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Age Dating Oil and Gas Wastewater Spills Using Radium Isotopes and Their Decay Products in Impacted Soil and Sediment

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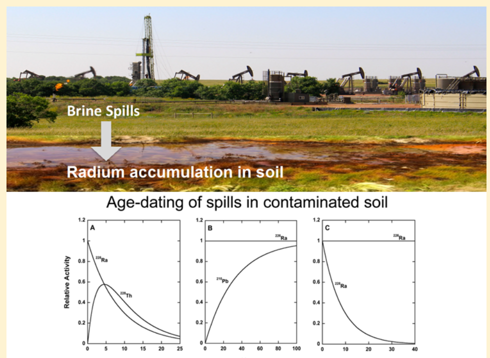
Supporting Information

ABSTRACT: Spills from oil and gas operations can contaminate water resources, sediment, and soil, but in many cases, information about spill sources and environmental impacts is not available. Here we present age dating methods to estimate the time since the accumulation of radium in impacted soils and sediments from oil and gas wastewater spills. The retention of unsupported ^{226}Ra and ^{228}Ra from spill water to soil and sediment and the ingrowth of Ra progeny result in three independent age dating methods using the ^{228}Th/^{228}Ra, ^{210}Pb/^{226}Ra, and ^{228}Ra/^{226}Ra activity ratios. We tested the ^{228}Th/^{228}Ra method on spill sites in North Dakota and West Virginia, where the dates of the spills are known. The ^{228}Th/^{228}Ra method yields ages similar to the documented spill ages and can reveal the initial ^{228}Ra/^{226}Ra ratios of the spill waters, validating the notion that Ra isotopes and their decay products in contaminated soils and sediments can reveal the ages and origins of spills.



INTRODUCTION

One of the environmental risks associated with the rise of unconventional shale gas and tight oil extraction by hydraulic fracturing is the increased frequency of inadvertent releases of oil and gas wastewater (OGW) to the environment.[1,2] OGW includes produced and flowback waters that are composed of injected water and naturally occurring brines from the targeted formations. In addition to salts, trace elements, and organics,[3−6] these fluids typically contain elevated levels of radium isotopes, ^{226}Ra ($t_{1/2}$ = 1600 years) and ^{228}Ra ($t_{1/2}$ = 5.75 years), with total Ra activities (^{228}Ra+^{226}Ra) of up to about 400 Bq/L reported in Marcellus waters.[7] The combination of high U concentrations in shales,[8,9] reducing and highly saline conditions that enhance mobilization of radium from the host rocks to formation waters, and the differential solubility of other U−Th series elements results in U−Th series disequilibrium in formation waters with high Ra yet low Th and U activities.[7,10,11] Following the release of Ra-bearing OGW to the environment through spills or disposal, the unsupported Ra accumulates in the soil and sediment through adsorption as well as coprecipitation and generation of authigenic Ra-rich barite.[12−15]

Previous studies have recognized applications of U−Th series disequilibrium in OGW associated with conventional oil and gas. Radium isotopes and radium−daughter disequilibrium have been used to estimate the age of Ra-bearing barite in contaminated soils, oil field sludges, and scales.[16,17] Additionally, ^{228}Ra in pit sediments was used as an indicator of the recent formation of Ra-bearing barite and burial rates,[15] and ^{228}Ra−^{228}Th disequilibrium was used to detect the age of contamination in soils and stream sediments in the vicinity of ponds used to store produced water.[17] The ability to verify the age and source of contamination is vital for linking contamination directly to oil and gas operations. Additionally, distinguishing recent contamination related to hydraulic fracturing from older contamination related to conventional oil and gas operations is particularly challenging in areas with a history of conventional oil and gas exploration and new unconventional development. For example, reports of elevated radioactivity in stream sediments from OGW disposal sites in western Pennsylvania[12] have triggered debate about whether the high radioactivity results from disposal of recent hydraulic fracturing fluids or previous conventional OGW.[18,19]

