

EXHIBIT A

Disequilibrium of Naturally Occurring Radioactive Materials (NORM) in Drill Cuttings from a Horizontal Drilling Operation

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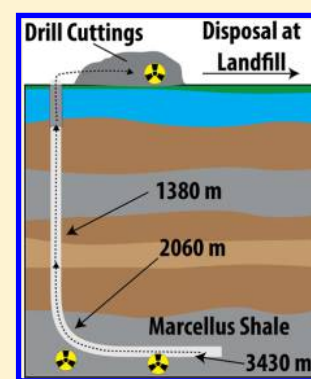
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Supporting Information

ABSTRACT: Naturally occurring radioactive materials (NORM) in solid waste or “drill cuttings” produced from unconventional drilling for natural gas extraction wells potentially pose environmental contamination risks; however, the composition and mobility of NORM in these solid wastes are poorly understood. In this study, the composition of NORM, including uranium, thorium, radium, lead, and polonium isotopes, was evaluated in three samples of drill cuttings extracted from a well drilled into the Marcellus Shale formation. Leachability of NORM in drill cuttings was characterized by leaching the solid waste with dilute acetic acid at four different pH values. The uranium-series radionuclides in cuttings and leachate samples displayed isotopic disequilibrium, suggesting some environmental mobility of radionuclides in these shale formations. Our results indicate that isotopic analysis of uranium-series radionuclides is needed for a more complete understanding of the potential environmental contamination risks associated with these solid wastes.



INTRODUCTION

Although there are numerous socioeconomic benefits related to increased domestic energy production, unconventional drilling produces large volumes of waste that may result in long-term undesirable environmental impacts.^{1–3} While a range of chemical contaminants have been documented in both solid and liquid wastes, naturally occurring radioactive materials (NORM) from the uranium 238 (²³⁸U) and thorium 232 (²³²Th) series may also be cause for concern.^{4,5} Liquid waste (produced fluids and flowback waters) from unconventional wells has received considerable attention from numerous stakeholders because of the large volumes of radium (Ra)-enriched fluids that are produced and the risks these fluids pose to riparian environments.^{6–16} Less attention has been paid to the levels of NORM in solid wastes (termed drilling cuttings). Despite the 2.37 million tons of drill cutting extracted in Pennsylvania (PA) in 2011 alone, very little information about the radiochemical profile of these materials is available.¹⁷

Accurate analysis of NORM in drill cuttings and leachates from drill cuttings requires a multitude of radiochemical techniques that are tailored to the physicochemical and/or radiochemical nature of any given isotope. In 2015, PA and WV (West Virginia) released studies on the NORM content of Marcellus Shale cuttings, indicating that radioactivity levels in cuttings from horizontal portions of an unconventional well were higher than those from vertical portions.^{18,19} The studies also concluded that drill cuttings pose minimal risk to the general public. Although this conclusion may be the case, these reports focused on only several long-lived radionuclides from the ²³⁸U series, specifically, ²³⁸U and ²²⁶Ra. Other key

series radionuclides, such as pure α -emitting radionuclides, ²³⁴U, thorium 230 (²³⁰Th), and polonium 210 (²¹⁰Po) and the low-energy β -emitter, lead 210 (²¹⁰Pb), were not explicitly reported. The PA and WV reports also indicated that leachates from landfills accepting drill cuttings contained NORM, and in some cases, the ²²⁶Ra concentrations in these samples were above action levels.^{18,19} WV and PA did not report levels of ²³⁸U in leachates; however, results from sequential leach studies suggest that ²³⁸U in Marcellus Shale cuttings is relatively mobile and may contribute to elevated levels of ²³⁸U in landfill leachates.²⁰ While new information about ²³⁸U and ²²⁶Ra in Marcellus Shale cuttings and leachates is emerging, relative concentrations and mobility of other environmentally persistent radionuclides in the ²³⁸U series, including ²³⁴U, ²³⁰Th, ²¹⁰Pb, and ²¹⁰Po, remain unexplored. These radionuclides may provide important information for environmental contamination risk and source apportionment.

