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Water quality assessment downstream of oil and gas produced water discharges intended for beneficial reuse in arid regions

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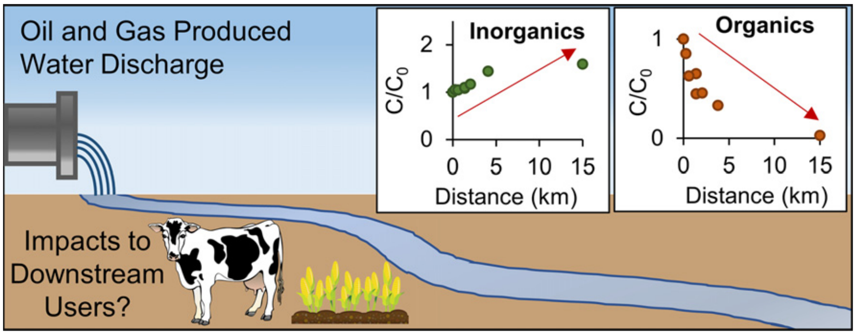
HIGHLIGHTS

- Effects of oil and gas produced water releases for beneficial use are complex.
- Concentrations of organic chemicals generally decreased downstream.
- Concentrations of Na, SO_4, Cl, B, Mn, Se increased downstream due to evaporation.
- Ba, Sr, Ra, and total alkalinity decreased downstream due to co-precipitation.
- Absent regulatory thresholds, toxicity assays are necessary to determine impacts.

GRAPHICAL ABSTRACT



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ABSTRACT

Produced water (PW) is the largest waste stream associated with oil and gas extraction and contains organics, salts, metals and radioactive materials. In the United States, west of the 98th meridian, the National Pollutant Discharge Elimination System exemption allows for release of PW to surface waters for agricultural beneficial reuse if it is "of good enough quality". Due to the complex and variable composition of PW, the downstream impacts of these releases are not fully understood. In this study, a detailed chemical analysis was conducted on a stream composed of PW released for agricultural beneficial reuse. Over 50 geogenic and anthropogenic organic chemicals not specified in the effluent limits were detected at the discharge including hydrocarbons, halogenated compounds, and surfactants. Most were removed within 15 km of the discharge due to volatilization, biodegradation, and sorption to sediment. Inorganics detected at the discharge were within regulatory effluent limits. While some inorganic species (i.e., strontium, barium and radium) decreased in concentration downstream due to co-precipitation, concentrations of many inorganic species including sodium, sulfate and boron increased due to water evaporation. Consequently, downstream water quality changes need to be considered to adequately evaluate the potential impact of discharged PW. Regulatory health thresholds for humans, livestock, and aquatic species for most chemical species present at the discharge are still lacking. As a result, toxicity tests are necessary to determine the potential health impacts to downstream users.

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1. Introduction

Produced water (PW) originating from hydrocarbon reservoirs is extracted concurrently with oil and gas (O&G). This fluid contains elevated levels of chemicals naturally present in the formation, including hydrocarbons and their derivatives, salts, metals and naturally occurring radioactive materials (NORM) (Guerra et al., 2011). It also contains any remaining drilling, hydraulic fracturing, or well maintenance chemicals as well as their transformation products. Composition of this complex fluid varies with time, geologic formation, and variations in chemical use (Clark and Veil, 2009; Orem et al., 2014; Rosenblum et al., 2017; Oetjen et al., 2018). In the United States, total dissolved solids (TDS) in PW ranges between 100 and 400,000 mg/L (Benko and Drewes, 2008; Kahrilas et al., 2016); radium concentrations range between 3 Bq/L and 67 Bq/L (Rowan et al., 2011; Rosenblum et al., 2017); and total organic carbon (TOC) ranges from below detection limit to 2000 mg/L (Benko and Drewes, 2008). Chemical concentrations in PW are often well above safe drinking water thresholds for both humans and livestock. For TDS, the screening level for drinking water is 500 mg/L and the upper limit for livestock is 10,000 mg/L (Soltanpour and Raley, 1999). For radium, the drinking water screening level is 0.19 Bq/L and the limit for industrial effluent is 2.22 Bq/L (Rowan et al., 2011). TOC concentrations are generally not directly regulated in drinking water, however, individual organic species can be and many have been detected above maximum contaminant levels (MCLs) in PW.

On average in the U.S., over three trillion liters of PW are generated per year (Guerra et al., 2011). Management practices for this waste stream vary by region. Underground injection into Class II disposal wells is the most common management technique in the U.S.; however, high injection rates have been linked to induced seismicity (Weingarten et al., 2015). Treatment at wastewater treatment plants (WWTPs) is another common management approach, but has been shown to increase concentrations of salts, disinfection by-products, and radioactivity downstream (Warner et al., 2013; Parker et al., 2014; Burgos et al., 2017). Economic viability of O&G extraction is partly driven by the high costs of PW management practices at around one to fifteen U.S. Dollars ($) per m^3 of water (Dolan et al., 2018). This is especially true for older wells, which can generate 50 to 1000 times more PW than oil (Scanlon et al., 2014). Thus, operators are increasingly considering alternative options, including discharging PW for agricultural beneficial reuse (Dolan et al., 2018). Municipalities are also interested in this practice because many O&G producing formations in the U.S. are located in the arid West and in dire need of more water to meet demands from citizens, industry, and agriculture (Guerra et al., 2011).

Under the Clean Water Act it is illegal to discharge pollutants from a point source into a water of the United States unless the entity obtains a National Pollutant Discharge Elimination System (NPDES) permit. U.S. Code of Federal Regulations Title 40, Part 435, Oil and Gas Extraction Point Source Category states that "there shall be no discharge of waste water pollutants into navigable waters from any source associated with production, field exploration, drilling, well completion or well treatment (i.e., produced water, drilling muds, drill cuttings, and produced sand)." For onshore wells located west of the 98th meridian, however, the exemption in Subpart E allows for the discharge of PW for agricultural or wildlife propagation if PW (1) "is of good enough quality to be used for wildlife or livestock water or other agricultural uses", (2) "is actually put to use during period of discharge", and (3) does not exceed the effluent limitation of 35 mg/L oil and grease. Besides the oil and grease limitation, "of good enough quality" is not defined through any other federal regulatory limits. State and federal regulators, however, generally include additional effluent limits when writing NPDES O&G PW permits.

The lack of both legal definition and available data on the quality of PW discharged under the NPDES program motivated us to investigate the watershed around an O&G extraction site and NPDES PW release in Wyoming. The overarching goal of this study was to increase our understanding of potential impacts of PW beneficial reuse on downstream users and ecosystem services. Our specific objectives were to 1) characterize the chemical composition of the discharge that is being used for beneficial reuse, 2) assess the environmental fate of chemicals in the discharge stream along the flow path, and 3) conduct a systematic evaluation for potential health impacts to humans, livestock and aquatic life based on previously established thresholds and screening levels. As standard methods for produced water characterization are still critically missing, various analytical techniques were developed with the goal of identifying potential contaminants of concern. The health thresholds used in this study are from sources used by regulators when drafting NPDES permits and by farmers when determining safety for their livestock.

2. Materials and methods

2.1. Site description

This study was conducted at an undisclosed well field in Wyoming where over 10 NPDES PW discharges are located. At this site, O&G operations occur in a relatively remote location and there are few other sources of contamination. Analysis focused on one NPDES discharge and the surrounding watershed (Fig. 1). Multiple wells contribute PW to this NPDES release, one of which is 100 years old. The operator stated that the PW to oil ratio from this well is 1000:1 and that operation would be economically infeasible if beneficial reuse were not an option.

