.0004)
Mg	.26 (.0013)	Mg	.26 (.0014)
K	.24 (.0030)	Na	.24 (.0028)
Na	.23 (.0040)	U	.20 (.0132)
U	.19 (.0176)	K	.16 (.0497)

<sup>1</sup>Total Ra equals combined activities of Ra-226 and Ra-228

Ra-228 independent of pH. Highest activities of Ra are observed in samples containing DOC above the median DOC and having pH below the median pH (Fig. 4). Dissolved organic acids may enhance Ra mobility by complexation. Thurman (1985) estimated that 1 mg/L (milligram per liter) DOC has about 1 microequivalent of metal-binding capacity, although that capacity generally decreases with decrease in pH because of hydrogen-ion competition for binding sites. The degree of ion complexation varies depending upon pH, relative binding capacities, specific complexing agents, and competing ions present (Stumm and Morgan, 1970). Thus, Ra ions may be preferably complexed by organic acids even at low pH despite the abundance of competing cations (sample median is 0.8 milliequivalents).

Ra positively correlates with Ba and  $\text{SO}_4$ , which are positively correlated with each other ( $r_s = 0.38$ ) and negatively correlated with pH ( $r_s = -0.49$  and  $-0.20$ , respectively). These correlations reflect the similar chemical behavior of Ba (a common trace element) and Ra and suggest that the relatively insoluble barium and radium sulfates [ $\log K_{sp} = -10$  and  $-11.4$ , respectively (Riese, 1982)] are undersaturated in water with low pH. Even at saturation of barium and radium sulfates, high activities of Ra-226 and Ra-228 may occur. Riese (1982) states that Ra activity will be limited by precipitation of  $\text{RaSO}_4$  only in waters with elevated concentrations of  $\text{SO}_4$  or extremely elevated concentrations of Ra.

The presence of  $\text{SO}_4$  also may indicate pyrite oxidation and dissolution, a process that decreases ground-water pH and increases desorption of Ba and Ra from cation-binding minerals or dissolution of Ba- and Ra-bearing minerals. Pyrite dissolution in oxygen-rich ground water may result in the oxidation of dissolved ferrous Fe and precipitation of  $\text{Fe}(\text{OH})_3$  and further acidification. Oxidation of dissolved ferrous Fe is indicated by the significant negative correlations of total Fe with DO and Eh ( $r_s = -0.20$  and  $-0.30$ , respectively). The lack of significant correlations between dissolved or total Fe and  $\text{SO}_4$  or pH may be caused by other sources of or reactions controlling Fe and  $\text{SO}_4$ . For example, atmospheric deposition (acid rain) is a source of  $\text{SO}_4$  unaccompanied by Fe.

The positive correlation between Ra and Mn and negative correlation between Mn and pH ( $r_s = -0.31$ ) indicate that the mobility of Mn, like Ra, is greatest in more acidic water. Dissolution of some Mn-bearing minerals in low pH water may be accompanied by concurrent release of Ra that otherwise might be adsorbed by Mn oxides and hydroxides.

Ra correlates positively with specific conductance and TDS. Ra solubility may be greater in water with higher specific conductance because ion solubility tends to increase with increases in specific conductance and ionic strength. Increases in specific conductance also may be associated with increases in pH, although specific conductance does not correlate with pH. Ground water commonly acquires solutes (TDS) through weathering or dissolution of silicates and carbonates, reactions that consume hydrogen ions. Ra mobility is enhanced only in high specific-conductance waters of low pH (low alkalinity) because pH is a strong control on Ra desorption, as indicated by the relative strength of correlations between Ra and pH, and Ra and specific conductance .

