Supporting Information for

Influence of High Total Dissolved Solids Concentration and Ionic Composition on Gamma Spectroscopy Radium Measurements of Oil and Gas Produced Water

Moses A. Ajemigbitse,[*‡] Travis L. Tasker,[†] Fred S. Cannon,[‡] and Nathaniel R. Warner[‡]

[‡] Department of Civil and Environmental Engineering, Pennsylvania State University, 212 Sackett Building, University Park, Pennsylvania 16802, United States

[†] Department of Environmental Engineering, Saint Francis University, Science Center, Loretto, Pennsylvania 15940, United States

***Corresponding author:**

Moses A. Ajemigbitse

Department of Civil and Environmental Engineering, the Pennsylvania State University

University Park, Pennsylvania, 16802

Email: mosesajemigbitse@gmail.com

Telephone: (814) 321-4632

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Table S1: Gamma decay probability for Ra-226 and Ra-228 daughter decay products employed for efficiency determination. [1]

Nuclide	Ra-226	Pb-214	Pb-214	Bi-214	Ac-228	Bi-214	Bi-214
Energy Level (keV)	186.2	295.2	351.9	609.3	911.2	1120	1765
Probability	0.0364	0.1842	0.356	0.4549	0.258	0.1492	0.1530

Table S2: Elemental composition of the mixed-cation synthetic brines. The amount of each salt added to 1 L of Distilled-Deionized Water to create the brine at each given TDS concentration.

Salt mass added (g) to create 1 L of mixed-cation synthetic brines				
	50 g/L	100 g/L	200 g/L	300 g/L
NaCl	28.68	57.36	114.71	172.07
$CaCl_2$	10.89	21.78	43.57	65.35
$BaCl_2$	5.45	10.90	21.80	32.70
$MgCl_2$	1.87	3.74	7.48	11.21
$SrCl_2$	3.11	6.22	12.45	18.67

Table S3: Elemental composition of Appalachian oil and gas produced water. [2]

Source		TDS (mg/L)	Cl (mg/L)	Na (mg/L)	Ca (mg/L)	Sr (mg/L)	Ba (mg/L)	^{226}Ra (pCi/L)	^{228}Ra (pCi/L)	228 / 226
Produced Appalachian Basin	Mean	189,410	112,081	42,987	20,076	782	507	881	1,127	1.28
	Median	186,600	112,572	42,550	17,600	727	230	480	500	1.04
	Count	1,965	1,867	1,800	1,841	1,072	592	95	72	
Produced Marcellus	Mean	91,888	51,714	26,527	7,023	1,449	1,076	3,976	425	0.11
	Median	59,750	34,000	18,000	4,360	953	297	1,042	201	0.19
	Count	110	103	100	129	165	110	31	31	

Table S4: Results of the linear regression of efficiency versus TDS for the NaCl-only synthetic brine and the multi-cation synthetic brine. The TDS-influenced attenuation factor, α_{TDS}, its 95 % CI and p-values at each energy level are presented.

Energy Level (keV)		**186**	**295**	**351**	**609**	**911**	**1120**	**1764**
Multi-cation	$\alpha_{TDS} \times 10^{-4}$	-2.57	-1.66	-1.46	-0.523	0.0255	-0.3	-0.36
	95% CI $\times 10^{-6}$	2	12	14	8	6	16	30
	p-value	0.025	0.013	0.005	0.011	0.821	0.035	0.098
NaCl-only	$\alpha_{TDS} \times 10^{-4}$	-1.56	-1.27	-1.07	-0.375	-0.177	-0.24	-0.28
	95% CI $\times 10^{-6}$	0	4	10	2	4	16	32
	p-value	0.001	0.002	0.004	0.001	0.132	0.059	0.182

Table S5: Validation of the linear regressions of efficiency against TDS. The empirically calculated efficiency was divided by the efficiency predicted by the regression equation for each energy level and at each TDS level. These are the column values. Then the averages and 95% CI of these values were calculated, shaded in grey. Finally, the averages and 95% CI of all data points at all the energy levels was calculated, bolded and italicized.

Multi-Cation Synthetic brine

	TDS (g/L)	186 keV	295 keV	351 keV	609 keV	911 keV
	0	99%	105%	103%	105%	103%
	50	98%	99%	101%	100%	97%
	100	101%	93%	94%	92%	99%
	200	101%	98%	97%	100%	101%
	300	99%	105%	104%	104%	100%
Ave	***100%***	99.7%	100%	100%	100%	100%
95 CI	***7.01%***	2.4%	10.8%	8.35%	10.1%	5.17%

NaCl-only Synthetic brine

	TDS (g/L)	186 keV	295 keV	351 keV	609 keV	911 keV
	0	101%	101%	103%	102%	103%
	50	101%	100%	98%	99%	98%
	100	99%	99%	98%	99%	100%
	200	101%	97%	98%	99%	99%
	300	100%	103%	103%	102%	102%
Ave	***100%***	100%	100%	100%	100%	100%
95 CI	***2.85%***	1.62%	4.68%	5.22%	3.15%	4.18%

