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Radium-226 and low pH in groundwater due to oxidation of authigenic pyrite; Savannah River Site, South Carolina

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ABSTRACT

The origin of elevated radium-226 in groundwater beneath a sanitary landfill at the Savannah River Site (SRS) was investigated. Nearly one hundred monitoring wells are developed in the Steed Pond Aquifer (SPA), which consists of 100-150 ft of Coastal Plain sand, iron oxides, and minor clay. Wells screened in the upper and middle portions of the aquifer have average Ra-226 between 0.5 and 2.5 pCi/L, and average pHs above 4.7. However, wells screened near the base of the aquifer exhibit higher average Ra-226 concentrations of 2.5 to 4.6 pCi/L, with some measurements exceeding the MCL of 5 pCi/L, and show average pHs of 4.1 to 4.7. These wells are not downgradient of the landfill, and are not impacted by landfill leachate. The Crouch Branch Confining Unit (CBCU) underlies the aquifer, and is composed partly of reduced gray/brown clay with lignite and authigenic pyrite. Gamma ray logs show that the SPA has low gamma counts, but the CBCU is consistently elevated. Groundwater with high radium / low pH also contains elevated sulfate concentrations. pH calculations indicate that sulfate is in the form of sulfuric acid. A model for the origin of elevated Ra-226 levels in deeper SPA wells envisions infiltration of oxygenated SPA groundwater into reduced pyritic CBCU sediments, with consequent oxidative pyrite dissolution, and acidification of groundwater. Then, naturally occurring CBCU radium dissolves, and mixes into the Steed Pond Aquifer.

INTRODUCTION

Radium and gross alpha concentrations in groundwater sometimes exceed the EPA Maximum Contaminants Level (MCLs) due to naturally occurring radioactive material (Focazio et al, 2001; Michel, 1990). Several field studies show that concentrations are partially controlled by acidity, TDS (Total Dissolved Solids), and chloride (Senior and Vogel, 1995; Kozinski et al, 1995; Fisher, 1988; Bolton, 2000). Although acidity and high TDS may have natural sources, a possible manmade source is presented by leachate from municipal solid waste landfills. Therefore, in the vicinity of landfills, radium and/or gross alpha MCL exceedances in groundwater may be anthropogenic, even if no radium-bearing waste was disposed of in the landfill. In order to distinguish between naturally elevated radium and leachate-mobilized radium in groundwater below a landfill, careful interpretation of available data is necessary.

This paper presents a case study of a solid waste landfill in the South Carolina Coastal Plain. At this landfill, some monitoring wells show MCL exceedances of Ra-226 and gross alpha, and Ra-226 concentrations correlate with low pH. Since landfill leachate is often acidic, the data could be interpreted in terms of radium being mobilized by the leachate.

Nevertheless, considerations of spatial and temporal analyte distributions and mass balance calculations support a natural origin for the elevated Ra-226 concentrations, due to oxidation of authigenic pyrite below the water table.

SITE DESCRIPTION

The study area is located within the Savannah River Site (SRS), a Department of Energy nuclear facility in the South Carolina Coastal Plain (Figure 1). The SRS Sanitary Landfill (SLF) is 71 acres in area, and received solid waste generated from office, cafeteria, and routine industrial activities between 1974 and 1997 (Westinghouse Savannah River Company, 2004). The SLF is situated on terrain which slopes gently to the southeast, at elevations of 170 to 230 feet above sea level (Figure 2). The site is underlain by gently southeastward dipping Cenozoic sand and clay.

The water table, like the land surface and subsurface strata, also slopes gently to the southeast (Figure 2). Under most of the landfill, the water table is 25 to 40 feet below the surface. The water table aquifer is the Steed Pond Aquifer, which consists of sand, and extends down to about 50 ft above mean sea level; the aquifer thickness beneath the SLF is about 100 feet. Below that is the Crouch Branch Confining Unit (CBCU), consisting of clay and sand interbeds (Westinghouse Savannah River Company, 2004). Some groundwater monitoring wells beneath and/or to the southeast of the landfill show elevated levels of organic solvents, tritium, radium, iron, chloride, and acidity.

