

## Appendix E

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# Flowback and Produced Water Supplemental Tables and Information

## Appendix E. Flowback and Produced Water Supplemental Tables and Information

### E.1. Flowback and Long-Term Produced Water Volumes

- 1 The EPA ([2015g](#)) estimates of flowback volumes and long-term produced water volumes used to
- 2 generate the summaries appearing in Table 7-3 of Chapter 7 appear below in Table E-1.

**Table E-1. Flowback and long-term produced water characteristics for wells in unconventional formations, formation-level data.**Source: [U.S. EPA \(2015g\)](#).

Basin	Resource Type	Unconventional Formation	Drill Type	Fracturing Fluid (Mgal)			Flowback (% of Fracturing Fluid Returned)			Long-Term Produced Water Rates (gpd)		
				Median	Range	Number of Data Points	Median	Range <sup>a</sup>	Number of Data Points	Median	Range <sup>b</sup>	Number of Data Points
Anadarko	Shale	Woodford	H	4.7	1.0-12	2,239	34	20-50	3	5,500	3,200-6,400	198
	Tight	Cleveland	H	0.81	0.2-4.0	144	--	12-40	2	82	20-300	571
			V	0.69	0.11-3	4	--	--	2	32	6.6-170	390
		Granite Wash	H	6.2	0.2-9.4	77	--	7-22	2	1,300	0-2,200	273
			V	0.56	0.05-3	26	--	--	2	500	170-1,300	2,413
		Mississippi Lime	H	1.8	0.82-2.4	428	--	50	1	--	37,000-120,000	4
Appalachian	Shale	Marcellus	H	4.4	0.9-11	14,010	7	4-47	4,374	860	54-13,000	4,984
			V	2.6	0.53-6.6	66	40	21-60	7	230	100-1,200	714
		Utica	H	4.0	1.0-11	150	4	2-27	73	510	210-1,200	82
Arkoma	Shale	Fayetteville	H	5.1	1.7-11	1,668	--	10-20	2	430	150-2,300	2,305
Denver-Julesburg	Shale	Niobrara	H	2.6	0.73-3.4	69	13	6-25	16	680	260-810	250
			V	0.32	0.27-3.3	367	11	7-35	9	340	240-600	5,474
	Tight	Codell	D	0.28	0.21-0.46	78	--	--	0	--	--	0
			V	0.27	0.13-0.46	185	--	--	0	--	--	0
		Codell-Niobrara	H	2.6	0.15-2.7	62	7	--	32	34	19-140	32
	D		0.45	0.21-0.47	116	--	--	0	--	--	0	
	V		0.30	0.13-0.46	592	--	--	0	29	13-65	1,677	

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Basin	Resource Type	Unconventional Formation	Drill Type	Fracturing Fluid (Mgal)			Flowback (% of Fracturing Fluid Returned)			Long-Term Produced Water Rates (gpd)		
				Median	Range	Number of Data Points	Median	Range <sup>a</sup>	Number of Data Points	Median	Range <sup>b</sup>	Number of Data Points
Denver-Julesburg, cont.	Tight cont.	Muddy J	D	0.59	.025-0.62	162	--	--	0	230	64-390	3
			V	0.28	0.16-0.62	292	--	--	0	55	9.3-500	129
Fort Worth	Shale	Barnett	H	3.6	1-7.3	23,917	30	21-40	11	920	160-4,200	10,349
			V	1.3	0.4-1.9	3,589	--	--	0	250	170-580	3,318
Green River	Shale	Hilliard-Baxter-Mancos	H	1.7	1.0-5.6	2	--	--	0	37	15-58	7
	Tight	Lance	V	1.3	0.81-3.5	29	3	1-50	31	410	250-580	1,050
			D	1.2	0.76-1.9	180	6	1-17	170	860	360-1,200	1,140
Green River, cont.		Mesaverde	D	0.23	0.16-0.31	73	8	0-37	61	190	150-440	445
			V	0.17	0.081-0.29	14	21	6-83	11	290	140-610	1,081
Illinois	Shale	New Albany	H	--	--	0	--	--	0	--	2,900	2
Michigan	Shale	Antrim	V	--	0.05	1	--	25-75	2	--	4,600	1
Permian	Shale	Avalon & Bone Spring	D	2.2	0.94-4.5	20	13	5-31	16	950	220-2,400	183
			H	1.1	0.73-2.8	17	--	--	0	0	0-2,300	37
		Barnett-Woodford	H	2.1	0.5-4.5	2	--	--	0	--	--	0

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Basin	Resource Type	Unconventional Formation	Drill Type	Fracturing Fluid (Mgal)			Flowback (% of Fracturing Fluid Returned)			Long-Term Produced Water Rates (gpd)		
				Median	Range	Number of Data Points	Median	Range <sup>a</sup>	Number of Data Points	Median	Range <sup>b</sup>	Number of Data Points
Permian, cont.	Shale, cont.	Devonian (TX)	H	0.32	0.13-0.89	10	--	--	0	880	310-1,800	381
			V	0.27	0.12-1.0	16	--	--	0	400	150-3,000	162
		Wolfcamp	H	1.4	1.1-3.9	55	--	--	0	3,000	210-19,000	104
			D	1.3	0.26-1.7	12	16	15-20	3	310	22-8,700	259
			V	0.81	0.078-1.7	60	--	--	0	910	130-1,700	926
	Tight	Spraberry	V	--	1.0	1	--	--	0	870	100-4,000	66
San Juan	Tight	Mesaverde (San Juan)	D	--	--	0	--	--	0	18	12-260	48
		Dakota	V	0.2	0.063-0.22	19	--	--	0	65	29-120	6
			D	0.12	0.07-0.3	52	4	1-40	30	160	41-370	379
TX-LA-MS	Shale	Bossier	H	2.7	1.7-3.6	2	--	--	0	750	610-1,200	25
			V	0.4	0.19-1.7	16	--	--	0	470	180-1,100	1,203
			D	0.28	0.13-0.8	21	--	--	0	320	130-1,300	253
		Haynesville	H	5.3	0.95-15	3,222	5	5-30	3	1,700	84-1,800	1,249
			V	0.61	.14-3.5	9	--	--	0	210	56-850	263
		Tight	Cotton Valley	H	4.2	.25-6.0	30	--	<60	2	770	130-2,700
	D			.48	.084-4.0	24	--	<60	2	950	630-1,800	1801
	V			.28	.019-.94	76	--	<60	2	640	370-1,800	10,717

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Basin	Resource Type	Unconventional Formation	Drill Type	Fracturing Fluid (Mgal)			Flowback (% of Fracturing Fluid Returned)			Long-Term Produced Water Rates (gpd)		
				Median	Range	Number of Data Points	Median	Range <sup>a</sup>	Number of Data Points	Median	Range <sup>b</sup>	Number of Data Points
TX-LA-MS, cont.	Tight, cont.	Travis Peak	H	3.0	0.25-6	2	--	--	0	200	39-1,700	5
			V	0.9	0.2-4	2	--	--	0	980	330-1,800	1,380
Western Gulf	Shale	Eagle Ford	H	5.0	1.0-14	2,485	4	2-8	1,800	110	9.1-250	498
			V	2.9	2.0-4.1	9	--	--	0	--	--	0
		Pearsall	H	3.7	3.3-4.1	2	--	--	0	200	54-370	12
	Tight	Austin Chalk	H	0.94	0.58-1.3	15	--	--	0	720	290-2,400	1,097
		Vicksburg	V	.016	0.084-0.6	20	--	--	0	1,000	650-1,900	937
			D	0.11	0.1-0.13	4	--	--	0	--	--	0
			Wilcox Lobo	H	2.1	0.66-2.6	4	--	--	0	330	62-740
		V		0.21	0.06-0.6	14	--	--	0	620	330-1,400	1,514
		D		.058	.056-.076	3	--	--	0	--	--	0
		Olmos	V	--	0.15	2	--	--	0	--	--	0
Williston		Bakken	H	2.0	0.35-10	2,203	19	5-47	206	680	380-1,500	1,739
			V	1.1	.35-2.9	12	--	--	0	1,000	340-3,100	222

"--" indicates no data; H, horizontal well; D, directional well; V, vertical well.

<sup>a</sup> For some formations, if only one data point was reported, the EPA reported it in the range column and did not report a median value.

<sup>b</sup> For some formations, the number of data points was not reported in the data source. In these instances, the EPA reported the number of data points as equal to one, even if the source reported a range and median value.

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## **E.2. Produced Water Content**

### **E.2.1. Introduction**

1 In the main text of Chapter 7, we describe aspects of flowback and produced water composition,  
2 including temporal changes in water quality parameters of flowback (Section 7.5) and major classes  
3 of compounds in produced water (Section 7.6). In section 7.7 we describe variability as occurring  
4 on three levels: between different rock types (e.g., coal vs. sandstone), between formations  
5 composed of the same rock types (e.g., Barnett Shale vs. Bakken Shale), and within formations of  
6 the same rock type (e.g., northeastern vs. southwestern Marcellus Shale). In this appendix we  
7 present data from the literature which illustrates the differences among these three variability  
8 levels.

### **E.2.2. General Water Quality Parameters**

9 As noted in Chapter 7, the EPA identified data characterizing the content of unconventional  
10 flowback and produced water in a total of 12 shale and tight formations and coalbed methane  
11 (CBM) basins. These formations and basins span 18 states. Note that in this subsection we treat all  
12 fluids as produced water. As a consequence, the variability of reported concentrations is likely  
13 higher than if the data could be standardized to a specific point on the flowback-to-produced water  
14 continuum. Table E-2 and Table E-3 provide supporting data on general water quality parameters  
15 of produced water for 12 formations.

**Table E-2. Reported concentrations of general water quality parameters in produced water for unconventional shale and tight formations, presented as: average (minimum–maximum) or *median* (minimum–maximum).**

Parameter	Units	Shales					Tight formations			
		Bakken <sup>a</sup>	Barnett <sup>b</sup>	Fayetteville <sup>c</sup>	Marcellus		Cotton Valley Group <sup>f</sup>	Devonian Sandstone <sup>g</sup>	Mesaverde <sup>f</sup>	Oswego <sup>f</sup>
States	n/a	MT, ND	TX	AR	PA <sup>d</sup>	PA, WV <sup>e</sup>	LA, TX	PA	CO, NM, UT, WY	OK
Acidity	mg/L	-	NC (ND–ND)	-	NC (<5–473)	<b>162</b> (5–925)	-	-	-	-
Alkalinity	mg/L	-	<b>725</b> (215–1,240)	1,347 (811–1,896)	165 (8–577)	<b>99.8</b> (7.5–577)	-	99 (43–194)	-	582 (207–1,220)
Ammonium	mg/L	-	-	-	-	-	89 (40–131)	-	-	-
Bicarbonate	mg/L	291 (122–610)	-	-	-	-	-	524 (ND–8,440)	2,230 (1,281–13,650)	-
Biochemical oxygen demand (BOD)	mg/L	-	<b>582</b> (101–2,120)	-	-	<b>141</b> (2.8–12,400)	-	-	-	-
Carbonate	mg/L	-	-	-	-	-	-	-	227 (ND–1,680)	-
Chloride	mg/L	119,000 (90,000–133,000)	<b>34,700</b> (9,600–60,800)	9,156 (5,507–12,287)	57,447 (64–196,000)	<b>49,000</b> (64.2–196,000)	101,332 (3,167–221,498.7)	132,567 (58,900–207,000)	4,260 (8–75,000)	44,567 (23,000–75,000)
Chemical oxygen demand	mg/L	-	<b>2,945</b> (927–3,150)	-	15,358 (195–36,600)	<b>4,670</b> (195–36,600)	-	-	-	-

