Alice Zinnes

I thank the DRBC for banning fracking in the DRB. Peer-review studies after peer-review studies show that facking operations pollute the air, water and land with toxic chemicals, heavy metals and radioactive materials. It thus makes complete sense to ban fracking from our protected waters, the Delaware River.

However, and for similar reasons, it makes absolutely NO SENSE to allow -- even with regulations -- any frack wastewater into the Basin. This water holds the same chemicals, heavy metals and radioactive materials that give reason to ban fracking in the first place. Please see the attached policy analysis of the radioactivity in frack wastewater.

Environmental Science & Technology

Policy Analysis

Sources of Radium Accumulation in Stream Sediments near Disposal Sites in Pennsylvania: Implications for Disposal of Conventional Oil and Gas Wastewater

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Sources of Radium Accumulation in Stream Sediments near Disposal Sites in Pennsylvania: Implications for Disposal of Conventional Oil and Gas Wastewater

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KEY WORDS

Radium, Produced Water, Appalachian Basin, Marcellus Shale, Hydraulic Fracturing

ABSTRACT

In Pennsylvania, Appalachian oil and gas wastewaters (OGW) are permitted for release to surface waters after some treatment by centralized waste treatment (CWT) facilities. While this practice was largely discontinued in 2011 for unconventional Marcellus OGW, it continues for conventional OGW. This study aimed to evaluate the environmental implications of the policy allowing the disposal of conventional OGW. We collected stream sediments from three discharge sites receiving treated OGW between 2014-2017 and measured ^{228}Ra, ^{226}Ra, and their decay products, ^{228}Th and ^{210}Pb, respectively. We consistently found elevated activities of ^{228}Ra and ^{226}Ra in stream sediments in the vicinity of the outfall (total Ra = 90-25,000 Bq/kg) compared to upstream sediments (20-80 Bq/kg). In 2015 and 2017, ^{228}Th/^{228}Ra activity ratios in sediments from two disposal sites were relatively low (0.2-0.7), indicating that a portion of the Ra has accumulated in the sediments in recent (<3) years, when no unconventional Marcellus OGW was reportedly discharged. ^{228}Ra/^{226}Ra activity ratios were also higher than what would be expected solely from disposal of low ^{228}Ra/^{226}Ra Marcellus OGW. Based on these variations, we concluded that recent disposal of treated conventional OGW is the source of high Ra in stream sediments at CWT facility disposal sites. Consequently, policies pertaining to the disposal of only unconventional fluids are not adequate in preventing radioactive contamination in sediments at disposal sites, and the permission to release of treated Ra-rich conventional OGW through CWT facilities should be reconsidered.

INTRODUCTION

The large-scale development of unconventional shale gas in the Appalachian Basin has been associated with different types and mechanisms of water contamination, including the management and disposal of the oil and gas wastewater (OGW) that is comprised of flowback fluids and produced waters.[1-3] Flowback and produced waters from the Appalachian Basin are highly saline and enriched in naturally occurring radioactive materials (NORM).[4-7] Previous studies have demonstrated that NORM in formation waters mainly consists of radium-226 ($t_{1/2}$=1600 years) and radium-228 ($t_{1/2}$=5.8 years) from the uranium and thorium decay series.[7-9] Total Ra (^{228}Ra+^{226}Ra) activities have been measured in Appalachian Basin formation waters up to hundreds of Becquerels per liter (Bq/L; up to 660 Bq/L and 250 Bq/L for Marcellus and conventional produced waters, respectively)[7] that exceed by several orders of magnitude the activities typically measured in fresh surface waters (0.5- 20 mBq/L for ^{226}Ra) by several orders of magnitude.[10] Elevated ^{228}Ra and ^{226}Ra may pose environmental and human health risks if released to the environment, as they are carcinogenic,[11] bioaccumulate (concentration factors between sediment and aquatic plants and fish of 0.014 and 2.3-700, respectively),[12-17] persist in the environment due to their relatively long half lives, and decay into a suite of other radioactive elements including gaseous ^{222}Rn, ^{210}Pb, and ^{210}Po.

Due to their high salinity, unique chemistry, and immense volume, OGW pose significant management challenges when brought to the surface with hydrocarbons. In Pennsylvania, 43 million bbl of unconventional and 6.6 million bbl of conventional OGW were produced in 2014. A large fraction of this OGW (64% of unconventional OGW and 5% of conventional OGW; >50% of the combined total) was reused for hydraulic fracturing operations.[18] A major option for disposal is injection underground via EPA Class II deep-well injection wells, but since there are a relatively limited number of these disposal wells in Pennsylvania, the OGW is often transported to neighboring states for disposal. Therefore, alternative disposal options in Pennsylvania consist of spreading on roads as a deicing agent or dust suppressant and treatment by wastewater treatment plants, including centralized waste treatment (CWT) facilities.[18] Treatment of OGW at these facilities has been described previously[19-21] and often includes the addition of Na_2SO_4 to promote the precipitation of metals, as well as Ra, before the treated OGW is discharged to local surface waters.

Due to concerns of contamination, in the spring of 2011 the Pennsylvania Department of Environmental Protection (PADEP) requested unconventional well operators to cease sending Marcellus OGW to wastewater treatment facilities. Although participation was voluntary, treatment of Marcellus waste at many wastewater treatment plants in Pennsylvania nearly ended by the fall of 2011.[22] However, these facilities continued to receive, treat, and dispose conventional OGW to the local streams.[18]

Several studies addressing this issue were published in 2013, relatively soon after Marcellus OGW treatment and discharge was discontinued. These studies showed that the releases of highly saline effluent causes direct contamination of the stream water at disposal sites, [19, 20, 23, 24] and also increases the risk of the formation of disinfection byproducts in downstream communities.[25] In addition to degrading water quality, Warner et al.[20] found that the release of treated OGW to Blacklick Creek, a tributary of the Allegheny River in Josephine, PA, resulted in the accumulation of Ra (^{226}Ra activities of 544- 8,759 Bq/kg) in stream sediments in close vicinity (<200 m) to the outfall. Skalak et al.[26] found no increase in ^{226}Ra in stream sediments downstream of effluent sites from five wastewater treatment facilities. In two facilities, Skalak et al.[26] also collected sediments at the disposal sites, one of which was found to have ^{226}Ra activities slightly elevated (73 Bq/kg) above background (40 Bq/kg). These investigations, however, were conducted during the time period that Marcellus OGW were treated and discharged (2008-2011), or relatively soon after this practice was discontinued, and consequently the Ra accumulation in sediments has been attributed to contamination from the time period of high volumes of Marcellus OGW discharge.[20]

While much attention has been paid to understanding and mitigating contamination from unconventional OGW, the environmental impact from disposal of conventional OGW from CWT facilities has not been thoroughly investigated. Previous research has shown that conventional OGW from the Appalachian basin is also enriched in both ^{226}Ra and ^{228}Ra, with total Ra activities reaching 250 Bq/L (median 27 Bq/L).[7] Accordingly, we hypothesized that in spite of Marcellus OGW no longer being sent to wastewater treatment facilities, long-term release of conventional OGW by CWT facilities would still result in Ra accumulation in stream sediments at disposal sites.

In this study, we collected stream sediments from three disposal sites in PA receiving treated OGW. These include sediments from Blacklick Creek in Josephine, the Allegheny River in Franklin, and McKee Run in Creekside (Figure 1). Stream sediments were collected between 2014 and 2017 while the CWT facilities were not receiving Marcellus OGW but did report receipt of conventional OGW.[18] The objectives of this study were to (1) assess Ra accumulation and the ingrowth of Ra decay products in sediments of streams receiving treated conventional OGW; (2) use the U-Th series disequilibrium to constrain the timing of Ra accumulation and determine whether the Ra in stream sediments reflects ongoing conventional OGW disposal or legacy disposal of Marcellus OGW; and (3) use the data to evaluate the environmental implications of current policies that solely regulate and restrict unconventional fluids and allow continued disposal of treated conventional OGW to the environment.

