

Electronic Supplementary Information (ESI)

Constructed Wetlands for Polishing Oil and Gas Produced Water Releases

Molly C. McLaughlin^{1,2}, Bonnie McDevitt³, Hannah Miller⁴, Kaela K. Amundson⁴, Michael J. Wilkins⁴, Nathaniel R. Warner³, Jens Blotevogel¹, Thomas Borch^{1,4,5,*}

¹ Department of Civil and Environmental Engineering, Colorado State University, 1320 Campus Delivery, Fort Collins, CO, 80523, USA

² Present address: Abt Associates Inc., 2755 Canyon Blvd., Boulder, CO, 80301

³ Department of Civil and Environmental Engineering, The Pennsylvania State University, 212 Sackett Building, University Park, PA 16801, USA

⁴ Department of Soil and Crop Sciences, Colorado State University, 1170 Campus Delivery, Fort Collins, Colorado 80523, USA

⁵ Department of Chemistry, Colorado State University, 1872 Campus Delivery, Fort Collins, Colorado, 80523, USA

*Corresponding author: thomas.borch@colostate.edu

Materials and Methods

Site Description

At Discharge A, discharge rates average 1.5 million liters per day and range between 0.4 and 6.5 million liters per day. This discharge is released directly into a large (~40,000 m²) wetland. This wetland is shallow and carbonate-terraced. Dense vegetation, consisting mostly of cattails, surrounds the outer edge of this wetland, covering about 50% of the area. Closer to the center of the wetland, cattails are sparse. Based on the average discharge at DA-D, and assuming the area of DA-W1 with a water depth of ~0.33 m, the estimated hydraulic retention time in DA-W1 is about 9 days. Water then flows approximately 0.3 km into a ~200,000 m² wetland that is largely unvegetated, however some grasses are established towards the exterior of the wetland. After leaving the second wetland, water flows nearly 15 km and passes through additional CWs before it connects with a much larger perennial stream that is used as a drinking water intake downstream. There is little precipitation in the region (average 230 mm/year)¹ and no additional tributaries to the wetlands and streams discussed at these sites. As a result, the wetlands and streams downstream of all three discharges are composed entirely of O&G PW unless there has been a recent precipitation event.

At Discharge B, PW from 13 wells is combined, treated and released, resulting in a PW to oil ratio exceeding 20:1. On average, Discharge B releases 4.0 million liters per day directly into an ephemeral stream bed. The stream bed contains some vegetation, including many cattails. A 350 m² wetland is located 0.8 km downstream of DB-D and the cattails are more concentrated in this area. Assuming a 0.165 m wide and 0.165 m deep stream for 0.8 km, estimated hydraulic retention time in DB-W1 is 0.19 days or ~4.6 hours. Water exits the wetland through a culvert

and flows another 0.3 km to a pond that is unvegetated and was dry during the sampling event. At the time of sampling, multiple wells at this site were not operating due to low oil prices. This resulted in a lower than average discharge rate.

Discharge C was the focus of an extensive chemical and toxicological evaluation.^{2,3} At Discharge C, an average of 4.5 million liters of PW are released per day into an ephemeral stream bed. A 450 m² CW is located 1.8 km from the discharge, and contains many grasses, with vegetation covering about 50% of the CW area. The CW is followed by a dam that separates the discharge into two equal streams. One continues southeast for about 2 km before emptying into a playa lake which is a shallow, ephemeral lake, commonly found in the U.S. High Plains region.⁴ The other stream continues another 30 km until connecting with a larger perennial river that is used as the drinking water intake for thousands of people downstream. Along this 30 km stretch are a series of CWs, the first of which is located 5.2 km downstream of the discharge. This wetland is approximately 2500 m² and contains thick stands of cattails, as well as grasses. Over half of this CW is vegetated. At all three discharges, McDevitt et al. (2019)⁵ previously found that calcium carbonate dominated grab sediments near NPDES discharges and decreased with increasing distance from the discharges. In addition, only trace amounts of gypsum were found in grab sediments.

Permit Effluent Limits

Daily maximum effluent limits for these NPDES discharges are provided in Table S1. Effluent limits are the same between all permits except Discharge A has effluent limits for sulfide (as H₂S) and selenium, while the other two discharges do not. In addition to these effluent limits, the permit also states that no floating solids or visible foam can be discharged other than in trace amounts. Discharge rate must be reported monthly for Discharge A and Discharge C and every six months for Discharge B. For Discharge B and Discharge C, sulfide as H₂S must be reported quarterly. A toxic pollutants screen, which includes organic and inorganic pollutants outlined in U.S. Code of Federal Regulations Title 40, Part 122, Appendix D, must be conducted in the first, third and fifth years of the permit. Permits typically last four to five years. In addition to these chemical limits, acute whole effluent testing (WET) is required quarterly at the site. This involves an acute 48-hour static-renewal toxicity test using *Daphnia magna* and an acute 96-hour static-renewal toxicity test using *Pimephales promelas*. In the three years prior to this sampling event, violations to these permits were identified at both Discharge A and Discharge B. At Discharge A, the oil and grease effluent limits were exceeded. Violations at Discharge B included failed acute toxicity tests and exceedances for sulfate. No violations were reported at Discharge C in this time period.

Table S1. NPDES permit effluent limit daily maximums specific to the discharges in this study. If no limit listed, that parameter was not specified for that discharge.

Parameter	Discharge A	Discharge B	Discharge C
Specific Conductance	7500 $\mu\text{S}/\text{cm}$	7500 $\mu\text{S}/\text{cm}$	7500 $\mu\text{S}/\text{cm}$
Total Dissolved Solids	5,000 mg/L	5,000 mg/L	5,000 mg/L
Chloride	2,000 mg/L	2,000 mg/L	2,000 mg/L
Sulfate	2,500 mg/L	2,500 mg/L	2,500 mg/L
Total Radium 226	60 pCi/L ^a	60 pCi/L ^a	60 pCi/L ^a
Oil and Grease	10 mg/L ^b	10 mg/L ^b	10 mg/L ^b
pH	6.5 - 9.0 ^c	6.5 - 9.0 ^c	6.5 - 9.0 ^c
Sulfide (as H ₂ S)	200 mg/L	-	-
Selenium	5.0 $\mu\text{g}/\text{L}$	-	-

^a Values taken directly from the permit. 60 pCi/L = 2.22 Bq/L.

^b Permit also states that there cannot be a “visible sheen in the receiving waters or deposits on the bottom or shoreline of the receiving waters.”

^c pH range given. All other values are maxima.

Chemical Analysis

Non-purgeable Organic Carbon and Total Nitrogen Analyses of Water. Water samples for non-purgeable organic carbon (NPOC) and total nitrogen (TN) were collected in plastic bottles, acidified using HCl (pH < 2) in the field and immediately placed on ice. Samples were stored at -20°C in the lab and analyzed within 4 weeks of collection. NPOC and TN of water samples was determined using a Shimadzu TOC-L equipped with a platinum catalyst. Triplicate injections were performed at 720°C. Standardization was based on a 6-point calibration curve using aqueous potassium hydrogen phthalate (KHP) and potassium nitrate (KNO₃) stock standards. Dilutions were performed in the instrument and the limit of detection was approximately 0.2 mg/L. Each sample was analyzed three times to ensure data repeatability. Check standards were run every 10 samples.

