Supporting information for Geochemical and isotope analysis of produced water from the Utica and Point Pleasant Shale, Appalachian Basin

Tasker, T.L.*, Warner, N.R., Burgos, W.D.

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

*Current address of corresponding author: Department of Environmental Engineering, Saint Francis University, 117 Evergreen Drive, Loretto, PA 15940; Email: ttasker@francis.edu

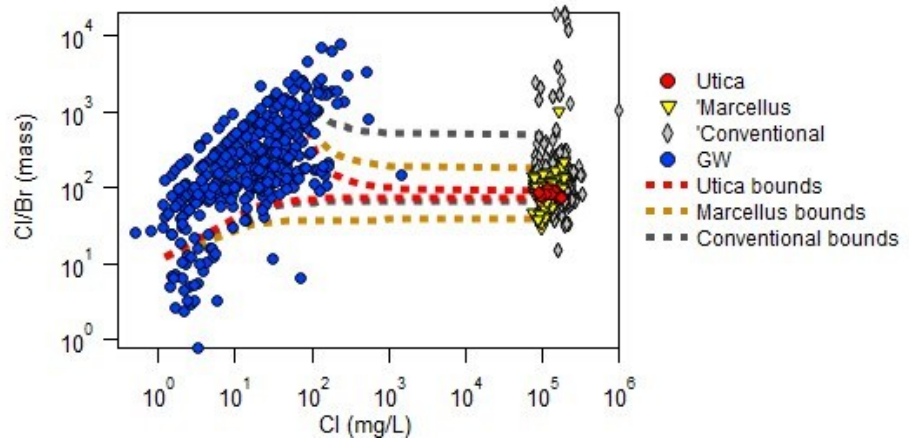

Figure S1. Conservative mixing trends between freshwaters and produced waters from UPP, Marcellus, and conventional O&G formations. Dashed lines represent mixing trends between 5th and 95th percentile concentrations in O&G produced water and freshwater.

Table S1. Chemistry of UPP produced waters analyzed in this study.

ID	State	County	Depth (feet)	Calculated TDS (mg/L)	Cl (mg/L)	Br (mg/L)	SO4 (mg/L)	Li (mg/L)	B (mg/L)
UPP 1	OH	Guernsey	7497	245093	151761	1660	<100	43.32	4.77
UPP 2	PA	Mercer	7591	251264	149545	1867	<100	62.72	4.92
UPP 3	PA	Mercer	7702	232485	147874	1879	<100	52.62	4.95
UPP 4	PA	Lawrence	7755	249255	152570	1903	<100	62.46	6.21
UPP 5	PA	Lawrence	7817	250939	154252	1906	<100	59.84	6.84
UPP 6	PA	Mercer	7877	240822	148271	1958	<100	62.19	5.54
UPP 7	PA	Lawrence	8003	264319	169798	2149	<100	43.35	61.27
UPP 8	PA	Lawrence	8014	262527	161783	1982	<100	53.45	59.29
UPP 9	PA	Lawrence	8074	234436	147630	1889	<100	69.12	7.26
UPP 10	PA	Lawrence	8098	232445	137766	1736	<100	77.60	7.33
UPP 11	OH	Noble	8365	224820	137740	1534	<100	60.80	7.48
UPP 12	OH	Harrison	8585	172367	106417	1318	<100	41.37	5.29
UPP 13	OH	Belmont	8755	158690	88305	1011	<100	34.60	6.25
UPP 14	OH	Belmont	8774	240181	99418	1137	<100	39.33	5.97
UPP 15	OH	Belmont	8868	192050	141980	1605	<100	62.07	10.16
UPP 16	OH	Belmont	9700	215394	114819	1212	<100	54.71	7.16
UPP 17	OH	Monroe	9814	285303	130163	1567	<100	57.71	8.90
UPP 18	OH	Jefferson	10088	283732	72968	886	<100	30.61	8.86
UPP 19	WV	Wetzel	11350	287576	106674	1303	<100	75.99	16.27
UPP 20	PA	Potter	11485	169347	171644	2239	<100	95.86	23.36
UPP 21	PA	Potter	11495	162378	170300	2209	<100	97.31	23.84
UPP 22	PA	Potter	11540	175165	176551	2375	<100	91.20	24.09
UPP 23	WV	Wetzel	12186	150107	91731	1215	<100	81.20	21.90
UPP 24	PA	Greene	13092	71445	42684	525	<100	41.75	15.43
UPP 25	PA	Greene	13308	147420	101285	1348	<100	99.64	28.19
UPP 26	PA	Greene	13503	118048	96624	1323	<100	100.13	30.31

Table S1 (Continued). Chemistry of UPP produced waters analyzed in this study.