MATERIALS AND METHODS

Site Selection. We investigated three sites where OGW effluents were released to surface waters from CWT facilities (Figure 1). The CWT facilities that were chosen are defined by Standard Industrial Classification (SIC) codes that only relate to oil and gas wastes. Although the possibility that these facilities received other undocumented wastes during the study period is unknown, we are not aware of any other NORM-rich wastewater sources in the study area. These facilities include (1) the Pennsylvania Brine Treatment Josephine Facility ("Josephine Facility") in Josephine, PA which discharges treated OGW to Blacklick Creek; (2) the Pennsylvania Brine Treatment Franklin Facility ("Franklin Facility") in Franklin, PA, which discharges to the Allegheny River; and (3) Hart Resource Technologies Creekside Facility ("Hart Facility") in Creekside, PA, which discharges to McKee Run (Figure 1).

In 2010, the PADEP issued regulations that required effluents from wastewater treatment plants have total dissolved solid (TDS) levels below 500 mg/L. However, the Josephine, Franklin, and Creekside facilities were 3 of initially 27 facilities grandfathered in to previous regulations that do not strictly limit the TDS of effluents.[27] These three investigated facilities also reported that they stopped receiving unconventional OGW by the end of 2011, following PADEP asking that well operators voluntarily stop sending unconventional OGW to wastewater treatment facilities grandfathered in to the less stringent TDS standards.[22, 27] Total conventional and unconventional waste sent to CWT facilities investigated in this study was compiled from the PADEP oil and gas reporting website for the years 2010-2016.[18] These data confirm that treatment of unconventional wastes at these three facilities diminished by 2012, while treatment of conventional waste and discharge of high salinity waters continued at consistent rates (Figure S1). Average annual discharge rates from 2012 to 2017 were of 236±61x10^6 L per year at the Franklin Facility and 174±29x10^6 L per year at the Josephine Facility.[28]

In each of the sites, effluents from the CWT facilities discharge to the local streams. The stream sediments in these areas are common to northern Appalachian watersheds. Grain size distribution analyses indicate that the stream sediments consistently range from 5-15% silt and clay across all streams. The remainder of the size fraction is fine to very coarse sand. Results in this study refer to the bulk sediments without analysis of selective grain-size fractions.

Sample Collection. Grab stream sediments were collected in May 2014 (Franklin n= 2, Josephine n=7, Hart n=2), June and August 2015 (Franklin n= 4, Josephine n=2, Hart n=2), and June 2017 (Franklin n= 4, Josephine n=3) from the three effluent sites. Approximately 100 grams of the top 2-4 cm of sediment were scooped with a shovel and stored in a polypropylene jar. Multiple sediment samples were similarly collected from various points upstream of the disposal site over the course of the sampling campaigns (Franklin n=5, Josephine n=7, Hart n=6). Upstream sediments are assumed to be unaffected by effluents and therefore are used as reference sites. However, other upstream sources such as coal mine discharges and other CWT facilities could potentially influence the "background".

One effluent sample was also collected from the Franklin Facility in 2015. The sample was collected unfiltered, prior to coming in contact with stream water. The effluent was diluted with freshwater to a specific conductivity less than seawater (<50 mS/cm) and passed through two sequential plastic columns each containing 10 grams of MnO_2 coated acrylic fiber that efficiently adsorbs Ra.[29-36] The flow rate through the columns was monitored periodically and kept at less than 1 L/min. Fibers were rinsed with DI water, hand squeezed to remove particulates and excess moisture, and stored in separate plastic bags prior to laboratory processing.

Radionuclide Analyses. Approximately 40-60 grams of sediment were oven dried at 105 degrees C and, if necessary, ground with a mortal and pestle to a diameter less than 5 mm. Samples were packed and weighed in plastic snap close Petri style dishes (6.5 cm in diameter and 2 cm in height) that were then sealed with electrical tape and coated in wax to prevent the escape of gaseous ^{222}Rn ($t_{1/2}$ =3.8 days) and ^{220}Rn ($t_{1/2}$=55 seconds). The MnO_2 coated fibers from the Franklin Facility were compressed and then packaged and incubated similarly to the sediment samples. The two fibers were packaged and analyzed separately to monitor for potential Ra bleed through that would result in underestimation of Ra activities.[34]

Sealed samples incubated for a minimum of 21 days to allow ^{226}Ra to reach radioactive secular equilibrium (i.e. the activity of the parent nuclide is equal to the activity of decay product) with ^{222}Rn along with other decay products, ^{214}Bi ($t_{1/2}$ = 19.9 minutes) and ^{214}Pb ($t_{1/2}$ = 27 minutes). This holding time also allows ^{228}Th to reach radioactive secular equilibrium with ^{224}Ra ($t_{1/2}$=3.6 days) and the succeeding short-lived radionuclides including ^{212}Pb ($t_{1/2}$=10.6 hours) and for ^{228}Ra to reach radioactive secular equilibrium with its immediate decay product ^{228}Ac ($t_{1/2}$=6.1 hours). If radioactive secular equilibrium is assumed in these sections of the U and Th decay series, ^{228}Ra, ^{226}Ra, and ^{228}Th can be measured through their decay products [36-39] when direct measurement is not feasible (e.g. the significant interference of ^{235}U (54% yield) on the 186 KeV peak).

Following incubation, samples were counted on a Canberra Broad Energy 5030 Germanium Gamma detector surrounded by 10 cm of lead shielding. Samples typically counted for 6- 48 hours so that counting errors (2σ) were less than 10%. ^{226}Ra activities were measured through the 351 KeV energy peak of ^{214}Pb. ^{228}Ra activities were measured through the 911 KeV energy peak of ^{228}Ac. ^{228}Th activities were measured through the 239 KeV energy peak of ^{212}Pb. Finally, ^{210}Pb ($t_{1/2}$ = 22 years) activities were measured directly through the 47 KeV energy peak. The detector efficiencies were determined using a U-Th reference ore material (DL-1a) prepared by the Canadian Certified Reference Materials Project (CCRMP) that was packaged and incubated in a container identical to the samples. Background and efficiency checks were performed routinely prior to and during the time frame of sample analyses.

We accounted for attenuation of gamma photons by the sample itself at each energy investigated in this study using U and Th point sources according to methods described in Cutshall et al.[40] At low energies (<200 KeV; ^{210}Pb), differences in sample density and composition between the standard and samples of interest resulted in significant attenuation differences. However, we found at higher energies (>200 KeV), these differences were generally minor (i.e. within statistical counting error) for our sample set.

RESULTS AND DISCUSSION

Accumulation of Ra and decay products in sediments at OGW disposal sites. At all three investigated sites, we consistently find elevated Ra activities in stream sediments collected near effluent pipes at the outfall sites (^{226}Ra = 57-14,949 Bq/kg; n= 26) compared to upstream sediments (^{226}Ra = 9-41 Bq/kg; n=18) (Figure 2). Sediments from the Franklin effluent site had ^{226}Ra activities ranging from 269-14,949 Bq/kg (n=10), sediments the Josephine effluent site had ^{226}Ra activities ranging from 119- 10,747 Bq/kg (n=12), and sediments from the Hart effluent site had ^{226}Ra activities ranging from 57-351 Bq/kg (n=4). We did not observe any apparent trends in activities increasing or decreasing with time.

