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

Title: Partitioning of Naturally-Occurring Radionuclides (NORM) in Marcellus Shale Produced Fluids Influenced by Chemical Matrix

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44   **Abstract:** Naturally-occurring radioactive materials (NORM) associated with

45   unconventional drilling produced fluids from the Marcellus Shale have raised

46   environmental concerns. However, few investigations into the fundamental chemistry of

47   NORM in Marcellus Shale produced fluids have been performed. Thus, we performed

48   radiochemical experiments with Marcellus Shale produced fluids to understand the

49   partitioning behavior of major radioelements of environmental health concern (uranium

50   (U), thorium (Th), radium (Ra), lead (Pb), and polonium (Po)). We applied a novel

51   radiotracer, ^{203}Pb, to understand the behavior of trace-levels of ^{210}Pb in these fluids.

52   Ultrafiltration experiments indicated U, Th, and Po are particle reactive in Marcellus

53   Shale produced fluids and Ra and Pb are soluble. Sediment partitioning experiments

54   revealed that >99% of Ra does not adsorb to sediments in the presence of Marcellus

55   Shale produced fluids. Further experiments indicated that although Ra adsorption is

56   related to ionic strength, the concentrations of heavier alkaline earth metals (Ba, Sr) are

57   stronger predictors of Ra solubility.

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63 **Main Text:**

64 **Introduction:**

65   The levels of radium (Ra) isotopes and other naturally-occurring radioactive

66 materials (NORM) in flowback and produced fluids from the Marcellus Shale are an

67 emerging environmental concern.[1-9] Recent reports demonstrated that Marcellus Shale

68 produced fluids from unconventional drilling are enriched in Ra isotopes (^{228}Ra, ^{226}Ra,

69 ^{224}Ra) and devoid of most other long-lived NORM, such as certain U, Th, Pb and Po

70 isotopes.[1, 9-11] Despite research interest in radionuclides contained in Marcellus Shale

71 produced fluids, there have been few laboratory-based studies that characterize the

72 fundamental chemical behavior of NORM in Marcellus Shale produced fluids.

73 Information has been gleaned about the chemical behavior of NORM in these fluids from

74 environmental studies; however, even well designed environmental studies may not

75 accurately characterize the chemical behavior of unconventional drilling wastes due to

76 uncertainty and complexity of environmental sites in a region of the United States that

77 has a long history with the extractive industries. That is, unknown treatment levels (i.e.,

78 speciation and composition) of waste source terms, ongoing and legacy pollution from

79 mixed sources (natural gas and coal extraction industries), and misinformation can

80 complicate the interpretation of results from environmental studies of unconventional

81 drilling wastes.[12, 13] Due to the limitations of environmental studies, we decided to

82 explore information about the chemical behavior of NORM in produced fluids through

83 laboratory-based partitioning studies. Although such experiments may lack

84 generalizability, they provide important clues about behavior of radioactive elements

85 without the challenges of accounting for uncontrolled environmental inputs, radioactive

86 decay, and decay product ingrowth.

87   One of the major chemical parameters of interest for predicting the fate and

88 transport of NORM in unconventional drilling wastes is ionic strength. A wide body of

89 literature exists on the effects of ionic strength on the fate and transport of NORM in the

90 environment. With respect to Ra, adsorption and desorption from sediments has been of

91 great interest to environmental scientist and oceanographers.[14-20] Ra adsorption studies

92 show that Ra generally partitions through an ion exchange mechanism to the aqueous

93 phase as ionic strength increases, yet most empirical data stops at ionic strengths

3

94   comparable to those of seawater. Further, most studies have only explored the effects of

95   ionic strength by considering concentration of Na with little attention to high molarities

96   of alkaline earth metals (Mg, Ca, Sr, Ba). It is unclear whether these models are

97   appropriate for Marcellus Shale produced fluids which may have ionic strengths up to 10

98   times that of seawater and levels of alkaline earth metals in the g/L range.[8, 9, 21] Despite

99   years of research into NORM, the current understanding of Ra chemistry in Marcellus

100   Shale produced fluids is murky and the understanding of the chemical behavior of U, Th,

101   Pb, and Po in these fluids is largely unexplored.

102   In this study, we characterize the chemical composition of Marcellus Shale

103   produced fluids and suspended particulates by high resolution transmission electron

104   microscopy (HRTEM) and powder x-ray diffraction (PXRD). We describe the

105   partitioning of U, Th, Ra, Pb, and Po in Marcellus Shale produced fluids using

106   radiotracers and ultrafiltration (0.1 μm filter pore size). We then applied sequential

107   extraction and radiotracer techniques to determine the potential for Ra, Pb, and Po

108   adsorption-desorption on a variety of sediment textures and mineral compositions. Note,

109   we applied an underused radiotracer, ^{203}Pb, to understand the behavior of trace levels of

110   ^{210}Pb in these fluids. ^{203}Pb has been applied as a tracer of Pb in environmental systems;[22]

111   however, lack of access to the isotope has stymied its use. With the increase in medical

112   imaging applications of ^{203}Pb, in our laboratory in particular, ^{203}Pb is now more readily

113   attainable. Next, we investigated the effect of ionic strength on Ra using a chemical

114   matrix characteristic of Marcellus Shale fluids. Finally, we explored the role of

115   exchangeable cations (Na, Mg, Ca, Sr, Ba) at a range of concentrations (0.01 M, 0.1 M,

116   and 1 M) on the partitioning of Ra.