ID	Na (mg/L)	K (mg/L)	Mg (mg/L)	Ca (mg/L)	Sr (mg/L)	$^{87}Sr/^{86}Sr$	$^{87}Sr/^{86}Sr$ (±)	Ba (mg/L)
UPP 1	54089	769	2943	30410	3259	0.711680	1.08E-05	57
UPP 2	58950	1022	3139	32107	4136	0.711610	3.07E-05	214
UPP 3	47526	725	2706	27739	3730	0.710880	1.80E-05	94
UPP 4	55528	1009	2939	29302	5238	0.710970	1.10E-05	567
UPP 5	52544	884	3331	30879	6462	0.710310	2.11E-05	445
UPP 6	54213	850	2586	28260	4266	0.711130	1.30E-05	213
UPP 7	49822	3059	3936	31959	3046	0.710980	2.42E-05	372
UPP 8	53206	2967	4160	34187	3478	0.710880	1.85E-05	559
UPP 9	52759	988	2324	21561	4940	0.711260	1.81E-05	2004
UPP 10	56484	1081	2678	24159	5936	0.710970	1.82E-05	2226
UPP 11	55202	914	2541	22915	3047	0.712300	7.30E-06	739
UPP 12	39292	553	2050	19100	3097	0.711390	1.31E-05	318
UPP 13	36192	582	1580	16823	2447	0.711610	1.41E-05	281
UPP 14	34695	681	1979	17230	2988	0.710950	2.04E-05	372
UPP 15	60842	1041	2851	25296	4704	0.711720	1.71E-05	1666
UPP 16	47705	760	2174	18961	4807	0.710850	2.08E-05	1402
UPP 17	54759	900	2091	19369	4949	0.711020	1.69E-05	1401
UPP 18	27232	460	1133	11215	3780	0.709650	1.09E-05	189
UPP 19	46673	688	1456	11618	5018	0.710603	8.11E-06	1286
UPP 20	77080	3245	1378	20995	5862	0.711424	1.12E-05	2612
UPP 21	77065	3155	1380	20833	5874	0.711406	9.02E-06	2665
UPP 22	75538	3179	1316	20139	5770	0.711435	1.63E-05	2511
UPP 23	39917	573	973	9623	4917	0.710345	7.42E-06	855
UPP 24	21105	451	319	3747	1999	0.710847	1.31E-05	339
UPP 25	46660	918	1021	10840	5966	0.710873	7.28E-06	1113
UPP 26	45341	818	862	10519	5640	0.710979	7.39E-06	1052

Table S1 (Continued). Chemistry of UPP produced waters analyzed in this study.

ID	^{226}Ra (pCi/L)	^{228}Ra (pCi/L)	TotRa (pCi/L)	Fe (mg/L)	Cu (mg/L)	As (mg/L)	Cd (mg/L)	Pb (mg/L)	U (mg/L)
UPP 1	1026	1194	2220	98	<0.1	<0.1	<0.01	<0.1	<0.01
UPP 2	1424	1688	3111	217	<0.1	<0.1	<0.01	0.102	<0.01
UPP 3	1261	1357	2618	155	1.27	0.144	<0.01	0.288	<0.01
UPP 4	1555	1812	3367	132	0.132	<0.1	<0.01	<0.1	<0.01
UPP 5	1725	1591	3316	169	0.201	<0.1	<0.01	<0.1	<0.01
UPP 6	1470	1410	2880	137	0.175	<0.1	<0.01	<0.1	<0.01
UPP 7	3295	1167	4462	72	0.288	<0.1	<0.01	0.152	<0.01
UPP 8	2063	942	3006	91	0.138	<0.1	<0.01	<0.1	<0.01
UPP 9	1941	2114	4055	266	1.12	<0.1	<0.01	0.319	<0.01
UPP 10	1816	2148	3964	295	1.59	<0.1	<0.01	0.547	<0.01
UPP 11	1282	1816	3098	120	0.249	<0.1	<0.01	<0.1	<0.01
UPP 12	826	885	1712	175	0.145	<0.1	<0.01	<0.1	<0.01
UPP 13	406	676	1083	159	<0.1	<0.1	<0.01	<0.1	<0.01
UPP 14	724	813	1537	146	<0.1	<0.1	<0.01	<0.1	<0.01
UPP 15	1684	2124	3808	125	0.363	<0.1	<0.01	<0.1	<0.01
UPP 16	1662	1731	3393	148	0.212	<0.1	<0.01	<0.1	<0.01
UPP 17	1799	1842	3641	130	0.229	<0.1	<0.01	<0.1	<0.01
UPP 18	308	354	662	145	<0.1	<0.1	<0.01	<0.1	<0.01
UPP 19	1288	1542	2830	357	0.217	<0.1	<0.01	<0.1	<0.01
UPP 20	3867	3537	7404	129	0.412	<0.1	<0.01	<0.1	<0.01
UPP 21	4052	3613	7665	130	0.441	<0.1	<0.01	<0.1	<0.01
UPP 22	3035	3450	6484	82	0.386	<0.1	<0.01	<0.1	<0.01
UPP 23	1030	1095	2124	201	0.285	<0.1	<0.01	<0.1	<0.01
UPP 24	563	751	1314	221	0.515	<0.1	<0.01	<0.1	<0.01
UPP 25	1511	1514	3026	68	0.174	<0.1	<0.01	<0.1	<0.01
UPP 26	1146	1411	2557	68	0.17	<0.1	<0.01	<0.1	<0.01