Because Ra is significantly higher in sediments from disposal sites compared to sediments from upstream sites (up to ~650 times compared to the average ^{226}Ra background activity at the Franklin Facility), combined with direct evidence for water contamination from OGW effluents in the stream water,[20, 41] we suggest that the CWT facility discharges are the source for the elevated Ra in the impacted stream sediments. While total Ra activities in conventional OGW can be found up to 250 Bq/L, low ^{226}Ra activities in the discharged effluents from Josephine site were reported by Warner et al[20] (0.13-0.19 Bq/L), which indicate substantial Ra removal as part of the CWT treatment. Similarly, we found relatively low activities of ^{226}Ra and ^{228}Ra (0.4 Bq/L and 0.6 Bq/L, respectively) in effluents collected from the Franklin Site in 2015. In spite of the large removal of Ra from the treated effluents, Ra in sediments collected from the disposal sites was still elevated. These data suggest that the release of low Ra effluents can potentially results in high Ra accumulation in sediments at the disposal sites. However, we cannot exclude the possibility of infrequent pulses of high Ra effluents to the streams as a major contributor to the Ra activities measured in sediments from the disposal sites.

We conducted mass-balance calculations to evaluate the possibility that the ongoing release of low-Ra effluents is responsible for the elevated Ra observed in the sediments near the effluents discharge sites. Our model (see SI for details) takes into account the Ra loading to the stream (based on the Ra activities and volume of the discharge effluents), variable salinity ranges that control the Ra adsorption coefficient (K_d)[42], and the volume of impacted sediments. We find that the Ra activities in impacted stream sediments modeled from these mass-balance calculations are similar to the measured Ra activities in the sediments, supporting the notion that Ra accumulation at the levels observed in this study is possible from long-term discharge of treated OGW effluents even with low Ra activities. Our model does not account for any sediment losses from the system due to continuous downstream transport. A previous study estimated sedimentation rates at 5 to 8 cm per year in a location downstream of the discharge site of Blacklick Creek[43], suggesting that there is likely some transport of sediments to and from the discharge sites, which could effectively be "diluting" the Ra activities at the discharge sites.

The retention of Ra in stream sediments following OGW disposal can be obtained by (1) Ra adsorption to clays and/or manganese and iron oxides;[42, 44, 45] (2) incorporation of Ra into secondary minerals such as barite ((Ba,Ra)SO_4) that could be generated upon the blending of Ba-rich OGW with high-sulfate river water; [46] and/or (3) episodic or ongoing addition of extremely fine-grained barite particles that were generated during the treatment process, suspended in the liquid effluents, and then transported to the stream sediments. While determining the mechanism of Ra accumulation to sediments is outside the scope of this study, future research should investigate whether Ra is incorporated into sediments in these streams through adsorption, authigenic barite formation, or effluent-transported solid barite particles. Such a distinction could have important implications for mitigating future contamination.

In addition to ^{226}Ra and ^{228}Ra, elevated activities of Ra decay products, ^{210}Pb and ^{228}Th, were detected in the sediments collected from two CWT disposal sites at substantially elevated activities compared to the upstream sediments (Figure 2). Sediments from the Franklin site had ^{228}Th activities ranging from 91-4591 Bq/kg and ^{210}Pb activities ranging from 117-1593 Bq/kg, and sediments the Josephine effluent site had ^{228}Th activities ranging from 32- 2614 Bq/kg and ^{210}Pb activities ranging from 33-82 Bq/kg. Upstream ^{228}Th and ^{210}Pb activities ranged from 9-38 Bq/kg and 14-81 Bq/kg, respectively, at both sites. Given the low solubility of Th and Pb and their negligible levels in OGW[8], we assume that the accumulation of ^{228}Th and ^{210}Pb in the stream sediments is likely due to Ra decay and subsequent ingrowth in situ, rather than the transport and addition of these nuclides via retention from discharged effluents.

Source and Age Constraints of Radionuclide Accumulation. Determination of the timing of Ra accumulation has important implications for assessing the source of Ra contamination in the investigated streams. If elevated Ra activities are found to be solely due to legacy contamination from Marcellus OGW treatment and disposal, then the end of this practice in 2011 should have prevented any additional contamination from OGW disposal after 2011. However, if the age of the contamination is relatively recent, then the elevated Ra activities in stream sediments at the disposal sites can be attributed to continued disposal of treated conventional OGW.

The ^{228}Th/^{228}Ra activity ratios have been previously used to determine the age and source of OGW spills and radioactive barite associated with oil and gas development.[38, 47, 48] Unsupported ^{228}Ra decays into ^{228}Th, and the ^{228}Th/^{228}Ra activity ratio can serve as a chronometer of contamination events[8, 38, 47, 49] due to the insolubility and suitable 1.9 year half-life of ^{228}Th.[45, 50-52] With time, ^{228}Th approaches transient equilibrium with ^{228}Ra, and the ^{228}Th/^{228}Ra activity ratio will approach ~1.5 after about 15 years. Changes in the ^{228}Th/^{228}Ra activity ratio with time can be modeled according the Equation 1.

$$\frac{228Th}{228Ra} = \frac{\lambda_{Th228}}{\lambda_{Th228}-\lambda_{Ra228}}\left[1 - e^{(\lambda_{228Ra}-\lambda_{Th228})t}\right] \qquad \text{(Eq. 1)}$$

Previous studies have typically employed this ^{228}Th/^{228}Ra dating technique on relatively specific events,[38, 47, 48] while its application to dating contamination events derived from OGW effluents that have been released over multiple years is less established. Here we develop the use of the ^{228}Th-^{228}Ra disequilibrium to constrain the age of ongoing contamination from discharging effluents. If all the excess Ra measured in the sediments from the disposal sites was solely accumulated between 2008 and 2011, when the Marcellus OGW was discharged, then observed ^{228}Th/^{228}Ra activity ratios would fall within the range of 0.8-1.2 in 2015 and 1.1-1.3 in 2017 (Figure 3). However, the relatively low ^{228}Th/^{228}Ra activity ratios (0.3-0.7 in 2015 and 0.2-0.4 in 2017) found in impacted sediments at the Franklin and Josephine sites indicate that at least a portion of the measured Ra has accumulated during the ~0.5 to 3 years prior to sample collection. These relatively low ^{228}Th/^{228}Ra activity ratios observed in the stream sediments rule out the possibility that the elevated Ra activities in the sediments is entirely derived from legacy contamination from documented Marcellus OGW, and rather suggests that at least a portion of the excess radioactivity in sediments from the disposal sites is derived from recent disposal of conventional OGW.

^{228}Th/^{228}Ra age dating assumes a closed system with no losses of ^{228}Ra or external source of ^{228}Th in the impacted sediments. Adsorption/desorption is heavily controlled by the ionic strength of the fluid, among other parameters such as pH and the cation exchange capacity (CEC) of the sediment.[42, 44, 45, 53] For example, in groundwater systems, the sediment partition coefficient (K_d; the ratio of the adsorbed nuclide to the nuclide in the dissolved phase) for Ra exponentially increased from 1.4 at TDS~200,000 mg/L to >500 at TDS<1000 mg/L.[42] We posit that the dilution of highly saline OGW with stream water following discharge permits Ra adsorption to stream sediment. Subsequent desorption of Ra or ingrown ^{228}Th is possible following fluctuations in salinity or pH. However, Th is far less mobile than Ra,[52, 54] and losses to the system from desorption would more heavily affect Ra rather than Th. In such a case, the ^{228}Th/^{228}Ra activity ratios measured in this study would be artificially high and derived age constraints would be artificially old (i.e., indicating even younger ages than our evaluation assuming no Ra lost). Additionally, ^{228}Th/^{228}Ra age dating in this system assumes a fixed sediment substrate despite potential transport of sediments downstream. Regardless, the results from this study indicate that contamination has occurred on a recent time scale and cannot solely be attributed to discharges of Marcellus OGW from 2008-2011.

