Contribution of Naturally Occurring Radioisotopes to Gross Alpha-Particle Activity in Ground Water in Bedrock Aquifers of Northern New Jersey

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ABSTRACT

Elevated gross alpha-particle activity in ground water, greater than the U.S. Environmental Protection Agency Maximum Contaminant Level (MCL) of 15 pCi/L (picocuries per liter), was documented from widely scattered areas in the bedrock aquifers of northern New Jersey consisting of crystalline-rock (granite, gneiss, marble) aquifers in the Highlands Province and sandstone and mudstone aquifers in the Piedmont (Mesozoic Basin) Province. Forty samples were collected from each Province from 2007 to 2011. Most of the measured alpha-particle activity in the waters was attributable to the long-lived isotopes of uranium (U), with maximum (mass) concentration of 623 ug/L (micrograms per liter)), and to a lesser extent, radium-226 (Ra-226), with maximum concentration, 51.1 pCi/L. Bedrock composition (mineralogy, lithology, and mineral surface coatings) and geochemical conditions (pH, oxidation-reduction potential) in the aquifer directly affect the occurrence (variable concentration in groundwater) and distribution (between rock and groundwater, and aqueous mobility) of naturally occurring radionuclides in ground water used in the region for drinking water.

In the Highlands Province, eight samples (of 40, 20%) had U concentrations in excess of 30 ug/L, the MCL. Alpha-emitting long-lived Ra-226 and short-lived Ra-224 was present in detectable concentrations in the water at 7 and 4 (17.5% and 10 %) of 40 sites, respectively, with maximum, 17.3 and 2.4 pCi/L, respectively. For those sites where the water was at or near saturation with dissolved oxygen (greater than 8 mg/L), isotopes of U accounted for nearly all the gross alpha-particle activity, and Ra-226 was only detected once. For those sites where water was not near saturation with dissolved oxygen (DO), concentrations of Ra-226 were detected more frequently. The mobility of U in the ground waters of the Highlands and the Piedmont was not only sensitive to concentrations of DO, but also, concentrations were generally highest where pH was slightly alkaline, generally equal to or greater than about 7.3 (Fig. 6), and waters had considerable carbonate alkalinity. The range of U-234:U-238 isotopic activity ratios was from 0.94 to 2.95, with median 1.39. When the measured isotopic activity ratios of the U isotopes were considered, gross alpha-particle activity was completely accounted for by the uranium activity except at those few sites where alpha-particle emitting isotopes of Ra were also present. In the Piedmont Province, three samples (of 40, 7.5%) had U concentrations in excess of 30 ug/L. In 7 of the 8 samples in which the concentration of Ra-226 was greater than the 5 pCi/L MCL, dissolved oxygen concentration was less than 0.5 mg/L. Detections for concentrations of Ra-226 greater than 0.3 pCi/L were noted in 24 samples (61.5% of 39 samples). At a few sites where Ra-224 was present in concentrations greater than 3 pCi/L, it made considerable contribution to gross alpha-particle activity measured 48 hours after sample collection. The gross alpha-particle activity was thus rarely accounted for by only the uranium activity. The range of U-234:U-238 isotopic activity ratios was from 0.94 to 8.45, with median 2.19. The quantification of “excess” U234 isotope concentration more accurately characterized the source of the gross alpha-particle activities, and in about 7.5% of the samples affected compliance with the “uranium-activity adjusted” gross alpha-particle MCL.

The inexpensive U mass analysis (in ug/L) coupled with determination of pH, iron, manganese, and bicarbonate alkalinity concentration, and perhaps DO, might be suitable initial water-quality indicators at most sites in the region to indicate the most substantial radionuclide contaminant, allowing some residents to avoid additional (high) laboratory costs when choosing a treatment system to decrease radiation exposure by removing uranium or radium. Awareness is needed that extreme U234:238U isotope ratios as high as 8.45 in a small percentage of waters from the Piedmont Province can be a considerable source of gross alpha-particle activity not accounted for by analyses for radium isotopes or uranium mass, and may give the faulty impression that the treatment system is ineffective.

1. INTRODUCTION

The U.S. Environmental Protection Agency (USEPA), on the basis of cancer risk (Mays and Rowland, 1985), finalized a Maximum Contaminant Level (MCL) for gross alpha (15 pCi/L), for combined radium (Ra-226 + Ra-228) (5 pCi/L), and for uranium (U) mass (30 ug/L) (U mass as a kidney toxin has as much risk as the radioactivity-based cancer risk from U; USEPA, 2000a;b). Compliance for the gross alpha-particle activity MCL of 15 pCi/L includes "adjustment" for the emitted alpha-particle radioactivity of the U, which can vary on the basis of the variability in the ratio of the shorter lived U-234 progeny and the longer lived U-238 parent isotope; only the latter is detected in the "mass" based analysis for concentration of U. For compliance purposes, the USEPA does allow for the conversion from U mass to U alpha activity using the factor of 0.672 pCi/ug of measured U mass reported in ug/L concentration units. This "natural" U conversion factor (CF_n), however, assumes that the radioactivity of both the U-234 and the U-238 are present in equal amount (1:1 activity ratio).

The common occurrence of naturally occurring radionuclides in principal aquifers of New Jersey and the considerable reliance of the dense population on ground-water resources for drinking water have made research necessary to define the aquifers or portions of aquifers most vulnerable to such contamination. The large geological, geochemical, and hydrological variability in this relatively small State, especially in the northern part where more than 100 different geologic formations are mapped (Drake et al., 2000), each with differing hydrogeochemical attributes (Serfes, 2004), has required definition of various radionuclide occurrences in numerous environmental settings. Gaining understanding of the occurrence and identifying the master geochemical variable(s) that may be indicative of preferential occurrence in a certain type of environment may guide monitoring efforts toward (or away from) similar environments elsewhere.

Elevated gross alpha-particle activity in ground water has recently been documented from scattered areas in northern New Jersey (Barker Hamill, oral commun., 2004; New Jersey Department of Environmental Protection Safe Drinking Water Program, 2004; New Jersey Department of Environmental Protection, 2008). The State of New Jersey already mandates the analysis of gross alpha within 48 hours for utilities and for residents in counties where the gross alpha-particle activity test is a requirement of the Private Well Testing Act (PWTA) (New Jersey Department of Environmental Protection, 2002a) to capture the effects of alpha-particle emissions from Ra-224 and its progeny. The occurrence of Ra-224 is widespread in the acidic ground water of the quartzose sand aquifers of southern New Jersey. A separate MCL has not been set for Ra-224. It is not known whether in northern New Jersey, gross alpha activity is as useful an indicator for radionuclide occurrence as it is in southern New Jersey. In southern New Jersey, the gross alpha test within 48 hours is adequate to account for Ra-226 and Ra-224 because U is not present (Szabo et al., 2005). Complementary information on various radioisotope occurrence is needed if alpha-particle activity in northern New Jersey is attributable to a mixture of, for example, long-lived isotopes of U, and the long-lived progeny, Ra-226, or even short-lived Ra-224. The gross alpha-particle activity analysis, while procedurally simple and inexpensive (ASTM, 1999), is subject to complicated errors and biases that are at least partly sample composition dependent (Arndt, 2010), and needs further evaluation of significance in any region where complex mixtures of radionuclides are expected.

Remediation options are widely different for U and Ra. Thus, in northern New Jersey where high gross alpha-particle activity is present, it is critical to determine what portion of the alpha activity is from U and from Ra to assess the best treatment option for risk reduction. Sampling programs to date have not been geared to determine the amount of contribution to elevated gross alpha-particle activity by isotopes of uranium or radium in Physiographic Provinces in northern New Jersey but have rather determined only the gross alpha-particle activity (Serfes, 2004). This sampling program reported in this article assessed the occurrence of U, Ra, and high activities of gross alpha-particles in ground water in northern New Jersey from the crystalline-rock aquifers of the Highlands Province and the sedimentary rocks of the Piedmont Province (Fig. 1).

2. STUDY AREA

The mountainous ridges in the Highlands Province are mostly comprised of Middle Proterozoic (1600 to 900 million years old) metamorphic and igneous rocks. The valleys are mostly underlain by Early to Middle Paleozoic (570 to 360 million years old, mostly Cambrian and Ordovician age) sedimentary and meta-sedimentary rocks, predominantly limestone and marble, that are more easily eroded. The exceptions to this trend are the mountainous ridges in the Green Pond Mountain region in the northeastern part of the Highlands which are underlain by Paleozoic (mostly Silurian age) conglomerate formations (Green Pond Conglomerate). The Middle Proterozoic rocks are heterogeneous metasedimentary and metavolcanic gneisses and granofels, mostly composed of quartz- and feldspar-rich gneisses and occasionally pyroxene or amphibolite-rich gneisses, and also granites (Fig. 1).

3.1. Geohydrology

Ground water in the fractured crystalline-rock aquifers of the Highlands Province and Mesozoic sedimentary-rock aquifers of the Piedmont Province occurs under unconfined and confined conditions, with some storage of water in glacial overburden or soil layer, and water transmission along fractures. The water table rises and falls rapidly depending on the amount of rainfall because fractures have little storage. Ground water generally flows from the upland areas down into the valleys, where it eventually discharges to surface water. Geological controls on ground water flow include: the orientation, density, inter-connectiveness and openness of fractures, and layering of bedrock, and the permeability and distribution of overlying glacial sediments. About 16.4 billion gallons were reportedly withdrawn from these aquifers in 1996, a major source of water to the State (Zapecza et al., 2002), with the marble aquifers locally providing significant quantities of water (Watt, 2000). Small quantities of water can be extracted from the other rock types for domestic use.

The natural ground water quality is mainly a function of the composition and mineralogy of the aquifer matrix and the residence time of ground water in the aquifer. Therefore, the chemistry of ground water is characteristic of a particular rock aquifer and location along the ground water flow path. The general water-quality characteristics for the crystalline bedrock aquifers in the Highlands Province are: high dissolved oxygen concentration; low to moderate pH; low to moderate alkalinity; and highly variable major ion content (Oden et al., 2000; Serfes, 2004), and high radon content (Bell et al., 1992; Szabo et al., 2006). Non-point and point sources of pollution (from human activities at the surface) affect ground water quality because of rapid recharge through the fracture network. Elevated sodium and chloride concentrations (from road salting), and elevated nitrate concentrations have been detected (Oden et al., 2000). The use of nitrogen-based fertilizers in agricultural and urban areas, and possibly septic system and sewer system leakage in urban and suburban areas are considered the major nitrate sources. Waters from the Piedmont Province tend to be more mineralized and more alkaline (Serfes, 1994) than in the Highlands.

3.1. Bedrock Radioactivity Occurrences

Accessory minerals containing radioactive elements (magnetite, titanite, allanite, zircon, apatite, and even uraninite; see Eby et al., 1992; Vassilou, 1980) are found in a variety of crystalline rocks in the Highlands, and therefore the potential exists for radionuclide release to ground water. Potassium-rich granite, granitic pegmatite, alaskite and some quartzo-feldspathic gneisses usually with (but occasionally without) hornblende are associated with elevated radionuclide-bearing mineral occurrences in the Highlands Province (Muessig et al., 1992). Numerous abandoned U mine sites are spread throughout the Highlands area in northern New Jersey (Bell, 1983) and extend into southern New York State (Gilchrist et al., 2009). Proposals as to the nature of U enrichment in this region have been made, and include the concept of igneous differentiation and tectonic enrichment processes, including mylonization (Vassilou, 1980; Gates and Gundersen, 1989; Wanty et al., 1991). The latter is of interest because structural features may also create pathways for radionuclide mobility in water. Accessory minerals containing radioactive elements (magnetite, titanite, allanite, zircon, apatite, and even uraninite; see Eby et al., 1992; Vassilou, 1980) are found in a variety of crystalline rocks in the Highlands, and therefore the potential exists for radionuclide release to ground water. A maximum of 85 pCi/L of gross alpha particle activity has been detected in water from a well in the Province in previous monitoring efforts (Serfes, 2004). Radon concentration values in a regional sampling program conducted in 1987 ranged from 36 to 24,000 pCi/L, with a median value of 1600 pCi/L (Bell et al., 1992). The highest concentrations of Rn-222 were found in waters from granites (Bell et al., 1992; Szabo et al., 2006). Occurrence of radon in bedrock aquifers, especially in granites, is a well-known water-quality issue in the northern United States (Ayotte et al., 2007) and the southeastern Appalachian region (Chapman et al., 2013).

3. METHODS FOR SAMPLING AND ANALYSIS

Samples were collected and analyzed for U isotopes (U-234, -235, and –238), short-term (within 48 hours) gross alpha-particle activity, isotopes of Ra (-224, -226, and -228), As species, Fe, Mn, and anions. Characterization of gross alpha-particle activity and concentrations of U and Ra in aquifers in northern NJ along with pH and Eh conditions and the concentrations of bicarbonate, sulfate, iron, and manganese (as possible indicators of oxidation-reduction potential and alkalinity; see Hem (1985) and McMahon and Chapelle, 2008) were critical in identifying aquifers geochemically vulnerable to U occurrence. Table 1 lists analytical methods. Details of approaches to sampling, sampling, analysis, data analysis, and QA specific to the study are provided.

3.1. Approach to sampling

Because the study is intended to supply basic information that might be useful for future monitoring and water-treatment efforts for limiting ingestion risk for potable water supplies, a broad variety of wells serving small water supplies were targeted for sampling, whether they be small public or non-transient non-community water suppliers, or private self-supply (domestic). Emphasis was given to sampling wells in a fashion to provide rough geographic distribution across the entire Highlands Province so that a typical pattern of radionuclide occurrence can be partly defined both geographically and geologically. For purposes of this study, sampling was focused on only three major rock types in the Highlands: granites, metamorphic rocks, and carbonate rocks (Fig. 1). Furthermore, for purposes of this study, sampling was focused on only two major rock types in the Piedmont: black shale representing organic-carbon-rich former lake bed deposits and red shale representing former sabkha and mudflat deposits. Sampling emphasis in the Piedmont Province was given to the south central part of the province where the black and red mudstone representing lake and sabkha deposits respectively are located (Fig. 1). Much of the northern and eastern part of the Province in New Jersey has either conglomeratic deposits or basalts, neither of which are known to contain radionuclides in substantive levels. Finally, the wells selected were known to have high levels of gross alpha particle activity or were near wells that had previously been shown to have radiological problems. A total of 40 wells were targeted for sampling in each Province, the NJ Highlands from 2007 to 2011, and the NJ Piedmont from 2009 to 2011.

3.2. Sample Collection

Water sampling was conducted using appropriate (USGS) “trace-element-clean” ground-water sampling techniques (U.S. Geological Survey, 2004). Sampling tubing (high-density polypropylene) is to be cleaned following a series of steps: an initial deionized water (DIW) rinse, soap-solution rinse, 1 percent nitric acid solution rinse, and a final DIW rinse flushing the tubing three times for twenty minutes. The high-density white polyethylene plumbing fittings, used to connect sample tubing to the sampling port of public-supply wells, will be cleaned before use by soaking overnight in a 1 percent nitric acid solution followed by copious DIW rinse.

Measurements of numerous characteristics including pH, Eh, and turbidity were conducted in the field during sampling. A flow-through chamber was used for monitoring field parameters except turbidity (U.S. Geological Survey, 2004). After one to three casing volumes are purged and all the monitored field parameters have stabilized, including turbidity; final measurements were recorded, then water sampling commenced.

3.3. Sample Analysis

Analysis consisted of uranium concentrations, uranium isotope ratios, radium isotopes, gross alpha-particle activity, radon-222 concentration, arsenic concentration and arsenic speciation, and analysis of ancillary constituents to more thoroughly characterize geochemical characteristics of the ground water. The analysis of U and U isotopes by ICP-MS was the technique of choice because it is quick and inexpensive, and analysis was completed using the methods of Kraemer et al. (2002). The analysis of U mass (as U238) by ICP-MS is already USEPA approved (USEPA Method 200.8). For isotopic determination, U radionuclides were separated from other possible radionuclides and purified using ion-exchange columns (strongly basic anion exchange medium in the Cl- form) and extraction of the sorbed U was with 10 mL of 0.1 N HCl followed by 20 mL of distilled water. The U-bearing extract was injected directly into the ICP/MS through an ultrasonic nebulizer. The instrument was tuned and calibrated by running a blank followed by an 80-*u*g/L solution of NIST 4321B (Natural Uranium) as a standard. A secondary standard calibrated against NIST 4321B was run after every third sample. When drift was found the instrument was re-standardized.

The gross alpha-particle activities in this study were analyzed by co-precipitation procedure (Parsa et al., 2004; USEPA, 1997, method 900.1) or planchet evaporation (Krieger and Whittaker, 1980; USEPA, 1997, method 900.0) with low-background alpha counting in a low-background gas-flow proportional alpha-beta detector no more than 48-72 hours after sample collection using the Th-230 calibration curve (Parsa, 1998; USEPA, 2000a). The count within 48-72 hours is used to determine gross alpha-particle activity in those areas where the presence of Ra-224 or other short-lived radionuclides in the sample are suspected to be present (USEPA, 2000b). The LRL for typical gross alpha-particle activity measurements with 100 min (minute) counting time is about 3 pCi/L. Individual SSMDCs were lower than the LRL because of the long counting times; samples were counted 16 hours overnight when possible. The individual SSMDCs were thus on the order of 1 to 1.5 pCi/L. Similarly precision estimates (pe's) were substantially smaller than is typical for the gross count with 100 min counting time, on the order of ± 10% as opposed to ± 30%. Both the LRL and the SSMDC for these gross measurements are still higher than that for the U mass and U isotope activity measurements because of the absence of sample purification steps for the gross activity measurement and because the analytical equipment (low background alpha-beta gas proportional counter) used is not as sensitive as either an alpha spectrometer or a mass spectrometer. The co-precipitation procedure provides slightly better results for samples with high dissolved solids, which were commonly encountered (Arndt, 2010).

Radium-isotope concentrations from the Highlands Region were determined by gamma-ray spectroscopy (Parsa et al., 2004, modified from Standard Method 7500-E (APHA, 2004)). Radium-isotope concentrations from the Piedmont Region were determined by alpha spectroscopy, radon de-emanation, and beta-counting, respectively, for Ra-224, Ra-226, and Ra-228, respectively (Sill et al., 1979; USEPA, 1997, methods 903.0 and 904.0). The SSMDC is generally somewhat higher with this technique than other alpha- or beta-particle counting techniques for these isotopes, and are also higher than those for the U isotopes determined by ICP-MS. The median SSMDCs were 0.85, 0.54, and 1.1 pCi/L for Ra-224, Ra-226, and Ra-228, respectively. Nevertheless, with the generally high gross alpha-particle activity, the gamma spectroscopy method was considered reasonably sensitive for the Ra isotope analysis for these generally strongly radioactive water samples. Where a negative result was obtained, it was recorded as the "raw" unrounded value in the database, though for non-parametric statistical applications, negative results were simply coded as equaling the "minimum" value for ranking purposes. For a detailed explanation of the derivation of negative results, the authors refer the reader to Troyer et al. (1991).

A portable RAD-7 (Durridge Co., Bedford, Mass.) alpha-spectrometer radon-in-air monitor was used to determine the Rn-222 concentrations in the water (Burnett and Dulaiova, 2003; Lee and Kim, 2006; Schubert et al., 2006). For detection with the RAD-7, the Rn-222 was stripped from water and was circulated via air in the alpha-spectrometer counting cell. A small portion of the Rn-222 decays nearly instantaneously to Po-218, which is electrostatically deposited onto the semiconductor-based alpha-particle detector. The detector specifically records the decay of the Po-218, which is easy to detect because it occurs at high energy (6.00 MeV; Burnett and Dulaiova, 2003), during a set time interval. A correction is made for the Bi-212 progeny, which has similar alpha energy. Because the Po-218 only has a 3-minute half-life, it too rapidly decays, allowing both detection of the Rn-222 and maintaining a low alpha background (avoiding high bias) because of the rapid decay rate.

Concentration levels of Rn-222 were pre-screened in the field for those wells where steady purging could be maintained for more than 20 minutes using continuous flow counting methods (Burnett and Dulaiova, 2003; Burnett et al., 2007). The water-air exchanger simply has a spray nozzle inside a PVC Water was pumped continuously through a narrow spray nozzle into a clear acrylic cylinder that served as the water-air exchanger and a stream of air was pumped through the water-air exchanger by the built-in air pump in the RAD-7. The pumped air was then forced through a PVC tube filled with desiccant (calcium sulfate) and then into the chamber housing the alpha-spectrometry counting unit in the RAD-7. After about 20 minutes of time, the radon progeny (Po-218) concentration in the air in the chamber reaches secular equilibrium with the radon concentration of the air that had been passing through the water, thereby reaching equilibrium with the radon in the water, with the ratio at equilibrium being determined by the water temperature. The detector records the same high energy decays of Po-218 and Po-214 as before, but continuously during the purging period as opposed to a fixed time interval.