After extraction from the wells, the oil-gas-PW mixture is combined and sent to the treatment system. Treatment includes a three-phase separator (oil, gas, water) which uses heat, gravity, and emulsion-breaking chemicals. Once separated, half of the PW is reinjected into the O&G wells for enhanced oil recovery. The other half is sent to a series of settling ponds where additional oil is removed via flotation and skimming. On average, 4.5 million L per day of treated PW is released into an ephemeral stream bed from this NPDES discharge. This volume has remained relatively steady since 2005, ranging between 3.6 and 5.5 million L per day. There is little precipitation in the region (average 230 mm/year) (NOAA, 2018) and no additional tributaries to this stream. A previous study conducted at this site analyzed $^{228}Ra/^{226}Ra$ in water samples which indicated that the discharge was sourced from oil and gas reservoirs and that additional sources of water had minimal to no impact on inorganic chemistry downstream (McDevitt et al., 2019). Additionally, it should be noted that Wyoming state records show there are 203 oil and gas wells located in this well field, most of which are no longer in operation and located upstream of the NPDES discharge site. During the sampling events, no other sources of surface water were observed entering the stream. As a result, the majority of the discharge stream is composed of O&G PW unless there has been a recent precipitation or snowmelt event.

A wetland is located about 2 km from the discharge, 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 that is used by cattle, horses, waterfowl and other wildlife for drinking. Playa lakes are shallow, ephemeral lakes, commonly found in the U.S. High Plains region (Osterkamp and Wood, 1987). The other stream continues 30 km until connecting with a larger perennial river. Along this 30 km stretch are a series of wetlands that contain fish and serve as watering holes for cattle and other wildlife. The perennial river is used as the drinking water intake for thousands of people downstream. In October 2016 the flow rate of the discharge stream and perennial river were 0.03 $m^3 s^{-1}$ (at site D1.4) and 8.5 $m^3 s^{-1}$ (USGS, 2018), respectively. The flow rate in the perennial river was an estimated 6.7 $m^3 s^{-1}$ (USGS, 2018) in February 2018. Flow measurements were not taken in the discharge stream in 2018.

The daily maximum effluent limits for this specific NPDES permit are shown in Table 1. In addition to these effluent limits, the permit also states that no floating solids or visible foam can be discharged other

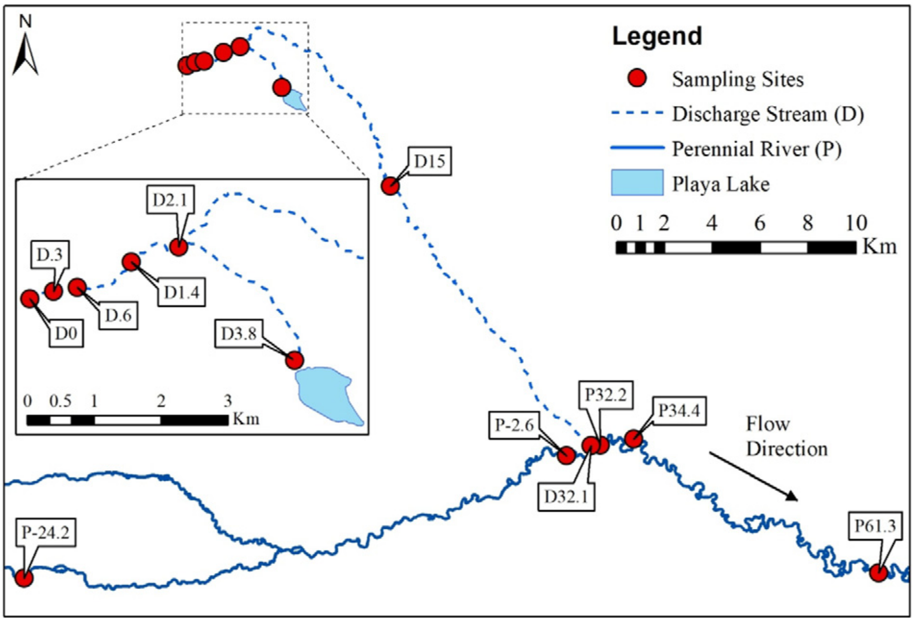

Fig. 1. Map of sampling locations at an undisclosed well field in Wyoming. Surface water samples were collected in October 2016 and February 2018 from the discharge (ephemeral) stream (D) and perennial river (P). Site D0 was collected directly from the discharge culvert before entering the stream. All other sites were collected at the indicated distance from the discharge (e.g. D.3 was collected 0.3 km downstream). Sites prefaced with a P were collected on the perennial river, with positive values indicating samples collected downstream of the confluence between the two water bodies (e.g. P32.2 is collected on the perennial river, 32.2 km downstream of the discharge) and negative values indicating samples collected upstream of the confluence (e.g. P-2.6 is collected on the perennial river, 2.6 km upstream of the confluence).

than in trace amounts. The discharge rate must be reported monthly and sulfide as H_2S 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*. Corrective actions must be taken if mortality of 50% or greater is observed for either species.

2.2. Site sampling

Water samples were collected 11 times between 2013 and 2018 including May and November 2013, July and October 2014, July and October 2015, June, August and October 2016 and February 2018. This study focuses on surface water samples that were collected in October 2016 and February 2018 from the discharge stream (D) and perennial river (P). These sampling events were selected because chronic toxicity assays, as discussed in a collaborative manuscript, were only conducted at these time points (McLaughlin et al., 2019). Additionally, flow and bulk parameters (e.g. specific conductance and diesel range organics) in the discharge stream remained relatively steady between 2013 and 2016 and no major trends were observed with season. Site D0 was collected directly from the discharge culvert before entering the stream. All other sites were collected at the indicated distance from the discharge (e.g. D.3 was collected 0.3 km downstream, see Table 2). Sites prefaced with a P were collected on the perennial river, with positive values indicating samples collected downstream of the confluence between the two water bodies (e.g. P32.2 is collected on the perennial river, 32.2 km downstream of the discharge) and negative values indicating samples collected upstream of the confluence (e.g. P-2.6 is collected on the perennial river, 2.6 km upstream of the confluence). Field and holding blanks were also collected and processed alongside each analysis. During the 2016 sampling event, the discharge stream and perennial river were not connected via surface water. A direct observation could not be made in 2018 due to unsafe road conditions. The streams have been connected during previous sampling events.

Table 1
NPDES permit effluent limits specific to the discharge in this study.

Parameter	Effluent limitation Daily maximum
Specific conductance	7500 μS/cm
Total dissolved solids	5000 mg/L
Chloride	2000 mg/L
Sulfate	1800 mg/L
Total radium 226	60 pCi/L[a]
Oil and grease	10 mg/L[b]
pH	6.5–9.0[c]

[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.

Based on the results of the previous sampling events, samples were collected at additional locations between the discharge and the playa lake during the 2018 sampling event. In 2018, one of the downstream samples (D15) was not accessible and was not sampled. Additionally, the control site location was different between the two sampling events. In 2016, the control site was located on the perennial river 2.6 km upstream of the confluence between the two streams (P-2.6). Although this site was not influenced by surface water from the discharge stream, it was likely influenced by anthropogenic activity from the nearby town. In 2018, a control site was selected 24.2 km upstream of the confluence (P-24.2), in a location that is upstream of most human activity.

In the discharge stream, water samples were collected in the center of the stream. In the larger perennial river, samples were collected where the water was flowing freely. Samples for organic analysis were collected in glass bottles with Teflon-lined caps. Samples for inorganic analysis were collected in plastic bottles. Samples were stored on ice in the field and refrigerated at 4 °C in the lab until analysis. Duplicate samples were collected from site D0 and P61.3 during the 2016 sampling event and at site D.3 during the 2018 sampling event. The results from these samples are presented as averages in the figures. Raw data

Table 2
Field parameters from October 2016 and February 2018 sampling events. Negative distance values indicate distance upstream of the confluence between the discharge stream and the perennial river. These samples (P-2.6 and P-24.2) were used as control sites.

Site name	Distance from discharge (km)	Temperature (°C)	pH	Conductivity (μS/cm)	Dissolved oxygen (mg/L)
			October 2016		
D0	0	39.4	7.87	2150	0.57
D1.4	1.4	31.0	8.14	2070	4.62
D15	15	24.6	8.62	3200	6.73
D32.1	32.1	------------------------------------Dry------------------------------------			
P-2.6	–2.6	11.8	8.27	420	8.61
P32.2	32.2	6.8	8.09	480	9.60
P61.3	61.3	12.3	8.24	710	8.68
			February 2018		
D0	0	35.6	7.92	2180	0.83
D.3	0.3	33.3	8.38	2050	1.82
D.6	0.6	30.4	8.33	2050	2.69
D1.4	1.4	25.8	8.28	2060	3.44
D2.1	2.1	17.6	7.99	1500	3.58
D3.8	3.8	7.0	7.82	2090	4.99
P-24.2	–24.2	0.3	8.32	180	9.30
P34.4	34.4	0.2	8.19	500	9.00

are shown in the Supporting Information. At each site, a Hanna HI98194 probe was used to measure temperature, pH, dissolved oxygen and specific conductivity of the water.