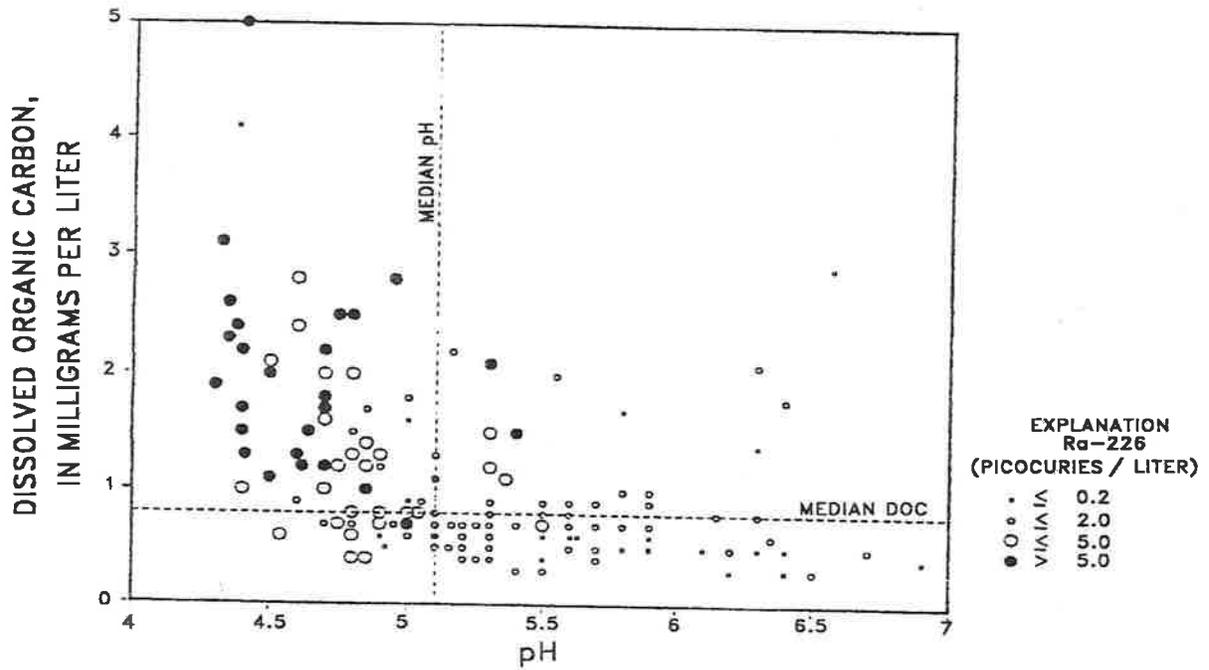
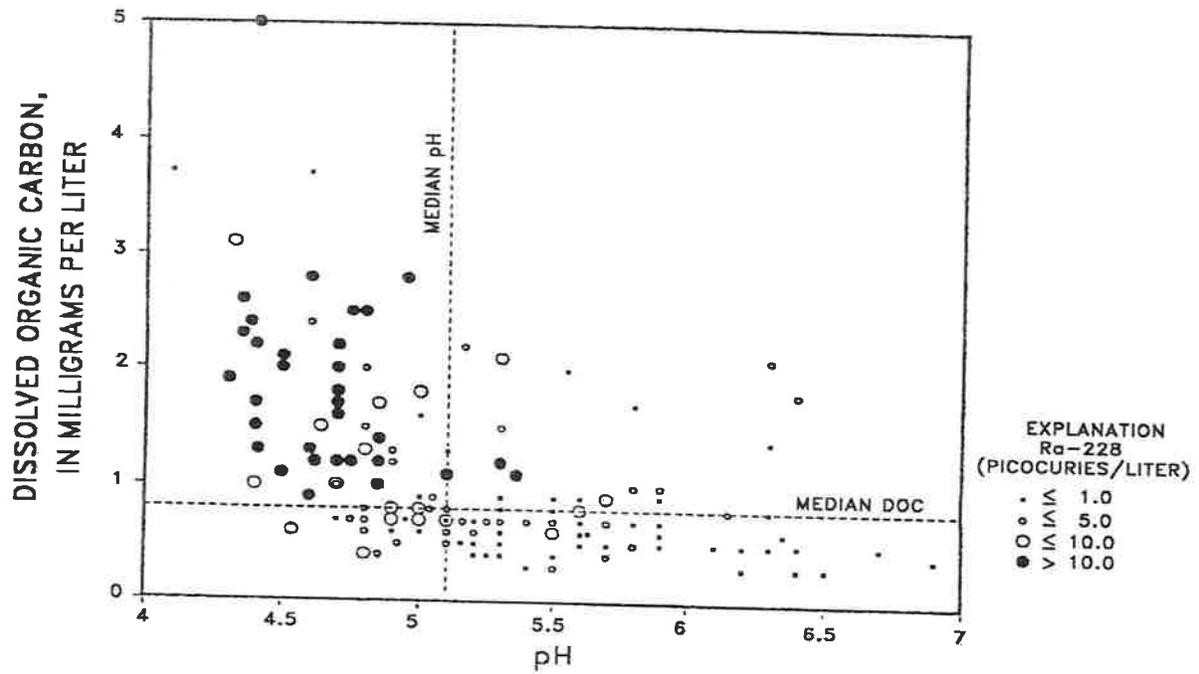


