Supporting information for accuracy of methods for reporting inorganic element concentrations and radioactivity in oil and gas wastewaters from the Appalachian Basin, U.S. based on an inter-laboratory comparison

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Table S1. Methods used for cation and anion analyses. Numbers below each lab identification represents the different types of equipment used by individual labs including ICP-MS/MS (identified as 1), ICP-MS (2), Direct Plasma Spectrometry (3), ICP-OES (4), XRF (5), Neutron Activation (6), or Ion chromatography (7).

Analyte	L1	L2	L3	L4	L5	L6	L7	L8	L9	L10	L11	L13	L13	L14	L15
Li	1	2		2	4	4	4	4	2	4		4		2	6
B	1			2	4	4		2	2	4		4		2	6
Na	1		7	3	4	4	4	4	2	4	5	4		4	6
K	1	2	7		4	4	4	4	2	4	5	4			6
Mg	1	2	7	3	4	4	4	4	2	4	5	4		4	6
Ca	1	2	7	3	4	4	4	4	4	4	5	4		4	6
Sr	1	2	7	3	4	4	4	4	2	4	5	4		4	6
Ba	1			3	4	4	4	2	2	4	5	4		2	6
Al	1			2	4	4		4	2	4		4		2	6
Fe	1	2		3	4	4	4	4	2	4	5	4		2	6
Mn	1	2		3	2	4	4	4	2		5	4		2	6
Cr	1	2		2	2	4		2	2		5	2	4	2	6
Ni	1	2		2	2	4		2	2	4	5	2	4		6
Cu	1	2		2	2			2	2		5	2	4	2	6
Zn	1	2		2	2	4		2	2	4	5	2	4	2	6
As	1	2			2	4		2	2		5	2	4	2	6
Cd	1	2		2	2			2	2		5	2	4	2	6
Pb	1			2	2	4		2	2		5	2	4	2	6
Cl	7	7		7	7	7		7	7	7	5	7		7	6
Br	1	7		7	7	7		7	7	7	5	7		7	6
SO4	7	7		7	7	7		7	7	7	5	7		7	6

Table S2. Chemistry of Appalachian Basin O&G wastewaters as reported in the United States Geological Survey's produced water database[1].

Analyte	Median	Q1	Q2
Br	841	327	1580
Cl	99600	51300	159000
SO4	115	20.3	337
Na	38900	22400	57500
K	840	221	1740
Mg	1920	871	3530
Ca	13600	5360	27800
Sr	813	175	1290
Ba	331	45.7	1130
Li	50.0	23.0	81.6
B	18.1	6.77	30.6
Al	0.80	0.25	4.00
Fe	45.0	9.48	131
Mn	11.7	3.00	41.0
Ni	0.15	0.03	0.40
Cu	0.23	0.04	0.25
Zn	0.80	0.12	2.00
As	0.10	0.05	0.10
Pb	0.03	0.02	0.03
226Ra	658	190	1780
228Ra	248	39.4	821

Table S3. Range in percent difference for various analytes in the most recent USGS inter-laboratory comparison for freshwaters[2]. The range in percent difference is based on reported data with acceptable quality (i.e., $z < 2$ or $z > -2$).

Element	Sample	Units	MPV	F	Acceptable quality concentration range	% difference
Br	M-226	mg/L	0.06	0.03	0 - 0.12	>±109
Cl	M-226	mg/L	26.2	0.96	24.3 – 28.1	±7.36
SO4	M-226	mg/L	14.2	0.45	13.3 – 15.1	±6.27
Na	T-233	mg/L	16	0.46	15.1 – 16.9	±5.70
K	T-233	mg/L	1.58	0.07	1.45 – 1.71	±8.48
Mg	T-233	mg/L	6.71	0.15	6.41 – 7.01	±4.53
Ca	T-233	mg/L	16.7	0.45	15.8 – 17.6	±5.33
Sr	T-233	µg/L	94	3.22	87.6 – 100	±6.85
Ba	T-233	µg/L	27.4	0.74	25.9 – 28.9	±5.41
Li	T-233	µg/L	2.57	0.03	2.52 – 2.62	±2.02
B	T-233	µg/L	22	1.56	18.9 – 25.1	±14.2
Al	T-233	µg/L	481	21.5	438 – 524	±8.94
Fe	T-233	µg/L	279	10.6	258 – 300	±7.60
Mn	T-233	µg/L	18.5	0.96	16.6 – 20.4	±10.3
Ni	T-233	µg/L	1.99	0.27	1.44 – 2.54	±27.5
Cu	T-233	µg/L	3.98	0.19	3.60 – 4.36	±9.60
Zn	T-233	µg/L	19.7	1.85	16.0 – 23.4	±18.8
As	T-233	µg/L	4.10	0.22	3.66 – 4.54	±10.7
Pb	T-233	µg/L	0.33	0.02	0.29 – 0.38	±12.6

