## **Appendices for:**

## The Impact of Commercially Treated Oil and Gas Produced Water Discharges on Bromide Concentrations and Modeled Brominated Trihalomethane Disinfection Byproducts at two Downstream Municipal Drinking Water Plants in the Upper Allegheny River, Pennsylvania, USA

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Site	CWTF Discharge Distance (km)	Allegheny River km
River Gage #03025500	-3.1	200.2
S01 - Upstream	-1.6	198.7
S02 - CWTF	0	197.1
S03 - Downstream1	12.3	184.8
S04 - Downstream2	43.5	153.6
S05 - PDW1	51.8	145.3
River Gage #03031500	62.9	134.2
S06 - PDW2	149.6	47.5

Table Appendix A.1. Distances of Allegheny River sampling sites and USGS gage stations from the CWTF discharge.

Table Appendix A.2. YSI multi-parameter instrument summary statistics for Allegheny River sites.

Site	Season	n	pН	Specific Conductivity (µs cm <sup>-1</sup> )	Total Dissolved Solids (g l <sup>-1</sup> )	Temperature (°C)
<b>S01</b> Upstream	Spring	8	$7.8 \pm 0.3$	$130 \pm 11$	$0.075 \pm 0.031$	$13.2 \pm 2.9$
	Summer	8	$8.9 \pm 0.3$	$170 \pm 10$	$0.110 \pm 0.007$	$28.5 \pm 1.1$
	Fall	3	$8.9\pm0.2$	$179 \pm 23$	$0.117 \pm 0.015$	$18.7 \pm 1.4$
S02 CWTF	Spring	6	$8.7 \pm 0.3$	$109548 \pm 6193$	$71.178 \pm 4.024$	$15.6 \pm 3.5$
	Summer	5	$8.6 \pm 0.1$	$136256 \pm 9945$	$88.530 \pm 6.461$	$26.9\pm0.7$
	Fall	3	$8.4\pm0.6$	$130854 \pm 5306$	$85.021 \pm 3.447$	$17.6\pm2.0$
S03 Downstream 1	Spring	7	$7.8\pm0.3$	$140 \pm 16$	$0.091 \pm 0.011$	$13.1 \pm 2.7$
	Summer	9	$8.3\pm0.4$	$173 \pm 10$	$0.112 \pm 0.007$	$26.8\pm1.1$
	Fall	4	$8.2\pm0.3$	$219 \pm 49$	$0.142\pm0.032$	$18.1\pm2.5$
<b>S04</b> Downstream 2	Spring	7	$7.8 \pm 0.2$	$139 \pm 12$	$0.090\pm0.008$	$14.9\pm2.6$
	Summer	8	$8.7 \pm 0.3$	191 ± 9	$0.124 \pm 0.006$	$27.3\pm0.7$
	Fall	4	$8.4\pm0.3$	$203 \pm 20$	$0.132\pm0.013$	$18.1\pm2.6$
<b>S05</b> PDW 1	Spring	6	$7.5 \pm 0.1$	$159 \pm 13$	$0.103\pm0.008$	$13.8\pm2.3$
	Summer	7	$7.8 \pm 0.3$	$215 \pm 32$	$0.140\pm0.020$	$26.4 \pm 1.4$
	Fall	4	$8.2\pm0.3$	$209 \pm 22$	$0.136\pm0.014$	$18.4\pm2.1$
<b>S06</b> PDW 2	Spring	5	$7.5\pm0.2$	$184 \pm 26$	$0.120\pm0.017$	$14.8 \pm 2.5$
	Summer	6	$7.3 \pm 0.1$	$344 \pm 65$	$0.223 \pm 0.042$	$27.8\pm0.9$
	Fall	5	$7.4\pm0.1$	$303 \pm 24$	$0.197\pm0.015$	$18.9\pm1.8$

Table Appendix A.3. Dionex Model ICS-2000 ion chromatography method performance characteristics.