Age constraints determined from the ^{228}Th/^{228}Ra activity ratios can be corroborated with ^{228}Ra/^{226}Ra activity ratios, which also suggest that Ra is being continually introduced to the stream sediments from the disposal of conventional OGW. While distinctly low ^{228}Ra/^{226}Ra activity ratios (typically less than 0.3) characterize OGW from the Marcellus Shale, higher ^{228}Ra/^{226}Ra (~1) activity ratios have been reported for OGW from conventional formations.[6, 7, 55] The ^{228}Ra/^{226}Ra activity ratios in the impacted sediments are expected to mimic the ratios of the OGW, combined with the decay of ^{228}Ra over time. Following the retention of Ra to the stream sediments, unsupported ^{228}Ra decays with a half-life of 5.8 years, while ^{226}Ra is relatively unchanged over this time scale. Therefore, the ^{228}Ra/^{226}Ra activity ratio in contaminated sediment is expected to decrease with time according the Equation 2, where lambda is the ^{228}Ra decay constant (0.12 yr^{-1}) and t is time.

$$\frac{228Ra}{226Ra} = \left(\frac{228Ra}{226Ra}\right)_o e^{-\lambda_{Ra228} t} \qquad \text{(Eq.2)}$$

Therefore, if all excess Ra was accumulated in the sediments during the period of Marcellus OGW disposal (2008 to 2011), we would expect ^{228}Ra/^{226}Ra activity ratios to be well below 0.3 as ^{228}Ra decays with time. Instead, we observed ^{228}Ra/^{226}Ra activity ratios ranging from 0.4-0.9 in sediments collected in 2015 and 2017, which are higher than typical Marcellus ^{228}Ra/^{226}Ra ratios (< 0.3), suggesting that Ra in the sediments was derived from relatively recent conventional OGW with a relatively high ^{228}Ra/^{226}Ra activity ratio of ~1 (Figure 4).

Policy Implications for Disposal of Conventional OGW from CWT Facilities. Previous[20] and new data presented in this study indicate that the disposal of OGW to the environment results in the accumulation of Ra and Ra-decay products in the upper section of impacted stream sediments. Our data indicate that in spite of the removal of a large fraction of Ra from treated OGW, the discharge of effluents results in accumulation of Ra (^{226}Ra up to 15,000 Bq/kg) in impacted sediments. This observation is supported by a Ra mass-balance model (See SI for details) that shows that the modeled Ra accumulation in the stream sediments is similar to the observed Ra activities in the impacted sediments. While there is no federal regulation, several states have developed limits for solids containing NORM, which typically range from 185-1850 Bq/kg (5 pCi/g to 50 pCi/g).[56] Our data indicate that the disposal of treated OGW results in elevated NORM activities in impacted stream sediments above the 1850 Bq/kg threshold. Waste materials with ^{226}Ra above 1850 Bq/kg should be transferred to a licensed radioactive waste disposal facility that has strict requirements related to site location and the following features: (1) lined walls, back up lining, and a cover, (2) a leachate collection system, and (3) leak detector systems.[57]

Relatively low ^{228}Th/^{228}Ra and high ^{228}Ra/^{226}Ra activity ratios measured in sediments collected from two CWT discharge sites in PA indicate that at least a portion of the Ra measured in sediments has accumulated in recent (0.5-3) years when no Marcellus OGW was reportedly discharged, suggesting that conventional OGW discharges are a noteworthy source of radium accumulation. Accordingly, data from this study indicate that restricting treatment to only conventional OGW at CWT facilities does not prevent the large accumulation of Ra in stream sediments from disposal sites. Our data and previous data[20] also suggest that the large Ra removal from the disposed effluents potentially does not mitigate the high NORM accumulation in sediments at the disposal sites, although we cannot rule out the possibility of infrequent pulses of high-Ra effluents as a major contributor of Ra to the sediments rather than long-term discharge and accumulation from low-Ra effluent.

In addition to treatment at wastewater treatment plants, unconventional OGW is also prohibited from being used as a deicing agent or dust suppressant on roads, while untreated conventional OGW is permitted for application to roads.[26] While the fate of NORM following the use of OGW as deicing agents and dust suppressants remains a major question, data from this study suggests that permission of conventional OGW will not protect the environment from radioactive contamination. In an initial assessment, Skalak et al. [26] found elevated Ra (1.2x), Sr, Ca, and Na in roadside sediments in Vernon County, PA, where OGW was applied to roads for dust suppression when compared to background sites. Future research addressing the application of OGW to roads as a deicing agent and dust suppressant is important to fully understand the impact of OGW related NORM on soils and sediments and the human and environmental health implications of this practice.

Overall, this study shows consistently elevated activities of Ra and their decay products in stream sediments at three disposal sites of CWT facilities in PA receiving conventional OGW, up to five years after unconventional Marcellus OGW were no longer discharged. The $^{228}Th/^{228}Ra$ and $^{228}Ra/^{226}Ra$ activity ratios in the sediments suggest that at least a portion of the Ra has accumulated in recent years when no Marcellus OGW were reportedly discharged, indicating that permitting CWT facilities to treat and release only conventional OGW does not prevent radioactive contamination and accumulation in the upper portion of sediments at disposal sites. In order to prevent radionuclide accumulation in the environment, we suggest that disposal restrictions should apply to any type of Ra-rich water, regardless of source, and that current policies differentiating the treatment and disposal of conventional OGW from unconventional OGW should be reconsidered.

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SUPPORTING INFORMATION AVAILABLE

Expanded information on the Ra mass balance calculations, 1 figure, and 1 table are available.