The concentration of Rn-222 was also determined by the traditional liquid scintillation technique (Pritchard and Gesell, 1977) for a subset of samples with Rn-222 concentration results estimated in the field to be over 10,000 pCi/L. When concentrations exceed 10, 000 pCi/L for Rn-222, some high bias for the alpha spectroscopy method is possible because of overlapping alpha-energy peaks of the Po isotope progenies (Kiliari and Pashalidis, 2008), making comparison among results of the methods especially important in these radioactive waters.

Determination of the concentration and speciation of arsenic (As) was determined in this study using primarily the field-extraction technique of Garbarino et al. (2002), though for a small subset of samples, the laboratory-extraction technique was used. The sample was extracted and preserved in the field in order to avoid the laboratory preservation problems noted by Edwards et al. (1998). The chemical compound EDTA was added to the sample in an opaque bottle for preservation of As(III) species. The As(V) was extracted from the water sample onto an anion-sorbing resin cartridge in the field. The As(V) was extracted from the resin in the laboratory; typically using dilute sulfuric acid. Phosphate was the dominant component of the carrier solutions as the As-bearing aliquots were passed through a chromatography column, then analyzed immediately primarily by collision-cell ICP-MS (Garbarino et al., 2006), though routine ICP-MS was used for some samples with Cl correction.

The concentrations of ancillary constituents were critical in characterizing aquifers geochemically. Concentrations of sulfate, iron, manganese, nitrate, arsenic, dissolved oxygen, and bicarbonate, and pH were used as possible indicators of oxidation-reduction potential and alkalinity (Hem, 1985; McMahon and Chapelle, 2008). The samples were grouped geochemically on the basis of concentrations of these constituents.

3.4. Quality Assurance

Equipment-blank samples have routinely been collected in the past and have not shown measurable amounts of the Ra isotopes (though for Ra-228, this result is in part due to the high detection level (SSMDC)) (Szabo et al., 2005). The RPD (relative percent difference) of the concentration between the environmental samples and the corresponding replicate samples were equal to the less than the analytical error (pe) for each Ra isotope. The maximum RPD (relative percent difference) of the concentration between the environmental samples and the corresponding replicate samples for U mass determination was 7.02%. The large analytical error (pe) typical for Ra analysis, especially for the Ra-228 concentrations, resulted in the acceptability of even relatively large RPD for Ra analysis (as compared to most other inorganic constituents analyzed). Except for one sample, all the remaining RPDs were less than 5 %. Results for the duplicate analyses illustrate how the imprecise analysis poses a limit to the characterization of the natural concentration distribution of Ra in the environment, including ground water.

3.5. Statistical Analysis

Correlations among Ra radionuclides and other constituents were calculated using the Spearman correlation coefficient (correlation of the ranks of the data, not the actual values), which is a measure of the degree to which the two data sets increase (or decrease) together. For a small number of Ra analyses, mostly but not exclusively for Ra-228, a negative value was reported; these were set equal to the same lowest ranked value that represented concentrations less than the SSMDC. Group-comparison tests such as the Wilcoxon and Kruskal-Wallis tests were used to determine whether Ra isotope concentration distributions from two or more groups were significantly different (Helsel and Hirsch, 1992). The Tukey-Kramer test was used on the ranks of the data to identify which group means were significantly different relative to other groups (Helsel and Hirsch, 1992).

3.6. Computations of Alpha-Particle Activities from Uranium

To determine compliance with the gross alpha-particle activity MCL, the total U activity (all isotopes of naturally occurring U emit alpha particles) is subtracted from the measured gross alpha activity, resulting in the “adjusted” gross alpha activity used to determine compliance with the standard (USEPA, 2000a). The “adjustment” for the emitted alpha-particle radioactivity of the U may be computed in differing ways depending upon the information available. The difference between gross alpha-particle activity and total U was computed by two separate techniques. First, the total U (mass) was converted to a calculated alpha radioactivity based on the assumed U isotope activity ratio of 1, or that of “natural” U.

Second, the total U (mass) was converted to a calculated alpha radioactivity based on the actual measured U isotope mass ratio (U-234/U-238) as determined by ICP-MS and was verified in a few instances by alpha spectroscopy. From the actual measured U isotope mass ratio, the actual U isotope activity ratio and the actual alpha radioactivity emitted by the U isotopes could be determined.

The USEPA does allow for the conversion from U mass to U alpha activity directly using the single factor of: 0.672 pCi/ug of measured U mass reported in ug/L concentration units to obtain "activity". The use of this single factor, known as the "natural" U conversion factor (CF_n) assumes that the U in solution is in fact "natural U" where the shorter lived U-234 progeny of the longer lived U-238 parent isotope are in secular equilibrium, that is, the radioactivity of both are equal (1:1 activity ratio). The assumption of secular (radioactive-decay-based) equilibrium for "natural U" is presumed on the basis that U234:U238 activity (and thereby mass) ratios are fixed because the bulk of the U has been isolated within mineral grains from dispersive processes for the hundreds of thousands of years required for the U-234 to reach the secular equilibrium with the U-238.

If the actual water sample has a measured U234:U238 activity ratio, then the measured conversion factor (CF) can be calculated as an actual value, and not just assigned the constant value. The CF is defined in terms of the measured U234:U238 isotope activity ratio as:

$$CF = 0.336(1 + (A, U234/A, U238))$$

where CF is the conversion factor, and the U isotope activity ratio is defined by (A, U234/A, U238). With use of the CF, the calculated activity is an actual value, and not an assumed value assigned on the basis of a "constant". In general, the principle of secular equilibrium does not hold for most ground water where advection predominates because dispersive processes (dissolution/desorption/recoil) all can occur on the flow path on the micro-second scale of time (Krisnashwami et al., 1991) thereby preventing the U isotopes from reaching secular equilibrium. In addition, the process of recoil releases U234 isotopes directly to pore spaces (water filled) at an enhanced rate relative to dissolution alone for the U238 isotope (Fleischer, 1980; Osmond and Cowart, 1976), resulting in "excess" U234 in most ground waters relative to the U238. For natural water samples with high U concentrations (at or near the U mass MCL of 30 ug/L) and highly variable U isotope ratios, this calculation ("adjustment") can result in one of the largest uncertainties as to whether or not a sample is indeed in compliance or non-compliance with the 15 pCi/L gross alpha-particle activity MCL. Therefore, computation and comparison of results for actual samples using both techniques was a vital evaluation for assessing the importance of actually measuring the U isotope activity ratio.

4. RADIONUCLIDE OCCURRENCE AND OCCURRENCE OF ANCILLARY CONSTITUENTS

4.1. Highlands

The collected water-quality data from the 40 wells sampled in the NJ Highlands indicates that the occurrence of radionuclides is an important issue for ground water in the Highland Physiographic Province, especially the occurrence of uranium. A statistical description of the population characteristics for the water quality results are provided in Table 2. The most important items of the occurrence data are summarized below.

Water from 14 (35%) of 40 wells exceeded the (uncorrected) gross alpha standard of 15 pCi/L (picocuries per liter), and 10 (25%) of samples exceeded or equaled an activity of 20.0 pCi/L. The median gross alpha-particle activity was 8.1 pCi/L and the maximum value was 232 pCi/L. (The well with the maximum value has been re-sampled outside the time frame of this study and has had activities as high as about 500 pCi/L.)

Uranium appears to be the predominant source of gross alpha-particle activity in water sampled in the NJ Highlands. Water from 8 (20%) of the 40 wells exceeded the Uranium MCL of 30 ug/L (micrograms per liter), with 5 (12.5%) samples exceeding 60 ug/L, and 3 (7.5%) samples exceeding 100 ug/L, and fully 25% (10) of the samples equaled or exceeded 20 ug/L. The median value of U concentration was 5.8 ug/L, and the maximum value was 623 ug/L. Uranium-238 is the only isotope whose concentration is determined with the mass (ICP-MS) measurement of U concentration. Analyses of U isotope activity ratios indicate U-234 isotope is present in excess relative to U-238 in all but 2 of 33 samples from the NJ Highlands in which it was measured. The excess U-234 isotope can cause an increase in gross alpha-particle activity above that expected from “natural” U for which the activity ratio is 1:1. In 18% (6 of 33) of the samples for which the ratio was determined, Uranium-234 isotope activity was more than double the U-238 isotope activity, and in 25 % of the samples, the U isotope activity ratios were greater than 1.84, with the maximum U isotope activity ratio of 2.95. The median value of the U isotope activity ratio was 1.36. In 82 percent of the samples the U isotope activity ratio was greater than 1.2, the global median groundwater uranium isotope activity ratio reported by Osmond and Cowart (1968).

Concentrations of combined Ra (Ra-226+Ra-228) in water from 3 wells exceeded the MCL of 5 pCi/L, and concentration in water from a fourth well was 3.3 pCi/L, though concentrations in water from the remaining 36 wells did not exceed 3 pCi/L. At least one isotope of radium was detectable in 17 of 40 wells. Most frequently detected was Ra-226 (17 times), and it was present in the maximum concentration (17.43 pCi/L). Samples collected in areas underlain by uranium-rich felsic granites, granite gneisses, and marbles in the Highlands generally had concentrations of radium-226 that were substantially higher than the associated concentrations of radium-228, consistent with the notion of uranium enrichment relative to thorium in these rock types, both in unweathered minerals, but especially along the surface of weathered minerals and fracture faces, and hence there was a plentiful source of radium-226.

Samples from 13 (36%) of the 36 wells that had levels of Rn-222 determined greater than 10,000 pCi/L, 23 (64%) had concentrations > 4000 pCi/L, the proposed USEPA AMCL, and 32 (89%) had concentrations > 800 pCi/L, the 20th percentile of the proposed USEPA AMCL. Only 1 sample had a concentration <300 pCi/L, the proposed USEPA MCL. The median concentration was 6700 pCi/L.

The concentrations of additional ancillary constituents were critical in characterizing potable quality of water from the aquifers as well as defining the geochemical environment. Water from 2 wells exceeded the NJ arsenic MCL of 5ug/l (NJDEP, 2002b) (maximum, 14.9 ug/L, all as arsenate). Only one well had water in which both inorganic species of arsenic were detected and the arsenite concentration was considerably greater than the arsenate; this water sample also had the lowest uranium concentration (<0.04 ug/L), the highest manganese concentration (445 ug/L) and the second highest iron concentration (500 ug/L) among the samples from the NJ Highlands, and also had low concentration of dissolved oxygen (0.68 mg/L). Water from 6 wells had detections for total coliform, and 1 had detection for fecal coliform, consistent with the results of Atherholt et al. (2013) that indicate coliform bacteria are commonly detected in this region. Water from 21 (53%) wells had nitrate concentration greater than 1 mg/L, though only 23 percent of the samples had a nitrate concentration greater than 3 mg/L, with the maximum value of 6.86 mg/L. Concentrations of ammonia were infrequently detected (7 of 40, or 17.5%). Water samples from 3 wells had chloride concentration that exceeded the 250 mg/L secondary standard, and the median and 3rd quartile concentrations were also high, 73 and 140 mg/L, respectively. Water samples from 7 wells exceeded the 50 ug/L secondary standard for manganese, and 3 exceeded the secondary standard of 300 ug/L for iron, though 2 of these 3 samples were turbid (turbidity was greater than 5 NTUs (Nephelometric Turbidity Units)) indicating that some iron may have passed the filters used during sampling in colloidal form.

4.2. Piedmont

The collected water-quality data from the 40 wells sampled in the NJ Piedmont (Mesozoic Basin) indicates that the occurrence of radionuclides is an important issue for ground water in this Province of New Jersey as well, especially the occurrence of radium (Ra-226 radionuclide most specifically). A statistical description of the population characteristics for the water quality results are provided in Table 2. The most important items of the occurrence data are summarized below.

Water from 13 (33%) of 39 wells exceeded the (uncorrected) gross alpha standard of 15 pCi/L, and 25 % of samples exceeded or equaled an activity of 20.0 pCi/L (analysis was not completed from 1 sample). The median gross alpha-particle activity was 5.6 pCi/L and the maximum value was 225 pCi/L.Water from 3 (7.5%) of the 40 wells exceeded the Uranium MCL of 30 ug/L, with 1 sample exceeding 100 ug/L (maximum, 225 ug/L). The median value of U concentration was 3.03 ug/L, and the 3rd quartile value was 6.87 ug/L, or about equal to the median for the NJ Highlands Province. Analyses of U isotope activity ratios indicate U-234 isotope is present in excess relative to U-238 in all but 1 sample. In 60% (18 of 30) of the samples for which the ratio was determined, U-234 isotope activity was more than double the U-238 isotope activity, and 25 % were greater than 3.42, with the maximum U isotope activity ratio of 8.45. The median value of the U isotope activity ratio was 2.19. In 93 percent of the samples the U isotope activity ratio was greater than 1.19. The well with the maximum activity ratio was re-sampled and the same high activity value was measured again. Finally, re-analysis with alpha spectrometry matched the ratio determined with mass spectrometry.

Concentrations of combined Ra (Ra-226+Ra-228) in samples of water from 8 (20.5%) wells exceeded the MCL of 5 pCi/L, and in 7 of the 8 samples, the concentration of Ra-226 was greater than the 5 pCi/L by itself. At least one isotope of radium was detectable in all but 1 of the wells; the most frequently detected isotope was Ra-226. Detections of concentrations of Ra-226 greater than or equal to 0.3 pCi/L were measured in 24 of the 39 samples (61.5%) for which the analysis was completed. The Ra-226 isotope was present in higher concentrations than the Ra-224 and Ra-228 in all but 2 samples and the Ra-226 to Ra-228 ratio on occasion was greater than 5:1, with a maximum ratio of 28. The maximum Ra-226 concentration was 51.1 pCi/L, and 25% of the samples exceeded a concentration of 1.2 pCi/L, but the median was only 0.43 pCi/L. Only in 1 sample for which the Ra-226 concentration was less than 1 pCi/L was the concentration of Ra-224 and Ra-228 greater than 1 pCi/L. Samples collected in areas underlain by organic-carbon-rich siltstone and mudstone in the Early Mesozoic basin aquifers generally had concentrations of radium-226 that were substantially higher than the associated concentrations of radium-228, consistent with the notion of uranium enrichment relative to thorium in these organic-carbon-rich sedimentary rock types, and hence the plentiful source of radium-226.Samples from 4 (28%)

of the 14 wells that had levels of Rn-222 determined were greater than 10,000 pCi/L, 6 (43%) had concentrations > 4000 pCi/L, the proposed USEPA AMCL, and all but 1 (93%) had concentrations > 800 pCi/L, the 20th percentile of the proposed USEPA AMCL. Only 1 sample had a concentration <300 pCi/L. The median concentration was 3340 pCi/L, as with U, almost exactly half that in the water samples from the NJ Highlands.

The concentrations of additional ancillary constituents were critical in characterizing potable quality of water from the aquifers as well as defining the geochemical environment. Water from 15 (37.5%) wells exceeded the NJ arsenic MCL of 5ug/L (NJDEP, 2002b) (maximum, 24.7 ug/L) and 5 exceeded the USEPA arsenic MCL of 10 ug/L. The median arsenic concentration was 2.8 ug/L and 25% of samples exceeded a concentration of 7 ug/L. Only three wells had water in which the concentration of arsenite was considerably greater than that of arsenate, however, and the two inorganic species were present in equal amounts in 1 other sample; all 4 of these samples had concentrations of manganese and iron greater than 50 ug/L, and all had non-detectable dissolved oxygen concentration (<0.1 mg/L). The highest manganese concentration was 738 ug/L) and the highest iron concentration was 3750 ug/L; 12 samples exceeded the 50 ug/L secondary standard for manganese, and 4 exceeded the secondary standard of 300 ug/L for iron. Low concentrations of dissolved oxygen (anoxic conditions) were almost equally prevalent with more oxic conditions; 17 (43.5%) samples had DO concentration less than 1 mg/L, and the median value was 1.3 mg/L. Water from 21 wells had nitrate concentration greater than 1 mg/L, though only 25 percent of the samples had a nitrate concentration greater than 2.5 mg/L, and only 10 percent of the samples had a concentration greater than 3 mg/L, with the maximum concentration of 5.6 mg/L. In contrast with the more oxic waters of the NJ Highlands where concentrations of ammonia were infrequently detected, in water from the NJ Piedmont, ammonia was detected in 35% of the samples (14 of 40). Water from 3 wells had chloride concentration that exceeded the 250 mg/L secondary standard, but the median and 3rd quartile concentrations, 41 and 81 mg/L, respectively, were not as high as in the NJ Highlands (Table 2).

5. DISCUSSION AND IMPLICATIONS

The water-quality results indicate that elevated gross alpha-particle activity and elevated concentrations of radionuclides are a potential health-risk issue for residents using ground water from the bedrock aquifers in northern New Jersey, including in both the NJ Highland and Piedmont (Mesozoic Basin) Physiographic Province, with 27 (33.8%) of 80 samples having measured gross alpha-particle activity greater than 15 pCi/L. A general pattern of radionuclide occurrence with respect to U and Ra can be partly defined based on geology and geochemistry of these regions. Excess U-234 isotope was present in most samples and can cause an increase in gross alpha-particle activity above that expected from the chemically determined U mass in presumed secular equilibrium. A general pattern of occurrence of considerably greater uranium isotope activity ratios was defined for the Piedmont Province.

5.1.Geochemical Comparisons by Region

The physicochemical properties (oxidation-reduction potential, dissolved oxygen concentration, pH, specific conductance, alkalinity, turbidity, and residue on evaporation [ROE, dissolved solids]) measured in groundwater sampled from all 80 wells varied considerably for some of the constituents resulting in considerable differences in geochemical environments (table 2). Among the most noticeable was the considerable difference in dissolved oxygen concentration among the Highlands and Piedmont Provinces, with the median value almost 5-fold higher in the Highlands than in the Piedmont, and nearly half (43.5%) the samples collected from the Piedmont having DO less than or equal to 1 mg/L, classified as “anoxic” for purposes of this study, whereas only 16 percent of the samples from the Highlands fit this description. Most wells sampled from the Piedmont Early Mesozoic basin siliciclastic-rock aquifers had groundwater that was classified as hard (calcium carbonate equivalent 150 to 300 mg/L) and alkaline, with median pH of 7.6, and very few samples having pH less than 7.0. Samples of water from the crystalline-rock aquifers from the Highlands frequently were bimodal with respect to pH and hardness, about half characterized as hard and alkaline (pH greater than 7.0) and about half characterized as soft and mildly to moderate acidic having pH values less than 6.5. The median pH was 7.0, with range from 5.2 to 7.9. The pH, alkalinity, and hardness was especially bimodal for the water samples from the granites. Among the granites, water with low pH was more common than from among other rock types.

5.2.1. Relations among Radionuclides and Gross Alpha Particle Activity

The conventional measurements of the general amount of radioactivity in the water, such as measurements of gross alpha-particle activity, did reliably indicate the presence elevated concentration of one or more radionuclide, but gave no further information for identifying specifically which radionuclides were present, and whether radionuclide concentrations might exceed the combined radium MCL or the uranium MCL. The identity of which of these nuclides is predominant and contributes the most to the radioactivity of the water sample cannot be established on the basis of the gross alpha-particle activity measurement alone. Additional information was gained by directly measuring the concentrations of the most likely of these radionuclides to be present in considerable concentrations.

The radionuclide concentrations in this study indicate that in the waters from the northern New Jersey bedrock area, where the gross alpha-particle activity is high, U is likely (though not exclusively) to be the source. Of the 11 samples with the highest measured (uncorrected) gross alpha-particle activities, (all over 60 pCi/L), 7 had among the highest uranium concentrations, with these 7 samples having uranium concentrations greater than the 30 ug/L MCL. Of the water samples from the 14 wells from the NJ Highlands that exceeded the (uncorrected) gross alpha standard of 15 pCi/L, 8 (57%) contained U in concentrations greater than the 30 ug/L MCL and 3 more had U concentrations equal to or greater than 17.5 ug/L (79%, or 11 of these samples had considerable U). Seven of the samples also had detectable Ra-226 and/or Ra-224 concentration, but only 1 sample had a concentration of Ra-226 that exceeded 5 pCi/L. Of the 13 wells from the NJ Piedmont that exceeded the (uncorrected) gross alpha standard of 15 pCi/L, 3 (23%) contained U in concentrations greater than the 30 ug/L MCL and 3 more had U concentrations equal to or greater than 11.5 ug/L (46%, or 6 of these samples had considerable U). Seven of the samples had concentrations of Ra-226 in excess of 5 pCi/L, and 3 more had Ra-226 concentration in excess of the median value of 1.3 pCi/L. Additional information from chemical surrogates suggestive of specific occurrence of one or the other of these radioelements were further investigated.