117

118   **Experimental**

119   *General.* Sediments were taken from the Dunkard Creek near Wana, West Virginia, USA

120   in May 2014 or from collections at the University of Iowa Quaternary Materials

121   Laboratory. Dunkard Creek sediments were collected from the site of a spill that occurred

122   in 2009.[23] The Dunkard Creek spill was speculated to be related to unconventional

123   drilling and/or coal wastes;[23] however, the etiology of this spill is beyond the scope of

124   this study. Grain size, PXRD, and HRTEM were performed at the University of Iowa

125   using standard techniques.[24, 25] The Marcellus Shale produced fluids described herein

126   were previously characterized for NORM and matrix composition.[1,5] Sequential

127   extractions were based on previously published methods.[26] In partitioning and sequential

128   extraction experiments, ^{226}Ra was determined by ^{222}Rn emanation,[5] ^{203}Pb by NaI gamma

129   spectrometry based on standard laboratory methods,[27] and ^{nat}U, ^{nat}Th, and ^{210}Po by

130   preconcentration and alpha spectrometry.[1, 28]

131

132   *Grain size*. Sediment grain-size distribution was analyzed using the pipette method with

133   size fraction breaks at <2μ (clay), 2-20μ (fine silt), 20-50μ (coarse silt) and 50μ-2mm

134   (sand) at the University of Iowa Quaternary Materials Laboratory**.**

135

136   *PXRD* Sediments, Marcellus Shale produced fluids fines (0.1 μm polypropylene filter),

137   and Marcellus Shale produced fluids solid-state evaporites were prepared for power X-

138   ray diffraction (PXRD) by mortar and pestle (under acetone). Diffractograms were

139   collected on a Bruker Advance Diffractometer equipped with CuKα radiation (λ =

140   1.54056 Å) and a LynxEye detector. Scans were performed from 5-60° 2θ with a step

141   size of 0.02° and collection time of 1 sec/step. Major mineral phases present in the solid

142   samples were identified using the Bruker Eva software **(Fig. S1, Fig. S2, Fig. S3, Table**

143   **S1).**

144

145   *High Resolution Transmission Electron Microscopy*. Morphological features of the Fe

146   particulates were determined using high resolution transmission electron microscopy

147   (HRTEM) at the University of Iowa Central Microscopy Research Center. A 1 mg mL^{-1}

148   colloidal suspension of the particulates was prepared in ultrapure water and sonicated for

149   30 min to improve dispersion. Holey carbon copper grids (Ted Pella, Inc 01824, UC-A

150   on holey, 400 mesh Cu) were loaded with 5 µL aliquots of the suspension and evaporated

151   to dryness in air. HRTEM investigations were carried out by a JEOL JEM 2100F

152   equipped with a cold Schottky cathode, field emission gun, and operated at a 200 kV

153   accelerating voltage. Gatan DigitalMicrograph software was utilized for image

154   acquisition in congruency with an externally inserted Orius camera cooled to -25 ºC.

155

156

157 ***Produced Fluids Filtration U, Th, Ra, Pb, Po.*** ^{232}U (Eckert and Ziegler 92403), ^{228}Th (in

158 ^{232}U tracer/endogenous), ^{226}Ra (endogenous), ^{203}Pb Lantheus Medical Imaging, Billerica,

159 MA), and ^{210}Po (from ^{210}Pb source NPL A13959) were added to Marcellus Shale

160 produced fluids (20 mL, except ^{226}Ra 35 mL), stirred (6-18 hours, room temperature, 220

161 RPM), and ultra-filtered (0.1 μm, filtration Resolve Eichrom). Filters and supernatant

162 samples requiring analysis by alpha spectrometry were then traced with ^{nat}U (Eckert and

163 Ziegler 92564), ^{230}Th (NIST SRM 4342A), or ^{209}Po (Eckert and Ziegler 92565) and

164 prepared using methods previously described.[1] ^{203}Pb samples were quantitated by NaI

165 gamma spectrometry. ^{226}Ra samples were analyzed by RAD7 (Durridge Company, Inc.,

166 Billerica, MA, USA).

167

168

169 ***Sediment Sequential Extraction of Ra.*** Selected homogenized sediments were placed

170 into 50 mL conicals (n=3, 3.5 g) **(Fig. S4)**. Marcellus Shale produced fluids (35 mL)

171 were added to each conical before shaking on a rotating table (1 hr, room temperature,

172 220 RPM). Conicals were then centrifuged (5 min, 3400 x *g*), and the supernatant was

173 transferred to clean vials (40 mL, glass VOC). To prevent foaming during counting by

174 RAD7, anti-foam solution (Sigma, emulsion B, 1 mL 25%) was added to each vial before

175 topping with H_2O and hermetically sealing. Ra was then sequentially extracted from

176 sediment based on methods previously described.[26] Briefly, sediment was treated three

177 times with water-soluble-phase extractant (0.4 M $MgCl_2$, pH 5.5), once with carbonate-

178 phase extractant (1M NH_4Ac in 25% v/v acetic acid), once with reducible-phase

179 extractant (0.01 M NH_2OH in 25% v/v acetic acid), once with organic-phase extractant

180 (30% v/v H_2O_2, 0.02 M HNO_3) and finally with acid-digestible phase (4 M HNO_3).

