IMPACTS OF SHALE GAS WASTEWATER DISPOSAL ON WATER QUALITY IN WESTERN PENNSYLVANIA

Supporting Information

Nathaniel R. Warner[+*^], Cidney A. Christie[+], Robert B. Jackson[+], and Avner Vengosh[+*]

[+] Division of Earth and Ocean Sciences, Nicholas School of the Environment, Duke University, Durham, NC 27708, United States

[^] Current address: Department of Earth Sciences, Dartmouth College, Hanover, NH 03755, United States

* Corresponding authors.

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1. Background

Pennsylvania is a historical oil and gas producer and is currently at the center of Marcellus Shale gas exploration. The volume of wastewater produced from conventional wells was ~800 million liters per year (ML/yr) prior to 2007.[1]However, the rapid expansion of unconventional oil and gas from the Marcellus Formation has increased the wastewater volume to between three and five billion L/yr.[1, 2] Each Marcellus gas well typically produces 0.65, 1.68, and 2.87 ML of drilling fluid, flowback, and produced water, respectively.[1] Combining these waste types represents an increase in wastewater volumes of over 570% compared to the conventional oil and gas waste stream.[1] Maloney and Yoxtheimer (2012) estimated the complete development of the Marcellus play in Pennsylvania (an estimated total of 60,000 wells) would result in over 62,600 ML of produced water and 54,300 ML of flowback.

In the United States, oil and gas exploration and production (E&P) wastewaters are exempt from regulation as a hazardous waste under Subtitle C of the Federal Resource Conservation and Recovery Act (RCRA). The RCRA exemption allows the operator to choose waste management and disposal options that are potentially less stringent and costly than those required under RCRA Subtitle C (http://www.epa.gov/osw/nonhaz/industrial/special/oil/oil-gas.pdf). There are several E&P wastewater management and disposal options such as W injection into underground deep disposal wells, direct discharge to nearby surface water bodies, treatment either at publicly-owned treatment works (POTW) that were originally designed for sewage treatment (i.e., municipal waste water treatment plants), or commercial treatment facilities (centralized waste treatment facility [brine treatment facility]), or reused, often after some treatment [3, 4] (Table S8). Certain POTWs originally accepted wastewater associated with unconventional Marcellus Shale gas wells until May 2011, when the Pennsylvania Department of Environmental Protection (PADEP) requested that oil and gas operators voluntarily cease disposal of wastewater from unconventional wells (i.e., Marcellus wastewater) to POTWs. However, private companies (that operated brine treatment facilities for several decades) still operate in western Pennsylvania treating conventional oil and gas produced water.

References

1. Lutz, B. D.; Lewis, A. N.; and Doyle, M. W. Generation, transport, and disposal of wastewater associated with Marcellus Shale gas development. *Water Resour Res* **2013**, *49*, (2), 647-656.
2. Maloney, K. and Yoxtheimer, D.,Production and disposal of waste materials from gas and oil extraction from the Marcellus Shale play in Pennsylvania. *Environ. Pract.* **2012**, *14*, 278-287.
3. Ferrar, K. J.; Michanowicz, D. R.; Christen, C. L.; Mulcahy, N.; Malone, S. L.; and Sharma, R. K. Assessments of effluent contaminants from three wastewater treatment plants discharging Marcellus Shale wastewater to surface waters in Pennsylvania. *Environ. Sci. & Technol.* **2013**, *47*, (7), 3472–3481.
4. Veil, J. *Water Management Technologies Used by Marcellus Shale Gas Producers*; prepared for US Department of Energy Office of Fossil Fuel Energy, National Energy Technology Laboratory: **2010**.

Table S1: Complete chemical and isotopic data set.