5.1.1. Relations among Concentrations of Uranium, Radium, Dissolved Oxygen, Manganese, and Iron

The U is somewhat more likely to be the source of the gross alpha-particle activity in the NJ Highlands than the NJ Piedmont province primarily because of the difference in geochemistry among the two regions. The U is most likely to be the predominant to exclusive source of the alpha radiation present when the water is at or near saturation with oxygen (>8 mg/L), as Ra-226 was virtually never detected in the most oxic water (fig. 2a). This condition is most often met in the crystalline rocks (granites, gneisses, marbles –all generally organic-carbon poor) of the Highlands. When consumption of DO was noted and the samples were not near saturation with oxygen (dissolved oxygen concentration ranging from 1-6 mg/L, with most of these concentrations ranging between 1 and 4 mg/L in the Highlands), radium-226 was detected somewhat more commonly (fig. 2a). Radium-226, when detected in concentration of 1 pCi/L or greater, was in all but one case in water that was anoxic/reducing (concentration of DO less than 1 mg/L; fig 3a). When low DO was noted in the Highlands, then there was a substantial likelihood that at least one Ra isotope concentration was detectable or on occasion elevated (fig. 2a).

In the occasionally organic-carbon rich sedimentary rocks of the NJ Piedmont (Mesozoic Basin), the alpha activity in water samples is likely from a combination of the presence of isotopes of U and Ra, especially in water that is either anoxic (DO less than or equal to 1 mg/L) or at least is well below saturation with DO (1-4 mg/L), because Ra was commonly detected in those waters (Fig. 2b). The elevated (> 2 pCi/L) concentrations of Ra isotopes were especially common when DO concentrations were less than 1 mg/L (Fig. 3b). The nearly hyperbolic trend among the concentrations of radium and dissolved oxygen observed especially in the Piedmont is a consistent and strongly definable trend (fig. 3b), and to a lesser degree is also notable in the samples from the Highlands crystalline-rock aquifers (fig. 3a). Of the 9 samples in the northern bedrock region of NJ in which the Ra-226 concentration exceeded the level of 5 pCi/L, 7 samples had DO concentrations less than 0.5 mg/L (fig. 3), and the maximum concentration was 2.3 mg/L. Conversely, Ra-226 was generally not detected, and when detected did not exceed a concentration of 1 pCi/L, in all but 1 collected samples of water that were saturated or nearly saturated with DO (concentration of DO greater than 4 mg/L; fig. 2b).

The presence of elevated concentrations of Fe and Mn generally corresponded to the lowest DO and highest Ra concentrations in waters from especially the Piedmont bedrock aquifers, and to a lesser extent, from the Highlands aquifers. Elevated concentrations of Fe and/(or) Mn were present in almost all the ground-water samples that had detectable Ra-226 concentrations greater than 1 pCi/L in the NJ Piedmont; in those Ra-rich samples, concentrations of Mn were as high as 738 ug/L and were detected in every sample, and concentrations of Fe were as high as 3,750 ug/L, and were detected in all but 3 samples. Ra concentrations corresponded most strongly with the concentrations of Mn, especially in the Piedmont (fig. 4), though correspondence with Fe was nearly as strong. Elevated concentrations of Fe and/(or) Mn were present in almost all the ground-water samples that had detectable Ra-226 concentrations greater than 1 pCi/L in the NJ Highlands also; in those Ra-rich samples, concentrations of Mn were as high as 165 ug/L, and were detected in every sample (more than half with concentrations greater than 50 ug/L), and concentrations of Fe were also as high as 2056 ug/L, and were similarly detected in all the samples, though exhibited greater variability in concentration than Mn. Of the 9 samples in the northern bedrock region of NJ in which the Ra-226 exceeded the level of 5 pCi/L, 7 samples had concentrations of Mn greater than 50 ug/L and 5 samples had concentrations of Fe greater than or equal to 250 ug/L.

The correspondence of Ra occurrence with low to moderate levels of DO is indicative of ongoing geochemical process that mobilizes Ra in reducing waters. The presence of elevated concentrations of Fe and Mn can be representative of anoxic Fe- and Mn-reducing environments and they reasonably correspond to the lowest DO and highest Ra in waters from the Highlands, and even more so, the Piedmont, aquifers. Desorption or release of Ra from Fe- and Mn-hydroxides driven by "reductive dissolution" of those amorphous solids, or lack of adsorption to these hydroxides in the first place, is considered a critical mechanism that explains the presence or absence of Ra in many aquifers (Landa et al., 1991; Szabo et al., 2012). Ra in the natural environment is present only as the moderately sorbed Ra^{+2} cation that does not form ion-pair associations with other anions across the range of most naturally occurring pH (Langmuir and Riese, 1985), and does not undergo redox transformations, indicating the relation with anoxic conditions is controlled by the chemistry of the sorbent materials. Laboratory studies have shown that while Ra was adsorbed by all the secondary minerals typically found in aquifers, amorphous Fe hydroxides and Mn oxides adsorbed far more Ra than any of the clay minerals (Ames et al., 1983; Moore, 1976), but these oxides in turn dissolve in anoxic conditions. High concentrations of divalent calcium and magnesium compete with the Ra for sorption/exchange sites, and in anoxic conditions with the dissolution of these oxides, the number of these sorption sites are diminished (Szabo et al., 2012).

The concentrations of U were typically higher in waters that contained abundant DO (Fig. 5) and concentrations of Mn and Fe were less than 50 ug/L, especially in the Highlands Province where the above conditions held in all but 2 cases. To a lesser extent, the same was true in the Piedmont, though evidence was more abundant there that waters of different redox characteristics were mixed in wells, and U was on occasion detected in waters with low DO (fig. 5). With respect to geochemical characteristics representing redox conditions, Ra exhibited occurrence opposite that of U in especially the Piedmont Province (Fig. 6), but also in the Highlands Province. The exceptions were where mixing of waters with different redox conditions were indicated, and where gross alpha-particle activity was greater than 100 pCi/L indicating strongly radioactive source rock with such an abundance of radionuclides that conceivably the available sorption sites were overwhelmed.

The anoxic conditions appeared to be strongly indicative of the occurrence for radium occurrence. A suite of indicators of anoxia were useful as geochemical “surrogates” for radium occurrence at concentrations of concern. The surrogates considered for evaluation of anoxia were the following: DO, less than or equal to 1 mg/L; iron and manganese concentrations greater than or equal to 50 ug/L; and ammonia concentrations greater than or equal to 0.02 mg/L. A boxplot (Fig. 7) of Ra-226 concentrations by groupings of the surrogate redox classes shows the importance of dissolution of iron and manganese amorphous oxide grain coatings for Ra occurrence. The median concentration of Ra-226 for the group for which concentrations of either iron or manganese or both is equal to or greater than 50 ug/L (iron and manganese reducing class) is about 0.9 pCi/L. The strongest likelihood that Ra concentrations of concern, 2.5 pCi/L (or half the MCL value for combined Ra), was found in the subset of samples that met all the redox criteria. For the remaining two groups (suboxic and oxic, defined below) the median is less than half that for the most anoxic group, about 0.4 and 0.3 pCi/L, respectively. These remaining two groups might be defined as suboxic and/or nitrate reducing class, with concentrations of DO less than 1 mg/L and concentrations of ammonia greater than 0.02 mg/L, and oxic class, with concentrations of DO greater than 1mg/L. More importantly, while about 25 percent of samples from the iron and manganese reducing class has Ra-226 concentrations of 10 pCi/L or greater, less than 10 percent of the samples have concentrations greater than 2 pCi/L in the other two classes of samples. This information indicates the importance of redox surrogates, specifically iron and manganese concentration, for identifying the likely presence of the elevated concentrations of Ra in these bedrock aquifer systems. This information points to the importance of low DO (less than 1 mg/L), but also points out that the water needs to be reducing enough to reduce and dissolve iron and manganese in amorphous oxide grain coatings that are likely the main sorbents for the Ra, thereby diminishing the Ra retention capacity of the aquifer materials. It must be noted however that even for samples for which these surrogate indicators were present, half contained less than 1 pCi/L of Ra-226, and conversely, each of the more oxic classes had 1 sample for which the Ra-226 concentration was greater than 1 pCi/L. The presence of iron and manganese is a useful tool to indicate the much higher likelihood of the presence of elevated concentration of Ra, but is not definitive in all cases. Low or high values of Ra were possible even when all the geochemical criteria were met. It can generally be stated that the manganese- and iron-reducing geochemical environments are overall favorable for Ra mobilization and elevated occurrence in these aquifer system in northern New Jersey. Similar results have been noted in many aquifer types around the United States (Gilkeson and Cowart, 1987; Herczeg et al., 1991; Szabo et al., 2012).

5.1.2. Relations among pH and Concentrations of Uranium and Arsenic

Uranium in the Highlands crystalline-rock aquifers and Piedmont (Mesozoic basin) aquifers occurs most commonly in groundwater with oxic geochemical conditions that has somewhat alkaline values for pH, higher than about 7.3. The highest U concentrations in both Provinces were in the most alkaline (highest pH) waters (Fig. 8) and correlated positively with pH and alkalinity. Of the water samples from the Highlands crystalline-rock aquifers with the highest U concentrations (14 samples with concentration > 15 µg/L), the median pH was 7.4 in contrast to the median of 7.0 for the entire data set, and 64 percent (9) had pH values greater than or equal to 7.3, whereas only 21 percent (3) had pH values ranging from 6.2 to 6.8. In the grouping of samples in which the concentrations of uranium exceeded 30 µg/L, 75 percent (6 of 8) had pH values that were greater than or equal to 7.45. Conversely, in samples where uranium concentrations were low (less than 1 µg/L), the samples were overwhelmingly acidic, with pH less than 7.0 in all but 3, and having a median value of 6.2 and a minimum of 5.2. The uranium concentration distribution was somewhat bimodal for the water samples from the crystalline-rock aquifers of the Highlands on the basis of pH, especially among the granites. Among granites, when waters had low pH, the uranium concentrations were much less than when the pH was neutral or slightly alkaline. The highest uranium concentrations in water in the Highlands, 623 and 117 µg/L, were detected from granite and granite-gneiss, respectively; the associated pH values of 7.8 and 7.0, respectively, were relatively high for the granites and granite-gneisses. Among Despite the fact that in the Highlands Province, the metamorphic rocks, the interbedded marbles and gneisses of sedimentary origin contained less U than the granites (Duval and Riggle, 1999), generally waters from among these bedrock units had among the highest individual uranium concentrations and generally also had the highest associated values of pH. Uranium in the Piedmont (Mesozoic basin) aquifers occurred most commonly in ground waters that had the higher values of pH (greater than or equal to 7.4; fig. 7b) and oxic geochemical conditions. In the Piedmont, the large majority of samples had neutral to alkaline pH because of the considerable amount of calcite dispersed in these rocks. The median pH was 7.6, considerably higher than the 7.0 reported for the Highlands (Table 2). For samples where uranium concentrations were low (less than 1 µg/L), the median sample pH was lower (7.0) than even the first quartile value (7.15) for the entire Piedmont data set. The observed high concentrations of U in association with pH values of about 7.3 and above are consistent with the similar association observed for the Highlands in this study as well as observed for water samples from crystalline-rock aquifers throughout the Appalachian Piedmont and Blue Ridge Provinces from Georgia to New Jersey by Chapman and others (2013).

The correspondence between U concentrations and pH in the groundwater is not surprising because of the important role pH and alkalinity play in the formation of carbonate and bicarbonate soluble ion pairs (carbonate complexation) resulting in geochemical mobilization of U. Uranium tends to be most mobile only as the oxidized U(VI) specie as soluble phosphate and carbonate ion pairs (complexes) (Langmuir, 1978). Whereas U strongly sorbs to Fe-hydroxides, laboratory experiments have shown that U is readily desorbed from the Fe hydroxides in the presence of carbonate alkalinity (Hsi and Langmuir, 1985; Echevarria et al., 2001). In field studies, Curtis et al. (2004) measured increasing U desorption from Fe-hydroxide coated sand that was progressively brought into contact with natural waters bearing increasing amounts of carbonate alkalinity.

Uranium concentrations were positively correlated with pH and concentrations of alkalinity, but also specific conductance, and concentrations of calcium, and the trace element, arsenic (As). Higher concentrations (greater than the respective median values) of U and As tend to associate in water with pH that were greater than about 7.3. Uranium and arsenic, and additional trace elements including boron, vanadium, and molybdenum, all form oxyanions (neutral to negatively charged anion pairs or complexes) (Hodge and others, 1998) that tend to be most mobile in alkaline environments.

Of the water samples from the Highlands rock aquifers with the highest As concentrations (6 samples with > 0.65 µg/L), 67 percent (4) had pH values greater than or equal to 7.3, and an additional sample had pH 7.2 (fig. 9a). The highest As concentrations in water in the Highlands, 14.9 and 7.1 µg/L, were detected from granite and granite-gneiss, respectively, with pH 7.8 and 7.4, respectively, and were the only 2 samples (of 39) to exceed the promulgated final standard for As in New Jersey of 5 ug/L (NJDEP, 2002). Conversely, in samples with As concentrations that were lowest (less than 0.3 µg/L), the samples were generally acidic, with median pH 6.6, and if only the samples where As was not detected (less than or equal to 0.06 µg/L) were considered, the median pH was 5.8. In the grouping of the 14 samples with the highest concentrations of U (greater than 15 µg/L), 86 percent (12) had detectable As concentrations, including the 2 highest values. -. In contrast, in the grouping of the 13 samples with the lowest concentrations of U (less than 1 µg/L), 23 percent (3) had detectable As concentrations. For the 15 samples (of 40, 37.5%) with the highest As concentrations in the Piedmont aquifers were in excess of the standard for As in New Jersey of 5 ug/L, they occurred in groundwaters that had the highest values of pH (all but 2 had pH values greater than or equal to 7.5; fig. 9b). For samples where As concentrations were lowest (less than 1 µg/L), the median sample pH of 7.25 was about equal to the first quartile for the entire data set (7.15). There was general correspondence of the highest concentrations of As and U as well as for the lowest concentrations.

Unlike many other trace elements, arsenic can be highly mobile in both oxic (arsenate, arsenic (V)) and reduced (arsenite, arsenic (III)) specie (Cherry and others, 1979; Masschelyn et al., 1991; Dixit and Herring, 2003). Both inorganic As species were detected. Arsenate (As(V)) was the most prevalent species of As, especially so in the more oxic waters of the Highlands Province (detected in 18 samples as opposed to in 4 samples for As(III)), and was also most prevalent in the Piedmont Province (detected in 29 samples as opposed to in 12 samples for arsenite (As(III)). In all but 11 samples with detections for arsenic species, however, either the reduced arsenite (As(III)) or the oxidized arsenate (As(V)) specie comprised all the arsenic present, and of the 11, the two species were present in nearly equal amounts in only 7 samples, mostly in the Piedmont. Arsenite (As(III)) was the most prevalent species of As in the water and exceeded a concentration of 1 ug/L from 5 samples from the black mudstones in the NJ Piedmont and all but one of these samples contained concentrations of manganese and iron greater than 50 ug/L and concentrations of DO less than 0.5 mg/L in all but one. The As(III) specie (not total As) concentration was greater than or equal to 1 ug/L only when all the redox surrogates indicating anoxia to the level of at least iron reduction (McMahon and Chappelle, 2008); As is desorbed from iron hydroxides and reduced (Masschelyn et al., 1991; Bowell, 1994). Thus the presence of the As(III) specie concentration greater than 1 ug/L in the Piedmont might be an indicator of water anoxic enough to have an increased likelihood of containing elevated amounts of Ra, though Fe and Mn occurrence is more commonplace and is less costly to determine. Detectable (>0.8ug/L) concentrations of arsenate was associated primarily with oxic water where DO was readily measurable in concentrations greater than 0.5 mg/L and pH was high (Fig. 9), prompting desorption (Jain and Loeppert, 2000).

Approximately 90 percent of the groundwater samples from the Highlands and 80 percent of the samples from the Piedmont had radon-222 concentrations that were greater than the proposed maximum contaminant level of 300 pCi/L. The maximum radon concentration was 138,000 pCi/L in a water sample from felsic granite in one of several large felsic intrusive complexes. Six of the seven wells with the highest radon concentrations, all greater than 10,000 pCi/L, were from granite. Radon concentrations were moderately correlated with those of U in the Highland crystalline-rock aquifers (Fig. 9a). The waters from the Piedmont (Mesozoic Basin) had a high median value for radon also, about 3,300 pCi/L, but radon concentrations did not correlate with those of U (fig. 9b). A favorable geochemical environment (with high pH and high concentrations of bicarbonate alkalinity and DO) is critical for mobilizing uranium, whereas radon is readily soluble in any type of water (either acidic or alkaline; oxic or anoxic) (Vinson et al., 2009; Chapman et al., 2013); hence the lack of correlation between radon and uranium concentrations, especially in the Piedmont, where anoxic conditions were common.

5.3. Excess 234U as a component of measured gross alpha particle activity

To determine compliance with the gross alpha-particle activity MCL, the total U activity (all isotopes of naturally occurring U emit alpha particles) is subtracted from the measured gross alpha activity, resulting in the "adjusted" gross alpha activity used to determine compliance with the standard (USEPA, 2000a). For natural water samples with high U concentrations (at or near the U mass MCL of 30 ug/L) and highly variable U isotope ratios, this calculation ("adjustment") can result in one of the largest uncertainties as to whether or not a sample is indeed in compliance or non-compliance with the 15 pCi/L gross alpha-particle activity MCL.

Because the half-life of U-234 is much shorter than that of U-238, and thereby its rate of radioactive decay is much greater (by nearly a factor of 10^4), an infinitesimal mass of "excess" U-234 can result in a substantial increase in the net amount of alpha-particle activity emitted by the mass of U in the sample. Most techniques of the mass measurement are only capable of measuring the mass of the U238 isotope, which provides 99.274 % of the overall mass of natural U.

The implication of the presence of a small "excess" U234 isotope is provided in an example. The details are provided in Table 3. A hypothetical sample has measured gross alpha-particle activity of 25 pCi/L and U mass of 12.5 ug/L. Using the assumed "natural U" conversion factor of 0.672 pCi/ug/L, a value of 8.4 pCi/L of gross alpha-particle activity originating from U is calculated, then by subtraction from the measured gross alpha-particle activity, a net 16.6 pCi/L is determined to be present from presumed radioisotope sources other than U. This result indicates the "adjusted" gross alpha particle-activity still exceeded the MCL. If the hypothetical water sample had a measured U234:U238 activity ratio, then the conversion factor (CF) can be calculated from the actual measured value using the above equation. If a measured ratio of 2 is reported, the CF is determined as 1.008 pCi/ug/L. The resulting alpha-particle activity originating from U can now be recalculated using the actual CF on the basis of measured isotope ratios, and is 12.6 pCi/L. A re-examination of compliance relative to the 15 pCi/L "adjusted" gross alpha particle MCL now indicates compliance (25 -12.6 = 12.4 pCi/L). This example illustrates that the presumed 1:1 U isotope activity ratio is “conservative” because it most likely underestimates the mass to alpha-activity conversion factor, thereby making it more likely that the “adjusted” gross alpha-particle activity is not in compliance with the MCL (a “false positive” result). Adjustment using the measured U isotope ratios accounts for the “excess” U-234 that is the alpha radioactivity source.

5.3.1. Examples from the Highlands: Mostly Uranium Occurrence in Oxic Waters

We now present discussion of compliance with gross alpha-particle activity MCL of the actual water samples from the northern New Jersey bedrock aquifers as an illustration of the complexity faced by a homeowner or utility trying to reasonably assess limiting risk once the gross alpha-particle activity measurement has been made. We begin with select data from the Highlands Province in Table 3 where oxic waters with elevated uranium was the most common water type of concern. In Example 1 (Sample 1), the sample had measured gross alpha-particle activity 48 hours after sample collection of 65.9 pCi/L and U mass of 86.7 ug/L. When using the assumed “natural U” conversion factor (CF_n) of 0.672 pCi/ug/L, a value of 57.94 pCi/L of gross alpha-particle activity originating from U is calculated. Subtracting this activity (57.94 pCi/L) from the measured gross alpha-particle activity (65.9 pCi/L) indicates a net 7.96 pCi/L of “adjusted” gross alpha-particle activity is calculated to be potentially present. This “adjusted” activity result does not any longer constitute a gross alpha particle-activity MCL exceedence, even though the “unadjusted” (initially determined raw) value did exceed the 15 pCi/L MCL. The further information obtained by analyses conducted during this study of the U234:U238 activity ratio showed that for this sample, the measured ratio was 1.32; thereby, the more appropriate conversion factor (CF) for the isotope activity ratio of 1.32, was the CF of 0.78 pCi/ug/L. Recalculating the alpha activity attributable to the 86.7 ug/L of U with the now measured U isotope activity ratio, it is determined that 67.09 pCi/L of alpha activity is feasibly derived from the uranium, which is almost identical to the 65.9 pCi/L measured for the gross alpha-particle activity (unadjusted). The result now indicates that the adjusted gross alpha activity equals about zero, and essentially all the measured gross alpha particle activity is attributable to the U isotopes. Even with the recalculation or “re-adjustment” of alpha activity, the sample of course still exceeds the MCL for U mass, but no further analysis or action is otherwise necessary. The concentrations of the Ra isotopes were determined for the sample for purposes of the study; neither Ra-224, nor Ra-226, nor Ra-228 were present in detectable amounts.Results from

Samples 4 and 7 also presented in Table 3 represent other samples typical of this commonplace scenario for water samples from the Highlands. In Sample 4, measured gross alpha-particle activity was 27.02 pCi/L and U mass was 31.6 ug/L exceeding the MCL for both gross alpha-particle activity and U, whereas for Sample 7, measured gross alpha-particle activity was 23.15 pCi/L and U mass was 26.08 ug/L, exceeding the MCL for gross alpha-particle activity, but not U. Using the assumed "natural U" conversion factor (CF) for Sample 4, a value of 21.49 pCi/L of gross alpha-particle activity originating from U is calculated, and by subtraction, a net 5.53 pCi/L is calculated to be present from radioisotope sources potentially other than U. The remaining gross alpha-particle activity is slightly greater than 5 pCi/L after adjustment using the "natural U" conversion factor but clearly the dominance of U as the source of alpha activity was demonstrated. The water sample 4 had a U234:U238 activity ratio of 1.31 resulting in a CF of 0.775 pCi/ug/L; the resulting alpha-particle activity originating from U (accounting for the "excess U") is calculated as 24.86 pCi/L indicating that nearly all or all the measured gross alpha particle activity is attributable to the U isotopes, and a similar result can be demonstrated for sample 7. A small amount of Ra-224 (1.58 pCi/L) and Ra-228 (2.27 pCi/L) were detected in sample 4, but no Ra-226, whereas a detectable amount of Ra-226 (1.76 pCi/L) was present in sample 7, but was small compared to U. It is important to note for sample 4 that the Ra-224 progeny of the Ra-228 radioisotope emits alpha particles and can serve as a "proxy" for Ra-228 occurrence, but the Ra-228 itself is a beta-particle emitter and cannot be detected by analysis of alpha-particle activity. The relatively poor precision of the radioactivity measurements are such that small amounts of radiation are readily within the margin of error of measurement, which is a limitation of this method of assessment.