Here, we characterized NORM in cuttings associated with horizontal drilling activities in the Marcellus Shale formation. First, using new and modified radiochemical methods, we quantitated and assessed the equilibrium status of environmentally persistent ²³⁸U-series radionuclides (²³⁸U, ²³⁴U, ²²⁶Ra, ²¹⁰Pb, and ²¹⁰Po) in three solid samples from a horizontal well within the Marcellus Shale formation (Figure 1). Second, the potential for NORM to leach from cuttings extracted from the

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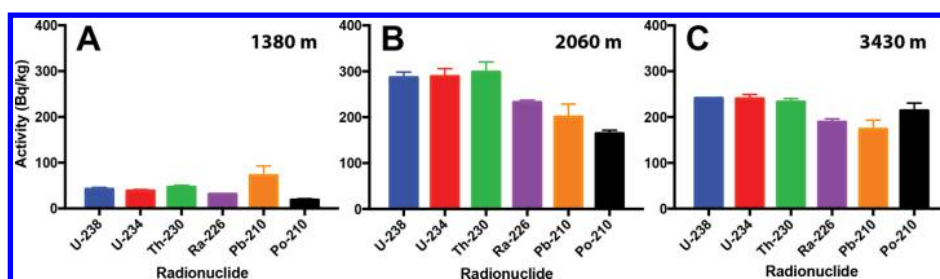


Figure 1. Levels of ^{238}U -series radionuclides in three drill cutting samples from an unconventional drilling operation targeting the Marcellus Shale: (A) sample from a vertical portion of the well at 1380 m, (B) sample from a horizontal drilled portion of the well at 2060 m, and (C) sample from a horizontal drilled portion of the well at 3430 m.

horizontal portion of the well was assessed using a modified U.S. Environmental Protection Agency (EPA) Toxicity Characteristic Leaching Procedure (TCLP).²¹ We hypothesized that ^{238}U -series radionuclides in Marcellus Shale drill cuttings would be in secular equilibrium (steady state) and that ^{238}U -series radionuclides would partition into TCLP leachates with decreasing pH.

MATERIALS AND METHODS

General. All chemicals were ACS reagent grade or higher. The University of Iowa State Hygienic Laboratory (SHL) analyzed the solid samples for the content of relevant metals, inorganics, and organics (Table S1 and Figure 2). High-purity

^{229}Th standard 4328C [National Institute of Standards and Technology (NIST), Gaithersburg, MD], ^{209}Po standard 92565 (E&Z), and the cyclotron-produced ^{203}Pb (Lantheus Medical Imaging, Billerica, MA). Emission energies and half-lives were taken from the NUDAT database from the U.S. National Nuclear Data Center (NNDC, Brookhaven National Laboratory, U.S. Department of Energy, Upton, NY).²² The only exception is for ^{209}Po , for which a half-life of 128.3 years was used, as evidence suggests that its half-life is longer than previously established.²³ All samples were decay corrected to the time of extraction using standard decay correction equations.²⁴

Drill Cutting Samples. Three solid samples were obtained from a single well in northern PA. The first sample was taken from the vertical, air-drilled section (1380 m) extracted in mid-November 2015, and the two other samples were extracted from the horizontal section (2060 and 3430 m) in mid-December 2015. Samples were received January 8, 2016, and homogenized. Subsamples for U, Th, Ra, and Pb isotopic analysis were dried at 110 °C until a stable weight was achieved. Because of the volatility of ^{210}Po , analysis was performed on the “wet” sample.