Total Organic and Inorganic Carbon of Sediments. Sediments for total carbon and total nitrogen were collected in glass bottles, stored on ice in the field and then stored at -20°C in the lab until analysis. Analysis was conducted using a LECO TruSpec CN. Wet sediments were dried in glass containers in the muffle furnace at 105°C, ground using a mortar and pestle and then sieved through 2 mm sieve. Samples ranging from 0.05 g to 0.2 g were weighed into tin sampling cups and placed in the autosampler for analysis. A Sidney High soil standard was used for calibration. A blank and check standard were run every ten samples. Blanks consisted of empty tin cups for TC and TN. Results are reported as percent of sediment mass on a dry weight basis.

Inorganic carbon (i.e., carbonate) content of soils was analyzed using a calcimeter, pressure transducer and voltage meter following methods in Sherrod, 2002.17. Samples ranging from 0.25 to 1.0 g were weighed into amber glass vials, depending on expected inorganic carbon concentration. Next, 2 mL of a 6N HCl + 3% ferrous chloride solution was added to a 0.5 dram (1.84 mL) vial, which was carefully placed into each amber vial to avoid spilling. Vials were

then capped using a rubber stopper and aluminum seal. Capped vials were shaken vigorously for one minute to ensure that the HCl solution had wet the entire sample. Vials were then allowed to rest for two hours while the reaction continued. After two hours, the voltage from each vial was measured using a voltage meter. A needle attached to the voltage meter was quickly inserted into the septa of each vial and the voltage was recorded. This needle was rinsed after each sample. Concentrations were determined using a 7-point CaCO₃ standard curve. Blanks consisted of empty headspace vials containing 2 mL of a 6N HCl + 3% ferrous chloride solution. Organic carbon concentrations for sediments were determined by subtracting the inorganic carbon value from the total organic carbon value.

Volatile Organic Compounds Analysis. Samples for volatile organic compound (VOC) analysis were collected without headspace, stored on ice in the field and stored at 4°C until analysis. Water samples were prepared following EPA Method 5021A using a Tekmar 7000 Headspace Autosampler and analyzed for volatile organics following EPA Method 8015 using an Agilent 6890N Network Gas Chromatography (GC) System with a Flame Ionization Detector (FID). Analysis parameters for the headspace analyzer are shown in Table S2. For GC-FID analysis, a Rtx-5 column (30 m length, 0.32 mm internal diameter, 0.25 µm film thickness, Restek) and the following temperature program were used: 40 °C (held for 2 min), then increased at 12°C min⁻¹ to 150°C, then increased at 30°C min⁻¹ to 250°C (held for 3 min). Ultra-high purity helium was used as a carrier gas at a constant flow rate of 3 mL/min. Sample injection volumes were 1 mL. Compound identification was achieved using retention times of analytical standards, including Gasoline Range Organics (Restek, Bellefonte, PA) and naphthalene (Alfa Aesar, Ward Hill, MA).

Table S2. Headspace analyzer parameters.

Variable	Value
Platen/Sample Temp	75°C
Valve Oven Temp	150°C
Transfer Line Temp	150°C
Standby Flow Rate	
Sample Equilibration Time	15 min.
Pressurize	10 psig
Pressurize Time	1 min.
Pressurize Equilibration Time	0.2 min.
Loop Fill Time	0.2 min.
Inject Time	1 min.
Mixer	ON
Mixing Time	2 min.
Mixer Level	3
Mixer Stabilize Time	0.1 min.
Constant Heat Time	ON

Non-Volatile Organic Compound Analysis. Both water and sediment samples were analyzed for non-volatile organic compounds. Water samples were collected without headspace, stored on ice in the field and stored at 4°C in the lab until analysis. Sediment samples were stored on ice in the field and at -20°C in the lab. Water samples were filtered through glass microfiber filters

(Whatman, Grade 934-AH) and then extracted. Solid phase extraction (SPE) was used to concentrate surfactants and reduce the salt concentrations in the samples. Glassware for surfactant analysis was pre-cleaned by washing with deionized water (3x), Milli-Q water (3x) and methanol (1x) followed by baking in a muffle furnace (400°C for 8 hours). Bottles were rinsed three times with sample water prior to collection. Prior to extraction, high purity hydrochloric acid was added to water samples to adjust to pH 3 in order to increase extraction efficiency. Supel Select HLB cartridges (200mg/6mL, Supelco, Bellefonte, PA) were conditioned with methanol (HPLC grade, Fisher) followed by Milli-Q water and Milli-Q water, adjusted to pH 3 using hydrochloric acid. A volume of 1000 mL of sample was applied to the cartridges (5-10 mL min⁻¹). Cartridges were washed with 50 mL of 5% methanol solution and then dried under vacuum for 15 minutes. Surfactants were eluted from the cartridge using 10 mL of methanol. Samples were stored at -20°C and analyzed within 24 hours.

Sediment extracts were prepared following methods described in Lara-Martin et al., 2011⁶. Sediment was freeze-dried, milled and sieved following the procedures described for SVOCs. Extraction was performed using three 30-minute cycles in a sonicator bath at 50°C. Methanol was used as the solvent. After each sonicator cycle, samples were centrifuged for 5 minutes at 8,000 rpm and the solvent was decanted. All three extracts were combined and then filtered through a glass microfiber filter (Whatman, Grade 934-AH). Samples were evaporated to 2 mL using a gentle stream of nitrogen and then reconstituted to 100 mL using Milli-Q water. Samples were extracted using the SPE method described for the water samples, with the wash volume reduced to 10 mL, and then evaporated down to 1 mL using a gentle stream of nitrogen. For both water and sediment extracts, octaethylene glycol monododecylether (Sigma Aldrich, Saint Louis, MO) was added as an internal standard.

Water and sediment methanol extracts were analyzed for NVOCs using a Quadrupole Time-of-Flight mass spectrometer (Q-ToF-MS). Extracts were analyzed using an Agilent 1290 Infinity Series liquid chromatograph coupled with an Agilent 6530 Quadrupole Time-of-Flight mass spectrometer (Q-ToF), using the method described in Thurman et al. (2014)⁷ with the following exceptions. Mobile phases were A (0.1% formic acid) and B (acetonitrile). A gradient elution method was developed with 0-2 minutes, 20% B; 2-15 min, 20-95% B; 15-22 min, 95% B; 22-25 min, 20% B. The flow rate was 0.6 mL/min, the injection volume was 20 µL, and the temperature of the drying gas was 325°C. Peaks were identified by accurate mass and potential chemical formulas, which were then verified using surfactant standards. An exact concentration of each surfactant series could not be determined due to a lack of commercial standards with known ethoxymer distribution. Instead, an estimated concentration was determined at the discharge using polyethylene glycol 400, polypropylene glycol (Alfa Aesar, Haverhill, MA), and 4-nonylphenol-polyethylene glycol (Sigma Aldrich, Saint Louis, MO) standards. For alkyldimethylbenzylammonium chloride (ADBAC), three different alkyl lengths (C10, C12, C14) were detected and a dodecyldimethyl-*n*-benzylammonium chloride (Alfa Aesar, Haverhill, MA) standard was used to estimate concentration. Relative concentrations (C/C_0) were determined for samples downstream since all samples were stored in the same manner and extracted and analyzed at the same time.