There were a small number (7) of samples with considerable alpha-particle activity not accounted for by the U isotopes, and all had a detectable amount of at least Ra-226, and three had detectable amounts of all three measured Ra isotopes, Ra-224, Ra-226, and Ra-228. In those well water samples where Ra was detected, the Ra generally contributed to the gross alpha-particle activity. The measured gross alpha-particle activity was 71.6 pCi/L and concentration of U (mass) was 64.78 ug/L for Sample 2, which also had the third highest combined Ra (Ra-226 + Ra-228) concentration (3.32 pCi/L) and second highest concentration of Ra-224 (2.4 pCi/L) among the 40 samples from the Highlands. Using either the assumed "natural U" CF of 0.672 pCi/ug/L, or the CF of 0.88 pCi/ug/L obtained from the measured U isotope activity ratio of 1.64, respectively, a net 28.96 pCi/L or a net 15.32 pCi/L gross alpha-particle activity is calculated to be present from radioisotope sources other than U. This sample thus still exceeds the gross alpha-particle activity MCL of 15 pCi/L regardless of the method employed to compute the alpha activity derived from U. The high remaining gross alpha-particle activity in water Sample 2 was mostly accounted for by the isotopes of Ra (and their presumed short-lived progeny). In this case, the well owner might derive benefit from the information that Ra isotopes were also present in the water at concentrations near to but not exceeding the MCL, pointing to the need for possible complex treatment system (capable of uranium and radium treatment), depending upon the degree of health risk the consumer is willing to tolerate. Analysis of the uranium isotope ratio was important for this sample (Table 3) in quantifying the large amount of “excess” U-234, but also in identifying that additional radionuclide sources (Ra was most likely) may have accounted for the considerable amount of (adjusted) gross alpha-particle activity. It is also important to note that this sample (2) did not have surrogate chemical indicators of the Ra occurrence

In a handful of samples, the concentration of U was low, and another alpha-particle emitting isotope was likely present. The concentration of U was relatively low, 4.29 ug/L, in Sample 18, which had gross alpha-particle activity of 14.74 pCi/L, or just slightly less than the MCL. The measured U isotope activity ratio of 2.32 for this sample was among the highest measured from the Highlands, but even using the high CF of 1.12 pCi/ug/L, the net remaining “adjusted” gross alpha-particle activity (after accounting for that from U including the “excess” U-234 is nearly 10 pCi/L (9.66 pCi/L)). An amount of Ra-226 (2.41 pCi/L) about half the combined Ra MCL was detected representing a level high enough that the well owner benefits from being aware of it even if treatment option is not required or chosen. Sample 34 had gross alpha-particle activity of 19.4 pCi/L, or slightly greater than the MCL, but the low concentration of U was low, 1.33 ug/L, and the low measured U isotope activity ratio of 1.25 indicated that little of the gross alpha-particle activity is accounted for by U (alpha) activity. Analysis for Ra was warranted and detectable amounts of all three Ra isotopes measured, Ra-224, Ra-226, and Ra-228, were found though not in amounts to exceed the combined Ra MCL. The presence of Ra-224 in Sample 34, just as for Sample 2, accounts for a considerable amount of the “adjusted” gross alpha particle activity. In this case, the well owner still benefits from being aware that multiple sources of alpha-emitting radionuclides are present in the water. Analysis of the uranium isotope ratio is of moderate importance for these samples (Table 3) in ruling out the possibility that an unusually large amount of “excess” U-234 is the source of much of the gross alpha-particle activity. It is also important to note that both these samples (18 and 34) have surrogate chemical indicators of Ra occurrence in that concentrations of dissolved oxygen are low (Fig. 3a) and concentrations of iron and manganese are elevated (Table 3; Fig. 7).

The drawback of the imprecision of radioactivity measurements is that the presence of Ra-226 might be missed in some samples on the basis of interpretation of measurement of only gross alpha-particle activity and U concentration or U isotope activity, especially when the gross alpha-particle activity and U isotope activity are both large values. Sample 36 represents such a "problematic" case. The high alpha activity from U isotopes appears to equal or exceed the measured gross alpha-particle activity (both in excess of 100 pCi/L; Table 3) suggesting that analysis for the presence of Ra-226 might not be necessary, but the presence of 7.31 pCi/L of Ra-226, a concentration greater than the MCL, was detected indicating lack of analysis would not have been prudent. For 6 samples, the gross alpha-particle activity predicted from uranium concentration is greater than the measured gross alpha-particle activity also illustrating the limitation imposed by the low precision of radioactivity measurement. "Patchy" planchet residues for gross alpha-particle activity determinations are just one example of several methodological limitations that result in decreased efficiency for detecting alpha particle emissions (Arndt and West, 2007; Zikovsky, 2000). For samples with extreme gross alpha-particle activity, the utility or homeowner is prudent to complete analysis for Ra as well as perhaps other radionuclides.

The examples just provided are the most common scenario for water samples with gross alpha-particle activities greater than 15 pCi/L collected from the NJ Highlands aquifers during this study. In the oxic ground waters from the Highlands Province, typically U activity accounts for nearly all the gross alpha-particle activity regardless of which conversion factor is used for the "adjustment" of the gross alpha-particle activity, and the "adjusted" gross alpha-particle activity is generally below the MCL. In 6 of the 10 samples for which the gross alpha-particle activity was greater than 15 pCi/L, the results were similar to Sample 1, in that U concentration was also greater than the 30 ug/L MCL, and when the U isotope activity ratio was considered to determine the amount of "excess U-234", the U isotopes were shown to account for essentially all the gross alpha-particle activity. Two samples were similar to Sample 7 in that even though the concentration of U (mass) did not exceed the MCL, but natural U and the excess U-234 accounted for nearly all the gross alpha-particle activity, and thus the adjusted gross alpha-particle activity did not exceed the MCL either. In fact, only 3 samples had remaining net gross alpha activity greater than 5 pCi/L when the "excess U-234" was accounted for, with only 1 sample (Sample 2) in excess of the 15 pCi/L MCL. In the extremely U-rich ground waters for which U activity can be shown to account for nearly all the gross alpha-particle activity even if only the simple “natural U” conversion factor is used, the practical utility for further “adjustment” of the gross alpha-particle activity using measured uranium isotope ratios is low (Table 3).

For residents of the Highlands Province in northern New Jersey consuming the ground water, it is most important to note that the samples are U rich and elevated gross alpha-particle activity is most likely from U, a constituent which has an MCL as well, and this MCL was exceeded frequently (7 of the 31 water samples, or 22.6%). Because the majority of the samples are so U rich, and in general, the U isotope activity ratios are not extreme relative to “natural U”, the effect that the U concentration has on calculated compliance with the gross alpha-particle MCL (“adjusted” for U activity) can often be evaluated even without determination of the amount of the “excess” U234 isotope. The calculated gross alpha particle activity on the basis of measured uranium concentrations matches closely the measured gross alpha particle activity for the large majority of samples of water from the Highlands crystalline fractured-rock aquifers, as indicated by the close value of the slope (m) of 0.82 to the slope of 1 (1:1 correlation line) and strong regression coefficients (R^2) also close to 1 (R^2, 0.87) in figure 11a. It is important to note the for the Highlands ground waters that no sample was encountered that would be an example of a “false positive” gross alpha-particle activity MCL exceedence. Even with the simple U mass measurement, in most cases (about 65 % in this study), the utility or homeowner might be able to avoid (with good reason) considerable expense trying to determine “unknown” radioisotope that results in the gross alpha-particle activity exceedence. For the remaining ground-water samples, the effect that the alpha activity from the “excess” U234 isotope has on calculated compliance with the gross alpha-particle MCL might need to be evaluated, especially if there is concern that the samples might contain Ra. There is actual benefit to the water-supply owner in actually knowing whether “excess U234” or Ra-226 or some other radioisotope is a major source of gross alpha activity. For this reason, any geochemical “proxy” that indicates the presence/absence of elevated Ra-226 has considerable benefit. The measured U (U-234/U-238) isotope ratios, which ranged from 1 to 2.9, with median value of 1.39, indicated that in general the amount of “excess U-234” was not large, nor was the effect with regards to “adjustment” for gross alpha-particle activity on the basis of the measured U isotope activity. The gross alpha particle activity determined on the basis of measured uranium isotope ratios matches the measured gross alpha particle activity almost exactly, with slope of this second regression line in figure 11a of 1.04 and R^2 of 0.90. The uranium activity is so high relative to Ra activity in these oxic waters that the small amounts of Ra make little contribution to the overall gross alpha-particle radioactivity of the “typical” sample for the region. The Ra-226 was not a major source for gross alpha-particle activity with the exception of 5 samples (12.5 percent), 3 of which are shown circled in Fig. 11a, and include Samples 2 and 34 discussed above. For samples with extreme gross alpha-particle activity, however, the utility or homeowner is prudent to complete analysis for Ra or even perhaps other radionuclides, as illustrated by sample 36 in Table 3 from the NJ Highlands.

5.3.2. Examples from the Piedmont (Mesozoic Basin): Impacts from 226Ra and 234U Excess in Anoxic or Mixed Redox Waters

We now present compliance discussion of the actual samples from the Piedmont (Mesozoic Basin) in Table 3 where anoxic or mixed redox waters with elevated radium occasionally also containing uranium was the most common water type of concern. Because the waters contained mixtures of elevated radium and also uranium, the uranium-corrected gross alpha-particle activity has considerably more significance than in the mostly oxic waters of the Highlands Province where uranium mostly was the only source of the alpha-particle activity. The implication of the presence of “excess” U-234 in the anoxic waters of the Piedmont terrane may be considerable when considering the source of gross alpha-particle activity, because of the multiple sources of activity.

A simple comparison of the composition of Sample 41 with Sample 9 indicates nearly identical concentrations of U, Ra-226, and Ra-224, yet there is considerable difference among the samples with regard to the gross alpha-particle activity, with Sample 41 having about 15 pCi/L more gross alpha-particle activity, 74.5 pCi/L as opposed to 58.6 pCi/L. Additional (costly) analyses for other alpha-particle emitting radionuclides, such as for Po-210, were considered by the homeowner of well 41. Measurement of the uranium isotope ratio demonstrated the implication of the presence of the “excess” U-234 in waters from this geological terrain. The considerable difference among the samples was determined to be the uranium isotope ratio, which was 6.20 for Sample 41, but was only 1.44 for Sample 9 (Table 3). The much higher gross alpha-particle activity in Sample 41 is contributed by “excess” U-234 that is not detected in the uranium mass concentration measurement. The CF of 2.42 pCi/ug/L obtained from use of the elevated uranium isotope ratio of 6.20 for Sample 41 accounted for more of the gross alpha-particle activity originating from U (16.3 pCi/L, or about 12 pCi/L more) than assumed before using the CF for “natural U”, which had implied very little (4.53 pCi/L) gross alpha-particle originated from U.

For both Sample 9 and Sample 41, it already stood to reason that other alpha-particle emitting isotopes than those from U, most likely Ra, were likely present. The concentrations of U at 7.5 and 6.66 ug/L, respectively, were moderate relative to many observed concentrations of U in the northern New Jersey region, and were low in relation to the measured gross alpha-particle activity. Constituents that may serve as surrogate chemical indicators of Ra occurrence in the Piedmont (Mesozoic Basin) were in fact in evidence from the water from both wells, including low concentration of DO and elevated concentrations of iron and manganese and detectable concentrations of ammonia and arsenite (the reduced form of arsenic). On the basis of the elevated gross alpha-particle activity, the relatively low concentrations of U, and the presence of numerous surrogate indicators of the likely presence of Ra, the well owners likely could identify the constituent of major health risk concern in the waters, the presence of Ra. Health risk for U ingestion in drinking water is set nationally by the 30 ug/L MCL for U mass but health risk from radioactivity from U has also been estimated (USEPA, 1999; 2000); to minimize radioactivity exposure and the associated health risk presumed to originate from uranium ingestion in water, the State of California has established an MCL of 20 pCi/L for the U activity (Wong et al., 1999; California Environmental Protection Agency, 2001). The typical U isotope ratio in California was 1.7, and numerous ground waters exceeded the 20 pCi/L MCL of California even if the U mass did not exceed 30 ug/L (Wong et al., 1999). The measured U isotope activity ratio of Sample 41 of 6.20 is surprisingly high and relatively rare in nature (Osmond and Cowart, 1976; Arndt, 2000). The U isotope ratio result may indicate the need for possible complex treatment system (capable of uranium and radium treatment simultaneously) for those homeowners concerned about the overall exposure to gross alpha radioactivity, not just that from Ra, and thus quantifying the uranium isotope ratio was moderately important for the situation of considerable “excess” U-234 activity as demonstrated by Sample 41 (Table 3). In addition, analyses for other alpha-particle emitting radionuclides (such as Po-210) were not pursued (minimizing laboratory cost burden).

Another example of the considerable implication of the presence of “excess” U-234 in the waters of the Piedmont is illustrated when considering the sample from well 13. The anoxic water sample from well 13 had high gross alpha-particle activity (56 pCi/L) with a concentration of U of 4.19 ug/L that was moderately low; this data indicated the likely presence of Ra. Further analysis confirmed the high Ra-226 concentration of 15.7 pCi/L and a lower Ra-224 concentration of 2.66 pCi/L. The cation exchange (water softener) treatment removed Ra so that Ra concentrations were not detectable in the treated (drinking) water represented by sample 13T (Table 3). The gross alpha-particle activity, however, while diminished after the cation exchange treatment was still elevated (25.4 pCi/L) and though the U levels were not changed the use of the “natural U” CF indicated the U concentration could not account for more than a small fraction of the gross alpha-particle activity. Follow-up analysis for Po-210 indicated concentration was not detectable. Attempts at re-engineering the system did not reduce the gross alpha-particle activity. Analysis of the U isotope activity ratio of treated water sample 13T resulted in a value of 8.06 (with actual CF, 3.04). The surprisingly high level of “excess” U-234 indicated that in fact the 4 ug/L of U present may result in 12.3 pCi/L of gross alpha-particle activity, which is about half the measured gross alpha-particle activity of the treated water. The “adjusted” gross alpha activity accounting for “excess” U-234 falls below the 15-pCi/L MCL. Quantifying the uranium isotope ratio was important for the situation of considerable “excess” U-234 activity for water from well 13 because the information enabled the consideration of redirection of resources toward provision of a more complex treatment system that was appropriate for the contaminant of concern (U).

Results from Samples 30 and 34 also presented in Table 3 represent other typical scenarios for water samples from the NJ Piedmont. In Sample 30, measured gross alpha-particle activity was 65.7 pCi/L and U mass was 48.22 ug/L exceeding the MCL for both gross alpha-particle activity and U, whereas for Sample 34, measured gross alpha-particle activity was 23.0 pCi/L and U mass was 11.36 ug/L, exceeding the MCL for gross alpha-particle activity, but not U. Using the assumed “natural U” conversion factor (CF) for Sample 30, a value of 21.49 pCi/L of gross alpha-particle activity originating from U is calculated. The remaining gross alpha-particle activity is greater than 15 pCi/L after adjustment using the “natural U” conversion factor. The water sample 30 had a U234:U238 activity ratio of 2.22 resulting in a CF of 1.02 pCi/ug/L; the resulting alpha-particle activity originating from U (accounting for the “excess U”) is calculated as 52.17 pCi/L indicating that the largest component of the measured gross alpha particle activity is attributable to the “excess” U-234 isotope, and a net 13.53 pCi/L is calculated to be present from radioisotope sources potentially other than U. A similar result can be demonstrated for sample 34. The dominance of U as the source of alpha activity was demonstrated in both samples, and for each, the “excess” U-234 isotope accounts for so much of the gross alpha-particle activity that the adjusted gross alpha-particle activity does not exceed 15 pCi/L. Constituents that may serve as surrogate chemical indicators of Ra occurrence in the Piedmont (Mesozoic Basin) were for these wells at levels where they were marginal or least reliable. A small amount of Ra-226 (0.43 pCi/L) and Ra-224 (0.2 pCi/L) were detected in sample 30. A detectable amount of Ra-226 (1.34 pCi/L) was present in sample 34, but was small compared to U. In each of these cases, resources could be directed towards addressing the contaminant of greatest concern, in these cases, the U (though for well 34, the U concentration was less than the MCL).

There were a considerable number (8) of samples that had large amounts of Ra-226 (greater than 5 pCi/L) and had detectable amounts of the other measured Ra isotopes, Ra-224 and Ra-228; for these samples the Ra-226 isotope accounted for the largest part of the alpha-particle activity, and small to neglible amount was accounted for by the U isotopes. An example is Sample 35 for which the Ra-226 concentration was 51.1 pCi/L, and U was detectable, but only at 2.5 ug/L, so despite the measured U isotope activity ratio of 2.18, the gross alpha-particle activity is not from U isotopes. A slightly lesser number of wells had water samples where both U and isotopes of Ra was detected in notable concentrations, and both contributed to the gross alpha-particle activity, which was slightly greater than the 15 pCi/L MCL. The use of the assumed "natural U" CF, or the CF obtained from the measured U isotope activity ratio (median of 2.2 in the NJ Piedmont). may have provided different outcomes when trying to determine if the "adjusted" gross alpha-particle activity exceeds the MCL of 15 pCi/L; examples are given in Table 3 (Samples 30, 34, and 13T) regardless of the method employed to compute the alpha activity derived from U. Analysis of the uranium isotope ratio is of importance for these samples (Table 3) in ruling out the possibility that a large amount of another radioisotope is present, and instead defining that "excess" U-234 is a source of an important part of the gross alpha-particle activity. The well owner still benefits from understanding the sources of alpha-emitting radionuclides present in the water, and can choose whether to invest in a complex treatment system (capable of uranium and radium treatment) in order to avoid radiation exposure from the "excess" U-234.

For residents of the Piedmont (Mesozoic Basin) Province of northern New Jersey consuming the ground water, it is most important to note that the samples are anoxic or mixed redox condition and are Ra rich, though U, a constituent which has an MCL as well, occurred and exceeded the MCL on occasion (3 of the 40 water samples, or 7.5%). Because the majority of the samples did contain a mix of Ra and U, and because in general, the amount of "excess" U234 isotope are on occasion extreme, determination of the U isotope activity ratios may be important in some cases. In the NJ Piedmont, in contrast to the Highlands ground waters, samples were encountered that were specific examples of a "false positive" for "adjusted" gross alpha-particle activity MCL exceedence, that is, it was mostly "excess" U234 that accounted for the majority of the "adjusted" gross alpha-particle activity. The calculated gross alpha particle activity on the basis of measured uranium concentrations does not match the measured gross alpha particle activity for the majority of samples of water from the Piedmont fractured-rock aquifers. The slope (m) of the line comparing these values is 0.25 and R^2 is small (R^2, 0.27) in figure 11b. The measured U (U-234/U-238) isotope ratios, which ranged from 1 to 8.45, with a median of 2.2, indicate that the alpha activity from the "excess" U234 isotope may be considerable, and can bias "adjusted" gross alpha-particle activities high. The use of gross alpha particle activity determined on the basis of measured uranium isotope ratios improves the match to the measured gross alpha particle activity for the samples considerably, raising the slope of the second regression line in figure 10b to 0.41 with a slightly improved R^2 of 0.29. The Ra activity in so many of the anoxic samples is so high relative to U activity that the small amounts of "natural" U and "excess" U-234 cannot explain the radionuclide contribution to the overall gross alpha-particle radioactivity for the "typical" sample for the region. The measured gross alpha particle activity for the majority of samples of water from the Piedmont fractured-rock aquifers is only approximately matched by the calculated gross alpha-particle activity contributions if alpha activity from "natural" U, "excess" U-234, and Ra isotopes are summed; the slope of this third regression line in figure 11b is nearly 1 (0.97) and the R^2 is strong (0.87). For samples with extreme gross alpha-particle activity, however, the concentration of Ra-226 was dominant (usually when gross alpha-particle activity was greater than 50 pCi/L). The utility or homeowner is prudent to complete analysis for Ra if a geochemical "proxy" is present that indicates the likely presence of elevated concentrations of Ra. Nevertheless, in some number of cases, the utility or homeowner might be able to avoid additional expense even with just the simple U mass measurement.