While previous studies have used Ra isotopes and their decay products to detect the age of soil and sediment contamination associated with storage and leakage of conventional OGW,[15−17] here we test the methods for age dating OGW spills associated with unconventional energy development. We present three age dating methods based on the decay of unsupported Ra and resulting changes in the ^{228}Th/^{228}Ra, ^{210}Pb/^{226}Ra, and ^{228}Ra/^{226}Ra activity ratios in impacted soils and sediments (all ratios presented hereafter are activity ratios). We demonstrate the validity of the ^{228}Th/^{228}Ra method for detecting the age of recent events in two case studies where sediment and soil have been impacted by unconventional OGW spills.

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■ MATERIALS AND METHODS

Grab soil and sediment samples were collected from two spill sites in West Virginia ($n = 1$ spill soil; $n = 1$ background soil) and North Dakota[20] ($n = 3$ spill sediments; $n = 3$ upstream and downstream sediments) in January 2014 and July 2015, respectively. The Tyler County spill in West Virginia occurred on January 2, 2014, when a storage tank on a drill pad exploded, flooding the surrounding area with flowback water. The Blacktail Creek spill in North Dakota, caused by a pipeline leak, was discovered on January 6, 2015, and released 3 million gallons of brine near the Blacktail Creek, a tributary of the Missouri River in Williams County, North Dakota.

Oven-dried soil and sediment samples (30−60 g) were packaged in Petri style dishes (6.5 cm in diameter, 2 cm in height) that were wrapped with electrical tape and coated in wax to prevent the escape of gaseous ^{222}Rn ($t_{1/2}$ = 3.8 days). Samples were incubated for at least 21 days to allow time for ^{226}Ra to reach secular equilibrium with its great granddaughter, ^{214}Pb, prior to being run on a Canberra broad energy germanium gamma detector for ∼24 h. ^{228}Ra was determined through the ^{228}Ac peak (911 kEv), ^{226}Ra through the ^{214}Pb peak (351 kEv), ^{228}Th ($t_{1/2}$ = 1.9 years) through the ^{212}Pb peak (239 kEv), and ^{210}Pb ($t_{1/2}$ = 22.2 years) directly through its own peak at 47 kEv. Activities were calculated by manually summing peak counts, subtracting background counts, and correcting for detector efficiency. Efficiencies were determined using a U−Th ore reference material (CCRMP DL-1a) packaged and incubated in the same geometry as the samples. We corrected for sample adsorption of the low-energy ^{210}Pb gamma emission using a ^{210}Pb point source.[21]

■ RESULTS AND DISCUSSION

U−Th Series Radionuclides in Spill Sites. Elevated activity concentrations of ^{228}Ra and ^{226}Ra (total Ra up to 4685 Bq/kg for Blacktail Creek[20] and 343 Bq/kg for Tyler County) were observed in sediments and soils from both spill sites compared to background sites (total Ra up to 47 Bq/kg for Blacktail Creek[20] and 101 Bq/kg for Tyler County), indicating the accumulation of Ra in impacted soils and sediments following spills. In all spill soil and sediment samples, $^{210}Pb/^{226}Ra$ (0.07−0.41) and $^{228}Th/^{228}Ra$ (0.33−0.82) ratios were less than 1 (uncorrected for background activities), indicating disequilibrium between radium isotopes and their corresponding daughters. Additionally, $^{228}Ra/^{226}Ra$ ratios in spill sediments (0.24−0.70) were found to be lower than $^{228}Ra/^{226}Ra$ ratios in background samples (0.75−1.0) (Table S1).