Methods of Analysis. Uranium and Thorium. ^{238}U , ^{234}U , and ^{230}Th were prepared by a slightly modified rapid method developed for the analysis of actinides in asphalt.²⁵ First, 50 mBq each of ^{232}U and ^{229}Th tracer were added to the samples (1.0 g), and the dried drill cuttings were ashed in a muffle furnace (600 °C, 1 h) in a platinum crucible. The samples were then rapidly fused in NaOH (10 g, 600 °C, 15 min), before removal from the salt matrix using H_2O . Initially, the samples were precipitated with calcium phosphate [$\text{Ca}_3(\text{PO}_4)_2$], followed by a second precipitation with cerium fluoride (CeF_3). CeF_3 solids were then dissolved [10 mL, 3 M HNO_3 /0.175% boric acid; 10 mL, 3 M HNO_3 /1 M $\text{Al}(\text{NO}_3)_3$] and separated by Eichrom method ACW01.²⁶ Elemental fractions were prepared for α spectrometry by CeF_3 micro-precipitation as previously described.²⁷

Radium. Samples (1000 cm^3) for ^{226}Ra analysis were dried, sealed (>21 days, for ^{222}Rn ingrowth), and quantitated by HPGe γ spectrometry (SHL) as previously described.^{10,11}

Lead. ^{210}Pb was separated and quantitated by PACE Analytical according to Eichrom method PBS01.²⁸

Polonium. ^{209}Po tracer (~50 mBq) was added to 0.5 g subsamples and then digested with 11 mL of aqua regia overnight on hot plate. Samples were then precipitated [few drops of H_2O_2 , $\text{Fe}(\text{OH})_3$, manganese dioxide (MnO_2), and NH_4OH], centrifuged, and washed (H_2O) as described for the methodology developed for Marcellus Shale-produced fluids.¹¹ Pellets were dissolved [20 mL of 0.1 M HCl and 2 mL of 25%

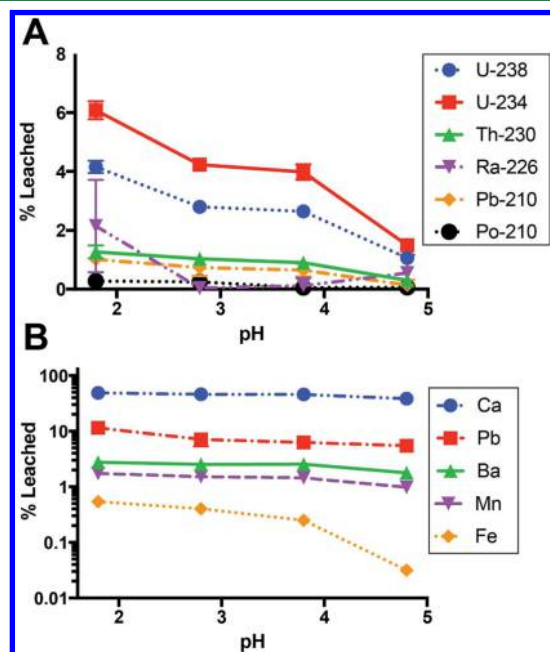


Figure 2. Percentage of (A) radionuclides (Figure 1) and (B) metals leached by acetate buffer at pH 1.8, 2.8, 3.8, and 4.8 from 2060 m drill cuttings (normalized to dry weight).

germanium (HPGe) γ spectrometry of drill cuttings was performed at the SHL using 500 cm^3 Marinelli beakers on an ORTEC system calibrated to a mixed γ source [Standard Reference Source 101582, Eckert and Ziegler (E&Z), Atlanta, GA] using a previously described methodology.^{10,11} Separation and gas flow proportional counting (GFPC) of ^{210}Pb in drill cuttings were performed by PACE Analytical (Greensburg, PA). α spectrometry was performed at the University of Iowa. Radionuclide tracers included ^{232}U standard 92403 (E&Z),

(w/v) hydroxylamine ($\text{NH}_2\text{OH}\cdot\text{Cl}$), autodeposited onto nickel (Ni) disks, and counted by high-resolution α spectrometry.¹¹

Leaching Studies. Leaching was performed using a modified EPA TCLP.²¹ Centrifugation was used instead of filtration to allow for inclusion of colloid-bound radionuclides. For Pb, Po, U, and Th leaches, 100 mL of acetate buffer adjusted to pH 1.8, 2.8, 3.8, and 4.8 ($n = 4$) was added to 10.0 g of sample. Because of the higher detection limits for ²²⁶Ra, samples were increased to 20.0 g of drill cuttings and 200 mL of acetate buffer. All samples were then mixed for 24 h and centrifuged, and the leachates were placed into glass beakers prior to separation and quantitation.