Location Number	Location Type	Sample Type	Distance Downstream (m)	Date Sampled	TDS calculated (mg/L)	Cl (mg/L)	Br (mg/L)	SO4 (mg/L)	Alkalinity (mg/L)	Ca(mg/L)	Mg(mg/L)	Sr(mg/L)	Na(mg/L)	Ba (mg/L)	$^{87}Sr/^{86}Sr$	$\delta^{2}H$	$\delta^{18}O$
AMD-1	AMD	SW		2011	659	26	0.14	441		114	28	0.6	14	0.1	0.714474	-59.4	-9.2
AMD-2	AMD	SW		2012	164	17	0.07			80	24	0.5	11	0.0	0.714549		
AMD-3	AMD	SW		2012	539	15	0.05	377		73	23	0.4	9	0.0			
US-1	Upstream	SW	-25	2011	403	17	0.10	244	22	59	14	0.3	43	0.1	0.713120	-49.9	-8.1
US-2	Upstream	SW	-25	2010	194	17	0.02	118		25	7	0.1	16	3.4			
US-3	Upstream	SW	-50	2012	240	15	0.04	161	4	34	10	0.2	12	0.1	0.713096		
US-4	Upstream	SW	-100	2010	189	17	0.02	115		25	7	0.1	15	2.8			
US-5	Upstream	SW	-100	2010	197	17	0.03	119		26	8	0.1	16	2.8			
US-6	Upstream	SW	-25	2012	117	20	0.05		3	52	13	0.3	22	0.0	0.713155		
US-7	Upstream	SW	-25	2012	119	21	0.06		3	53	14	0.3	23	0.0	0.713000		
EFF-1	Effluent	Brine Discharge	0	2011	94079	61260	522	585	241	16837	653	2230	11702	1	0.710124	-40.9	-4.4
EFF-2	Effluent	Brine Discharge	0	2010	131362	74309	602	1013	250	16957	1087	2326	34727	13	0.710185	-44.3	-4.3
EFF-3	Effluent	Brine Discharge	0	2010					250	13996	919	1871	29520	7			
EFF-4	Effluent	Brine Discharge	0	2010					250	10245	682	1340	22601	6		-44.6	-3.8
EFF-5	Effluent	Brine Discharge	0	2010					250	12693	832	1686	27143	6		-44.9	-3.7
EFF-6	Effluent	Brine Discharge	0	2010	86438	60751	474	1118	250	6663	455	856	15682	4	0.710183	-45.7	-4.4
EFF-7	Effluent	Brine Discharge	0	2010	108412	55077	477	200	250	16127	1050	2197	32980	14	0.710597	-45.6	-3.7
EFF-8	Effluent	Brine Discharge	0	2010	126829	74026	605	746	250	15490	1016	2120	32485	14	0.710831	-43.5	-4.3
EFF-9	Effluent	Brine Discharge	0	2010					250	16330	1063	2296	34718	14	0.710883	-46.4	-4.2
EFF-10	Effluent	Brine Discharge	0	2011	144559	85656	674	1136	272	15813	961	1419	38495	21	0.710500	-44.3	-4.3
EFF-11	Effluent	Brine Discharge	0	2011					257	13420	860	1155	33523	21		-39.1	-3.8
EFF-12	Effluent	Brine Discharge	0	2011	135909	89299	738	1010	269	12233	689	976	30584	19	0.710800	-40.8	-4.2
EFF-13	Effluent	Brine Discharge	0	2011	120290	78827	609	928	241	10276	612	777	27907	19		-39.8	-3.9
EFF-14	Effluent	Brine Discharge	0	2011	127026	75277	622	1103	252	13619	783	1031	34234	20	0.710800	-45.7	-4.4
EFF-15	Effluent	Brine Discharge	0	2011	183648	150153	1266	2911	249	7611	624	612	20134	17		-39.7	-3.9
EFF-16	Effluent	Brine Discharge	0	2011	104919	76877	605	1116	268	7003	565	632	17743	17	0.710579	-43.5	-4.3
EFF-17	Effluent	Brine Discharge	0	2011	90406	67773	543	1405	273	5509	517	542	13752	17	0.710197	-46.4	-4.2
EFF-18	Effluent	Brine Discharge	0	2011	151009	97756	632	1012	249	15336	1200	912	33900	12	0.711100		
DS-1	Downstream	SW	1	2012	13343	8193	69	194	27	1421	106	114.2	3216	1.9	0.711000		
DS-2	Downstream	SW	10	2012	8131	5000	42	208	17	890	70	69.6	1832	1.1			
DS-3	Downstream	SW	20	2011	4409	2403	18	260	33	555	39	49.4	1048	0.6	0.710258	-47.0	-8.0
DS-4	Downstream	SW	180	2012	900	367	2.42	153	5	123	19	6.3	219	0.2			
DS-5	Downstream	SW	300	2012	248	97	0.58		2	71	15	1.4	53	0.1			
DS-6	Downstream	SW	300	2012	240	95	0.58		2	69	15	1.3	51	0.1			
DS-7	Downstream	SW	1	2010		75085	650	397									
DS-8	Downstream	SW	10	2010	7076	4191	36	199		837	92	78.0	1584	27.3			
DS-9	Downstream	SW	20	2010	4375	2411	17			664	82	55.8	1100	23.4			
DS-10	Downstream	SW	100	2010	810	401	3.32	112		100	13	9.7	160	2.8			
DS-11	Downstream	SW	600	2010	52					27	8	0.1	14	0.0			
DS-12	Downstream	SW	300	2010	78					35	9	1.2	30	0.1	0.711181		
DS-13	Downstream	SW	300	2010	52					27	8	0.2	14	0.0	0.713004		
DS-14	Downstream	SW	300	2010	206	17	0.04	118		32	9	0.1	18	3.4	0.710207		
DS-15	Downstream	SW	600	2010	304	85	0.58	110		40	9	1.6	46	3.1	0.710362		
DS-16	Downstream	SW	600	2010	189	18	0.03	105		29	8	0.2	18	3.0	0.712109		
DS-17	Downstream	SW	600	2010	197	16	0.03	114		29	9	0.1	17	3.1	0.713002		
DS-18	Downstream	SW	1780	2012	543	233	1.43	157	3	73	23	0.4	9	0.0			
BG-1	Background	SW		2011	360	32	0.12	144	79	48	11	0.3	43	0.0	0.714500	-41.7	-6.4
BG-2	Background	SW		2011	127	24	0.02	10	59	18	3	0.1	12	0.0	0.712545	-55.0	-8.5
BG-3	Background	SW		2011	184	28	0.11	11	93	29	5	0.1	16	0.1	0.712880	-60.8	-9.2
BG-4	Background	SW		2011	91	13	0.02	9	44	13	3	0.0	8	0.0	0.713900	-45.4	-7.3
BG-5	Background	SW		2011	376	37	0.21	189	44	57	17	0.3	29	0.1	0.712200	-45.3	-7.8