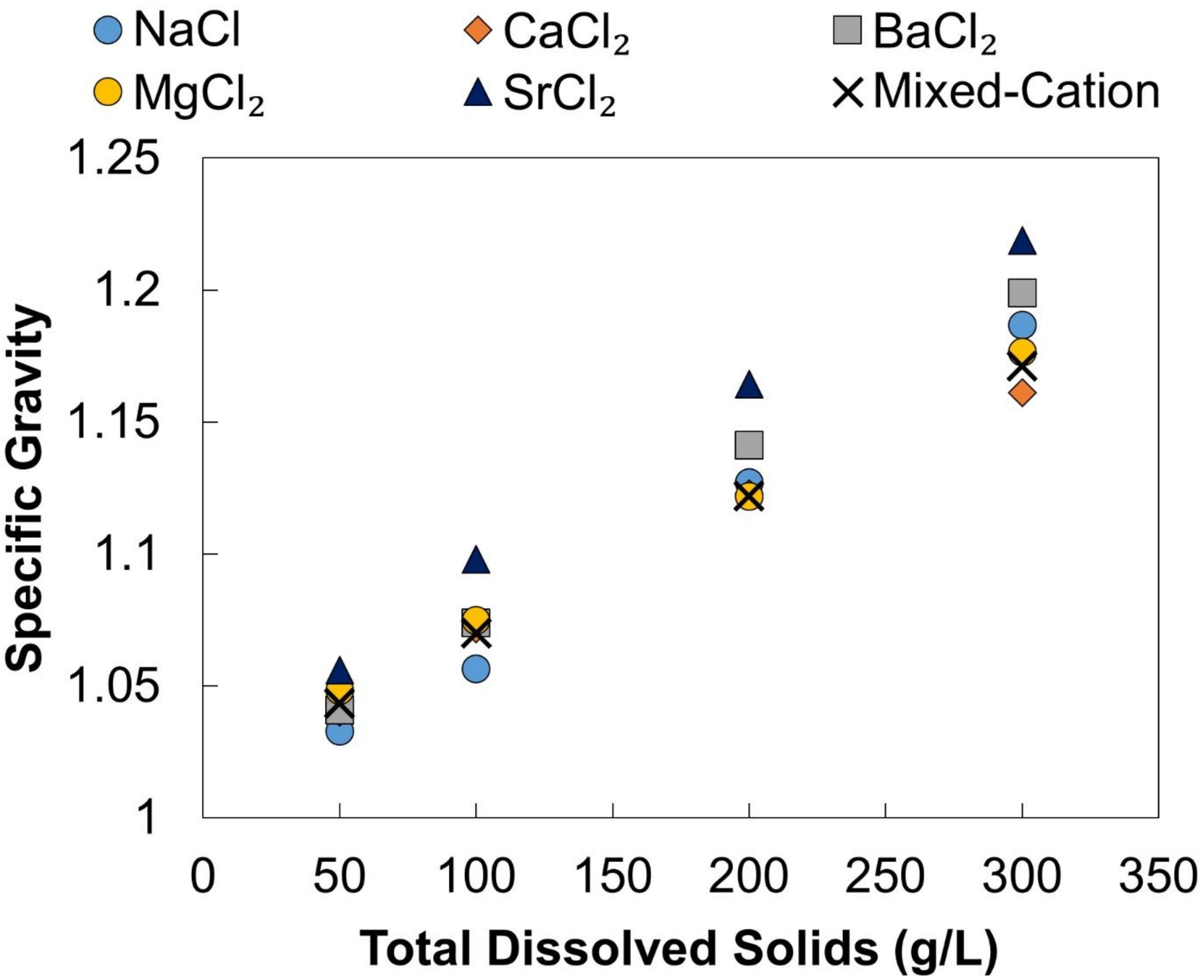

Figure S1: The TDS and specific gravities of NaCl, $CaCl_2$, $BaCl_2$, $MgCl_2$, $SrCl_2$, and mixed Na-Ca-Ba-Mg-Sr-Cl brine solutions.

Calculating the attenuation factor by the theoretical approach of Appleby *et al.* 1992 [3] and Hubbell 1981 [4]

Appleby *et al.* in their paper put forth a theoretical model to calculate the self-adsorption factor for a well-detector γ-spec. In their paper, they introduce a geometric parameter, k shown in Eq. (S1) and (S2), which characterizes the dimensions of the well detector/sample holder. This parameter was defined theoretically and then determined empirically. For a gamma ray beam of incident intensity I_0, they derive the attenuation factor I/I_0, as being dependent on sample mass and the mass attenuation coefficient, μ. The mass attenuation coefficients can be obtained from Hubbell's work, provided the exact elemental composition of the sample is known.