Figure 4. -- Relation between dissolved organic carbon and pH, and radium-226 and radium-228.

Ra does not correlate with Ca, even though both have similar chemical behavior as alkaline earth metals. Ca, unlike Ra, correlates positively with alkalinity and pH ( $r_s = 0.29$  and  $0.20$ , respectively). The correlation suggests that pH increases through the buffering reaction associated with calcium carbonate or silicate dissolution and Ra mobility decreases. The piper diagrams (Fig. 3) show that higher Ra activities occur in water with relatively low concentrations of Ca and bicarbonate. Riese (1982) found that Ca competes with Ra for adsorption sites on silica in the pH range from 3 to 9, and that total Ra adsorption declines with decreasing pH. Thus, Ra mobility is enhanced only in Ca-rich waters with low pH (and low alkalinity).

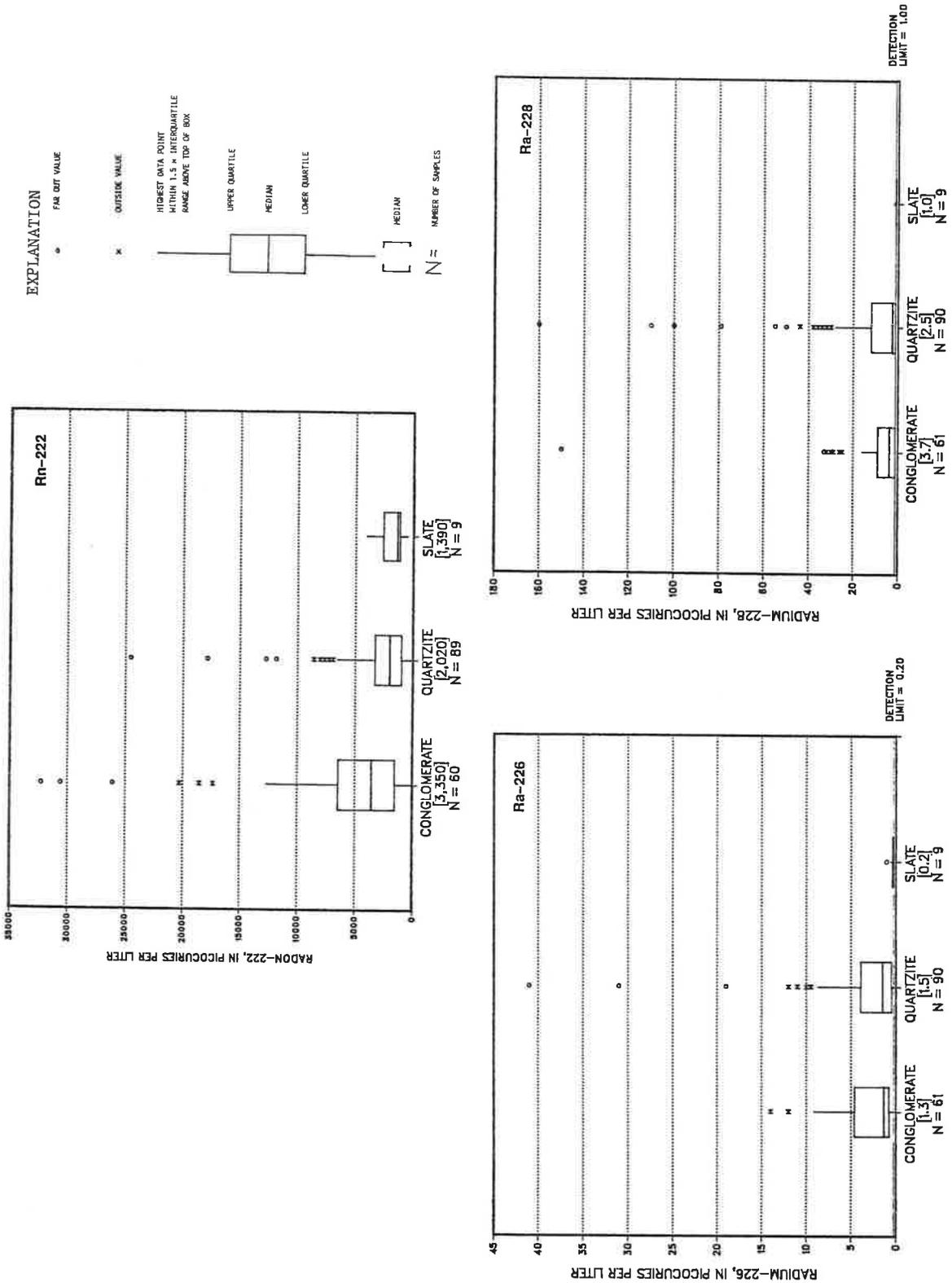
Positive correlations between Ra with  $\text{NO}_3$  and Eh are not well understood, but suggest Ra mobility increases in ground water whose quality is influenced by surface or near-surface sources such as acid rain, agriculture, and septic systems.  $\text{NO}_3$  does not correlate with pH. Eh correlates negatively with pH ( $r_s = -0.51$ ) and positively with DO ( $r_s = 0.52$ ). Relatively higher Eh could be associated with oxygenated recharge waters or may indicate aeration during sampling.