Table S4. Elemental ratios (mass/mass) as measured by labs in this study that reported acceptable quality values (i.e., z score that was between -2 and 2 was considered acceptable quality). In instances where no ratios are reported for a lab, the reported values were either of unacceptable or questionable quality or they did not analyze one of the cations or anions needed for calculating the ratio. S1, S2, and S3 represent samples 1, 2, and 3.

	Cl/Br			Sr/Ca			B/Cl		
	Sample #			Sample #			Sample #		
LAB	S1	S2	S3	S1	S2	S3	S1	S2	S3
1	99.1	95.1	96		0.19	0.05		5.36E-05	8.60E-05
2	79.5	82.7	78.5						
3				0.22	0.19	0.05			
4	92.8		92.6	0.21	0.18	0.05	7.01E-05		9.76E-05
5	87.0	85.7	85.7		0.20	0.05			
7				0.23	0.19	0.05			
8	86.7	90.6	87.2	0.21	0.18	0.05	7.73E-05	6.09E-05	8.65E-05
9	105	75.4	86.6		0.17	0.04	7.72E-05	5.98E-05	8.57E-05
10				0.22	0.19				
11			90.4						
13	90.9	92.9		0.20	0.18	0.05	7.43E-05	7.01E-05	
14	87.7	95.9	100	0.22	0.19	0.05	7.47E-05	6.83E-05	8.71E-05

Table S5. Methods used for radium analyses in liquids.

Lab	Equipment	Sample prep	Measurement
Lab 3	Gamma Spectroscopy	Samples sealed in 55 mL polypropylene jars. Jar threads sealed with vacuum grease. >21 day storage	^{226}Ra (609 keV and 351 keV) and ^{228}Ra (911 keV)
Lab 4	Gamma Spectroscopy	>21 day storage. >48 hour counting time. Sealed in 2 oz sediment jar to prevent ^{222}Rn gas release.	^{226}Ra (186 keV) and ^{228}Ra (911 keV)
Lab 5	Gamma Spectroscopy	3 L of sample sealed in 4 L Marinelli beaker. 30 day storage.	^{226}Ra (weighted average of 609 Kev, 351 keV, 295 keV, and 242 keV), ^{228}Ra (911 keV)
Lab 7a	Gamma Spectroscopy	No sample prep. Direct counting in 125 mL geometry	^{226}Ra (186 keV) and ^{228} Ra (911 keV)
Lab 7b	Gamma Spectroscopy	Co-precipitation with barium sulfate. ^{133}Ba yield monitor. Precipitate filtered onto 47 mm filter and analyzed on gamma spec.	^{226}Ra (186 keV) and ^{228} Ra (911 keV)
Lab 8	Low-level proportional counters (^{228}Ra) and radon flask counters (^{226}Ra)	Co-precipitation with barium sulfate (^{226}Ra and ^{228}Ra). EPA methods 904.0 and 903.1	^{226} Ra (^{222}Radon scintillation counting) ^{228}Ra (^{228}Ac daughter counted with low background proportional counter)
Lab 9	Canberra LB5100 gas flow counter (^{228}Ra) and EG&G Ortec alpha detectors	Pre-concentrated with MnO_2 and traced with ^{225}Ra (^{226}Ra) and co-precipitation with barium sulfate (^{228}Ra)	^{226}Ra (alpha spectrometry) and ^{228}Ra (gas flow proportional counter)
Lab 10	Gamma Spectroscopy	Evaporation and analysis of 6 grams of solid.	^{226}Ra (186 keV) and ^{228}Ra (911 keV)
Lab 11	Gamma Spectroscopy	3.5 L of sample sealed in 4L Marinelli beaker for 21 days. EPA method 901.1.	Not reported
Lab 12	Gamma Spectroscopy	500 mL. 24 hour counting time.	^{226}Ra (186 keV) and ^{228}Ra (911 keV)
Lab 13	Gamma Spectroscopy	20 mL of sample sealed in liquid scintillation vial. EPA method 901.1. Counting time of 4-10 hours.	^{226}Ra (351 keV and 609 keV) and ^{228}Ra (911 keV)
Lab 14a	Gamma Spectroscopy	3 L of sample sealed in a 4 L Marinelli beaker. >21 day storage. Counting time of 3 to 18 hours.	^{226}Ra (609 keV), ^{228}Ra (911 keV)
Lab 14b	Gamma Spectroscopy	3 L of sample sealed in a 4 L Marinelli beaker. Direct counting with no storage. Counting time of 3 to 18 hours.	^{226}Ra (186 keV)
Lab 15	Neutron activation followed by gamma spectroscopy	Sample evaporation. Counting time of 3 to 18 hours.	Not reported