GROUNDWATER RADIOACTIVITY AND CHEMISTRY

Limited groundwater monitoring at SLF began in 1984, and expanded in 1987. A series of wells was installed within, surrounding, and downgradient of the landfill. Wells which penetrate the landfill, or surround its perimeter, are mostly less than 60 feet deep; however, downgradient of the landfill, a series of well clusters was installed with shallow screen zones (about 20-30 feet deep), as well as deeper screen zones which sample depths of 40 to 100 feet.

Monitoring for tritium and gross alpha began in 1987. Tritium was found consistently above the MCL in some near-source wells. During the next few years, a few near-source wells also showed repeated detections of gross alpha (GA) above the 15 pCi/L MCL, as high as 30 pCi/L. Therefore, monitoring of radium-226 and radium-228 began in 1992. Since then, the concentration of Ra-226 plus Ra-228 has exceeded the 5 pCi/L MCL in 26% of analyses; GA has exceeded 15 pCi/L in 3% of analyses.

Figure 3 shows the relationship between Ra-226 and Ra-228 concentrations in SLF wells. Each point represents the average radium concentration at a single well, for the period 1992-2005. The poor correlation between Ra-226 and Ra-228 shows that those two isotopes are not co-located at SLF; in general terms, their concentrations are not controlled by the same source or process. Ra-228 concentrations are highest in shallow wells; whereas Ra-226

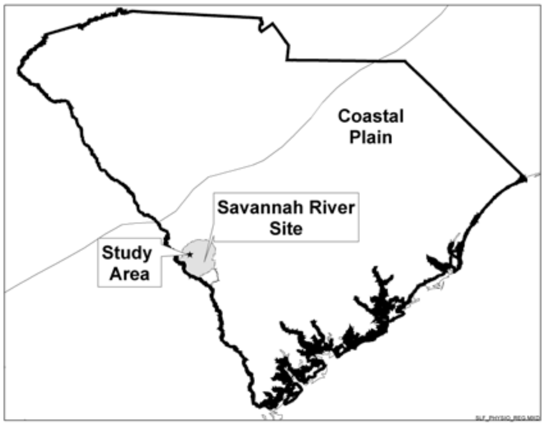

Figure 1. Location map.

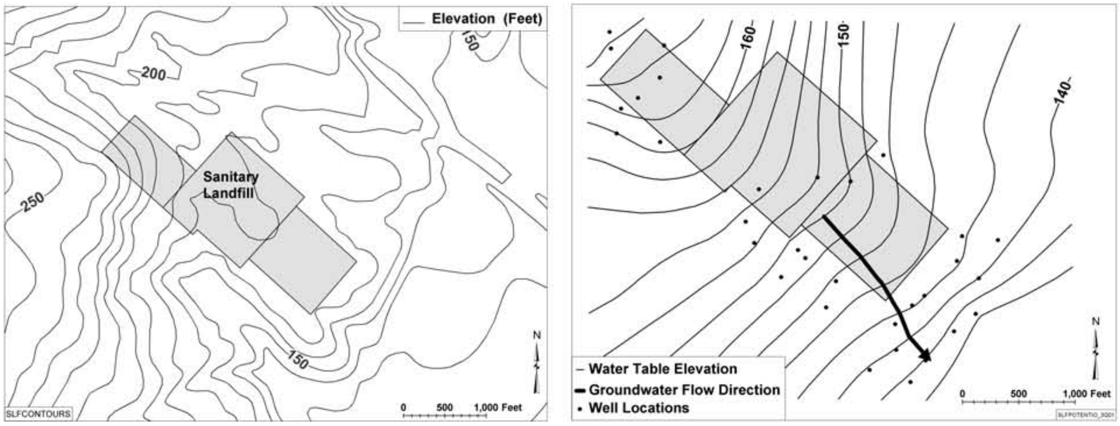

Figure 2. Surface topography at SLF (left), and 2001 water table surface (right).