2.3. Organic analysis

For all analyses, U.S. EPA standard methods were applied when available. Details on sample preservation, preparation and analytical methods are provided in Table S1. Volatile organic compounds (VOCs) were analyzed by gas chromatography/mass spectrometry (GC–MS). Samples for semi-volatile organic compound (SVOCs) analysis were first liquid-liquid extracted into dichloromethane and then analyzed by GC–MS. Samples for gasoline range organics (GRO) and diesel range organics (DRO) were acidified in the field using HCl to $pH < 2$. GRO samples were prepared using purge-and-trap followed by gas chromatographic analysis. Samples for DRO analysis were extracted into dichloromethane and analyzed using gas chromatography with flame ionization detector (GC-FID). Samples collected for VOC and GRO analysis were collected without headspace. Some compounds were analyzed via multiple methods (e.g. benzene was analyzed by EPA method 8260B and 8021B). The results for these compounds are presented as averages in the figures. Raw data are shown in the Supporting Information.

Solid phase extraction (SPE) was used to concentrate surfactants and reduce the salt concentrations in the samples. Water samples were extracted using Supel Select HLB cartridges (200 mg/6 mL, Supelco, Bellefonte, PA) and analyzed using liquid chromatography/quadrupole time-of-flight mass spectrometry (LC/Q-ToF-MS). Detailed methods are provided in the Supporting Information. 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 standards (Sigma Aldrich, Saint Louis, MO). Relative concentrations (C/C_0) were determined for samples downstream.

2.4. Inorganic analysis

Samples for cation analysis were filtered in the field using 0.45-μm filters and acidified to $pH < 2$ with HNO_3. Cations were analyzed by inductively coupled plasma-atomic emission spectrometry (ICP-AES) and by inductively coupled plasma-mass spectrometry (ICP-MS). Samples for major anions were filtered in the field (0.45 μm) and analyzed by ion chromatography. Samples for ammonia as nitrogen were acidified with H_2SO_4 in the field and analyzed colorimetrically, following EPA method 350.1. Alkalinity was analyzed via titration. Radium-228 and Radium-226 were analyzed following EPA NAREL SOP 13 and 14, respectively.

3. Results and discussion

3.1. Field parameters

Field parameters for the sampling sites are shown in Table 2. The water temperature was elevated at the discharge (39.4 °C, 2016; 35.6 °C, 2018), due to downhole conditions and heat added during separation, and decreased with distance downstream. At D15, the discharge stream sample farthest from the NPDES release and 15 km downstream, water temperature remained elevated as compared to the perennial river (24.6 °C vs. 11.8 °C). In 2016, pH was 7.87 and increased slightly downstream to 8.62 at D15. In 2018, pH was 7.92 at the discharge and increased until D1.4 ($pH = 8.28$) but then decreased in the wetland (D2.1, $pH = 7.99$) and playa lake (D3.8, $pH = 7.82$). All sampling sites were within the range of the pH permitted at the effluent ($pH = 6.5–9$). Conductivity was elevated at the discharge (2150 μS/cm, 2016; 2180 μS/cm, 2018) as compared to the perennial river (average ~500 μS/cm) but below the permit effluent limit (7500 μS/cm) and near the minimum value for PW in the U.S. (Benko and Drewes, 2008). In 2016, conductivity increased nearly 50% between the discharge and site D15, due to water evaporation downstream (McDevitt et al., 2019). In 2018, conductivity remained relatively stable in the discharge stream, except for a decrease of ~500 μS/cm at site D2.1. Dissolved oxygen (DO) was depleted at the discharge (0.57 mg/L, 2016; 0.83 mg/L, 2018) and increased with distance downstream, likely due to aeration in short waterfalls along the flow path, decreasing temperature, and atmospheric equilibration. At D15, DO remained lower than in the perennial stream (6.73 mg/L vs. 8.61 mg/L). In 2016, daytime air temperature ranged between 4.5 °C and 13 °C. In 2018, daytime air temperature ranged between −12 °C and −4 °C.

3.2. Organic chemistry of the discharge

Gas chromatography analysis revealed numerous organic chemicals present at the discharge (Fig. 2). The majority of these chemicals were geogenic hydrocarbons (i.e. benzene, DRO, etc.)

and many have previously been reported in PW (Orem et al., 2007; Benko and Drewes, 2008; Orem et al., 2014; Elliott et al., 2016; Luek and Gonsior, 2017). In general, concentrations of individual organic species were low in comparison to available health thresholds, ranging from 0.29 μg/L (methyl acrylate, 2018) to 49.8 μg/L (acetone, 2018). DRO (C_{10} to C_{28} alkanes; boiling point range ~170 °C–430 °C) in the discharge was detected at 1560 μg/L in 2016 and 1430 μg/L in 2018. GRO (C_6 to C_{10} alkanes; boiling point range ~60 °C–170 °C) in the discharge was detected at 156 μg/L in 2016 and 94.2 μg/L in 2018.

Concentrations of VOCs, SVOCs, DRO and GRO at the discharge were relatively consistent between the two sampling events. The discharge is sourced from conventional wells that have been operating for decades and it was expected that concentration of geogenic compounds would remain steady between sampling events. Two chemical species were only observed at one sampling event. This includes 1,2-dichloroethane (0.56 μg/L), which was detected at the discharge in 2016 but not in 2018, and carbazole, which was detected in the discharge only during the 2018 sampling event (3.03 μg/L). Carbazole has many potential sources including crude oil and 1,2-dichloroethane was most likely used as a solvent (Frolov et al., 1989). Common chemical additives including 2-butoxyethanol and acetone were also detected at the discharge (Drollette et al., 2015). 2-Butoxyethanol is a product stabilizer, solvent and surfactant. Acetone is a commonly used solvent. It is also a known transformation product of polypropylene glycol surfactants, which were also detected, so may not have been directly used as a well maintenance chemical (Heyob et al., 2017).

Liquid chromatography analysis was conducted on all samples collected in 2018 and only on the discharge sample in 2016. Analysis revealed the presence of polyethylene glycols (PEG), polypropylene glycols (PPG) and nonylphenol ethoxylates (NPEO). These nonionic surfactant species were present in the discharge at an estimated concentration of 9 μg/L (2016) and 2 μg/L (2018) PEGs; 9 μg/L (2016) and 5 μg/L (2018) PPGs, and 12 μg/L (2016) and 8 μg/L (2018) NPEOs (Fig. 3). PEG, PPG and NPEO are surfactants commonly used by the oil and gas industries as emulsifiers, wetting agents and corrosion inhibitors (Heyob et al., 2017).

3.3. Organic contaminant changes downstream

3.3.1. Volatile organic chemistry

Out of the 13 individual VOCs detected at the discharge in 2018, only eight were detected at the next sampling site located 0.3 km downstream. This included 1,2,4-trimethylbenzene, 2-butanone, acetone, benzene, toluene, ethylbenzene, *m*,*p*-xylene and *o*-xylene. Fig. S1 shows that benzene, toluene, ethylbenzene and xylenes (BTEX) concentrations decreased with increasing distance downstream. BTEX are a component of crude oil and commonly employed as an indicator of oil and gas releases (Gross et al., 2013). In both 2016 and 2018, all BTEX chemicals were detected in the discharge at concentrations of 48.0 μg/L and 31.0 μg/L, respectively. In 2018, BTEX were also detected 0.3 km downstream, albeit at a much lower concentration (1.6 μg/L) than at the discharge (see Table S2 for organic chemical data). No BTEX chemicals were detected farther than 0.3 km from the discharge or in the perennial river.