181 Extractions were performed at room temperature on a rotating table (1 hr, 220 RPM),

182 each time centrifuging and transferring supernatant to clean glass vials (40 mL, VOC).

183 Vials containing acetic acid, H_2O_2, or HNO_3 were taken to complete dryness before

184 topping with H_2O and hermetically sealing. Samples were held 30+ days to ensure

185 secular equilibrium between ^{222}Rn and ^{226}Ra before counting by RAD7 (Durridge,

186 Billerica, MA) as previously described.[5] Assessment of adsorption kinetics was

187 performed on DC6 sediment similarly as described above, yet samples were incubated

188 with Marcellus Shale produced fluids and the extractants for 168 hours *en lieu* of 1 hour.

189

190 ***Sediment Sequential Extraction of Ba, Pb, Po.*** Sediment from Dunkard Creek was

191 placed into conicals (50 mL, n=3, 2 g). Marcellus Shale produced fluids (20 mL) and

192 radiotracers ([133]Ba Eckert and Ziegler 6133, [203]Pb (Lantheus Medical Imaging), [210]Po

193 (supported by ^{210}Pb, NPL A13959) traced with [209]Po Eckert and Ziegler 92565)) were

194 added to each conical before shaking on a rotating table (1 hr, room temperature, 220

195 RPM). Conicals were then centrifuged (5 min, 3400 x *g*), the supernatant was transferred

196 to clean liquid scintallation (LS) vials (20 mL, glass). LS vials were then counted by a

197 well-type sodium iodide (NaI) detector (Ortec) and gamma-emitting radionuclides were

198 quantitated using standard radioactivity measurement techniques, similarly as described

199 previously.[27] Po was separated and quantitated using standard methods previously

200 described.[1] The radionuclides adsorbed to the sediment were then sequentially extracted

201 based on methods previously described.[26] Extractions were performed at room

202 temperature on a rotating table (1 hr, 220 RPM), each time centrifuging and transferring

203 supernatant to clean glass vials (20 mL, LS).

204

205 ***Ionic Strength and Ra Partitioning.*** All experiments investigating Ra partitioning were

206 performed on DC6 sediment (n=3, 3.5 g), with the indicated salt solution (35 mL), and

207 [226]Ra standard (37.3 Bq, NIST traceable standard, Eckert & Ziegler 1742-75). Marcellus

208 Shale produced fluids surrogate matrix consisted of reagent grade (or higher) chloride

209 form salts with the following concentrations: Na^+ (1300 mM), K^+ (4 mM), Mg^{2+} (35

210 mM), Ca^{2+} (320 mM), Sr^{2+} (410 mM), Ba^{2+} (66 mM), Fe^{3+} (0.78 mM), Cl^- (4100 mM).

211 Note, surrogate matrix was only used in experiments described in this paragraph.

212 Surrogate matrix was used so that [226]Ra activity (37.3 Bq) could be controlled despite

213 dilution of the matrix solution. Separate select cations (Na^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+})

214 were prepared by serial dilution to the following concentrations: 1 M, 0.1 M, and 0.01 M.

215 All samples were shaken on a rotating table (1 hour, room temperature, 220 RPM),

216 centrifuged (3400 x *g*), and the supernatant was transferred to clean glass vials (40 mL,

217   glass VOC). Anti-foaming solution (1 mL) was added to each vial before topping with

218   anti-foam (1 mL), hermetically sealing (30+ days), and counting by RAD7.

219

220   **Results and Discussion:**

221   **NORM in Produced Fluids**

222   Very little is known about the concentrations of most NORM in Marcellus Shale

223   fluids, and less information is available regarding NORM partitioning between aqueous

224   and particulate phases. Several studies have developed a general understanding of how

225   NORM levels in produced fluids change throughout the lifecycle of the unconventional

226   drilling process.[7-9] For example, Ra isotope concentrations steadily increase concurrently

227   with the age of the well and concentration of total dissolved solids (TDS) and alkaline

228   earth metals.[7, 8] In contrast, U levels have been reported to spike briefly at the beginning

229   of the flowback stage and then decrease over time.[11] Lastly, an analysis of late stage

230   Marcellus Shale fluids by Nelson *et al.* (2015) reported U, Th, Pb, and Po isotopes were

231   initially absent, but certain isotopes (^{228}Th, ^{210}Pb, ^{210}Po) increase by radiochemical decay

232   product ingrowth processes.[1] Collectively, these reports provide important clues about the

233   behavior of NORM within Marcellus Shale fluids at the point source, particularly at

234   increased pressure, higher temperature, and altered redox conditions that occur in the

235   subsurface environment.

236   It is unclear how U, Th, Ra, Pb, and Po behave when produced fluids enter low-

237   temperature geochemical environments. Although we anticipate the majority of U and Th

238   isotopes (with the exception of ^{228}Th) will remain at depth or be adsorbed to solid waste

239   products,[1] understanding the solubility of U and Th in Marcellus Shale produced fluids

240   under surface conditions is important, particularly in cases where there are significant

241   interactions between the waste forms. To understand the basic partitioning of U, Th, Ra,

242   Pb, and Po in surface waters, we spiked homogenized Marcellus Shale produced fluids

243   with appropriate radiochemical tracers. Spiked fluids underwent ultrafiltration (0.1 μm)

244   and particulate and aqueous phases were analyzed by alpha or gamma spectrometry. U,

245   Th, and Po associated with the particulates (98%, 97% and >99%, respectively) and Ra

246   and Pb remained in solution (99% and 97%, respectively) (**Fig. 1A**).