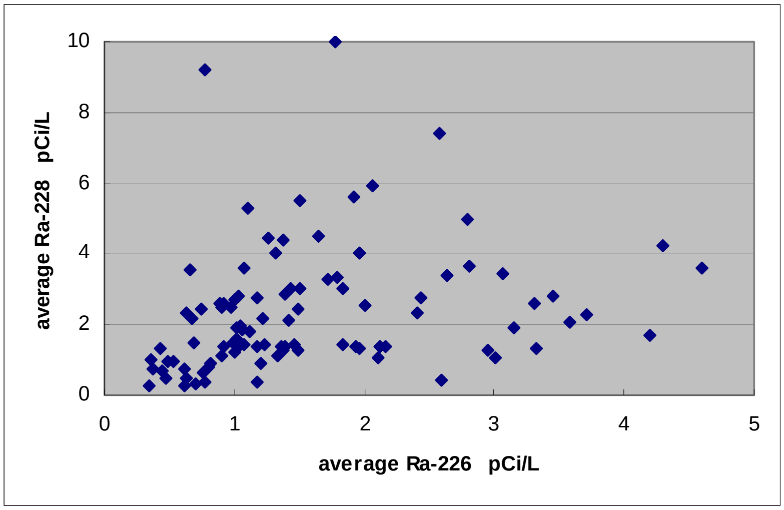

Figure 3. Average SLF groundwater Ra-226 and Ra-228 concentrations, 1992-2005.

is most concentrated in deeper wells. The origin of Ra-228 at SLF is beyond the scope of this report; the focus of the investigation will be on Ra-226.

Ninety-nine SLF wells have been monitored for Ra-226 since 1992. Individual analytical results range from nondetect up to 28 pCi/L. Over the 1992-2005 period, most wells have average Ra-226 concentrations below 2 pCi/L, with some as low as 0.5 pCi/L. However, 11 wells have average Ra-226 concentrations exceeding 3 pCi/L, and as high as 4.6 pCi/L. Radium-226 is not distributed randomly; rather, it is concentrated in wells southeast of the SLF, with relatively deep screen zones (top of screen zone below 95 ft elevation). Shallower wells at the same locations have less radium-226. Wells with elevated Ra-226 are acidic, having average pHs in the range of 4.1 to 4.7, whereas wells with low Ra-226 have pHs at or above the rainfall value of 4.7. Upgradient wells northwest of the landfill have low average Ra-226 (0.6 to 1.8 pCi/L for designated background wells). The average pH of background wells is 4.7 or higher.

Since Ra-226 concentrations are highest southeast of the landfill, and correlate with low pH, and since Ra-226 is not elevated in the background wells, one might conclude that the radium has been mobilized by downgradient flow of acidic landfill leachate. However, detailed inspection of available data indicates that the radium is naturally elevated. Spatial and chemical arguments will be presented to show that landfill leachate cannot account for the observed acidity in wells elevated in Ra-226.

Figure 4 is a cross-section along a NW-SE plane, with selected monitoring well clusters projected onto the section. Groundwater flow is from left to right. Average Ra-226 concentrations during the period 1992-2005 are shown. The highest concentrations are found in wells southeast of the landfill, but confined to deeper wells. Wells which penetrate the landfill (10A, 18, and 21), and other wells near the landfill, exhibit lower levels of Ra-226. Upgradient wells (43, 31) are also low in Ra-226, but those wells do not penetrate to the depths characterized by high Ra-226. At the Sanitary Landfill, wells with elevated Ra-226 do not have an appropriate background well for comparison. Figures 5 and 6 show average pH values during the periods 1993-6, and 2002-5. Comparison of the two graphs shows that pH values were stable during the investigation period. Like radium-226, pH values below 4.7 are limited to deeper wells. Groundwater distribution of selected landfill contaminants, 1,4-dioxane and chloride, are shown in Figures 7 and 8. For these constituents, as well as others not shown, groundwater beneath the landfill (wells 10A, 18, and 21) is clearly contaminated, and a plume extends into shallow and middle wells southeast of the landfill. However, deeper wells are unaffected. It is concluded that the deep wells which show elevated concentrations of Ra-226 and low pH are not situated along contaminant flow paths issuing from the landfill.