The primary removal mechanism for BTEX chemicals from surface water is volatilization as evidenced by the Henry's constants ($5.2–6.6 \times 10^{-3}$ atm-m^3/mol, see Table S4 for organic chemical properties) (ATSDR, 2007a, 2007b; Hosseini et al., 2010; ATSDR, 2017). Short (0.25–1.0 m) waterfalls have been constructed throughout the discharge stream to increase volatilization of chemicals in the water. Aerobic biodegradation is another possible removal mechanism; however, previous studies have shown that the rate of BTEX biodegradation is likely insignificant as compared to the rate of volatilization (ATSDR, 2007a) (Table S4). Once in the atmosphere, BTEX react readily with hydroxyl radicals and have a half-life on the order of hours to days, depending on the concentration of hydroxyls present (ATSDR, 2007a, 2007b; Hosseini et al., 2010; ATSDR, 2017). Oil and gas production has previously been shown to be a significant source of BTEX releases in the U.S. (Hildenbrand et al., 2016; Marrero et al., 2016). 1,2,4-Trimethylbenzene was detected only at the discharge and 0.3 km downstream (Fig. S2). This chemical has a Henry's constant within the range of the BTEX chemicals and is likely removed from the discharge stream via volatilization.

Other VOCs that were detected past the discharge point include 2-butanone and acetone. 2-Butanone was highest at the discharge (11.9 μg/L in 2016; 13.4 μg/L in 2018) and detected as far as 3.8 km

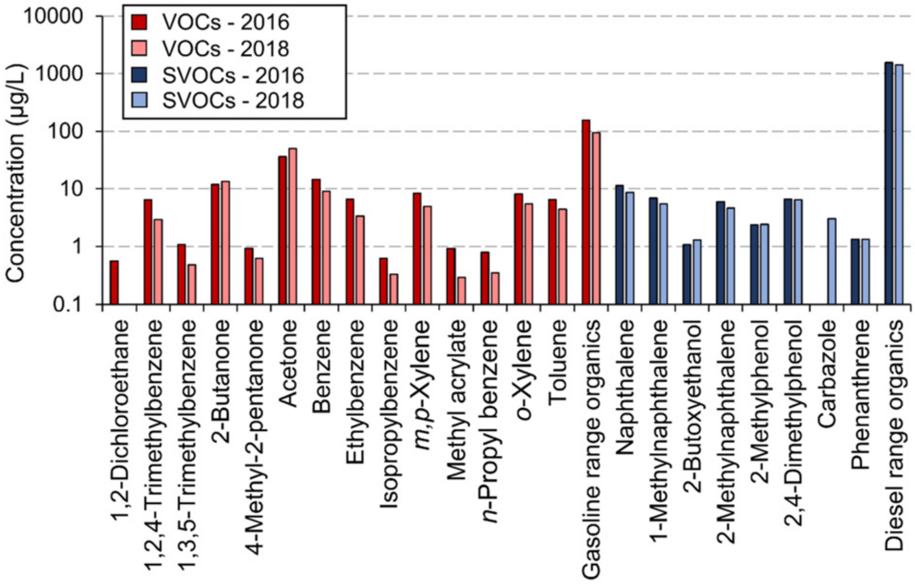

Fig. 2. Concentrations of volatile organic chemicals (VOCs), semi-volatile organic chemicals (SVOCs), gasoline range organics (GRO) and diesel range organics (DRO) at the NPDES PW discharge during the October 2016 and February 2018 sampling events. VOCs and GRO are shown in red. SVOCs and DRO are shown in blue.

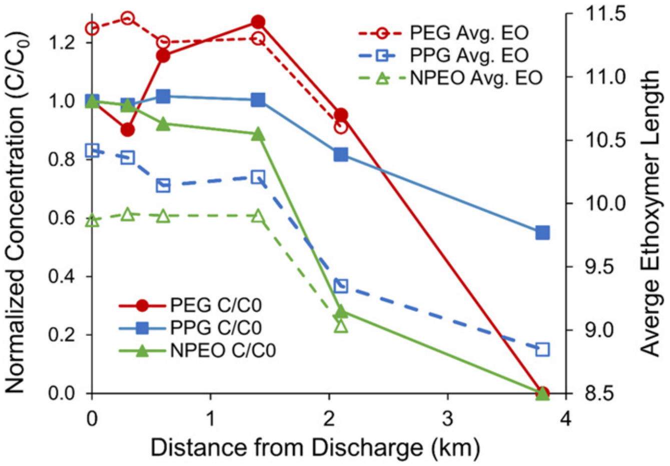

Fig. 3. Relative concentration of polyethylene glycols (PEG), polypropylene glycols (PPG) and nonylphenol ethoxylates (NPEO) as well as average ethoxymer (EO) length for each surfactant group versus distance from the NPDES discharge (km) during the February 2018 sampling event. PEG and NPEO were below detection limit 3.8 km downstream and therefore no average ethoxymer length is shown. PEG, PPG and NPEO were all below detection in the control site sample. These surfactants were also detected at the discharge in October 2016 (data not shown). A wetland is located ~1.8 km downstream and may be the source of surfactant removal between 1.5 km and 2.1 km.

downstream (1.69 μg/L, 2018) (Fig. S2). 2-Butanone is geogenic and has previously been reported in PW (Elliott et al., 2016). Acetone was the most dominant VOC in the discharge (36.3 μg/L, 2016; 49.8 μg/L, 2018) and one of two organic chemicals detected in both the discharge and perennial streams. As discussed above, acetone may be a chemical additive or a by-product of PPG degradation (Heyob et al., 2017). In 2016, acetone concentrations were steady at all locations in the perennial river, ranging from 0.9 to 1.09 μg/L. In 2018, acetone was below detection limit at both sites in the perennial river. Acetone is a by-product of fat metabolism in animals and is also sourced from plants, trees, insects and forest fires (ATSDR, 1994). One or all of these are the most likely sources of acetone in the control site samples.

Acetone and 2-butanone persisted farther downstream than BTEX. This can be explained partly by their Henry's constants, which are two orders of magnitude less than BTEX (~10^{-5} atm-m^3/mol). Volatilization and biodegradation are the primary removal mechanisms for these species. Once in the atmosphere, the residence time of 2-butanone is expected to be less than a day. Acetone has an average residence time of 45 days and therefore has the potential to be transported farther from the NPDES release point (ATSDR, 1994).

Carbon disulfide, a VOC that has been detected in PW and in air samples collected near oil and gas activity (Rich et al., 2016; Butkovskyi et al., 2017), was not detected at the discharge during either sampling event, but was detected downstream (Fig. S2). It can be produced by reaction between methane and hydrogen sulfide, but only at much higher temperature than at the discharge point. Thus, its detection downstream is not due to formation in the stream. More likely, losses of this highly volatile compound occurred during sampling at the discharge since the sample was collected directly from the discharge as the water fell from the culvert into the streambed. In 2016, carbon disulfide was detected at a concentration of 0.54 μg/L at site D1.4 and 0.25 μg/L at site D15. It was not detected in the perennial river. In 2018, carbon disulfide was first detected in D.3 at an average concentration of 50.9 μg/L. Carbon disulfide was detected at all sites on the discharge stream as well as P34.4, but not in the control site sample. The Henry's constant (1.22×10^{-3} atm-m^3/mol) of carbon disulfide indicates that it will quickly partition from water to air via volatilization (ATSDR, 1996).

3.3.2. Semi-volatile organic compounds

Of the eight SVOCs detected at the discharge in 2018, seven were detected at the next sampling site 0.3 km downstream. This included polycyclic aromatic hydrocarbons (PAHs), which were detected in the discharge stream and have previously been found in PW (Elliott et al., 2016). PAHs detected at the discharge included naphthalene, phenanthrene, 1-methylnapthalene and 2-methylnaphthalene (Fig. S3). Naphthalene was the most dominant PAH at the discharge (11.4 μg/L, 2016; 8.72 μg/L, 2018) and was detected as far as 1.4 km downstream, making it the most persistent of the PAHs. Phenanthrene was the least concentrated among the detected PAHs at the discharge (1.34 μg/L, 2016; 1.32 μg/L, 2018) and below detection limit (1 μg/L) by 0.6 km downstream. 1- and 2-methylnaphthalene persisted until 0.6 km and 0.3 km downstream, respectively.