Figures

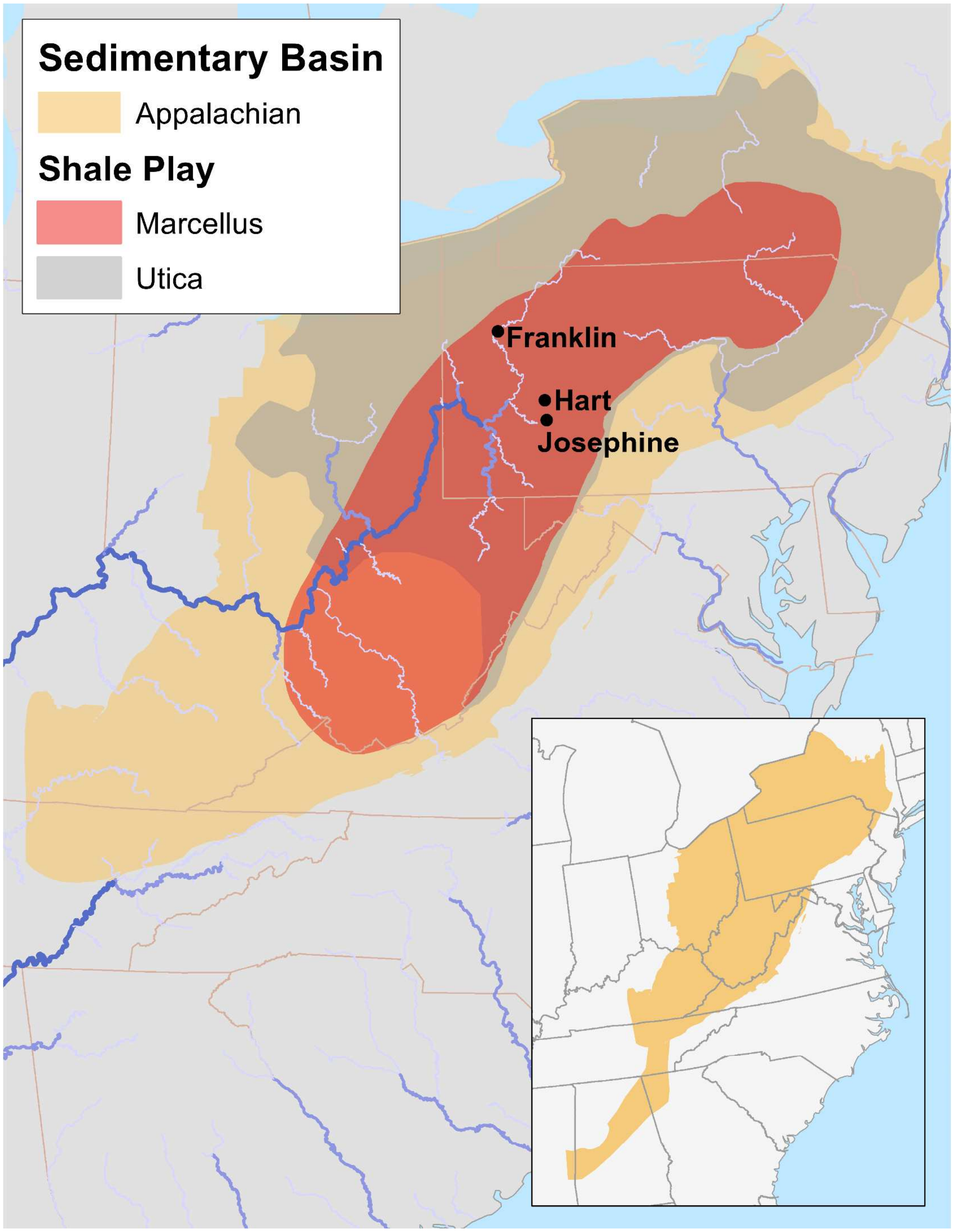


Figure 1. A map of the northern Appalachian Basin and major shale plays in the eastern United States. Inset map shows the entirety of the Appalachian Basin, that extends from New York southward through Pennsylvania, Maryland, Ohio, West Virginia, Virginia, Kentucky, and Tennessee before terminating in Alabama. The location of the three CWT facilities investigated in this study are also shown.

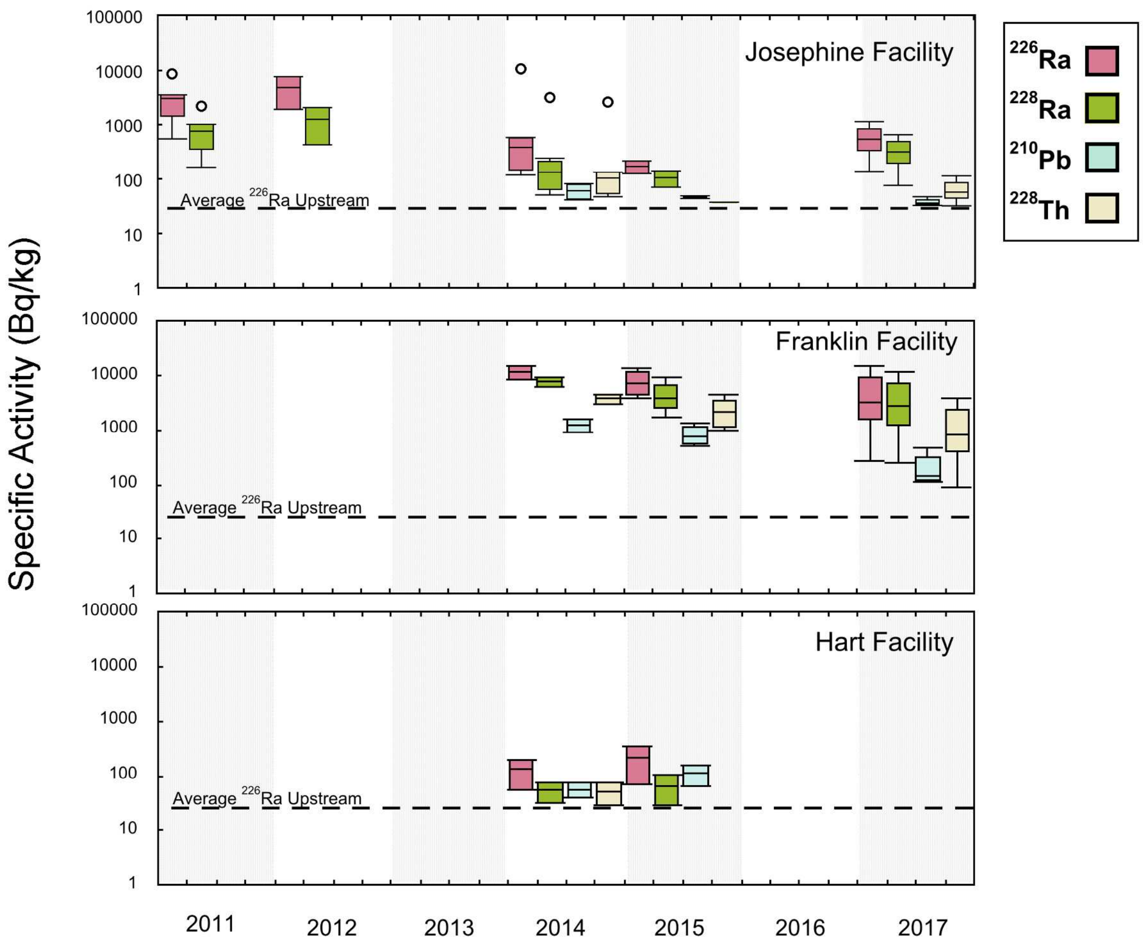


Figure 2. ^{226}Ra, ^{228}Ra, ^{210}Pb, and ^{228}Th in sediments collected from three streams receiving OGW discharged by CWTs in 2014, 2015, and 2017. Josephine data from 2011 and 2012 were compiled from the literature.[18] The boxplots indicate the middle 50% and the median of the data. Boxplot whiskers indicate the minimum and maximum values, excluding outliers which are indicated by open circles. Dashed lines show the average ^{226}Ra activity of upstream samples, assumed to be unaffected by treated OGW effluents. Elevated activities were measured at all three effluent sites compared to upstream sites.

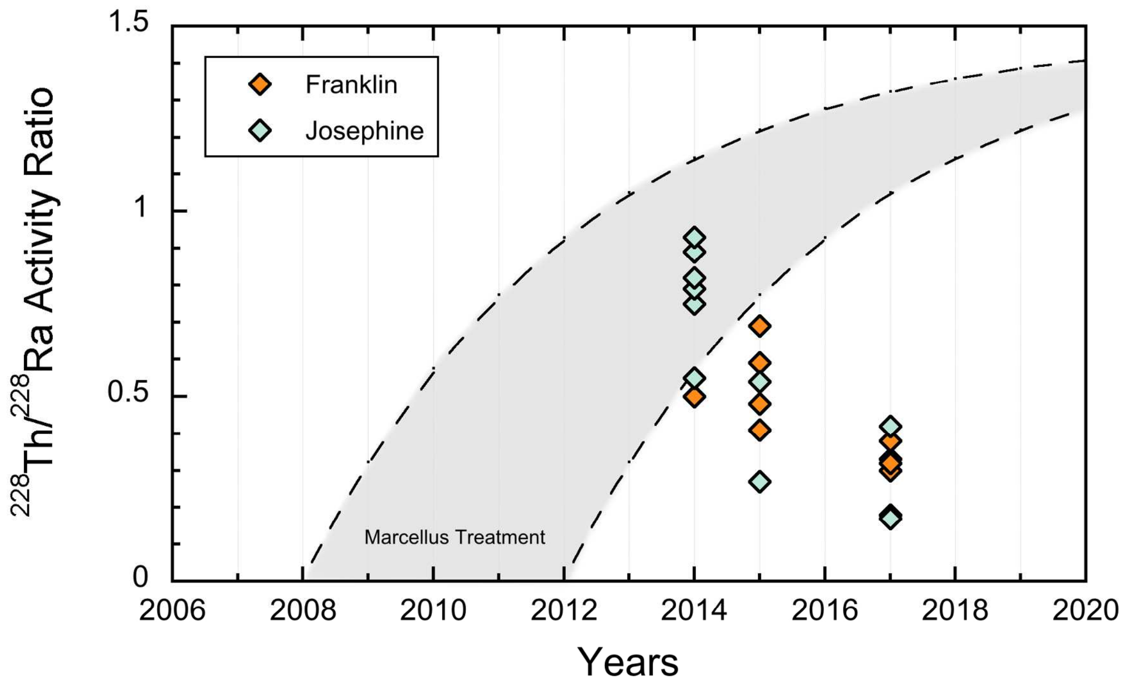


Figure 3. ^{228}Th/^{228}Ra activity ratios in sediments collected from the Franklin and Josephine CWT facilities in 2014, 2015, and 2017. Ratios that fall within the gray band reflect contamination that can be dated to the time period of high discharges of treated unconventional Marcellus OGW (2008-2011). Sediments collected in 2015 and 2017 had ^{228}Th/^{228}Ra activity ratios that fall below the expected range if contamination was solely from Marcellus OGW contamination. These relatively low ratios suggest that at least a portion of the Ra that has accumulated in the sediments is from relatively recent releases of conventional OGW.