Groundwater directly beneath the landfill has been less acidic than rainwater since 1987, but prior to that, acidic pHs around 4.0 were recorded there. Acidic leachate is a common occurrence downgradient of municipal landfills; acetic acid is the dominant species. No analytical data are available for acetic acid at SLF, but Total Organic Carbon (TOC) measurements were made during 1991-6. Average TOC concentrations in wells deeper than 95 ft MSL are about 0.2 to 0.3 mg/L. If all TOC were attributed to acetic acid, 0.3 mg/L

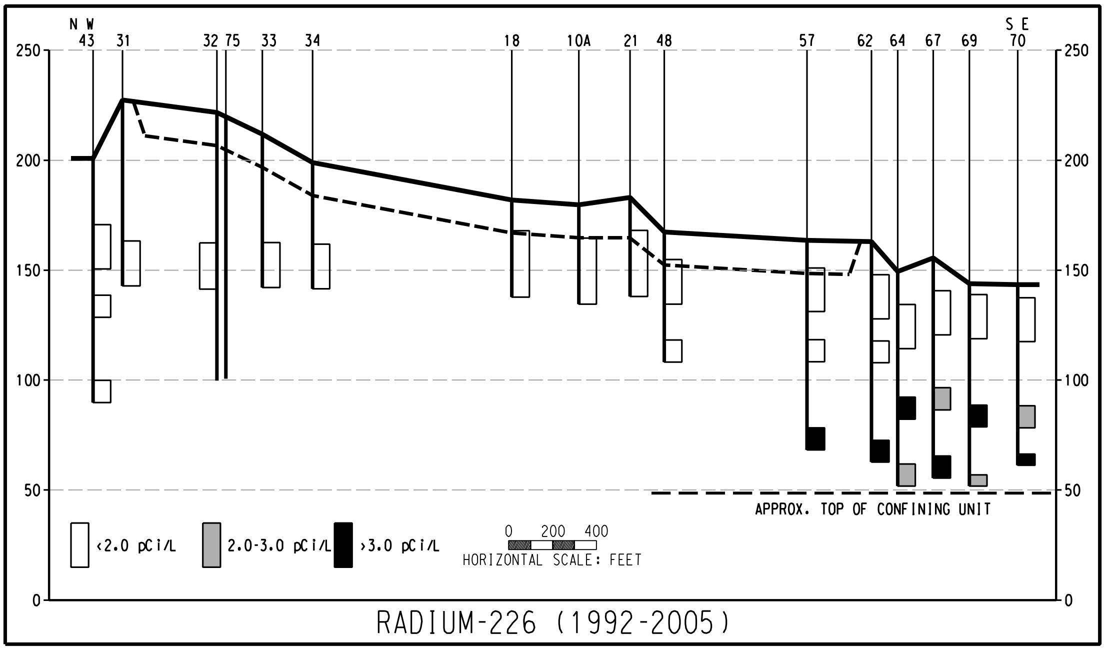

Figure 4. Cross-section of SLF with average Ra-226 groundwater concentrations, 1992-2005.

