Published in final edited form as:

Environ Sci Process Impacts. 2016 April ; 18(4): 456–463. doi:10.1039/c5em00540j.

Partitioning of naturally-occurring radionuclides (NORM) in Marcellus Shale produced fluids influenced by chemical matrix†

Andrew W. Nelson^a, Adam J. Johns^b, Eric S. Eitrheim^b, Andrew W. Knight^b, Madeline Basile^b, E. Arthur Bettis III^c, Michael. K. Schultz^{a,b,d,*}, and Tori Z. Forbes^b

^aInterdisciplinary Human Toxicology Program, University of Iowa, ML B180 FRRB, 500 Newton Road, Iowa City, Iowa, USA 52242

^bDepartment of Chemistry, University of Iowa, Iowa City, Iowa, USA 52242

^cDepartment of Earth and Environmental Sciences, IIHR Hydrosience and Engineering, University of Iowa, Iowa City, Iowa, USA 52242

^dDepartments of Radiology and Radiation Oncology, Free Radical and Radiation Biology Program, Medical Scientist Training Program, University of Iowa, Iowa City, Iowa, USA 52240

Abstract

Naturally-occurring radioactive materials (NORM) associated with unconventional drilling produced fluids from the Marcellus Shale have raised environmental concerns. However, few investigations into the fundamental chemistry of NORM in Marcellus Shale produced fluids have been performed. Thus, we performed radiochemical experiments with Marcellus Shale produced fluids to understand the partitioning behavior of major radioelements of environmental health concern (uranium (U), thorium (Th), radium (Ra), lead (Pb), and polonium (Po)). We applied a novel radiotracer, ²⁰³Pb, to understand the behavior of trace-levels of ²¹⁰Pb in these fluids. Ultrafiltration experiments indicated U, Th, and Po are particle reactive in Marcellus Shale produced fluids and Ra and Pb are soluble. Sediment partitioning experiments revealed that >99% of Ra does not adsorb to sediments in the presence of Marcellus Shale produced fluids. Further experiments indicated that although Ra adsorption is related to ionic strength, the concentrations of heavier alkaline earth metals (Ba, Sr) are stronger predictors of Ra solubility.

Introduction

The levels of radium (Ra) isotopes and other naturally-occurring radioactive materials (NORM) in flowback and produced fluids from Marcellus Shale are an emerging environmental concern.^{1–9} Recent reports demonstrated that Marcellus Shale produced fluids from unconventional drilling are enriched in Ra isotopes (²²⁸Ra, ²²⁶Ra, ²²⁴Ra) and devoid of most other long-lived NORM, such as certain U, Th, Pb and Po isotopes.^{1,9–11} Despite research interest in radionuclides contained in Marcellus Shale produced fluids,

†Electronic supplementary information (ESI) available. See DOI: 10.1039/c5em00540j

Michael-schultz@uiowa.edu; Tel: +1 319 335 8017.

The other authors declare they have no actual or potential competing financial interests.

there have been few laboratory-based studies that characterize the fundamental chemical behavior of NORM in Marcellus Shale produced fluids. Information has been gleaned about the chemical behavior of NORM in these fluids from environmental studies; however, even well designed environmental studies may not accurately characterize the chemical behavior of unconventional drilling wastes due to uncertainty and complexity of environmental sites in a region of the United States that has a long history with the extractive industries. That is, unknown treatment levels (*i.e.*, speciation and composition) of waste source terms, ongoing and legacy pollution from mixed sources (natural gas and coal extraction industries), and misinformation can complicate the interpretation of results from environmental studies of unconventional drilling wastes.^{12,13} Due to the limitations of environmental studies, we decided to explore information about the chemical behavior of NORM in produced fluids through laboratory-based partitioning studies. Although such experiments may lack generalizability, they provide important clues about behavior of radioactive elements without the challenges of accounting for uncontrolled environmental inputs, radioactive decay, and decay product ingrowth.

One of the major chemical parameters of interest for predicting the fate and transport of NORM in unconventional drilling wastes is ionic strength. A wide body of literature exists on the effects of ionic strength on the fate and transport of NORM in the environment. With respect to Ra, adsorption and desorption from sediments has been of great interest to environmental scientist and oceanographers.^{14–20} Ra adsorption studies show that Ra generally partitions through an ion exchange mechanism to the aqueous phase as ionic strength increases, yet most empirical data stops at ionic strengths comparable to those of seawater. Further, most studies have only explored the effects of ionic strength by considering concentration of Na with little attention to high molarities of alkaline earth metals (Mg, Ca, Sr, Ba). It is unclear whether these models are appropriate for Marcellus Shale produced fluids which may have ionic strengths up to 10 times that of seawater and levels of alkaline earth metals in the g L^{-1} range.^{8,9,21} Despite years of research into NORM, the current understanding of Ra chemistry in Marcellus Shale produced fluids is murky and the understanding of the chemical behavior of U, Th, Pb, and Po in these fluids is largely unexplored.

