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Wastewater Disposal from Unconventional Oil and Gas Development Degrades Stream Quality at a West Virginia Injection Facility

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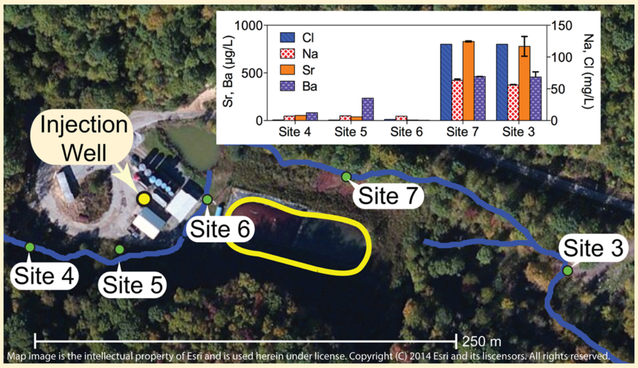
Supporting Information

ABSTRACT: The development of unconventional oil and gas (UOG) resources has rapidly increased in recent years; however, the environmental impacts and risks are poorly understood. A single well can generate millions of liters of wastewater, representing a mixture of formation brine and injected hydraulic fracturing fluids. One of the most common methods for wastewater disposal is underground injection; we are assessing potential risks of this method through an intensive, interdisciplinary study at an injection disposal facility in West Virginia. In June 2014, waters collected downstream from the site had elevated specific conductance (416 μS/cm) and Na, Cl, Ba, Br, Sr, and Li concentrations, compared to upstream, background waters (conductivity, 74 μS/cm). Elevated TDS, a marker of UOG wastewater, provided an early indication of impacts in the stream. Wastewater inputs are also evident by changes in $^{87}Sr/^{86}Sr$ in streamwater adjacent to the disposal facility. Sediments downstream from the facility were enriched in Ra and had high bioavailable Fe(III) concentrations relative to upstream sediments. Microbial communities in downstream sediments had lower diversity and shifts in composition. Although the hydrologic pathways were not able to be assessed, these data provide evidence demonstrating that activities at the disposal facility are impacting a nearby stream and altering the biogeochemistry of nearby ecosystems.



INTRODUCTION

Increasing demand for fossil fuels and depletion of traditional oil and gas reservoirs has driven the development of shale gas, coal-bed methane (CBM), and other unconventional oil and gas (UOG) resources using technologies such as directional drilling and hydraulic fracturing e.g., ref 1. These resources are an important part of the United States' energy resource portfolio. While CBM production is estimated to remain at current levels of national gas production (8%), development of shale gas is estimated to account for at least 50% of all natural gas produced in the U.S. by 2040.[2] Production of UOG resources results in liquid (e.g., produced waters or wastewaters), solid (e.g., drill cuttings), and gaseous wastes, which pose unknown risks and potential consequences to the quality of atmospheric, groundwater, surface water, soil, and environmental resources.

Wastewaters from UOG production are mixtures of residual fluids used to complete the well and formation brine.[1,3−7] Initially, these wastewaters reflect the composition of the injected fluid, then over time, the chemistry shifts to reflect the chemical composition of the formation, e.g.,.[5] Wastewaters from the Marcellus Shale typically have elevated total dissolved solids (TDS, up to 300 000 mg/L),[5,8−10] variable concentrations of organic compounds,[6,11] and naturally occurring radioactive material (NORM[12]). An average well producing from the Marcellus Shale yields approximately 5 million liters of wastewater over its lifetime; these large volumes of returned fluids, with complex chemistries, present water management challenges. The chemistry can affect the suitability of wastewaters for reuse or the strategy for disposal.[3,4,13,14]

UOG wastewaters are managed in a variety of ways including treatment and reuse for new well completions,[15] disposal through publicly owned or commercial wastewater treatment plants,[14,15] or disposal in Class II underground injection control (UIC) wells.[4,14,15] Class II disposal wells are estimated to be disposing of over 2 billion gallons of wastewater from oil and gas operations every day.[16] They are located across the United States and there are approximately 36 000 Class II UIC wells handling wastewaters from UOG operations.[16] Impacts on

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environmental health from accidental or intentional releases during handling, disposal, treatment, or reuse are poorly documented, with few reports in the literature.[17] Potential pathways for wastewater to enter surface water or groundwater include: (1) releases from pipelines or tanker trucks transporting fluids, (2) leakage from wastewater storage ponds through compromised liners and overflows from the ponds, or (3) migration of the fluids through the subsurface at the injection depth or through failed injection well casings. Research is needed to examine the potential impacts of wastewater releases on environmental health, which are likely to accelerate with the growing pace of UOG development.

Near Lochgelly, West Virginia, wastewaters from UOG development are disposed of in a Class II UIC well. A small stream runs through the facility and provides an opportunity to sample surface water and sediments near a wastewater disposal operation (Figure 1). This study is a part of a larger effort by the US Geological Survey (USGS) and university researchers to quantify biogeochemical and human health changes resulting from UOG wastewater disposal.[18] Here, we used key field and inorganic chemical signatures, as well as microbial community compositions, to identify UOG wastewater impacts to stream biogeochemistry by characterizing differences between sites within the disposal facility and background sites located upstream or in a separate drainage with no known inputs from oil and gas development. Although the pathway of contaminants from the disposal facility to the stream could not be assessed, these results clearly demonstrate that wastewater handling practices at the site affect stream and sediment quality.