Herein, we attempt to derive the attenuation coefficient for the 300 g/L mixed-cation synthetic brine based on the theoretical work of Appleby and Hubbell.

$$k_t = \frac{1}{\lambda \pi a L} \tag{S1}$$

$$k_e = \frac{0.133}{a^2}(\lambda L/a)^{-0.687} \tag{S2}$$

$$0 < \lambda \leq 1 \tag{S3}$$

$$\frac{I}{I_0} = f(m)\begin{cases} e^{-k\mu m} & \text{for} \quad k\mu m < 0.28 \\ \left(1 + \frac{(k\mu m)^2}{4}\right)e^{-k\mu m} & \text{for} \quad 0.28 < k\mu m < 1.15 \end{cases} \tag{S4}$$

Where,

k_t is the theoretical derivation for the geometric parameter

k_e is the empirical derivation for the geometric parameter

λ describes the depth to which the sample holder has been filled

a is the radius of the sample holder

L is the depth of the sample holder

μ is the mass attenuation coefficient

m is the sample mass

Table S6: The dimensional characteristics of our well detector and the geometric parameter based on theoretical or empirical relationships of Eq. (1) – Eq. (3).

Parameter	Value		
a	1.675 cm	0.0469	0.0258
L	4.05 cm		
λ	1		

Table S7: The sample mass attenuation factor, μm, for the 300 g/L mixed-cation synthetic brine at 150 keV and at 200 keV.

Element		(cm^2/g)		(cm^2)	
	grams	150 keV	200 keV	150 keV	200 keV
Na	1.45	*0.1335*	*0.1199*	*0.193*	*0.174*
Ba	0.0356	*0.7827*	*0.4045*	*0.0279*	*0.0144*
Mg	0.103	*0.1393*	*0.1245*	*0.0143*	*0.0128*
Ca	0.877	*0.1671*	*0.1374*	*0.147*	*0.1205*
Sr (Br*)	0.113	*0.2889**	*0.1834**	*0.0325*	*0.0207*
K	0.0129	*0.1579*	*0.1318*	*0.00204*	*0.00170*
Cl	4.42	*0.1479*	*0.1265*	*0.655*	*0.560*
H_20	20.4	*0.1504*	*0.1370*	*3.07*	*2.79*
Plastic Container	8.5	*0.1534*	*0.1401*	*1.304*	*1.191*
			Total	***4.14***	***3.70***

*Sr data was not provided. Bromine data was used instead as it was the closest atomic number.

Table S8: The self-adsorption factor at 150 keV and 200 keV for the 300 g/L mixed-cation synthetic brine calculated for the theoretical and empirical derivations of the geometric parameter. The empirical derivations predicted 9 – 10% attenuation while the theoretical derivation predicted 20 – 22 % attenuation in the 150 – 200 keV range. Our TDS-influenced attenuation factor predicted ~23 % at 186 keV, placing it within range of the empirical values.

	150 keV	200 keV	150 keV	200 keV	150 keV	200 keV
k_t	*0.254*	*0.228*	*0.776*	*0.796*	**22%**	**20%**
k_e	*0.140*	*0.1256*	*0.870*	*0.882*	**13%**	**12%**

Error Propagation for reporting error of measured ^{226}Ra activities

Radium-226 activities of all solid samples were determined by gamma spectroscopy on a Canberra ultra-low background small anode, high purity germanium (HPGe) well detector, after the incubation period of three weeks. The reported ^{226}Ra activity was the average of the daughter products activities (^{214}Bi at 295.2 keV and 351.9 keV, ^{214}Po at 609.3 keV). The standard errors (in %) reported by the software (Genie 2000) at each energy level were used to calculate the counting error. This counting error was calculated as follows:

$$\epsilon_{counting}[\%] = \sqrt{\left(\frac{1}{3}\right)^2 (\epsilon_{295}^2 + \epsilon_{351}^2 + \epsilon_{609}^2)} \qquad (5)$$

Where:

ϵ_{295} was the standard error in % at 295.2 keV

ϵ_{351} was the standard error in % at 351.9 keV

ϵ_{609} was the standard error in % at 609.3 keV

The total error included the error from counting, mass measurement and uncertainty of the detector efficiency:

$$\epsilon_{total}\left[\frac{Bq}{g}\right] = \frac{Activity\ [cps]}{mass\ [g] \times eff[\frac{cps}{Bq}]}\sqrt{\epsilon_{counting}{}^2 + \left(\frac{\epsilon_{eff}}{eff}\right)^2 + \left(\frac{\epsilon_{mass}}{mass}\right)^2} \qquad (6)$$

We found that the error from mass measurement and the uncertainty of the detector efficiency were small compared to the counting error, thus this simplified the total error to:

$$\epsilon_{total}\left[\frac{Bq}{g}\right] = \frac{Activity\ [cps]}{mass\ [g] \times eff[\frac{cps}{Bq}]} \times \epsilon_{counting}[\%] \qquad (7)$$

SI References

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