In this study, we characterize the chemical composition of Marcellus Shale produced fluids and suspended particulates by high resolution transmission electron microscopy (HRTEM) and powder X-ray diffraction (PXRD). We describe the partitioning of U, Th, Ra, Pb, and Po in Marcellus Shale produced fluids using radiotracers and ultrafiltration (0.1 μm filter pore size). We then applied sequential extraction and radiotracer techniques to determine the potential for Ra, Pb, and Po adsorption–desorption on a variety of sediment textures and mineral compositions. Note, we applied an underused radiotracer, ^{203}Pb , to understand the behavior of trace levels of ^{210}Pb in these fluids. ^{203}Pb has been applied as a tracer of Pb in environmental systems;²² however, lack of access to the isotope has stymied its use. With the increase in medical imaging applications of ^{203}Pb , in our laboratory in particular, ^{203}Pb is now more readily attainable. Next, we investigated the effect of ionic strength on Ra using a chemical matrix characteristic of Marcellus Shale fluids. Finally, we explored the role of exchangeable cations (Na, Mg, Ca, Sr, Ba) at a range of concentrations (0.01 M, 0.1 M, and 1 M) on the partitioning of Ra.

Experimental

General

Sediments were taken from the Dunkard Creek near Wana, West Virginia, USA in May 2014 or from collections at the University of Iowa Quaternary Materials Laboratory. Dunkard Creek sediments were collected from the site of a spill that occurred in 2009.²³ The Dunkard Creek spill was speculated to be related to unconventional drilling and/or coal wastes;²³ however, the etiology of this spill is beyond the scope of this study. Grain size, PXRD, and HRTEM were performed at the University of Iowa using standard techniques.^{24,25} The Marcellus Shale produced fluids described herein were previously characterized for NORM and matrix composition.^{1,5} Sequential extractions were based on previously published methods.²⁶ In partitioning and sequential extraction experiments, ²²⁶Ra was determined by ²²²Rn emanation,⁵ ²⁰³Pb by NaI gamma spectrometry based on standard laboratory methods,²⁷ and ^{nat}U, ^{nat}Th, and ²¹⁰Po by preconcentration and alpha spectrometry.^{1,28}

Grain size

Sediment grain-size distribution was analyzed using the pipette method with size fraction breaks at <2 μ (clay), 2–20 μ (fine silt), 20–50 μ (coarse silt) and 50 μ –2 mm (sand) at the University of Iowa Quaternary Materials Laboratory.

PXRD

Sediments, Marcellus Shale produced fluids fines (0.1 μ m polypropylene filter), and Marcellus Shale produced fluids solid-state evaporites were prepared for power X-ray diffraction (PXRD) by mortar and pestle (under acetone). Diffractograms were collected on a Bruker Advance Diffractometer equipped with CuK α radiation (λ = 1.54056 Å) and a LynxEye detector. Scans were performed from 5–60° 2 θ with a step size of 0.02° and collection time of 1 s per step. Major mineral phases present in the solid samples were identified using the Bruker Eva software (Fig. S1–S3, Table S1†).

High resolution transmission electron microscopy

Morphological features of the Fe particulates were determined using high resolution transmission electron microscopy (HRTEM) at the University of Iowa Central Microscopy Research Center. A 1 mg mL^{−1} colloidal suspension of the particulates was prepared in ultrapure water and sonicated for 30 min to improve dispersion. Holey carbon copper grids (Ted Pella, Inc 01824, UC-A on holey, 400 mesh Cu) were loaded with 5 μ L aliquots of the suspension and evaporated to dryness in air. HRTEM investigations were carried out by a JEOL JEM 2100F equipped with a cold Schottky cathode, field emission gun, and operated at a 200 kV accelerating voltage. Gatan DigitalMicrograph software was utilized for image acquisition in congruency with an externally inserted Orius camera cooled to −25 °C.

Produced fluids filtration U, Th, Ra, Pb, Po

²³²U (Eckert and Ziegler 92403), ²²⁸Th (in ²³²U tracer/endogenous), ²²⁶Ra (endogenous), ²⁰³Pb (Lantheus Medical Imaging, Billerica, MA), and ²¹⁰Po (from ²¹⁰Pb source NPL A13959) were added to Marcellus Shale produced fluids (20 mL, except ²²⁶Ra

35 mL), stirred (6–18 hours, room temperature, 220 RPM), and ultra-filtered (0.1 μm , filtration Resolve Eichrom). Filters and supernatant samples requiring analysis by alpha spectrometry were then traced with $^{\text{nat}}\text{U}$ (Eckert and Ziegler 92564), ^{230}Th (NIST SRM 4342A), or ^{209}Po (Eckert and Ziegler 92565) and prepared using methods previously described.¹ ^{203}Pb samples were quantitated by NaI gamma spectrometry. ^{226}Ra samples were analyzed by RAD7 (DurrIDGE Company, Inc., Billerica, MA, USA).