247   Low particle reactivity of Ra and Pb led us to probe the mineral composition of

248 particulates and dissolved solids in the Marcellus Shale fluids. Powder X-ray diffraction

249 (PXRD) of the solid evaporites from the produced fluids revealed the presence of halite

250 salts containing predominately alkali and alkali earth cations **(Fig. 1B, Fig. S3)**. The

251 diffractogram of the Fe particulates include a relatively high background due to

252 fluorescence, but the presence of two broad peaks suggests the presence of an amorphous

253 Fe oxyhydroxide **(Fig. 1C, Table S1)**. In addition, weaker reflections correspond to the

254 mineral akaganeite (β-FeO(OH, Cl)), which requires the presence of 1-9 wt% chloride in

255 solution for formation of this phase to be favored over goethite and other Fe^{3+}

256 oxhydroxide species.[29] Akaganeite is most commonly observed as a corrosion product in

257 marine environments,[30] but the high ionic strength of the produced fluids contains

258 concentrations of chloride to support the formation of akaganeite. The high-resolution

259 transmission electron microscopy (HRTEM) image of the Fe particulates reveals the

260 formation of bladed aggregates that are approximately 20-50 nm in width (**Fig. 1 D**).

261 Akaganeite has previously been reported to form elongated aggregates with longitudinal

262 striations and are similar to the morphology of the Fe particulates obtained from the

263 produced fluids.[31, 32] We attribute the low observed adsorption of Pb and Ra to the

264 akaganeite and amorphous iron oxides to matrix effects (competition with exchange

265 cations), similarly as observed for ferrihydrite and goethite.[16]

266

267 **Environmental Fate of NORM**

268   The gross levels of radionuclides in unconventional drilling wastes may be

269 inappropriate for assessing environmental impact given the possibility for surface

270 adsorption and sedimentation.[26] To understand the potential fate of radionuclides

271 introduced into the environment, it is important to determine partitioning within soil and

272 colloidal phase reservoirs through sequential extraction experiments.[26, 33] Initially our

273 sequential extraction experiments focused exclusively on Dunkard Creek sediments, as

274 these sediments were collected from a stream that has geology more consistent with sites

275 in the region of the United States overlaying the Marcellus Shale (i.e., sites that are more

276 likely to contact Marcellus Shale produced fluids). We applied sequential extraction

277 techniques to determine ^{226}Ra concentrations in water-soluble, carbonate, Fe and Mn

278 oxides, organic, and strong acid-digestible residue fractions for Dunkard Creek

279 sediments. ^{226}Ra was measured in each sequentially extracted fraction by ^{222}Rn

280 emanation, to allow for accurate, trace-level radiochemical experiments **(Fig. S4 of**

281 **Supporting Information)**. Sequential extractions of ^{226}Ra (1 hour) indicated >90% of

282 ^{226}Ra remained in the load solution (Marcellus produced fluids) and nearly all the

283 residual ^{226}Ra (>99%) was removed in the water-exchangeable fractions **(Fig. 2A).** The

284 high observed solubility of ^{226}Ra^{2+} led us to explore additional chemical parameters

285 important for the adsorption of cations to sediments—kinetics, sediment

286 mineralogy/texture, ionic strength, and chemical matrix.

287   The role of kinetics on the observed solubility was investigated in a time

288 dependence study, where we performed the same sequential extraction experiment for

289 168 hours (one week) instead of 1 hour. The same trend occurred in the extended reaction

290 time, with >90% of ^{226}Ra removed in the load solution and residual ^{226}Ra was observed

291 in the remaining water-exchangeable fractions such that >99% was recovered. This result

292 suggests that kinetics have minimal effects on Ra adsorption-desorption in this system,

293 which is in agreement with other studies that find Ra adsorption to sediments occurs

294 within minutes.[14, 17]

295   We further investigated the mineralogy and soil characteristics of the sediments,

296 because both characteristics greatly affect the speciation and adsorption of Ra.[26, 34] Soil

297 texture and PXRD analysis indicated that four Dunkard Creek sediments were loam to

298 sandy-loam, primarily consisting of quartz. Given that loams have lower binding capacity

299 for ^{226}Ra than clay-rich sediments,[15, 16] we included seven different sediments of different

300 mineralogy, and diverse texture (97% sand (sediment 7), to 60% clay (sediment 5), to

301 86% silt (sediment 3)) **(Fig 3, Fig. S4 of Supporting Information)**. Regardless of soil

302 texture and mineralogy, >90% of Ra remained in the load solution and nearly all the

303 remaining ^{226}Ra was removed in the water exchangeable fractions. This suggested to us

304 that some chemical parameter(s) of the Marcellus Shale produced fluids overwhelm the

305 binding capacity of soil minerals.