5.5. Remediation Options and Future Research Needs

Conventional measurements of the general amount of radioactivity in the water, such as measurements of gross alpha-particle activity, did not prove to be reliable for identifying specifically where concentrations might exceed the combined radium MCL or the uranium MCL. Elevated gross alpha-particle activity indicates the presence of at least one or the other of these alpha-particle-emitting radioactive constituents in relatively high concentrations, but the identity of which of these nuclides is predominant and contributes the most to the radioactivity of the water sample cannot be established on the basis of the gross alpha-particle activity measurement alone.

Sample geochemistry (oxic or anoxic) and bedrock geology (crystalline or sedimentary) could be helpful in estimating the likelihood of which radionuclide is predominant. The geochemistry of radium and uranium differ, and either one or the other tends to predominate in many, but not all, cases. The inexpensive U mass analysis (in ug/L) with dissolved oxygen concentration, iron and manganese concentration, and pH determination might be suitable initial water-quality indicators at most sites in the region in addition to the gross alpha-particle activity determination, allowing some residents to avoid high laboratory costs when choosing a treatment system to minimize exposure to radioactivity from the ingested drinking-water source.

Anion-exchange systems did remove U and gross alpha-particle activity when uranium was the predominant source of the radiation. Cation-exchange (water softener) systems did not remove U, nor did they reduce gross alpha-particle activity when uranium was the predominant source of the radiation, though Ra and Ba were diminished in concentration. Because remediation options differ widely for U and Ra, in northern New Jersey where high gross alpha-particle activity is present, it is critical to determine the predominant source of the alpha activity, whether from U or Ra, to assess the best treatment option. The information regarding sample chemistry has value for designing As treatment for the homeowner as those media are also strongly influenced both by the speciation of the element as well as the composition of the water (Meng et al., 2000). Quality of water from domestic wells tends to be affected by radionuclides and arsenic in many principal aquifers of the United States (DeSimone, 2009), and improvements in understanding their occurrence that can offer guidance to homeowners is of substantial benefit.

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7. CONCLUSIONS

Elevated gross alpha-particle activity in ground water, greater than the U.S. Environmental Protection Agency Maximum Contaminant Level of 15 pCi/L, was documented from widely scattered areas in the crystalline-rock (granite, gneiss, marble) Highlands Province and in black mudstone in the Piedmont (Mesozoic Basin) of northern New Jersey. Most of this alpha-particle activity in the waters in the Highlands and Piedmont Provinces, respectively, was attributable to the long-lived isotopes of U (maximums, 623 ug/L and 237 ug/L, respectively), and to a lesser extent, Ra-226 (maximum, 17.4 and 51.1 pCi/L, respectively) and Ra-224, which is derived indirectly from Ra-228.

- U occurrence predominates where waters have high dissolved oxygen (DO). Ra-226 occurrence predominates where waters have low dissolved oxygen (DO).
- U activity does account for all the gross alpha-particle activity in the most oxic waters. U isotope ratios are extremely variable in some areas of the Piedmont and U may account for more of the gross alpha-particle activity in these areas than is evident from the simple mass measurement of uranium.
- U and As were higher more frequently in alkaline water with pH $\geq$ about 7.4 than in less alkaline water – these were more common in metamorphic than granitic rock in the Highlands, and mudstone than sandstone in the Piedmont.
- Ra-226 occurrence predominates where waters have low dissolved oxygen (DO) of < 1 mg/L, and other characteristics of these waters included filtered manganese and iron concentrations of 50 ug/L (micrograms per liter) and detectable ammonia.
- On rare occasions, all the constituents occurred together, possibly because of mixing of waters from different fracture zones.
- On rare occasions, extreme “excess” U-234 isotope concentration was detected. This phenomenon increases the measured gross alpha-particle activity without increasing the observed U concentration. This situation may cause homeowners and even knowledgeable treatment system operators confusion.
- For computing the “uranium-adjusted” gross alpha-particle activity, the “natural-U” isotope ratio is most conservative, but can be misleading when isotope ratios are highly variable.
- Anion exchange removed U and Cation exchange removed Ra. Homeowners need be aware of this critical difference.
- Some limited guidance as to occurrence of U and Ra is possible for home owners on the basis of gross alpha-particle activity, DO, and to lesser extent pH, bicarbonate alkalinity, filtered iron and/or manganese, and rock type -- but none of the “surrogates” are 100% definitive. Further investigations to improve understanding and further update guidance may have utility.

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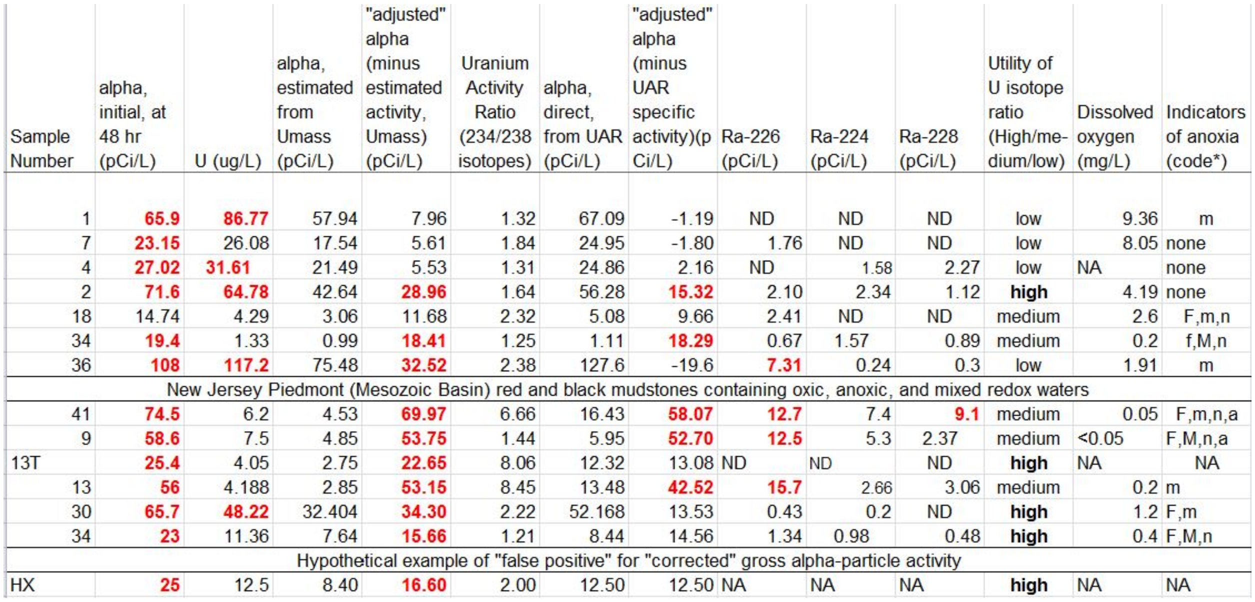
Table 1. Analytical technique and method reporting level of chemical analyses performed, U occurrence study, Highlands Province, northern New Jersey, 2007-08.

Constituent	**Method Reporting Level**	**Method**
Gross alpha, short term (48-hr) [with another sample bottle held for 30+ day analysis	3 pCi/L	Ba-sulfate co-precipitation & Low-background proportional count
Ra-226 Ra-228 Ra-224	0.3 pCi/L 0.5 pCi/L 0.5 pCi/L	Ba-sulfate co-precipitation & Gamma Spectroscopy
Uranium	0.3 ug/L	ICP-Mass Spectrometry
Manganese	0.2 ug/L	
Iron	10 ug/L	ICP - optical spectroscopy
Arsenic	0.1-0.3 ug/L	ICP-collision Mass Spectrometry
Sulfate	0.3 mg/L	Ion Chromatography
Nutrients, chloride	<0.1 mg/L	Colorimetry
Uranium isotopes	0.1 pCi/L	ICP-Mass Spectrometry
Arsenic species (optional)	0.1-0.3 ug/L	Field extraction; ICP-Mass Spectrometry
FIELD MEASUREMENTS		
Temperature	0.1 $^{\circ}$C	Field Meter
PH	0.1 units	
Dissolved oxygen	0.1 mg/L	
Eh	MV, ± 20	
Conductance	5 uS/cm	
Turbidity	0.1 NTU	
Alkalinity	0.1 mg/L	Titration
Rn-222	120 pCi/L	Alpha Spectrometry

Table 2. Statistical summary of radionuclides concentration distribution for water from the crystalline-rock aquifers of the Highlands Province, and Mesozoic sedimentary-rock aquifers, Piedmont Province, northern New Jersey, 2007-2011. [--, below variable detection level; nd, not determined in most samples]

Constituent	25th percentile	Median	75th percentile	90th percentile	Maximum
a) NJ Highlands, 40 wells					
Gross alpha	3.72	9.94	22.58	66.5	232
Radium-224	--	--	0.47	1.57	3.36
Radium-226	--	--	0.81	2.13	17.43
Radium-228	--	--	0.74	1.15	2.27
UAR	1.25	1.36	1.79	2.29	2.95
Uranium	0.88	5.84	19.70	69.1	623
Radon-222	2557	6677	17,512	28,675	154,600
pH	6.47	7.00	7.45	7.64	7.88
DO	3.05	5.50	8.14	9.50	10.90
SC	269	538	801	997	2350
Turbidity	0.38	1.12	3.57	7.0	52
Iron	5.70	6.95	27.0	83.7	2056
Manganese	0.69	2.62	27.4	117	445
Arsenic	<0.06	0.07	0.32	0.94	14.9
Chloride	8.24	72.8	139	192	712
Alkalinity	55	108	131	181	258
Calcium	27.0	53.4	80.7	93.7	109
Barium	3.12	11.77	21.23	88.05	116.4
Strontium	57.6	97.2	167	234	392
Silica	15.85	17.22	20.55	23.29	36.08
Nitrite plus nitrate	0.52	1.87	2.97	4.30	6.86
b) NJ Piedmont, 40 wells					
Gross alpha	3.83	5.58	19.95	69.9	222
Radium-224	--	0.25	1.00	3.83	19.2
Radium-226	0.19	0.43	1.22	12.72	51.1
Radium-228	*nd*	*nd*	*nd*	*nd*	9.10
UAR	1.48	2.19	3.42	5.99	8.45
Uranium	1.52	3.03	6.88	16.29	228
Radon-222	1930	3340	14,980	24,020	27,300
pH	7.15	7.60	7.68	7.90	8.10
DO	0.17	1.34	4.95	6.62	7.60
SC	360	474	595	959	1620
Turbidity	0.13	0.22	0.70	3.17	9.30
Iron	<3	<4	17.1	274	3747

Manganese	0.41	4.52	59.8	220	738
Arsenic	1.22	2.83	7.08	10.32	24.7
Chloride	9.64	41.2	81.9	224	401
Alkalinity	130	149	165	182	200
Calcium	39.3	55.0	76.0	125	190
Barium	38.2	109.6	162	332	1162
Strontium	247	524	770	2098	6174
Silica	19.08	22.10	27.11	37.73	45.39
Nitrite plus nitrate	0.75	1.69	2.57	3.19	5.60



Sample Number	alpha, initial, at 48 hr (pCi/L)	U (ug/L)	alpha, estimated from Umass (pCi/L)	"adjusted" alpha (minus estimated activity, Umass) (pCi/L)	Uranium Activity Ratio (234/238 isotopes)	alpha, direct, from UAR (pCi/L)	"adjusted" alpha (minus UAR specific activity)(pCi/L)	Ra-226 (pCi/L)	Ra-224 (pCi/L)	Ra-228 (pCi/L)	Utility of U isotope ratio (High/medium/low)	Dissolved oxygen (mg/L)	Indicators of anoxia (code*)
1	**65.9**	**86.77**	57.94	7.96	1.32	67.09	-1.19	ND	ND	ND	low	9.36	m
7	**23.15**	26.08	17.54	5.61	1.84	24.95	-1.80	1.76	ND	ND	low	8.05	none
4	**27.02**	**31.61**	21.49	5.53	1.31	24.86	2.16	ND	1.58	2.27	low	NA	none
2	**71.6**	**64.78**	42.64	**28.96**	1.64	56.28	**15.32**	2.10	2.34	1.12	**high**	4.19	none
18	14.74	4.29	3.06	11.68	2.32	5.08	9.66	2.41	ND	ND	medium	2.6	F,m,n
34	**19.4**	1.33	0.99	**18.41**	1.25	1.11	**18.29**	0.67	1.57	0.89	medium	0.2	f,M,n
36	**108**	**117.2**	75.48	**32.52**	2.38	127.6	-19.6	**7.31**	0.24	0.3	low	1.91	m
New Jersey Piedmont (Mesozoic Basin) red and black mudstones containing oxic, anoxic, and mixed redox waters													
41	**74.5**	6.2	4.53	**69.97**	6.66	16.43	**58.07**	**12.7**	7.4	**9.1**	medium	0.05	F,m,n,a
9	**58.6**	7.5	4.85	**53.75**	1.44	5.95	**52.70**	**12.5**	5.3	2.37	medium	<0.05	F,M,n,a
13T	**25.4**	4.05	2.75	**22.65**	8.06	12.32	13.08	ND	ND	ND	**high**	NA	NA
13	**56**	4.188	2.85	**53.15**	8.45	13.48	**42.52**	**15.7**	2.66	3.06	medium	0.2	m
30	**65.7**	**48.22**	32.404	**34.30**	2.22	52.168	13.53	0.43	0.2	ND	**high**	1.2	F,m
34	**23**	11.36	7.64	**15.66**	1.21	8.44	14.56	1.34	0.98	0.48	**high**	0.4	F,M,n
Hypothetical example of "false positive" for "corrected" gross alpha-particle activity													
HX	**25**	12.5	8.40	**16.60**	2.00	12.50	12.50	NA	NA	NA	**high**	NA	NA

Table 3. Example computations of “adjusted” gross alpha-particle activity with subtraction of alpha-particle activity contributed by U. Adjusted gross alpha-particle activity was determined using: 1) measured uranium mass assuming “natural” U-2324/U-238 activity ratio of 1; and 2) measured U-234/U-238) isotope activity ratios (UAR), which ranged from 1 to 8.45 (median, 1.9). Concentrations that exceed a Maximum Contaminat Level are indicated in bold. Further explanation is given in text.[pCi/L, picocuries per liter; ug/L, micrograms per liter; mg/L, milligrams per liter; ND, not detected; NA, not analyzed. Anoxia code: f, iron concentration > 50 ug/L; F, iron concentration > 100 ug/L; m, manganese concentration > 50 ug/L; M, manganese concentration > 100 ug/L; n, ammonia concentration > 0.02 mg/L; a, arsenite concentration > 0.5 ug/L.]

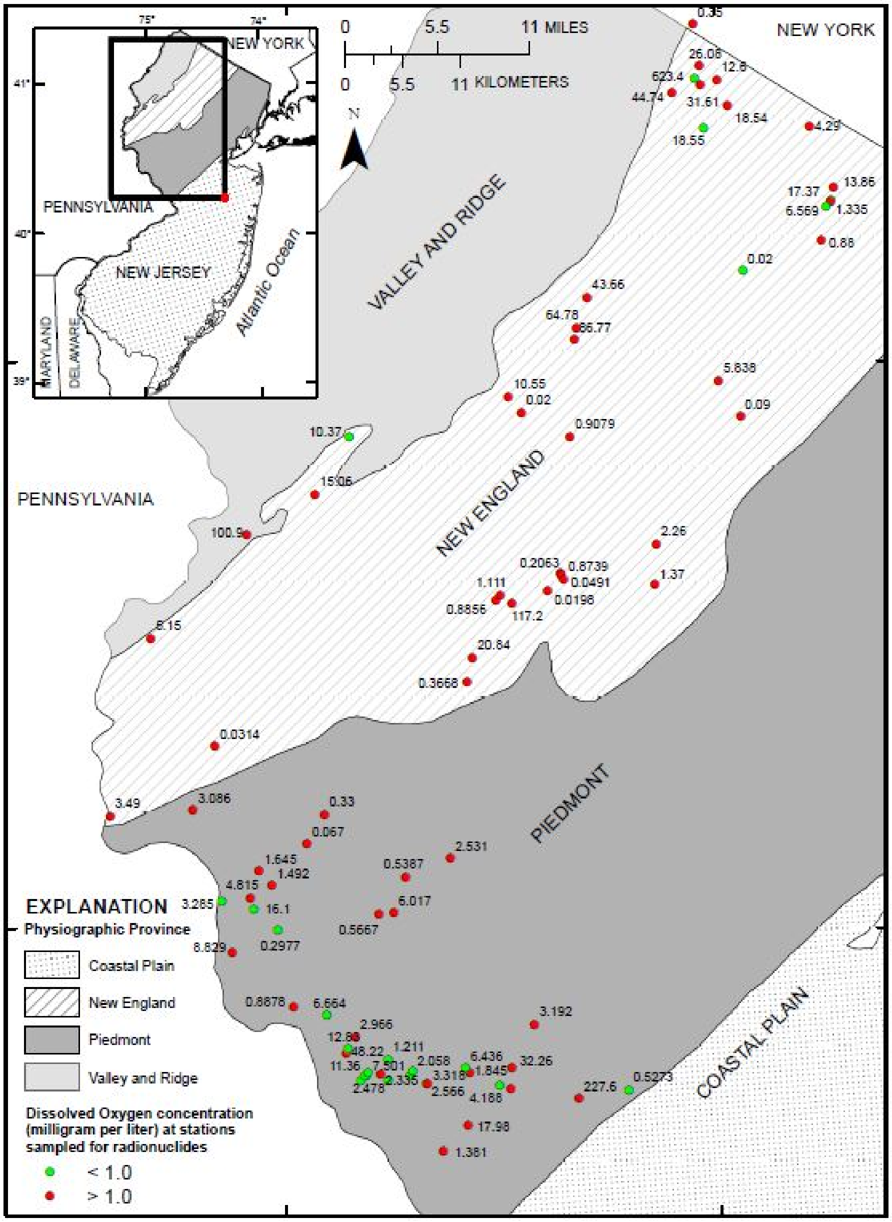


Fig. 1. Map showing location of wells sampled for, and distribution of, U in water from the fractured felsic crystalline-rock aquifers of the Highlands Province and the Mesozoic fluvial and lacustrine sedimentary-rock aquifers of the Piedmont Province, northern New Jersey, 2007-2011.

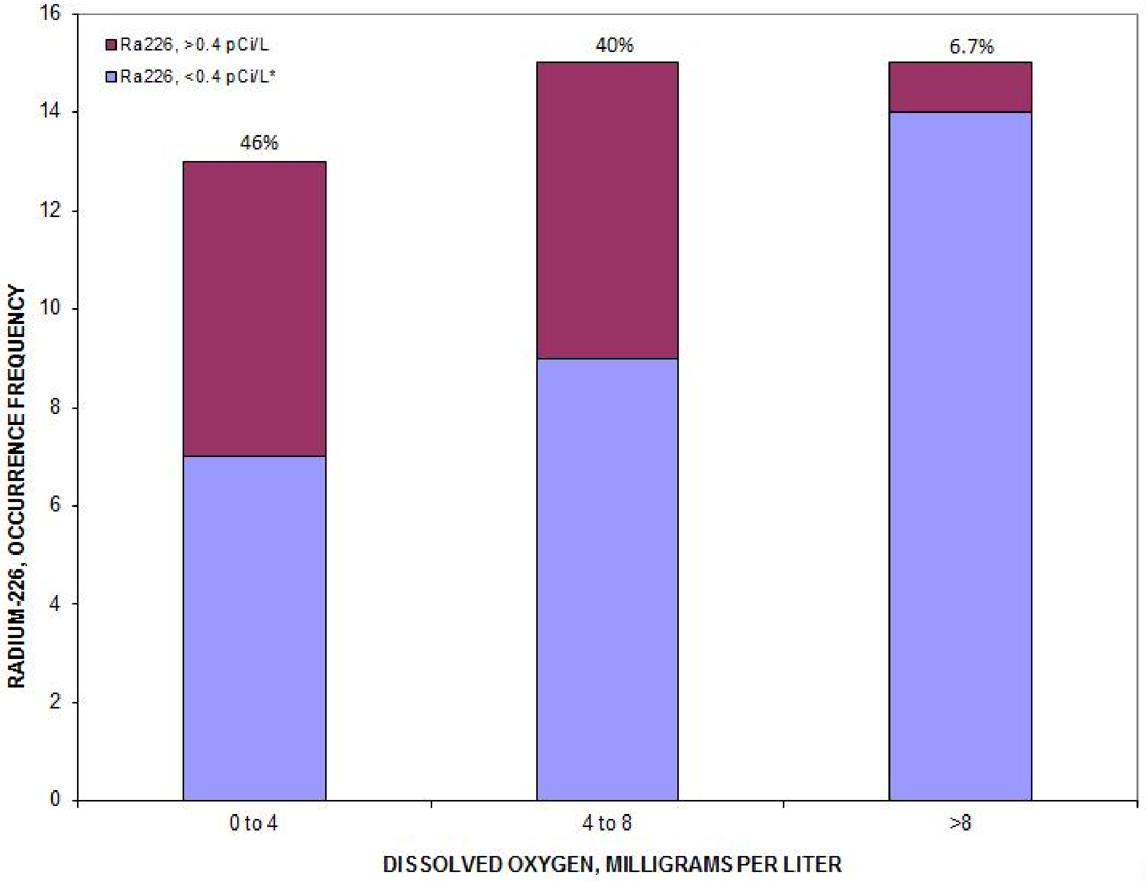


Fig. 2a. Frequency of detection of Radium-226 (Ra-226) in samples of water collected from Highlands crystalline fractured-rock aquifers, northern New Jersey, 2007-2011, grouped by dissolved oxygen concentration. Note the wells are long open boreholes resulting in mixing of oxygen-rich and oxygen-poor waters at some locales. [*, Ra-226 in 2 samples with reported concentration greater than 0.4 pCi/L had high background radioactivity and were considered not to represent actual detection].