Table S2: Results of STATA non-parametric comparison of mean ranks between concentrations (activities for 226Ra and 228Ra) of discharge effluent to Northern Appalachian Basin: flowback and produced water from Marcellus wells (top row), produced water from Upper Devonian formations (second row), produced water from Lower Devonian and older formations (3rd row), and produced and flowback waters from all groups combined (4th row). Evidence of significant differences ($p<0.05$) between the effluent and the four groups of wastewaters are shown in bold font. The sample group with the larger mean is also shown immediately below the p-value. For example, the first comparison between effluent Cl concentrations to Marcellus Cl concentrations yielded a p-value of 0.087 (not a significant difference), with a higher value of the mean Cl concentration in the effluent. Produced water major element chemistry data compiled from Dresel and Rose (2010)[1] and Osborn et al., (2010)[2]. Values for radium isotopes in produced waters compiled from Dresel and Rose (2010)[1] and Rowan et al., (2012)[3].

Effluent Compared to:		Cl	Br	SO4	Ca	Mg	Sr	Na	Ba	226 Ra	228 Ra
Marcellus	p-value	0.087	0.312	**<0.001**	**0.013**	0.325	0.346	0.985	**<0.001**	**0.025**	**0.046**
	Larger Mean	Effluent	Marcellus	Effluent	Effluent	Marcellus	Marcellus	Marcellus	Marcellus	Marcellus	Marcellus
Upper Devonian Produced Water	p-value	1.000	**0.025**	**<0.001**	0.883	**<0.001**	**<0.001**	0.283	0.107	0.564	
	Larger Mean		UD	Effluent	Effluent	UD	UD	UD	UD	UD	
Lower Devonian and older Produced Water	p-value	**0.003**	**0.004**	**<0.001**	**<0.001**	**<0.001**	0.768	**<0.001**	0.401	0.064	
	Larger Mean	LD	LD	Effluent	LD	LD	LD	LD	LD	LD	
Combined: Marcellus, Upper Devonian and Lower Devonian or Older	p-value	0.702	**0.019**	**<0.001**	0.471	**<0.001**	0.108	0.293	**<0.001**	**0.037**	**0.046**
	Larger Mean	Effluent	App	Effluent	Effluent	App	Effluent	App	App	App	App

1. Dresel, P.,and Rose, A. *Chemistry and origin of oil and gas well brines in western Pennsylvania: Pennsylvania Geological Survey*; Pennsylvania Department of Conservation and Natural Resources: 2010.

2. Osborn, S. G., and McIntosh, J. C. Chemical and isotopic tracers of the contribution of microbial gas in Devonian organic-rich shales and reservoir sandstones, northern Appalachian Basin. *Appl. Geochem.* **2010,** *25*, (3), 456-471.

3. Rowan, E., Engle, M., Kirby, C., and Kraemer, T. *Radium content of oil- and gas-field produced waters in the northern Appalachian Basin (USA)—Summary and discussion of data: U.S. Geological Survey Scientific Investigations Report 2011–5135*; U.S. Geological Survey 2011.

