

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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2 **Disposal Sites in Pennsylvania: Implications for Disposal of**
3 **Conventional Oil and Gas Wastewater**

4

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22 **KEY WORDS**

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

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26 **ABSTRACT**

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

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49 INTRODUCTION

50 The large-scale development of unconventional shale gas in the Appalachian
51 Basin has been associated with different types and mechanisms of water contamination,
52 including the management and disposal of the oil and gas wastewater (OGW) that is
53 comprised of flowback fluids and produced waters.¹⁻³ Flowback and produced waters
54 from the Appalachian Basin are highly saline and enriched in naturally occurring
55 radioactive materials (NORM).⁴⁻⁷ Previous studies have demonstrated that NORM in
56 formation waters mainly consists of radium-226 ($t_{1/2}=1600$ years) and radium-228
57 ($t_{1/2}=5.8$ years) from the uranium and thorium decay series.⁷⁻⁹ Total Ra ($^{228}\text{Ra}+^{226}\text{Ra}$)
58 activities have been measured in Appalachian Basin formation waters up to hundreds of
59 Becquerels per liter (Bq/L; up to 660 Bq/L and 250 Bq/L for Marcellus and conventional
60 produced waters, respectively)⁷ that exceed by several orders of magnitude the activities
61 typically measured in fresh surface waters (0.5- 20 mBq/L for ^{226}Ra) by several orders of
62 magnitude.¹⁰ Elevated ^{228}Ra and ^{226}Ra may pose environmental and human health risks if
63 released to the environment, as they are carcinogenic,¹¹ bioaccumulate (concentration
64 factors between sediment and aquatic plants and fish of 0.014 and 2.3-700,
65 respectively),¹²⁻¹⁷ persist in the environment due to their relatively long half lives, and
66 decay into a suite of other radioactive elements including gaseous ^{222}Rn , ^{210}Pb , and ^{210}Po .
67 Due to their high salinity, unique chemistry, and immense volume, OGW pose
68 significant management challenges when brought to the surface with hydrocarbons. In
69 Pennsylvania, 43 million bbl of unconventional and 6.6 million bbl of conventional OGW
70 were produced in 2014. A large fraction of this OGW (64% of unconventional OGW and
71 5% of conventional OGW; >50% of the combined total) was reused for hydraulic

72 fracturing operations.¹⁸ A major option for disposal is injection underground via EPA
73 Class II deep-well injection wells, but since there are a relatively limited number of these
74 disposal wells in Pennsylvania, the OGW is often transported to neighboring states for
75 disposal. Therefore, alternative disposal options in Pennsylvania consist of spreading on
76 roads as a deicing agent or dust suppressant and treatment by wastewater treatment
77 plants, including centralized waste treatment (CWT) facilities.¹⁸ Treatment of OGW at
78 these facilities has been described previously¹⁹⁻²¹ and often includes the addition of
79 Na₂SO₄ to promote the precipitation of metals, as well as Ra, before the treated OGW is
80 discharged to local surface waters.

81 Due to concerns of contamination, in the spring of 2011 the Pennsylvania
82 Department of Environmental Protection (PADEP) requested unconventional well
83 operators to cease sending Marcellus OGW to wastewater treatment facilities. Although
84 participation was voluntary, treatment of Marcellus waste at many wastewater treatment
85 plants in Pennsylvania nearly ended by the fall of 2011.²² However, these facilities
86 continued to receive, treat, and dispose conventional OGW to the local streams.¹⁸

87 Several studies addressing this issue were published in 2013, relatively soon after
88 Marcellus OGW treatment and discharge was discontinued. These studies showed that
89 the releases of highly saline effluent causes direct contamination of the stream water at
90 disposal sites,^{19, 20, 23, 24} and also increases the risk of the formation of disinfection
91 byproducts in downstream communities.²⁵ In addition to degrading water quality, Warner
92 et al.²⁰ found that the release of treated OGW to Blacklick Creek, a tributary of the
93 Allegheny River in Josephine, PA, resulted in the accumulation of Ra (²²⁶Ra activities of
94 544- 8,759 Bq/kg) in stream sediments in close vicinity (<200 m) to the outfall. Skalak et

95 al.²⁶ found no increase in ²²⁶Ra in stream sediments downstream of effluent sites from
96 five wastewater treatment facilities. In two facilities, Skalak et al.²⁶ also collected
97 sediments at the disposal sites, one of which was found to have ²²⁶Ra activities slightly
98 elevated (73 Bq/kg) above background (40 Bq/kg). These investigations, however, were
99 conducted during the time period that Marcellus OGW were treated and discharged
100 (2008-2011), or relatively soon after this practice was discontinued, and consequently the
101 Ra accumulation in sediments has been attributed to contamination from the time period
102 of high volumes of Marcellus OGW discharge.²⁰