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Parameter	Units	Shales					Tight formations			
		Bakken <sup>a</sup>	Barnett <sup>b</sup>	Fayetteville <sup>c</sup>	Marcellus		Cotton Valley Group <sup>f</sup>	Devonian Sandstone <sup>g</sup>	Mesaverde <sup>f</sup>	Oswego <sup>f</sup>
States	n/a	MT, ND	TX	AR	PA <sup>d</sup>	PA, WV <sup>e</sup>	LA, TX	PA	CO, NM, UT, WY	OK
DO	mg/L	-	-	-	-	-	-	0.8 (0.2–2.5)	-	-
DOC	mg/L	-	<b>11.2</b> (5.5–65.3)	-	-	<b>117</b> (3.3–5,960)	-	-	-	-
Hardness as CaCO <sub>3</sub>	mg/L	-	<b>5,800</b> (3,500–21,000)	-	34,000 (630–95,000)	<b>25,000</b> (156–106,000)	-	-	-	-
Oil and grease	mg/L	-	<b>163.5</b> (88.2–1,430)	-	74 (5–802)	<b>16.85</b> (4.7–802)	-	-	-	-
pH	SU	5.87 (5.47–6.53)	<b>7.05</b> (6.5–7.2)	-	6.6 (5.1–8.4)	<b>6.5</b> (4.9–7.9)	-	6.3 (5.5–6.8)	8 (5.8–11.62)	6.3 (6.1–6.4)
Specific conductivity	µS/cm	213,000 (205,000–220,800)	<b>111,500</b> (34,800–179,000)	-	-	<b>183,000</b> (479–763,000)	-	184,800 (118,000–211,000)	-	-
Specific gravity	--	1.13 (1.0961–1.155)	-	-	-	-	-	-	-	-
TDS	mg/L	196,000 (150,000–219,000)	<b>50,550</b> (16,400–97,800)	13,290 (9,972–15,721)	106,390 (680–345,000)	<b>87,800</b> (680–345,000)	164,683 (5,241–356,666)	235,125 (106,000–354,000)	15,802 (1,032–125,304)	73,082 (56,541–108,813)
Total Kjeldahl nitrogen	mg/L	-	<b>171</b> (26–298)	-	-	<b>94.9</b> (5.6–312)	-	-	-	-

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Parameter	Units	Shales					Tight formations			
		Bakken <sup>a</sup>	Barnett <sup>b</sup>	Fayetteville <sup>c</sup>	Marcellus		Cotton Valley Group <sup>f</sup>	Devonian Sandstone <sup>g</sup>	Mesaverde <sup>f</sup>	Oswego <sup>f</sup>
States	n/a	MT, ND	TX	AR	PA <sup>d</sup>	PA, WV <sup>e</sup>	LA, TX	PA	CO, NM, UT, WY	OK
TOC	mg/L	-	<b>9.75</b> (6.2–36.2)	-	160 (1.2–1,530)	<b>89.2</b> (1.2–5,680)	198 (184–212)	-	-	-
Total suspended solids	mg/L	-	<b>242</b> (120–535)	-	352 (4–7,600)	<b>127</b> (6.8–3,220)	-	-	-	-
Turbidity	NTU	-	<b>239</b> (144–314)	-	-	<b>126</b> (2.3–1,540)	-	-	-	-

n/a, not applicable; -, no value available; NC, not calculated; ND, not detected., SU= standard units, **bolded italic** numbers are medians

<sup>a</sup> [Stepan et al. \(2010\)](#). *n* = 3. Concentrations were calculated based on Stepan et al.'s raw data. Samples had charge balance errors of 1.74, -0.752, and -0.220%

<sup>b</sup> [Hayes and Severin \(2012b\)](#). *n* = 16. This data source reported concentrations without direct presentation of raw data.

<sup>c</sup> [Warner et al. \(2013\)](#). *n* = 6. Concentrations were calculated based on Warner et al.'s raw data. Both flowback and produced water included.

<sup>d</sup> [Barbot et al. \(2013\)](#). *n* = 134–159. This data source reported concentrations without direct presentation of raw data.

<sup>e</sup> [Hayes \(2009\)](#). *n* = 31–67. Concentrations were calculated based on Hayes's raw data. Both flowback and produced water included. Non-detects and contaminated blanks omitted.

<sup>f</sup> [Blondes et al. \(2014\)](#). Cotton Valley Group, *n*=2; Mesa Verde, *n* = 1–407; Oswego, *n* = 4–30. Concentrations were calculated based on raw data presented in the U.S. Geological Survey (USGS) National Produced Water Database v2.0.

<sup>g</sup> [Dresel and Rose \(2010\)](#). *n* = 3–15. Concentrations were calculated based on Dresel and Rose's raw data.

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**Table E-3. Reported concentrations of general water quality parameters in produced water for unconventional coalbed basins, presented as: average (minimum–maximum).**

Parameter	Units	Black Warrior <sup>a</sup>	Powder River <sup>b</sup>	Raton <sup>b</sup>	San Juan <sup>b</sup>
States	n/a	AL, MS	MT, WY	CO, NM	AZ, CO, NM, UT
Alkalinity	mg/L	355 (3–1,600)	1,384 (653–2,672)	1,107 (130–2,160)	3,181 (51–11,400)
Ammonium	mg/L	3.60 (0.16–8.91)	-	-	-
Bicarbonate	mg/L	427 (2–1,922)	1,080 (236–3,080)	1,124 (127–2,640)	3,380 (117–13,900)
Carbonate	mg/L	3 (0–64)	2.17 (0.00–139.0)	51.30 (1.30–316.33)	40.17 (0.00–1,178)
Chloride	mg/L	9,078 (11–42,800)	21 (BDL–282)	787 (4.8–8,310)	624 (BDL–20,100)
Chemical oxygen demand	mg/L	830 (0–10,500)	-	-	-
Dissolved oxygen	mg/L	-	1.07 (0.11–3.48)	0.39 (0.01–3.52)	0.51 (0.04–1.69)
DOC	mg/L	3.37 (0.53–61.41)	3.18 (1.09–8.04)	1.26 (0.30–8.54)	3.21 (0.89–11.41)
Hardness as CaCO <sub>3</sub>	mg/L	871 (3–6,150)	-	-	-
Hydrogen sulfide	mg/L	-	-	4.41 (BDL–190.0)	23.00 (23.00–23.00)
Oil and grease	mg/L	-	-	9.10 (0.60–17.6)	-
pH	SU	7.5 (5.3–9.0)	7.71 (6.86–9.16)	8.19 (6.90–9.31)	7.82 (5.40–9.26)
Phosphate	mg/L	0.435 (0.026–3.570)	BDL (BDL–BDL)	0.04 (BDL–1.00)	1.89 (BDL–9.42)
Specific conductivity	μS/cm	20,631 (718–97,700)	1,598 (413–4,420)	3,199 (742–11,550)	5,308 (232–18,066)
TDS	mg/L	14,319 (589–61,733)	997 (252–2,768)	2,512 (244–14,800)	4,693 (150–39,260)
Total Kjeldahl nitrogen	mg/L	6.08 (0.15–38.40)	0.48 (BDL–4.70)	2.61 (BDL–26.10)	0.46 (BDL–3.76)
TOC	mg/L	6.03 (0.00–103.00)	3.52 (2.07–6.57)	1.74 (0.25–13.00)	2.91 (0.95–9.36)
Total suspended solids	mg/L	78 (0–2,290)	11.0 (1.4–72.7)	32.3 (1.0–580.0)	47.2 (1.4–236.0)
Turbidity	NTU	74 (0–539)	8.2 (0.7–57.0)	4.5 (0.3–25.0)	61.6 (0.8–810.0)

n/a, not applicable; -, no value available; BDL, below detection limit.

<sup>a</sup> [DOE \(2014\)](#).  $n = 206$ . Concentrations were calculated based on raw data presented in the reference.

<sup>b</sup> [Dahm et al. \(2011\)](#). Powder River,  $n = 31$ ; Raton,  $n = 40$ ; San Juan,  $n = 20$ . This data source reported concentrations without presentation of raw data.

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### E.2.3. Salinity and Inorganics

1 Table E-4 and Table E-5 provide supporting data on salinity and inorganic constituents of produced  
2 water for 12 formations.

#### E.2.3.1. Processes Controlling Salinity and Inorganics Concentrations

3 Multiple mechanisms likely control elevated salt concentrations in flowback and produced water  
4 and are largely dependent upon post-injection fluid interactions and the formation's stratigraphic  
5 and hydrogeologic environment ([Barbot et al., 2013](#)). High inorganic ionic loads observed in  
6 flowback and produced water are expressed as TDS.

7 Subsurface brines or formation waters are saline fluids associated with the targeted formation.  
8 Shale and sandstone brines are typically much more saline than coalbed waters. After hydraulic  
9 fracturing fluids are injected into the subsurface, the injected fluids (which are typically not sources  
10 of high TDS) mix with in situ brines, which typically contain high ionic loads ([Haluszczak et al.,  
11 2013](#)).

12 Deep brines, present in over- or underlying strata, may naturally migrate into targeted formations  
13 over geologic time or artificially intrude if a saline aquifer is breached during hydraulic fracturing  
14 ([Chapman et al., 2012](#); [Maxwell, 2011](#); [Blauch et al., 2009](#)). Whether it is through natural or induced  
15 intrusion, saline fluids may contact the producing formation and introduce novel salinity sources to  
16 the produced water ([Chapman et al., 2012](#)).

17 The dissolution salts associated with formation solids both increases TDS concentrations and alters  
18 formation porosity and permeability ([Blauch et al., 2009](#)). Additionally, the mobilization of connate  
19 fluids (deposition-associated pore fluids) and formation fluids during hydraulic fracturing likely  
20 contributes to increased TDS levels ([Dresel and Rose, 2010](#); [Blauch et al., 2009](#)). Despite the general  
21 use of fresh water for hydraulic fracturing fluid, some elevated salts in produced water may result  
22 from the use of reused saline flowback or produced water as a hydraulic fracturing base fluid  
23 ([Hayes, 2009](#)).

**Table E-4. Reported concentrations (mg/L) of inorganic constituents contributing to salinity in unconventional shale and tight formations produced water, presented as: average (minimum–maximum) or *median* (minimum–maximum).**

Parameter	Shale					Tight Formations			
	Bakken <sup>a</sup>	Barnett <sup>b</sup>	Fayetteville <sup>c</sup>	Marcellus		Cotton Valley Group <sup>f</sup>	Devonian Sandstone <sup>g</sup>	Mesaverde <sup>f</sup>	Oswego <sup>f</sup>
States	MT, ND	TX	AR	PA <sup>d</sup>	PA, WV <sup>e</sup>	LA, TX	PA	CO, NM, UT, WY	OK
<b>Bromide</b>	-	<b>589</b> (117–798)	111 (96–144)	511 (0.2–1,990)	<b>512</b> (15.8–1,990)	498 (32–1,338)	1,048 (349–1,350)	-	-
<b>Calcium</b>	9,680 (7,540–13,500)	<b>1,600</b> (1,110–6,730)	317 (221–386)	7,220 (38–41,000)	<b>7,465</b> (173–33,000)	19,998 (181–51,400)	20,262 (8,930–34,400)	212 (1.01–4,580)	5,903 (3,609–8,662)
<b>Chloride</b>	119,000 (90,000–133,000)	<b>34,700</b> (9,600–60,800)	9,156 (5,507–12,287)	57,447 (64–196,000)	<b>49,000</b> (64.2–196,000)	101,332 (3,167–221,498.7)	132,567 (58,900–207,000)	4,260 (8–75,000)	44,567 (23,000–75,000)
<b>Fluoride</b>	-	<b>3.8</b> (3.5–12.8)	-	-	<b>0.975</b> (0.077–32.9)	-	-	-	-
<b>Iodine</b>	-	-	-	-	-	20 (1–36)	39 (11–56)	1.01 (1.01–1.01)	-
<b>Nitrate as N</b>	-	-	NC (ND–ND)	-	<b>1.7</b> (0.65–15.9)	-	-	0.6 (0.6–0.6)	-
<b>Nitrite as N</b>	-	<b>4.7</b> (3.5–38.1)	-	-	<b>11.8</b> (1.1–146)	-	-	-	-
<b>Phosphorus</b>	NC (ND–0.03)	<b>0.395</b> (0.19–0.7)	-	-	<b>0.3</b> (0.08–21.8)	-	-	-	-
<b>Potassium</b>	2,970 (0–5,770)	<b>316</b> (80–750)	-	-	<b>337</b> (38–3,950)	1,975 (8–7,099)	858 (126–3,890)	160 (4–2,621)	-

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Parameter	Shale					Tight Formations			
	Bakken <sup>a</sup>	Barnett <sup>b</sup>	Fayetteville <sup>c</sup>	Marcellus		Cotton Valley Group <sup>f</sup>	Devonian Sandstone <sup>g</sup>	Mesaverde <sup>f</sup>	Oswego <sup>f</sup>
States	MT, ND	TX	AR	PA <sup>d</sup>	PA,WV <sup>e</sup>	LA, TX	PA	CO, NM, UT, WY	OK
Silica	7 (6.41–7)	-	52 (13–160)	-	-	4 (4–4)	-	-	-
Sodium	61,500 (47,100–74,600)	<b>18,850</b> (4,370–28,200)	3,758 (3,152–4,607)	21,123 (69–117,000)	<b>21,650</b> (63.8–95,500)	39,836 (1,320–85,623.24)	58,160 (24,400–83,300)	5,828 (132–48,817)	19,460 (13,484–31,328)
Sulfate	660 (300–1,000)	<b>709</b> (120–1,260)	NC (ND–3)	71 (0–763)	<b>58.9</b> (2.4–348)	407 (ND–2,200.46)	20 (1–140)	837 (ND–14,612)	183 (120–271)
Sulfide	-	NC (ND–ND)	-	-	<b>3.2</b> (1.6–5.6)	-	0.7 (0.1–2.5)	-	-
Sulfite	-	-	-	-	<b>12.4</b> (5.2–73.6)	-	-	-	-
TDS	196,000 (150,000–219,000)	<b>50,550</b> (16,400–97,800)	13,290 (9,972–15,721)	106,390 (680–345,000)	<b>87,800</b> (680–345,000)	164,683 (5,241–356,666)	235,125 (106,000–354,000)	15,802 (1,032–125,304)	73,082 (56,541–108,813)

-, no value available; NC, not calculated; ND, not detected. **Bolded italic** numbers are medians.