306   We suspected the high ionic strength in Marcellus Shale produced fluids could be

307 responsible for the low Ra adsorption in this system; therefore, we tested Ra adsorption

308 to sediment (DC6) with variable ionic strengths. A surrogate matrix comprised of the

309 same chemical parameters as Marcellus Shale produced fluids (ionic strength = 4.4 M)

310 was adjusted by serial dilution (1:1, 1:10, 1:100, 1:1000, and 1:10000) and spiked with a

311 known amount of ^{226}Ra (37 Bq per sample). Sediments incubated with dilute surrogate

312 (0.044 M and less) retained nearly all the ^{226}Ra (>97%), which agrees with many studies

313 that show ^{226}Ra is particle reactive at ionic strengths typical of groundwater and

314 freshwater (**Fig. 2B**). However, at an ionic strength of 0.44 M (slightly less than a typical

315 seawater of 0.7 M), 70% of ^{226}Ra remained in the aqueous phase (**Fig. 2B**). Sediments

316 incubated with undiluted surrogate matrix (4.4 M) retained only 2% of the the ^{226}Ra (**Fig.**

317 **2B**). Although Webster *et al.* (1995) have shown that seawater can solubilize

318 approximately 10-25% ^{226}Ra,[14] the high solubility of ^{226}Ra at ionic strengths less than

319 seawater prompted us to probe deeper into the role that chemical composition of the

320 produced fluids plays on the adsorption process.

321   The chemical matrix of Marcellus Shale produced fluids is dominated by Na^+,

322 Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+} cations and Cl^- anions.[8, 9] Thus, we tested the effects of

323 individual ions on competition with Ra^{2+} for adsorption sites in Dunkard Creek

324 sediments. We incubated sediments with solutions of chloride salts (0.01 M, 0.1 M, and 1

325 M), resulting in ionic strengths of 0.01 M, 0.1 M, and 1 M for Na solutions and 0.03 M,

326 0.3 M, and 3 M for alkaline earth solutions. Two clear trends emerged: (1) as cation

327 concentration (and thus ionic strength) increased, the amount of $^{226}Ra^{2+}$ in solution

328 increased; and (2) as the ionic radius of the cation approached that of $^{226}Ra^{2+}$, the amount

329 of $^{226}Ra^{2+}$ in solution increased **(Fig. 2C).** The effect of concentrations of Ba^{2+} is quite

330 dramatic, even at concentrations as low as 10 mM (typical Ba^{2+} concentration of late-

331 stage Marcellus Shale produced fluids [8]). Importantly, samples of relatively low ionic

332 strength but considerable levels of Ba^{2+}, may not behave as expected based on ionic

333 strength alone. These chemical experiments suggest that in holding ponds containing

334 untreated Marcellus Shale produced fluids, Ra^{2+} will not adsorb to solid mineral surfaces

335 according to models developed for seawater matrices. In other words, the chemical

336 composition of Marcellus Shale produced fluids (i.e., high concentrations of divalent

337 alkaline earth metals) enhances the aqueous phase concentrations of Ra^{2+}. Consideration

338 of Ba^{2+} concentrations, in particular, may be important for understanding the potential for

339 Ra^{2+} to adsorb to the sediment-mineral interface in environmental settings (**Fig. 4**).

340   Furthermore, accurate measurement of Ba^{2+} concentration in produced fluids may be

341   more important than ionic strength when assessing treatment goals and potential

342   environmental impact. Future modeling studies will explore the effects of dilution and

343   environmentally relevant anion concentrations (particularly SO_4^{2-}) on bulk transport of

344   Ra^{2+} in riparian environments.

345   Fate and transport of ^{226}Ra decay products, ^{210}Pb and ^{210}Po, from Marcellus Shale

346   produced fluids are important to consider as these isotopes are well-known to

347   bioaccumulate.[35] ^{210}Pb is challenging to study in environmental systems due to its

348   radiochemical properties. Similarly, ^{210}Po is often neglected as specific instrumentation

349   and chemical separations (alpha spectrometry and autodeposition) are required for its

350   analysis. Thus instead of measuring ^{210}Pb, we employed a cyclotron-produced isotope—

351   ^{203}Pb. The short half-life of ^{203}Pb (51.92 hour) makes this isotope effectively a "massless"

352   tracer and more representative than stable Pb tracers when investigating the fate of

353   naturally-occurring low-mass-abundance (parts-per-quadrillion or less), radioactive Pb

354   isotopes. Sequential extraction experiments were also performed for ^{203}Pb and ^{210}Po using

355   a similar process as described above. Results for ^{203}Pb indicated that $45 \pm 2\%$ of ^{203}Pb

356   remained in the produced fluids **(Fig. 2D)**. The remainder of the ^{203}Pb was removed in

357   the carbonate or strong acid phases ($25 \pm 1\%$ and $17 \pm 1\%$, respectively). Isotope-dilution

358   alpha spectrometry indicated that ^{210}Po (traced with ^{209}Po) largely associated with

359   carbonate and strong acid ($25 \pm 4\%$ and $52 \pm 2\%$, respectively) phases **(Fig. 2D)**. These

360   results demonstrate that ^{210}Pb and ^{210}Po have different environmental fate and transport

361   processes that may lead to radiochemical disequilibrium (non-steady state). More work is

362   needed to understand the potential for these isotopes to migrate through the environment.

363

364   **Conclusion**

365   This study investigated the fundamental partitioning behavior of critical

366   radioelements (U, Th, Ra, Pb, Po) contained in unconventional drilling wastes. In

367   agreement with findings from an earlier study on NORM contained in Marcellus Shale

368   produced fluids, we find that U, Th, and Po are insoluble (particle reactive) and Ra is

369   soluble.[1] It is unclear why the high observed solubility of trace-level Pb (as measured by

370   ^{203}Pb) in these fluids differs from earlier observations that ^{210}Pb was absent in produced

12

371   fluids. The studies described herein were performed at room temperature, atmospheric

372   pressure, and normoxic conditions on sediments from West Virginia to maintain

373   relevance to potentially impacted riparian environments. These conditions are inherently

374   different than those within the Marcellus Shale. Future studies should explore the

375   solubility and partitioning behavior of NORM between interstitial fluids and particulate

376   phases, under the pressures, temperatures, and anoxic conditions relevant to

377   unconventional reservoirs.