Species	IDL	MDL	n	<b>Analytical Precision</b>	n	<b>Collocated Precision</b>
	(ppb)	(ppb)*		(%)		(%)
Chloride	2.2	25.8	130	$100 \pm 1$	122	$99 \pm 2$
Bromide	1.5	6.3	58	$99 \pm 2$	117	$98 \pm 6$
Sulfate	0.7	12.9	120	$100 \pm 1$	117	$96 \pm 10$

\*CWTF samples were diluted 1000x, therefore the raw sample MDLs are ppm

Table Appendix A.4. Disinfection byproduct empirical raw water model input parameters.

Site	Condition	Bromide (ppb)	pН	Temp (°C)	DOC (mg liter <sup>-1</sup> )	Chlorine (mg liter <sup>-1</sup> )	Contact Time (hours)
S05-PDW1	Baseline	70	8.0	26.4	3.00	3.5	24
	CWTF Impacted	93	8.0	26.4	3.00	3.5	24
S06-PDW2	Baseline	83	7.5	27.8	2.98	8.0	16
	<b>CWTF</b> Impacted	132	7.3	27.8	2.98	8.0	16

Figure Appendix B.1. Relationship between Onset in-river sonde and Isco sample bottle conductivity. 1:1 line is plotted.



Corresponding Onset Sonde Specific Conductivity (mS cm<sup>-1</sup>)

Figure Appendix B.2. Allegheny River and tributary mean water discharge (m<sup>3</sup> min<sup>-1</sup>) line diagram for study domain during high and low (in parenthesis) discharge sampling campaigns.



Tributary Name	USGS Gage Station
Allegheny River (Franklin, PA)	03025500
Clarion River (Piney, PA)	03030500
Allegheny River (Parker, PA)	03031500
Redbank Creek (St. Charles, PA)	03032500
Mahoning Creek (Mahoning Dam, PA)	03036000
Crooked Creek (Crooked Creek Dam, PA)	03039000
Kiskiminetas River (Vandergrift, PA)	03048500
Blacklick Creek (Josephine, PA)	03042000
Buffalo Creek (Freeport, PA)	03049000
Allegheny River (Natrona, PA)	03049500





\*USGS Provisional Data





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Figure Appendix B.4a. Comparison of Allegheny River high and low river discharge regimes specific conductivity by site location. Dashed lines indicates median "baseline" values at S01-upstream1 site during each flow regime.



Figure Appendix B.4b. Comparison of Allegheny River high and low river discharge regimes chloride by site location. Dashed lines indicates median "baseline" values at S01-upstream1 site during each flow regime.



Figure Appendix B.4c. Comparison of Allegheny River high and low river discharge regimes bromide by site location. Dashed lines indicates median "baseline" values at S01-upstream1 site during each flow regime.



Figure Appendix B.4d. Comparison of Allegheny River high and low river discharge regimes Cl<sup>-</sup>/Br<sup>-</sup> ratio by site location. Dashed lines indicates median "baseline" values at S01upstream1 site during each flow regime. The S02-CWTF discharge Cl<sup>-</sup>/Br<sup>-</sup> ratio was 110.6  $\pm$  6.2 and 90.4  $\pm$  2.4 for the high and low river discharge regimes, respectively.



Figure Appendix B.4e. Comparison of Allegheny River high and low river discharge regimes sulfate by site location. Dashed lines indicates median "baseline" values at S01-upstream1 site during each flow regime.



Figure Appendix B.5. Plot depicting example in-river sonde specific conductivity observations at S03-Downstream1 during high discharge sampling campaign demonstrating how the collocated Isco sampling times were offset from periods of maximum CWTF discharge impact. Drop down lines represent Isco sampling times (09:00 & 12:00 EST) and the grey boxes represent the plume transport time corrected CWTF discharge impact periods.



Figure Appendix B.6. Time series plot of PDW2 quarterly THM prior to installation of new microfiltration treatment plant in 2013-Q3. The box delineates the two quarters during the 2012 EPA field sampling campaigns.



Figure Appendix B.7. Time series plot of S06-PDW2 quarterly mean bromide and total organic carbon (trend is not significant at  $\alpha = 0.05$ ). The box delineates the two quarters during the 2012 EPA field sampling campaigns.