Uranium and Thorium. ²³²U and ²²⁹Th tracers were added, and the sample was subjected to a $\text{Fe}(\text{OH})_3$ and $\text{Ca}_3(\text{PO}_4)_2$ coprecipitation. The resulting solid pellets were dissolved [10 mL, 3 M HNO_3 /1 M $\text{Al}(\text{NO}_3)_3$], separated, and prepared for α spectrometry as described above.

Radium. Leachates were prepared by the EPA 903.0 method by SHL.²⁹ The only modification to this procedure was that yields were determined by barium 133 (¹³³Ba) using HPGe γ spectrometry en lieu of gravimetric determinations. ²²⁶Ra was quantitated by GFPC.

Lead. ²⁰³Pb tracer was added, and then the leachates were then subjected to a $\text{Fe}(\text{OH})_3$ precipitation. The resultant pellet that was dissolved in 10 mL of 1 M HCl and separated on Pb resin according to Eichrom method PBW01.³⁰ Yields of ²⁰³Pb were determined by sodium iodide (NaI) γ spectrometry.⁹ Activities of ²¹⁰Pb were determined by ingrowth of ²¹⁰Po via liquid scintillation on an α/β discriminating liquid scintillation counter at SHL.

Polonium. ²⁰⁹Po was added as a tracer, and the leachate was acidified to pH 1–2 using HCl. $\text{NH}_2\text{OH}\cdot\text{Cl}$ was added [5 mL, 25% (w/v)], and Po was then autodeposited at 90 °C on a Ni planchet and quantitated by α spectrometry.¹¹

Metals. Using the modified EPA TCLP,²¹ each acetate buffer (10 mL, pH 1.8, 2.8, 3.8, and 4.8; $n = 3$ for each pH) was added to the drill cuttings (2060 m sample) and homogenized for 24 h. The samples were then centrifuged, decanted, and acidified (100 μL of 16 M HNO_3) prior to analysis by SHL.

RESULTS AND DISCUSSION

Chemical Characterization. Cuttings from each location were analyzed for common organic and inorganic constituents that could interfere with radiochemical separations. The shallowest sample (1380 m) was extracted by air drilling from the vertical portion of the well, whereas the two deeper samples from the horizontal section (2060 and 3430 m) were removed by diesel-based drilling techniques. All three samples had high levels of organic fractions, with levels of ethylbenzene (38000–63000 $\mu\text{g}/\text{kg}$), xylenes (270000–450000 $\mu\text{g}/\text{kg}$), diesel fuel (70000–120000 $\mu\text{g}/\text{kg}$), and total extractable hydrocarbons (70000–120000 $\mu\text{g}/\text{kg}$) notably elevated (Table S1). The 1380 m sample is chemically distinct from the deeper Marcellus Shale samples (2060 and 3430 m), which were characteristic of marine black shales as evidenced by enrichment of trace elements cadmium (Cd), copper (Cu), vanadium (V), zinc (Zn), arsenic (As), and selenium (Se).³¹