Results & Discussion

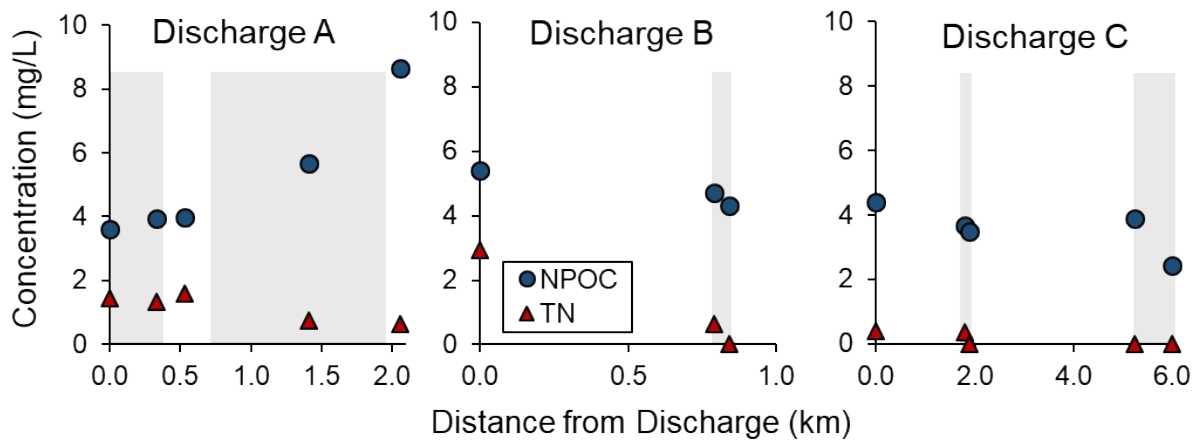


Figure S1. Non-purgeable organic carbon (NPOC) and total nitrogen (TN) in water samples collected at the three discharges. Wetlands are represented by grey boxes.

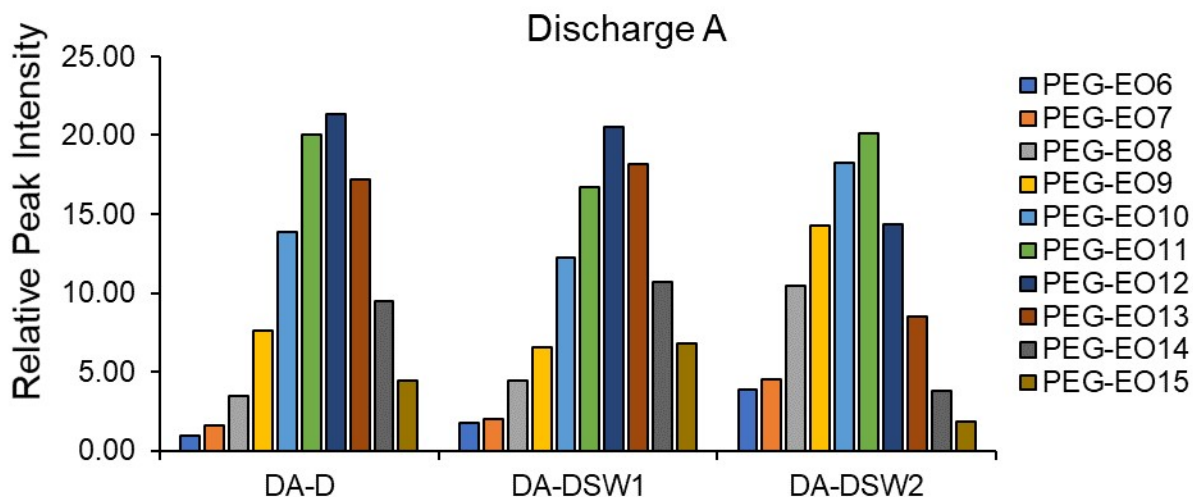


Figure S2. Polyethylene glycol (PEG) relative peak intensity at the discharge (DA-D), downstream of the first wetland (DA-DSW1) and downstream of the second wetland (DA-DSW2) at Discharge A. Shorter homologues (EO 6-10) increase with distance downstream and larger homologues (EO 12-15) decrease with distance downstream, indicating biodegradation as a removal mechanism for PEG in this system.

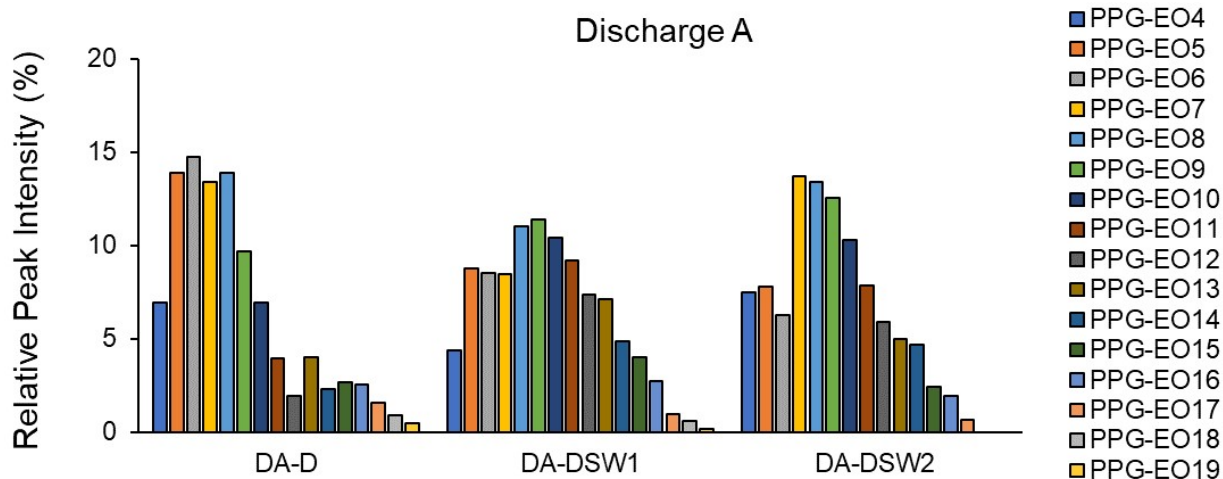


Figure S3. Polypropylene glycol (PPG) relative peak intensity at the discharge (DA-D), downstream of the first wetland (DA-DSW1) and downstream of the second wetland (DA-DSW2) at Discharge A.

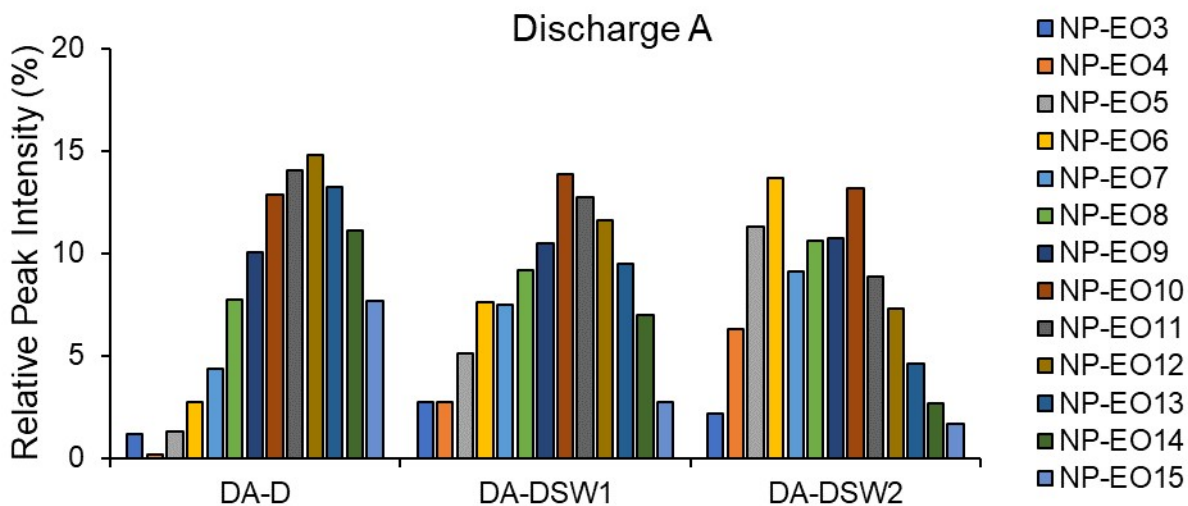


Figure S4. Nonylphenol ethoxylate (NPEO) relative peak intensity at the discharge (DA-D), downstream of the first wetland (DA-DSW1) and downstream of the second wetland (DA-DSW2) at Discharge A. Shorter homologues (EO 3-9) increase with distance downstream and larger homologues (EO 11-15) decrease with distance downstream, indicating biodegradation as a removal mechanism for NPEO in this system.