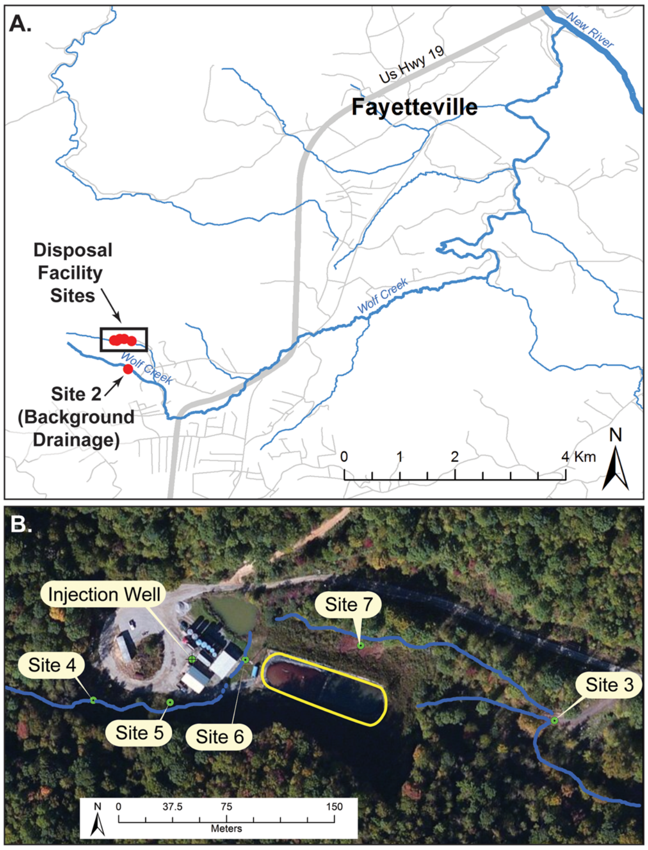

Figure 1. Map of sampling locations near Fayetteville, WV within the Wolf Creek watershed (A) and specific sites (B) in a stream running adjacent to a class II disposal facility. Panel A shows that Site 2 was located in a separate drainage from the disposal facility sites (outlined in black box), which are shown in panel B (Sites 4, 5, 6, 7 and 3). In panel B, the blue line highlights the stream, and the yellow outline is the location of the former impoundment ponds. Source: Esri. DigitalGlobe, GeoEy, i-cubed, Earthstar Geographies, CNES/Airbus DS, USDA, USGS, AEX, Getmapping, Aerogrid, IGN, IGP, swisstopo, and the GIS User Community.

■ MATERIALS AND METHODS

Site Description. The study area is located near a UOG wastewater UIC facility (disposal facility) in central West Virginia (Figures 1 and S10 of the Supporting Information). The disposal well was originally drilled in 1981 as a natural gas production well to a depth of 990.6 m. The well was reworked as a Class II injection well in 2002, with fluids injected into a sandstone reservoir at a depth of 792.5 m. In addition to the disposal well, the facility has brine storage tanks, an access road, and two small, lined impoundment ponds. Until the spring of 2014, a portion of the wastewaters were temporarily stored in the holding ponds prior to injection to allow for settling of particulates that could potentially clog the pore space in the receiving reservoir. The ponds operated from 2002 to spring 2014 when they were removed and the area recontoured and planted with grass.

A certified record inventory for the site was obtained from the West Virginia Environmental Quality Board (WVEQB), which provided API numbers for 25 wells shipping wastewaters to the facility. Between 2002 and 2014 the UIC well injected approximately 1.5 million barrels (equal to ∼178 million liters) of wastewater from the 25 production wells located in West Virginia. Information about these production wells was obtained from the West Virginia Department of Environmental Protection (WVDEP), Office of Oil and Gas permit database ((http://tagis.dep.wv.gov/oog/) as detailed in Table S1. All of the wells are producing natural gas, with 15 wells producing coal bed methane, while four wells are producing from the Marcellus Shale. An additional 4 wells are characterized as horizontal gas wells producing from the Lower Huron shale formation (Lower Huron is WVDEP nomenclature, USGS usage is Huron Member of the Ohio Shale). We were unable to find records for the remaining two wells listed in the WVEQB document.

The Wolf Creek watershed encompasses 4430 ha with Wolf Creek flowing to the northeast and joining the New River ∼10 km downstream from the facility (Figure S10). The New River is used for recreation and is a local drinking-water source. The headwaters of Wolf Creek flow through areas of past surface coal mining that have since been covered or reclaimed and are primarily residential or agricultural land.[19] Despite reclamation, Wolf Creek was classified as biologically impaired by the WVDEP in 2008, due to high levels of iron and dissolved aluminum,[20] which may be due to acid mine drainage from the Summerlee coal mine.[21]

An initial reconnaissance-sampling trip conducted in September 2013 indicated potential impacts to the headwaters requiring additional investigation (Table 1, Figure 1). To further study impacts from the disposal facility, samples were collected from two locations within the Wolf Creek watershed: 1) a small tributary that runs through the disposal facility and 2) a separate drainage (referred to as "background drainage"), Site 2, with no potential impact from the disposal facility (Figure 1A, Table 1). The tributary begins upstream from the disposal facility and runs adjacent to the disposal well, then