Characterization of NORM. Environmentally persistent radionuclides from the natural ²³⁸U series (²³⁸U, ²³⁴U, ²³⁰Th, ²²⁶Ra, ²¹⁰Pb, and ²¹⁰Po) were quantified in each drill cutting location (Figure 2A,B and Table S2). On the basis of the chemical analysis and the potential for interference of organic

constituents with radiochemical separations, the cutting samples were fired in a muffle furnace. NaOH fusion, based on methods developed for actinide analysis in asphalt, was used to ensure total dissolution of solid material.²⁵ Drill cuttings are exceptionally challenging samples for radiochemical separations. For example, radiochemical yields for uranium in this study were $40 \pm 10\%$. Previous radiochemical analysis of drill cutting material reported substantially lower radiochemical yields (i.e., $\sim 2\%$ recovery).¹⁸ These results suggest that new, more robust methods for analysis of drill cutting solid waste are needed. ²²⁶Ra analyses are simplified for this complex matrix by elevated abundance and the high-energy γ emissions of ²²⁶Ra decay products (²¹⁴Bi and ²¹⁴Pb) for HPGe γ spectrometry with little sample preparation (apart from a 30 day hold to allow for decay product ingrowth). The high density of the drill cuttings can interfere with direct measurement of ²¹⁰Pb (46 keV, 4%) by γ spectrometry,^{32,33} therefore, ²¹⁰Pb was quantitated by methods developed for ²¹⁰Pb in soil.²⁸ ²¹⁰Po was extracted with aqua regia and H_2O_2 , because ²¹⁰Po can adhere to organic matter in the soil³⁴ and volatilize in dry samples through elevated temperatures (>100 °C)³⁵ or by biological processes under ambient conditions.³⁶

The deep drill cuttings (2060 and 3430 m) have levels of ²³⁸U-series radionuclides significantly higher than those of the shallower location (1380 m). These results are consistent with the WV and PA studies that indicate horizontal drill cuttings from the Marcellus Shale have elevated levels of ²³⁸U and ²²⁶Ra relative to those of the vertical portions.^{18,19} The lower level of ²²⁶Ra relative to ²³⁸U is likely attributable to the partitioning of ²²⁶Ra into Marcellus Shale brines that have characteristically elevated levels of ²²⁶Ra.^{6,8,10,11} As expected, the horizontal portions are also elevated in environmentally persistent radionuclides, ²³⁴U, ²³⁰Th, ²¹⁰Pb, and ²¹⁰Po. Contrary to our hypothesis, the ²³⁸U-series radionuclides were not in secular equilibrium. In all samples, ²²⁶Ra levels were lower than ²³⁸U, ²³⁴U, and ²³⁰Th levels, which is consistent with other observations.^{18,19} Similarly, levels of ²¹⁰Pb and ²¹⁰Po were decreased relative to the ²²⁶Ra level. This disequilibrium is likely attributable to partitioning of the noble gas, radon 222 (²²²Rn), in the subsurface as is expected of gaseous hydrocarbons. The disequilibrium between ²²⁶Ra and ²¹⁰Pb is likely explained by partitioning of ²²²Rn and could be explored as a tool for determining gas migration in the subsurface.³⁷ These results suggest that radiochemical equilibrium of ²³⁸U-series radionuclides cannot be assumed in Marcellus Shale drill cuttings; accurate assessment of environmental contamination risk by ²³⁸U-series radionuclides must include detailed radiochemical analyses.

Leaching. Drill cuttings in the Marcellus Shale region are primarily (98.4%) deposited in landfills;³⁸ however, the stability of NORM in drill cuttings is uncertain. To assess the potential for ²³⁸U-series radionuclides to leach from drill cuttings, we employed a simple, acetate buffer leaching protocol based on the EPA TCLP method,²¹ which the EPA believes simulates the leaching that occurs in landfills.³⁹ We chose to analyze the 2060 m sample as it had the highest levels of all ²³⁸U-series radionuclides and would allow for shorter counting times and lower detection limits. In general, we observed negative correlations for the percent radionuclide leached with respect to pH for the ²³⁸U-series radionuclides tested ($R^2 = -0.96$ for ²³⁸U; $R^2 = -0.96$ for ²³⁴U; $R^2 = -0.95$ for ²³⁰Th; $R^2 = -0.62$ for ²²⁶Ra; $R^2 = -0.96$ for ²¹⁰Pb; $R^2 = -0.91$ for ²¹⁰Po) (Figure 2A).