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

111 In this study, we collected stream sediments from three disposal sites in PA
112 receiving treated OGW. These include sediments from Blacklick Creek in Josephine, the
113 Allegheny River in Franklin, and McKee Run in Creekside (Figure 1). Stream sediments
114 were collected between 2014 and 2017 while the CWT facilities were not receiving
115 Marcellus OGW but did report receipt of conventional OGW.¹⁸ The objectives of this
116 study were to (1) assess Ra accumulation and the ingrowth of Ra decay products in
117 sediments of streams receiving treated conventional OGW; (2) use the U-Th series

118 disequilibrium to constrain the timing of Ra accumulation and determine whether the Ra
119 in stream sediments reflects ongoing conventional OGW disposal or legacy disposal of
120 Marcellus OGW; and (3) use the data to evaluate the environmental implications of
121 current policies that solely regulate and restrict unconventional fluids and allow
122 continued disposal of treated conventional OGW to the environment.

123

124 **MATERIALS AND METHODS**

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

136 In 2010, the PADEP issued regulations that required effluents from wastewater
137 treatment plants have total dissolved solid (TDS) levels below 500 mg/L. However, the
138 Josephine, Franklin, and Creekside facilities were 3 of initially 27 facilities grandfathered
139 in to previous regulations that do not strictly limit the TDS of effluents.²⁷ These three
140 investigated facilities also reported that they stopped receiving unconventional OGW by

141 the end of 2011, following PADEP asking that well operators voluntarily stop sending
142 unconventional OGW to wastewater treatment facilities grandfathered in to the less
143 stringent TDS standards.^{22, 27} Total conventional and unconventional waste sent to CWT
144 facilities investigated in this study was compiled from the PADEP oil and gas reporting
145 website for the years 2010-2016.¹⁸ These data confirm that treatment of unconventional
146 wastes at these three facilities diminished by 2012, while treatment of conventional waste
147 and discharge of high salinity waters continued at consistent rates (Figure S1). Average
148 annual discharge rates from 2012 to 2017 were of $236 \pm 61 \times 10^6$ L per year at the Franklin
149 Facility and $174 \pm 29 \times 10^6$ L per year at the Josephine Facility.²⁸

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

156

157 **Sample Collection.** Grab stream sediments were collected in May 2014 (Franklin n= 2,
158 Josephine n=7, Hart n=2), June and August 2015 (Franklin n= 4, Josephine n=2, Hart
159 n=2), and June 2017 (Franklin n= 4, Josephine n=3) from the three effluent sites.

160 Approximately 100 grams of the top 2-4 cm of sediment were scooped with a shovel and
161 stored in a polypropylene jar. Multiple sediment samples were similarly collected from
162 various points upstream of the disposal site over the course of the sampling campaigns
163 (Franklin n=5, Josephine n=7, Hart n=6). Upstream sediments are assumed to be

164 unaffected by effluents and therefore are used as reference sites. However, other
165 upstream sources such as coal mine discharges and other CWT facilities could potentially
166 influence the “background”.

167 One effluent sample was also collected from the Franklin Facility in 2015. The
168 sample was collected unfiltered, prior to coming in contact with stream water. The
169 effluent was diluted with freshwater to a specific conductivity less than seawater (<50
170 mS/cm) and passed through two sequential plastic columns each containing 10 grams of
171 MnO₂ coated acrylic fiber that efficiently adsorbs Ra.²⁹⁻³⁶ The flow rate through the
172 columns was monitored periodically and kept at less than 1 L/min. Fibers were rinsed
173 with DI water, hand squeezed to remove particulates and excess moisture, and stored in
174 separate plastic bags prior to laboratory processing.

175

176 **Radionuclide Analyses.** Approximately 40-60 grams of sediment were oven dried at 105
177 degrees C and, if necessary, ground with a mortar and pestle to a diameter less than 5
178 mm. Samples were packed and weighed in plastic snap close Petri style dishes (6.5 cm in
179 diameter and 2 cm in height) that were then sealed with electrical tape and coated in wax
180 to prevent the escape of gaseous ²²²Rn (t_{1/2}=3.8 days) and ²²⁰Rn (t_{1/2}=55 seconds). The
181 MnO₂ coated fibers from the Franklin Facility were compressed and then packaged and
182 incubated similarly to the sediment samples. The two fibers were packaged and analyzed
183 separately to monitor for potential Ra bleed through that would result in underestimation
184 of Ra activities.³⁴

185 Sealed samples incubated for a minimum of 21 days to allow ²²⁶Ra to reach
186 radioactive secular equilibrium (i.e. the activity of the parent nuclide is equal to the

187 activity of decay product) with ^{222}Rn along with other decay products, ^{214}Bi ($t_{1/2} = 19.9$
188 minutes) and ^{214}Pb ($t_{1/2} = 27$ minutes). This holding time also allows ^{228}Th to reach
189 radioactive secular equilibrium with ^{224}Ra ($t_{1/2}=3.6$ days) and the succeeding short-lived
190 radionuclides including ^{212}Pb ($t_{1/2}=10.6$ hours) and for ^{228}Ra to reach radioactive secular
191 equilibrium with its immediate decay product ^{228}Ac ($t_{1/2}=6.1$ hours). If radioactive secular
192 equilibrium is assumed in these sections of the U and Th decay series, ^{228}Ra , ^{226}Ra , and
193 ^{228}Th can be measured through their decay products ³⁶⁻³⁹ when direct measurement is not
194 feasible (e.g. the significant interference of ^{235}U (54% yield) on the 186 KeV peak).