<sup>a</sup> [Stepan et al. \(2010\)](#).  $n = 3$ . Concentrations were calculated based on Stepan et al.'s raw data. Samples had charge balance errors of 1.74, -0.752, and -0.220%

<sup>b</sup> [Hayes and Severin \(2012b\)](#).  $n = 16$ . This data source reported concentrations without presentation of raw data.

<sup>c</sup> [Warner et al. \(2013\)](#).  $n = 6$ . Concentrations were calculated based on Warner et al.'s raw data. Both flowback and produced water included.

<sup>d</sup> [Barbot et al. \(2013\)](#).  $n = 134–159$ . This data source reported concentrations without presentation of raw data.

<sup>e</sup> [Hayes \(2009\)](#).  $n = 8–65$ . Concentrations were calculated based on Hayes's raw data. Both flowback and produced water included. Non-detects and contaminated blanks omitted.

<sup>f</sup> [Blondes et al. \(2014\)](#) Cotton Valley Group,  $n = 2$ ; Mesa Verde,  $n = 1–407$ ; Oswego,  $n = 4–30$ . Concentrations were calculated based on raw data presented in the USGS National Produced Water Database v2.0.

<sup>g</sup> [Dresel and Rose \(2010\)](#).  $n = 3–15$ . Concentrations were calculated based on Dresel and Rose's raw data.

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**Table E-5. Reported concentrations (mg/L) of inorganic constituents contributing to salinity in produced water for unconventional CBM basins, presented as: average (minimum–maximum).**

Parameter	Black Warrior <sup>a</sup>	Powder River <sup>b</sup>	Raton <sup>b</sup>	San Juan <sup>b</sup>
State	AL, MS	MT, WY	CO, NM	AZ, CO, NM, UT
Barium	45.540 (0.136–352)	0.61 (0.14–2.47)	1.67 (BDL–27.40)	10.80 (BDL–74.0)
Boron	0.185 (0–0.541)	0.17 (BDL–0.39)	0.36 (BDL–4.70)	1.30 (0.21–3.45)
Bromide	-	0.09 (BDL–0.26)	4.86 (0.04–69.60)	9.77 (BDL–43.48)
Calcium	218 (0–1,640)	32.09 (2.00–154.0)	14.47 (0.81–269.0)	53.29 (1.00–5,530)
Chloride	9,078 (11–42,800)	21 (BDL–282)	787 (4.8–8,310)	624 (BDL–20,100)
Fluoride	6.13 (0.00–22.60)	1.57 (0.40–4.00)	4.27 (0.59–20.00)	1.76 (0.58–10.00)
Magnesium	68.12 (0.18–414.00)	14.66 (BDL–95.00)	3.31 (0.10–56.10)	15.45 (BDL–511.0)
Nitrate	8.70 (0.00–127.50)	-	-	-
Nitrite	0.03 (0.00–2.08)	-	-	-
Phosphorus	0.32 (0.00–5.76)	-	-	-
Potassium	12.02 (0.46–74.00)	11.95 (BDL–44.00)	6.37 (BDL–29.40)	26.99 (BDL–970.0)
Silica	8.66 (1.04–18.10)	6.46 (4.40–12.79)	7.05 (4.86–10.56)	12.37 (3.62–37.75)
Sodium	4,353 (126–16,700)	356 (12–1,170)	989 (95–5,260)	1,610 (36–7,834)
Strontium	11.354 (0.015–142.000)	0.60 (0.10–1.83)	5.87 (BDL–47.90)	5.36 (BDL–27.00)
Sulfate	5.83 (0.00–302.00)	5.64 (BDL–300.0)	14.75 (BDL–253.00)	25.73 (BDL–1,800)
TDS	14,319 (589–61,733)	997 (252–2,768)	2,512 (244–14,800)	4,693 (150–39,260)

-, no value available; BDL, below detection limit.

<sup>a</sup> [DOE \(2014\)](#).  $n = 206$ . Concentrations were calculated based on the authors' raw data.

<sup>b</sup> [Dahm et al. \(2011\)](#). Powder River,  $n = 31$ ; Raton,  $n = 40$ ; San Juan,  $n = 20$ . This data source reported concentrations without presentation of raw data.

#### E.2.4. Metals and Metalloids

- 1 Table E-6 and Table E-7 provide supporting data on metal constituents of produced water for 12
- 2 formations.

**Table E-6. Reported concentrations (mg/L) of metals and metalloids from unconventional shale and tight formation produced water, presented as: average (minimum–maximum) or *median* (minimum–maximum).**

Note that calcium, potassium, and sodium appear in Table E-4.

Parameter	Shale					Tight Formation			
	Bakken <sup>a</sup>	Barnett <sup>b</sup>	Fayetteville <sup>c</sup>	Marcellus		Cotton Valley Group <sup>f</sup>	Devonian Sandstone <sup>g</sup>	Mesaverde <sup>f</sup>	Oswego <sup>f</sup>
States	MT, ND	TX	AR	PA <sup>d</sup>	PA, WV <sup>e</sup>	LA, TX	PA	CO, NM, UT, WY	OK
Aluminum	-	<b>0.43</b> (0.37–2.21)	-	-	<b>2.57</b> (0.22–47.2)	-	-	-	-
Antimony	-	NC (ND–ND)	-	-	<b>0.028</b> (0.018–0.038)	-	-	-	-
Arsenic	-	NC (ND–ND)	-	-	<b>0.101</b> (0.013–0.124)	-	-	-	-
Barium	10 (0–24.6)	<b>3.6</b> (0.93–17.9)	4 (3–5)	2,224 (0.24–13,800)	<b>542.5</b> (2.590–13,900)	160 (ND–400.52)	1,488 (7–4,370)	139 (4–257)	-
Beryllium	-	NC (ND–ND)	-	-	-	-	-	-	-
Boron	116 (39.9–192)	<b>30.3</b> (7.0–31.9)	4.800 (2.395–21.102)	-	<b>12.2</b> (0.808–145)	37 (2–100)	-	10 (1–14.2)	-
Cadmium	-	NC (ND–ND)	-	-	-	-	-	-	-
Chromium	-	<b>0.03</b> (0.01–0.12)	-	-	<b>0.079</b> (0.011–0.567)	-	-	-	-
Cobalt	-	<b>0.01</b> (0.01–0.01)	-	-	-	-	-	-	-

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Parameter	Shale					Tight Formation			
	Bakken <sup>a</sup>	Barnett <sup>b</sup>	Fayetteville <sup>c</sup>	Marcellus		Cotton Valley Group <sup>f</sup>	Devonian Sandstone <sup>g</sup>	Mesaverde <sup>f</sup>	Oswego <sup>f</sup>
States	MT, ND	TX	AR	PA <sup>d</sup>	PA, WV <sup>e</sup>	LA, TX	PA	CO, NM, UT, WY	OK
<b>Copper</b>	NC (ND-0.21)	<b>0.29</b> (0.06-0.52)	-	-	<b>0.506</b> (0.253-4.150)	0.7 (0.48-1)	0.04 (0.01-0.13)	-	-
<b>Iron</b>	96 (ND-120)	<b>24.9</b> (12.1-93.8)	7 (1-13)	-	<b>53.65</b> (2.68-574)	-	188 (90-458)	9 (1-29)	61 (41-78)
<b>Lead</b>	-	<b>0.02</b> (0.01-0.02)	-	-	<b>0.066</b> (0.003-0.970)	-	0.02 (0.01-0.04)	-	-
<b>Lithium</b>	-	<b>19.0</b> (2.56-37.4)	9.825 (2.777-28.145)	-	<b>53.85</b> (3.410-323)	23 (1-53)	97.8 (20.2-315)	3 (1-33)	-
<b>Magnesium</b>	1,270 (630-1,750)	<b>255</b> (149-755)	61 (47-75)	632 (17-2,550)	<b>678</b> (40.8-2,020)	1,363 (27-3,712.98)	2,334 (797-3,140)	74 (1-2,394)	753 (486-1,264)
<b>Manganese</b>	7 (4-10.2)	<b>0.86</b> (0.25-2.20)	2 (2-3)	-	<b>2.825</b> (0.369-18.600)	30.33 (30.33-30.33)	19 (5.6-68)	-	-
<b>Mercury</b>	-	NC (ND-ND)	-	-	<i>0.00024</i>	-	-	-	-
<b>Molybdenum</b>	NC (ND-<0.2)	<b>0.02</b> (0.02-0.03)	-	-	-	-	-	-	-
<b>Nickel</b>	-	<b>0.04</b> (0.03-0.05)	-	<b>0.1815</b> (0.007-0.137)	<b>0.419</b> (0.068-0.769)	-	-	-	-
<b>Selenium</b>	-	<b>0.03</b> (0.03-0.04)	-	-	<i>0.004</i>	-	-	-	-
<b>Silver</b>	-	-	-	-	<b>4</b> (3-6)	-	-	-	-

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Parameter	Shale					Tight Formation			
	Bakken <sup>a</sup>	Barnett <sup>b</sup>	Fayetteville <sup>c</sup>	Marcellus		Cotton Valley Group <sup>f</sup>	Devonian Sandstone <sup>g</sup>	Mesaverde <sup>f</sup>	Oswego <sup>f</sup>
States	MT, ND	TX	AR	PA <sup>d</sup>	PA, WV <sup>e</sup>	LA, TX	PA	CO, NM, UT, WY	OK
Strontium	764 (518–1,010)	<b>529</b> (48–1,550)	27 (14–49)	1,695 (0.6–8,460)	<b>1,240</b> (0.580–8,020)	2,312 (39–9,770)	3,890 (404–13,100)	-	-
Thallium	-	NC (ND–0.14)	-	-	<i>0.168</i>	-	-	-	-
Tin	-	NC (ND–ND)	-	-	-	-	-	-	-
Titanium	-	<b>0.02</b> (0.02–0.03)	-	-	-	-	-	-	-
Zinc	7 (2–11.3)	<b>0.15</b> (0.10–0.36)	-	-	<b>0.391</b> (0.087–247)	-	0.20 (0.03–1.26)	-	-

-, no value available; NC, not calculated; ND, not detected; BDL, below detection limit. ***Bolded italic*** numbers are medians.

<sup>a</sup> [Stepan et al. \(2010\)](#). *n* = 3. Concentrations were calculated based on Stepan et al.'s raw data.

<sup>b</sup> [Hayes and Severin \(2012b\)](#). *n* = 16. This data source reported concentrations without presentation of raw data.

<sup>c</sup> [Warner et al. \(2013\)](#). *n* = 6. Concentrations were calculated based on Warner et al.'s raw data. Both flowback and produced water included.

<sup>d</sup> [Barbot et al. \(2013\)](#). *n* = 134–159. This data source reported concentrations without presentation of data.