Table 1. Site Descriptions, Field Parameters and NVDOC of Water Samples Collected in September 2013, June 2014, and September 2014 in Tributaries of Wolf Creek[a]

sample	type, location	pH			conductivity (μS/cm)			temp. (°C)			NVDOC[b] (mg/L)		
		Sept. 2013	June 2014	Sept. 2014	Sept. 2013	June 2014	Sept. 2014	Sept. 2013	June 2014	Sept. 2014	Sept. 2013	June 2014	Sept. 2014
site 2	background, separate drainage	7.8	6.5	ND[c]	216	109	ND	14.1	16.0	ND	2.65	1.42	ND
site 4	background, upstream of disposal facility	ND	6.5	6.7	ND	74.0	125	ND	18.2	16.0	ND	1.13	1.60
site 5	adjacent to the disposal facility	ND	6.2	ND	ND	90.0	ND	ND	20.3	ND	ND	3.31	ND
site 6	adjacent to the injection well shed	ND	6.9	ND	ND	82.0	ND	ND	20.1	ND	ND	2.20	ND
site 7	adjacent to the former impoundment ponds	5.8	6.4	6.5	1750	416	1040	21.0	24.1	17.4	7.35	2.49	3.10
site 3	downstream of the disposal facility	6.4	6.1	6.5	1210	379	1110	25.0	22.9	17.7	3.85	3.24	3.40
field equipment blank	blank	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.86	0.50	0.70

[a]Site locations are indicated in Figure 1. All field parameter values are the median of three individual measurements. Sites 7 and 3 were sampled in duplicate in June 2014 and values presented are averages. [b]NVDOC = non volatile dissolved organic carbon. [c]ND = not determined.

downhill from the two former impoundments (Figure 1B). The background drainage-stream meets the disposal-facility-stream prior to joining the main stem of Wolf Creek, ~1000 m downstream from the facility (Figure 1A). No samples were obtained for the current study below Site 3 due to other industrial activities in the area (e.g., an automotive junkyard).

Site Sampling and Analysis. The disposal facility and background drainage streams (Site 2) were sampled in June 2014 at five points within the disposal facility, including locations upstream (Site 4), within (Site 5 and 6), and downstream (Sites 7 and 3) from the disposal facility (Figure 1B, Table 1). Conductivity, pH, and aqueous Fe^{2+} were determined in the field as described in the SI Methods. Water samples were collected from the approximate center of the stream for analysis of alkalinity, cations, anions, strontium (Sr), oxygen (O) and hydrogen (H) isotopes, nonvolatile dissolved organic carbon (NVDOC), trace inorganic elements, and disinfection byproducts (DBP) as described in the SI Methods. Additional field measurements and water samples for NVDOC and major and minor cations were collected in September 2013 and 2014 at Sites 2, 7, and 3. Streambed sediment samples were collected for carbon, nitrogen, and sulfur elemental analysis (CNS), Fe speciation, total inorganic elements, and microbial community analysis as described in the SI Methods. Detailed sampling, quality assurance/quality control (QA/QC) procedures, and analytical methods are described in the SI Methods. No hydrologic measurements were conducted or groundwater sampled during the September and June sampling efforts. Further investigations into the hydrology of the site were not possible due to site access limitations. The microbial community sequence data set was deposited in the National Center for Biotechnology Information (NCBI) Sequence Read Archive (SRA) under accession number SRP073303.

RESULTS AND DISCUSSION

Impacts to Stream Water Quality. Tributaries of Wolf Creek that were sampled in September 2013, June 2014, and September 2014 showed impacts on the tributary downstream from the injection disposal facility (Figure 1, Table 1). In September 2013 exploratory sampling indicated that there was elevated specific conductance at Sites 7 and 3 compared to the background drainage Site 2 (Table 1). Intensive sampling in June 2014 revealed that background sites located in the separate drainage (Site 2) or upstream (Site 4), with no known UOG wastewater inputs, exhibited no visual signs of impacts or disturbance due to anthropogenic activity. Waters at these sites had neutral pH and specific conductance (~80 μS/cm, Table 1) in line with that of minimally impacted streams in the area. Sites 5, 6, 7 and 3, which were located on the facility, adjacent to the disposal injection well, adjacent to the former holding ponds, or downstream, respectively, all exhibited visual signs of impacts. All 4 of these sites had red-orange sediments and waters characterized by neutral pH (Table 1). At Sites 6, 7, and 3 there were hydrocarbon odors once the sediment was disturbed, although Site 6 waters had a specific conductance in line with background sites and Site 5. Waters from sites downstream from the former impoundments (Sites 7 and 3) had elevated specific conductance (~400 μS/cm) indicating that visual impacts at these sites were associated with alterations to the stream chemistry. The elevated specific conductance provided the field evidence that impacts to the stream are due to UOG wastewaters, because produced waters from both conventional and unconventional oil and gas wells in the Appalachian Basin are characterized by high salinity.[5,6,10,22−26] Specific conductance at all of the sites was lowest at the June 2014 sampling time point, likely due to the fact that 3.0 cm of precipitation fell in 24 h on June 12, 2014 in nearby Beckley, WV,[27] less than 1 week prior to our sampling on June 17, 2014.

Water samples collected in June 2014 showed clear differences in chemistry upgradient and downgradient from the waste-disposal facility (Figures 2 and 3 and Table S2). Streams in this region are naturally low in NVDOC: below 1.5 mg/L at both background sites at the time of sampling (Figure 3a, Table S2). Concentrations increased to 2.2−3.3 mg/L at sites on and downgradient from the facility. In contrast, nitrate (NO_3^-) and sulfate (SO_4^{2-}) concentrations in the stream decreased on and below the disposal facility. Total Fe concentrations adjacent to the former impoundments were 8.1 mg/L, far in excess of the 0.13 mg/L found upstream from the facility (Table S2).