Table S3. Radium isotope data of effluents from Josephine Brine Treatment Facility and river sediments collected upstream, adjacent to, and downstream of the discharge site of the treated effluent. Also included are measurements from background stream sediments throughout western Pennsylvania (see location in Figure 1 and S1).

Location Number	Location Type	Sample Type	Distance Downstream	Year Sampled	Effluent 226Ra (Bq/L)	Effluent 228Ra (Bq/L)	Sediment 226Ra (Bq/kg)	Sediment 228Ra (Bq/kg)	228Ra/226Ra
EFF-1	Effluent	Discharge	0	2011	0.11	0.04			0.39
EFF-18	Effluent	Discharge	0	2011	0.19	0.13			0.7
BG-1	Background	Sediment		2011			26	24	0.92
BG-2	Background	Sediment		2011			32	18	0.56
BG-3	Background	Sediment		2011			22	13	0.61
BG-4	Background	Sediment		2011			27	19	0.73
BG-5	Background	Sediment		2011			44	33	0.77
US-1	Upstream	Sediment	-25	2011			34	22	0.66
US-3	Upstream	Sediment	-50	2012			31	25	0.82
USS-1	Upstream	Sediment	-50	2012			34	33	0.98
US-7	Upstream	Sediment	-25	2012			27	24	0.89
AMD-1	AMD	Sediment		2011			34	30	0.88
AMD-3	AMD	Sediment		2012			41	33	0.82
EFF-1	Effluent	Sediment	0	2011			8759	2187	0.25
EFF-18	Effluent	Sediment	0	2011			3497	1016	0.29
EFFS-2	Effluent	Sediment	0	2011			3497	1016	0.29
EFFS-3	Effluent	Sediment	1	2011			1419	355	0.25
EFFS-4	Effluent	Sediment	5	2011			3036	757	0.25
EFFS-5	Effluent	Sediment	0	2012			7708	2083	0.27
EFFS-6	Effluent	Sediment	1	2012			1908	426	0.22
EFFS-1	Effluent	Sediment	5	2011			544	164	0.30
DS-1	Downstream	Sediment	1	2012			5967	1617	0.27
DS-2	Downstream	Sediment	10	2012			1923	478	0.25
DS-3	Downstream	Sediment	20	2011			299	75	0.25
DS-4	Downstream	Sediment	180	2012			348	87	0.25
DS-5	Downstream	Sediment	300	2012			38	22	0.57
DS-6	Downstream	Sediment	300	2012			53	34	0.63
DS-18	Downstream	Sediment	1780	2012			33	22	0.67

Table S4. Estimated total annual discharge (reported discharge volume x discharge concentration) from the Josephine Brine Treatment Facility for Cl and Br.

	Chloride	Bromide
Average measured concentrations in treated effluent from 2010-2012	81,771 (mg/L)	643 (mg/L)
Grams per liter	81.77	0.64
Kilograms per liter	0.08	6.43E-4
Metric tons per liter	8.18E-5	6.43E-7
Reported discharge volume per day (liters)	5.85E+5	5.85E+5
Estimated tons discharged per day (measured tons per liter x reported liters per day)	47.84	0.38
Estimated tons discharged per year (tons per liter x liters per year)	17,460	137

Table S5: Estimated total yearly volumes of Marcellus wastewater disposed in brine treatment facilities and corresponding estimated total flux (in tons) of chloride and bromide released to surface water. Marcellus wastewater is eventually discharged to western Pennsylvania surface water and into the Ohio River that passes through Pittsburgh. The effect of the Marcellus wastewater disposal leads to an increase in flux of chloride (4.65%) and bromide (19.5%) above estimated background.

	Chloride	Bromide
Total volume disposed at brine treatment facilities (liters per year)	3.90E+08	3.90E+08
Average concentration in effluent (mg/L)	81,771 (mg/L)	643 (mg/L)
Estimated total discharge mass per year (mg) (total volume liters per year x average mg/L in effluent)	3.19E+13	2.51E+11
Estimated total flux to surface water from disposal of Marcellus wastewater (tons/year)	31,891	251
Estimated background concentration of western Pennsylvania streams (mg/L)	24 (mg/L)	0.045 (mg/L)
Estimated total background flux in the Ohio River at Pittsburgh (mg/year) 2.85E+13 liters/year x mg/L	6.86E+14	1.29E+12
Estimated total background flux in the Ohio River at Pittsburgh (tons/year)	6.86E+05	1.29E+03
Estimated annual average increase of mass flux in the Ohio River at Pittsburgh because of disposal of Marcellus wastewater to surface water in western Pennsylvania	4.65%	19.5%

Table S6: Results of STATA non-parametric comparison of mean ranks between concentrations (activities for 226Ra and 228Ra) of discharge effluent and upstream and downstream (between 1 and 1780 meters downstream) values from Blacklick Creek. Evidence of significant differences ($p<0.05$) between the groups are shown in bold. Values less than 0.001 are shown as <0.001.