Like acetone and 2-butanone, volatilization and biodegradation are the most important removal mechanisms for low molecular weight PAHs (ATSDR, 1995). As indicated by the atmospheric hydroxylation rate of these compounds, the half-lives of phenanthrene and naphthalene compounds in the atmosphere are <1 day. Previous studies have shown that atmospheric concentrations of PAHs are elevated by at least one order of magnitude in areas near oil and gas operations (Paulik et al., 2015). These compounds exhibit a moderate potential to sorb to sediment and a previous study found PAHs, including naphthalene and phenanthrene, sorbed to sediment in a lake downstream of a wastewater treatment plant processing oil and gas wastewater (Burgos et al., 2017).

Phenol, 2-methylphenol, and 2,4-dimethylphenol were also detected in the discharge stream (Fig. S4). Phenol was not detected at the discharge but was detected in 2018 at site D.3 at a concentration of 1.03 μg/L, indicating it may be an intermediate of benzene biodegradation. Both 2-methylphenol (2.36 μg/L, 2016; 2.41 μg/L, 2018) and 2,4-dimethylphenol (6.57 μg/L, 2016; 6.45 μg/L, 2018) were highest at the discharge. 2,4-Dimethylphenol was present at 2 to 3 times greater concentration than 2-methylphenol and persisted farther in the discharge stream (3.8 km vs. 1.4 km). These species may also be biodegradation intermediates of the respective methylated parents as xylenes were also present at a 2 to 3 times higher concentration than toluene (ATSDR, 2007a, 2008a).

The main removal mechanism for phenol and the substituted phenol compounds is biodegradation (ATSDR, 2008a, 2008b). Volatilization from water will occur but at a slower rate than chemicals previously mentioned in this manuscript as indicated by the lower Henry's constants (10^{-6}–10^{-7} atm-m^3/mol). The phenol compounds are also relatively mobile in soil (K_{oc}: 25–175) but degrade quickly in both soils and groundwater, and thus are not expected to persist in the groundwater (ATSDR, 2008b). For the portion of these compounds that volatilize, atmospheric hydroxylation occurs quickly, and removal will occur within a day.

Two well maintenance chemicals, 2-butoxyethanol and bis(2-ethylhexyl)phthalate, were also detected in the discharge stream. 2-Butoxyethanol is a surfactant and solvent while bis(2-ethylhexyl) phthalate is a diverter and used in PVC piping (Elsner and Hoelzer, 2016; Butkovskyi et al., 2017). It is also possible that bis(2-ethylhexyl) phthalate is a contaminant from a plastic coating used for sample collection, however, this is unlikely since it was only found in two samples and not in the blanks. Both of these compounds have previously been reported in O&G wastewater (Orem et al., 2014). 2-Butoxyethanol has also been found in a water well contaminated by oil and gas activity in Pennsylvania (Llewellyn et al., 2015). In 2016, 2-butoxyethanol was only detected at the discharge (1.07 μg/L). In 2018, however, it was detected as far as 1.4 km downstream, ranging between 1.07 and 1.65 μg/L over this distance (Fig. S4). Bis(2-ethylhexyl)phthalate was not detected at the discharge but was detected 15 km downstream in 2016 (4.99 μg/L) and 2.1 km downstream in 2018 (5.13 μg/L). The main removal mechanism for 2-butoxyethanol from water is biodegradation. For bis(2-ethylhexyl)phthalate, the main removal mechanism is sorption to soil, as indicated by its high soil adsorption coefficient. Volatilization of both chemicals occurs very slowly and is not a major removal mechanism for either compound (ATSDR, 1998, 2002).

3.3.3. Diesel and gasoline range organics

Both gasoline range organics (GRO) and diesel range organics (DRO) were detected in the discharge stream at a maximum concentration of 156 μg/L (GRO) and 1560 μg/L (DRO) at the discharge (Fig. 4). DRO was detected in the perennial river in 2018 but was not analyzed in 2016. The concentration of DRO at the background and in the site downstream of the confluence was 37.8 μg/L and 37.3 μg/L, respectively. The perennial river is surrounded by agricultural production, flows through a downstream town and passes under multiple bridges, thus, the background DRO is likely sourced from cars or other common uses of oil. The combined concentration of GRO and DRO was below the effluent limit in the permit for oil and grease (10 mg/L).

GRO did not persist as far as DRO. The more volatile and biodegradable compounds were removed first, as indicated by the Henry's constants (K_H: 0.487 to 0.151 atm-m^3/mol for GRO; 0.151 to 7.36×10^{-7} atm-m^3/mol for DRO) and the biodegradation half-lives (7–9 days for GRO; 9 to 125 days for DRO) (Williams et al., 2017). This agrees with the overall trend that more volatile and biodegradable chemicals were removed first, emphasizing the importance of volatilization and biodegradation as the dominant removal pathways for organic chemicals. DRO were likely removed by a combination of biodegradation, volatilization and sorption as indicated by previous studies and the physiochemical properties listed in Table S4 (Balseiro-Romero et al., 2018).

3.3.4. Surfactants

Downstream samples were analyzed for surfactants only in 2018. Results showed that concentrations of PPGs and NPEOs were highest at the discharge and decreased with distance (Fig. 3). The concentration of PEGs decreased initially and then increased between 0.3 and 1.4 km downstream, reaching a maximum normalized concentration of 1.27 (estimated 2.54 μg/L) at site D1.4. The increase in PEGs may be a result of NPEO biodegradation. Previous studies provided evidence for a central fission mechanism for NPEO degradation, which would result in direct generation of PEGs and nonylphenol (NP), an endocrine disruptor (Franska et al., 2003; Wyrwas et al., 2011). A shift in PEGs speciation towards the major NPEOs homologues (EO8–EO11) was observed (Figs. S9–S11) and NPEOs average ethoxymer length remained steady over this distance, indicating that central fission is a potential mechanism for PEG generation. The concentration of PEGs increased by an estimated 1.4 nM over this distance, while NPEOs only decreased by 1.1 nM. This suggests that other mechanisms, such as variability in discharge composition, influenced the concentration of PEGs as well. The well maintenance schedule is not provided in the permit for this discharge, however, permits for other NPDES PW discharges in the area report that well-maintenance chemicals are used on a biweekly or bimonthly basis, indicating that discharge composition would vary with time.

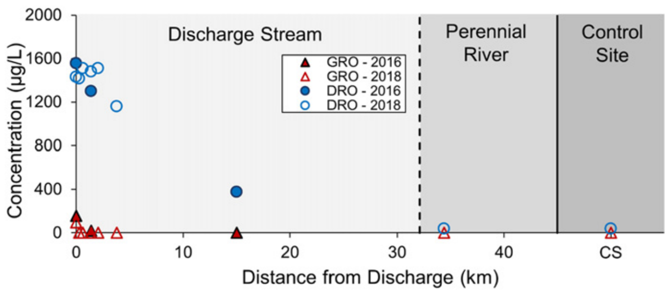

Fig. 4. Concentrations of gasoline range organics (GRO) and diesel range organics (DRO) with distance from the NPDES discharge point (km). In October 2016, GRO and DRO were not measured in the perennial river and control site samples. The dashed line indicates the location of the confluence between the discharge stream and the perennial river (see Fig. 1). Data points to the right of the solid line correspond to the concentration of GRO and DRO in the February 2018 control site (CS) samples.

As shown in Fig. 3, the concentration of surfactant species decreased significantly between 1.4 and 2.1 km downstream, as compared to the overall decrease upstream of this section. The first wetland at the site is located about 1.7 km from the discharge, with site D2.1 located at the end of this wetland. The decrease is most apparent for NPEOs, which were present at 0.88 normalized concentration at site D1.4, decreased to 0.28 by site D2.1 (60% removed), and were fully removed by site D3.8. PEG and PPG removal increases in the wetland as well, but to a lesser degree than NPEOs.