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

206 We accounted for attenuation of gamma photons by the sample itself at each
207 energy investigated in this study using U and Th point sources according to methods
208 described in Cutshall et al.⁴⁰ At low energies (<200 KeV; ^{210}Pb), differences in sample
209 density and composition between the standard and samples of interest resulted in

210 significant attenuation differences. However, we found at higher energies (>200 KeV),
211 these differences were generally minor (i.e. within statistical counting error) for our
212 sample set.

213

214 **RESULTS AND DISCUSSION**

215 **Accumulation of Ra and decay products in sediments at OGW disposal sites.** At all
216 three investigated sites, we consistently find elevated Ra activities in stream sediments
217 collected near effluent pipes at the outfall sites ($^{226}\text{Ra} = 57\text{-}14,949$ Bq/kg; $n=26$)
218 compared to upstream sediments ($^{226}\text{Ra} = 9\text{-}41$ Bq/kg; $n=18$) (Figure 2). Sediments from
219 the Franklin effluent site had ^{226}Ra activities ranging from 269-14,949 Bq/kg ($n=10$),
220 sediments the Josephine effluent site had ^{226}Ra activities ranging from 119- 10,747 Bq/kg
221 ($n=12$), and sediments from the Hart effluent site had ^{226}Ra activities ranging from 57-
222 351 Bq/kg ($n=4$). We did not observe any apparent trends in activities increasing or
223 decreasing with time.

224 Because Ra is significantly higher in sediments from disposal sites compared to
225 sediments from upstream sites (up to ~650 times compared to the average ^{226}Ra
226 background activity at the Franklin Facility), combined with direct evidence for water
227 contamination from OGW effluents in the stream water,^{20, 41} we suggest that the CWT
228 facility discharges are the source for the elevated Ra in the impacted stream sediments.
229 While total Ra activities in conventional OGW can be found up to 250 Bq/L, low ^{226}Ra
230 activities in the discharged effluents from Josephine site were reported by Warner et al²⁰
231 (0.13-0.19 Bq/L), which indicate substantial Ra removal as part of the CWT treatment.
232 Similarly, we found relatively low activities of ^{226}Ra and ^{228}Ra (0.4 Bq/L and 0.6 Bq/L,

233 respectively) in effluents collected from the Franklin Site in 2015. In spite of the large
234 removal of Ra from the treated effluents, Ra in sediments collected from the disposal
235 sites was still elevated. These data suggest that the release of low Ra effluents can
236 potentially results in high Ra accumulation in sediments at the disposal sites. However,
237 we cannot exclude the possibility of infrequent pulses of high Ra effluents to the streams
238 as a major contributor to the Ra activities measured in sediments from the disposal sites.

239 We conducted mass-balance calculations to evaluate the possibility that the
240 ongoing release of low-Ra effluents is responsible for the elevated Ra observed in the
241 sediments near the effluents discharge sites. Our model (see SI for details) takes into
242 account the Ra loading to the stream (based on the Ra activities and volume of the
243 discharge effluents), variable salinity ranges that control the Ra adsorption coefficient
244 (K_d)⁴², and the volume of impacted sediments. We find that the Ra activities in impacted
245 stream sediments modeled from these mass-balance calculations are similar to the
246 measured Ra activities in the sediments, supporting the notion that Ra accumulation at
247 the levels observed in this study is possible from long-term discharge of treated OGW
248 effluents even with low Ra activities. Our model does not account for any sediment
249 losses from the system due to continuous downstream transport. A previous study
250 estimated sedimentation rates at 5 to 8 cm per year in a location downstream of the
251 discharge site of Blacklick Creek⁴³, suggesting that there is likely some transport of
252 sediments to and from the discharge sites, which could effectively be “diluting” the Ra
253 activities at the discharge sites.

254 The retention of Ra in stream sediments following OGW disposal can be obtained
255 by (1) Ra adsorption to clays and/or manganese and iron oxides;^{42, 44, 45} (2) incorporation

256 of Ra into secondary minerals such as barite ((Ba,Ra)SO₄) that could be generated upon
257 the blending of Ba-rich OGW with high-sulfate river water;⁴⁶ and/or (3) episodic or
258 ongoing addition of extremely fine-grained barite particles that were generated during the
259 treatment process, suspended in the liquid effluents, and then transported to the stream
260 sediments. While determining the mechanism of Ra accumulation to sediments is outside
261 the scope of this study, future research should investigate whether Ra is incorporated into
262 sediments in these streams through adsorption, authigenic barite formation, or effluent-
263 transported solid barite particles. Such a distinction could have important implications for
264 mitigating future contamination.