		TDS (mg/L)	Cl (mg/L)	Br (mg/L)	SO4 (mg/L)	Alkalinity (mg/L)	Ca(mg/L)	Mg(mg/L)	Sr(mg/L)	Na(mg/L)	Ba (mg/L)	87Sr/86Sr	Sediment 226Ra (Bq/kg)	Sediment 228Ra (Bq/kg)	228Ra/ 226Ra
Effluent versus Upstream	p-value	**<0.001**	**<0.001**	**<0.001**	**<0.001**	**<0.001**	**<0.001**	**<0.001**	**<0.001**	**<0.001**	**<0.001**	**<0.001**	**0.001**	**0.001**	**0.001**
	Larger Mean	Effluent	Effluent	Effluent	Effluent	Effluent	Effluent	Effluent	Effluent	Effluent	Effluent	Up	Effluent	Effluent	Up
Effluent versus Downstream	p-value	**<0.001**	**<0.001**	**<0.001**	**<0.001**	**<0.001**	**<0.001**	**<0.001**	**<0.001**	**<0.001**	**<0.001**	0.076	**0.001**	**0.025**	**0.001**
	Larger Mean	Effluent	Effluent	Effluent	Effluent	Effluent	Effluent	Effluent	Effluent	Effluent	Effluent	Down	Effluent	Effluent	Up
Upstream versus Downstream	p-value	0.069	**0.001**	**0.001**	0.235	0.090	**0.008**	**0.017**	**0.001**	**0.013**	0.144	**0.007**	**0.004**	**0.032**	**0.011**
	Larger Mean	Down	Down	Down	Down	Up	Down	Down	Down	Down	Down	Up	Down	Up	Up

Table S7: Classification of sediment sample grain size.

Location from Discharge	Grain Size (mm)	Classification Range
Downstream	0.25 - 10	fine sand - pebble
Near Discharge	0.15 - 6	fine sand - pebble
Upstream	0.25 - 9	medium sand - pebble
AMD	0.10 - 6	very fine sand - pebble

Table S8: Terminology of treatment facilities used in this study.

Facility Type	Description	Typical Treatment
Oil and gas water pollution control facilities	Facilities in Pennsylvania permitted to treat oil and gas wastewater. This designation includes both publically owned treatment works (POTWs) that are typically sewage treatment plants as well as wastewater treatment plants (WWTPs) that may be privately or publically owned. Many WWTPs were designed to treat acid mine drainage, industrial waste, or brine, which typically comes from both conventional oil and gas produced water as well as unconventional Marcellus wells. Pennsylvania previously designated brine treatment facilities as centralized waste treatment facilities (CWT), but in 2011 that designation changed to treatment for reuse.[1]	Various methods to remove oils and metals
POTW	Publically owned treatment works – typically sewage treatment plants	Flocculation, aeration
WWTP	Wastewater treatment plants, includes industrial brine treatment facilities.	Removal of oils and metals

1. Wilson, J.M. and J. M. VanBriesen, Oil and Gas Produced Water Management and Surface Drinking Water Sources in Pennsylvania. *Environmental Practice*, **2012**, 14, 288-300.