$^{228}Ra/^{226}Ra$ ratios in soils and sediments impacted by OGW spills reflect the ratios of the OGW source combined with ^{228}Ra decay, while the $^{210}Pb/^{226}Ra$ and $^{228}Th/^{228}Ra$ ratios reflect the subsequent ingrowth of the Ra progeny with time. We conducted time series measurements ($n = 3$) of a single soil sample impacted by the Tyler County spill. We found that, with time, estimated unsupported ^{226}Ra activity is constant, unsupported ^{228}Ra activity is decreasing, and ^{228}Th is approaching equilibrium with ^{228}Ra (Figure 1). ^{210}Pb ingrowth over this relatively short time scale was not statistically significant; however, one would expect ^{210}Pb activities to be increasing from ^{226}Ra decay. Given the known half-lives of these radionuclides and their observed ingrowth and decay, the $^{228}Th/^{228}Ra$, $^{210}Pb/^{226}Ra$, and $^{228}Ra/^{226}Ra$ ratios in contaminated soils and sediments can be potentially used to date a spill event.

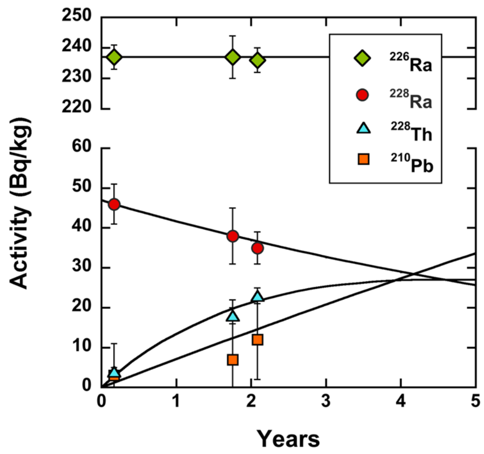

Figure 1. Time series data of the ingrowth and decay of excess U−Th series radionuclides in impacted soil from the Tyler County, West Virginia, spill. Data points represent the same sample measured on three different occasions. Black curves represent modeled decay and ingrowth of respective radionuclides. Excess activities were calculated by subtracting an estimated background of 31 Bq/kg from ^{228}Ra, ^{226}Ra, and ^{228}Th activities, and 98 Bq/kg from ^{210}Pb activities. Background activities were back-calculated using knowledge of when the spill occurred. ^{210}Pb ingrowth over this time scale was not statistically significant, further indicating that the $^{210}Pb/^{226}Ra$ ratio is not suitable for age dating young spills. Error bars represent 95% confidence intervals.

Using the $^{228}Th/^{228}Ra$, $^{210}Pb/^{226}Ra$, and $^{228}Ra/^{226}Ra$ ratios directly measured in soil and sediment to calculate spill age can be misleading because of the natural occurrence of these radionuclides from in situ U and Th decay. Therefore, excess ^{226}Ra, ^{228}Ra, ^{210}Pb, and ^{228}Th relative to background values must be estimated and accounted for in age dating calculations for spills of unknown age, unless the magnitude of Ra accumulation and daughter ingrowth are so high that background levels are negligible compared to contamination levels. Background radionuclides in soil and sediment can be estimated on the basis of the average activity concentrations measured in nearby uncontaminated soils or upstream sediments, assuming that background samples have a similar grain size distribution, mineralogy, and degree of weathering to spill samples.

$^{228}Th/^{228}Ra$ Method. The $^{228}Th/^{228}Ra$ method relies on the decay of ^{228}Ra into its granddaughter ^{228}Th (Figure 2A). This model assumes that Th is insoluble in the formation water, and therefore, ^{232}Th and ^{228}Th activities in the OGW spill water are zero. The insolubility of Th in brines and other natural waters has been well documented in previous studies.[22,23] Because ^{228}Ra ($t_{1/2}$ = 5.75 years) cannot be considered stable over this time scale, ^{228}Th approaches transient equilibrium with ^{228}Ra. Transient equilibrium is a condition under which the half-life of the daughter is shorter than that of the parent but cannot be considered negligible. As a result, the $^{228}Th/^{228}Ra$ dating method accounts for both the ingrowth of ^{228}Th and the decay of ^{228}Ra, and the $^{228}Th/^{228}Ra$ ratio in contaminated soils and sediments will approach an equilibrium value of ∼1.5 after approximately 20 years (Figure S2). The relationship between the $^{228}Th/^{228}Ra$ activity ratio and time can be expressed using the equation $^{228}Th/^{228}Ra = \lambda_{^{228}Th}/(\lambda_{^{228}Th} - \lambda_{^{228}Ra})[1 - e^{(\lambda_{228Ra} - \lambda_{228Th})t}]$, where λ is the decay constant for the respective nuclides and t is time (this notation is consistent for all equations hereafter).