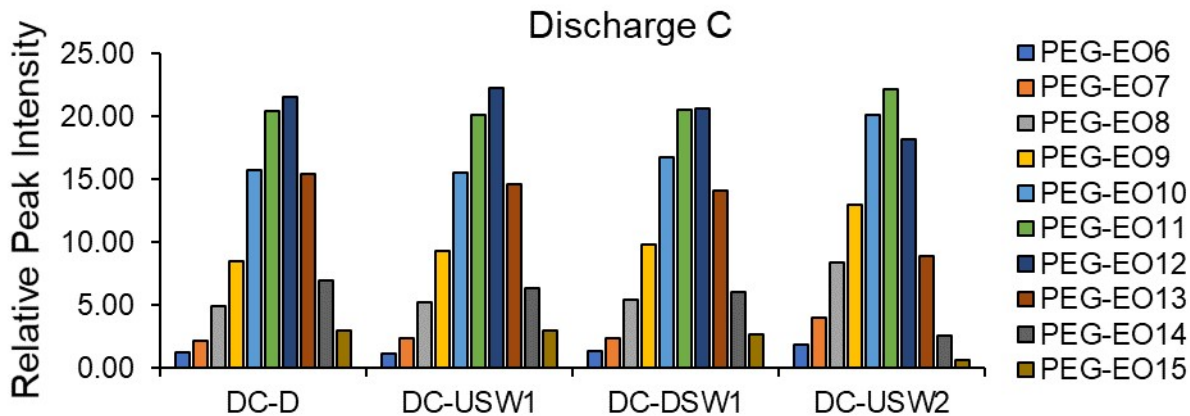


Figure S5. Polyethylene glycol (PEG) relative peak intensity at the discharge (DC-D), upstream of the first wetland (DC-USW1), downstream of the first wetland (DC-DSW1) and upstream of the second wetland (DC-USW2) at Discharge C. Shorter homologues (EO 6-11) increase with distance downstream and larger homologues (EO 12-15) decrease with distance downstream, indicating biodegradation as a removal mechanism for PEG in this system.

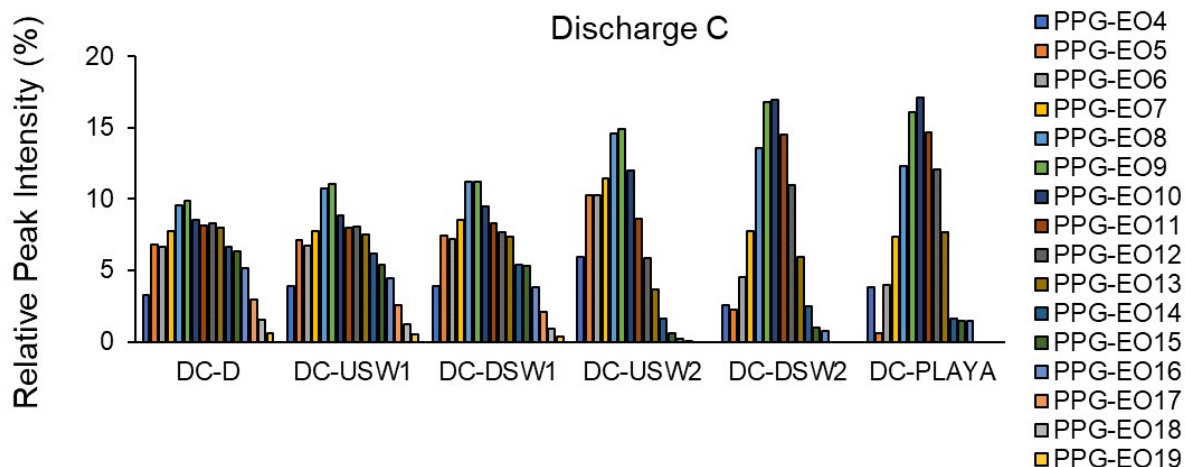


Figure S6. Polypropylene glycol (PPG) relative peak intensity at the discharge (DC-D), upstream of the first wetland (DC-USW1), downstream of the first wetland (DC-DSW1), upstream of the second wetland (DC-USW2), downstream of the second wetland (DC-DSW2), and in the playa lake (DC-PLAYA) at Discharge C.

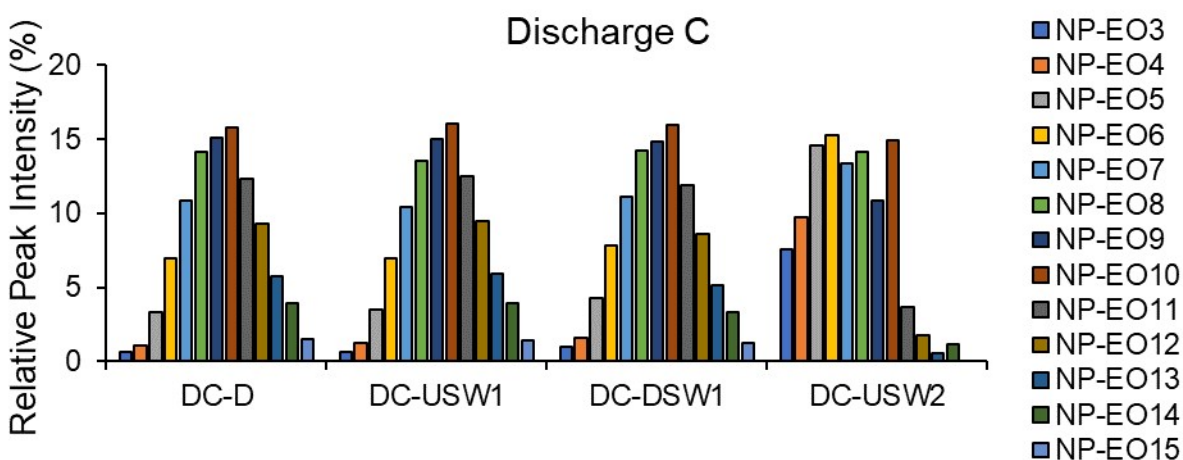


Figure S7. Nonylphenol ethoxylate (NPEO) relative peak intensity at the discharge (DC-D), upstream of the first wetland (DC-USW1), downstream of the first wetland (DC-DSW1), upstream of the second wetland (DC-USW2), downstream of the second wetland (DC-DSW2), and in the playa lake (DC-PLAYA) at Discharge C. Shorter homologues (EO 3-7) increase with distance downstream and larger homologues (EO 11-15) decrease with distance downstream, indicating biodegradation as a removal mechanism for NPEO in this system.

Table S3. Chromatographic retention times and ToF-MS data for polyethylene glycols (PEGs).