Sediment sequential extraction of Ra

Selected homogenized sediments were placed into 50 mL conicals ($n = 3$, 3.5 g) (Fig. S4†). Marcellus Shale produced fluids (35 mL) were added to each conical before shaking on a rotating table (1 h, room temperature, 220 RPM). Conicals were then centrifuged (5 min, $3400 \times g$), and the supernatant was transferred to clean vials (40 mL, glass VOC). To prevent foaming during counting by RAD7, anti-foam solution (Sigma, emulsion B, 1 mL 25%) was added to each vial before topping with H_2O and hermetically sealing. Ra was then sequentially extracted from sediment based on methods previously described.²⁶ Briefly, sediment was treated three times with water-soluble-phase extractant (0.4 M MgCl_2 , pH 5.5), once with carbonate-phase extractant (1 M NH_4Ac in 25% v/v acetic acid), once with reducible-phase extractant (0.01 M NH_2OH in 25% v/v acetic acid), once with organic-phase extractant (30% v/v H_2O_2 , 0.02 M HNO_3) and finally with acid-digestible phase (4 M HNO_3). Extractions were performed at room temperature on a rotating table (1 h, 220 RPM), each time centrifuging and transferring supernatant to clean glass vials (40 mL, VOC). Vials containing acetic acid, H_2O_2 , or HNO_3 were taken to complete dryness before topping with H_2O and hermetically sealing. Samples were held 30+ days to ensure secular equilibrium between ^{222}Rn and ^{226}Ra before counting by RAD7 (DurrIDGE, Billerica, MA) as previously described.⁵ Assessment of adsorption kinetics was performed on Dunkard Creek sediment B sediment similarly as described above, yet samples were incubated with Marcellus Shale produced fluids and the extractants for 168 hours *en lieu* of 1 hour.

Sediment sequential extraction of Ba, Pb, Po

Sediment from Dunkard Creek was placed into conicals (50 mL, $n = 3$, 2 g). Marcellus Shale produced fluids (20 mL) and radiotracers (^{133}Ba Eckert and Ziegler 6133, ^{203}Pb (Lantheus Medical Imaging), ^{210}Po (supported by ^{210}Pb , NPL A13959) traced with ^{209}Po (Eckert and Ziegler 92565)) were added to each conical before shaking on a rotating table (1 h, room temperature, 220 RPM). Conicals were then centrifuged (5 min, $3400 \times g$), the supernatant was transferred to clean liquid scintillation (LS) vials (20 mL, glass). LS vials were then counted by a well-type sodium iodide (NaI) detector (Ortec) and gamma-emitting radionuclides were quantitated using standard radioactivity measurement techniques, similarly as described previously.²⁷ Po was separated and quantitated using standard methods previously described.¹ The radionuclides adsorbed to the sediment were then sequentially extracted based on methods previously described.²⁶ Extractions were performed at room temperature on a rotating table (1 h, 220 RPM), each time centrifuging and transferring supernatant to clean glass vials (20 mL, LS).

Ionic strength and Ra partitioning

All experiments investigating Ra partitioning were performed on Dunkard Creek sediment B sediment ($n = 3$, 3.5 g), with the indicated salt solution (35 mL), and ^{226}Ra standard (37.3 Bq, NIST traceable standard, Eckert & Ziegler 1742–75). Marcellus Shale produced fluids surrogate matrix consisted of reagent grade (or higher) chloride form salts with the following concentrations: Na^+ (1300 mM), K^+ (4 mM), Mg^{2+} (35 mM), Ca^{2+} (320 mM), Sr^{2+} (410 mM), Ba^{2+} (66 mM), Fe^{3+} (0.78 mM), Cl^- (4100 mM). Note, surrogate matrix was only used in experiments described in this paragraph. Surrogate matrix was used so that ^{226}Ra activity (37.3 Bq) could be controlled despite dilution of the matrix solution. Separate select cations (Na^+ , Mg^{2+} , Ca^{2+} , Sr^{2+} , and Ba^{2+}) were prepared by serial dilution to the following concentrations: 1 M, 0.1 M, and 0.01 M. All samples were shaken on a rotating table (1 hour, room temperature, 220 RPM), centrifuged ($3400 \times g$), and the supernatant was transferred to clean glass vials (40 mL, glass VOC). Anti-foaming solution (1 mL) was added to each vial before topping with anti-foam (1 mL), hermetically sealing (30+ days), and counting by RAD7.