<sup>e</sup> [Hayes \(2009\)](#). *n* = 48. Concentrations were calculated based on Hayes's raw data. Both flowback and produced water included. Non-detects and contaminated blanks omitted.

<sup>f</sup> [Blondes et al. \(2014\)](#). Cotton Valley Group, *n* = 2; Mesa Verde, *n* = 1–407; Oswego, *n* = 4–30. Concentrations were calculated based on raw data presented in the USGS National Produced Water Database v2.0.

<sup>g</sup> [Dresel and Rose \(2010\)](#). *n* = 3–15. Concentrations were calculated based on Dresel and Rose's raw data.

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**Table E-7. Reported concentrations (mg/L) of metals and metalloids from unconventional coalbed produced water, presented as: average (minimum–maximum).**

Parameter	Black Warrior <sup>a</sup>	Powder River <sup>b</sup>	Raton <sup>b</sup>	San Juan <sup>b</sup>
States	AL, MS	MT, WY	CO, NM	AZ, CO, NM, UT
Aluminum	0.037 (0–0.099)	0.018 (BDL–0.124)	0.193 (BDL–2,900)	0.069 (BDL–0.546)
Antimony	0.006 (0.00–0.022)	BDL (BDL–BDL)	BDL (BDL–BDL)	BDL (BDL–BDL)
Arsenic	0.002 (0.0–0.085)	0.001 (BDL–0.004)	0.010 (BDL–0.060)	0.001 (BDL–0.020)
Barium	45.540 (0.136–352)	0.61 (0.14–2.47)	1.67 (BDL–27.40)	10.80 (BDL–74.0)
Beryllium	0.0 (0.0–0.008)	BDL (BDL–BDL)	BDL (BDL–BDL)	BDL (BDL–BDL)
Boron	0.185 (0–0.541)	0.17 (BDL–0.39)	0.36 (BDL–4.70)	1.30 (0.21–3.45)
Cadmium	0.001 (0.00–0.015)	BDL (BDL–0.002)	0.002 (BDL–0.003)	0.002 (BDL–.006)
Calcium	218 (0–1,640)	32.09 (2.00–154.0)	14.47 (0.81–269.0)	53.29 (1.00–5,530)
Cesium	0.011 (0.0–0.072)	-	-	-
Chromium	0.002 (0.0–0.351)	0.012 (BDL–0.250)	0.105 (BDL–3.710)	0.002 (BDL–0.023)
Cobalt	0.023 (0.00–0.162)	BDL (BDL–BDL)	0.001 (BDL–0.018)	0.001 (BDL–0.017)
Copper	0.001 (0.0–0.098)	0.078 (BDL–1.505)	0.091 (BDL–4.600)	0.058 (BDL–0.706)
Iron	8.956 (0.045–93.100)	1.55 (BDL–190.0)	7.18 (0.09–95.90)	6.20 (BDL–258.0)
Lead	0.008 (0.00–0.250)	BDL (BDL–BDL)	0.023 (BDL–0.233)	0.023 (BDL–0.390)
Lithium	1.157 (0–8.940)	0.13 (BDL–0.34)	0.32 (0.01–1.00)	1.61 (0.21–4.73)
Magnesium	68.12 (0.18–414.00)	14.66 (BDL–95.00)	3.31 (0.10–56.10)	15.45 (BDL–511.0)
Manganese	0.245 (0.006–4.840)	0.02 (BDL–0.16)	0.11 (0.01–2.00)	0.19 (BDL–1.34)
Mercury	0.000 (0.000–0.000)	-	-	-
Molybdenum	0.002 (0–0.083)	0.005 (BDL–0.029)	0.002 (BDL–0.035)	0.020 (BDL–0.040)
Nickel	0.015 (0.0–0.358)	0.141 (BDL–2.61)	0.015 (0.004–0.11)	0.020 (BDL–0.13)
Potassium	12.02 (0.46–74.00)	11.95 (BDL–44.00)	6.37 (BDL–29.40)	26.99 (BDL–970.0)
Rubidium	0.013 (0.0–0.114)	-	-	-
Selenium	0.002 (0.00–0.063)	0.006 (BDL–0.046)	0.017 (BDL–0.100)	0.018 (BDL–0.067)
Silver	0.015 (0.0–0.565)	0.003 (0.003–0.003)	0.015 (BDL–0.140)	BDL (BDL–BDL)
Sodium	4,353 (126–16,700)	356 (12–1,170)	989 (95–5,260)	1,610 (36–7,834)
Strontium	11.354 (0.015–142.000)	0.60 (0.10–1.83)	5.87 (BDL–47.90)	5.36 (BDL–27.00)
Thallium	-	-	-	-
Tin	0.00 (0.00–0.009)	0.006 (BDL–0.028)	0.008 (BDL–0.021)	0.017 (BDL–0.039)
Titanium	0.003 (0.0–0.045)	BDL (BDL–0.002)	BDL (BDL–0.002)	0.004 (BDL–0.020)

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Parameter	Black Warrior <sup>a</sup>	Powder River <sup>b</sup>	Raton <sup>b</sup>	San Juan <sup>b</sup>
States	AL, MS	MT, WY	CO, NM	AZ, CO, NM, UT
Vanadium	0.001 (0.0–0.039)	BDL (BDL–BDL)	0.001 (BDL–0.013)	BDL (BDL–BDL)
Zinc	0.024 (0.0–0.278)	0.063 (BDL–0.390)	0.083 (0.010–3.900)	0.047 (0.005–0.263)

-, no value available; BDL, below detection limit.

<sup>a</sup> DOE (2014).  $n = 206$ . Concentrations were calculated based on the authors' raw data.

<sup>b</sup> Dahm et al. (2011). Powder River,  $n = 31$ ; Raton,  $n = 40$ ; San Juan,  $n = 20$ . This data source reported concentrations without presentation of raw data.

#### E.2.4.1. Processes Controlling Mineral Precipitation and Dissolution

1 Hydraulic fracturing treatments introduce fluids into the subsurface that are not in equilibrium  
 2 with respect to formation mineralogy. Subsurface geochemical equilibrium modeling and  
 3 saturation indices are therefore used to assess the solution chemistry of unconventional produced  
 4 water and the subsequent likelihood of precipitation and dissolution reactions (Engle and Rowan,  
 5 2014; Barbot et al., 2013). Dissolution and precipitation reactions between fracturing fluids,  
 6 formation solids, and formation water contribute to the chemistry of flowback and produced water.

7 For example, early flowback fluids may be under-saturated with respect to certain constituents or  
 8 minerals associated with formation solids. Through time, as fluid-rock geochemistry returns to  
 9 equilibrium, formation minerals will dissolve into solution and return in flowback.

10 Depending upon the formation chemistry and composition of the hydraulic fracturing fluid, the  
 11 hydraulic fracturing fluid may initially have a lower ionic strength than existing formation fluids.  
 12 Consequently, salts, carbonate, sulfate, and silicate minerals may undergo dissolution or  
 13 precipitation. Proppants may also undergo dissolution or serve as nucleation sites for precipitation  
 14 (McLin et al., 2011).

15 Currently, relatively little literature quantitatively explores subsurface dissolution and  
 16 precipitation reactions between hydraulic fracturing fluids and formation solids and water.  
 17 However, the processes that take place will likely be a function of the solubilities of the minerals,  
 18 the chemistry of the fluid, pH, redox conditions, and temperature.

19 Documented dissolution processes in unconventional resources include the dissolution of feldspar  
 20 followed by sodium enrichment in coalbed produced water (Rice et al., 2008). Dissolution of  
 21 barium-rich minerals (barite ( $\text{BaSO}_4$ ) and witherite ( $\text{BaCO}_3$ )), and strontium-rich minerals (celestite  
 22 ( $\text{SrSO}_4$ ) and strontianite ( $\text{SrCO}_3$ )) are known to enrich shale produced waters in barium and  
 23 strontium (Chapman et al., 2012).

24 Known precipitation processes in unconventional resources include the precipitation of carbonate  
 25 and subsequent reduction of calcium and magnesium concentrations in coalbed produced water  
 26 (Rice et al., 2008). Additionally, calcium carbonate precipitation is suspected to cause declines in pH  
 27 and alkalinity levels in shale produced water (Barbot et al., 2013).

1 The subsurface processes associated with fluid-rock interactions take place over a scale of weeks to  
2 months through the generation of flowback and produced water. Note that the types and extent of  
3 subsurface dissolution and precipitation reactions change with time, from injection through  
4 flowback and production. For instance, [Engle and Rowan \(2014\)](#) found that early Marcellus Shale  
5 flowback was under-saturated with respect to gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ), halite ( $\text{NaCl}$ ), celestite,  
6 strontianite, and witherite, indicating that these minerals would dissolve in the subsurface. Fluids  
7 were oversaturated with respect to barite. Saturation indices for gypsum, halite, celestite, and  
8 barite all increased during production. Knowing when dissolution and precipitation will likely  
9 occur is important, because dissolution and precipitation of minerals change formation  
10 permeability and porosity, which can affect production ([André et al., 2006](#)).

11 Additionally, pyrite ( $\text{FeS}_2$ ) is an important minor mineral in reduced sedimentary rocks. Pyrite is  
12 the primary form of sulfur and iron occurrence in shales ([Leventhal and Hosterman, 1982](#)) and is  
13 also a common mineral phase generated in coals in which organic matter is closely associated  
14 ([Ward, 2002](#)). Pyrite content in shales can vary from less than 1% to several percent ([Chermak and](#)  
15 [Schreiber, 2014](#); [Vulgamore et al., 2007](#)). Researchers have found a strong association of trace  
16 metals (i.e., nickel, copper, cadmium, chromium, cobalt, lead, selenium, vanadium, and zinc) with  
17 pyrite in shales ([Chermak and Schreiber, 2014](#); [Tuttle et al., 2009](#); [Leventhal and Hosterman, 1982](#)).

18 Although studies considering pyrite oxidation within the context of hydraulic fracturing are  
19 currently lacking, it is likely that the introduction of oxygenated fluids to freshly exposed surfaces  
20 in the subsurface during hydraulic fracturing can initiate limited, short-term pyrite oxidation or  
21 dissolution. Pyrite dissolution may increase iron and trace element concentrations and acidity in  
22 produced waters ([Nordstrom and Alpers, 1999](#); [Moses and Herman, 1991](#)).

23 The extent to which the oxidative dissolution of pyrite would exert a control on post-injection  
24 subsurface fluid chemistry is unknown, although an ongoing U.S. Geological Survey (USGS) study  
25 anticipates it may be more significant than previously hypothesized ([Li and Brantley, 2011](#)).  
26 Regardless, relative to other reactions contributing to the composition of flowback and produced  
27 water (i.e., dissolution of salts), pyrite oxidation appears to be less significant. Ultimately, reactions  
28 resulting from temporary changes in subsurface redox conditions will be less important relative to  
29 other reactions that are less redox-dependent.

## **E.2.5. Naturally Occurring Radioactive Material (NORM) and Technically Enhanced Naturally Occurring Radioactive Material (TENORM)**

### ***E.2.5.1. Formation Solids Levels of NORM***

30 Elevated uranium levels in formation solids have been used to identify potential areas of natural  
31 gas production for decades ([Fertl and Chilingar, 1988](#)). Marine black shales are estimated to contain  
32 an average of 5–20 ppm uranium depending on depositional conditions, compared to an average of  
33 less than 5 ppm among all shales ([USGS, 1961](#)). Shales that bear significant levels of uranium  
34 include the Barnett in Texas, the Woodford in Oklahoma, the New Albany in the Illinois Basin, the  
35 Chattanooga Shale in the southeastern United States, and a group of black shales in Kansas and  
36 Oklahoma ([Swanson, 1955](#)).

1 [Bank et al. \(2012\)](#) identified Marcellus samples with uranium ranging from 4–72 ppm, with an  
2 average of 30 ppm. Additionally, shale samples taken from three counties within the Marcellus  
3 Shale had uranium concentrations ranging from 8 to 84 ppm ([BTGS, 2011](#); [Hatch and Leventhal,  
4 1981](#)). [Chermak and Schreiber \(2014\)](#) compiled mineralogy and trace element data available in the  
5 literature for nine U.S. hydrocarbon-producing shales. In this combined data set, uranium levels  
6 among different shale plays were found to vary over three orders of magnitude, with samples of the  
7 Utica Shale containing approximately 0–5 ppm uranium and samples of the Woodford Shale  
8 containing uranium in the several-hundred-ppm range.