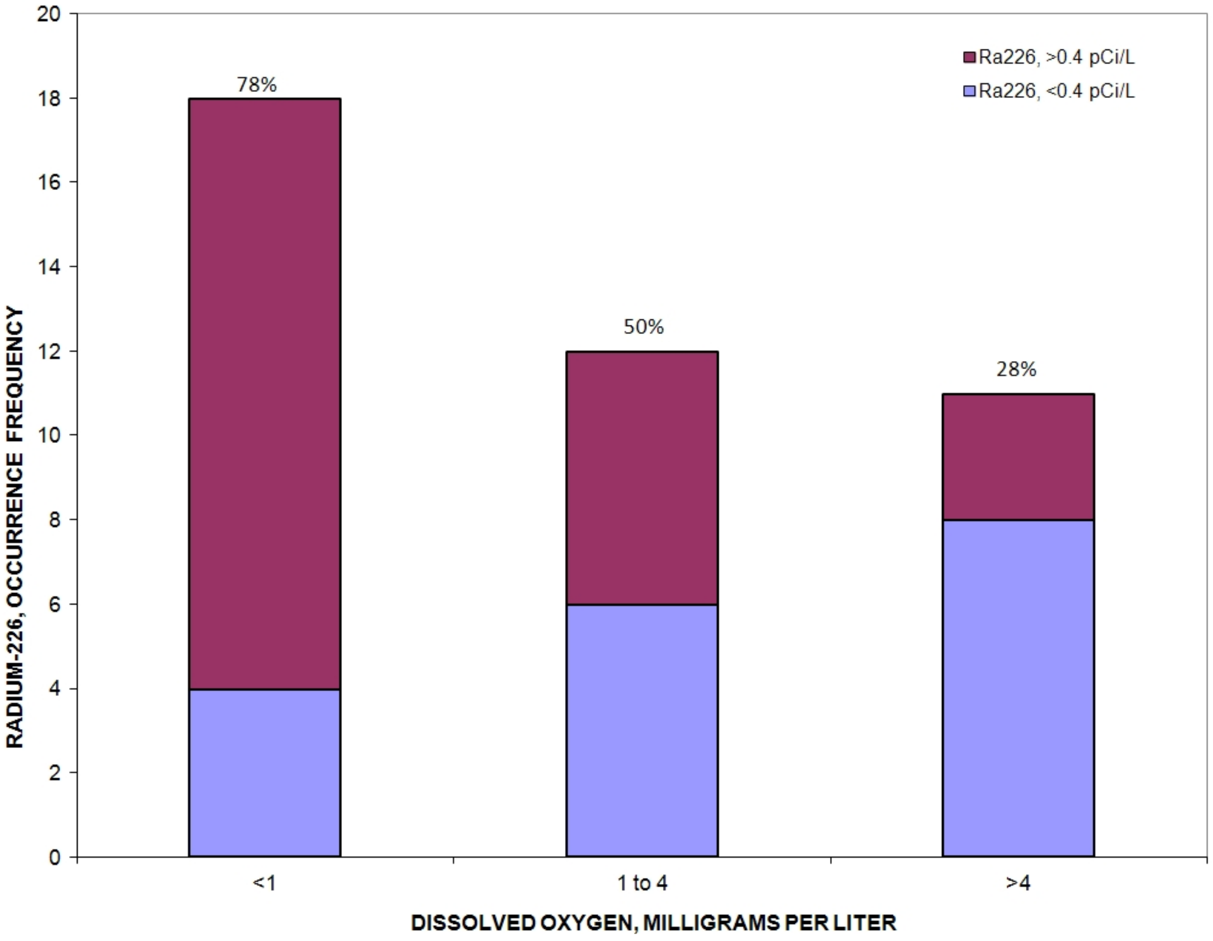


Fig. 2b. Frequency of detection of Radium-226 in samples of water collected from Piedmont Mesozoic age sedimentary fractured-rock aquifers, northern New Jersey, 2009-2011, grouped by dissolved oxygen concentration. Note the wells are long open boreholes resulting in mixing of oxygen-rich and oxygen-poor waters at some locales.

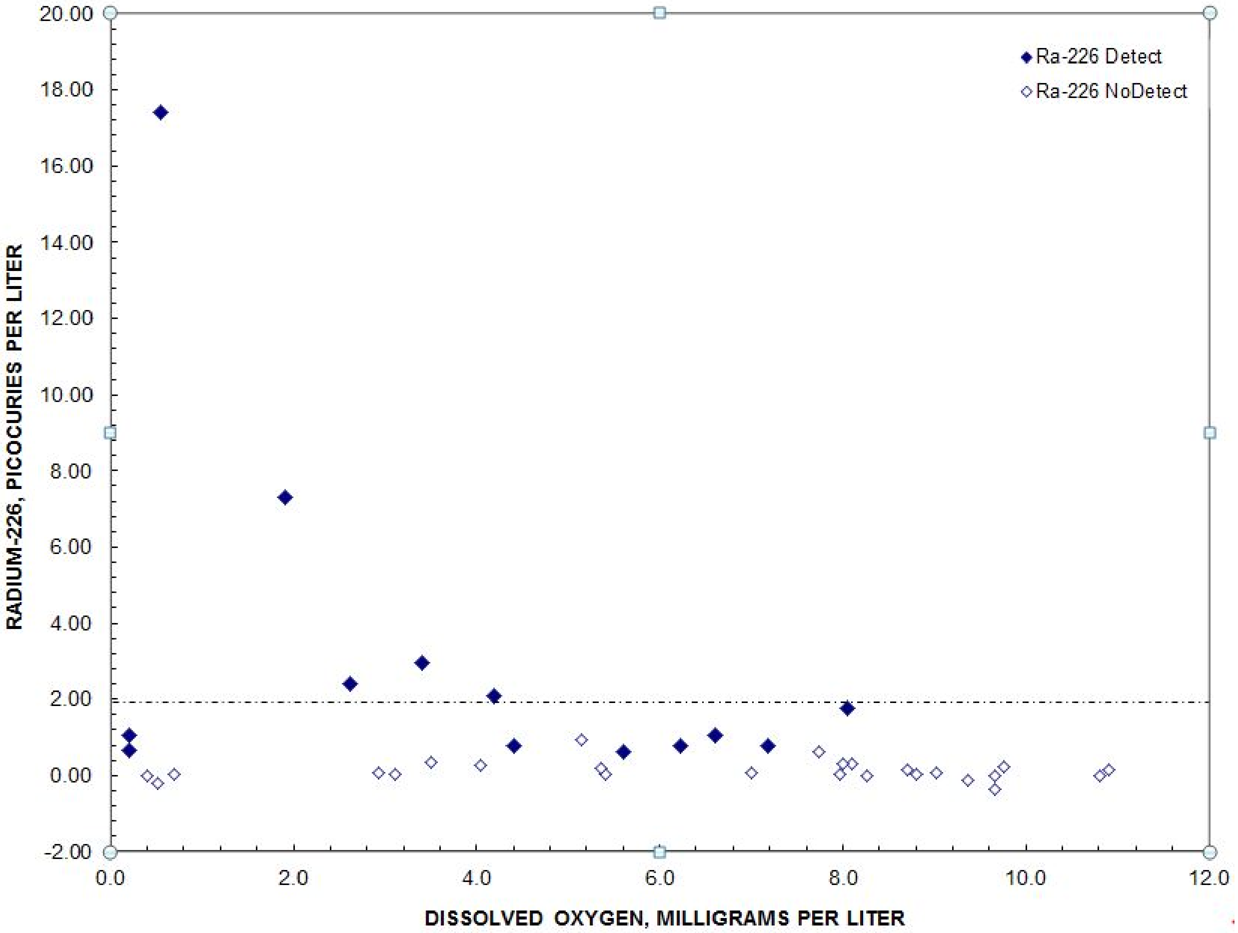


FIG. 3a. Concentrations of Ra-226 as a function of dissolved oxygen concentrations in water from the fractured crystalline-rock aquifers of the Highlands Province, northern New Jersey, 2007-2011.

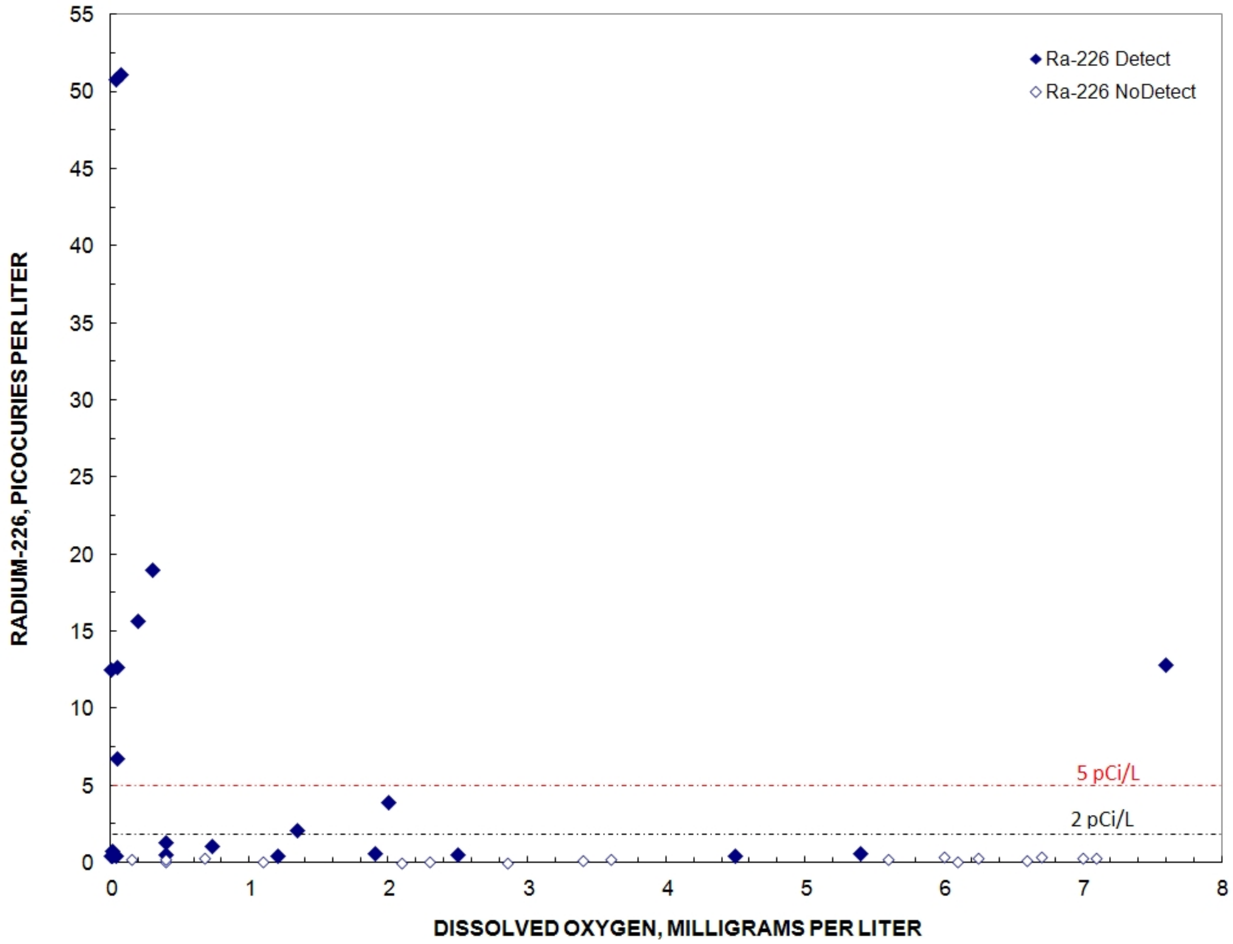


FIG. 3b. Concentrations of Ra-226 as a function of dissolved oxygen concentrations in water from the Mesozoic sedimentary fractured-rock aquifers of the Piedmont Province, northern New Jersey, 2009-2011.

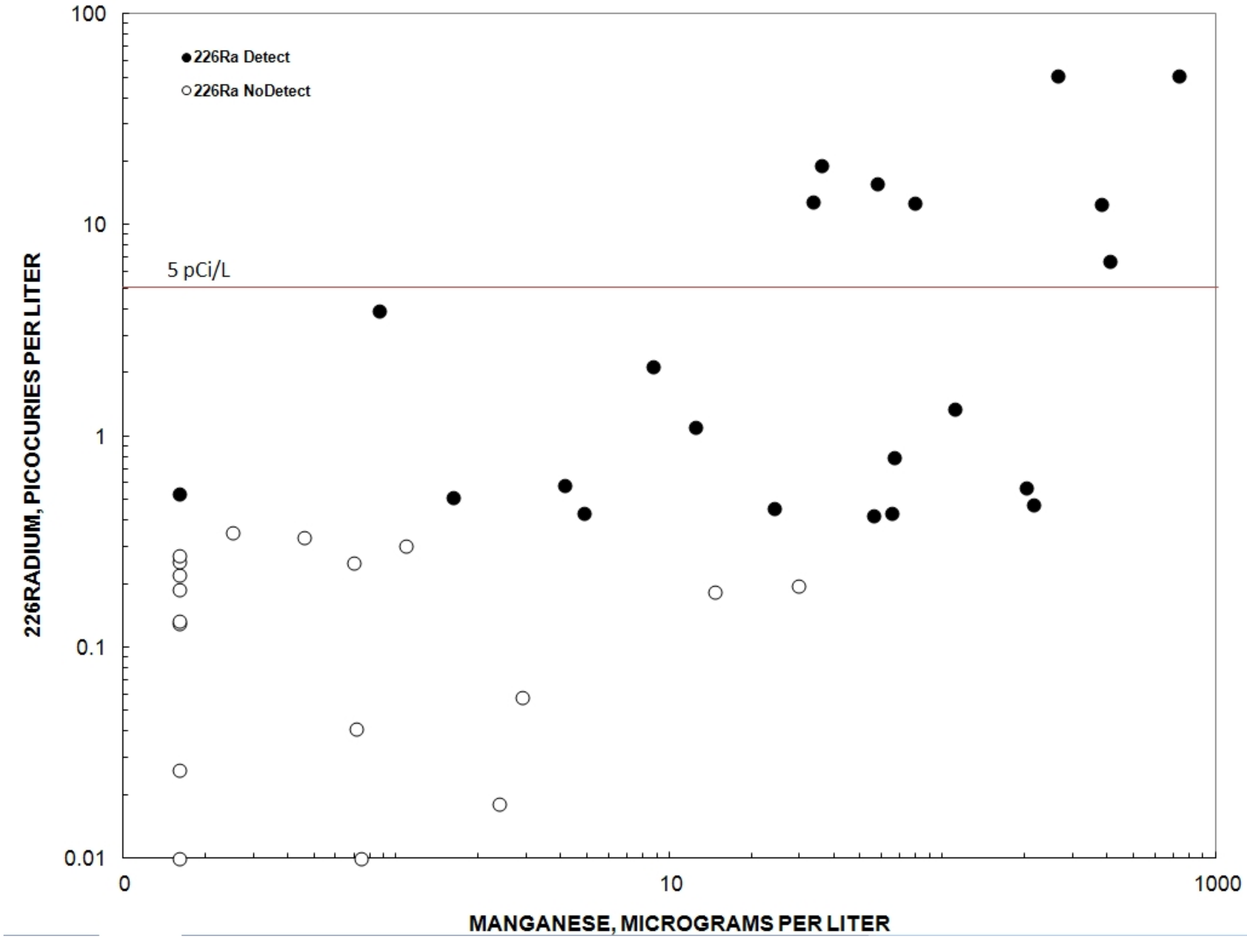


FIG. 4. Concentrations of Ra-226 as a function of manganese concentrations in water from the sedimentary fractured-rock aquifers of the Piedmont Province, northern New Jersey, 2009-2011.

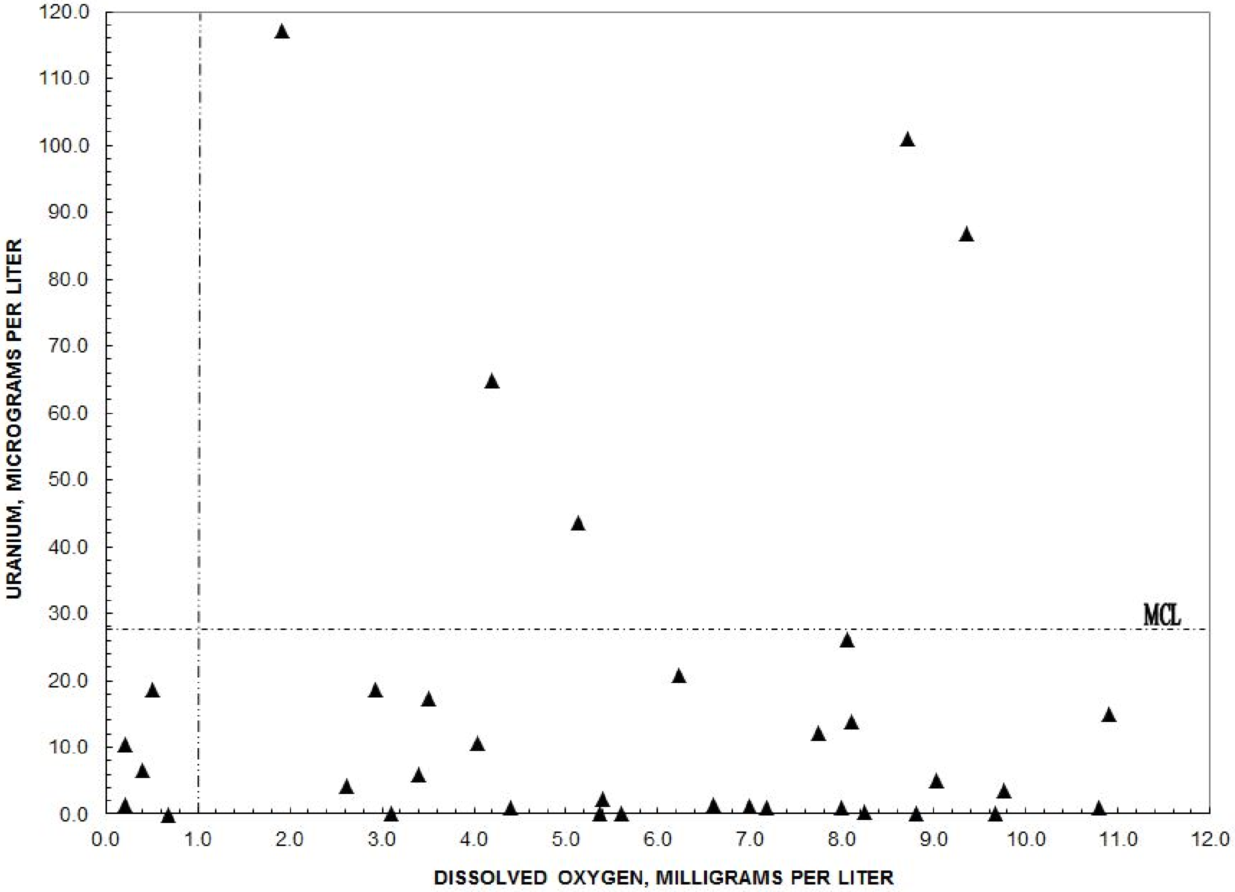


FIG. 5a. Concentrations of uranium as a function of dissolved oxygen concentrations in water from the crystalline-rock aquifers of the Highlands Province, northern New Jersey, 2007-2011.