Surfactant Species	Retention Time (min.)	Base Peak	Base Peak Formula	Observed m/z	Theoretical m/z	Error (ppm)
--------------------	-----------------------	-----------	-------------------	----------------	-------------------	-------------

PEG-EO8	4.3	[M+Na] ⁺	C ₁₆ H ₃₄ O ₉ Na ⁺	393.2099	393.2095	-1
PEG-EO9	4.5	[M+NH ₄] ⁺	C ₁₈ H ₃₈ O ₁₀ NH ₄ ⁺	432.2803	432.2803	0
PEG-EO10	4.8	[M+NH ₄] ⁺	C ₂₀ H ₄₂ O ₁₁ NH ₄ ⁺	476.3069	476.3065	-0.8
PEG-EO11	5.1	[M+NH ₄] ⁺	C ₂₂ H ₄₆ O ₁₂ NH ₄ ⁺	520.3325	520.3328	0.6
PEG-EO12	5.6	[M+NH ₄] ⁺	C ₂₄ H ₅₀ O ₁₃ NH ₄ ⁺	564.3595	564.359	-0.9
PEG-EO13	6.1	[M+NH ₄] ⁺	C ₂₆ H ₅₄ O ₁₄ NH ₄ ⁺	608.3849	608.3852	0.5
PEG-EO14	6.5	[M+NH ₄] ⁺	C ₂₈ H ₅₈ O ₁₅ NH ₄ ⁺	652.4113	652.4114	0.2

Table S4. Chromatographic retention times and ToF-MS data for polypropylene glycols (PPGs).

Surfactant Species	Retention Time (min.)	Base Peak	Base Peak Formula	Observed <i>m/z</i>	Theoretical <i>m/z</i>	Error (ppm)
PPG-EO4	7.6	[M+Na] ⁺	C ₁₂ H ₂₆ O ₅ Na ⁺	273.167	273.1672	0.7
PPG-EO5	8.5	[M+Na] ⁺	C ₁₅ H ₃₂ O ₆ Na ⁺	331.2086	331.2091	1.5
PPG-EO6	9.4	[M+Na] ⁺	C ₁₈ H ₃₈ O ₇ Na ⁺	389.2506	389.251	1
PPG-EO7	10.3	[M+Na] ⁺	C ₂₁ H ₄₄ O ₈ Na ⁺	447.2927	447.2928	0.2
PPG-EO8	11.1	[M+NH ₄] ⁺	C ₂₄ H ₅₀ O ₉ NH ₄ ⁺	500.3785	500.3793	1.6
PPG-EO9	12	[M+NH ₄] ⁺	C ₂₇ H ₅₆ O ₁₀ NH ₄ ⁺	558.4213	558.4212	-0.2
PPG-EO10	12.8	[M+NH ₄] ⁺	C ₃₀ H ₆₂ O ₁₁ NH ₄ ⁺	616.4632	616.463	-0.3
PPG-EO11	13.6	[M+NH ₄] ⁺	C ₃₃ H ₆₈ O ₁₂ NH ₄ ⁺	674.5053	674.5049	-0.6
PPG-EO12	14.5	[M+NH ₄] ⁺	C ₃₆ H ₇₄ O ₁₃ NH ₄ ⁺	732.5468	732.5468	0
PPG-EO13	15.3	[M+NH ₄] ⁺	C ₃₉ H ₈₀ O ₁₄ NH ₄ ⁺	790.5888	790.5886	-0.3
PPG-EO14	16.2	[M+NH ₄] ⁺	C ₄₂ H ₈₆ O ₁₅ NH ₄ ⁺	848.6301	848.6305	0.5
PPG-EO15	17.1	[M+NH ₄] ⁺	C ₄₅ H ₉₂ O ₁₆ NH ₄ ⁺	906.6722	906.6724	0.2
PPG-EO16	18.2	[M+NH ₄] ⁺	C ₄₈ H ₉₈ O ₁₇ NH ₄ ⁺	964.7141	964.7142	0.1
PPG-EO17	18.9	[M+NH ₄] ⁺	C ₅₁ H ₁₀₄ O ₁₈ NH ₄ ⁺	1022.7564	1022.7561	-0.3
PPG-EO18	20	[M+NH ₄] ⁺	C ₅₄ H ₁₁₀ O ₁₉ NH ₄ ⁺	1080.7977	1080.798	0.3

Table S5. Chromatographic retention times and ToF-MS data for nonylphenol ethoxylates (NPEOs).

Surfactant Species	Retention Time (min.)	Base Peak	Base Peak Formula	Observed <i>m/z</i>	Theoretical <i>m/z</i>	Error (ppm)
NP-EO17	16.3	[M+NH ₄] ⁺	C ₄₉ H ₉₂ O ₁₈ NH ₄ ⁺	986.6615	986.6622	0.7
NP-EO16	16.4	[M+NH ₄] ⁺	C ₄₇ H ₈₈ O ₁₇ NH ₄ ⁺	942.6354	942.636	0.6

NP-EO15	16.6	[M+NH ₄] ⁺	C ₄₅ H ₈₄ O ₁₆ NH ₄ ⁺	898.6097	898.6098	0.1
NP-EO14	16.7	[M+NH ₄] ⁺	C ₄₃ H ₈₀ O ₁₅ NH ₄ ⁺	854.5832	854.5835	0.4
NP-EO13	16.9	[M+NH ₄] ⁺	C ₄₁ H ₇₆ O ₁₄ NH ₄ ⁺	810.5575	810.5573	-0.2
NP-EO12	17	[M+NH ₄] ⁺	C ₃₉ H ₇₂ O ₁₃ NH ₄ ⁺	766.5312	766.5311	-0.1
NP-EO11	17.2	[M+NH ₄] ⁺	C ₃₇ H ₆₈ O ₁₂ NH ₄ ⁺	722.5049	722.5049	0
NP-EO10	17.3	[M+NH ₄] ⁺	C ₃₅ H ₆₄ O ₁₁ NH ₄ ⁺	678.4782	678.4787	0.7
NP-EO9	17.5	[M+NH ₄] ⁺	C ₃₃ H ₆₀ O ₁₀ NH ₄ ⁺	634.4525	634.4525	0
NP-EO8	17.7	[M+NH ₄] ⁺	C ₃₁ H ₅₆ O ₉ NH ₄ ⁺	590.4265	590.4263	-0.3
NP-EO7	17.8	[M+NH ₄] ⁺	C ₂₉ H ₅₂ O ₈ NH ₄ ⁺	546.4003	546.4	-0.5
NP-EO6	18	[M+NH ₄] ⁺	C ₂₇ H ₄₈ O ₇ NH ₄ ⁺	502.374	502.3738	-0.4

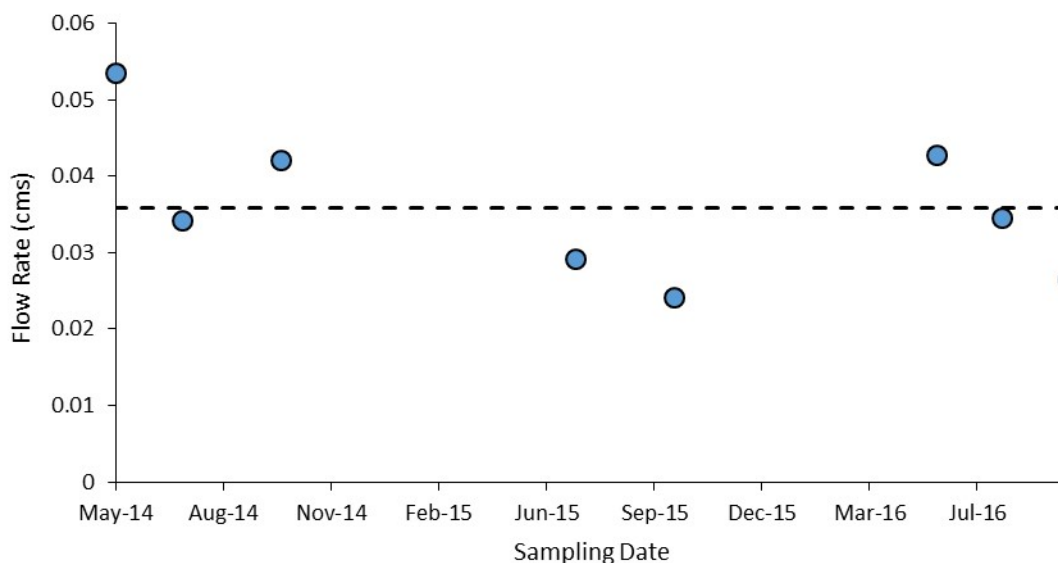


Figure S8. Flow rate at DC-D between May 2014 and October 2016.