The 1.9 year half-life of ^{228}Th suggests that the $^{228}Th/^{228}Ra$ dating method is useful for dating relatively recent spills up to ∼10 years old. The major limitation of this method is the

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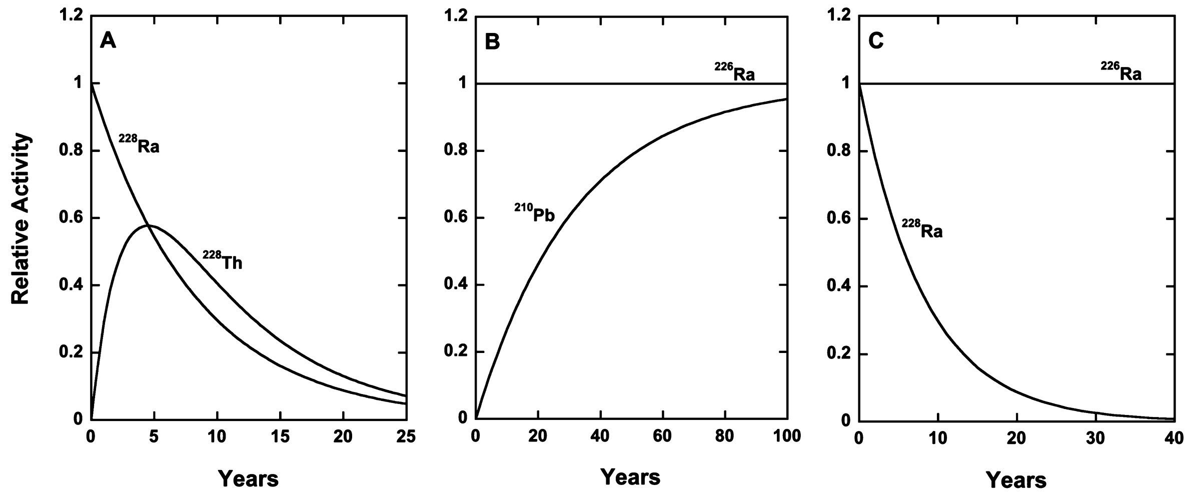

Figure 2. Modeled ingrowth and decay of U−Th radionuclides in sediments affected by OGW spills for the three proposed age dating methods. (A) Ingrowth of ^{228}Th as a result of ^{228}Ra decay. After approximately 20 years, ^{228}Th/^{228}Ra ratios will approach 1.5, indicating transient equilibrium. (B) Ingrowth of ^{210}Pb as a result of ^{226}Ra decay. After approximately 100 years, ^{210}Pb/^{226}Ra ratios will approach ∼1, indicating secular equilibrium. (C) Decay of unsupported ^{228}Ra and persistence of ^{226}Ra with time. ^{228}Ra/^{226}Ra ratios will approach 1/infinity after approximately 40 years.

relatively lower levels of ^{228}Ra compared to that of ^{226}Ra in OGW generated from the shale reservoirs, including the Marcellus (^{228}Ra/^{226}Ra ∼ 0.2).[7] Therefore, in smaller spills of unconventional fluids, excess ^{228}Ra activities may be close to supported (background) ^{228}Ra activities. The ^{228}Ra/^{228}Th ratio is most effective for dating recent, large spills where the magnitude of Ra accumulation in the soil and sediment is high.