265 In addition to ²²⁶Ra and ²²⁸Ra, elevated activities of Ra decay products, ²¹⁰Pb and
266 ²²⁸Th, were detected in the sediments collected from two CWT disposal sites at
267 substantially elevated activities compared to the upstream sediments (Figure 2).
268 Sediments from the Franklin site had ²²⁸Th activities ranging from 91-4591 Bq/kg and
269 ²¹⁰Pb activities ranging from 117-1593 Bq/kg, and sediments the Josephine effluent site
270 had ²²⁸Th activities ranging from 32- 2614 Bq/kg and ²¹⁰Pb activities ranging from 33-82
271 Bq/kg. Upstream ²²⁸Th and ²¹⁰Pb activities ranged from 9-38 Bq/kg and 14-81 Bq/kg,
272 respectively, at both sites. Given the low solubility of Th and Pb and their negligible
273 levels in OGW⁸, we assume that the accumulation of ²²⁸Th and ²¹⁰Pb in the stream
274 sediments is likely due to Ra decay and subsequent ingrowth in situ, rather than the
275 transport and addition of these nuclides via retention from discharged effluents.

276

277 **Source and Age Constraints of Radionuclide Accumulation.** Determination of the
278 timing of Ra accumulation has important implications for assessing the source of Ra

279 contamination in the investigated streams. If elevated Ra activities are found to be solely
280 due to legacy contamination from Marcellus OGW treatment and disposal, then the end
281 of this practice in 2011 should have prevented any additional contamination from OGW
282 disposal after 2011. However, if the age of the contamination is relatively recent, then
283 the elevated Ra activities in stream sediments at the disposal sites can be attributed to
284 continued disposal of treated conventional OGW.

285 The $^{228}\text{Th}/^{228}\text{Ra}$ activity ratios have been previously used to determine the age and
286 source of OGW spills and radioactive barite associated with oil and gas development.^{38,}
287 ^{47, 48} Unsupported ^{228}Ra decays into ^{228}Th , and the $^{228}\text{Th}/^{228}\text{Ra}$ activity ratio can serve as a
288 chronometer of contamination events^{8, 38, 47, 49} due to the insolubility and suitable 1.9 year
289 half-life of ^{228}Th .^{45, 50-52} With time, ^{228}Th approaches transient equilibrium with ^{228}Ra ,
290 and the $^{228}\text{Th}/^{228}\text{Ra}$ activity ratio will approach ~ 1.5 after about 15 years. Changes in the
291 $^{228}\text{Th}/^{228}\text{Ra}$ activity ratio with time can be modeled according to the Equation 1.

$$292 \quad \frac{^{228}\text{Th}}{^{228}\text{Ra}} = \frac{\lambda_{\text{Th}228}}{\lambda_{\text{Th}228} - \lambda_{\text{Ra}228}} [1 - e^{(\lambda_{\text{Ra}228} - \lambda_{\text{Th}228})t}] \quad (\text{Eq. 1})$$

293 Previous studies have typically employed this $^{228}\text{Th}/^{228}\text{Ra}$ dating technique on
294 relatively specific events,^{38, 47, 48} while its application to dating contamination events
295 derived from OGW effluents that have been released over multiple years is less
296 established. Here we develop the use of the ^{228}Th - ^{228}Ra disequilibrium to constrain the
297 age of ongoing contamination from discharging effluents. If all the excess Ra measured
298 in the sediments from the disposal sites was solely accumulated between 2008 and 2011,
299 when the Marcellus OGW was discharged, then observed $^{228}\text{Th}/^{228}\text{Ra}$ activity ratios
300 would fall within the range of 0.8-1.2 in 2015 and 1.1-1.3 in 2017 (Figure 3). However,
301 the relatively low $^{228}\text{Th}/^{228}\text{Ra}$ activity ratios (0.3-0.7 in 2015 and 0.2-0.4 in 2017) found

302 in impacted sediments at the Franklin and Josephine sites indicate that at least a portion
303 of the measured Ra has accumulated during the ~0.5 to 3 years prior to sample collection.
304 These relatively low $^{228}\text{Th}/^{228}\text{Ra}$ activity ratios observed in the stream sediments rule out
305 the possibility that the elevated Ra activities in the sediments is entirely derived from
306 legacy contamination from documented Marcellus OGW, and rather suggests that at least
307 a portion of the excess radioactivity in sediments from the disposal sites is derived from
308 recent disposal of conventional OGW.