Chloride (Cl^-, 115 mg/L) and bromide (Br^-, 0.80 mg/L) concentrations were elevated adjacent to the former impoundments (Site 7), compared to 0.88 mg/L Cl^- and <0.03 mg/L Br^- at Site 4, upstream from the facility (Figure 3b,c and Table S2). The concentrations at Site 7 correspond to a Cl/Br ratio (mass basis) of ~144, which is in-line with produced waters

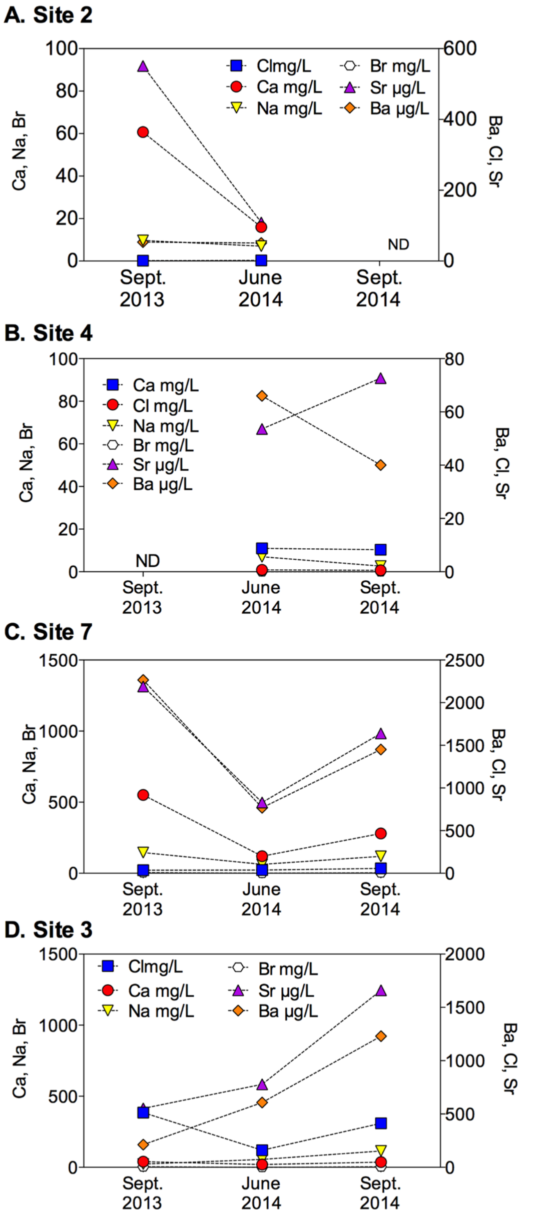

Figure 2. Major anion and cation concentrations over time at Sites 2 (A), 4 (B), 7 (C), and 3 (D). Samples were collected in September 2013, June 2014, and September 2014 at all sites with the exception of Sites 2 and 4, which were only sampled in Sept. 2013 and June 2014 and June and September 2014, respectively (ND = not determined). Note the different scales in panels A and B.

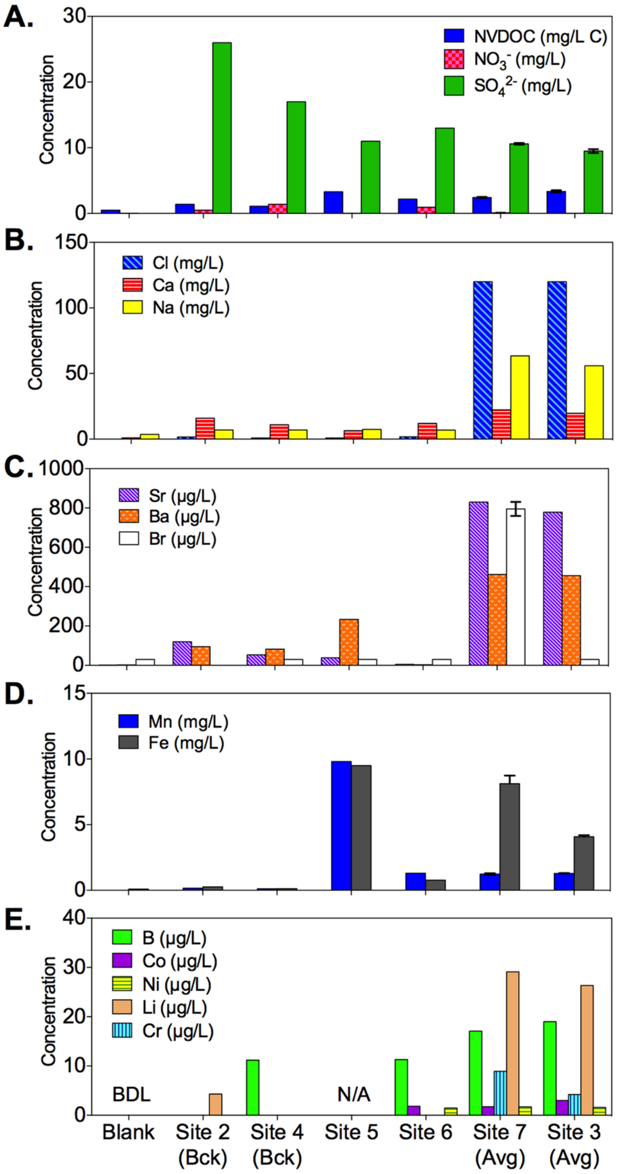

Figure 3. Chemistry in waters collected in June 2014 from a stream adjacent to the disposal facility. (A) Concentrations of nonvolatile dissolved organic carbon (NVDOC), sulfate, and nitrate; (B) chloride, calcium, and sodium concentrations; (C) strontium, barium, and bromide concentrations; (D) concentrations of dissolved Mn and Fe; and (E) trace element concentrations. Site locations are indicated in Figure 1 and Sites 2 and 4 are background (Bck) sampling locations. Site 2 is located in a separate drainage, whereas Site 4 is upstream of the disposal facility. Sites 7 and 3 were sampled in duplicate and averages (Avg) of individual measurements are presented. The blank is the field equipment blank.