Table S2. Molar ratios in the UPP produced waters analyzed in this study.

ID	Na/Cl	Cl/Br	B/Cl	(Ca+Mg)/Cl	(Ba+Sr)/Mg	Sr/Ca	Sr/Cl	Ba/Cl
UPP 1	0.55	206	1.03E-04	0.21	0.31	0.05	0.0087	9.70E-05
UPP 2	0.61	181	1.08E-04	0.22	0.38	0.06	0.0112	3.69E-04
UPP 3	0.50	177	1.10E-04	0.19	0.39	0.06	0.0102	1.65E-04
UPP 4	0.56	181	1.33E-04	0.20	0.53	0.08	0.0139	9.60E-04
UPP 5	0.53	182	1.45E-04	0.21	0.56	0.10	0.0170	7.45E-04
UPP 6	0.56	171	1.23E-04	0.19	0.47	0.07	0.0116	3.70E-04
UPP 7	0.45	178	1.18E-03	0.20	0.23	0.04	0.0073	5.66E-04
UPP 8	0.51	184	1.20E-03	0.22	0.26	0.05	0.0087	8.93E-04
UPP 9	0.55	176	1.61E-04	0.15	0.74	0.10	0.0135	3.50E-03
UPP 10	0.63	179	1.74E-04	0.18	0.76	0.11	0.0174	4.17E-03
UPP 11	0.62	202	1.78E-04	0.17	0.38	0.06	0.0090	1.39E-03
UPP 12	0.57	182	1.63E-04	0.19	0.45	0.07	0.0118	7.72E-04
UPP 13	0.63	197	2.32E-04	0.19	0.46	0.07	0.0112	8.22E-04
UPP 14	0.54	197	1.97E-04	0.18	0.45	0.08	0.0122	9.66E-04
UPP 15	0.66	199	2.35E-04	0.19	0.56	0.09	0.0134	3.03E-03
UPP 16	0.64	213	2.04E-04	0.17	0.73	0.12	0.0169	3.15E-03
UPP 17	0.65	187	2.24E-04	0.16	0.77	0.12	0.0154	2.78E-03
UPP 18	0.58	186	3.98E-04	0.16	0.95	0.15	0.0210	6.70E-04
UPP 19	0.68	185	5.00E-04	0.12	1.11	0.20	0.0190	3.11E-03
UPP 20	0.69	173	4.46E-04	0.12	1.51	0.13	0.0138	3.93E-03
UPP 21	0.70	174	4.59E-04	0.12	1.52	0.13	0.0140	4.04E-03
UPP 22	0.66	168	4.47E-04	0.11	1.55	0.13	0.0132	3.67E-03
UPP 23	0.67	170	7.83E-04	0.11	1.56	0.23	0.0217	2.41E-03
UPP 24	0.76	183	1.19E-03	0.09	1.93	0.24	0.0189	2.05E-03
UPP 25	0.71	169	9.13E-04	0.11	1.81	0.25	0.0238	2.84E-03
UPP 26	0.72	165	1.03E-03	0.11	2.03	0.25	0.0236	2.81E-03

Table S3. Summary statistics for all produced waters with greater than 76,800 mg/L Chloride (i.e., 5th percentile concentration the 26 UPP produced waters analyzed in this study). All analyte concentration units are in mg/L except radium (pCi/L).