309 $^{228}\text{Th}/^{228}\text{Ra}$ age dating assumes a closed system with no losses of ^{228}Ra or external
310 source of ^{228}Th in the impacted sediments. Adsorption/desorption is heavily controlled by
311 the ionic strength of the fluid, among other parameters such as pH and the cation
312 exchange capacity (CEC) of the sediment.^{42, 44, 45, 53} For example, in groundwater
313 systems, the sediment partition coefficient (K_d ; the ratio of the adsorbed nuclide to the
314 nuclide in the dissolved phase) for Ra exponentially increased from 1.4 at TDS~200,000
315 mg/L to >500 at TDS<1000 mg/L.⁴² We posit that the dilution of highly saline OGW
316 with stream water following discharge permits Ra adsorption to stream sediment.
317 Subsequent desorption of Ra or ingrown ^{228}Th is possible following fluctuations in
318 salinity or pH. However, Th is far less mobile than Ra,^{52, 54} and losses to the system from
319 desorption would more heavily affect Ra rather than Th. In such a case, the $^{228}\text{Th}/^{228}\text{Ra}$
320 activity ratios measured in this study would be artificially high and derived age
321 constraints would be artificially old (i.e., indicating even younger ages than our
322 evaluation assuming no Ra lost). Additionally, $^{228}\text{Th}/^{228}\text{Ra}$ age dating in this system
323 assumes a fixed sediment substrate despite potential transport of sediments downstream.
324 Regardless, the results from this study indicate that contamination has occurred on a

325 recent time scale and cannot solely be attributed to discharges of Marcellus OGW from
326 2008-2011.

327 Age constraints determined from the $^{228}\text{Th}/^{228}\text{Ra}$ activity ratios can be
328 corroborated with $^{228}\text{Ra}/^{226}\text{Ra}$ activity ratios, which also suggest that Ra is being
329 continually introduced to the stream sediments from the disposal of conventional OGW.
330 While distinctly low $^{228}\text{Ra}/^{226}\text{Ra}$ activity ratios (typically less than 0.3) characterize OGW
331 from the Marcellus Shale, higher $^{228}\text{Ra}/^{226}\text{Ra}$ (~ 1) activity ratios have been reported for
332 OGW from conventional formations.^{6, 7, 55} The $^{228}\text{Ra}/^{226}\text{Ra}$ activity ratios in the impacted
333 sediments are expected to mimic the ratios of the OGW, combined with the decay of
334 ^{228}Ra over time. Following the retention of Ra to the stream sediments, unsupported
335 ^{228}Ra decays with a half-life of 5.8 years, while ^{226}Ra is relatively unchanged over this
336 time scale. Therefore, the $^{228}\text{Ra}/^{226}\text{Ra}$ activity ratio in contaminated sediment is expected
337 to decrease with time according the Equation 2, where lambda is the ^{228}Ra decay constant
338 (0.12 yr^{-1}) and t is time.

$$339 \quad \frac{{}^{228}\text{Ra}}{{}^{226}\text{Ra}} = \left(\frac{{}^{228}\text{Ra}}{{}^{226}\text{Ra}}\right)_0 e^{-\lambda_{\text{Ra}} 228t} \quad (\text{Eq.2})$$

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

347

348 **Policy Implications for Disposal of Conventional OGW from CWT Facilities.**

349 Previous²⁰ and new data presented in this study indicate that the disposal of OGW to the
350 environment results in the accumulation of Ra and Ra-decay products in the upper
351 section of impacted stream sediments. Our data indicate that in spite of the removal of a
352 large fraction of Ra from treated OGW, the discharge of effluents results in accumulation
353 of Ra (²²⁶Ra up to 15,000 Bq/kg) in impacted sediments. This observation is supported by
354 a Ra mass-balance model (See SI for details) that shows that the modeled Ra
355 accumulation in the stream sediments is similar to the observed Ra activities in the
356 impacted sediments. While there is no federal regulation, several states have developed
357 limits for solids containing NORM, which typically range from 185-1850 Bq/kg (5 pCi/g
358 to 50 pCi/g).⁵⁶ Our data indicate that the disposal of treated OGW results in elevated
359 NORM activities in impacted stream sediments above the 1850 Bq/kg threshold. Waste
360 materials with ²²⁶Ra above 1850 Bq/kg should be transferred to a licensed radioactive
361 waste disposal facility that has strict requirements related to site location and the
362 following features: (1) lined walls, back up lining, and a cover, (2) a leachate collection
363 system, and (3) leak detector systems.⁵⁷

364 Relatively low ²²⁸Th/²²⁸Ra and high ²²⁸Ra/²²⁶Ra activity ratios measured in
365 sediments collected from two CWT discharge sites in PA indicate that at least a portion
366 of the Ra measured in sediments has accumulated in recent (0.5-3) years when no
367 Marcellus OGW was reportedly discharged, suggesting that conventional OGW
368 discharges are a noteworthy source of radium accumulation. Accordingly, data from this
369 study indicate that restricting treatment to only conventional OGW at CWT facilities does
370 not prevent the large accumulation of Ra in stream sediments from disposal sites. Our

371 data and previous data²⁰ also suggest that the large Ra removal from the disposed
372 effluents potentially does not mitigate the high NORM accumulation in sediments at the
373 disposal sites, although we cannot rule out the possibility of infrequent pulses of high-Ra
374 effluents as a major contributor of Ra to the sediments rather than long-term discharge
375 and accumulation from low-Ra effluent.