Results and discussion

NORM in produced fluids

Very little is known about the concentrations of most NORM in Marcellus Shale fluids, and less information is available regarding NORM partitioning between aqueous and particulate phases. Several studies have developed a general understanding of how NORM levels in produced fluids change throughout the lifecycle of the unconventional drilling process.^{7–9} For example, Ra isotope concentrations steadily increase concurrently with the age of the well and concentration of total dissolved solids (TDS) and alkaline earth metals.^{7,8} In contrast, U levels have been reported to spike briefly at the beginning of the flowback stage and then decrease over time.¹¹ Lastly, an analysis of late stage Marcellus Shale fluids by Nelson *et al.* (2015) reported U, Th, Pb, and Po isotopes were initially absent, but certain isotopes (^{228}Th , ^{210}Pb , ^{210}Po) increase by radiochemical decay product ingrowth processes.¹ Collectively, these reports provide important clues about the behavior of NORM within Marcellus Shale fluids at the point source, particularly at increased pressure, higher temperature, and altered redox conditions that occur in the subsurface environment.

It is unclear how U, Th, Ra, Pb, and Po behave when produced fluids enter low-temperature geochemical environments. Although we anticipate the majority of U and Th isotopes (with the exception of ^{228}Th) will remain at depth or be adsorbed to solid waste products,¹ understanding the solubility of U and Th in Marcellus Shale produced fluids under surface conditions is important, particularly in cases where there are significant interactions between the waste forms. To understand the basic partitioning of U, Th, Ra, Pb, and Po in surface waters, we spiked homogenized Marcellus Shale produced fluids with appropriate radiochemical tracers. Spiked fluids underwent ultrafiltration (0.1 μm) and particulate and aqueous phases were analyzed by alpha or gamma spectrometry. U, Th, and Po associated with the particulates (98%, 97% and >99%, respectively) and Ra and Pb remained in solution (99% and 97%, respectively) (Fig. 1A).

Low particle reactivity of Ra and Pb led us to probe the mineral composition of particulates and dissolved solids in the Marcellus Shale fluids. Powder X-ray diffraction (PXRD) of the solid evaporites from the produced fluids revealed the presence of halite salts containing predominately alkali and alkali earth cations (Fig. 1B and S3[†]). The diffractogram of the Fe particulates include a relatively high background due to fluorescence, but the presence of two broad peaks suggests the presence of an amorphous Fe oxyhydroxide (Fig. 1C, Table S1[†]). In addition, weaker reflections correspond to the mineral akaganeite (β -FeO(OH, Cl)), which requires the presence of 1–9 wt% chloride in solution for formation of this phase to be favored over goethite and other Fe³⁺ oxyhydroxide species.²⁹ Akaganeite is most commonly observed as a corrosion product in marine environments,³⁰ but the high ionic strength of the produced fluids contains concentrations of chloride to support the formation of akaganeite. The high-resolution transmission electron microscopy (HRTEM) image of the Fe particulates reveals the formation of bladed aggregates that are approximately 20–50 nm in width (Fig. 1D). Akaganeite has previously been reported to form elongated aggregates with longitudinal striations and are similar to the morphology of the Fe particulates obtained from the produced fluids.^{31,32} We attribute the low observed adsorption of Pb and Ra to the akaganeite and amorphous iron oxides to matrix effects (competition with exchange cations), similarly as observed for ferrihydrite and goethite.¹⁶

Environmental fate of NORM

The gross levels of radionuclides in unconventional drilling wastes may be inappropriate for assessing environmental impact given the possibility for surface adsorption and sedimentation.²⁶ To understand the potential fate of radionuclides introduced into the environment, it is important to determine partitioning within soil and colloidal phase reservoirs through sequential extraction experiments.^{26,33} Initially our sequential extraction experiments focused exclusively on Dunkard Creek sediments, as these sediments were collected from a stream that has geology more consistent with sites in the region of the United States overlaying the Marcellus Shale (*i.e.*, sites that are more likely to contact Marcellus Shale produced fluids). We applied sequential extraction techniques to determine ²²⁶Ra concentrations in water-soluble, carbonate, Fe and Mn oxides, organic, and strong acid-digestible residue fractions for Dunkard Creek sediments. ²²⁶Ra was measured in each sequentially extracted fraction by ²²²Rn emanation, to allow for accurate, trace-level radiochemical experiments (Fig. S4 of ESI[†]). Sequential extractions of ²²⁶Ra (1 hour) indicated >90% of ²²⁶Ra remained in the load solution (Marcellus produced fluids) and nearly all the residual ²²⁶Ra (>99%) was removed in the water-exchangeable fractions (Fig. 2A). The high observed solubility of ²²⁶Ra²⁺ led us to explore additional chemical parameters important for the adsorption of cations to sediments—kinetics, sediment mineralogy/texture, ionic strength, and chemical matrix.