Fe and Mn displayed similar trends with greater percentages leaching as pH decreased ($R^2 = -0.99$ for Fe; $R^2 = -0.95$ for Mn) (Figure 2B). The partitioning of ^{238}U -series radionuclides into the acetate solution may in part be explained by the desorption from hydrous Fe and Mn oxide minerals, which are well-known to adsorb heavy metals.⁴⁰

Uranium and Thorium. We observed that ^{238}U and ^{234}U were the most leachable radionuclides (4.2 and 6.1% leached at pH 1.8, respectively), which may be explained by the increased solubility of U when it is complexed with the acetate anion.⁴¹ Interestingly, ^{234}U had a mean radioactivity concentration 1.5 ± 0.1 times higher than that of ^{238}U across all leachate samples. This result was unexpected because ^{234}U and ^{238}U were in secular equilibrium in the drill cuttings. However, the isotopic enrichment of ^{234}U is well-known in natural systems because of α recoil enrichment,⁴² which occurs when ^{238}U decays and releases high-energy α particles that break chemical bonds. This allows decay products (i.e., ^{234}U) to be forcefully extruded from the crystal lattice and deposits larger amounts of ^{234}U on the outside of the mineral grain, leading to higher leaching rates. ^{230}Th was not leached as readily as U, as expected because of the relatively low solubility of ^{230}Th in environmental systems. Th is particle reactive in most environmental systems and tends to remain adsorbed onto mineral surfaces at pH >2.⁴³

Radium, Lead, and Polonium. Interestingly, only $2.1 \pm 1.6\%$ of ^{226}Ra leached at pH 1.8, which is consistent with the analogous Ba data, which indicated that the percent leached was $2.76 \pm 0.03\%$. This is surprising, given that high levels of Ba and Ra isotopes were previously reported in Marcellus Shale-produced fluids.^{6,10} The amount of ^{210}Pb leached was positively correlated with stable Pb extraction ($R^2 = 0.84$), though in much smaller quantities ($1.0 \pm 0.1\%$, vs $11.5 \pm 0.6\%$ for ^{210}Pb). The difference in extractability between ^{210}Pb and stable Pb may be a reflection of their geochemical microenvironment, which has been observed for other radionuclides.⁴⁴ ^{210}Po was the least soluble radionuclide tested in this system, with only $0.28 \pm 0.01\%$ leached at pH 1.8. We expected ^{210}Po to partition into the acetate buffers as ^{210}Po is known to be soluble in acetate,³⁵ yet the low solubility of ^{210}Po can be explained by its strong particle reactivity and tendency to adhere strongly to organics.³⁴ Interestingly, recent reports have indicated that ^{210}Po in reduced sediments can be volatilized by aerobic marine microorganisms.³⁶ Drill cuttings from the Marcellus Shale could serve as an interesting medium for future studies of the volatility of Po from ancient marine sediments.

Although previous studies have suggested that NORM in drill cuttings pose a minimal health risk to the general public when deposited in landfills,^{18,19,45} our results indicate that Marcellus Shale drill cuttings warrant further radiochemical investigation. More studies are needed to develop robust, rapid methods that are suitable for a variety of complex matrices typified by drill cuttings. Additionally, field studies are needed to determine the stability of radionuclides in landfills and the potential for NORM from drill cuttings to migrate into landfill leachates. Studies assessing the risks of exposure to NORM should include analysis of pure α emitters (^{234}U , ^{230}Th , and ^{210}Po) and the low-level β emitter (^{210}Pb). For example, the most leachable isotope in these drill cuttings was ^{234}U , which is typically not detected or reported by standard environmental monitoring methods. Accurate assessment of the human health risks associated with drill cuttings should include isotopic analysis of all environmentally persistent radionuclides.

■ ASSOCIATED CONTENT

📄 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.estlett.6b00439.

Metal, organic, and inorganic composition of drill cuttings (Table S1) and radioactivity concentrations in drill cuttings (Table S2) (PDF)

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Notes

The authors declare no competing financial interest.

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