Ra-226 correlates positively, but weakly, with U, its primary parent. Ra and U may enter ground water from the same source area in the aquifer but be separated because of differences in chemical behavior in the aqueous phase. U commonly forms anion complexes, especially in oxidizing solutions, whereas Ra commonly occurs as a free cation (Riese, 1982). U, unlike Ra, correlates positively with Ca and alkalinity ( $r_s = 0.38$  and  $0.22$ , respectively). U mobility is enhanced in the presence of bicarbonate (Chatham and others, 1981). Ra-226 does not correlate with Rn-222, its daughter in solution, although there is an inverse relation in many samples. Increased Rn-222 activity in ground water is expected where Ra-226 is concentrated in aquifer materials and not necessarily where Ra-226 is dissolved.

#### Relations of Ra-226, Ra-228, and Rn-222 in Water and Rock

The source of Ra and Rn in the ground water is Th- and U-bearing minerals in the Chickies Quartzite. Solid-phase analysis (Table 2) indicates that the Th/U ratio of the solid phase ranges from average to enriched in Th relative to bulk crustal composition. The Ra-228/Ra-226 activity ratios in ground water (median is 2.7) are even greater than calculated Th-232/U-238 activities in the solid phase (median is 1.1), suggesting different solubility controls, such as different host minerals, for Ra-228 and Ra-226. Th concentrations in solid phase and Ra-228 activities in ground water are more variable than U concentrations in solid phase or Ra-226 activities in ground water.

The distribution of Ra-226, Ra-228, and Rn-222 activities in ground water is related to lithology. Data were divided into three groups on the basis of the mapped areas of the three lithologies--conglomerate, quartzite, and slate. Boxplots displaying Ra-226, Ra-228, and Rn-222 activities in ground water by lithology are shown in Figure 5. Median and range of Rn-222 activity in ground water increases from the slate to the quartzite to the



**Figure 5.** -- Distribution of radon-222, radium-226 and radium-228 activities in ground water from the conglomerate, quartzite, and slate lithologies of the Chickies Quartzite.

conglomerate. Median and range of Ra-226 and Ra-228 activity in ground water increases from the slate (median is below detection limit) to the conglomerate and quartzite.