The role of kinetics on the observed solubility was investigated in a time dependence study, where we performed the same sequential extraction experiment for 168 hours (one week) instead of 1 hour. The same trend occurred in the extended reaction time, with >90% of ²²⁶Ra removed in the load solution and residual ²²⁶Ra was observed in the remaining water-exchangeable fractions such that >99% was recovered. This result suggests that kinetics have minimal effects on Ra adsorption–desorption in this system, which is in

agreement with other studies that find Ra adsorption to sediments occurs within minutes.^{14,17}

We further investigated the mineralogy and soil characteristics of the sediments, because both characteristics greatly affect the speciation and adsorption of Ra.^{26,34} Soil texture and PXRD analysis indicated that four Dunkard Creek sediments were loam to sandy-loam, primarily consisting of quartz. Given that loams have lower binding capacity for ²²⁶Ra than clay-rich sediments,^{15,16} we included seven different sediments of different mineralogy, and diverse texture (97% sand (sediment 7), to 60% clay (sediment 5), to 86% silt (sediment 3)) (Fig. 3 and S4 of ESI†). Regardless of soil texture and mineralogy, >90% of Ra remained in the load solution and nearly all the remaining ²²⁶Ra was removed in the water exchangeable fractions. This suggested to us that some chemical parameter(s) of the Marcellus Shale produced fluids overwhelm the binding capacity of soil minerals.

We suspected the high ionic strength in Marcellus Shale produced fluids could be responsible for the low Ra adsorption in this system; therefore, we tested Ra adsorption to sediment (Dunkard Creek sediment B) with variable ionic strengths. A surrogate matrix comprised of the same chemical parameters as Marcellus Shale produced fluids (ionic strength = 4.4 M) was adjusted by serial dilution (1 : 1, 1 : 10, 1 : 100, 1 : 1000, and 1 : 10 000) and spiked with a known amount of ²²⁶Ra (37 Bq per sample). Sediments incubated with dilute surrogate (0.044 M and less) retained nearly all the ²²⁶Ra (>97%), which agrees with many studies that show ²²⁶Ra is particle reactive at ionic strengths typical of groundwater and freshwater (Fig. 2B). However, at an ionic strength of 0.44 M (slightly less than a typical seawater of 0.7 M), 70% of ²²⁶Ra remained in the aqueous phase (Fig. 2B). Sediments incubated with undiluted surrogate matrix (4.4 M) retained only 2% of the ²²⁶Ra (Fig. 2B). Although Webster *et al.* (1995) have shown that seawater can solubilize approximately 10–25% ²²⁶Ra,¹⁴ the high solubility of ²²⁶Ra at ionic strengths less than seawater prompted us to probe deeper into the role that chemical composition of the produced fluids plays on the adsorption process.

The chemical matrix of Marcellus Shale produced fluids is dominated by Na⁺, Mg²⁺, Ca²⁺, Sr²⁺, and Ba²⁺ cations and Cl[−] anions.^{8,9} Thus, we tested the effects of individual ions on competition with Ra²⁺ for adsorption sites in Dunkard Creek sediments. We incubated sediments with solutions of chloride salts (0.01 M, 0.1 M, and 1 M), resulting in ionic strengths of 0.01 M, 0.1 M, and 1 M for Na solutions and 0.03 M, 0.3 M, and 3 M for alkaline earth solutions. Two clear trends emerged: (1) as cation concentration (and thus ionic strength) increased, the amount of ²²⁶Ra²⁺ in solution increased; and (2) as the ionic radius of the cation approached that of ²²⁶Ra²⁺, the amount of ²²⁶Ra²⁺ in solution increased (Fig. 2C). The effect of concentrations of Ba²⁺ is quite dramatic, even at concentrations as low as 10 mM (typical Ba²⁺ concentration of late-stage Marcellus Shale produced fluids⁸). Importantly, samples of relatively low ionic strength but considerable levels of Ba²⁺, may not behave as expected based on ionic strength alone. These chemical experiments suggest that in holding ponds containing untreated Marcellus Shale produced fluids, Ra²⁺ will not adsorb to solid mineral surfaces according to models developed for seawater matrices. In other words, the chemical composition of Marcellus Shale produced fluids (*i.e.*, high concentrations of divalent alkaline earth metals) enhances the aqueous phase concentrations

of Ra^{2+} . Consideration of Ba^{2+} concentrations, in particular, may be important for understanding the potential for Ra^{2+} to adsorb to the sediment–mineral interface in environmental settings (Fig. 4). Furthermore, accurate measurement of Ba^{2+} concentration in produced fluids may be more important than ionic strength when assessing treatment goals and potential environmental impact. Future modeling studies will explore the effects of dilution and environmentally relevant anion concentrations (particularly SO_4^{2-}) on bulk transport of Ra^{2+} in riparian environments.