Decreases in relative concentration were accompanied by decreases in average ethoxymer length (Fig. 3). At the discharge, average PEG ethoxymer length was 11.4. This remained steady for the first 1.4 km of the discharge stream and then decreased to an average of 10.6 at site D2.1. Average PPG ethoxymer length at the discharge was 10.4, decreasing to 9.3 at site D2.1 and 8.8 at site D2.8. NPEO average ethoxymer length was 9.9 at the discharge and remained steady until site D2.1 where it dropped to an average of 9.0. These decreases in average ethoxylate number provide evidence that the concentration decreases were due to transformation rather than dilution. All three surfactant species are known to biodegrade via sequential ethoxylate chain shortening, which leads to changes in homolog distribution (McLaughlin et al., 2016; Heyob et al., 2017). In addition, sorption to sediment is an important removal mechanism for NPEOs and may also account for an appreciable portion of PPG removal (Heyob et al., 2017). A previous study reported NPEOs sorbed to sediment downstream of an O&G wastewater treatment plant (Burgos et al., 2017). NPEOs are commonly used by other industries and have been found in sediments around the world (Ferguson and Brownawell, 2003). For PPGs, increasing sorption to sediment with an increase in ethoxylate chain length has been reported, which would support the decrease in average ethoxylate number observed in the water samples (Heyob et al., 2017). Significant sorption or other abiotic removal mechanisms are not expected for PEGs (McLaughlin et al., 2016), so that their decrease in concentration and average ethoxylate number can likely be linked to biodegradation processes only. A previous study reported that the half-life of NPEO was shorter than that of PEGs under aerobic conditions in the presence of DRO (Wyrwas et al., 2011).

3.4. Inorganic chemistry of the discharge and changes downstream

The TDS of the discharge was 1200 mg/L and 870 mg/L during 2016 and 2018 (Fig. 5), respectively, which is near the minimum of TDS values observed in PWs in the U.S. (Kahrilas et al., 2016) and below the effluent limit for this NPDES permit (5000 mg/L). Median TDS values in Wyoming O&G basins are 10,000 mg/L or below, which is an order of magnitude lower than values observed in most other Western U.S. basins (Benko and Drewes, 2008). Salinity has a major impact on the feasibility of PW treatment and reuse. The relatively low TDS of the PW at this site is a major reason why beneficial reuse of this water is economically viable. TDS concentrations in the discharge stream increased downstream, reaching a maximum of 1930 mg/L at site D15. Alkalinity was highest at the discharge (375 mg/L in 2016; 510 mg/L in 2018) and decreased downstream (Fig. 5).

Sodium, chloride and sulfate were the most concentrated ions at the discharge site (Fig. 6). Previous studies have shown that these are the dominant ions in most Wyoming PW (Benko and Drewes, 2008). At the discharge, concentrations of sodium were 273 mg/L in 2016 and 285 mg/L in 2018, which is an order of magnitude lower than the median sodium concentrations for PW in the Western U.S. (Benko and Drewes, 2008). Compared to background, sodium concentrations were elevated by a factor of 15 to 30. This range is due to the fact that ions were generally more concentrated in the 2016 control site sample than the 2018 control site sample. Sodium concentrations in the

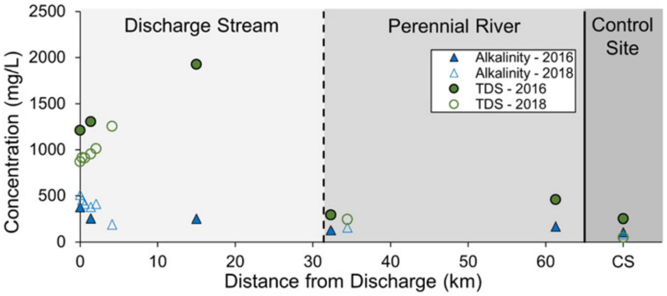

Fig. 5. Changes in total dissolved solids (TDS) and alkalinity versus distance in the discharge and perennial streams. The dashed line indicates the location of the confluence between the discharge stream and the perennial river (see Fig. 1). TDS increases in the discharge stream (to the left of the dashed line) and alkalinity decreases slightly over this same distance. Data points to the right of the solid line correspond to the concentration of TDS and alkalinity in the control site (CS) samples.

discharge stream increased with distance downstream, reaching a maximum of 454 mg/L at site D15.

Concentrations of chloride at the discharge were 182 mg/L in 2016 and 156 mg/L in 2018, which is two orders of magnitude lower than median values for the Western U.S. and an order of magnitude lower than the permit effluent limit (2000 mg/L) (Benko and Drewes, 2008). Chloride concentrations were elevated by a factor of 30 to 40 as compared to the control sites. Similar to sodium and TDS, chloride concentrations in the discharge stream increased with distance downstream, reaching a maximum of 251 mg/L at site D15.Sulfate concentrations were near median values for the Western U.S. at the discharge (305 mg/L, 2016; 420 mg/L, 2018) and an order of magnitude below the effluent limit in the permit (1800 mg/L) (Benko and Drewes, 2008). This element is elevated by a factor of 4 to 22 as compared to the background. Sulfate concentrations in the discharge stream also increased with distance downstream.

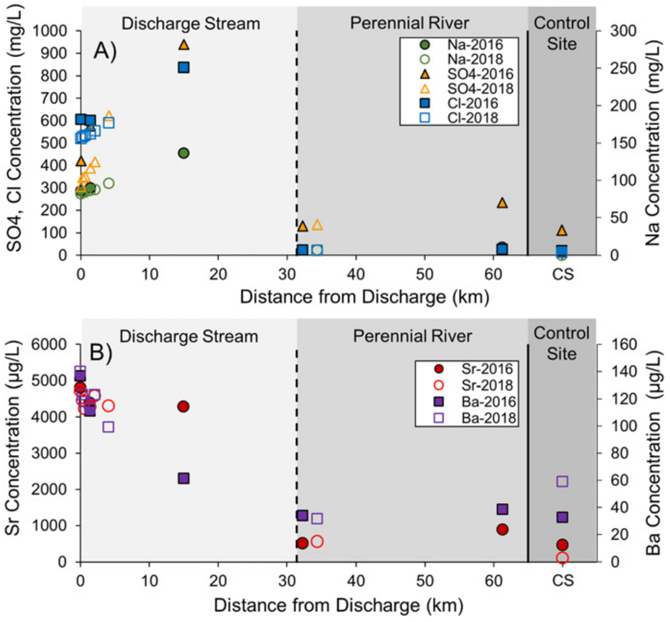

Fig. 6. Concentrations of A) sodium (Na), sulfate (SO4), chloride (Cl) and B) strontium (Sr), and barium (Ba) versus distance downstream from the NPDES produced water discharge (km) from 2016 (closed symbols) and 2018 (open symbols). The dashed line indicates the location of the confluence between the discharge stream and the perennial river (see Fig. 1). In the discharge stream (to the left of the dashed line), concentrations of sodium, sulfate and chloride increase, whereas concentrations of strontium and barium decrease in the discharge stream (to the left of the dashed line). Concentrations in the perennial stream (to the right of the dashed line) are provided to show that concentrations of most inorganic species are elevated at the discharge as compared to the perennial river. Data points to the right of the solid line correspond to the concentration of these species in the control site (CS) samples.

Other major ions that were elevated in the discharge as compared to background include potassium (27.1 mg/L in 2016; 25.7 mg/L in 2018; elevated by a factor of 15 to 25), calcium (74.3 mg/L in 2016; 75.1 mg/L in 2018; elevated by a factor of 2 to 4) and magnesium (32.0 mg/L in 2016; 32.5 mg/L in 2018; elevated by a factor of 2 to 4). Ammonia as nitrogen was absent from the control site sample but present at 360 μg N/L in the discharge (only measured in 2016). These species have previously been reported at elevated concentrations in PW (Akob et al., 2016; Cozzarelli et al., 2017). There was no clear trend in calcium concentration downstream (Fig. S5). Ammonia concentrations decreased with distance downstream (Fig. S5). Potassium and magnesium increased with distance downstream in the discharge stream, both reaching a maximum at site D15 (30.3 mg/L for potassium; 51.8 mg/L for magnesium; Fig. S6).

