

PAPER

View Article Online
View Journal | View Issue



Cite this: *Environ. Sci.: Processes Impacts*, 2017, **19**, 605

Uranium mobility and accumulation along the Rio Paguete, Jackpile Mine in Laguna Pueblo, NM†

Johanna M. Blake,^a Cherie L. De Vore,^b Sumant Avasarala,^b Abdul-Mehdi Ali,^c Claudia Roldan,^a Fenton Bowers,^d Michael N. Spilde,^c Kateryna Artyushkova,^e Matthew F. Kirk,^f Eric Peterson,^g Lucia Rodriguez-Freire^b and José M. Cerrato^{*b}

The mobility and accumulation of uranium (U) along the Rio Paguete, adjacent to the Jackpile Mine, in Laguna Pueblo, New Mexico was investigated using aqueous chemistry, electron microprobe, X-ray diffraction and spectroscopy analyses. Given that it is not common to identify elevated concentrations of U in surface water sources, the Rio Paguete is a unique site that concerns the Laguna Pueblo community. This study aims to better understand the solid chemistry of abandoned mine waste sediments from the Jackpile Mine and identify key hydrogeological and geochemical processes that affect the fate of U along the Rio Paguete. Solid analyses using X-ray fluorescence determined that sediments located in the Jackpile Mine contain ranges of 320 to 9200 mg kg⁻¹ U. The presence of coffinite, a U(IV)-bearing mineral, was identified by X-ray diffraction analyses in abandoned mine waste solids exposed to several decades of weathering and oxidation. The dissolution of these U-bearing minerals from abandoned mine wastes could contribute to U mobility during rain events. The U concentration in surface waters sampled closest to mine wastes are highest during the southwestern monsoon season. Samples collected from September 2014 to August 2016 showed higher U concentrations in surface water adjacent to the Jackpile Mine (35.3 to 772 µg L⁻¹) compared with those at a wetland 4.5 kilometers downstream of the mine (5.77 to 110 µg L⁻¹). Sediments co-located in the stream bed and bank along the reach between the mine and wetland had low U concentrations (range 1–5 mg kg⁻¹) compared to concentrations in wetland sediments with higher organic matter (14–15%) and U concentrations (2–21 mg kg⁻¹). Approximately 10% of the total U in wetland sediments was amenable to complexation with 1 mM sodium bicarbonate in batch experiments; a decrease of U concentration in solution was observed over time in these experiments likely due to re-association with sediments in the reactor. The findings from this study provide new insights about how hydrologic events may affect the reactivity of U present in mine waste solids exposed to surface oxidizing conditions, and the influence of organic-rich sediments on U accumulation in the Rio Paguete.

Received 15th November 2016
Accepted 5th March 2017

DOI: 10.1039/c6em00612d

rsc.li/process-impacts

Environmental impact

Uranium mobility and accumulation in the environment can affect surface water and sediment chemistry. Here, we investigated the mobility of uranium in water and accumulation on sediments along the Rio Paguete and within a wetland and reservoir 5 km south of the Jackpile Mine. Main findings of the study suggest that ore and mine waste from surficial locations of the Jackpile Mine are the source of uranium in the surface water. Additionally, the concentration of uranium in the Rio Paguete varies seasonally, with higher concentrations during the southwestern monsoon season. The uranium concentration in surface water decreases downstream of the mine and adsorption of uranium to organic-containing sediments in a wetland 5 km downstream contributes to this decrease. These results have important implications to better understand the mobility and accumulation of uranium in the environment.

^aDepartment of Chemistry, MSC03 2060, University of New Mexico, Albuquerque, New Mexico 87131, USA. E-mail: jmtblake@usgs.gov

^bDepartment of Civil Engineering, MSC01 1070, University of New Mexico, Albuquerque, New Mexico 87131, USA. E-mail: jcerrato@unm.edu

^cDepartment of Earth and Planetary Sciences, MSC03 2040, University of New Mexico, Albuquerque, New Mexico 87131, USA

^dDepartment of Nuclear Engineering, MSC01 1120, University of New Mexico, Albuquerque, New Mexico 87131, USA

^eDepartment of Chemical and Biological Engineering, MSC01 1120, University of New Mexico, Albuquerque, New Mexico 87131, USA

^fDepartment of Geology, Kansas State University, 108 Thompson Hall, Manhattan, KS 66506-3201, USA

^gDepartment of Chemical and Biological Engineering, Center for Microengineered Materials, University of New Mexico, MSC 01 1120, Albuquerque, New Mexico 87131, USA

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c6em00612d

‡ Present address: U.S. Geological Survey, 6700 Edith Blvd., NE Albuquerque, New Mexico 87113, USA.