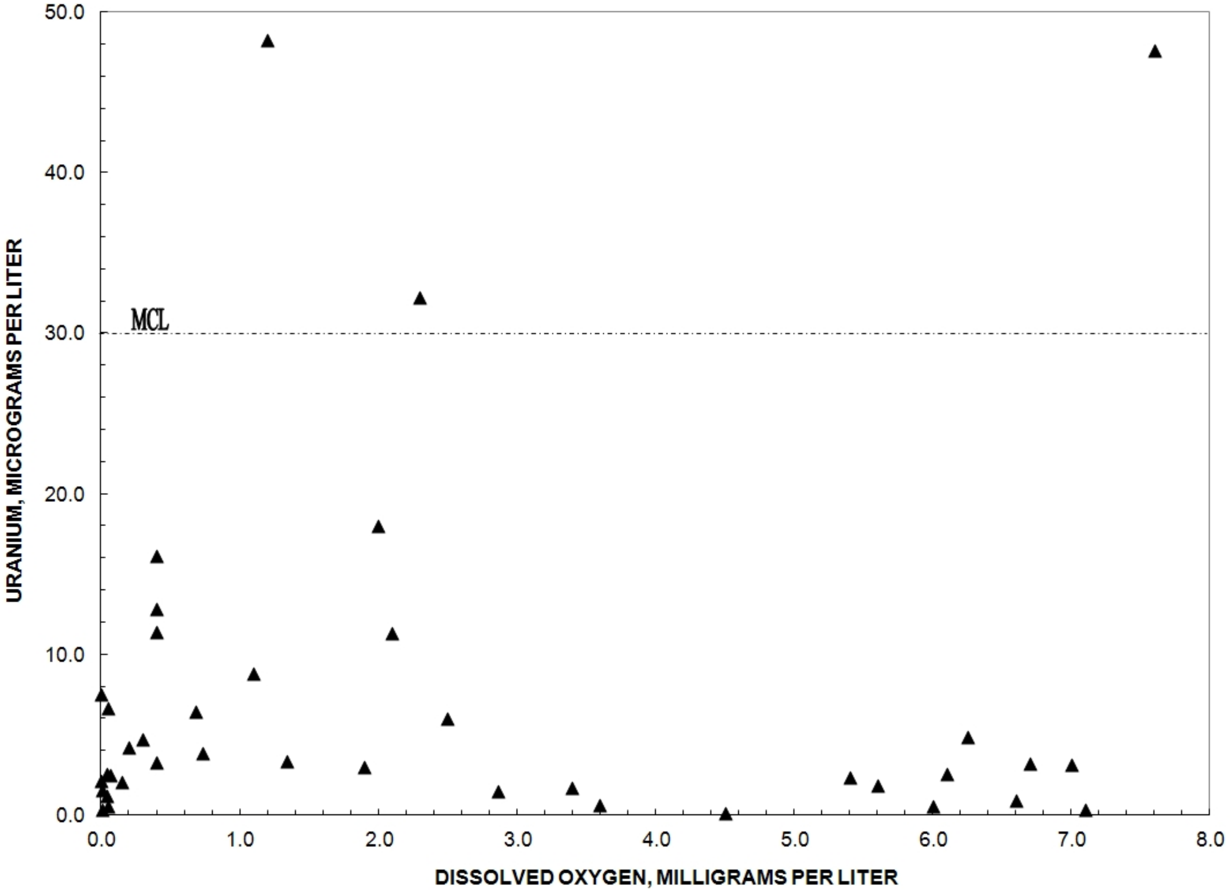


FIG. 5b. Concentrations of uranium as a function of dissolved oxygen concentrations in water from the Mesozoic sedimentary fractured-rock aquifers of the Piedmont Province, northern New Jersey, 2009-2011.

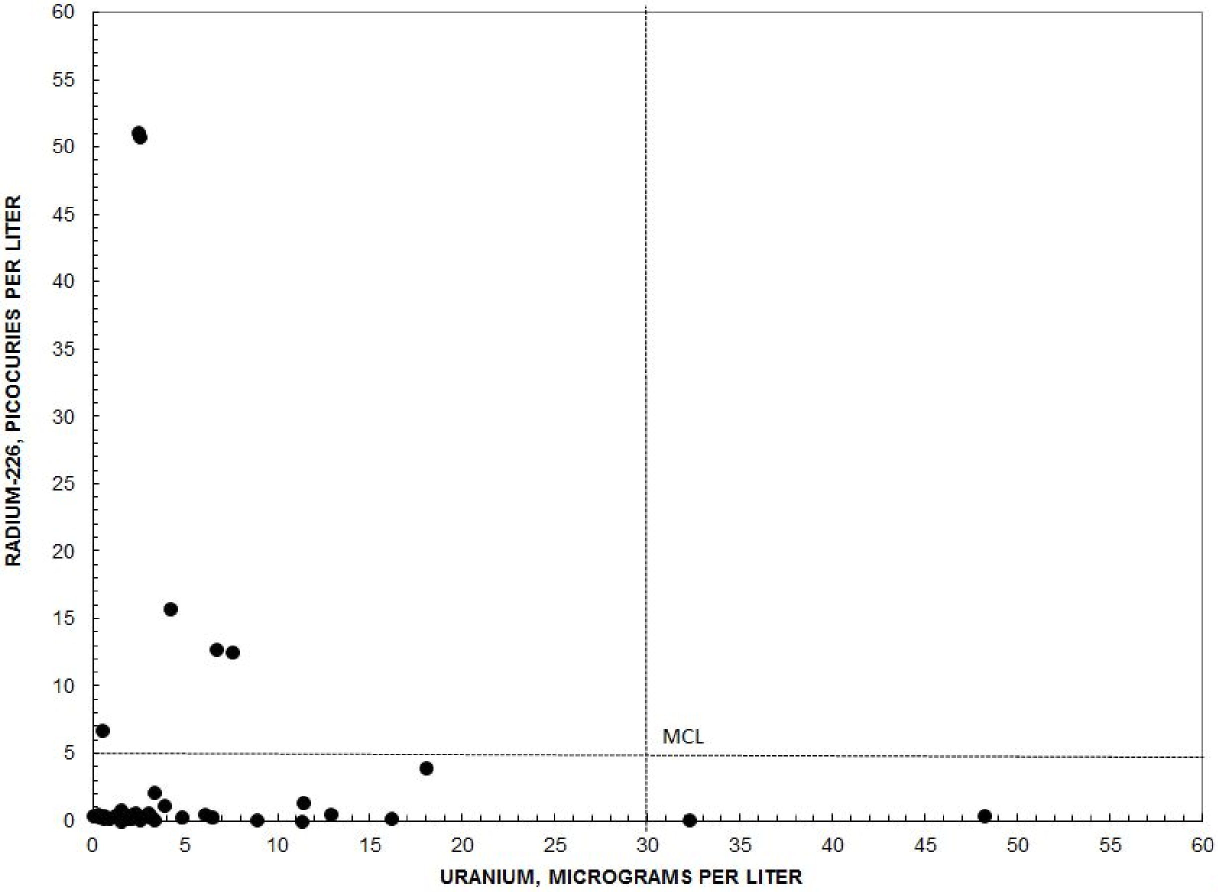


FIG. 6. Concentrations of radium-226 as a function of the concentrations of uranium in water from the Mesozoic sedimentary fractured-rock aquifers of the Piedmont Province, northern New Jersey, 2009-2011.

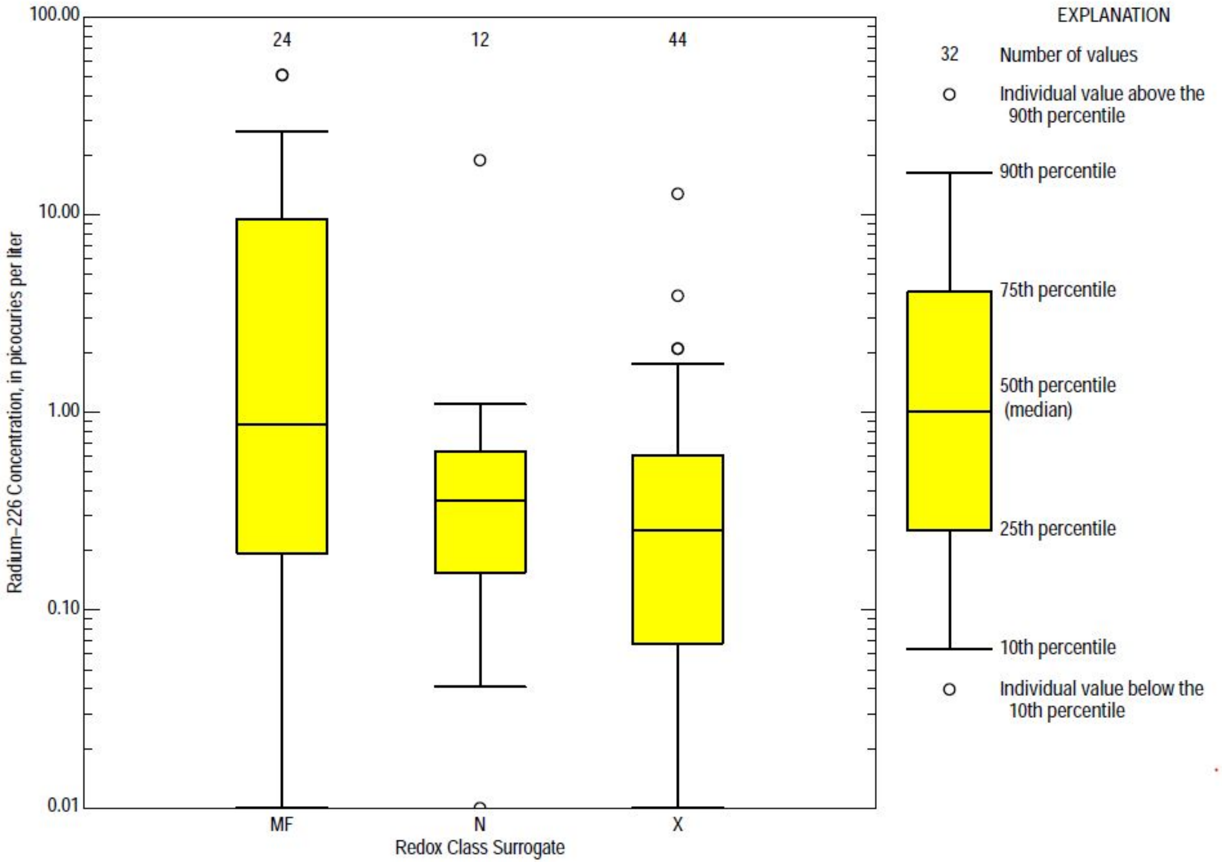


Fig. 7. Concentrations of radium-226 as a function of the redox class, bedrock aquifers, Highlands and Piedmont Provinces, northern New Jersey, 2007-2011. [Redox classes: MF, iron and manganese concentration ≥ 50 ug/L and dissolved oxygen (DO) ≤ 1mg/L; N, DO and nitrate (as nitrogen(N)) concentration ≤ 1mg/L and ammonia concentration ≥ 0.02 mg/L; X, DO concentration > 1mg/L and other components in concentrations less than the given criteria]

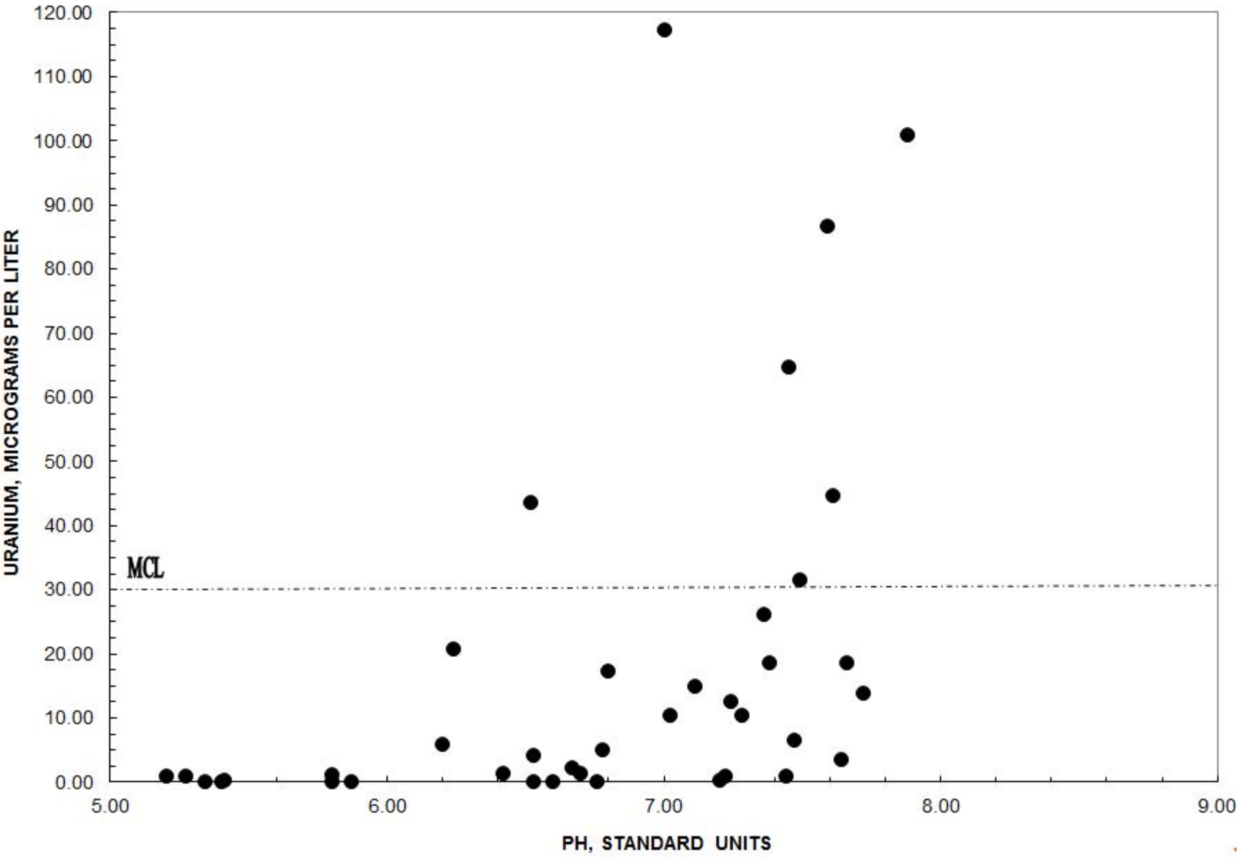


FIG. 8a. Concentrations of uranium as a function of pH in water from the crystalline-rock aquifers of the Highlands Province, northern New Jersey, 2007-2011.

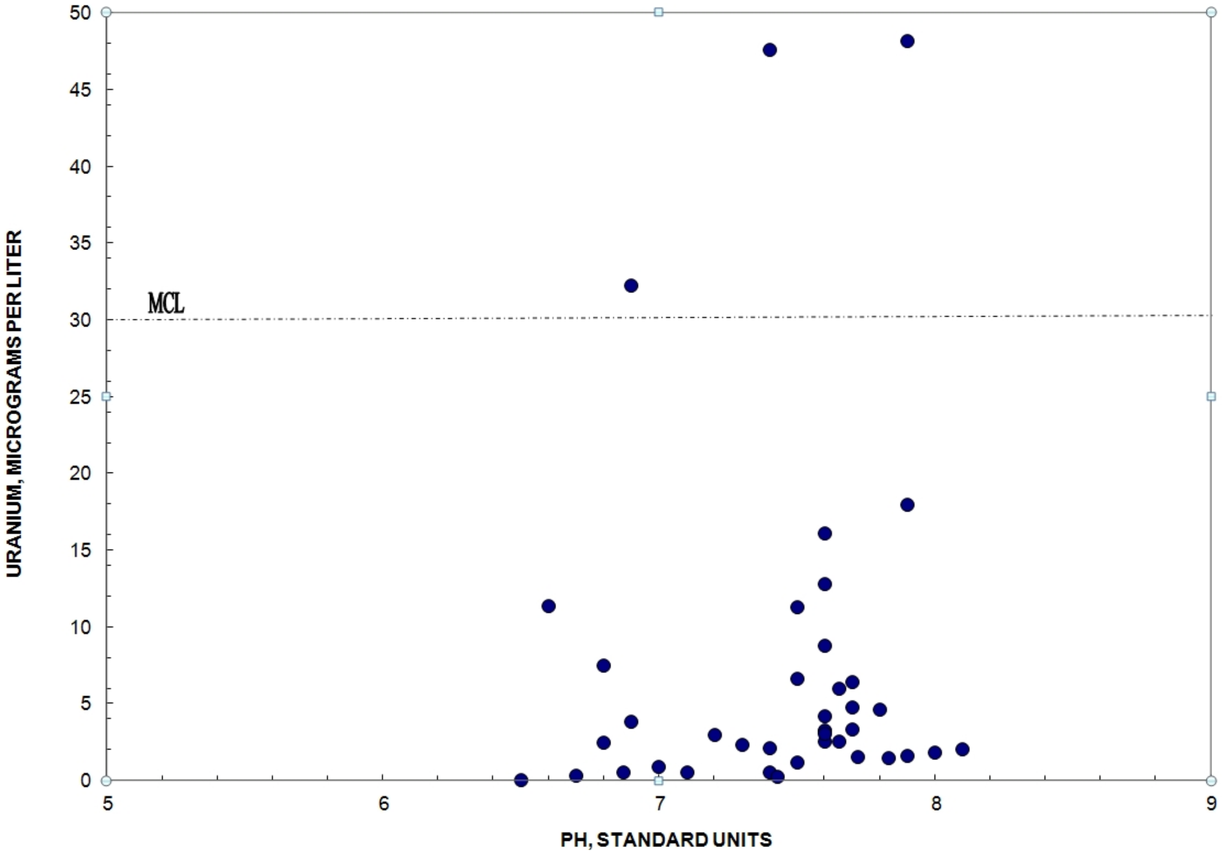


FIG. 8b. Concentrations of uranium as a function of pH in water from the Mesozoic sedimentary fractured-rock aquifers of the Piedmont Province, northern New Jersey, 2009-2011.

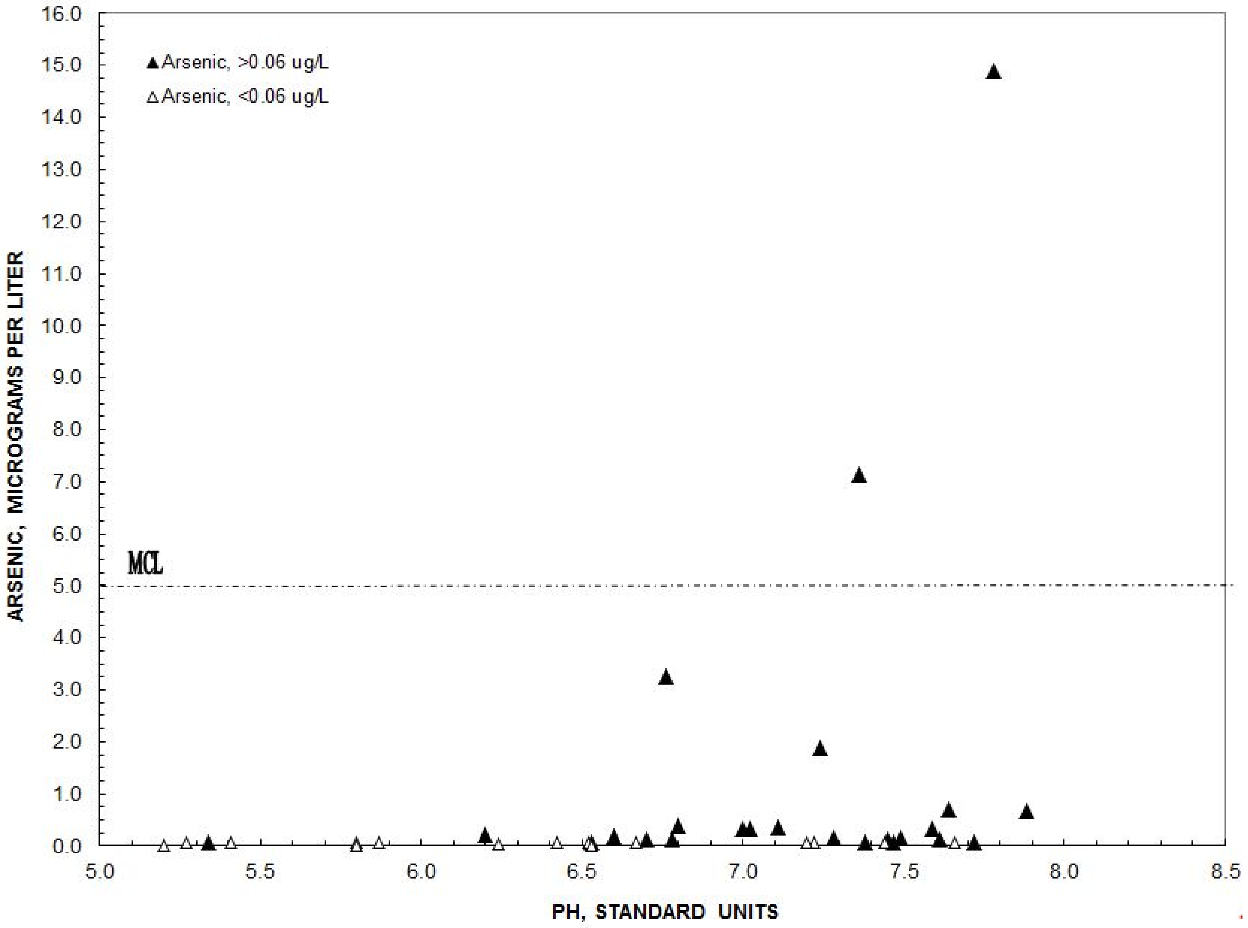


FIG. 9a. Concentrations of arsenic as a function of pH in water from the crystalline-rock aquifers of the Highlands Province, northern New Jersey, 2007-2011.