The discharge contained elevated concentrations of minor elements as well, including boron (0.94 mg/L in 2016; 0.95 mg/L in 2018; elevated by a factor of 10 to 20), manganese (4.6 μg/L in 2016; 6.0 μg/L in 2018; elevated by a factor of 3 in 2018) and selenium (4.8 μg/L in 2016; 1.9 μg/L in 2018; elevated by a factor of 1.5 to 5). Concentrations of all three elements increased downstream in the discharge stream (Fig. S7). Boron reached a maximum of 1300 μg/L at site D15. Manganese reached a maximum concentration of 229 μg/L in the playa lake and selenium reached a maximum of 12.8 μg/L at site D15. In addition to being sourced from PW, selenium is also naturally elevated in Wyoming soils (Raisbeck et al., 2008).

Strontium, barium and total radium (^{226}Ra + ^{228}Ra) were elevated at the discharge and decreased downstream (Figs. 6 and S8). These elements have previously been reported at elevated levels in PW (Cozzarelli et al., 2017; McDevitt et al., 2019). Strontium concentrations at the discharge were 4.8 mg/L and 4.7 mg/L in 2016 and 2018, respectively. Barium concentrations at the discharge were 138 μg/L in 2016 and 143 μg/L in 2018., Total radium (^{226}Ra + ^{228}Ra) concentration was 0.50 Bq/L at the discharge in 2016 which is below the permitted effluent limit of 2.22 Bq/L (60 pCi/L). Increased total radium concentrations are an indicator of PW impacts and a study has been conducted on the fate and transport of radium at this site. This study showed that radium, strontium and barium in the discharge stream were removed via co-precipitation with carbonate, and to a lesser extent, sulfate minerals (McDevitt et al., 2019). Radium was not analyzed in 2018. Other trace inorganic elements including arsenic were analyzed in the water samples. Data for all inorganic analyses is provided in Table S3.

Many of the elements found in the discharge, including chloride, sulfate, sodium, boron, potassium, magnesium, and manganese and selenium, increased in concentration downstream in the discharge stream. The radium study conducted at this site showed that increases in TDS, chloride and sulfate were due to progressive evaporation downstream (McDevitt et al., 2019). Previous studies on coalbed methane PW discharges in Wyoming have attributed increases in selenium and other inorganic chemicals downstream to both evaporation and increased leaching of naturally present species in the soil and rock, as a result of the PW (Jackson and Reddy, 2007; Ramirez, 2013).

3.5. Health threshold comparison

A systematic evaluation for potential health impacts to downstream users was conducted by comparing concentrations of chemicals detected at the discharge to previously established thresholds and screening levels, including MCL for drinking water, surface water acute and chronic thresholds for aquatic species, risk-based screening levels (RBSLs)/livestock upper limits and the human health consumption of fish threshold (Tables 3 and 4). A complete set of health thresholds reviewed here were only available for eight chemicals (BTEX, arsenic, cadmium, selenium and zinc), showing that an assessment of potential toxicological impacts is currently limited for most species in this stream.

For chemicals where thresholds were available, eight species were detected above the MCL at some point in the discharge stream including benzene, aluminum, chloride, fluoride, iron, manganese, sulfate and radium. Benzene and radium were above the MCL at D0 (benzene) and D0 and D1.4 (radium), while chloride and manganese were only above this threshold further downstream, as a result of increasing concentrations. Fluoride and sulfate were above their respective MCLs throughout the discharge stream and aluminum and iron were above this threshold at site D2.1 only.

Four species were detected above the acute aquatic threshold including boron and fluoride which were above this threshold throughout the discharge. Carbon disulfide and barium were both above this threshold closer to the discharge and below within 0.6 km and 2.1 km downstream, respectively, as concentrations of these species decreased downstream.

Seventeen species were detected above the chronic threshold for aquatic species; however, six of these (e.g. aluminum, iron, lead, molybdenum, uranium, and vanadium) are naturally elevated and not likely sourced from produced water. Organics above this threshold included toluene, xylenes, carbon disulfide, 1-methylnaphthalene, naphthalene and bis(2-ethylhexyl) phthalate. Bis(2-ethylhexyl) phthalate was only detected at two sites and was above the chronic threshold in both. All other species were above this threshold near the discharge and below it within 1.4 km downstream, as concentrations decreased with distance. In contrast, manganese and selenium were only above this threshold at site D3.8 (manganese) and D1.4 and D15 (selenium), as a result of increasing concentrations downstream. Boron, strontium and barium were above this threshold throughout the discharge stream and barium was also above the chronic threshold in the perennial stream. Previous studies have reported sublethal effects from flowback water including immobility in *Daphnia magna* and oxidative stress in rainbow trout (Blewett et al., 2017; Blewett et al., 2018). Finally, bis (2-ethylhexyl) phthalate was the only species detected above the human health consumption of fish threshold.

Fluoride was the only species detected above the livestock upper limit and was above this threshold through the discharge stream. BTEX concentrations at the discharge were at least three orders of magnitude below their respective RBSLs for cattle. Concentrations of low molecular weight PAHs (defined as PAH with two or three rings) were two orders of magnitude below the combined RBSL. GRO and DRO were one order of magnitude below the crude oil RBSL for calves. Application of these RBSLs is limited since they have been defined for livestock in the event of an accidental release and not for livestock who consistently drink this water, as is occurring at this site (Pattanayek and DeShields, 2004). Additionally, as with all health thresholds available, the RBSLs only pertain to one chemical and do not consider potential synergistic and antagonistic toxicological effects due to mixtures.

Finally, it was notable that few regulatory thresholds were available for chemical additives detected in the discharge including 2-butoxyethanol, PEG, PPG and NPEOs, despite the fact that these chemicals are commonly used in the oil and gas industry. While these species are unregulated in the U.S., NPEOs have been banned in Europe, mainly due to their potential to transform into NP, an endocrine disruptor (Soares et al., 2008).

3.5.1. Risk assessment in the playa lake

Multiple inorganic species including barium, boron, fluoride, manganese, molybdenum, strontium, sulfate and uranium were above at least

Table 3

Highest observed values for volatile and semi-volatile organic chemicals detected in the discharge or perennial streams compared to human, aquatic and livestock health thresholds. Values in bold exceed at least one criterion.

Chemical species	Highest concentration observed (μg/L)	Location of highest concentration	SL/MCL[a] (μg/L)	Surface water acute[b] (μg/L)	Surface water chronic[b] (μg/L)	RBSL (calves/beef cattle)[c] (ug/L)	Human health consumption of fish[d] (μg/L)
1,2,4-Trimethylbenzene	6.45	D0	56/—	–	–	–	–
1,2-Dichloroethane	**0.56**	D0	0.17/5	8800	100	–	37
1,3,5-Trimethylbenzene	1.07	D0	60/—	–	–	–	–
1-Methylnaphthalene	**6.92**	D0	1.1/—	37	2.1	–	–
2,4-Dimethylphenol	6.57	D0	360/—	212[e]	21[e]	–	850
2-Butanone	13.4	D0	5600/—	240,000	14,000	–	–
2-Butoxyethanol	1.28	D.3	2000/—	–	–	–	–
2-Methylnaphthalene	5.96	D0	36/—	–	330	–	–
2-Methylphenol	2.41	D0	930/—	230	13	–	–
4-Methyl-2-pentanone	0.93	D0	6300/—	2200	170	–	–
Acetone	49.8	D0	14,000/—	28,000	1500	–	–
Benzene	**14.6**	D0	0.46/5	2300	46	14,300/31,400	51
Bis(2-ethylhexyl) phthalate	**5.13**[f]	D2.1	5.6/6	27[e]	0.3	–	2.2
Carbazole	3.03	D0	—/—	–	–	–	–
Carbon disulfide	**50.9**[f]	D.3	810/—	17	0.92	–	–
Diesel range organics	1560	D0	—/—	–	–	29,300[g]/114,000[g]	–
Ethylbenzene	**6.6**	D0	1.5/700	130	7.3	11,700/25,600	2100
Gasoline range organics	156	D0	—/—	–	–	–	–
Isopropylbenzene	0.63	D0	450/—	–	–	–	–
Methyl acrylate	0.92	D0	42/—	–	–	–	–
Naphthalene	**11.4**	D0	0.17/—	190	1.1	–	–
n-Propyl benzene	0.8	D0	660/—	–	–	–	–
Phenanthrene	1.34	D0	—/—	30	3.6	–	–
Phenol	1.03	D.3	5800/—	1020[e]	180	–	860,000
Toluene	**6.49**	D0	1000/1000	120	2	89,500/196,000	15,000
Xylenes	**20.4**	D0	190/10,000	230	13	71,700/157,000	–
LMW PAH[h]	25.6	D0	—/—	–	–	2010/4400	–

[a] Screening level (SL) for tap water and Maximum Contaminant Level (MCL) (Williams et al., 2017). SLs are reported with Target Hazard Quotient = 1.