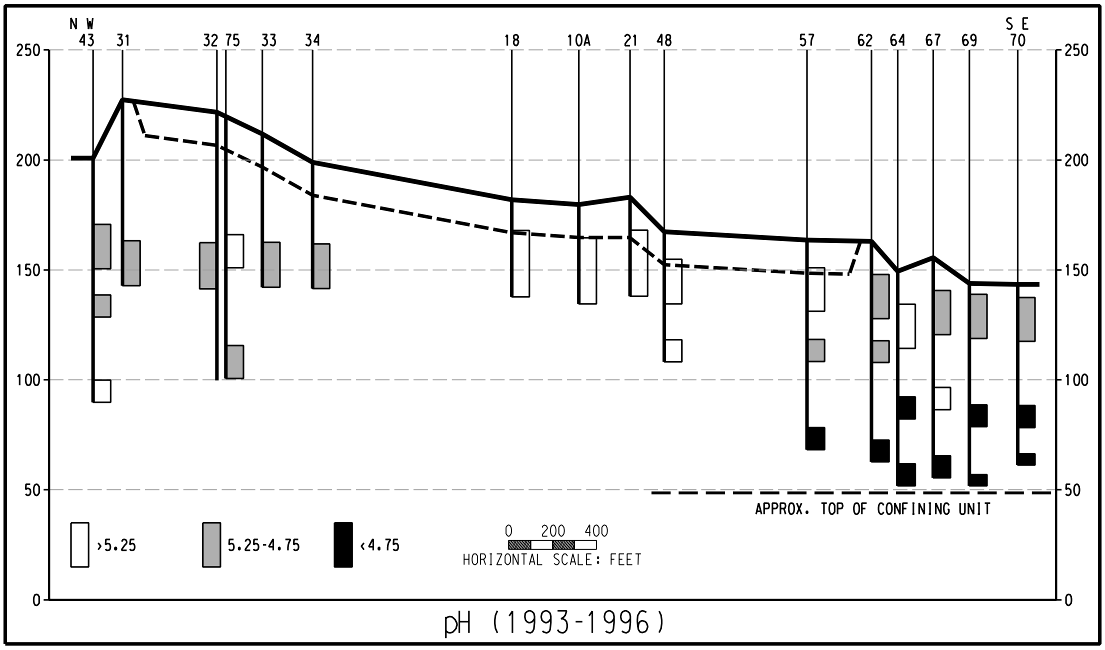

Figure 5. Average pH of SLF groundwater, 1993-1996.