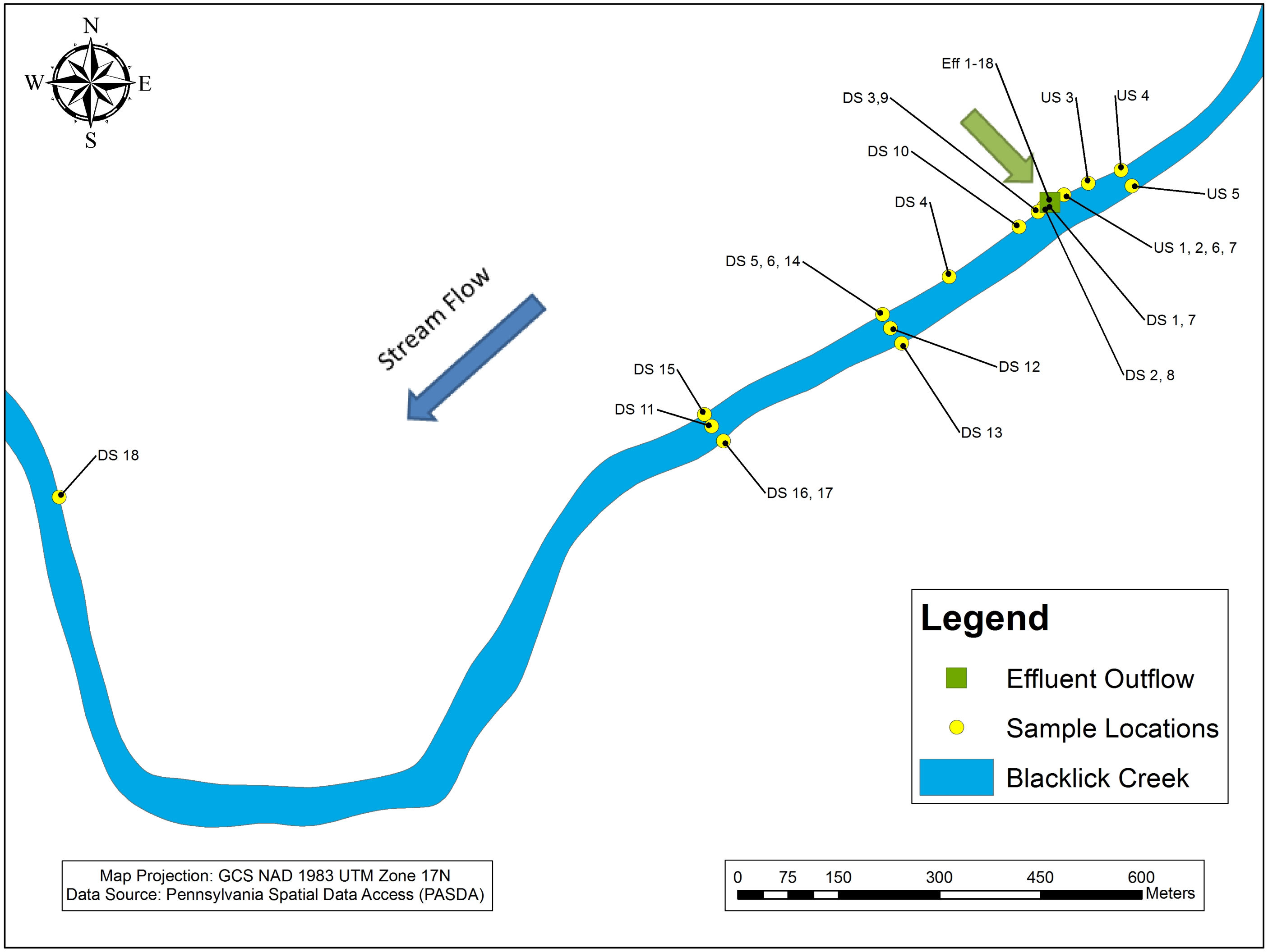

Figure S1: Location of the sampling sites in Blacklick Creek near Josephine Brine Treatment Facility in Western Pennsylvania. The USGS station 03042000 is located ~300 m downstream from sampling point DS-18.

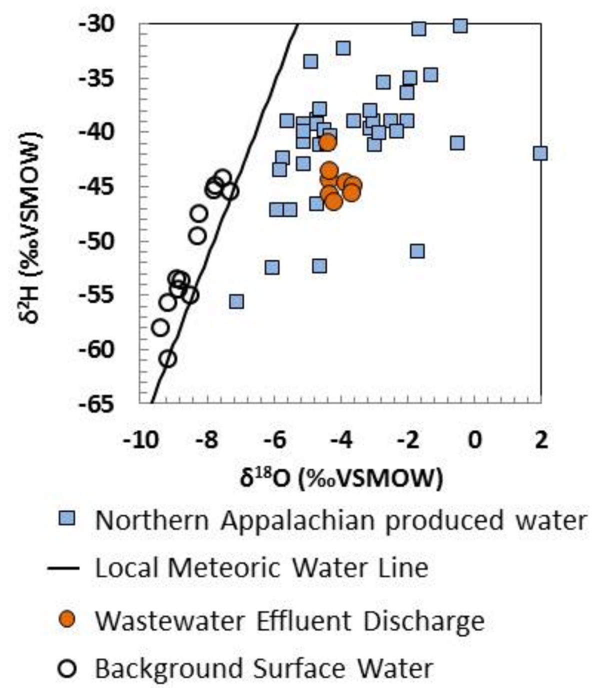

Figure S2. The values of δ^2H versus $\delta^{18}O$ normalized to Vienna Standard Mean Ocean Water (VSMOW)[1] in surface water samples collected from western PA streams (open black circles) and from wastewater discharged from the Josephine Brine Treatment Facility (orange circles), compared to the Local Meteoric Water Line (LMWL)[2] and produced and flowback waters from the Appalachian Basin[3,4] (blue squares).