9 [Vine \(1956\)](#) reported that the principal uranium-bearing coal deposits of the United States are  
10 found in Cretaceous and Tertiary formations in the northern Great Plains and Rocky Mountains; in  
11 some areas of the West, coal deposits have been found with uranium concentrations in the range of  
12 thousands of ppm or greater. In contrast, most Mississippian, Pennsylvanian, and Permian coals in  
13 the north-central and eastern United States contain less than 10 ppm uranium, rarely containing  
14 50 ppm or more.

#### **E.2.5.2. Produced Water Levels of TENORM**

15 Background data on NORM in the Marcellus Shale and Devonian sandstones are given in Table E-8.

**Table E-8. Reported concentrations (in pCi/L) of radioactive constituents in unconventional shale and sandstone produced water, presented as: average (minimum–maximum) or *median* (minimum–maximum).**

Parameter	Marcellus			Devonian Sandstone <sup>a</sup>		
	States	NY, PA <sup>b</sup>	PA NORM STUDY ( <a href="#">PA DEP, 2015</a> )			
			Flowback <sup>c</sup>		Conventional Produced Water <sup>d</sup>	Unconventional Produced Water <sup>e</sup>
Gross alpha		<b>6,845</b> (ND–123,000)	<b>10,700</b> (288–71,000)	<b>1,835</b> (465–2,570)	<b>11,300</b> (2,240–41,700)	-
Gross beta		<b>1,170</b> (ND–12,000)	<b>2,400</b> (742–21,300)	<b>909</b> (402–1,140)	<b>3,445</b> (1.5–7,600)	-
Radium-226		<b>1,869</b> (ND–16,920)	<b>4,500</b> (551–25,500)	<b>243</b> (81 – 819)	<b>6,300</b> (1,700–26,600)	<b>2,367</b> (200–5,000)
Radium-228		<b>557</b> (ND–2,589)	<b>633</b> (248–1,740)	<b>128</b> (26 – 896)	<b>941</b> (366–1,900)	-
Total Radium		<b>2,530</b> (0.192–18,045)	-	<b>371</b> (107 – 1,715)	<b>7,180</b> (2,336–28,500)	-
Uranium <sup>235</sup>		1 (ND–20)	-	-	-	-
Uranium <sup>238</sup>		42 (ND–497)	-	-	-	-

n/a, not applicable; -, no value available; BDL, below detection limit. ***Bolded italic*** numbers are medians.

<sup>a</sup> [Dresel and Rose \(2010\)](#). *n* = 3. Concentrations presented were calculated based on Dresel and Rose's raw data.

<sup>b</sup> [Rowan et al. \(2011\)](#). *n* = 51. Concentrations presented were calculated based on Rowan et al.'s raw data for Marcellus samples. Uranium data from Barbot et al. (2013) *n* = 14.

<sup>c</sup> [PA DEP \(2015\)](#). *n* = 9. Data reported in Table 3-14.

<sup>d</sup> [PA DEP \(2015\)](#). *n* = 9. Values calculated from Table 3-15 for unfiltered samples.

<sup>e</sup> [PA DEP \(2015\)](#). *n* = 4. Values calculated from Table 3-15 for unfiltered samples.

### **E.2.5.3. Mobilization of Naturally Occurring Radioactive Material**

1 Similar to conventional oil and gas production, in unconventional oil and gas production,  
2 radionuclides native to the targeted formation return to the surface with produced water. The  
3 principal radionuclides found in oil and gas produced waters include radium-226 of the uranium-  
4 238 decay series and radium-228 of the thorium-232 decay series ([White, 1992](#)). Levels of  
5 TENORM in produced water are controlled by geologic and geochemical interactions between  
6 injected and formation fluids, and the targeted formation ([Bank, 2011](#)). Mechanisms controlling  
7 NORM mobilization into produced water include (1) the TENORM content of the targeted  
8 formation; (2) factors governing the release of radionuclides, particularly radium, from the  
9 reservoir matrix; and (3) the geochemistry of the produced water ([Choppin, 2007, 2006](#); [Fisher,](#)  
10 [1998](#)).

11 Organic-rich shales and coals are enriched in uranium, thorium, and other trace metals in  
12 concentrations several times above those seen in typical shales or sedimentary rocks ([Diehl et al.,](#)  
13 [2004](#); [USGS, 1997](#); [Wignall and Myers, 1988](#); [Tourtelot, 1979](#); [Vine and Tourtelot, 1970](#)). Unlike  
14 shales and coals, sandstones are generally not organic-rich source rocks themselves. Instead,  
15 hydrocarbons migrate into these formations over long periods of time ([Clark and Veil, 2009](#)). Since  
16 TENORM and organic contents are typically positively correlated due to the original, reduced  
17 depositional environment ([Fertl and Chilingar, 1988](#)), it is unlikely that sandstones would be  
18 enriched in TENORM to the same extent as oil- and gas-bearing shales and coals. Therefore, concern  
19 related to TENORM within produced water is focused on operations targeting shales and coalbeds.

20 Radium is most soluble and mobile in chloride-rich, high-TDS, reducing environments ([Sturchio et](#)  
21 [al., 2001](#); [Zapeczka and Szabo, 1988](#); [Langmuir and Riese, 1985](#)). In formation fluids with high TDS,  
22 calcium, potassium, magnesium, and sodium compete with dissolved radium for sorption sites,  
23 limiting radium sorption onto solids and allowing it to accumulate in solution at higher  
24 concentrations ([Fisher, 1998](#); [Webster et al., 1995](#)). The positive correlation between TDS and  
25 radium is well established and TDS is a useful indicator of radium and TENORM activity within  
26 produced water, especially in lithologically homogenous reservoirs ([Rowan et al., 2011](#); [Sturchio et](#)  
27 [al., 2001](#); [Fisher, 1998](#); [Kraemer and Reid, 1984](#)).

28 Uranium and thorium are poorly soluble under reducing conditions and are therefore more  
29 concentrated in formation solids than in solution ([Fisher, 1998](#); [Kraemer and Reid, 1984](#); [Langmuir](#)  
30 [and Herman, 1980](#)). However, because uranium becomes more soluble in oxidizing environments,  
31 the introduction of relatively oxygen-rich fracturing fluids may promote the temporary  
32 mobilization of uranium during hydraulic fracturing and early flowback. In addition, the physical  
33 act of hydraulic fracturing creates fresh fractures and exposes organic-rich and highly reduced  
34 surfaces from which radionuclides could be released from the rock into formation fluids.

35 Produced water geochemistry determines, in part, the fate of subsurface radionuclides, particularly  
36 radium. Radium may remain in the host mineral or it may be released into formation fluids, where  
37 it can remain in solution as the dissolved  $Ra^{2+}$  ion, be adsorbed onto oxide grain coatings or clay  
38 particles by ion exchange, substitute for other cations during the precipitation of minerals, or form



1 complexes with chloride, sulfate, and carbonate ions ([Rowan et al., 2011](#); [Sturchio et al., 2001](#);  
2 [Langmuir and Riese, 1985](#)). Uranium- and thorium-containing materials with a small grain size, a  
3 large surface-to-volume ratio, and the presence of uranium and thorium near grain surfaces  
4 promote the escape of radium into formation fluids. [Vinson et al. \(2009\)](#) point to alpha decay along  
5 fracture surfaces as a primary control on radium mobilization in crystalline bedrock aquifers.  
6 Radium may also occur in formation fluids due to other processes, such as the decay of dissolved  
7 parent isotopes and adsorption-desorption reactions on formation surfaces ([Sturchio et al., 2001](#)).

8 Preliminary results from fluid-rock interaction studies ([Bank, 2011](#)) indicate that a significant  
9 percentage of uranium in the Marcellus Shale may be subject to mobilization by hydrochloric acid,  
10 which is used as a fracturing fluid additive. Understanding these processes will determine the  
11 extent to which such processes might influence the TENORM content of flowback and produced  
12 water.

### **E.2.6. Organics**

13 Background data on organics in seven formations is given in Table E-9.

**Table E-9. Concentrations of select organic parameters from unconventional shale, a tight formation, and coalbed produced water, presented as: average (minimum–maximum) or *median* (minimum–maximum).**

Parameter	Unit	Shale			Tight Formation	Coal			
		Barnett <sup>a</sup>	Marcellus		Cotton Valley Group <sup>d</sup>	Powder River <sup>e</sup>	Raton <sup>e</sup>	San Juan <sup>e</sup>	Black Warrior <sup>f</sup>
States	n/a	TX	PA <sup>b</sup>	PA, WV <sup>c</sup>	LA, TX	MT, WY	CO, NM	AZ, CO, NM, UT	AL, MS
<b>TOC</b>	mg/L	<b>9.75</b> (6.2–36.2)	160 (1.2–1,530)	<b>89.2</b> (1.2–5680)	198 (184–212)	3.52 (2.07–6.57)	1.74 (0.25–13.00)	2.91 (0.95–9.36)	6.03 (0.00–103.00)
<b>DOC</b>	mg/L	<b>11.2</b> (5.5–65.3)	43 (5–695)	<b>117</b> (3.3–5,960)	-	3.18 (1.09–8.04)	1.26 (0.30–8.54)	3.21 (0.89–11.41)	3.37 (0.53–61.41)
<b>BOD</b>	mg/L	<b>582</b> (101–2,120)	-	<b>141</b> (2.8–12,400)	-	-	-	-	-
<b>Oil and grease</b>	mg/L	<b>163.5</b> (88.2–1,430)	74 (5–802)	<b>16.9</b> (4.7–802)	-	-	9.10 (0.60–17.6)	-	-
<b>Benzene</b>	µg/L	680 (49–5,300)	-	<b>220</b> (5.8–2,000)	-	-	4.7 (BDL–220.0)	149.7 (BDL–500.0)	-
<b>Toluene</b>	µg/L	760 (79–8,100)	-	<b>540</b> (5.1–6,200)	-	-	4.7 (BDL–78.0)	1.7 (BDL–6.2)	-
<b>Ethylbenzene</b>	µg/L	29 (2.2–670)	-	<b>42</b> (7.6–650)	-	-	0.8 (BDL–18.0)	10.5 (BDL–24.0)	-

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Parameter	Unit	Shale			Tight Formation	Coal			
		Barnett <sup>a</sup>	Marcellus		Cotton Valley Group <sup>d</sup>	Powder River <sup>e</sup>	Raton <sup>e</sup>	San Juan <sup>e</sup>	Black Warrior <sup>f</sup>
States	n/a	TX	PA <sup>b</sup>	PA, WV <sup>c</sup>	LA, TX	MT, WY	CO, NM	AZ, CO, NM, UT	AL, MS
Xylenes	µg/L	360 (43–1,400)	-	<b>300</b> (15–6,500)	-	-	9.9 (BDL–190.0)	121.2 (BDL–327.0)	-
Average total BTEX <sup>g</sup>	µg/L	1,829	2,910	1,102	-	-	20.1	283.1	-

n/a, not applicable; -, no value available; BDL, below detection limit. ***Bolded italic*** numbers are medians.

<sup>a</sup> [Hayes and Severin \(2012b\)](#). *n* = 16. This data source reported concentrations without presentation of raw data.

<sup>b</sup> [Barbot et al. \(2013\)](#). *n* = 55; no presentation of raw data.

<sup>c</sup> [Hayes \(2009\)](#) *n* = 13-67. Concentrations were calculated based on Hayes' raw data. Both flowback and produced water included. Non-detects and contaminated blanks omitted.

<sup>d</sup> [Blondes et al. \(2014\)](#). *n* = 2. Concentrations were calculated based on raw data presented in the USGS National Produced Water Database v2.0.

<sup>e</sup> [Dahm et al. \(2011\)](#). Powder River, *n* = 31; Raton, *n* = 40; San Juan, *n* = 20. This data source reported concentrations without presentation of raw data.

<sup>f</sup> [DOE \(2014\)](#). *n* = 206. Concentrations were calculated based on the authors' raw data.

<sup>g</sup> Average total BTEX was calculated by summing the average/median concentrations of benzene, toluene, ethylbenzene, and xylenes for a unique formation or basin. Minimum to maximum ranges were not calculated due to inaccessible raw data.