The Kruskal-Wallis test, a nonparametric, one-way analysis of variance, was used to determine whether the mean rank (median) of Rn-222, Ra-226, and Ra-228 activities in ground water in the three lithologies are significantly different at the 95-percent confidence interval. If the null hypothesis was rejected, a nonparametric multiple comparison test (Campbell and Skillings, 1985) was used to determine which mean rank of the lithologic groups was different. Results of these tests show the following statistically significant differences: the mean rank of Rn-222 activity in ground water is greater for the conglomerate than it is for the quartzite and slate; the mean rank of both Ra-226 and Ra-228 activity in ground water is greater for the conglomerate and quartzite than it is for the slate. No significant differences are indicated between the mean ranks of Rn-222 activity in ground water from the quartzite and slate or between the mean ranks of Ra-226 and Ra-228 activity in ground water from the conglomerate and quartzite.

Differences in Rn-222 activity in ground water (Fig. 5) could be explained by physical properties of the lithologies (King, 1989), and (or) by differences in Ra-226 (and U-238) concentrations in the solid phase. Loomis (1987, p.33) found that "average radon concentration in ground water was consistent with relative abundance of U in rocks" and that "aquifer lithology was a useful predictor of radon concentration in ground water". The relative magnitudes of median Rn-222 activity in ground water from the three lithologies suggest that the U concentration in solid phase increases from the slate to the quartzite to the conglomerate. Distribution of Rn-222's parent, Ra-226, within the aquifer is controlled by occurrence of U-bearing minerals deposited during initial formation or introduced later, and by subsequent dissolution of U- and Ra-bearing minerals in ground water, ground-water transport of U and Ra, and adsorption of U, Ra, and Th onto aquifer materials.

Differences in Ra-226 and Ra-228 activities in ground water of the lithologies of the Chickies Quartzite are related to ground-water chemistry and to the U and Th content of the solid phase. The chemical character of ground water favoring Ra mobility, as defined by pH, and concentrations of DOC, Ba, and SO<sub>4</sub> (chemical variables most strongly statistically correlated with Ra activities) differs by lithology. The ground water in the conglomerate and quartzite is more acidic and contains more DOC, Ba, and SO<sub>4</sub> than the ground water in the slate (Fig. 6).

The conglomerate contains zones with higher concentrations of Th and U than present in the quartzite (Table 1). However, median Th and U contents of the conglomerate and quartzite appear similar and no significant differences were determined for Ra activities in ground water in the two lithologies. Greater variability of Ra-228 and Ra-226 activities in ground water in the quartzite than in the conglomerate, despite the greater range of Th and U concentrations in the conglomerate compared to the quartzite solid phase, suggests greater variability in geochemical controls on Ra mobility in the quartzite than the conglomerate.