Table S6. Methods used for Radium analyses in solids.

Lab #	Method	Sample prep	Measurement
Lab 3	Gamma Spectroscopy	Samples were packed into 40 mL jars	Count time of 48 hours. Detector calibrated using Canadian Certified Reference Materials Project. Attenuation correction was performed using the Cutshall point-source technique[3]
Lab 4	Gamma Spectroscopy	Samples were packed in petri dishes and incubated (>21 days)	Count time of 24-48 hours. Detector calibrated using Canadian Certified Reference Materials Project
Lab 5	Gamma Spectroscopy	Samples were packed into 200 mL HDPE vials	Count time of 16.7 hours. Detector calibrated using NIST standards (Eckert and Ziegler)
Lab 7a	Gamma Spectroscopy	Samples were packed into petri dishes	Count time of 48 hours. Detector calibrated using Canadian Certified Reference Materials Project. ^{226}Ra (weighted average of 295, 352, 609 keV) and 463 keV for ^{228}Ra. Attenuation correction was performed using the Cutshall point-source technique[3]
Lab 7b	Gamma Spectroscopy	Samples were packed into petri dishes	Count time of 48 hours. Detector calibrated using Canadian Certified Reference Materials Project. ^{226}Ra at 186 keV and ^{228}Ra at 911 keV. Attenuation correction was performed using the Cutshall point-source technique[3]
Lab 8	Low-level proportional counters (^{228}Ra) and radon flask counters (^{226}Ra)	Digestion according to EPA 3050B. Final liquid volume of 100mL	Count time of 100 min. ^{226} Ra (^{222}Radon scintillation counting) ^{228}Ra (^{228}Ac daughter counted with low background proportional counter)
Lab 9	Gamma Spectroscopy	Not described	Count time of 120 min. Detector was calibrated with NIST traceable soil (500g geometry)
Lab 10	Gamma Spectroscopy	Samples were packed into petri dishes	Count time of 24 hours.
Lab 11	Gamma Spectroscopy	Samples were packed into 0.5L Marinelli beakers	Count time of 1,000 min.
Lab 13	Gamma Spectroscopy	Samples were packed into 0.5L Marinelli beakers	Count time of 2 hours. Detector calibrated using Eckert and Ziegler standards. ^{226}Ra at 186 keV, ^{228}Ra at 911 keV
Lab 14	Gamma Spectroscopy	Samples were packed in scintillation vials and incubated (>21 days)	Count time of 7-36 hours. Detector calibrated using Canadian Certified Reference Materials Project. ^{226}Ra by average of ^{214}Bi at 609.3 keV, ^{214}Pb at 295.2 keV and 351.9 keV; ^{228}Ra by ^{228}Ac at 911.2 keV

References

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3. Cutshall, N. H.; Larsen, I. L.; Olsen, C. R., Direct analysis of 210Pb in sediment samples: self-absorption corrections. *Nuclear Instruments and Methods in Physics Research* **1983**, 206, (1-2), 309-312.