	Utica						Marcellus						Conventional					
Analyte	5th	25th	50th	75th	95th	n	5th	25th	50th	75th	95th	n	5th	25th	50th	75th	95th	n
Cl	92465	106610	144805	152991	171442	24	78390	88799	102000	130734	178800	127	85200	115616	153000	181792	212527	1123
Br	1148	1322	1698	1919	2235	24	663	901	1070	1600	2724	113	498	933	1440	1900	2915	875
SO4							32	42	50	84	149	37	45	91	232	460	926	689
Ca	10567	18528	21278	28520	32084	24	8572	12334	14650	19958	35050	126	10680	18455	26574	36796	49907	1099
Mg	980	1437	2249	2873	3845	24	800	1153	1479	1830	2885	126	1448	2360	3280	5310	9740	1075
Ba	112	359	797	1468	2597	24	77	1478	2680	5528	15085	124	2.0	22	513	1015	2311	258
Sr	2997	3423	4862	5673	5962	24	1525	2279	2870	4449	7901	120	260	720	960	1260	1890	651
Na	36657	46670	52982	55767	76836	24	27350	34505	39500	47580	75350	126	33351	43600	55272	66000	84188	1072
K	575	751	907	1051	3176	24	0.8	271	343	525	2198	79	200	950	1480	2416	4402	970
Li	40	53	62	78	99	24	47	75	95	157	254	98	19	32	51	75	167	353
B	4.9	6.1	7.4	23	55	24	3.4	6.0	16	21	89	48	16	26	37	54	123	78
Fe	69	115	134	171	291	24	27	54	97	148	194	126	4.7	36	111	237	641	429
Cu	0.138	0.175	0.239	0.393	1.286	20	0.027	0.082	0.250	0.499	0.703	42	0.010	0.010	0.045	0.135	2.800	24
Cd							0.002	0.003	0.009	0.050	0.050	24						
Pb	0.112	0.152	0.288	0.319	0.501	5	0.005	0.030	0.060	0.150	0.270	25	0.010	0.020	0.020	0.030	0.040	13
As	0.144	0.144	0.144	0.144	0.144	1	0.050	0.073	0.100	0.100	0.138	23						
U																		
226Ra	739	1232	1533	1847	3781	24	50.44	1141	1417	2390	4294	40	164	566	811	1988	4937	25
228Ra	824	1187	1566	1910	3524	24	0.65	18	229	344	1108	39	45	210	1194	1909	8515	20
TotRa	1563	2603	3105	3847	7266	24	163	1356	1794	2427	5355	40	240	961	2034	4215	7984	25

Table S4. P-values for pairwise comparisons between produced water chemistry from the various formations. Comparisons that are statistically different (i.e., <0.05) are highlighted red.

	p values		
Analyte	Utica - Conventional	Utica - Marcellus	Marcellus - Conventional
Cl	2.18E-01	2.10E-03	<2e-16
Br	1.25E-01	1.90E-03	7.20E-02
SO4			
Ca	8.12E-02	4.20E-03	<2e-16
Mg	9.00E-05	1.50E-03	<2e-16
Ba	9.78E-02	1.70E-04	< 2e-16
Sr	1.40E-15	7.30E-04	< 2e-16
Na	1.00E+00	2.40E-04	< 2e-16
K	2.7E-02	1.1E-07	< 2e-16
Li	1.3E-01	1.4E-05	< 2e-16
B	2.4E-07	1.0E+00	1.5E-10
Fe	4.8E-01	8.7E-03	5.8E-01
Cu	2.7E-03	1.0E+00	2.0E-02
Cd			
Pb	3.8E-03	3.3E-02	3.4E-02
As			
U			
226Ra	1.9E-01	1.0E+00	5.7E-01
228Ra	2.9E-01	6.7E-09	4.0E-03
TotRa	8.3E-02	6.6E-04	1.0E+00

Table S5. Summary statistics for all elemental and isotopic ratios in O&G produced water and freshwater. Ratios are for produced waters with greater than 76,800 mg/L Chloride (i.e., 5th percentile concentration the 26 UPP produced waters analyzed in this study). All ratios are in mol/mol except for radium (activity/activity).