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

388 Overall, this study shows consistently elevated activities of Ra and their decay
389 products in stream sediments at three disposal sites of CWT facilities in PA receiving
390 conventional OGW, up to five years after unconventional Marcellus OGW were no
391 longer discharged. The $^{228}\text{Th}/^{228}\text{Ra}$ and $^{228}\text{Ra}/^{226}\text{Ra}$ activity ratios in the sediments
392 suggest that at least a portion of the Ra has accumulated in recent years when no
393 Marcellus OGW were reportedly discharged, indicating that permitting CWT facilities to

394 treat and release only conventional OGW does not prevent radioactive contamination and
395 accumulation in the upper portion of sediments at disposal sites. In order to prevent
396 radionuclide accumulation in the environment, we suggest that disposal restrictions
397 should apply to any type of Ra-rich water, regardless of source, and that current policies
398 differentiating the treatment and disposal of conventional OGW from unconventional
399 OGW should be reconsidered.

400

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406 of this manuscript.

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408 **SUPPORTING INFORMATION AVAILABLE**

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

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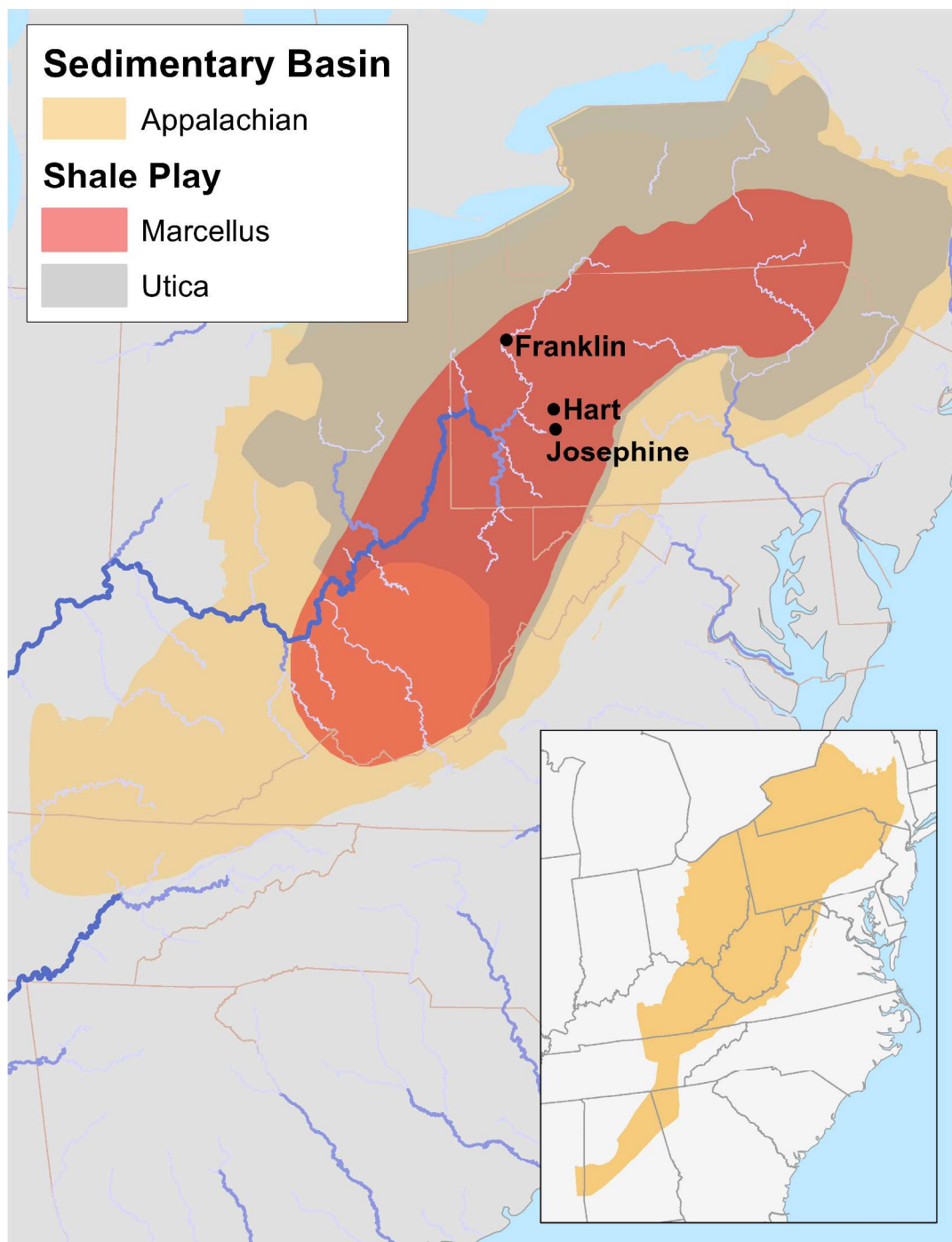
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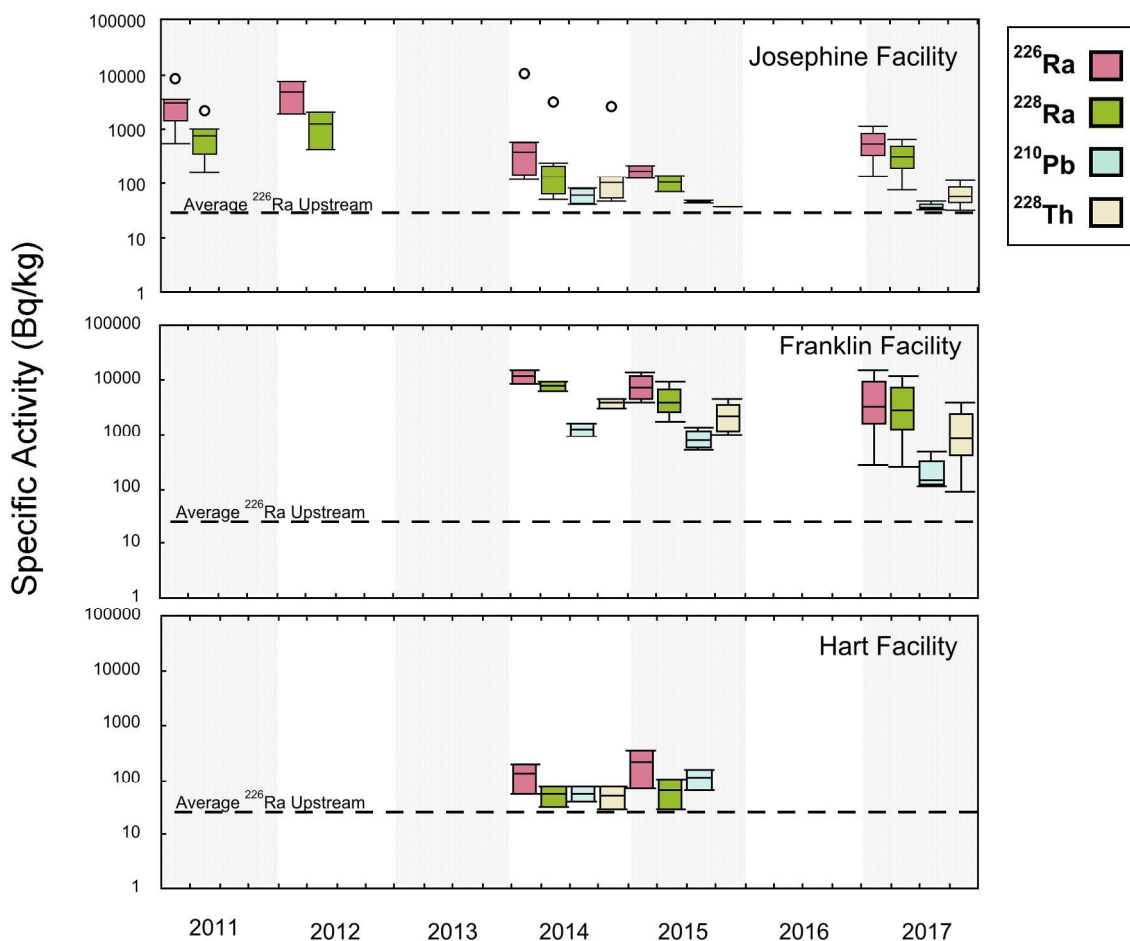
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417 **Figures**
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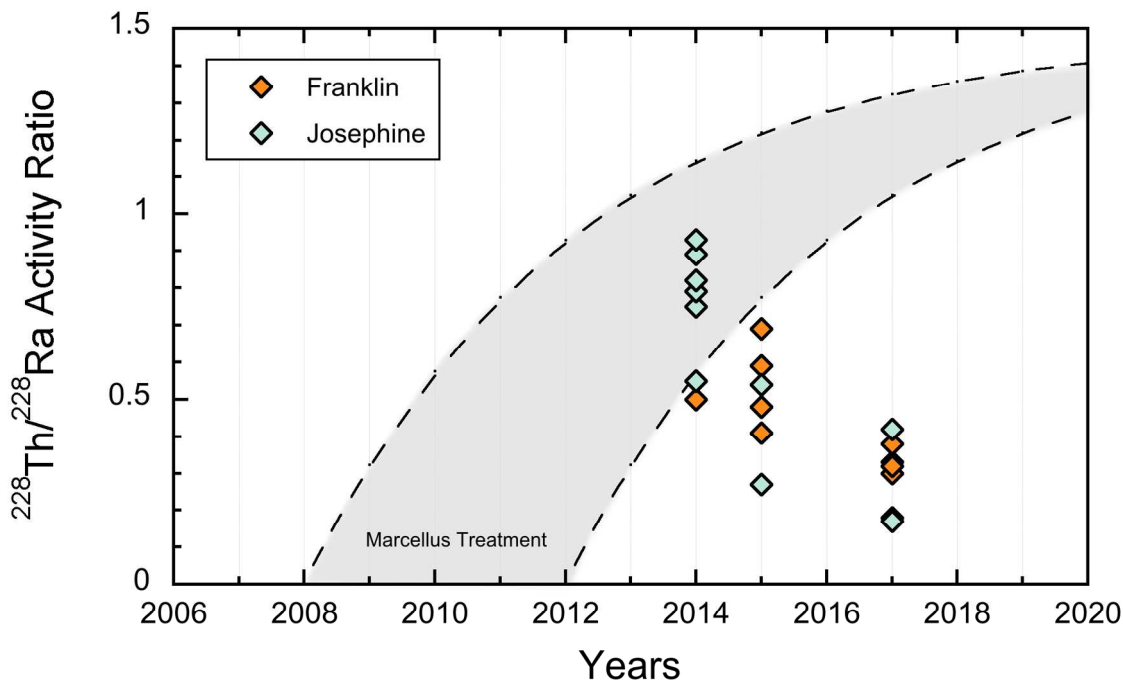
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Figure 1. A map of the northern Appalachian Basin and major shale plays in the eastern United States. Inset map shows the entirety of the Appalachian Basin, that extends from New York southward through Pennsylvania, Maryland, Ohio, West Virginia, Virginia,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