Table S6. Values used for stream segment retention time calculations at Discharge C. Average stream width and depth are based on observations while sampling. Width and length of wetlands are based off of Google Maps.

Parameter	Length
Width of stream (m)	1
depth of stream (m)	0.33
Width of W1 (m)	69
Length of W1 (m)	61
Depth of W1 (m)	0.33

Width of W2 (m)	61
Length of W2 (m)	632.1
Depth of W2 (m)	0.33

Table S7. Calculated segment volumes and retention time in Discharge C segments based on flow rate presented in Figure S8 and values presented in Table S6.

Segment Type	Segment Description	Distance (km)	Length of segment (km)	Volume of segment (m³)	Time in segment (days)
NA	Discharge Point	0.00			
Stream	Between Discharge and Upstream of W1	1.79	1.79	590	0.19
Wetland	W1 (Upstream to Downstream of W1)	1.90	0.11	1380	0.44
Stream	Downstream of W1 to Upstream of W2	5.24	3.34	1100	0.36
Wetland	W2 (Upstream to Downstream of W2)	6.00	0.76	12720	4.10

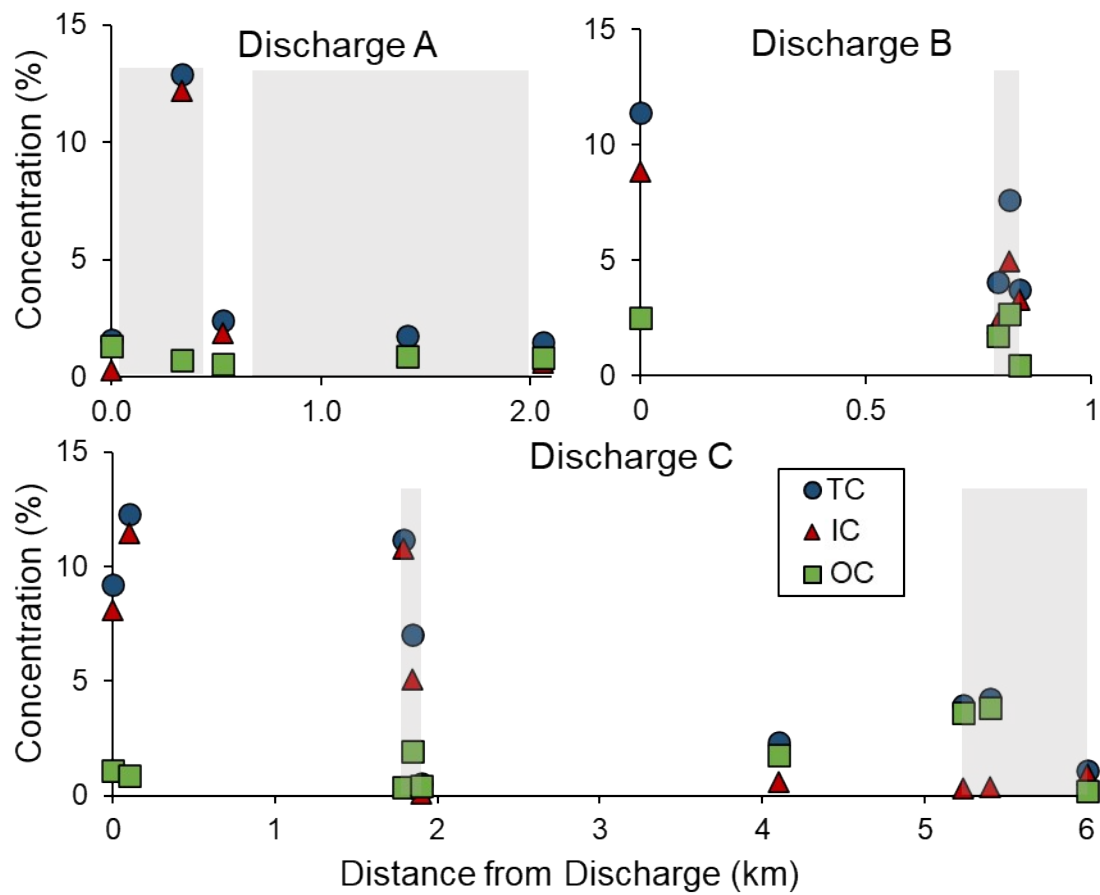


Figure S9. Total carbon (TC), inorganic carbon (IC), and organic carbon (OC) in sediment samples downstream of all three discharges. The grey boxes represent the locations of the wetlands.