Fate and transport of ^{226}Ra decay products, ^{210}Pb and ^{210}Po , from Marcellus Shale produced fluids are important to consider as these isotopes are well-known to bioaccumulate.³⁵ ^{210}Pb is challenging to study in environmental systems due to its radiochemical properties. Similarly, ^{210}Po is often neglected as specific instrumentation and chemical separations (alpha spectrometry and autodeposition) are required for its analysis. Thus instead of measuring ^{210}Pb , we employed a cyclotron-produced isotope— ^{203}Pb . The short half-life of ^{203}Pb (51.92 hour) makes this isotope effectively a “massless” tracer and more representative than stable Pb tracers when investigating the fate of naturally-occurring low-mass-abundance (parts-perquadrillion or less), radioactive Pb isotopes. Sequential extraction experiments were also performed for ^{203}Pb and ^{210}Po using a similar process as described above. Results for ^{203}Pb indicated that $45 \pm 2\%$ of ^{203}Pb remained in the produced fluids (Fig. 2D). The remainder of the ^{203}Pb was removed in the carbonate or strong acid phases ($25 \pm 1\%$ and $17 \pm 1\%$, respectively). Isotope-dilution alpha spectrometry indicated that ^{210}Po (traced with ^{209}Po) largely associated with carbonate and strong acid ($25 \pm 4\%$ and $52 \pm 2\%$, respectively) phases (Fig. 2D). These results demonstrate that ^{210}Pb and ^{210}Po have different environmental fate and transport processes that may lead to radiochemical disequilibrium (non-steady state). More work is needed to understand the potential for these isotopes to migrate through the environment.

Conclusion

This study investigated the fundamental partitioning behavior of critical radioelements (U, Th, Ra, Pb, Po) contained in unconventional drilling wastes. In agreement with findings from an earlier study on NORM contained in Marcellus Shale produced fluids, we find that U, Th, and Po are insoluble (particle reactive) and Ra is soluble.¹ It is unclear why the high observed solubility of trace-level Pb (as measured by ^{203}Pb) in these fluids differs from earlier observations that ^{210}Pb was absent in produced fluids. The studies described herein were performed at room temperature, atmospheric pressure, and normoxic conditions on sediments from West Virginia to maintain relevance to potentially impacted riparian environments. These conditions are inherently different than those within the Marcellus Shale. Future studies should explore the solubility and partitioning behavior of NORM between interstitial fluids and particulate phases, under the pressures, temperatures, and anoxic conditions relevant to unconventional reservoirs.

Without a firm understanding of the basic chemistry of produced fluids, it is difficult to predict the fate and transport of NORM in the environment when these fluids are the source of NORM. We investigated the partitioning behavior of Ra, Pb, and Po from Marcellus Shale produced fluids to the sediment– mineral interface through bench-scale studies. We found

that Ra was exceptionally soluble in the Marcellus Shale fluids and >90% was retained in the load solution. The remaining Ra was easily extracted by water-exchangeable washes, such that >99% was extracted in all water-soluble phases. Further experiments indicated that the high solubility of Ra was associated with ionic strength. However, careful consideration into the chemical composition of the Marcellus Shale produced fluids indicated the solubility of Ra was likely attributable to competition with other divalent cations (most profoundly by Ba), rather than ionic strength *per se*. Although wastes may not initially contain ^{210}Pb and ^{210}Po , due to radiochemical ingrowth processes, the environmental impacts of ^{210}Pb and ^{210}Po must be considered in wastes containing ^{226}Ra . We found that $(17 \pm 1\%)$ Pb associated with phases only extractable by strong acid (4 M HNO_3), suggesting that radiochemical disequilibrium between ^{226}Ra and ^{210}Pb is likely to occur (even after accounting for losses from ^{222}Rn). Even greater portions ($52 \pm 2\%$) of ^{210}Po associated with strong acid-extractable phases, suggesting radiochemical disequilibrium between ^{210}Pb and ^{210}Po should be expected.