^{210}Pb/^{226}Ra Method. The ^{210}Pb/^{226}Ra method is based on the decay of ^{226}Ra into its short-lived daughters and eventually ^{210}Pb (Figure 2B). This model assumes that Pb is negligible in OGW such that the original ^{210}Pb/^{226}Ra ratio is zero. The ^{210}Pb/^{226}Ra dating method can be modeled using the equation $^{210}\mathrm{Pb}/^{226}\mathrm{Ra} = \lambda^{^{210}\mathrm{Pb}}/(\lambda_{^{210}\mathrm{Pb}} - \lambda_{^{226}\mathrm{Ra}})[1 - e^{(\lambda_{226\mathrm{Ra}} - \lambda_{210\mathrm{Pb}})t}]$. The long half-life of ^{226}Ra compared to that of ^{210}Pb allows for the simplification of this model to $^{210}\mathrm{Pb}/^{226}\mathrm{Ra} = 1 - e^{-\lambda_{210\mathrm{Pb}}t}$ and indicates that secular equilibrium between ^{226}Ra and ^{210}Pb (i.e., ^{210}Pb/^{226}Ra ∼ 1) will be reached after approximately 100 years, after which the ^{210}Pb/^{226}Ra ratio is no longer a sensitive dating method. Additionally, because of the ∼22 year half-life of ^{210}Pb, ^{210}Pb ingrowth for detecting recent spills (<5 years) may not be statistically significant unless initial Ra adsorption was relatively high.

Several limitations arise in attempting to implement the ^{210}Pb/^{226}Ra dating method for spills. First, the escape of gaseous ^{222}Rn can reduce the level of accumulation of ^{210}Pb. ^{222}Rn emanation coefficients for disaggregated soil were found to range from 0.15 to 0.25, and ^{222}Rn emanation is expected to be more effective when Ra is distributed on grain surfaces.[24,25] The second limitation is the wider range of ^{210}Pb activities that can be naturally present in soil due to fallout ^{210}Pb. For example, Moore and Poet[26] documented ^{210}Pb in surface soils ranging from 40 to 250 Bq/kg that were ∼2−6 times greater than measured ^{226}Ra activities. The third limitation is the assumption of negligible ^{210}Pb in OGW. While ^{210}Pb activities are often not reported, detectable ^{210}Pb in geothermal brines has been measured up to ∼100 Bq/L,[27,28] suggesting that lead solubility can vary in OGW.

^{228}Ra/^{226}Ra Method. ^{228}Ra decays with a short half-life of 5.75 years compared to that of ^{226}Ra ($t_{1/2}$ = 1600 years). As a result, the ^{228}Ra/^{226}Ra ratio in contaminated soils and sediments will decrease with time as unsupported ^{228}Ra decays and ^{226}Ra remains essentially stable (Figure 2C). If the formation source of the OGW is known, then the original ^{228}Ra/^{226}Ra ratios can be estimated, and the change in the ^{228}Ra/^{226}Ra activity ratio can be modeled with time according to the equation $^{228}\mathrm{Ra}/^{226}\mathrm{Ra} = (^{228}\mathrm{Ra}/^{226}\mathrm{Ra})_o e^{-\lambda_{228\mathrm{Ra}}t}$, where $(^{228}\mathrm{Ra}/^{226}\mathrm{Ra})_o$ is the original ^{228}Ra/^{226}Ra ratio of the spilled fluid at time zero. This method is appropriate for dating spills up to ∼40 years old, after which nearly all unsupported ^{228}Ra will have decayed.

The major limitation of the ^{228}Ra/^{226}Ra method is defining the initial ratio of the spilled fluid, which can result in large errors.[16] Typically, OGWs from unconventional oil and gas operations have a low ^{228}Ra/^{226}Ra ratio of ∼0.2 that reflects the low Th/U ratio of shale formations.[7] Conventional OGWs are often extracted from sandstone formations and consequently have higher ^{228}Ra/^{226}Ra ratios that reflect the higher Th/U ratios of sandstones (∼1).[29−31] However, these ratios can vary substantially, from ∼0.1 to 0.3 for shale reservoirs and from 0.5 to 2.0 for sandstone reservoirs. If the source of the spill water is unknown or if the initial ^{228}Ra/^{226}Ra ratio of the spill water cannot be well-defined, we propose that the ^{228}Ra/^{226}Ra ratio is more useful as an indicator of the source of the fluid. The spill age can be estimated by ^{228}Th/^{228}Ra or ^{210}Pb/^{226}Ra ratios, and the original ^{228}Ra/^{226}Ra ratio can be calculated to reveal the source of contamination (Figure 3).