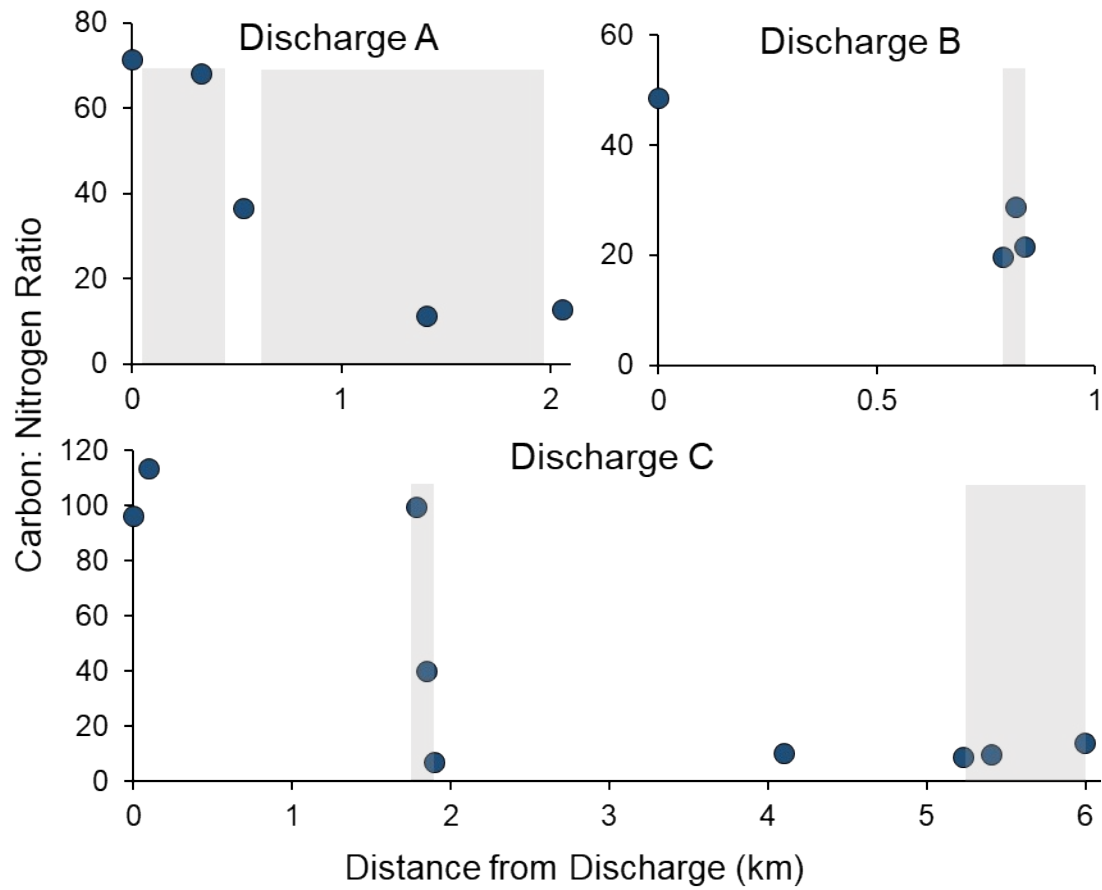


Figure S10. Carbon to nitrogen (C:N) ratios in sediment samples collected downstream of all three discharges. The grey boxes represent the locations of the wetlands.

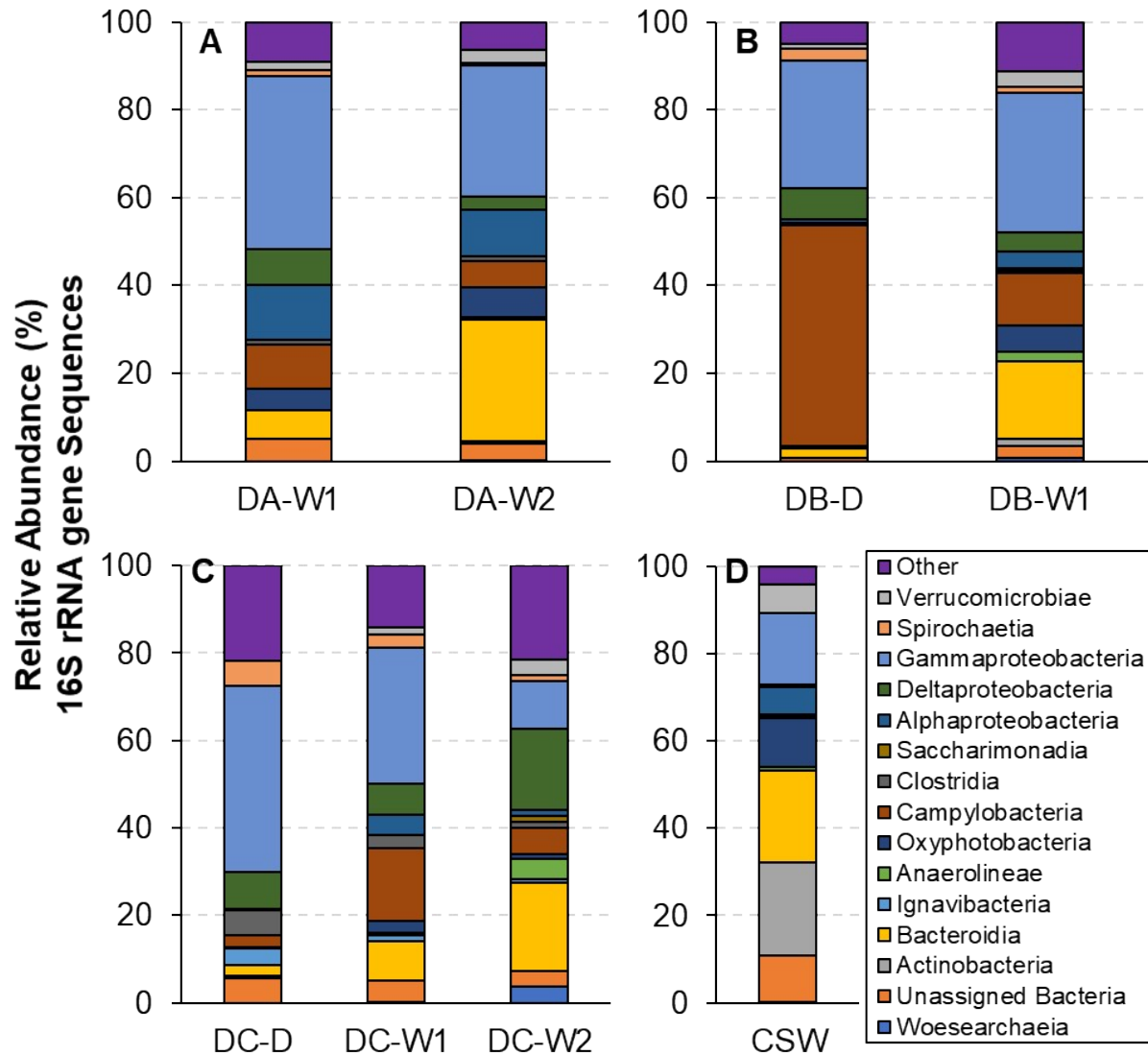


Figure S11. Microbial community composition (based on relative abundance of 16S rRNA gene sequences) for water extracts by class for A) Discharge A, B) Discharge B, C) Discharge C and D) Control Site Wetland. Sites are arranged from closest to the discharge (left) to farthest from the discharge (right). The water extract for DA-D is currently being re-run due to evaporation issues during the first round of analysis.