378   Without a firm understanding of the basic chemistry of produced fluids, it is

379   difficult to predict the fate and transport of NORM in the environment when these fluids

380   are the source of NORM. We investigated the partitioning behavior of Ra, Pb, and Po

381   from Marcellus Shale produced fluids to the sediment-mineral interface through bench-

382   scale studies. We found that Ra was exceptionally soluble in the Marcellus Shale fluids

383   and >90% was retained in the load solution. The remaining Ra was easily extracted by

384   water-exchangeable washes, such that >99% was extracted in all water-soluble phases.

385   Further experiments indicated that the high solubility of Ra was associated with ionic

386   strength. However, careful consideration into the chemical composition of the Marcellus

387   Shale produced fluids indicated the solubility of Ra was likely attributable to competition

388   with other divalent cations (most profoundly by Ba), rather than ionic strength *per se*.

389   Although wastes may not initially contain ^{210}Pb and ^{210}Po, due to radiochemical ingrowth

390   processes, the environmental impacts of ^{210}Pb and ^{210}Po must be considered in wastes

391   containing ^{226}Ra. We found that (17 ± 1%) Pb associated with phases only extractable by

392   strong acid (4 M HNO$_3$), suggesting that radiochemical disequilibrium between ^{226}Ra and

393   ^{210}Pb is likely to occur (even after accounting for losses from ^{222}Rn). Even greater

394   portions (52± 2 %) of ^{210}Po associated with strong acid-extractable phases, suggesting

395   radiochemical disequilibrium between ^{210}Pb and ^{210}Po should be expected.

396   The key finding from this study is that Ra is more soluble in Marcellus Shale

397   produced fluids than predicted by conventional adsorption-desorption models. Consistent

398   with adsorption-desorption models generated with seawater matrices, we found that as

399   ionic strength increases, the level of Ra in the aqueous phase increases. However, the

400   level of Ra in the aqueous phases exceeded the amount predicted by seawater models.

401   This suggests that the chemical matrix of produced fluids plays an important role in the

402   adsorption of Ra to environmental materials. Careful consideration of the levels of

403   divalent cations in Marcellus Shale produced fluids, particularly Ba, is important for

404   assessing the potential impacts of concentrated Marcellus Shale produced fluids releases

405   into the environment.