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1 Several classes of naturally occurring organic chemicals are present in conventional and  
2 unconventional produced waters, with large concentration ranges ([Lee and Neff, 2011](#)). These  
3 organic classes include total organic carbon (TOC); saturated hydrocarbons; BTEX (benzene,  
4 toluene, ethylbenzene, and xylenes); and polyaromatic hydrocarbons (PAHs) (see Table E-9). While  
5 TOC concentrations in produced water are detected at the milligrams to grams per liter level,  
6 concentrations of individual organic compounds are typically detected at the micrograms to  
7 milligrams per liter level.

8 TOC indicates the level of dissolved and undissolved organics in produced water, including non-  
9 volatile and volatile organics ([Acharya et al., 2011](#)). TOC concentrations in conventional produced  
10 water vary widely from less than 0.1 mg/L to more than 11,000 mg/L. Average TOC concentrations  
11 in unconventional produced water range from less than 2.00 mg/L in the Raton CBM basin to  
12 approximately 200 mg/L in the Cotton Valley Group sandstones, although individual measurements  
13 have exceeded 5,000 mg/L in the Marcellus Shale (see Table E-9).

14 Dissolved organic carbon (DOC) is a general indicator of organic loading and is the fraction of  
15 organic carbon available for complexing with metals and supporting microbial growth. DOC values  
16 in unconventional produced water range from less than 1.50 mg/L (average) in the Raton Basin to  
17 more than 115 mg/L (median) in the Marcellus Shale (see Table E-9). Individual DOC  
18 concentrations in the Marcellus Shale produced water approach 6,000 mg/L. For comparison, DOC  
19 levels in fresh water systems are typically below 5 mg/L, while raw wastewater can exceed  
20 50 mg/L ([Katsoyiannis and Samara, 2007](#); [Muylaert et al., 2005](#)).

21 Biochemical oxygen demand (BOD) is a conventional pollutant under the U.S. Clean Water Act. It is  
22 an indirect measure of biodegradable organics in produced water and an estimate of the oxygen  
23 demand on a receiving water. Median BOD levels for Barnett and Marcellus Shales produced water  
24 exceed 30 mg/L, and both reported maximum concentrations exceeding 12,000 mg/L (Table E-9).  
25 In some circumstances wide variation in produced water median BOD levels may be reflective of  
26 flowback reuse in fracturing fluids ([Hayes, 2009](#)).

27 Lastly, BTEX is associated with petroleum. Benzene was found in produced water from several  
28 basins: average produced water benzene concentration from the Barnett Shale was 680 µg/L, from  
29 the Marcellus Shale was 220 µg/L (median), and from the San Juan Basin was 150 µg/L (see Table  
30 E-9). Total BTEX concentrations for conventional produced water vary widely from less than  
31 100 µg/L to nearly 580,000 µg/L. For comparison, average total BTEX concentrations in  
32 unconventional produced water range from 20 µg/L in the Raton Basin to nearly 3,000 µg/L in the  
33 Marcellus play (see Table E-9). From these data, average total BTEX levels in shale produced water  
34 are one to two orders of magnitude higher than those in CBM produced water.

35 In addition to abundant BTEX, a variety of volatile and semi-volatile organic compounds VOCs and  
36 SVOCs have been detected in shale and coalbed produced water. Shale produced water contains  
37 naphthalene, alkylated toluenes, and methylated aromatics in the form of several benzene and  
38 phenol compounds, as shown in Table E-10. Like BTEX, naphthalene, methylated phenols, and  
39 acetophenone are associated with petroleum. Detected shale produced water organics such as

- 1 acetone, 2-butanone, carbon disulfide, and pyridine are potential remnants of chemical additives  
 2 used as friction reducers or industrial solvents ([Hayes, 2009](#)).

**Table E-10. Reported concentrations ( $\mu\text{g/L}$ ) of organic constituents in produced water for two unconventional shale formations, presented as: average (minimum–maximum) or median (minimum–maximum).**

Parameter	Barnett <sup>a</sup>	Marcellus <sup>b</sup>
	States TX	MD, NY, OH, PA, VA, WY
Acetone	145 (27–540)	<b>83</b> (14–5,800)
Carbon disulfide	-	<b>400</b> (19–7,300)
Chloroform	-	28
Isopropylbenzene	35 (0.8–69)	<b>120</b> (86–160)
Naphthalene	238 (4.8–3,100)	<b>195</b> (14–1,400)
Phenolic compounds	<b>119.65</b> (9.3–230)	-
1,2,4-Trimethylbenzene	173 (6.9–1,200)	<b>66.5</b> (7.7–4,000)
1,3,5-Trimethylbenzene	59 (6.4–300)	<b>33</b> (5.2–1,900)
1,2-Diphenylhydrazine	4.2 (0.5–7.8)	-
1,4-Dioxane	6.5 (3.1–12)	-
2-Methylnaphthalene	1,362 (5.4–20,000)	<b>3.4</b> (2–120)
2-Methylphenol	28.3 (5.8–76)	<b>13</b> (11–15)
2,4-Dichlorophenol	(ND–15)	-
2,4-Dimethylphenol	14.5 (8.3–21)	12
3-Methylphenol and 4-Methylphenol	41 (7.8–100)	<b>11.5</b> (0.35–16)
Acetophenone	(ND–4.6)	<b>13</b> (10–22)
Benzidine	(ND–35)	-
Benzo(a)anthracene	(ND–17.0)	-
Benzo(a)pyrene	(ND–130.0)	6.7
Benzo(b)fluoranthene	42.2 (0.5–84.0)	10
Benzo(g,h,i)perylene	42.3 (0.7–84.0)	6.9
Benzo(k)fluoranthene	32.8 (0.6–65.0)	5.9
Benzyl alcohol	81.5 (14.0–200)	<b>41</b> (17–750)
Bis(2-Ethylhexyl) phthalate	210 (4.8–490)	<b>20</b> (9.6–870)
Butyl benzyl phthalate	34.3 (1.9–110)	-

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Parameter	Barnett <sup>a</sup>	Marcellus <sup>b</sup>
States	TX	MD, NY, OH, PA, VA, WY
Chrysene	120 (0.57–240)	-
Di-n-octyl phthalate	(ND–270)	15
Di-n-butyl phthalate	41 (1.5–120)	<b>14</b> (11–130)
Dibenz(a,h)anthracene	77 (3.2–150)	<b>3.2</b> (2.3–11)
Diphenylamine	5.3 (0.6–10.0)	-
Fluoranthene	(ND–0.18)	6.1
Fluorene	0.8 (0.46–1.3)	8.4
Indeno(1,2,3-cd)pyrene	71 (2.9–140)	<b>3.1</b> (2.4–9.5)
N-Nitrosodiphenylamine	8.9 (7.8–10)	2.7
N-Nitrosomethylethylamine	(ND–410)	-
Phenanthrene	107 (0.52–1,400)	<b>9.75</b> (3–22)
Phenol	63 (17–93)	<b>10</b> (2.4–21)
Pyrene	0.2 (ND–0.18)	13
Pyridine	413 (100–670)	<b>250</b> (10–2,600)

-, no value available; ND, not detected.

<sup>a</sup> [Hayes and Severin \(2012b\)](#). *n* = 16. Data from days 1–23 of flowback. This data source reported concentrations without presentation of raw data.

<sup>b</sup> [Hayes \(2009\)](#). *n* = 1–35. Data from days 1–90 of flowback. Concentrations were calculated from Hayes' raw data. Non-detects and contaminated blanks omitted.

1 The organic profile of CBM produced water is characterized by high levels of aromatic and  
2 halogenated compounds compared to other unconventional produced waters ([Sirivedhin and](#)  
3 [Dallbauman, 2004](#)). PAHs and phenols are the most common organic compounds found in coalbed  
4 produced water. Produced water from coalbeds in the Black Warrior Basin mainly contains  
5 phenols, multiple naphthalic PAHs, and various decanoic and decenoic fatty acids (see Table E-11).  
6 CBM-associated organics are also known to include biphenyls, alkyl aromatics, hydroxypyridines,  
7 aromatic amines, and nitrogen-, oxygen-, and sulfur-bearing heterocyclics ([Orem et al., 2014](#);  
8 [Pashin et al., 2014](#); [Benko and Drewes, 2008](#); [Orem et al., 2007](#); [Fisher and Santamaria, 2002](#)).

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**Table E-11. Reported concentrations of organic constituents in 65 samples of produced water from the Black Warrior CBM Basin, presented as average (minimum–maximum).**

Parameter	Number of observations	Concentration (µg/L) <sup>a</sup>
States	-	AL, MS
Benzothiazole	45	0.25 (0.01–3.04)
Caprolactam	10	0.75 (0.02–2.39)
Cyclic octaatomic sulfur	29	1.06 (0.10–9.63)
Dimethyl-naphthalene	39	0.79 (0.01–9.51)
Diethyl phthalate	57	0.21 (0.01–2.30)
Dodecanoic acid	30	1.13 (0.67–2.52)
Hexadecanoic acid	50	1.58 (1.17–3.02)
Hexadecenoic acid	25	1.69 (1.13–8.37)
Methyl-biphenyl	18	0.25 (0.01–2.13)
Methyl-naphthalene	52	0.77 (0.01–15.55)
Methyl-quinoline	31	0.96 (0.03–3.75)
Naphthalene	49	0.41 (0.01–6.57)
Octadecanoic acid	32	1.95 (1.62–3.73)
Octadecenoic acid	29	1.87 (1.60–3.47)
Phenol, 2,4-bis(1,1-dimethyl)	21	0.45 (0.01–4.94)
Phenol, 4-(1,1,3,3-tetramethyl)	17	1.65 (0.01–18.34)
Phenolic compounds	-	19.06 (ND–192.00)
Tetradecanoic acid	53	1.51 (0.94–5.32)
Tributyl phosphate	23	0.26 (0.01–2.66)
Trimethyl-naphthalene	23	0.65 (0.01–4.49)
Triphenyl phosphate	6	1.18 (0.01–6.77)

-, no value available.

<sup>a</sup> [DOE \(2014\)](#). Concentrations were calculated based on the authors' raw data.

1 [Hayes \(2009\)](#) characterized the content of Marcellus Shale produced water including organics (see  
2 Table E-10). The author tested for the majority of VOCs and SVOCs, pesticides and PCBs, based on  
3 the recommendation of the Pennsylvania and West Virginia Departments of Environmental  
4 Protection. Only 0.5% of VOCs and 0.03% of SVOCs in the produced water were detected above  
5 1 mg/L. Approximately 96% of VOCs, 98% of SVOCs, and virtually all pesticides and PCBs were at  
6 nondetectable levels.

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### E.2.7. Chemical Reactions

1 Section E.2.7.1 describes general aspects of subsurface chemical reactions that might occur during  
2 hydraulic fracturing operations. Here we augment the discussion by describing subsurface chemical  
3 processes.

#### E.2.7.1. Injected Chemical Processes

4 Hydraulic fracturing injects relatively oxygenated fluids into a reducing environment, which may  
5 mobilize trace or major constituents into solution. Injection of oxygenated fluids may lead to  
6 short-term changes in the subsurface redox state, as conditions may shift from reducing to  
7 oxidizing. The chemical environment in hydrocarbon-rich unconventional reservoirs, such as black  
8 shales, is generally reducing, as evidenced by the presence of pyrite and methane ([Engle and  
9 Rowan, 2014](#); [Dresel and Rose, 2010](#)). For black shales, reducing conditions are a product of  
10 original accumulations of organic matter whose decay depleted oxygen to create rich organic  
11 sediments within oil- and gas-producing formations ([Tourtelot, 1979](#); [Vine and Tourtelot, 1970](#)).  
12 Yet reactions resulting from temporary redox shifts are likely to be less important than those  
13 resulting from other longer-term physical and geochemical processes. Temporary subsurface redox  
14 shifts may be due to the short timeframe for fluid injection (a few days to a few weeks) and the use  
15 of oxygen scavengers to prevent downhole equipment corrosion.