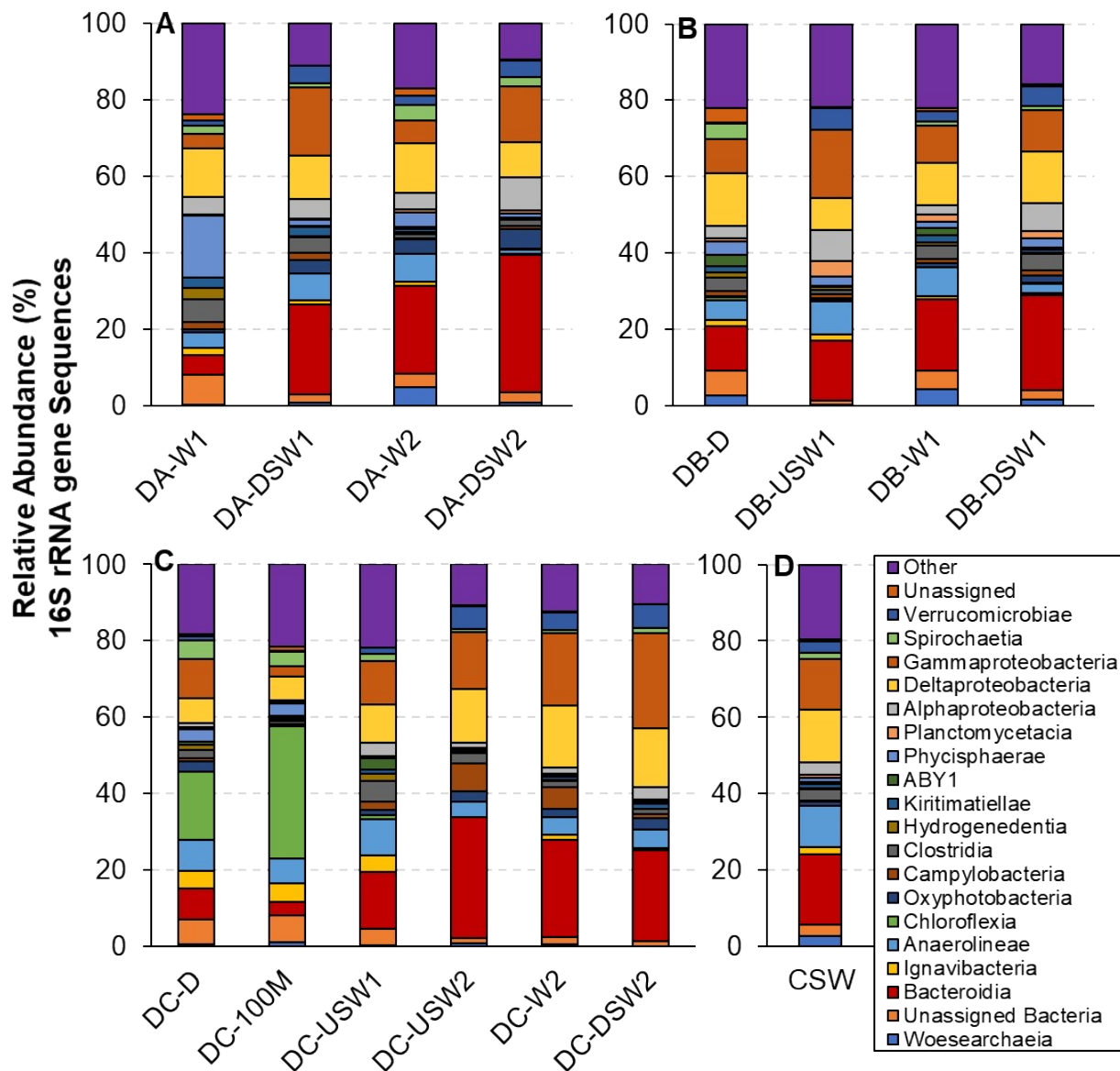


Figure S12. Relative abundance plots for 16S rRNA gene sequencing sediment extracts by class for A) Discharge A, B) Discharge B, C) Discharge C and D) Control Site Wetland. Sites are arranged from closest to the discharge (left) to farthest from the discharge (right). Due to low amplification, some samples could not be included in this analysis.

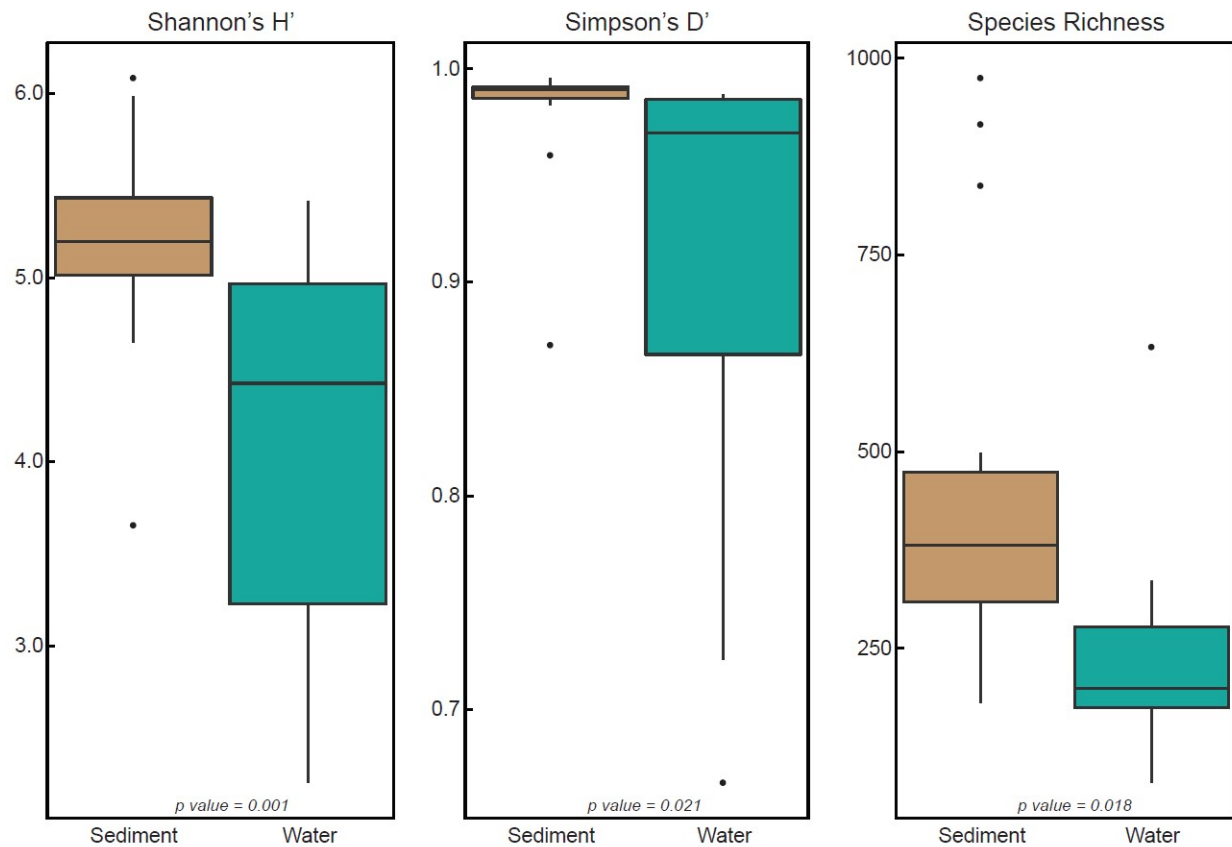


Figure S13. Alpha diversity metrics (Shannon's H, Simpson's D and Species Richness) between water and sediment samples.

Supplemental References

1. NOAA, Past Weather by Zip Code - Data Table, <https://www.climate.gov/>, (accessed Sept. 22, 2018).
2. M. C. McLaughlin, J. Blotevogel, R. A. Watson, B. Schell, T. A. Blewett, E. J. Folkerts, G. G. Goss, L. Truong, R. L. Tanguay, J. L. Argueso and T. Borch, Mutagenicity assessment downstream of oil and gas produced water discharges intended for agricultural beneficial reuse, *The Science of the total environment*, 2020, **715**, 136944.
3. M. C. McLaughlin, T. Borch, B. McDevitt, N. R. Warner and J. Blotevogel, Water quality assessment downstream of oil and gas produced water discharges intended for beneficial reuse in arid regions, *The Science of the total environment*, 2020, **713**, 136607.
4. W. R. Osterkamp and W. W. Wood, Playa-lake basins on the Southern High Plains of Texas and New Mexico: Part I. Hydrologic, geomorphic, and geologic evidence for their development, *GSA Bulletin*, 1987, **99**, 215-223.
5. B. McDevitt, M. McLaughlin, C. A. Cravotta, M. A. Ajemigbitse, K. J. Van Sice, J. Blotevogel, T. Borch and N. R. Warner, Emerging investigator series: radium accumulation in carbonate river sediments at oil and gas produced water discharges: implications for beneficial use as disposal management, *Environmental Science: Processes & Impacts*, 2019, **21**, 324-338.
6. P. A. Lara-Martín, E. González-Mazo and B. J. Brownawell, Multi-residue method for the analysis of synthetic surfactants and their degradation metabolites in aquatic systems by liquid chromatography–time-of-flight-mass spectrometry, *Journal of Chromatography A*, 2011, **1218**, 4799-4807.
7. E. M. Thurman, I. Ferrer, J. Blotevogel and T. Borch, Analysis of Hydraulic Fracturing Flowback and Produced Waters Using Accurate Mass: Identification of Ethoxylated Surfactants, *Analytical Chemistry*, 2014, **86**, 9653-9661.