derived from evaporated paleoseawater.[28] Dissolved calcium (Ca^{2+}), sodium (Na^{+}), strontium (Sr^{2+}), and barium (Ba^{2+}) concentrations were also elevated at Sites 7 and 3 (Figure 3b,c). Due to the very low concentrations of Cl^{-} and Na^{+} in the background water, these elements and Br^{-}, Sr^{2+} and Ba^{2+}, serve as a good local tracer of UOG wastewater impacts.[29] Iodine can be another indicator of UOG wastewater impacts;[30] however, concentrations were below the detection limit of 1 mg/L at all sites. Concentrations of several trace elements were also elevated above background, particularly lithium (Li^{+}), which is present at over 6 times the background concentration at Site 7 (Table S2, Figure 3e). Increased trace element concentrations in surface waters may be due to mobilization from sediments by the wastewater-derived inorganic salts, similar to what has been observed for roadside soils impacted by deicing salts.[31−39] Increased concentrations of Cl^{-}, Br^{-}, Sr^{2+}, and Ba^{2+} have been found in Pennsylvania streams downstream from wastewater treatment plants.[30,40] Elevated Br^{-} concentrations in UOG wastewaters can lead to increases in disinfection byproducts (DBP) downstream from wastewater treatment plants,[41] however DBP were not observed at any of the sites sampled in the Wolf Creek tributary.[42]

Although the concentrations of Cl^{-} between Sites 7 and 3 did not change (indicating minimal dilution between the sites), concentrations of Ca^{2+} and Na^{+} decreased by 12%, Ba^{2+} and Li^{+}

by 9% and Sr^{2+} by 6%. Bromide decreased to below detection at Site 3. The losses from solution of these elements indicate potential for incorporation into the stream-bed sediments. Skalak et al. 2014,[43] found the accumulation of Sr, Ca, and Na (in addition to Ra) in soils in areas of Pennsylvania where road spreading of produced-water brines was a common approach for deicing. Comparing the June 2014 results to those from September 2013 and 2014 shows that most elements that were elevated compared to background sites in June were lower in absolute concentration than observed during the September samplings (Figure 2), indicating dilution associated from recent rain events prior to the June 2014 sampling.[27]

Isotopic Indicators of UOG Wastewater Sources. Isotopic data for H, O, and Sr in samples collected in June 2014 show marked differences (Figure 4; Tables S2 and S5). Background samples from Sites 2 (background drainage) and 4 (upstream), exhibit lower Sr concentrations and higher $^{87}Sr/^{86}Sr$ (>0.713), than the samples on or below the disposal facility suggesting contribution from additional sources of water into the stream. Because Sr isotopes do not fractionate appreciably in the environment, sources of Sr-rich water with a lower $^{87}Sr/^{86}Sr$ ratio appear to contribute to the stream near Site 6 and again below the disposal facility (Sites 3 and 7). For context, these data are compared against late stage produced waters from the Marcellus Shale from Greene County, Pennsylvania and mine drainage water from the various Pennsylvanian age coals in the area (external Sr data from[44]). There is some spatial variability in strontium isotope geochemistry across the Marcellus Shale, so data from the closest county (Greene) were used. On this type of plot ($^{87}Sr/^{86}Sr$ vs 1/Sr), mixtures between any two end-members plot as straight lines (Figure 4a). The data point for the Site 6 sample falls along a mixing line between upstream water (Site 4) and Marcellus Shale produced waters. End-member mixing calculations suggest the sample from Site 6 is the result of a small contribution of Marcellus Shale produced waters (0.004%). Such small contributions can be identified because of the high concentration of Sr in Marcellus Shale produced water (>1500 mg/L) relative to the streamwater (<0.1 mg/L). The Sr signatures for samples from Sites 3 and 7, downstream from the disposal site are markedly different from the Site 6 sample. Their compositions overlap with data from Pittsburgh coal mine water, potentially suggesting an input of up to 50% of CBM produced waters in these samples. Loss of the apparent Sr signature from Marcellus Shale produced waters in these samples relative to the upstream Site 6 sample may be due to an overprinting by the relatively Sr-rich coal-sourced water (~1.2 mg/L coal-sourced water contribution vs ~0.1 mg/L contribution from the Marcellus Shale produced water).