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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.¹⁸⁷ 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.



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450 **Figure 3.** $^{228}\text{Th}/^{228}\text{Ra}$ activity ratios in sediments collected from the Franklin and
 451 Josephine CWT facilities in 2014, 2015, and 2017. Ratios that fall within the gray band
 452 reflect contamination that can be dated to the time period of high discharges of treated
 453 unconventional Marcellus OGW (2008-2011). Sediments collected in 2015 and 2017 had
 454 $^{228}\text{Th}/^{228}\text{Ra}$ activity ratios that fall below the expected range if contamination was solely
 455 from Marcellus OGW contamination. These relatively low ratios suggest that at least a
 456 portion of the Ra that has accumulated in the sediments is from relatively recent releases
 457 of conventional OGW.

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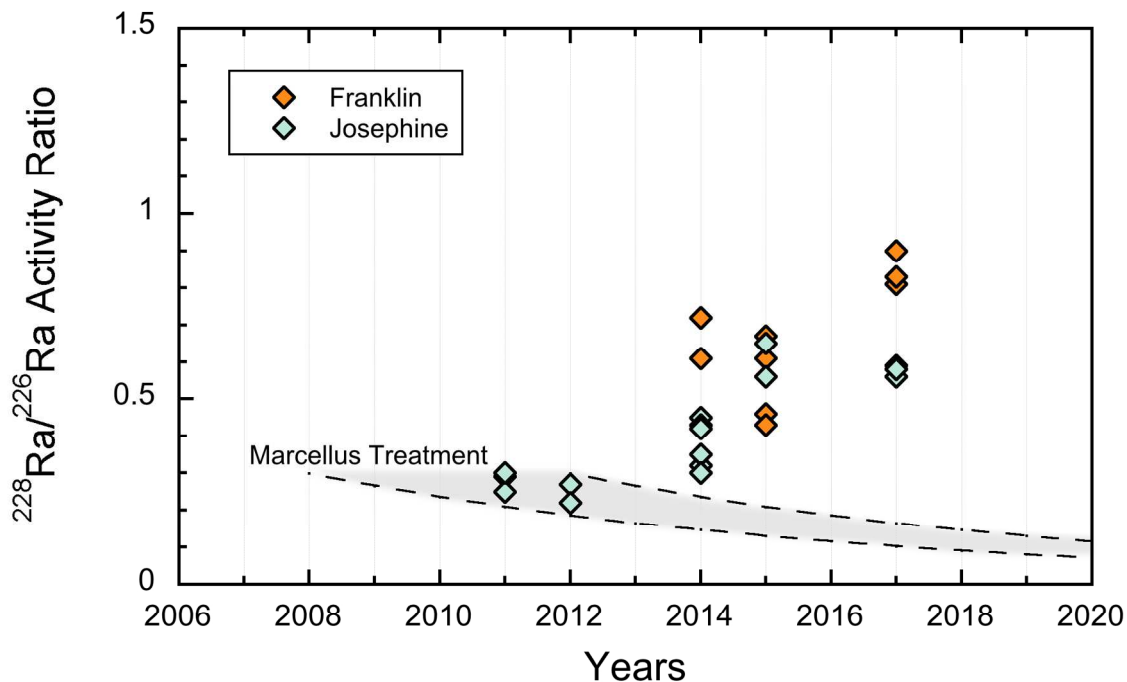
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Figure 4. $^{228}\text{Ra}/^{226}\text{Ra}$ activity ratios in sediments collected from the Franklin and Josephine CWT facilities in from 2011-2017. 2011 and 2012 data are compiled from Warner et al. (2013).²⁰ Ratios that fall within the gray band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

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