16 Hydraulic fracturing fluid injection introduces novel chemicals into the subsurface.<sup>1</sup> As such, the  
17 geochemistry of injected and native fluids will not be in equilibrium. Over the course of days to  
18 months, a complex series of reactions will equilibrate disparate fluid chemistries. The evolution of  
19 flowback and produced water geochemistry are dependent upon the exposure of formation solids  
20 and fluids to novel chemicals within hydraulic fracturing fluid. Chemical additives interact with  
21 reservoir solids and either mobilize constituents or themselves become adsorbed to solids. Such  
22 additives include metallic salts, elemental complexes, salts of organic acids, organometallics, and  
23 other metal compounds ([Montgomery, 2013](#); [House of Representatives, 2011](#)).

24 The salts, elemental complexes, organic acids, organometallics, and other metal-containing  
25 compounds may interact with metals and metalloids in the target formation through processes  
26 such as ion exchange, adsorption, desorption, chelation, and complexation. For instance, natural  
27 organic ligands (e.g., citrate) are molecules that can form coordination compounds with heavy  
28 metals such as cadmium, copper, and lead ([Martinez and McBride, 2001](#); [Stumm and Morgan, 1981](#);  
29 [Bloomfield et al., 1976](#)). Citrate-bearing compounds are used in hydraulic fracturing fluids as  
30 surfactants, iron control agents, and biocides. Studies of the additives' interactions with formation  
31 solids at concentrations representative of hydraulic fracturing fluids are lacking.

32 Furthermore, pH will likely play a role in the nature and extent of these processes, as the low pH of  
33 hydraulic fracturing fluids may mobilize trace constituents. The pH of injected fluids may differ  
34 from existing subsurface conditions due to the use of dilute acids (e.g., hydrochloric or acetic) used  
35 for cleaning perforations and fractures during hydraulic fracturing treatments ([Montgomery, 2013](#);

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<sup>1</sup> For more information on chemical additive usage, refer to Chapter 5 (Chemical Mixing).



1 [GWPC and ALL Consulting, 2009](#)). Metals within formation solids may be released through the  
2 dissolution of acid-soluble phases such as iron and manganese oxides or hydroxides ([Yang et al.,  
3 2009](#); [Kashem et al., 2007](#); [Filgueiras et al., 2002](#)). Thus, the pH of hydraulic fracturing fluids, or  
4 changes in system pH that may occur as fluid recovery begins, may influence which metals and  
5 metalloids are likely to be retained within the formation and which may be recovered in flowback.  
6 Ultimately, more research is needed to fully understand how the injection of hydraulic fracturing  
7 fluids affects subsurface geochemistry and resultant flowback and produced water chemistry.

### **E.2.8. Microbial Community Processes and Content**

8 By design, hydraulic fracturing releases hydrocarbons and other reduced mineral species from  
9 freshly fractured shale, sandstone, and coal, resulting in saltier in situ fluids, the release of  
10 formation solids, and increased interconnected fracture networks with rich colonization surfaces  
11 that are ideal for microbial growth ([Wuchter et al., 2013](#); [Curtis, 2002](#)). Depending upon the  
12 formation, microorganisms may be native to the subsurface and/or introduced from non-sterile  
13 equipment and fracturing fluids. Additionally, microorganisms compete for novel organics in the  
14 form of chemical additives ([Wuchter et al., 2013](#); [Arthur et al., 2009](#)). Since large portions of  
15 hydraulic fracturing fluid can remain emplaced in the targeted formation, long-term microbial  
16 activity is supported through these novel carbon and energy resources ([Orem et al., 2014](#); [Murali  
17 Mohan et al., 2013a](#); [Struchtemeyer and Elshahed, 2012](#); [Bottero et al., 2010](#)). Such physical and  
18 chemical changes to the environment at depth stimulate microbial activity and influence flowback  
19 and produced water content in important ways.

20 Several studies characterizing produced water from unconventional formations (i.e., the Barnett,  
21 Marcellus, Utica, and Antrim Shales) indicate that taxa with recurring physiologies compose shale  
22 flowback and produced water microbial communities ([Murali Mohan et al., 2013b](#); [Wuchter et al.,  
23 2013](#)). Such physiologies include sulfur cyclers (e.g., sulfidogens: sulfur, sulfate, and thiosulfate  
24 reducers); fermenters; acetogens; hydrocarbon oxidizers; methanogens; and iron, manganese, and  
25 nitrate reducers ([Davis et al., 2012](#)).

26 Based on their physiologies, microorganisms cycle substrates at depth by mobilizing or  
27 sequestering constituents in and out of solution. Mobilization can occur through biomethylation,  
28 complexation, and leaching. Sequestration can occur through intracellular sequestration,  
29 precipitation, and sorption to biomass.

30 The extent to which constituents are mobilized or sequestered depends upon the prevailing  
31 geochemical environment after hydraulic fracturing and through production. Significant  
32 environmental factors that influence the extent of microbially mediated reactions are increases in  
33 ionic content (i.e., salinity, conductivity, total nitrogen, bromide, iron, and potassium); decreases in  
34 acidity, and organic and inorganic carbon; the availability of diverse electron acceptors and donors;  
35 and the availability of sulfur-containing compounds ([Cluff et al., 2014](#); [Murali Mohan et al., 2013b](#);  
36 [Davis et al., 2012](#)). Examples follow that illustrate how subsurface microbial activity influences the  
37 content of produced water.

1 Under prevailing anaerobic and reducing conditions, microorganisms can mobilize or sequester  
2 metals found in unconventional produced water ([Gadd, 2004](#)). Microbial enzymatic reduction  
3 carried out by chromium-, iron-, manganese-, and uranium-reducing bacteria can both mobilize and  
4 sequester metals ([Vanengelen et al., 2008](#); [García et al., 2004](#); [Mata et al., 2002](#); [Gauthier et al.,  
5 1992](#); [Myers and Nealson, 1988](#); [Lovley and Phillips, 1986](#)). For instance, iron and manganese  
6 species go into solution when reduced, while chromium and uranium species precipitate when  
7 reduced ([Gadd, 2004](#); [Newman, 2001](#); [Ahmann et al., 1994](#)).

8 Metals can also be microbially solubilized by complexing with extracellular metabolites,  
9 siderophores (metal-chelating compounds), and microbially generated bioligands (e.g., organic  
10 acids) ([Glorius et al., 2008](#); [Francis, 2007](#); [Gadd, 2004](#); [Hernlem et al., 1999](#)). For example,  
11 *Pseudomonas* spp. secrete acids that act as bioligands to form complexes with uranium(VI) ([Glorius  
12 et al., 2008](#)).

13 Many sulfur-cycling taxa have been found in hydraulic fracturing flowback and produced water  
14 communities ([Murali Mohan et al., 2013b](#); [Mohan et al., 2011](#)). Immediately following injection,  
15 microbial sulfate reduction is stimulated by diluting high-salinity formation waters with fresh  
16 water (high salinities inhibit sulfate reduction). Microbial sulfate reduction oxidizes organic matter  
17 and decreases aqueous sulfate concentrations, thereby increasing the solubility of barium ([Cheung  
18 et al., 2010](#); [Lovley and Chapelle, 1995](#)).

19 Sulfidogens also reduce sulfate, as well as elemental sulfur and other sulfur species (e.g.,  
20 thiosulfate) prevalent in the subsurface, contributing to biogenic sulfide or hydrogen sulfide gas in  
21 produced water ([Alain et al., 2002](#); [Ravot et al., 1997](#)). Sulfide can also sequester metals in sulfide  
22 phases ([Ravot et al., 1997](#); [Lovley and Chapelle, 1995](#)). Sources of sulfide also include formation  
23 solids (e.g., pyrite in shale) and remnants of drilling muds (e.g., barite and sulfonates), or other  
24 electron donor sources ([Davis et al., 2012](#); [Kim et al., 2010](#); [Collado et al., 2009](#); [Grabowski et al.,  
25 2005](#)).

26 Additionally, anaerobic hydrocarbon oxidizers associated with shale produced water can readily  
27 degrade simple and complex carbon compounds across a considerable salinity and redox range  
28 ([Murali Mohan et al., 2013b](#); [Fichter et al., 2012](#); [Timmis, 2010](#); [Lalucat et al., 2006](#); [Yakimov et al.,  
29 2005](#); [McGowan et al., 2004](#); [Hedlund et al., 2001](#); [Cayol et al., 1994](#); [Gauthier et al., 1992](#); [Zeikus et  
30 al., 1983](#)).

31 Lastly, microbial fermentation produces organic acids, alcohols, and gases under anaerobic  
32 conditions, as is the case during methanogenesis. Some nitrogen-cycling genera have been  
33 identified in unconventional shale gas systems. These include genera involved in nitrate reduction  
34 and denitrification ([Kim et al., 2010](#); [Yoshizawa et al., 2010](#); [Yoshizawa et al., 2009](#); [Lalucat et al.,  
35 2006](#)). These genera likely couple sugar, organic carbon, and sulfur species oxidation to nitrate  
36 reduction and denitrification processes.

1 Consequently, using a variety of recurring physiologies, microorganisms mobilize and sequester  
2 constituents in and out of solution to influence the content of flowback and produced water in  
3 important ways.

### E.3. Produced Water Content Spatial Trends

#### E.3.1. Variability between Plays of the Same Rock Type

##### E.3.1.1. Shale Formation Variability

4 The content of shale produced water varies geographically, as shown by data from four formations  
5 (the Bakken, Barnett, Fayetteville, and Marcellus Shales; see Table E-2, Table E-4, Table E-6, Table  
6 E-9, Table E-10). For several constituents, variability between shale formations is common. The  
7 average/median TDS concentrations in the Marcellus (87,800 to 106,390 mg/L) and Bakken  
8 (196,000 mg/L) Shales are one order of magnitude greater than the average TDS concentrations  
9 reported for the Barnett and Fayetteville Shales (see Table E-2). As Fayetteville produced water  
10 contains the lowest reported average TDS concentration (13,290 mg/L), average concentrations for  
11 many inorganics (i.e., bromide, calcium, chloride, magnesium, sodium, and strontium) that  
12 contribute to dissolved solids loads are the lowest compared to average concentrations for the  
13 same inorganics in Bakken, Barnett, and Marcellus produced water (see Table E-4 and Table E-6).  
14 Average concentrations for metals reported within Bakken and Marcellus produced water are also  
15 higher than those within the Barnett or Fayetteville formations (see Table E-6).

16 Additionally, Marcellus produced water is enriched in barium (average concentration of 2,224 mg/l  
17 in [Barbot et al. \(2013\)](#) or median calculated from [Hayes \(2009\)](#) of 542.5 mg/L) and strontium  
18 (average concentration of 1,695 mg/L ([Barbot et al., 2013](#)) or median calculated from [Hayes  
19 \(2009\)](#) of 1,240 mg/L) by one to three orders of magnitude compared to Bakken, Barnett, and  
20 Fayetteville produced water (see Table E-6). Subsequently, radionuclide variability expressed as  
21 isotopic ratios (e.g., radium-228/radium-226, strontium-87/strontium-86) are being used to  
22 determine the reservoir source for produced water ([Chapman et al., 2012](#); [Rowan et al., 2011](#);  
23 [Blauch et al., 2009](#)). Lastly, Barnett and Bakken produced waters are enriched in sulfate.

24 Although organic data are limited, average BTEX concentrations are higher in Marcellus compared  
25 to Barnett produced water by one order of magnitude, whereas concentrations of benzene alone  
26 are marginally higher in Barnett compared to Marcellus produced water (see Table E-9 and Table  
27 E-10).

##### E.3.1.2. Tight Formation Variability

28 The average concentrations for various constituents in tight formation produced water vary  
29 geographically between sandstone formations (the Cotton Valley Group, Devonian sandstone, and  
30 the Mesaverde and Oswego), as shown in Table E-2, Table E-4, and Table E-6. The average TDS  
31 concentrations in the Devonian sandstone (235,125 mg/L) and Cotton Valley Group  
32 (164,683 mg/L) are one to two orders of magnitude greater than the average TDS concentrations  
33 reported for the Mesaverde (15,802 mg/L) and Oswego Formations (73,082 mg/L) (see Table E-2).

1 Mesaverde produced water also contained the lowest average concentrations for many of the  
2 inorganic components of TDS (i.e., calcium, chloride, iron, magnesium, and sodium; see Table E-4  
3 and Table E-6).

4 Little variability was reported in pH between these four tight formations (see Table E-2).  
5 Mesaverde produced water was enriched in sulfate, with an average concentration of 837 mg/L  
6 (see Table E-4), whereas Devonian produced water was enriched in barium, which had an average  
7 concentration of 1,488 mg/L (see Table E-6).