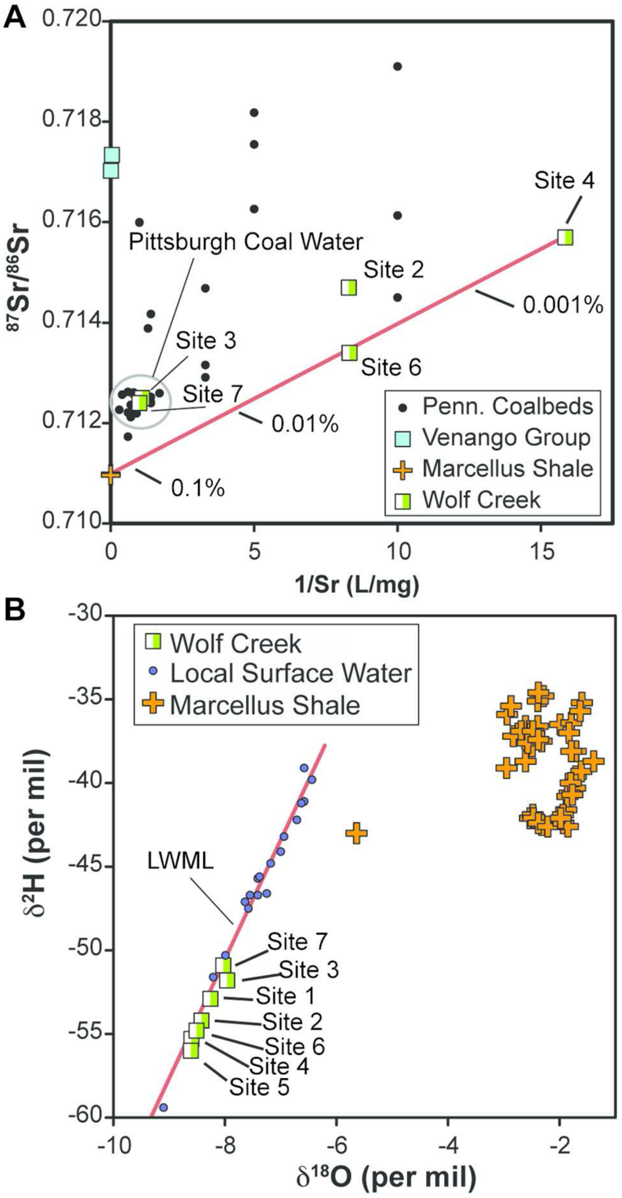

Figure 4. Two-component mixing plots of $^{87}Sr/^{86}Sr$ against 1/Sr concentration for Wolf Creek tributary water samples (green/white squares). Values for Pennsylvania coal beds (circles), Venango Group brines (blue squares), and Marcellus Shale produced waters (crosses) are provided for reference. Red line in panel A shows mixing pathway between Marcellus Shale produced water and Site 4. Percentages along the pathway indicate relative contribution of Marcellus Shale produced water in the mixture. Red line in panel B is the local meteoric water line (LMWL).

Results from the $\delta^{18}O$ and δ^2H analyses (Figure 4b) indicate that all of the samples collected are dominated by local meteoric water. Produced water samples from the Marcellus Shale from southwestern Pennsylvania are located distal to the local meteoric water line (LMWL) related to their origin from surface water mixing with formation water, which is highly evaporated paleoseawater.[5] No published $\delta^{18}O$ and δ^2H data exist for conventional oil and gas wells produced waters in nearby areas, but examination in other parts of the basin show overlap between Marcellus Shale produced waters and those from conventional oil and gas wells.[5,23] Thus, these data show no indication of mixing with substantial quantities of Marcellus Shale produced waters or likely any local conventional hydrocarbon produced waters. However, with a potential contribution of <1% such as possibly predicted from Sr isotopes at Site 6, no shift in $\delta^{18}O$ and δ^2H would be expected. Estimated recharge temperatures based on equations by Dansgaard[45] are slightly warmer at the sites below the disposal facility (mean = 8.1 °C) than those for the remaining sites (mean = 7.4 °C), and their compositions cover the range of local surface waters (data from ref 46) suggesting a relatively shallow recharge source for the waters from Sites 3 and 7, such as coal mine adits or CBM water, although no local $\delta^{18}O$ and δ^2H data are available for either.

Characterization of Stream Sediments. Sediment samples for total elemental analysis and extractable iron analyses were only obtained in June 2014. The percent carbon composition of the samples ranged from less than 1% to 5.4% with less than 1% of N and S. The C, N, and S contents of the sediments were consistent among sites with the exception of elevated C at site 6, which might be due to surface activities on site. The bulk sediment cation and trace element concentrations were similar between upstream, background and downstream streambed sediments (Figure S11 and Table S3), indicating no measurable impact from the waste disposal facility. Total Ca and Na concentrations observed were much lower (<2.5 mg/g; Table S3) than that observed in sediments impacted by oil and gas wastewaters (0.015−25 mg/g Ca and 0.01−48 mg/g Na;[43]).

Mercury and uranium concentrations (Table S4) in sediment samples were within the range of values estimated for average upper crustal rocks[47] and showed no overall differences between downstream, impacted and background sites (Table S4 and Figure 5). In contrast, the ^{226}Ra concentration at Site 6 was elevated well above background (^{228}Ra concentrations were below detection in all samples). In contrast to all other sites, ^{238}U/^{226}Ra in sediments at Site 6 were not in secular equilibrium (Table S4) indicating an external source of ^{226}Ra to the sediments. Elevated ^{226}Ra activity, a product of ^{238}U decay, is characteristic of produced water from the U-rich Marcellus Shale (e.g., ref 12), and elevated Ra concentrations were observed near a Marcellus Shale wastewater treatment facility discharge site[40] and in areas where conventional oil and gas wastewaters were used for road deicing.[43] The excess ^{226}Ra detected in sediments at Site 6 is consistent with the Sr isotope data that suggest a small contribution of Marcellus Shale produced water in water samples from the same location. The ^{226}Ra at Sites 3 and 7 appears to be in secular equilibrium with ^{238}U and suggests negligible input of external ^{226}Ra at these sites. This is consistent with input from coalbed methane produced waters, as they generally contain very little radium (<20 pCi/L).[48]