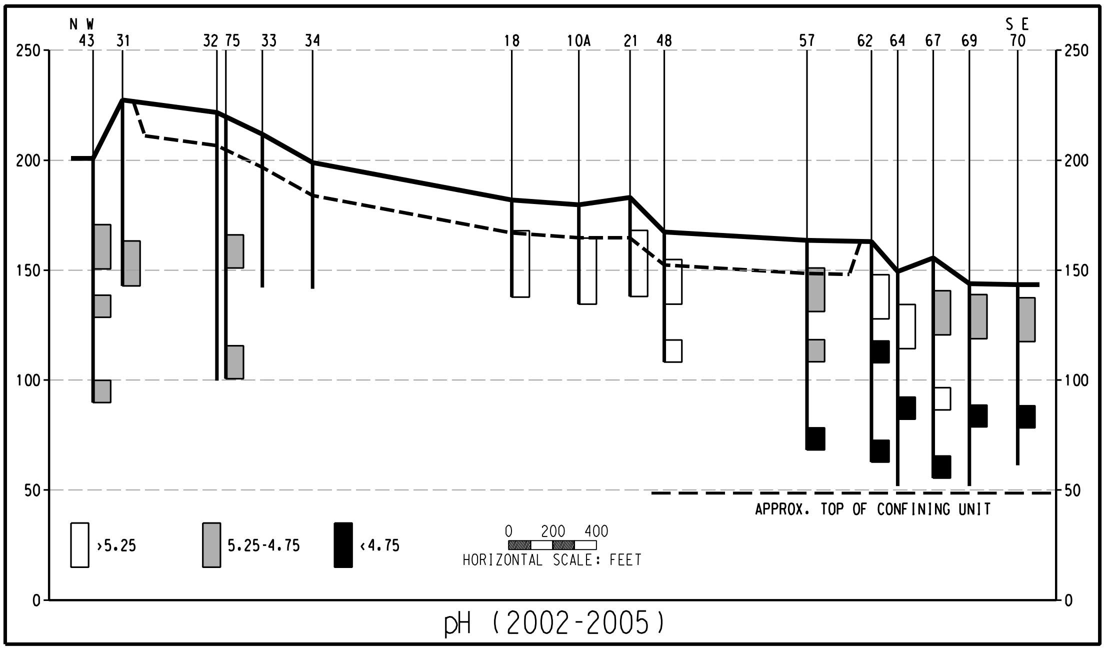

Figure 6. Average pH of SLF groundwater, 2002-2005.

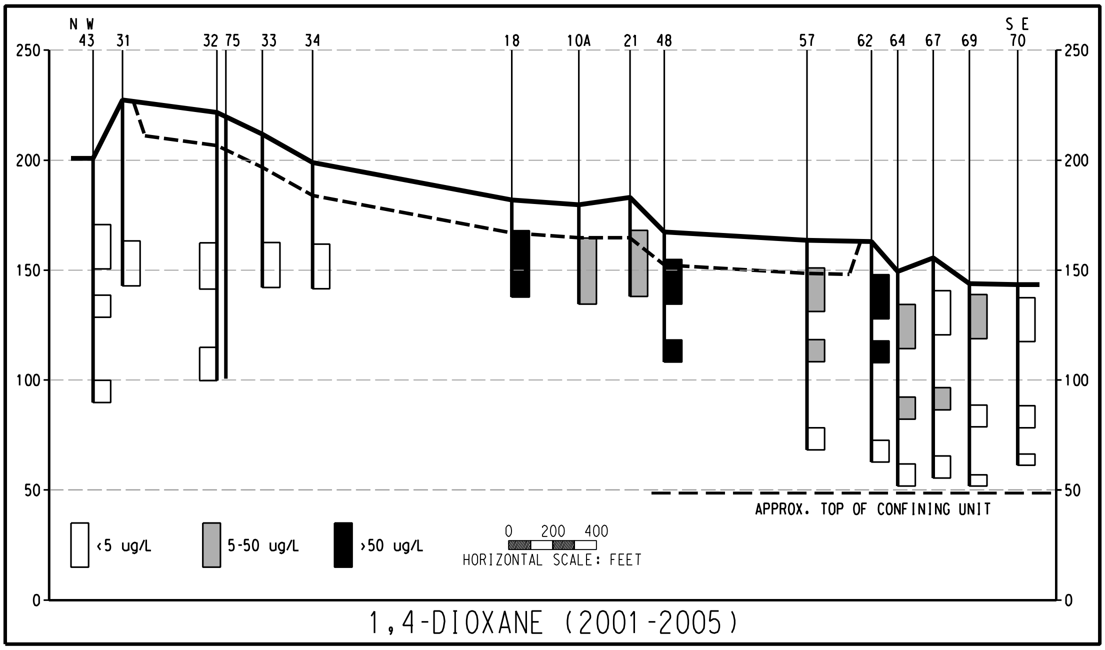

Figure 7. Maximum groundwater 1,4-dioxane concentrations, 2001-2005.