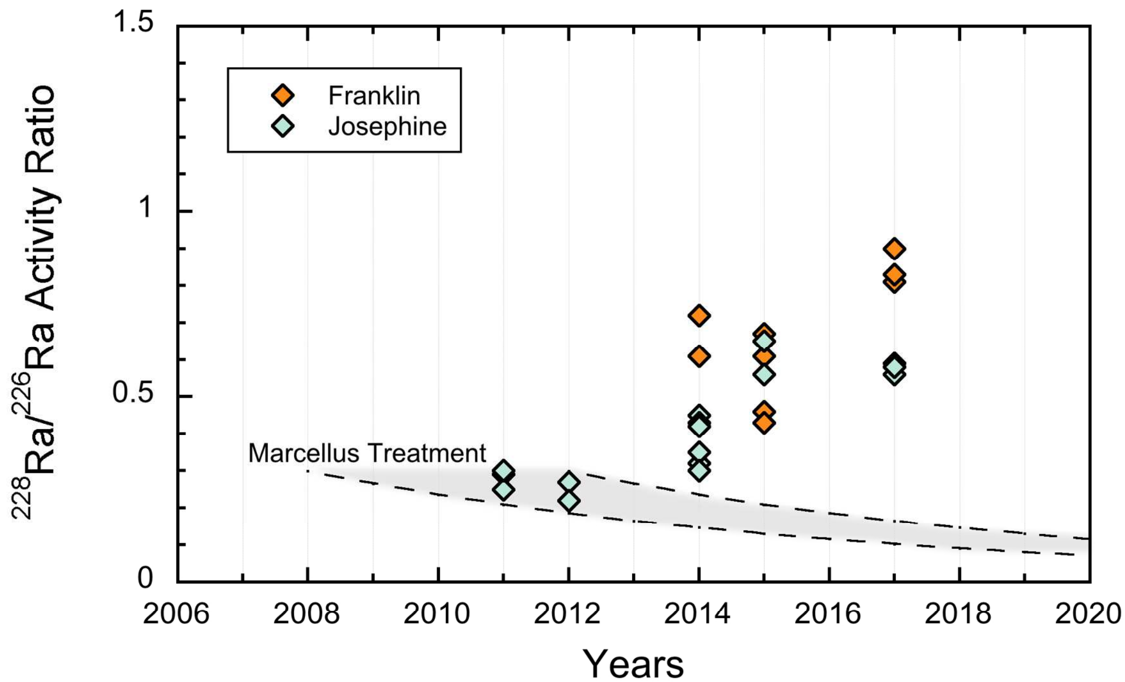


Figure 4. $^{228}Ra/^{226}Ra$ activity ratios in sediments collected from the Franklin and Josephine CWT facilities in from 2011-2017. 2011 and 2012 data are compiled from Warner et al. (2013).[20] Ratios that fall within the gray band reflect the ratios that would be expected from Marcellus OGW contamination from 2008-2011. Sediments from this study collected in 2014, 2015 and 2017 had $^{228}Ra/^{226}Ra$ activity ratios above the Marcellus range, suggesting that at least some of the contamination is sourced from conventional OGW with a relatively higher $^{228}Ra/^{226}Ra$ activity ratio (~1).

References

1. Vengosh, A.; Jackson, R. B.; Warner, N.; Darrah, T. H.; Kondash, A. A critical review of the risks to water resources from unconventional shale gas development and hydraulic fracturing in the United States. *Environ. Sci. Technol.* **2014,** *48*, (15), 8334-8348.

2. Brown, V. J. Radionuclides in fracking wastewater: Managing a toxic blend. *Environ. Health Perspect.* **2014,** *122*, (2), A50-A55.

3. Vidic, R.; Brantley, S.; Vandenbossche, J.; Yoxtheimer, D.; Abad, J. Impact of shale gas development on regional water quality. *Science* **2013,** *340*, (6134), 1235009.

4. Chapman, E. C.; Capo, R. C.; Stewart, B. W.; Kirby, C. S.; Hammack, R. W.; Schroeder, K. T.; Edenborn, H. M. Geochemical and strontium isotope characterization of produced waters from Marcellus shale natural gas extraction. *Environ. Sci. Technol.* **2012,** *46*, (6), 3545-3553.

5. Rowan, E. L.; Engle, M. A.; Kraemer, T. F.; Schroeder, K. T.; Hammack, R. W.; Doughten, M. W. Geochemical and isotopic evolution of water produced from Middle Devonian Marcellus shale gas wells, Appalachian Basin, Pennsylvania. *AAPG Bulletin* **2015**, (20,140,808).

6. Dresel, P. E.; Rose, A. W. *Chemistry and origin of oil and gas well brines in Western Pennsylvania: Pennsylvania Geological Survey*; Pennsylvania Department of Conservation and Natural Resources, **2010**.

7. Rowan, E.; Engle, M.; Kirby, C.; Kraemer, T. *Radium content of oil-and gas-field produced waters in the northern Appalachian Basin (USA)—summary and discussion of data: US Geological Survey Scientific Investigations Report* **2011,** *5135*, 15.

8. Nelson, A. W.; Eitrheim, E. S.; Knight, A. W.; May, D.; Mehrhoff, M. A.; Shannon, R.; Litman, R.; Burnett, W. C.; Forbes, T. Z.; Schultz, M. K. Understanding the radioactive ingrowth and decay of naturally occurring radioactive materials in the environment: An analysis of produced fluids from the Marcellus Shale. *Environ. Health Perspect.* **2015**.

9. Swann, C.; Matthews, J.; Ericksen, R.; Kuszmaul, J. *Evaluations of radionuclides of uranium, thorium, and radium associated with produced fluids, precipitates, and sludges from oil, gas, and oilfield brine injections wells in Mississippi*. MS: Mississippi Mineral and Resources Institute/Department of Pharmacology/Department of Geology and Geological Engineering, University of Mississippi, 2004.

10. IAEA *The environmental behavior of radium: Revised edition*; Vienna, 2014.

11. Raabe, O. G. Comparison of the carcinogenicity of radium and bone-seeking actinides. *Health physics* **1984,** *46*, (6), 1241-1258.

12. Bollhöfer, A.; Brazier, J.; Humphrey, C.; Ryan, B.; Esparon, A. A study of radium bioaccumulation in freshwater mussels, Velesunio Angasi, in the Magela Creek catchment, Northern Territory, Australia. *J. Environ. Radioact.* **2011,** *102*, (10), 964-974.

13. Jha, V.; Tripathi, R.; Sethy, N.; Sahoo, S.; Shukla, A.; Puranik, V. Bioaccumulation of ^{226}Ra by plants growing in fresh water ecosystem around the uranium industry at Jaduguda, India. *J. Environ. Radioact.* **2010,** *101*, (9), 717-722.