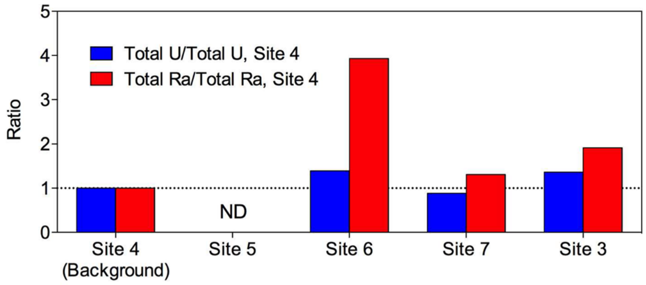

Figure 5. Ratios of total U and Ra in sediments collected from 5 sites along a stream adjacent to the disposal facility. Site locations are shown in Figure 1. Concentrations of total U and Ra are available in Table S4. No ^{228}Ra was detected so Total Ra equals ^{226}Ra.

Total iron concentrations were higher at Site 3 (Figure S11), but iron extractions showed that biogenic Fe(II) and bioavailable Fe(III) were elevated at Sites 7 and 3 (Table S4). Sites 7 and 3 had similar extractable Fe(III) concentrations, in agreement with the field observations of red-orange iron oxide-rich sediments. However, Site 7 duplicate field samples were highly variable visually (color, texture) and this is reflected in the variability seen in iron values between samples. One of the Site 7 samples was highly reduced, as shown by high Fe(II) contents (1340 μmol/g sediment; Table S4) and low % of Fe(III) and corresponded to a dark gray-black color of the sediments. The elevated iron contents at the site are likely associated with small-scale heterogeneities and potentially past coal mining in the area,[20,21] but wastewater contamination may drive the distribution between biogenic Fe(II) and bioavailable Fe(III).

Microbiology. Analysis of Illumina sequence reads of the 16S rRNA gene v4 region revealed striking differences in microbial community structure in the streambed sediments upstream and downstream of the disposal facility (Figure 6, Table S8). The alpha diversity was observed to be much lower at Site 7 (Inverse Simpson Index of 377), adjacent to the former impoundments, than either downstream at Site 3

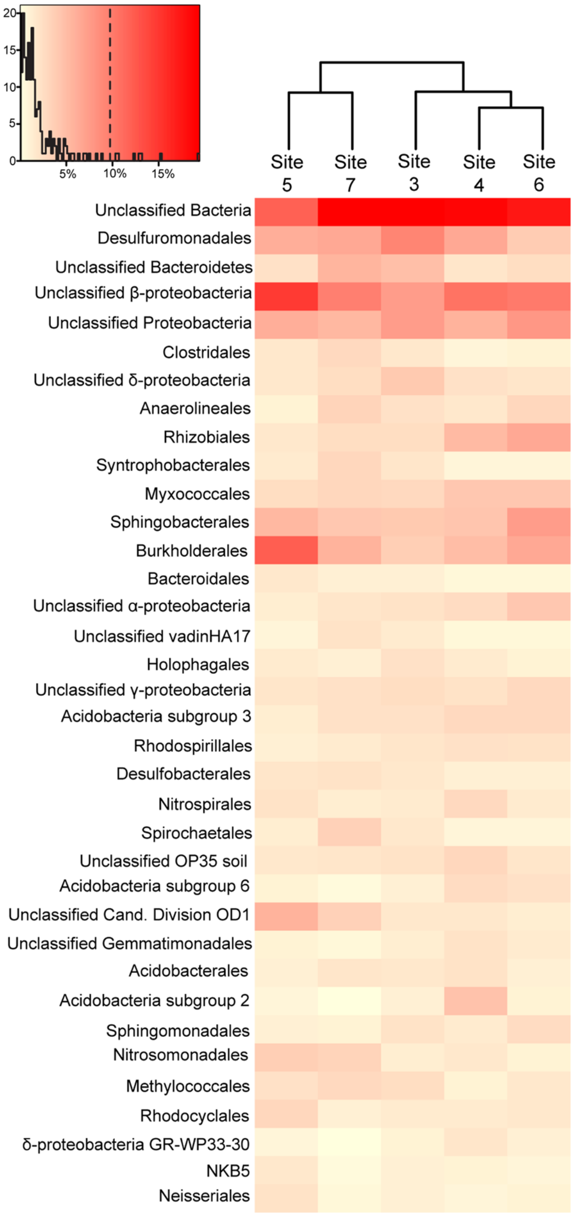

Figure 6. Heatmap and dendrogram of microbial orders comprising >1% of microbial communities in sediments collected from 5 sites along a stream adjacent to the disposal facility in June 2014. Site locations are indicated in Figure 1, and sediments were collected from the upper 5 cm of the streambed. Dendrogram represents relatedness of communities between sites.