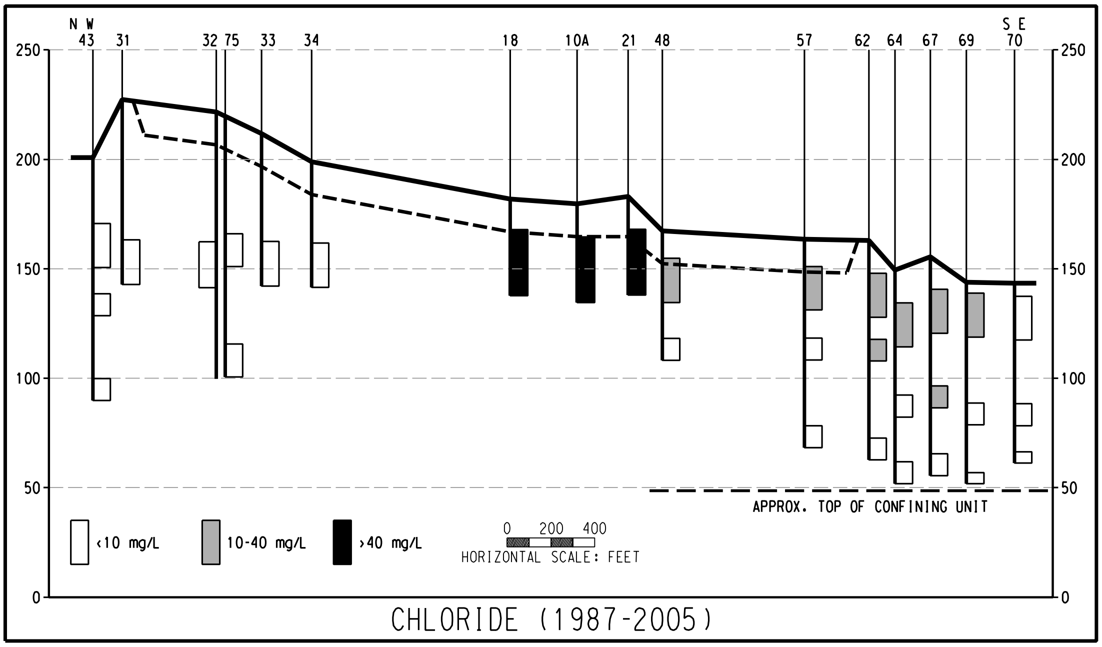

Figure 8. Maximum groundwater chloride concentrations, 1987-2005.

would correspond to a pH of 5.3, assuming complete dissociation. However, some of the deeper wells have average pHs as low as 4.1, and individual measurements go down to 2.8. There is not enough organic acid present in the deep wells to account for the observed pH.

Based on spatial and chemical arguments given above, it is concluded that elevated radium-226 concentrations and low pH in groundwater in deep SLF wells (screened below 95 ft elevation) are not related to landfill processes, but rather are naturally occurring.

PYRITE OXIDATION MODEL

A natural process for generating acid in groundwater is oxidation of pyrite or marcasite, to create sulfuric acid. This is well known to occur naturally, and is capable of lowering pH to below 3. Schroeder et al (2004) documented oxidation of pyrite contained within Coastal Plain clays in southern Georgia. At the SLF, deep wells which contain high Ra-226 and low pH also exhibit relatively high sulfate concentrations, but shallow wells are low in sulfate (Kubilius, 2005); this suggests that oxidation of sulfide is occurring in the subsurface.

Pyrite or marcasite is not expected to occur in oxidized sediments; they would persist only in a reduced setting. Although the Coastal Plain sedimentary package as a whole is quite oxidized, individual clay layers may preserve an original reducing mineralogy, due to low permeability. Chemically reduced clays may be recognized by their dark color due to carbonaceous material, glauconite, or sulfides. Deep wells at SLF are screened near the base of the Steed Pond Aquifer, just above the Crouch Branch Confining Unit (CBCU). According to Aadland et al (1995), the top of the CBCU corresponds to lignitic and iron-sulfide-bearing gray to black clays of the Paleocene Lang Syne/Sawdust Landing and Snapp Formations. In order to confirm whether these chemically reduced clays exist beneath SLF, we examined 6 sediment cores co-located with wells 35, 62, 64, 67, 71, and 72. In all cores, sediment of the SPA is uniformly oxidized, and is composed of quartz, kaolinite, and iron oxides. However, five cores contain dark brownish gray clay, indicative of reduced conditions, at depths corresponding to elevations of 34 to 55 ft, correlating with the top of the Crouch Branch Confining Unit (Westinghouse Savannah River Company, 2004), and slightly below the screen zone bottoms of the Ra-226-rich wells. In one core, lignite was visible. Although no pyrite was visible macroscopically, there was clear evidence of sulfide mineral oxidation. In four cores, abundant needles of gypsum ($CaSO_4 \cdot 2H_2O$) were present on the outer surface of the core. Melanterite(?) ($FeSO_4 \cdot 7H_2O$) was visible on one core, and jarosite ($KFe_3(SO_4)_2(OH)_6$) in another. All three minerals are hydrated sulfates, and form as oxidation products of sulfides. Two of them contain iron, indicating that they probably formed by oxidation of an iron mineral. All three minerals clearly crystallized after the core had been obtained, indicating that the sulfide precursor is present in the core itself. These observations indicate that reduced clays containing easily oxidizable iron sulfide exist beneath the SLF, and can account naturally for low pH conditions observed in deep wells.