	Utica						Marcellus					
Analyte	5th	25th	50th	75th	95th	n	5th	25th	median	75th	95th	n
Na/Cl	0.498	0.551	0.625	0.664	0.709	24	0.421	0.535	0.608	0.646	0.777	126
Cl/Br	168	174	181	190	206	24	82	191	222	271	340	113
B/Cl	1.08E-04	1.57E-04	2.14E-04	4.69E-04	1.16E-03	24	9.25E-05	1.44E-04	5.02E-04	7.16E-04	2.50E-03	48
Ba/Cl	1.96E-04	7.65E-04	1.90E-03	3.12E-03	4.02E-03	24	1.92E-04	3.41E-03	7.08E-03	1.42E-02	2.88E-02	124
(Ca+Mg)/Cl	0.109	0.120	0.183	0.195	0.219	24	0.097	0.131	0.150	0.176	0.208	126
Sr/Cl	0.009	0.011	0.013	0.017	0.023	24	0.006	0.010	0.012	0.015	0.021	120
(Ba+Sr)/Mg	0.264	0.432	0.561	1.213	1.776	24	0.261	0.525	1.017	1.432	2.509	126
Sr/Ca	0.047	0.065	0.090	0.128	0.244	24	0.052	0.070	0.091	0.120	0.156	120
87/86Sr	0.710384	0.71088	0.711	0.711426	0.711714	24	0.7101036	0.710705	0.711056	0.711167	0.711746	15
228Ra/226Ra	0.522	0.991	1.083	1.183	1.393	24	0.000	0.009	0.203	0.421	2.448	39
	Conventional						Freshwater					
Analyte	5th	25th	50th	75th	95th	n	5th	25th	median	75th	95th	n
Na/Cl	0.364	0.505	0.607	0.679	0.750	1070	0.504	0.811	0.973	1.213	4.390	2778
Cl/Br	138	197	227	316	590	874	27	223	476	1275	3812	459
B/Cl	3.04E-04	4.91E-04	6.91E-04	1.08E-03	2.09E-03	78						
Ba/Cl	4.13E-06	3.93E-05	1.23E-03	2.17E-03	4.72E-03	257						
(Ca+Mg)/Cl	0.120	0.156	0.192	0.241	0.301	1097	0.423	1.151	2.077	4.212	20.354	3075
Sr/Cl	0.001	0.002	0.003	0.003	0.005	651						
(Ba+Sr)/Mg	0.018	0.048	0.072	0.101	0.184	737	0.000	0.002	0.007	0.009	0.013	101
Sr/Ca	0.007	0.012	0.015	0.017	0.032	651	0.001	0.002	0.002	0.002	0.004	77
87/86Sr	0.709225	0.710085	0.71161	0.717892	0.719928	11	0.7091	0.7106	0.7129	0.7151	0.71872	37
228Ra/226Ra	0.064	0.266	1.153	2.823	13.065	20	4.010	5.606	12.198	15.418	26.753	25

Table S6. P-values for pairwise comparisons between elemental and isotopic ratios in produced water and freshwater. Comparisons that are statistically different (i.e., <0.05) are highlighted red.

	p values					
Analyte	Utica - Conventional	Utica - Groundwater	Utica - Marcellus	Marcellus - Conventional	Marcellus - Groundwater	Groundwater - Conventional
Na/Cl	1.00E+00	3.10E-11	1.00E+00	1.00E+00	< 2e-16	< 2e-16
Cl/Br	3.50E-07	2.00E-06	5.70E-04	1.36E-01	2.80E-15	< 2e-16
(Ca+Mg)/Cl	9.00E-02	5.10E-16	3.20E-01	< 2e-16	< 2e-16	< 2e-16
(Ba+Sr)/Mg	2.50E-15	1.90E-13	4.70E-01	< 2e-16	< 2e-16	< 2e-16
Sr/Ca	5.50E-15	1.00E-12	1.00E+00	< 2e-16	< 2e-16	< 2e-16
87/86Sr	1.00E+00	6.00E-02	1.00E+00	1.00E+00	9.70E-02	1.00E+00
228Ra/226Ra	1.00E+00	1.90E-13	1.10E-05	7.10E-03	1.60E-09	2.70E-06

Table S7. P-values for normality by Shapiro Wilk tests in RStudio. P-values greater than 0.05 indicate that the data is normally distributed.

Element	Utica	Marcellus	Conventional
Cl	0.05269	6.659e-09	2.2e-16
Ca	0.2914	4.874e-08	5.5e-14
Na	0.04073	1.785e-09	5.839e-15
Sr	0.1198	1.574e-10	2.2e-16