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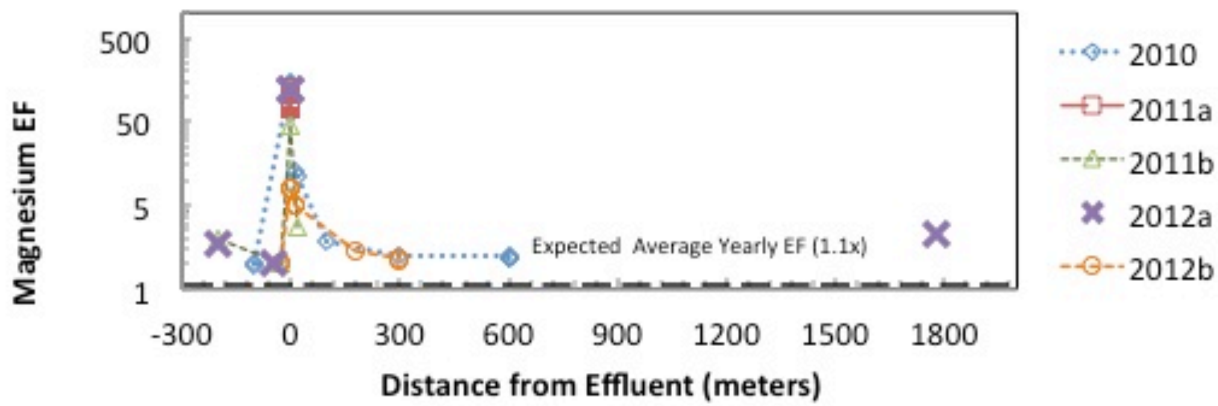
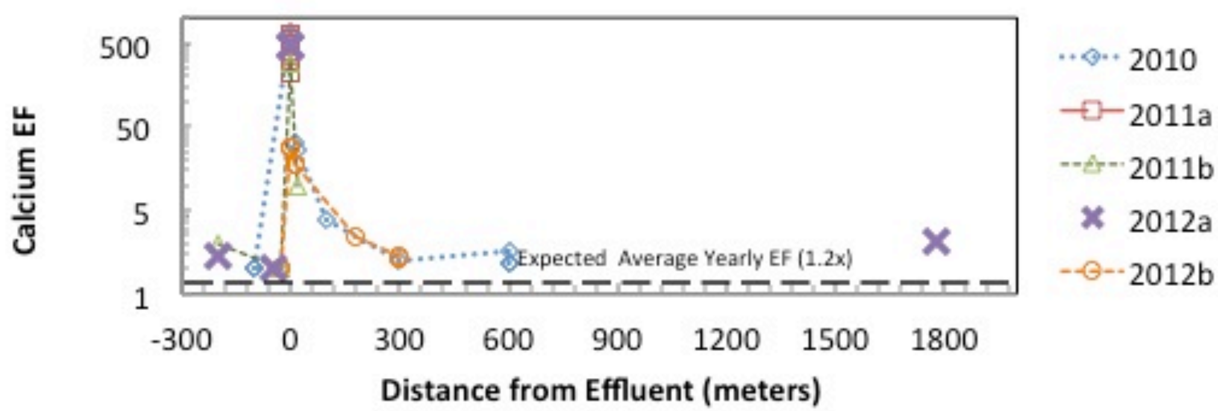

500
50
5
1
Magnesium EF
-300
0
300
600
900
1200
1500
1800
Distance from Effluent (meters)
Expected Average Yearly EF (1.1x)
2010
2011a
2011b
2012a
2012b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50
5
1
Calcium EF
-300
0
300
600
900
1200
1500
1800
Distance from Effluent (meters)
Expected Average Yearly EF (1.2x)
2010
2011a
2011b
2012a
2012b