### **E.3.1.3. Coalbed Variability**

8 Geochemical analysis showed that the Powder River Basin is predominately characterized by  
9 bicarbonate water types with a large intrusion of sodium-type waters across a large range of  
10 magnesium and calcium concentrations ([Dahm et al., 2011](#)).<sup>1</sup> In contrast, the Raton Basin is typified  
11 by sodium-type waters with low calcium and magnesium concentrations. A combination of Powder  
12 River and Raton produced water compositional characteristics typifies the San Juan Basin ([Dahm et](#)  
13 [al., 2011](#)). Lastly, Black Warrior Basin produced water is differentiated based upon its sodium  
14 bicarbonate- or sodium chloride-type waters ([DOE, 2014](#); [Pashin et al., 2014](#)).

15 Regional variability is observed in average produced water concentrations for various constituents  
16 of four CBM basins (Powder River, Raton, San Juan, and Black Warrior; see Table E-3, Table E-5,  
17 Table E-7, Table E-9, and Table E-11), but particularly between produced water of the Black  
18 Warrior Basin and the others. As the average TDS concentration in Black Warrior Basin produced  
19 water (14,319 mg/L) is one to two orders of magnitude higher than that of the other three  
20 presented in Table E-3, average concentrations for TDS contributing ions (i.e., calcium, chloride,  
21 and sodium) were also higher than in the Powder River, Raton, and San Juan Basins. These high  
22 levels follow from the marine depositional environment of the Black Warrior Basin ([Horsey, 1981](#)).

23 Powder River Basin produced water has the lowest average TDS concentration (997 mg/L), which  
24 is consistent with [Dahm et al. \(2011\)](#) reporting that nearly a quarter of all the produced water  
25 sampled from the Powder River Basin meets the U.S. drinking water secondary standard for TDS  
26 (less than 500 mg/L).<sup>2</sup> In addition, the Black Warrior Basin appears to be slightly enriched in  
27 barium, compared to the other three CBM basins (see Table E-5). Lastly, the three western CBM  
28 basins (Powder River, Raton, and San Juan) are much more alkaline and enriched in bicarbonate  
29 than their eastern counterpart (the Black Warrior Basin; see Table E-3).

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<sup>1</sup> Water is classified as a “type” if the dominant dissolved ion is greater than 50% of the total. A sodium-type water contains more than 50% of the cation milliequivalents (mEq) as sodium. Similarly, a sodium-bicarbonate water contains 50% of the cation mEq as sodium, and 50% of the anion mEq as bicarbonate ([USGS, 2002](#)).

<sup>2</sup> MCL refers to the highest level of a contaminant that is allowed in drinking water. MCLs are enforceable standards. These include primary MCLs for barium, cadmium, chromium, lead, mercury, and selenium. National Secondary Drinking Water Regulations (NSDWRs or secondary standards) are non-enforceable guidelines regulating contaminants that may cause cosmetic effects (such as skin or tooth discoloration) or aesthetic effects (such as taste, odor, or color) in drinking water. Secondary MCLs are recommended for aluminum, chloride, copper, iron, manganese, pH, silver, sulfate, TDS, and others. See <http://water.epa.gov/drink/contaminants/index.cfm#Primary> for more information.

1 Average concentrations of benzene, ethylbenzene, and xylenes are higher in San Juan compared to  
2 Raton produced water by two orders of magnitude, whereas concentrations of toluene are  
3 marginally higher in Raton compared to San Juan produced water (see Table E-9).

### E.3.2. Local Variability

4 Spatial variability of produced water content frequently exists within a single producing formation.  
5 For instance, Marcellus Shale barium levels increase along a southwest to northeast transect  
6 ([Barbot et al., 2013](#)). Additionally, produced water from the northern and southern portions of the  
7 San Juan Basin differ in TDS, due to ground water recharge in the northern basin leading to higher  
8 chloride concentrations than in the southern portion ([Dahm et al., 2011](#); [Van Voast, 2003](#)).

9 Spatial variability of produced water content also exists at a local level due to the stratigraphy  
10 surrounding the producing formation. For example, deep saline aquifers, if present in the over- or  
11 underlying strata, may over geologic time encroach upon shales, coals, and sandstones via fluid  
12 intrusion processes ([Blauch et al., 2009](#)). Evidence of deep brine migration from adjacent strata into  
13 shallow aquifers via natural faults and fractures has been noted previously in the Michigan Basin  
14 and the Marcellus Shale ([Vengosh et al., 2014](#); [Warner et al., 2012](#); [Weaver et al., 1995](#)). By  
15 extension, in situ hydraulic connectivity, which is stimulated by design during hydraulic fracturing,  
16 may lead to the migration of brine-associated constituents in under- and overlying strata into  
17 producing formations, as discussed in Chapter 6.

18 As hydrocarbon source rocks often form repeating sedimentary sequences, contact between these  
19 layers presents opportunities for an exchange of organics and inorganics ([Fredrickson and Balkwill,](#)  
20 [2006](#); [U.S. EPA, 2004](#)). For instance, diffusion of carbon sources and electron donors occurs at  
21 subsurface shale-sandstone interfaces, suggesting a stratigraphic role in the exchange of  
22 constituents between formations ([Fredrickson and Balkwill, 2006](#)).

## E.4. Example Calculation for Roadway Transport

23 This section provides background information for the roadway transport calculation appearing in  
24 Chapter 7.

### E.4.1. Estimation of Transport Distance

25 In a study of wastewater management for the Marcellus Shale, [Rahm et al. \(2013\)](#) used data  
26 reported to the Pennsylvania Department of Environmental Protection (PA DEP) to estimate the  
27 average distance wastewater was transported. For the period from 2008 to 2010, the distance  
28 transported was approximately 100 km, but it was reduced by 30% for 2011. The reduction was  
29 attributed to increased treatment infrastructure in Lycoming County, an area of intensive hydraulic  
30 fracturing operations in northeastern Pennsylvania. For the part of Pennsylvania within the  
31 Susquehanna River Basin, [Gilmore et al. \(2013\)](#) estimated the likely transport distances for drilling  
32 waste to landfills (256 km or 159 mi); produced water to disposal wells (388 km or 241 mi); and  
33 commercial wastewater treatment plants (CWTPs) (158 km or 98 mi). These distances are longer

1 than the values from [Rahm et al. \(2013\)](#), in part, because wells in the Susquehanna Basin are  
 2 further to the east of Ohio disposal wells and some CWTPs.

#### E.4.2. Estimation of Wastewater Volumes

3 In an example water balance calculation, [Gilmore et al. \(2013\)](#) used 380,000 gal of flowback as the  
 4 volume transported to CWTPs, 450,000 gal of flowback transported to injection wells, and 130,000  
 5 gal of un-reusable treated water also transported to injection wells for a total estimated wastewater  
 6 volume of 960,000 gal per well.

#### E.4.3. Estimation of Roadway Accidents

7 The U.S. Department of Transportation (DOT) published statistics on roadway accidents ([U.S.  
 8 Department of Transportation, 2012](#)) which indicate that the combined total of combination truck  
 9 crashes in 2012 was 179,736, or 110 per 100 million vehicle miles (1.77 million km) (see Table  
 10 E-12). As an indicator of the uncertainty of these data, DOT reported 122,240 large truck crashes  
 11 from a differing set of databases (see Table E-13), with a rate of 75 per 100 million vehicle miles,  
 12 which is 68% of the number of combination truck crashes.

**Table E-12. Combination truck crashes in 2012 for the 2,469,094 registered combination trucks, which traveled 163,458 million miles (U.S. Department of Transportation, 2012).<sup>a</sup>**

Type of crash	Combination trucks involved in crashes	Rates per 100 million vehicle miles traveled by combination trucks
Property damage only	135,000	82.8
Injury	42,000	25.5
Fatal	2,736	1.74
Total	179,736	110

<sup>a</sup> A combination truck is defined as a truck tractor pulling any number of trailers ([U.S. Department of Transportation, 2012](#)).

**Table E-13. Large truck crashes in 2012 (U.S. Department of Transportation, 2012).<sup>a</sup>**

Type of crash	Total crashes	Large trucks with cargo tanks	
		Number	Percentage
Towaway crashes	72,644	4,364	6.0%
Injury	45,794	3,245	7.1%
Fatal	3,802	360	9.5%
Totals	122,240	7,969	6.5%

<sup>a</sup> A large truck is defined as a truck with a gross vehicle weight rating greater than 10,000 pounds ([U.S. Department of Transportation, 2012](#)).

#### E.4.4. Estimation of Material Release Rates in Crashes

1 Estimates ranging from 5.6% to 36% have been made for the probability of material releases from  
 2 crashed trucks. [Craft \(2004\)](#) used data from three databases to estimate the probability of spills in  
 3 fatality accidents at 36%, which may overestimate the probability for all types of accidents ([Rozell  
 4 and Reaven, 2012](#)).<sup>1</sup> The [U.S. Department of Transportation \(2012\)](#) provides estimates of  
 5 hazardous materials releases from large truck crashes. For all types of hazardous materials carried,  
 6 408 of 2,903 crashes, or 14%, were known to have hazardous materials releases. The occurrence of  
 7 a release was unknown for 18% of the crashes. These crashes were not distinguished by truck type,  
 8 so they likely overestimated the number of tanker crashes. [Harwood et al. \(1993\)](#) used accident  
 9 data from three states (California, Illinois, and Michigan) to develop hazardous materials release  
 10 rate estimates for different types of roadways, accidents, and settings (urban or rural). For  
 11 roadways in rural settings the probability of release ranged from 8.1% to 9.0%, while in urban  
 12 settings the probability ranged from 5.6% to 6.9%.

#### E.4.5. Estimation of Volume Released in Accidents

13 Based on the estimated volume (960,000 gal (3.63 million L) per well) and disposal distances used  
 14 by [Rahm et al. \(2013\)](#) and [Gilmore et al. \(2013\)](#), and an assumed 20,000 L (5,300 gal)-containing  
 15 truck ([Gilmore et al., 2013](#)), the total travel distance by trucks ranges from 9,620 miles (14,900 km)  
 16 to 17,760 miles (28,570 km) per well (see Table E-14).

<sup>1</sup> The three databases were the Trucks Involved in Fatal Accidents developed by the Center for National Truck Statistics at the University of Michigan, the National Automotive Sampling System's General Estimates System (GES) produced by the National Highway Transportation Safety Agency, and the Motor Carrier Management Information System (MCMIS) Crash File produced by the Federal Motor Carrier Safety Administration.

**Table E-14. Estimate of total truck-travel miles per well in the Susquehanna River Basin based on the transport analysis performed by Gilmore et al. (2013).**

Action	Waste per well (million gal)	Trucks (20 m <sup>3</sup> /truck)	Miles traveled per truck	Total miles traveled (per well)	Material release rate bounds			
					5.6%		36%	
					Crashes per 100 million miles			
					75	110	75	110
<b><i>Gilmore et al. (2013) distance estimates</i></b>								
Produced water to CWTP	0.38	72	26.9	1,937				
Produced water to disposal well	0.45	85	147	12,495				
CWTP effluent to disposal well	0.13	25	133	3,325				
Total	0.96	182		17,757	3	4	18	27
<b><i>Rahm et al. (2013) distance estimates</i></b>								
Transport 100 km	0.96	182	62.1	11,300	2	3	12	17
Transport 70 km	0.96	182	43.5	9,620	1	2	8	12

- 1 The Susquehanna River Basin Commission reported 1,928 well pads permitted within the basin  
2 ([SRBC, 2012](#)). Assuming two wells per pad, the total distance traveled to haul hydraulic fracturing  
3 wastewater is 68.4 million miles (110 million km).
- 4 Combining these data with the DOT crash data gives an estimated 76 crashes per year using the  
5 combination truck crash rate or 52 per year using the DOT large truck crash rate. Based on the  
6 various assumptions of travel distances, crash rates, and estimated minimum and maximum  
7 material release rates, the number of crashes with releases ranges from 1 to 27 (see Table E-14).
- 8 Several limitations are inherent in this analysis, including differing rural road accident rates and  
9 highway rates, differing wastewater endpoints, and differing amounts of produced water transport.  
10 Further, the estimates present an upper bound on impacts, because not all releases of wastewater  
11 would reach or impact drinking water resources.

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