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491 **Figures and Figure Legends:**
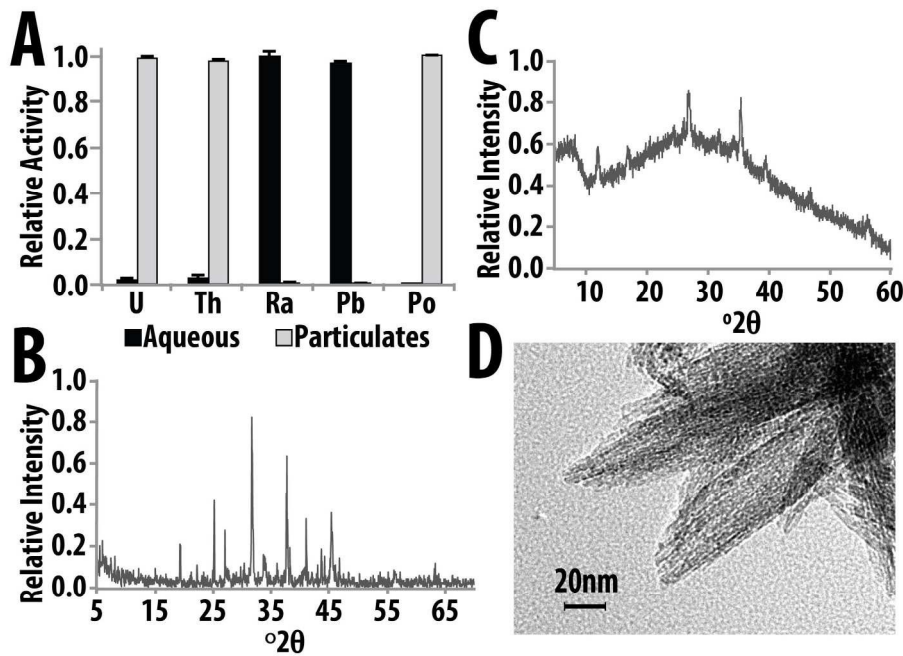
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495 **Fig. 1:** Partitioning within Marcellus Shale produced fluids. (A) Mean recoveries (with
496 standard deviations) of U, Th, Ra, Pb, and Po in aqueous or particulate phases of
497 radioisotope traced, filtered (0.1 μm) Marcellus Shale produced fluids. (B) pXRD
498 spectrum of evaporated (low heat), filtered (0.1 μm) produced fluids. (C) pXRD spectrum
499 of filtered (0.1 μm) produced fluid particulates. (D) TEM image of filtered (0.1 μm)
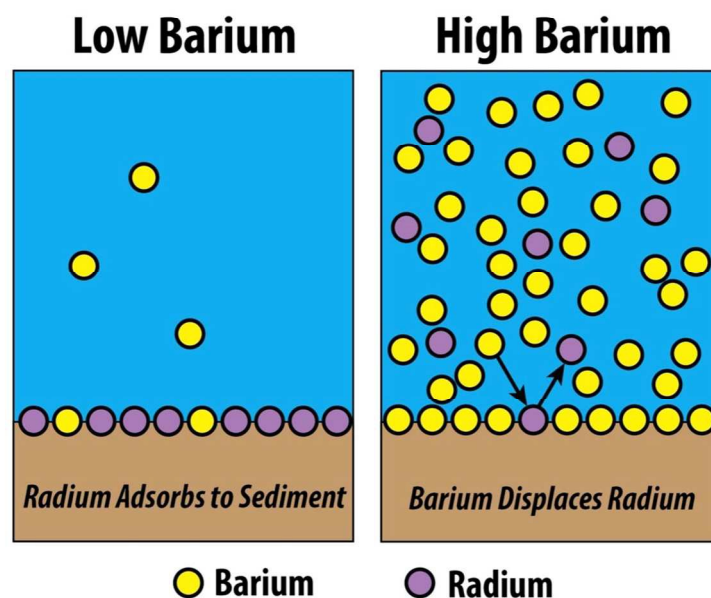500 produced fluid particulates.
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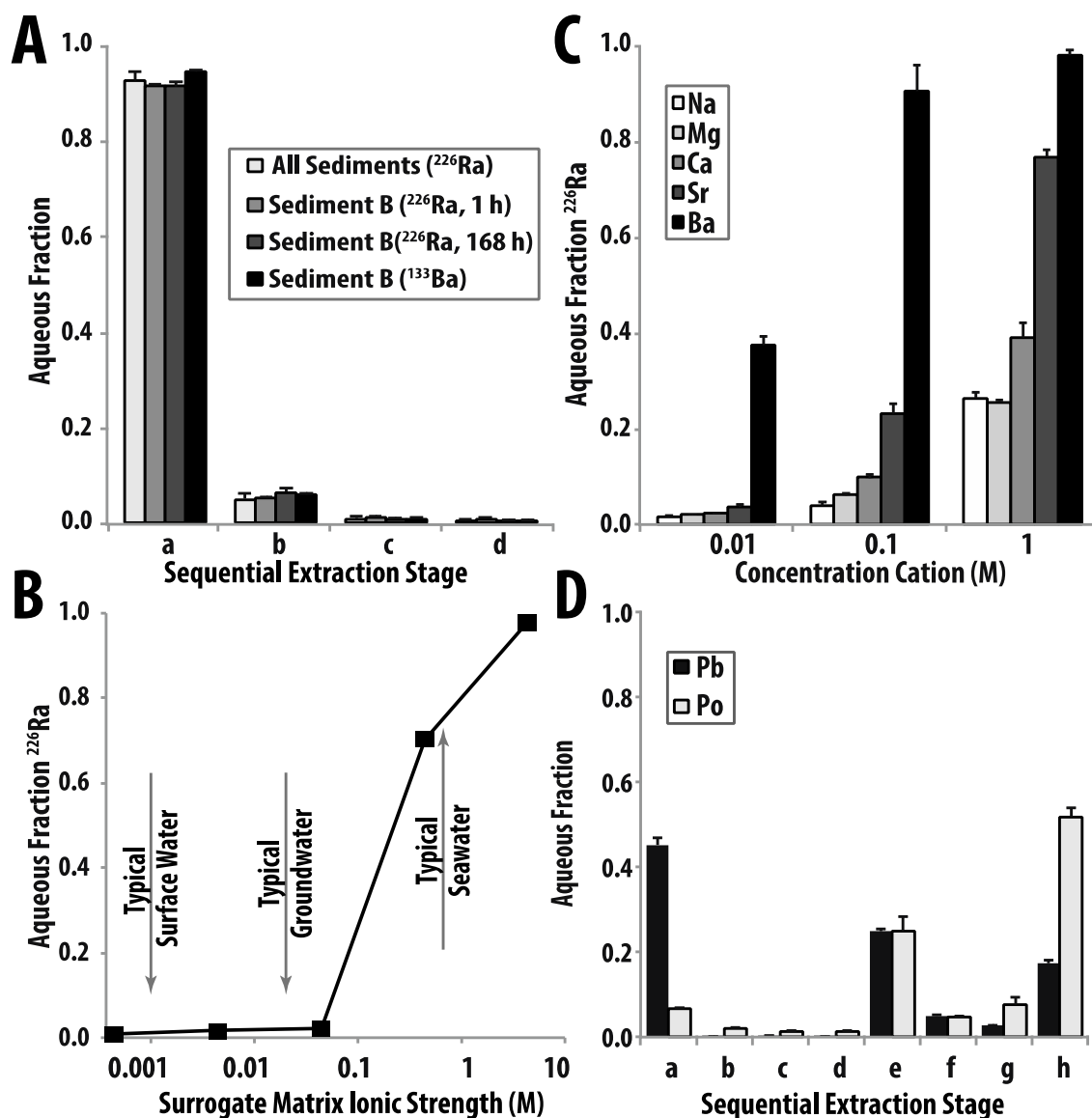
Fig. 2: Ra and Ra decay products partitioning between Marcellus Shale produced fluids (or surrogate) and sediments. (A) Sequential extractions of Ra or Ba on select sediments: the first three bars represent mean recoveries with standard deviations of [226]Ra from sequential extractions by [222]Rn emanation; values from left to right indicate Ra removal from 11 different sediments (n=3), Dunkard Creek sediment B (1 hour, n=3), Dunkard Creek sediment B (168 hour, n=4). Fourth bar represents mean recovery with standard deviation of Ba (traced with [133]Ba) from Dunkard Creek sediment B (n=3). (B) Aqueous fraction of surrogate fracturing matrix spiked with [226]Ra (37 Bq) and incubated with Dunkard Creek sediment B at various ionic strengths; values represent means (n=3) with standard deviations subsumed within squares. (C) Aqueous fraction of Na, Mg, Ca, Sr, or Ba chloride salts (0.01, 0.1, and 1 M) spiked with [226]Ra (37 Bq) and incubated with Dunkard Creek sediment B; values represent means (n=3) with standard deviations subsumed within squares. (D) Mean recovery with standard deviation of [203]Pb (n=3) and [210]Po (n=3, traced with [209]Po).