14. Jeffree, R. A.; Simpsonf, R. Radium-226 is accumulated in calcium granules in the tissues of the freshwater mussel, velesunio angasi: Support for a metabolic analogue hypothesis? *Comparative Biochemistry and Physiology Part A: Physiology* **1984,** *79*, (1), 61-72.

15. Johnston, A.; Murray, A.; Marten, R.; Martin, P.; Pettersson, H. Bioaccumulation of radionuclides and stable metals in the freshwater mussel, Velesunio Angasi. *Alligator Rivers Region Research Institute Annual Research Summary* **1986,** *87*, 69-74.

16. Williams, A. Radium uptake by freshwater plants. In *The environmental behaviour of radium* 1990, Vol. 1 .

17. Justyn, J.; Havlik, B., Radium uptake by freshwater fish. In *The environmental behaviour of radium*, 1990; Vol. 1.

18. PA DEP Oil & Gas Reporting Website: Statewide Data Downloads. https://www.paoilandgasreporting.state.pa.us/publicreports/Modules/Waste/WasteByWasteFacility.aspx (Accessed 10/2/2015).

19. Ferrar, K. J.; Michanowicz, D. R.; Christen, C. L.; Mulcahy, N.; Malone, S. L.; Sharma, R. K. Assessment of effluent contaminants from three facilities discharging Marcellus Shale wastewater to surface waters in Pennsylvania. *Environ. Sci. Technol.* **2013,** *47*, (7), 3472-3481.

20. Warner, N. R.; Christie, C. A.; Jackson, R. B.; Vengosh, A. Impacts of shale gas wastewater disposal on water quality in Western Pennsylvania. *Environ. Sci. Technol.* **2013,** *47*, (20), 11849-11857.

21. Veil, J. A. *Water management technologies used by Marcellus shale gas producers*; prepared for U.S. department of Energy Office of Fossil Fuel Energy, National Energy Technology Laboratory, 2010.

22. Pennsylvania DEP calls on natural gas drillers to stop giving treatment facilities wastewater. http://www.prnewswire.com/news-releases/pennsylvania-dep-calls-on-natural-gas-drillers-to-stop-giving-treatment-facilities-wastewater-120206249.html (Accessed September 10, 2017).

23. Olmstead, S. M.; Muehlenbachs, L. A.; Shih, J.-S.; Chu, Z.; Krupnick, A. J. Shale gas development impacts on surface water quality in Pennsylvania. *Proc. Natl. Acad. Sci.* **2013,** *110*, (13), 4962-4967.

24. Wilson, J. M.; Wang, Y.; VanBriesen, J. M. Sources of high total dissolved solids to drinking water supply in Southwestern Pennsylvania. *J. of Environ.l Eng.* **2013,** *140*, (5), B4014003.

25. Parker, K. M.; Zeng, T.; Harkness, J.; Vengosh, A.; Mitch, W. A. Enhanced formation of disinfection byproducts in shale gas wastewater-impacted drinking water supplies. *Environ. Sci. Technol.* **2014,** *48*, (19), 11161-11169.

26. Skalak, K. J.; Engle, M. A.; Rowan, E. L.; Jolly, G. D.; Conko, K. M.; Benthem, A. J.; Kraemer, T. F. Surface disposal of produced waters in Western and Southwestern Pennsylvania: Potential for accumulation of alkali-earth elements in sediments. *Int. J. Coal Geol.* **2014,** *126*, (0), 162-170.

27. Wilson, J. M.; VanBriesen, J. M. Oil and gas produced water management and surface drinking water sources in Pennsylvania. *Environ. Pract.* **2012,** *14*, (4), 288-300.

28. USEPA. Discharge monitoring report (DMR) pollutant loading tool. https://cfpub.epa.gov/dmr/ (Accessed 11/20/17).

29. Moore, W. S.; Reid, D. F. Extraction of radium from natural waters using manganese-impregnated acrylic fibers. *J. Geophys. Res.* **1973,** *78*, (36), 8880-8886.

30. Garcia-Solsona, E.; Garcia-Orellana, J.; Masqué, P.; Dulaiova, H. Uncertainties associated with ^{223}Ra and ^{224}Ra measurements in water via a delayed coincidence counter (RaDeCC). *Mar. Chem.* **2008,** *109*, (3), 198-219.

31. Vinson, D. S.; Vengosh, A.; Hirschfeld, D.; Dwyer, G. S. Relationships between radium and radon occurrence and hydrochemistry in fresh groundwater from fractured crystalline rocks, North Carolina (USA). *Chem. Geol.* **2009,** *260*, (3), 159-171.

32. Burnett, W. C.; Peterson, R.; Moore, W. S.; de Oliveira, J. Radon and radium isotopes as tracers of submarine groundwater discharge–results from the Ubatuba, Brazil SGD assessment intercomparison. *Est. Coast. Shelf Sci.* **2008,** *76*, (3), 501-511.

33. Gu, H.; Moore, W. S.; Zhang, L.; Du, J.; Zhang, J. Using radium isotopes to estimate the residence time and the contribution of submarine groundwater discharge (SGD) in the Changjiang effluent plume, East China Sea. *Cont. Shelf Res.* **2012,** *35*, 95-107.

34. Vinson, D. S.; Tagma, T.; Bouchaou, L.; Dwyer, G. S.; Warner, N. R.; Vengosh, A. Occurrence and mobilization of radium in fresh to saline coastal groundwater inferred from geochemical and isotopic tracers (Sr, S, O, H, Ra, Rn). *Appl. Geochem.* **2013,** *38*, 161-175.

35. Peterson, R. N.; Burnett, W. C.; Dimova, N.; Santos, I. R. Comparison of measurement methods for radium-226 on manganese-fiber. *Limnol. Oceanogr-Meth.* **2009,** *7*, (2), 196-205.

36. Dulaiova, H.; Burnett, W. C. An efficient method for γ ‐ spectrometric determination of radium ‐ 226,228 via manganese fibers. *Limnol. Oceanogr-Meth.* **2004,** *2*, (8), 256-261.

37. Reyss, J. L.; Schmidt, S.; Latrouite, D.; Floris, S. Age determination of crustacean carapaces using $^{228}Th/^{228}Ra$ measurements by ultra low level gamma spectroscopy. *Appl. Radiat. Isot.* **1996,** *47*, (9), 1049-1053.

38. Zielinski, R.; Otton, J.; Budahn, J. Use of radium isotopes to determine the age and origin of radioactive barite at oil-field production sites. *Environ. Pollut.* **2001,** *113*, (3), 299-309.

39. Zielinski, R. A.; Budahn, J. R. Radionuclides in fly ash and bottom ash: Improved characterization based on radiography and low energy gamma-ray spectrometry. *Fuel* **1998,** *77*, (4), 259-267.

40. Cutshall, N. H.; Larsen, I. L.; Olsen, C. R. Direct analysis of ^{210}Pb in sediment samples: Self-absorption corrections. *Nucl. Instrum. and Methods* **1983,** *206*, (1–2), 309-312.

41. Harkness, J. S.; Dwyer, G. S.; Warner, N. R.; Parker, K. M.; Mitch, W. A.; Vengosh, A. Iodide, bromide, and ammonium in hydraulic fracturing and oil and gas wastewaters: Environmental implications. *Environ. Sci. Technol.* **2015,** *49*, (3), 1955-1963.

42. Sturchio, N.; Banner, J.; Binz, C.; Heraty, L.; Musgrove, M. Radium geochemistry of ground waters in Paleozoic carbonate aquifers, Midcontinent, USA. *Appl. Geochem.* **2001,** *16*, (1), 109-122.

43. Burgos, W. D.; Castillo-Meza, L.; Tasker, T. L.; Geeza, T. J.; Drohan, P. J.; Liu, X.; Landis, J. D.; Blotevogel, J.; McLaughlin, M.; Borch, T. Watershed-scale impacts from surface water disposal of oil and gas wastewater in western Pennsylvania. *Environ. Sci. Technol.* **2017,** *51*, (15), 8851-8860.