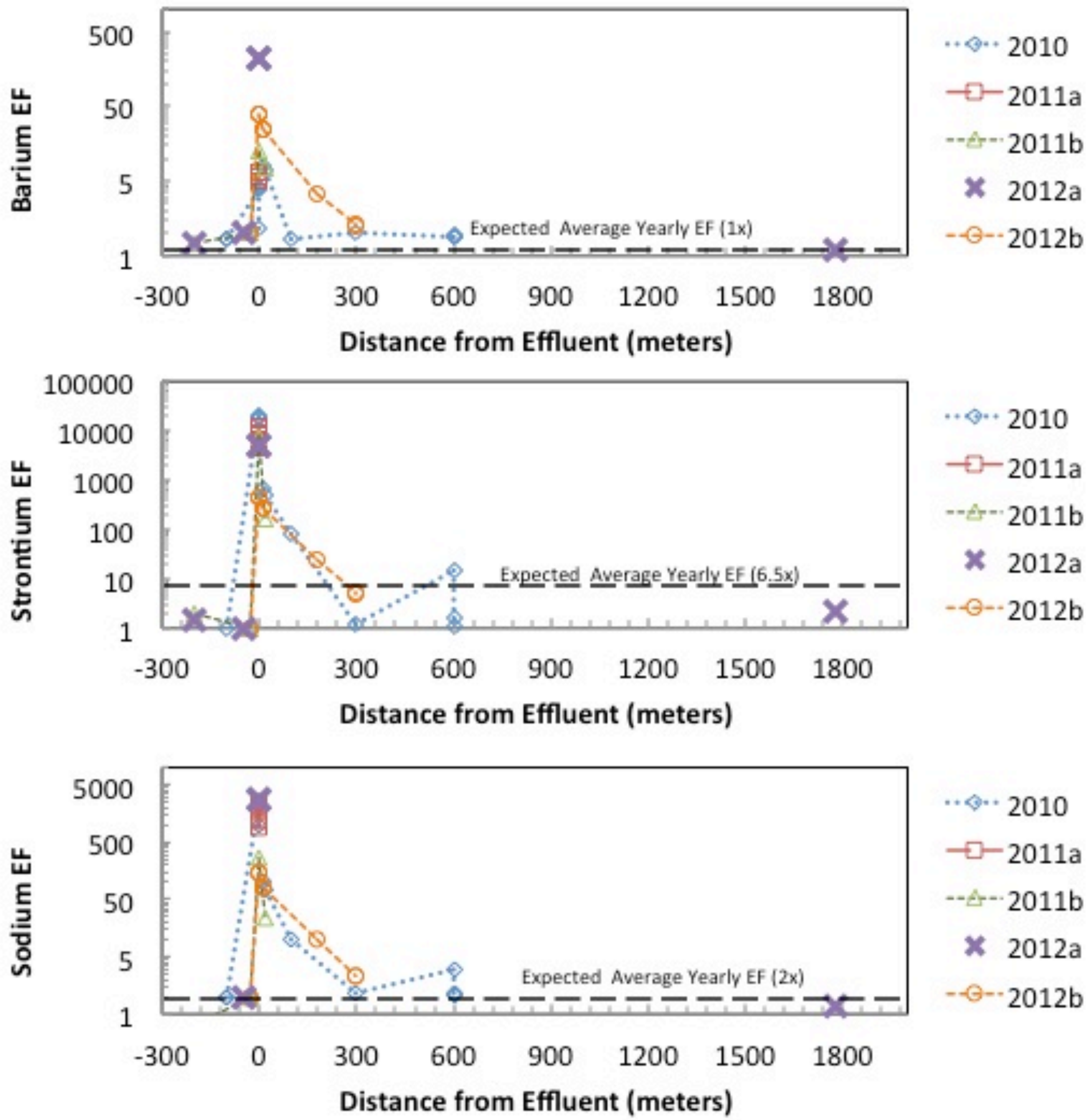
500
50
5
1
Barium EF
Expected Average Yearly EF (1x)
-300
0
300
600
900
1200
1500
1800
Distance from Effluent (meters)
2010
2011a
2011b
2012a
2012b
100000
10000
1000
100
10
1
Strontium EF
Expected Average Yearly EF (6.5x)
-300
0
300
600
900
1200
1500
1800
Distance from Effluent (meters)
2010
2011a
2011b
2012a
2012b
5000
500
50
5
1
Sodium EF
Expected Average Yearly EF (2x)
-300
0
300
600
900
1200
1500
1800
Distance from Effluent (meters)
2010
2011a
2011b
2012a
2012b

Figure S3 a through 3e. Surface water enrichment factors (EFs) in logarithmic scale of Mg, Ca, Ba, Sr, and Na plotted versus distance from the discharge site of the investigated treatment facility in western PA. EFs were calculated relative to upstream surface water concentrations for each of 5 sampling events. Samples plotted upstream (negative values on the X-axis) include surface water samples collected directly upstream of the discharge site and acid mine drainage contribution to the stream near the facility. The data show variability in concentrations during the same sampling event at the same distance downstream due to differential mixing of the effluents and river waters perpendicular to stream flow. Values of the expected average yearly EFs are marked in black dashed lines. These calculations use the permitted daily discharge volume multiplied by the average concentration measured in the effluent is mixed with the annual river flow with an average upstream concentration.