(Inverse Simpson Index of 1063) or upstream at Sites 4 and 6 (Inverse Simpson's Indices of 689 and 787, respectively). A heatmap was constructed to visualize differences in the structure of the microbial community using bacterial orders of greater than 1% abundance combined with cluster analysis (Figure 6). Notably, anaerobic orders including the Desulfuromonadales, Anaerolineales, and Syntrophobacterales were found at greater abundance at Sites 7 and 3, suggesting anaerobic conditions in the shallow streambed.[49−51] In addition, Clostridiales were observed in greater abundance at Sites 7 and 3, a finding similar to that in other UOG wastewater influenced systems.[6,52] In contrast, the predominantly aerobic Rhizobiales,[53] Myxococcales,[53] and Sphingobacteriales[54] were found in greater abundance at Sites 4 and 6.

Canonical correspondence analysis[55] and the ENVFIT function in the R vegan[56] package were utilized to relate differences in microbial community structure to the measured geochemical parameters of the streamwater (Figure S12). The community at Site 7 separates from Site 4 along axes 1 and 2, while the community at Site 3 separates from Site 4 along axes 1 and 3. In this analysis, the elevated dissolved metal concentrations observed at Sites 7 and 3 vary along axes 1 and 2, suggesting a relationship between the elevated metals found at these sites and the shifts in microbial community composition. Eigenvectors and loadings for Figure S12 are presented in Table S9.

Reactions That Control Element Stability/Fate and Transport. TCO_2 (total dissolved carbon dioxide) concentrations and P_{CO2} (partial pressure of carbon dioxide) values were calculated from the solution compositions (Table S7). P_{CO2} values at all sites ranged from 1.8% to 5.7%, substantially higher the atmospheric value of 0.04%, indicating the impact of respiration on the streamwater chemistry. Calcite, rhodocrosite ($MnCO_{3,s}$), and siderite ($FeCO_{3,s}$) were undersaturated but approached saturation with respect to rhodocrosite at Sites 5 and 6 and siderite at Sites 5 and 7. Saturation with respect to barite ($BaSO_{4,s}$), which can control both Ba^{2+} and Ra^{2+} concentrations and act as a reservoir for these elements in sediments,[57] was examined using the streamwater chemistry. Barite was undersaturated or slightly supersaturated at all sites, including the background sites (Table S7). Maximum saturation indices were observed at Site 7 in September 2014 (0.7) and Site 3 in June 2014 (0.2−0.5). Barite precipitation at these low degrees of saturation is unlikely given the inhibition by humic and fulvic acids, principal constituents of NVDOC, at NVDOC concentrations observed during this study (Table S2).[58] Thus, Sr^{2+}, Ba^{2+}, Ra^{2+}, and other metal ions elevated owing to UOG wastewater impacts are likely present as sorbed species in the sediments rather than incorporated into minerals and, as such, could be mobilized upon changing chemical conditions.

Implications. Multiple lines of evidence demonstrate that activities at the disposal facility are impacting the stream that runs through the area, as shown by changes in the inorganic chemistry and microbiology at the downstream sites. In addition, collaborative papers examining the organic chemistry and endocrine disrupting activity[59] in the same samples, provide additional lines of evidence demonstrating that activities at the disposal facility are impacting the nearby ecosystem. Many of the inorganic constituents known to be associated with UOG wastewaters and Appalachian Basin brines, e.g., Cl^-, Ca^{2+}, Na^+, Sr^{2+}, and Ba^{2+},[5,6,10,22−26,29,30] were elevated in streamwater samples downstream of the disposal facility, indicating that the impacts were associated with UOG wastewater inputs. Indeed, Site 7 waters had Cl^- and Br^- concentrations consistent with the influence of wastewater brines from conventional and unconventional resources, with concentrations consistent with coal bed methane,[25] Marcellus Shale produced waters,[9,30] and produced waters from Appalachian Basin conventional oil and gas wells.[23,30] However, the contribution of wastewaters to the stream chemistry is small, but still detectable, with less than 0.001 part brine to 0.999 parts freshwater needed to account for the observed stream Br^- and Cl^- contents.

Inorganic components of brine can immediately impact water quality, and can potentially alter ecosystem functions by impacting biogeochemical nutrient cycling. For example, increases in salinity due to deicing of roads are associated with disruptions in nitrogen cycling, likely due to alterations of microbial communities.[60,61] The alterations in sediment microbial communities at the downstream sites could impact nutrient cycling in the stream, highlighting the importance of understanding the link between microbial community structure and function in environments impacted by UOG wastewater releases. Increasing hardness and metal concentrations in ecosystems impacted by road salt were also shown to have toxic effects on aquatic organisms and terrestrial plants.[38,62,63] At Wolf Creek, organisms may be similarly impacted; similar components are elevated in stream waters due to disposal activities and wastewater inputs.

Our findings show that the disposal facility is impacting the stream but we are unable to identify a point source of contaminants to the stream. Disposal facilities offer multiple potential sources, including leaking wastewaters from storage ponds and tanks, as well as from fuel and motor oil from vehicles making frequent deliveries (e.g., wastewater transport). Contaminants from impoundment ponds or spills can reach streams by overland flow or through groundwater discharge that leach into the subsurface through failed or incomplete liners. In addition, background concentrations in streams may be elevated owing to previous land use, such as coal mining, which highlights the necessity of identifying and sampling an appropriate background site (e.g., upstream). Further investigations of potential contaminants, endocrine disruption activity of stream waters, as well as studies of aquatic organisms, and comparisons with impacts from other anthropogenic inputs are warranted to determine potential environmental health impacts of UOG wastewater disposal practices.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.6b00428.

> Detailed descriptions of site sampling, quality assurance/quality control (QA/QC) procedures and analytical methods; supporting references; Tables S1−S9 and Figures S10−S12 (PDF)

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Notes

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