The key finding from this study is that Ra is more soluble in Marcellus Shale produced fluids than predicted by conventional adsorption–desorption models. Consistent with adsorption–desorption models generated with seawater matrices, we found that as ionic strength increases, the level of Ra in the aqueous phase increases. However, the level of Ra in the aqueous phases exceeded the amount predicted by seawater models. This suggests that the chemical matrix of produced fluids plays an important role in the adsorption of Ra to environmental materials. Careful consideration of the levels of divalent cations in Marcellus Shale produced fluids, particularly Ba, is important for assessing the potential impacts of concentrated Marcellus Shale produced fluids releases into the environment.

Acknowledgments

The authors would like to acknowledge Dustin May, Marinea Mehrhoff, Mengshi Li, Michael Wichman, Adam Ward, and Sylvia Joun Lee, for their support. This research was partially supported by NSF Grant# EAR-1331906 for the Critical Zone Observatory for Intensively Managed Landscapes (IML-CZO), the Center for Health Effects of Environmental Contamination (CHEEC) at the University of Iowa, and the Center for Global and Regional Environmental Research (CGRER) at the University of Iowa. M. K. S. is a paid consultant for Speer Law Firm, PA, Kansas City, Missouri.

References

1. Nelson AW, Eitheim ES, Knight AW, May D, Mehrhoff MA, Shannon R, Litman R, Burnett WC, Forbes TZ, Schultz MK. Environ. Health Perspect. 2015; 123:689–696. [PubMed: 25831257]
2. Warner NR, Christie CA, Jackson RB, Vengosh A. Environ. Sci. Technol. 2013; 47:11849–11857. [PubMed: 24087919]
3. Zhang T, Gregory K, Hammack RW, Vidic RD. Environ. Sci. Technol. 2014; 48:4596–4603. [PubMed: 24670034]
4. Zhang T, Bain D, Hammack R, Vidic RD. Environ. Sci. Technol. 2015; 49:2969–2976. [PubMed: 25642997]
5. Nelson AW, May D, Knight AW, Eitheim ES, Mehrhoff M, Shannon R, Litman R, Schultz MK. Environ. Sci. Technol. Lett. 2014; 1:204–208.
6. Brown V. Environ. Health Perspect. 2014; 122:A50–A55. [PubMed: 24486733]
7. Rowan E, Engle M, Kirby C, Kraemer T. US Geological Survey Scientific Investigations Report 2011. 2011:5135.
8. Haluszczak LO, Rose AW, Kump LR. Appl. Geochem. 2013; 28:55–61.

9. Barbot E, Vidic NS, Gregory KB, Vidic RD. Environ. Sci. Technol. 2013; 47:2562–2569. [PubMed: 23425120]
10. Ziemkiewicz PF, Thomas He Y. Chemosphere. 2015; 134:224–231. [PubMed: 25957035]
11. Phan TT, Capo RC, Stewart BW, Graney JR, Johnson JD, Sharma S, Toro J. Appl. Geochem. 2015; 60:89–103.
12. Chapman EC, Capo RC, Stewart BW, Hedin RS, Weaver TJ, Edenborn HM. Appl. Geochem. 2013; 31:109–118.
13. Alley WM, Cherry JA, Parker BL, Ryan MC. Trans., Am. Geophys. Union. 2014; 95:264.
14. Webster IT, Hancock GJ, Murray AS. Geochim. Cosmochim. Acta. 1995; 59:2469–2476.
15. Powell BA, Miller T, Kaplan DI. Journal of the South Carolina Academy of Science. 2015; 13:4. [PubMed: 27540332]
16. Sajih M, Bryan ND, Livens FR, Vaughan DJ, Descostes M, Phommavanh V, Nos J, Morris K. Geochim. Cosmochim. Acta. 2014; 146:150–163.
17. Gonnea ME, Morris PJ, Dulaiova H, Charette MA. Mar. Chem. 2008; 109:250–267.
18. Sturchio NC, Banner JL, Binz CM, Heraty LB, Musgrove M. Appl. Geochem. 2001; 16:109–122.
19. Krishnaswami S, Bhushan R, Baskaran M. Chemical Geology Isotope Geoscience Section. 1991; 87:125–136.
20. Tamamura S, Takada T, Tomita J, Nagao S, Fukushima K, Yamamoto M. J. Radioanal. Nucl. Chem. 2014; 299:569–575.
21. Chapman EC, Capo RC, Stewart BW, Kirby CS, Hammack RW, Schroeder KT, Edenborn HM. Environ. Sci. Technol. 2012; 46:3545–3553. [PubMed: 22360406]
22. Little P, Wiffen RD. Atmos. Environ. 1977; 11:437–447. [PubMed: 71156]
23. Federman, A. [accessed February 2016] Earth Island Journal. 2012 Winter. 2012, http://www.earthisland.org/journal/index.php/eij/article/what_killed_dunkard_creek/
24. Soil Survey Staff, in Soil Survey Laboratory Methods Manual. U.S. Department of Agriculture, Natural Resources Conservation Service, National Soil Survey Center; Lincoln, Nebraska, USA: 1996. p. 35–37. Soil Survey Investigations Report No. 42, Version 3.0 Particle-Size Analysis, Particles <2 mm (pipet method) (3A), Air-Dry Samples (3A1)
25. Bish, DL., Post, JE. Reviews in Mineralogy. Vol. 20. Mineralogical Society of America; 1989. *Modern Powder Diffraction*
26. Schultz M, Burnett W, Inn K, Thomas J, Lin Z. J. Res. Natl. Inst. Stand. Technol. 1996; 101:707–715. [PubMed: 27805089]
27. Knight AW, Eitrheim ES, Nelson AW, Schultz MK. Nukleonika. 2015; 60:837–845.
28. Knight AW, Eitrheim ES, Nelson AW, Nelson S, Schultz MK. J. Environ. Radioact. 2014; 134:66–74. [PubMed: 24681438]
29. Schwertmann, U., Cornell, RM. Iron Oxides in the Laboratory. Vol. 9. Wiley-VCH Verlag GmbH; 2007. p. 113–119.
30. Refait P, Génin J-M. Corros. Sci. 1997; 39:539–553.
31. Holm NG. Origins Life Evol. Biosphere. 1985; 15:131–139.
32. Mohapatra M, Mohapatra L, Anand S, Mishra BK. J. Chem. Eng. Data. 2010; 55:1486–1491.
33. Zhang T, Hammack RW, Vidic RD. Environ. Sci. Technol. 2015; 49:9347–9354. [PubMed: 26154523]
34. Langmuir D, Riese AC. Geochim. Cosmochim. Acta. 1985; 49:1593–1601.
35. Seiler RL, Wiemels JL. Environ. Health Perspect. 2012; 120:1230–1237. [PubMed: 22538346]