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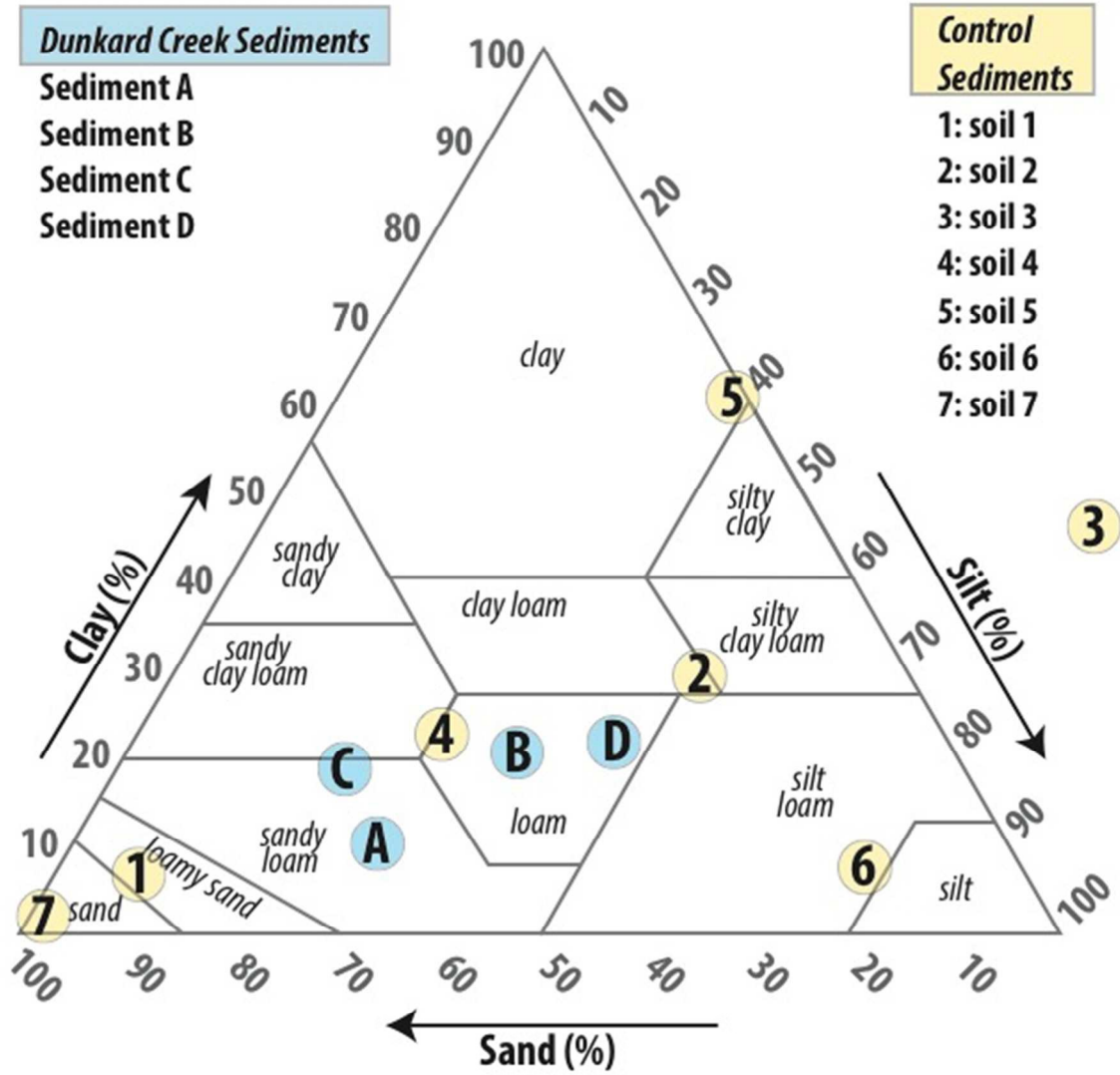
518
Fig 3. Grain Size Triangle Plot of Sediments from Quaternary Materials Laboratory at the
520   University of Iowa

Effect of Barium on Radium Adsorption

Low Barium | **High Barium**

Radium Adsorbs to Sediment | *Barium Displaces Radium*

🟡 **Barium**   🟣 **Radium**

521
522 **Fig. 4**: Theoretical depiction of Ba and Ra competition for adsorption on sediments in
523 high and low Ba concentrations.
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