Application to Oil and Gas Wastewater Spills. Results from unconventional OGW-impacted soils and sediments from North Dakota and West Virginia show that age dating techniques tested in this study could accurately evaluate the age of the spills. Both spills analyzed in this study have occurred in the past three years, making the ^{228}Th/^{228}Ra dating method the more appropriate dating tool because of the relatively shorter half-life of ^{228}Th compared to that of ^{210}Pb, and the higher sensitivity of the ^{228}Th/^{228}Ra ratio over this time scale. For the Tyler County spill, we back-calculated background activities of ^{228}Ra and ^{228}Th of 31 Bq/kg, based on knowledge of when the spill occurred, as the single background soil sample was not sufficient to estimate background activities. The time series measurements of a single sample yield ages of 0.2 ± 0.1, 1.5 ± 0.4, and 2.4 ± 0.5 years (actual times between the documented spill date and sample analysis were 0.2, 1.8, and 2.1 years, respectively). For the Blacktail Creek spill, three background stream sediments were

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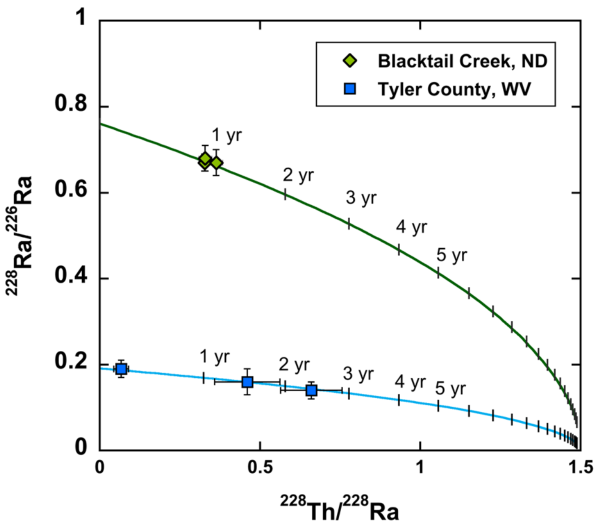

Figure 3. Background-corrected $^{228}Ra/^{226}Ra$ vs $^{228}Th/^{228}Ra$ in spill sediments from two sites in West Virginia (blue) and North Dakota (green). Lines represent modeled curves, and tick marks represent years. The use of the two independent age dating methods elucidates the original $^{228}Ra/^{226}Ra$ ratio of the OGW spill water and provides a constraint for detecting the source of the spill.

used to characterize the ^{228}Ra and ^{228}Th background (18 ± 5 Bq/kg). The background-corrected $^{228}Ra/^{228}Th$ ratios indicate an average age of 1.1 ± 0.1 years, which is consistent with the reported spill date (actual time between the documented spill date and sample analysis is 0.8 year). Using these ages to back-calculate the initial $^{228}Ra/^{226}Ra$ ratios, we find an initial $^{228}Ra/^{226}Ra$ ratio in the North Dakota spill water of ~0.8 and in the West Virginia spill water of ~0.2 (Figure 3). These ratios are relatively consistent with OGW from the Bakken and Marcellus formations, respectively.[7,20]

Given the high, unsupported Ra activities in OGW, the retention of radium in soil and sediments, and the different time scales for the ingrowth of Ra progeny, we demonstrate three independent age dating methods that can detect the age of OGW spills using impacted soil and sediment. We demonstrate the validity of the $^{228}Th/^{228}Ra$ age dating method for dating relatively young OGW spills, which is critical for linking spill contamination to recent unconventional oil and gas operations.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.estlett.6b00118.

Two figures and one table (PDF)

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Notes

The authors declare no competing financial interest.

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