Reduced sedimentary strata are often enriched in uranium (Krauskopf, 1967) and its daughter, Ra-226. Ten gamma ray well logs confirm that the top of the CBCU is elevated in natural radioactivity (Westinghouse Savannah River Company, 2004; Kubilius, 2005).

The co-occurrence of dissolved sulfate, low pH, Ra-226, sulfide-bearing clay, and gamma ray core log kicks in the vicinity of the deep well horizons, is regarded as strong evidence for a natural process involving oxidation of iron sulfide, which lowers groundwater pH and mobilizes Ra-226. Aerated groundwater near the base of the Steed Pond Aquifer, flowing southeastward through sand in the lower part of the SPA, comes in contact with the top of the brown/gray clay. Oxygen diffuses downward into the clay, and reacts with pyrite/marcasite. The decomposition of pyrite generates sulfuric acid at the weathering front, and H^+ and SO_4^{2-} both diffuse upward into the sand and into the deeper screen zones. The sulfuric acid mobilizes radium-226 which is naturally elevated in the reduced clay.

A test of this model is to determine if observed sulfate concentrations in deep wells can account for observed pHs, as sulfuric acid. Most of the deep wells have average sulfate concentrations of 6 to 13 mg/L (Kubilius, 2005). If sulfuric acid accounted for 100% of dissolved sulfate, 9 mg/L would generate a pH of 3.7. This indicates that observed low pHs in deep SLF wells can successfully be accounted for by the observed sulfate concentration.

CONCLUSION

At the Savannah River Site Sanitary Landfill, groundwater apparently downgradient of the waste unit exceeds the 5 pCi/L MCL for radium-226 plus radium-228, in part due to elevated concentrations of radium-226. Because the apparently downgradient wells also show anomalously low pH, it is possible to conclude that the elevated Ra-226 concentrations are due to advection of acidic landfill leachate into groundwater. However, examination of applicable spatial and chemical data shows that landfill leachate is not the source for either elevated Ra-226 or low pH in the affected wells; rather, a natural process of oxidation of authigenic pyrite is responsible for acidification of groundwater and dissolution of naturally occurring radioactive material. Salient points are:

- Spatial distribution of indicator contaminants (1,4-dioxane, chloride, and others) do not coincide with spatial distribution of Ra-226.
- Radium-226 is associated with low-pH groundwater, but total organic carbon concentrations cannot account for observed pHs in terms of acetic acid landfill leachate.
- Inspection of SLF core indicates oxidation of authigenic pyrite as a natural source for low pH in wells with elevated Ra-226.
- Sulfate concentrations in high-Ra-226 groundwater are sufficient to account for the low pH naturally, in the form of sulfuric acid.
- Gamma ray core logs show elevated natural radioactivity at the same depth as authigenic pyrite.

Due to the generation and advection of acidic leachate, groundwater downgradient of landfills is susceptible to contamination by naturally occurring toxic or radioactive metals such as radium, even if the materials were not disposed of in the waste unit. However, there are natural mechanisms for production of acidity and consequent dissolution of naturally occurring contaminants. Careful study of spatial and chemical information should be done before attributing elevated levels of contaminants near landfills to manmade processes.

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