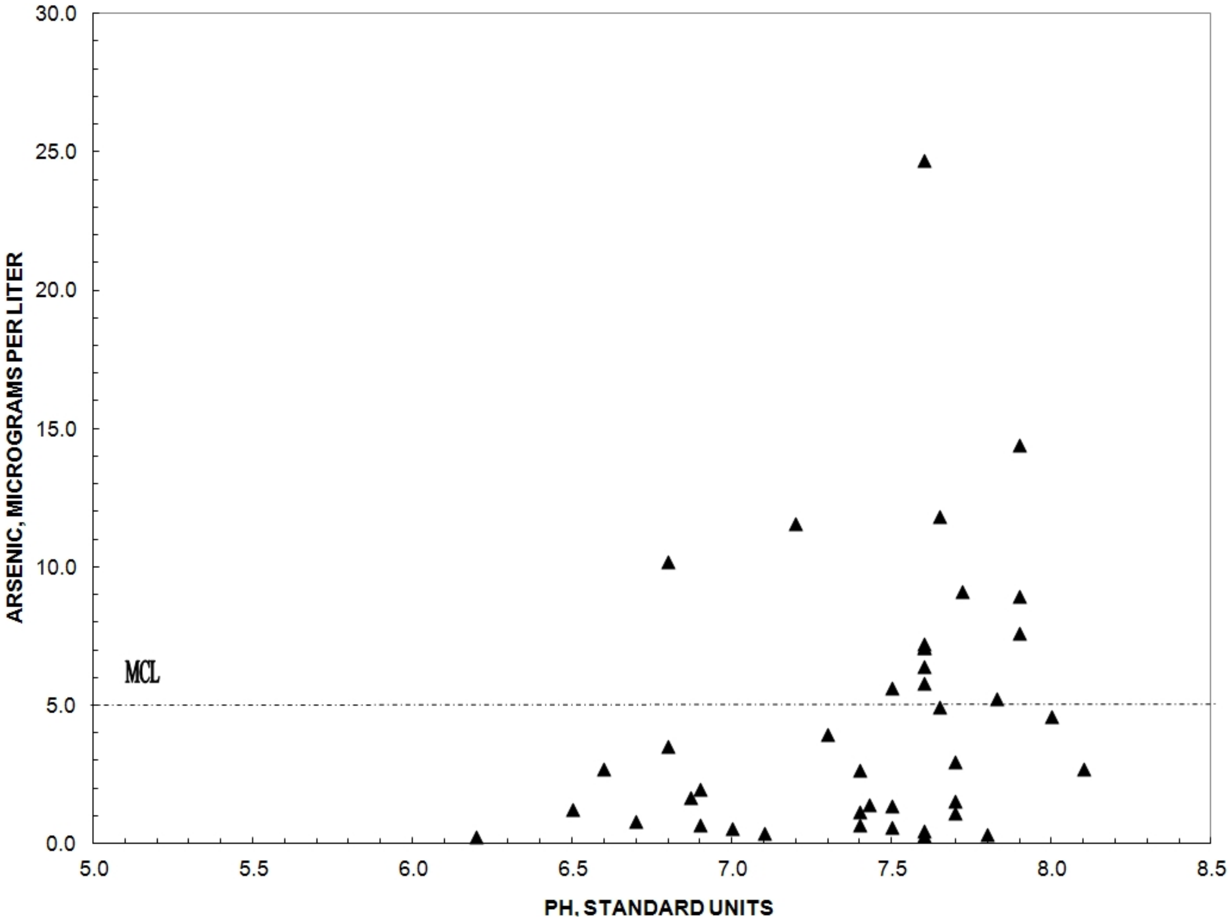


FIG. 9b. Concentrations of arsenic as a function of pH in water from the Mesozoic sedimentary fractured-rock aquifers of the Piedmont Province, northern New Jersey, 2009-2011.

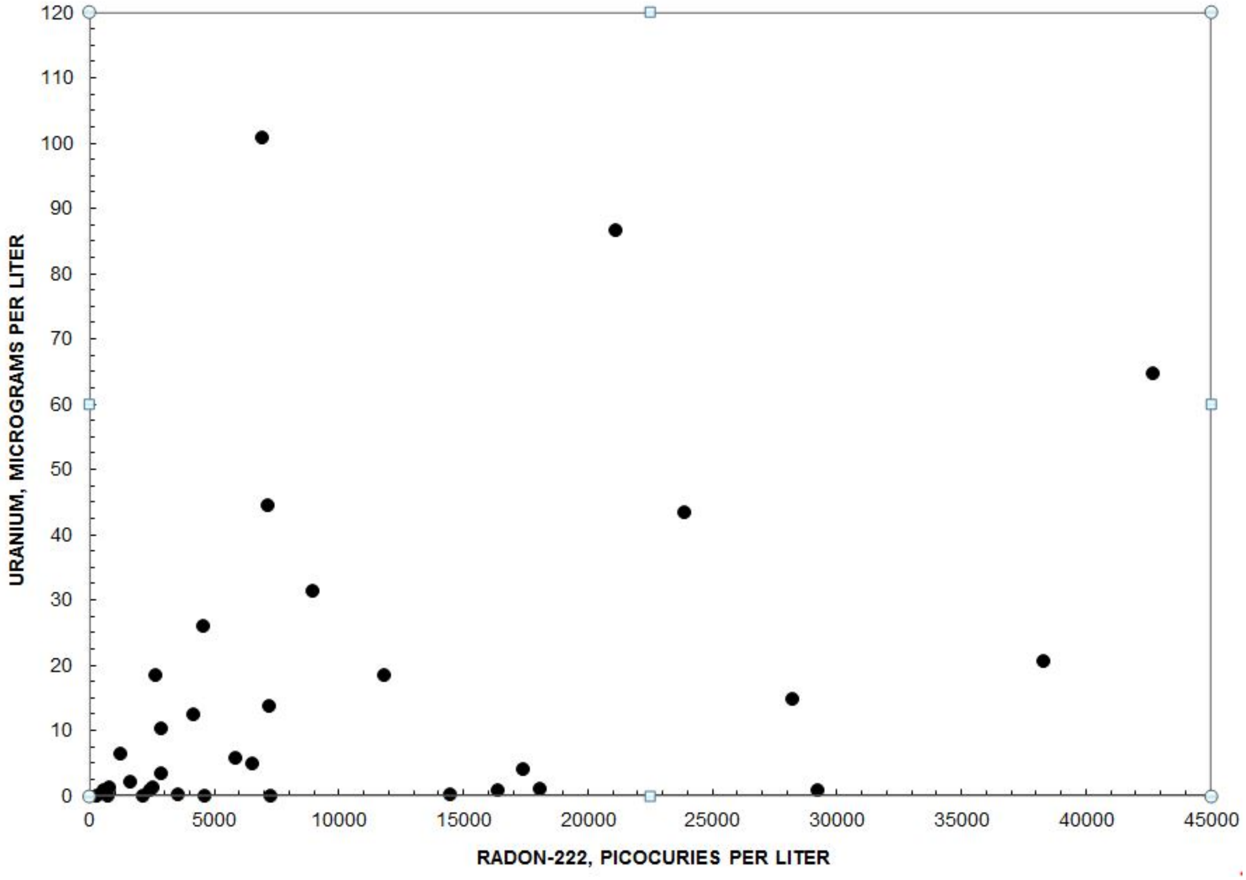


FIG. 10. Concentrations of uranium as a function of the concentrations of radon-222 in water from the (a) crystalline-rock aquifers of the Highlands Province, and the (b) sedimentary fractured-rock aquifers of the Piedmont Province, northern New Jersey, 2007-2011.

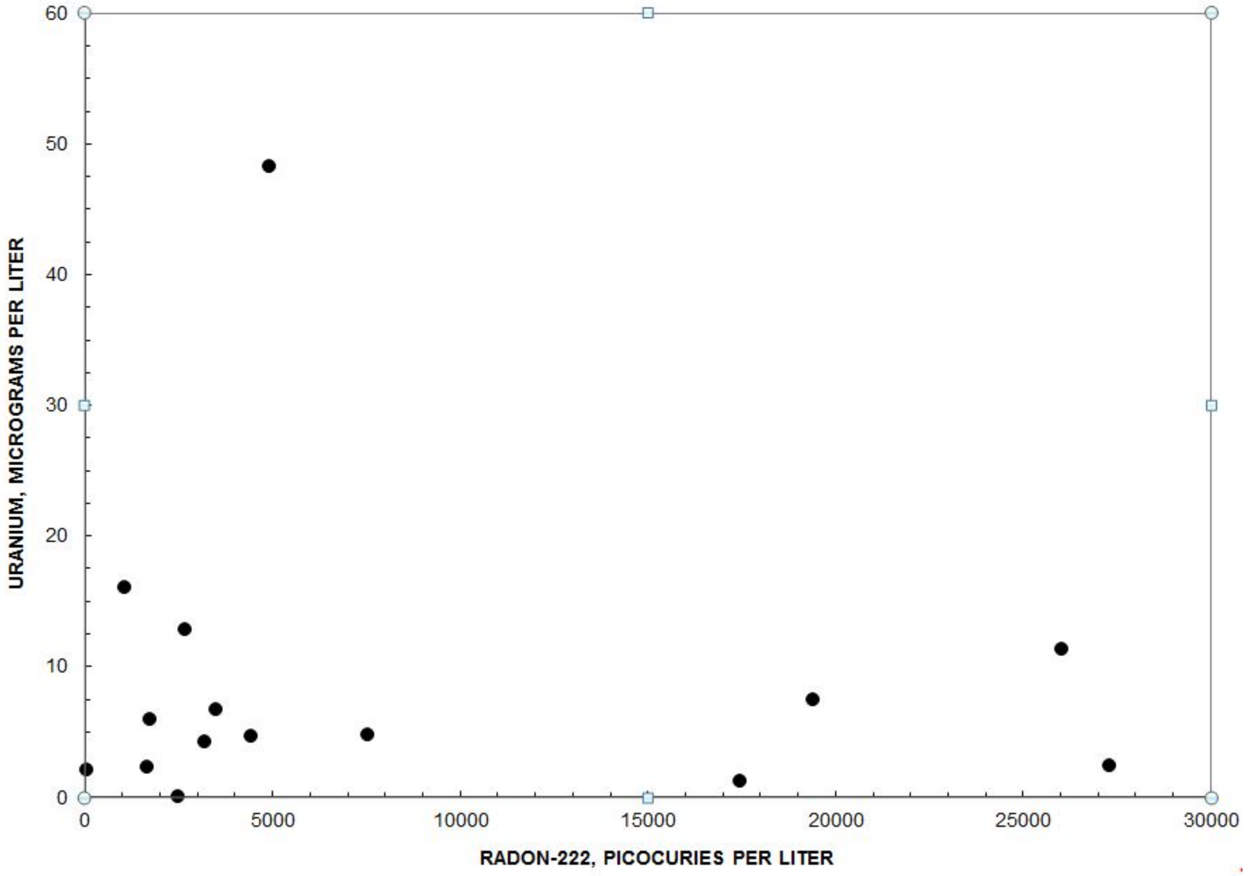


FIG. 10b. Concentrations of uranium as a function of the concentrations of radon-222 in water from the Mesozoic sedimentary fractured-rock aquifers of the Piedmont Province, northern New Jersey, 2009-2011.

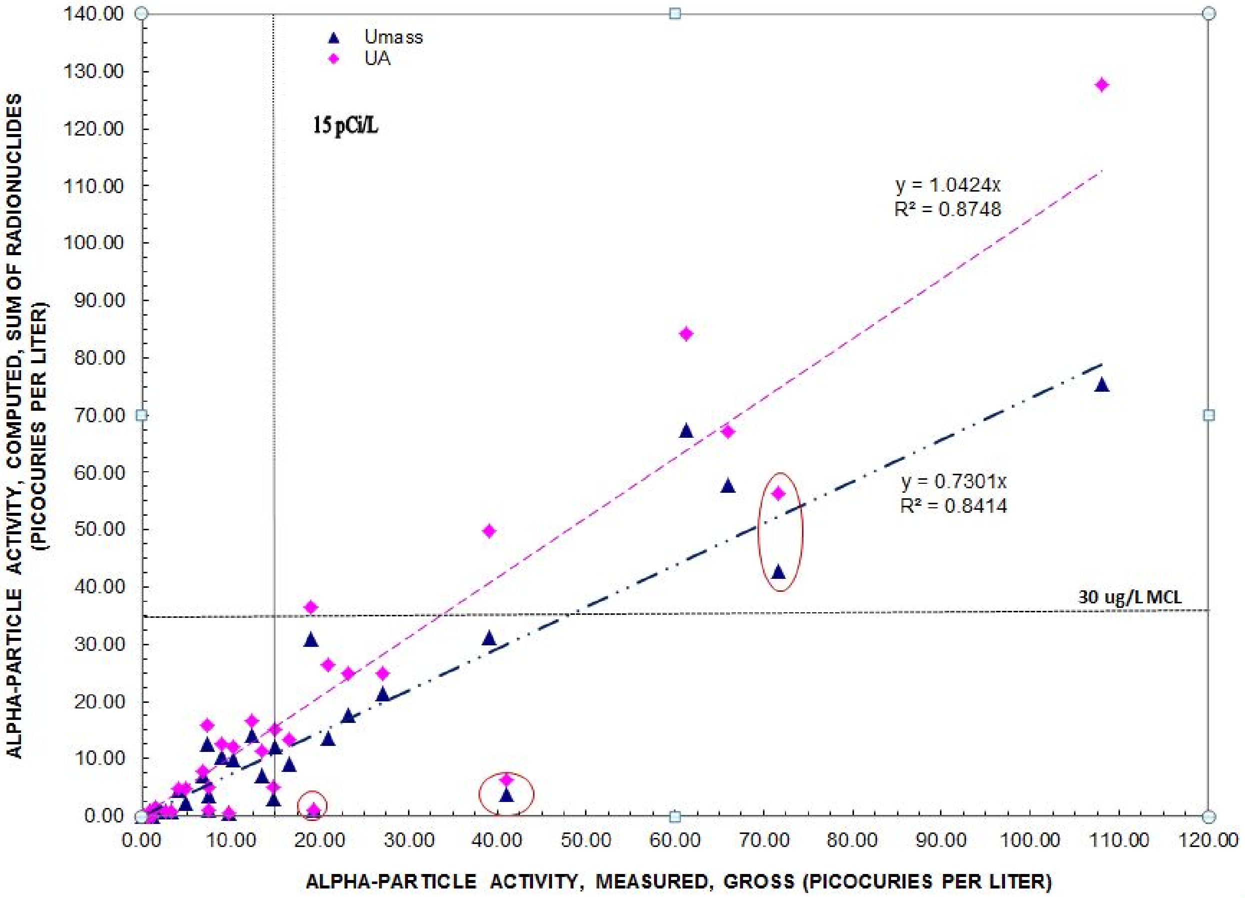


Fig. 11a. Calculated gross alpha particle activity on the basis of measured radionuclide concentrations as a function of the measured gross alpha particle activity (measured 24-48 hours after sample collection) for samples of water from the crystalline fractured-rock aquifers of the Highlands Province, northern New Jersey, 2007-11. The closer the slopes and regression coefficients are to 1, the closer the fit between the calculated and measured values. Calculated gross alpha-particle activity was determined using: 1) measured uranium mass assuming "natural" U-2324/U-238 activity ratio of 1 (blue triangles, labelled Umass); and 2) measured U-234/U-238) isotope ratios (pink diamonds, labelled UA), which ranged from 1 to 2.9, with median value of 1.4 in the Highlands Province. For the Highlands Province, the concentration of Ra-226 was not a major source for gross alpha-particle activity with the exception of 5 samples (12.5 percent), 3 of which are shown circled (and are discussed further in the text); otherwise Ra-226 activity is not included in this chart.

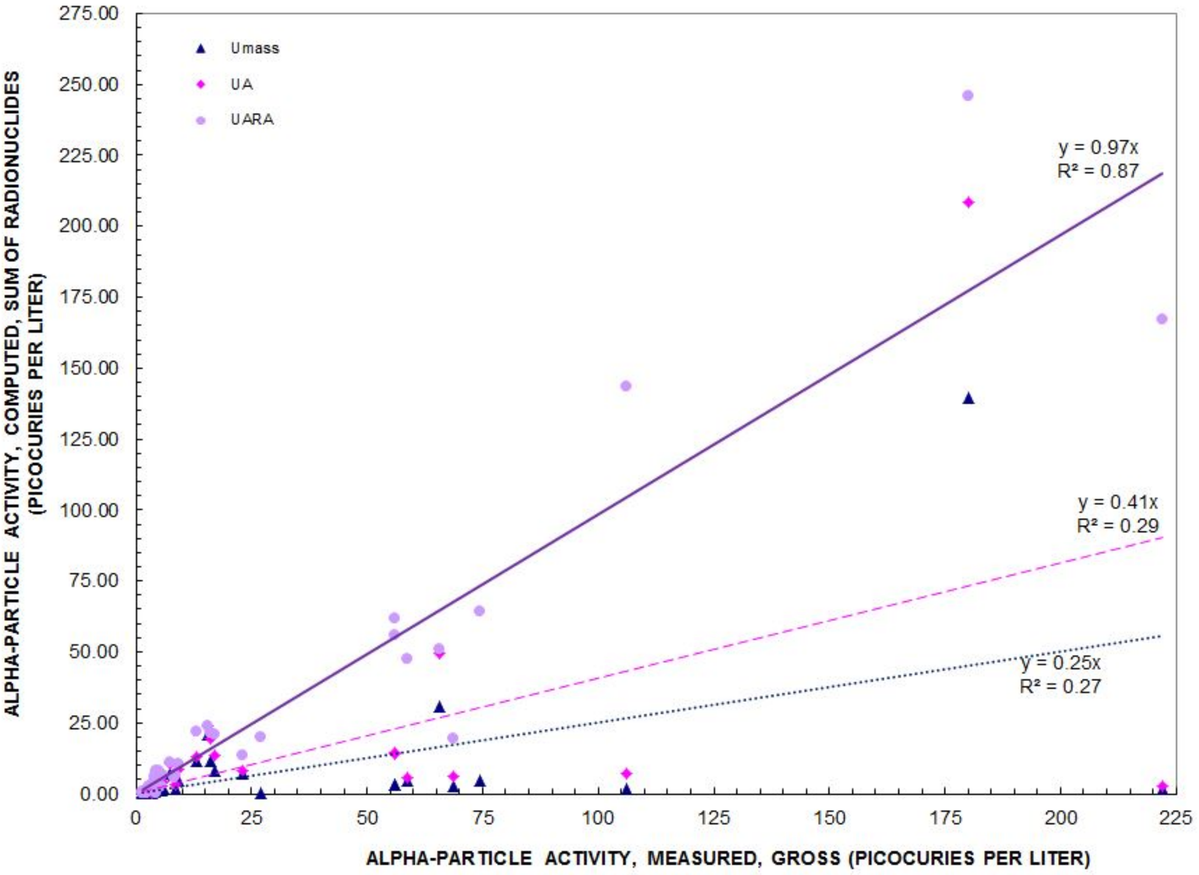


Fig. 11b. Calculated gross alpha particle activity on the basis of measured radionuclide concentrations as a function of the measured gross alpha particle activity (measured 24-48 hours after sample collection) for the Mesozoic fractured sedimentary-rock aquifers of the Piedmont Province, northern New Jersey, 2009-11. The closer the slopes and regression coefficients are to 1, the closer the fit between the calculated and measured values. Calculated gross alpha-particle activity was determined using: 1) measured uranium mass assuming “natural” U-2324/U-238 activity ratio of 1 (blue triangles, labelled Umass); and 2) measured U-234/U-238) isotope ratios (pink diamonds, labelled UA), which ranged from 1 to 8.5, with median value of 2.2 in the Piedmont Province. For the Piedmont Province, the concentration of Ra-226 was about an equal source for gross alpha-particle activity as were the isotopes of uranium, and tended to dominate when gross alpha-particle activity was greater than 50 pCi/L; contribution is shown (lilac circles, labelled UARA).