44. Landa, E.; Reid, D. Sorption of radium-226 from oil-production brine by sediments and soils. *Environ. Geol.* **1983,** *5*, (1), 1-8.

45. Krishnaswami, S.; Graustein, W. C.; Turekian, K. K.; Dowd, J. F. Radium, thorium and radioactive lead isotopes in groundwaters: Application to the in situ determination of adsorption ‐ desorption rate constants and retardation factors. *Water Resour. Res.* **1982,** *18*, (6), 1663-1675.

46. Kondash, A. J.; Warner, N. R.; Lahav, O.; Vengosh, A. Radium and barium removal through blending hydraulic fracturing fluids with acid mine drainage. *Environ. Sci. Technol.* **2013,** *48*, (2), 1334-1342.

47. Lauer, N.; Vengosh, A. Age dating oil and gas wastewater spills using radium isotopes and their decay products in impacted soil and sediment. *Environ. Sci. Technol. Lett.* **2016,** *3*, (5), 205-209.

48. Zielinski, R. A.; White, G. J.; Otton, J. K. In *Chemical and radiometric assessment of NORM in soils and sediments contacted by produced water, Teapot Dome, Wyoming*, Proceedings of the 5th International Petroleum Environmental Conference, Albuquerque, N.M., 1998.

49. Nelson, A. W.; Knight, A. W.; May, D.; Eitrheim, E. S.; Schultz, M. K., Naturally-occurring radioactive materials (NORM) associated with unconventional drilling for shale gas. In *Hydraulic fracturing: Environmental issues*, American Chemical Society: 2015; Vol. 1216, pp 89-128.

50. Porcelli, D.; Swarzenski, P. W. The behavior of U- and Th-series nuclides in groundwater. *Rev. Mineral. Geochem.* **2003,** *52*.

51. Laul, J.; Smith, M.; Hubbard, N. In *Behavior of natural uranium, thorium and radium isotopes in the Wolfcamp brine aquifers, Palo Duro Basin, Texas*, MRS Proceedings, 1984; Cambridge Univ Press: 1984; p 475.

52. Langmuir, D.; Herman, J. S. The mobility of thorium in natural waters at low temperatures. *Geochim. Cosmochim. Acta* **1980,** *44*, (11), 1753-1766.

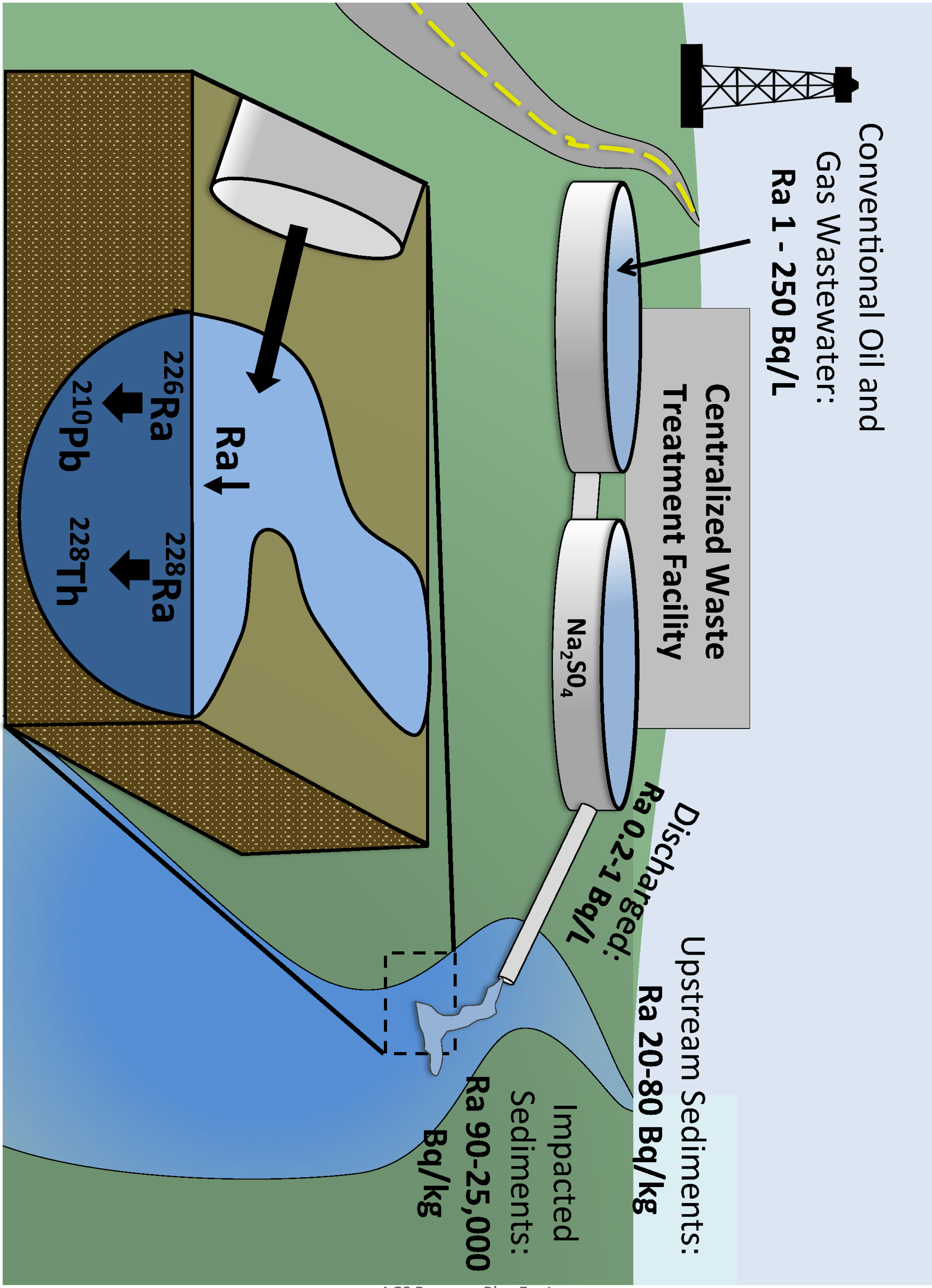
53. Webster, I. T.; Hancock, G. J.; Murray, A. S. Modelling the effect of salinity on radium desorption from sediments. *Geochim. Cosmochim. Acta* **1995,** *59*, (12), 2469-2476.

54. Lazar, B.; Weinstein, Y.; Paytan, A.; Magal, E.; Bruce, D.; Kolodny, Y. Ra and Th adsorption coefficients in lakes—Lake Kinneret (Sea of Galilee) "natural experiment". *Geochim. Cosmochim. Acta* **2008,** *72*, (14), 3446-3459.

55. Asikainen, M. Radium content and the $^{226}Ra/^{228}Ra$ activity ratio in groundwater from bedrock. *Geochim. Cosmochim. Acta* **1981,** *45*, (8), 1375-1381.

56. Smith, K. P.; Arnish, J. J.; Williams, G. P.; Blunt, D. L. Assessment of the disposal of radioactive petroleum industry waste in nonhazardous landfills using risk-based modeling. *Environ. Sci. Technol.* **2003,** *37*, (10), 2060-2066.

57. Michigan DEQ *Michigan TENORM disposal advisory panel white paper 2014-2015*; 2015.


Conventional Oil and
Gas Wastewater:
Ra 1 - 250 Bq/L
Centralized Waste
Treatment Facility
Na_2SO_4
Discharged:
Ra 0.2-1 Bq/L
Upstream Sediments:
Ra 20-80 Bq/kg
Impacted
Sediments:
Ra 90-25,000
Bq/kg
Ra↓
^{226}Ra
^{210}Pb
^{228}Ra
^{228}Th