[b] Data from NOAA Screening Quick Reference Tables (Buchman, 2008) unless noted. If multiple values available, lowest value was selected.

[c] Drinking water risk-based screening levels (RBSLs) for cattle and calves from the American Petroleum Institute (Pattanayek and DeShields, 2004).

[d] Obtained from State of Wyoming Surface Water Quality Standards (WDEQ, 2017).

[e] Data from the Baseline Ecological Risk Assessment for Non-Asbestos Contaminants (EPA, 2013).

[f] Maximum concentration was observed at a sampling site other than the discharge.

[g] Value for crude oil.

[h] Low molecular weight (LMW) polycyclic aromatic hydrocarbons (PAHs) are defined as PAHs with three or fewer rings.

Table 4
Highest observed values for inorganic chemicals detected in the discharge or perennial streams compared to human, aquatic and livestock health thresholds. Values in bold exceed at least one criterion.

Chemical species	Highest concentration observed (μg/L)	Location of highest concentration	SL/MCL[a] (μg/L)	Surface water acute[b] (μg/L)	Surface water chronic[b] (μg/L)	Livestock upper limit[c] (ug/L)	Human health consumption of fish (μg/L)
Aluminum	**1860**	D2.1	20,000/50[d]	750 (pH 6.5–9 only)	87 (pH 6.5–9 only)	5000	–
Ammonia as N	364.5	D0	–	–	–	–	–
Antimony	0.5	D2.1	7.8/6	88	30	–	640
Arsenic	**3.6**	D3.8	0.052/10	340	150	200	10
Barium	**140**	D0	3800/2000	110	3.9	–	–
Boron	**1310**	D15	4000/—	30	1.6	5000	–
Cadmium	**0.2**	D2.1	9.2/5	1.4[e]	0.19[e]	50	Hardness dependent
Calcium	75,700	D15	—/—	–	–	–	–
Chloride	**251,000**	D15	—/250,000[d]	–	–	–	–
Fluoride	**2910**	D2.1	800/2000[d]	200 (hardness < 50)	–	2000	–
Iron	**2620**	D2.1	14,000/300[d]	–	1000	–	–
Lead	**3.2**	D2.1	15/15	42 [e]	1.6[e]	50	–
Magnesium	51,800	D15	—/—	–	82,000[e]	–	Hardness dependent
Manganese	**229**	D3.8	430/50[d]	2300	80	–	–
Molybdenum	**84.9**	P34.4	100/—	16,000	34	–	–
Potassium	30,300	D15	—/—	373,000	53,000[e]	–	–
Selenium	**12.8**	D15	100/50	13	5	50	4200
Silica	39,900	D2.1	—/—	–	–	–	–
Sodium	454,000	D15	—/—	–	680,000[e]	–	–
Strontium	**4805**	D0	12,000/—	15,000	1500	–	–
Sulfate	**939,000**	D15	—/250,000[d]	–	–	–	–
Uranium	**5.2**	P61.3	—/—	46	0.5	–	–
Vanadium	**24.3**	D15	86/—	280	19	100	–
Zinc	67.3	P34.4	6000/5000[d]	85	85[e]	24,000	26,000
Radium	**0.50 Bq/L**	D0	0.19 Bq/L	–	–	–	–

[a] Screening level (SL) for tap water and Maximum Contaminant Level (MCL) (Williams et al., 2017). SLs are reported with Target Hazard Quotient = 1.

[b] Data from NOAA Screening Quick Reference Tables (Buchman, 2008) unless noted. If multiple values available, lowest value was selected.

[c] Drinking water risk-based screening levels for calves and cattle from the Colorado State University Extension Office (Soltanpour and Raley, 1999).

[d] Secondary MCL.

[e] Thresholds from the Baseline Ecological Risk Assessment for Non-Asbestos Contaminants (EPA, 2013).

one threshold in the playa lake, which is a major water source for livestock and wildlife in the area. Many of these chemicals reach their maximum value at site D2.1 or D3.8 showing that while the discharge may be safe, changes downstream could result in water that is unsuitable for beneficial reuse. Additionally, multiple organic species including acetone, 2-butanone, 2,4-dimethylphenol, DRO, PPGs and PEGs were detected in the playa lake. No organics were detected above available health thresholds; however, the complex chemistry in the playa lake once again highlights the limitations of health thresholds for individual chemical species since they do not consider mixture effects. As a result, a determination on potential health risks of this water for livestock cannot be made.

4. Conclusion

A comprehensive chemical analysis was conducted on a stream composed of treated PW released for agricultural beneficial reuse under U.S. EPA's NPDES program. This study aimed to characterize the discharge and assess potential health impacts to downstream users. Chemical concentrations at this discharge were near minimum values for PW in the U.S. Due to that and the fact that PW composition varies widely throughout the U.S., these results can be applied to this site only and are not representative of all NPDES PW discharges.

Over 20 different semi-volatile and volatile organic compounds, as well as three surfactant series (PEGs, PPGs and NPEOs), were detected in the discharge that were not specified in the effluent limits. Concentrations of organic chemicals generally decreased with distance from the discharge. Notable attenuation of organics was observed in the wetlands, indicating that constructed wetlands may be an effective strategy for managing PW discharge quality. However, the long-term fate of PW constituents regarding accumulation in sediments and infiltration to groundwater remains to be investigated.

Similar to concentrations of organics, the concentrations of some inorganic species associated with PW decreased downstream, including strontium, barium, total radium, and alkalinity. In contrast, however, concentrations of several inorganic species associated with the discharged PW increased with distance downstream, including four of the six chemicals or classes of chemicals with defined permit effluent limits (Table 1). At this site, all regulated chemicals remained below the permit effluent limits throughout the discharge stream; however, a subsequent study conducted at a separate NPDES PW discharge in the area revealed that specific conductance increased above the permissible discharge limit downstream of that discharge. This finding has major implications because reporting requirements for NPDES permits pertain to the discharge site only, while downstream changes are not considered. Consequently, our data reveal that changes in water quality downstream due to chemical, biological, physical, and hydrological processes must be assessed to fully understand the potential impact of these releases.

A systematic evaluation of health thresholds revealed that regulatory limits are currently unavailable for most species detected in this stream. Additionally, while the threshold values cited in this study are helpful guidelines, their applicability to this site is limited because they do not consider mixture effects. Numerous studies have shown that chemical species may have synergistic or antagonistic effects on the toxicity of other chemicals (Tang et al., 2013; Kassotis et al., 2015). Additionally, there are likely undetected chemicals and transformation products present in the discharge with unknown impacts on downstream users.

With the highly variable and complex nature of PW throughout the U.S., widely applicable chemical permit effluent limits are impractical for NPDES PW releases, and standardized analytical methods for many of these chemicals are still lacking. Thus, additional toxicity testing guidelines would add a critical line of evidence to determine if NPDES discharges are "of good enough quality." Currently, NPDES permits in Wyoming only require acute toxicity testing and do not consider chronic toxicity. Toxicity tests are well suited for complex waste streams with relatively low salinity, such as PW released for beneficial reuse. Thus, a companion study analyzed acute toxicity, mutagenicity and developmental toxicity in these samples.

In conclusion, this study shows that a critical amount of research regarding analytical characterization, environmental distribution, hydrological processes, toxicological effects and mechanisms, as well as bioaccumulation and uptake in organisms remains to be conducted before PWs can be deemed "of good enough quality" for environmental release.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2020.136607.

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