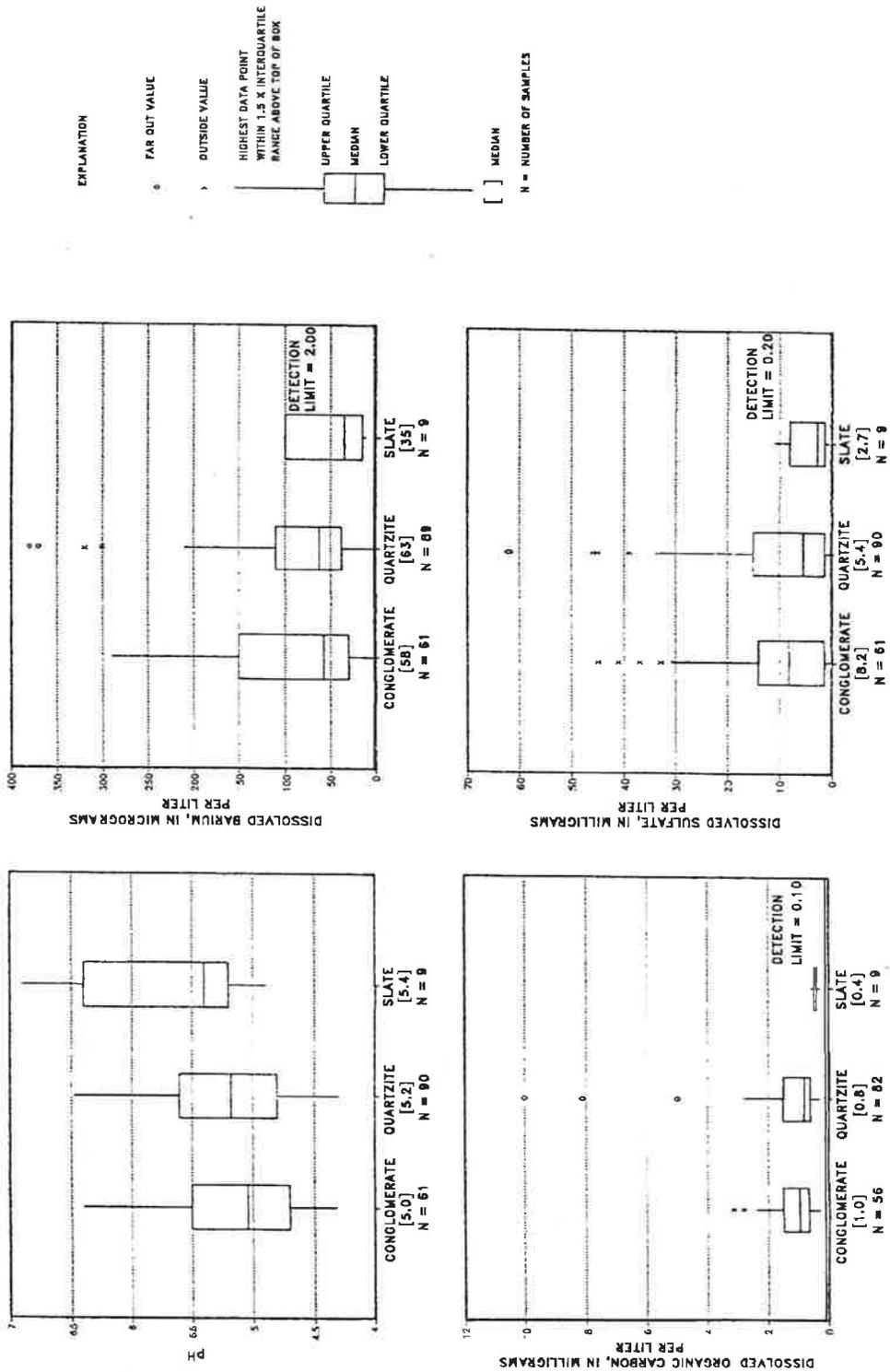


Figure 6. -- Distribution of pH, and concentrations of dissolved organic carbon, sulfate and barium in ground water in the conglomerate, quartzite, and slate of the Chickies Quartzite.

## SUMMARY

Radium-226 and radium-228 with combined activities greater than 5 pCi/L were detected in water samples from 47 percent of 160 wells penetrating the Chickies Quartzite in southeastern Pennsylvania. Activities up to 41 pCi/L for Ra-226, 160 pCi/L for Ra-228, and 32,280 pCi/L for radon-222 were measured. Nonparametric Spearman rho correlations between radium activities and chemical constituents and properties suggest that pH is the strongest control on Ra mobility and that dissolved organic carbon may enhance Ra mobility in low pH waters. Rn-222 activity does not correlate with Ra-226 activity in ground water.

The magnitudes of Ra-226, Ra-228, and Rn-222 activities differ in the ground water from three lithologies--conglomerate, quartzite, and slate-- of the Chickies Quartzite, reflecting varying geochemical controls on solubility and adsorption and varying uranium and thorium content. Median Rn-222 activity in ground water increases from the slate to the quartzite to the conglomerate, suggesting that the U content of the solid phase increases from the slate to the quartzite to the conglomerate. Rn-222 activity in ground water is statistically significantly greater for the conglomerate than it is for the slate and quartzite. Ra-226 and Ra-228 activities are significantly greater in ground water in the conglomerate and quartzite than in the slate. Ground water in the conglomerate and quartzite is more acidic (median pH = 5.0 and 5.2, respectively) than ground water in the slate (median pH = 6.4). Variable distribution of Th and U within the conglomerate and quartzite is indicated by natural gamma logs and solid-phase analysis, which show zones of Th enrichment. Ra-228 activity is greater than Ra-226 activity in most ground-water samples.

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