Environmental impact

Naturally-occurring radioactive materials (NORM) associated with unconventional drilling flowback and produced fluids from the Marcellus Shale have raised environmental health and waste management questions. Radium (Ra) has received considerable attention due to the challenges of removing it from produced fluids. Ra waste management challenges have largely been attributed to ionic strength; however, the apparent solubility of Ra in Marcellus Shale fluids exceeds that observed in other high ionic strength fluids. We herein report the effects of chemical matrices on Ra, as well as other NORM. We find that the concentration of Ba in these fluids is a more important predictor for Ra solubility than ionic strength.

Fig. 1.

Partitioning within Marcellus Shale produced fluids. (A) Mean recoveries (with standard deviations) of U, Th, Ra, Pb, and Po in aqueous or particulate phases of radioisotope traced, filtered (0.1 μm) Marcellus Shale produced fluids. (B) pXRD spectrum of evaporated (low heat), filtered (0.1 μm) produced fluids. (C) pXRD spectrum of filtered (0.1 μm) produced fluid particulates. (D) TEM image of filtered (0.1 μm) produced fluid particulates.

Fig. 2.

Ra and Ra decay products partitioning between Marcellus Shale produced fluids (or surrogate) and sediments. (A) Sequential extractions of Ra or Ba on select sediments: the first three bars represent mean recoveries with standard deviations of ^{226}Ra from sequential extractions by ^{222}Rn emanation; values from left to right indicate Ra removal from 11 different sediments ($n = 3$), Dunkard Creek sediment B (1 hour, $n = 3$), Dunkard Creek sediment B (168 hour, $n = 4$). Fourth bar represents mean recovery with standard deviation of Ba (traced with ^{133}Ba) from Dunkard Creek sediment B ($n = 3$). (B) Aqueous fraction of

surrogate fracturing matrix spiked with ^{226}Ra (37 Bq) and incubated with Dunkard Creek sediment B at various ionic strengths; values represent means ($n = 3$) with standard deviations subsumed within squares. (C) Aqueous fraction of Na, Mg, Ca, Sr, or Ba chloride salts (0.01, 0.1, and 1 M) spiked with ^{226}Ra (37 Bq) and incubated with Dunkard Creek sediment B; values represent means ($n = 3$) with standard deviations subsumed within squares. (D) Mean recovery with standard deviation of ^{203}Pb ($n = 3$) and ^{210}Po ($n = 3$, traced with ^{209}Po).

Fig. 3.
Grain size triangle plot of sediments from Quaternary Materials Laboratory at the University of Iowa.

Effect of Barium on Radium Adsorption

Fig. 4.

Theoretical depiction of Ba and Ra competition for adsorption on sediments in high and low Ba concentrations.