1. Introduction

The Abandoned Mine (AM) Land Inventory in the United States has listed over 28 000 AM sites and over 70 000 AM features as of 2011; 75% of these sites still need to be investigated and/or remediated.¹ The United States Environmental Protection Agency (USEPA), with information provided by other federal, state, and tribal agencies, has identified 15 000 mine locations with uranium occurrence in 14 western states. Most of those locations are found in Colorado, Utah, New Mexico, Arizona, and Wyoming, with about 75% of those on federal and tribal lands.¹ The uranium (U) concentration can be as high as 1 wt%, especially from mines before 1978 when the Uranium Mill Tailings Radiation Control Act (UMTRCA) was implemented. Elevated concentrations of metals in surface and groundwater sources located close to abandoned mine sites is a current problem in the Southwestern USA due to the extensive mining legacy.^{2–4} The semi-arid climate conditions and water scarcity in this region exacerbate the concern for the quality of the limited water sources.⁵ Additionally, a recent study in Navajo communities have linked exposure to mine waste to an increased potential of developing chronic diseases such as diabetes, hypertension, and kidney disease.⁶

The Jackpile Mine, Laguna Pueblo, northwestern New Mexico, was once the largest open pit U mine in the world, producing 25 million tons of U ore from 1953 to 1982.^{7–9} Reclamation actions performed in 1995 in the Jackpile Mine consisted of covering tailing piles with 0.3 m of topsoil and 1.2 m of overburden in addition to 0.3 m of topsoil on exposed Jackpile Sandstone, the formation containing the uranium ore, and fencing off the area from public access.^{7,10} Given the arid climate at this location, the neighboring villages (Paguate and Mesita) depend upon scarce surface water and groundwater for drinking, agriculture, and livestock activities. Surface water of the Rio Paguate and its tributary, the Rio Moquino, flows through areas affected by legacy mining of the Jackpile Mine (Fig. 1). Given that it is not common to identify elevated concentrations of U in surface water sources, the Rio Paguate is a unique site that concerns the Laguna Pueblo community. Hence, the need to better understand the mobility and accumulation of U and other metals along a stream reach of the Rio Paguate adjacent to the abandoned Jackpile Mine served as the motivation for this study.

Biogeochemical and physical processes can affect U mobility and accumulation in the Rio Paguate. The speciation and mobility of U and other metals can be affected by complexation with dissolved inorganic carbon and organic matter, and dissolution processes affected by redox conditions in surface oxic waters interacting with subsurface reducing environments.^{11–16} Hydrologic events cause variations in water flow through minerals exposed to surficial conditions, affecting precipitation/dissolution and adsorption/desorption processes.^{17–19} Microbiological processes can also affect redox reactions that affect the mobility of U and other metals.^{20–22} Oxidation of U(IV) to U(VI) can occur due to exposure of ores to surface oxidized conditions,^{23,24} which can affect the mobility of

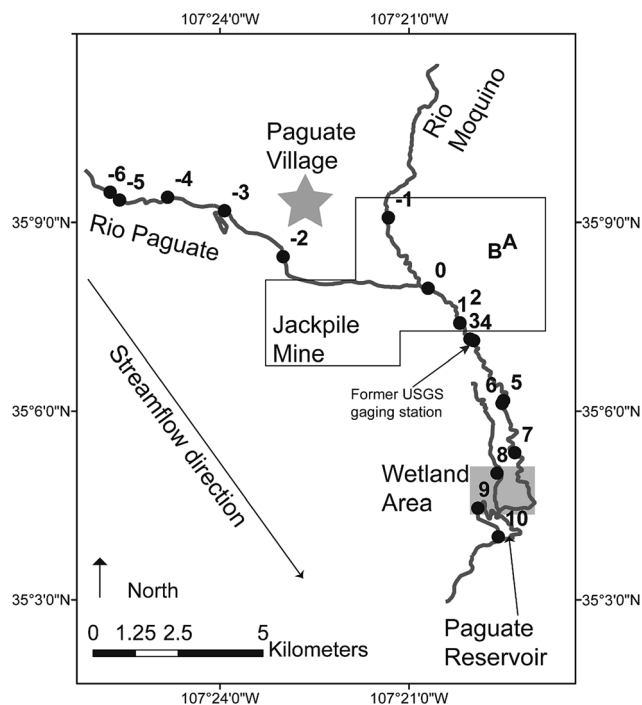


Fig. 1 Site map. Water and sediment samples were taken from locations –6 to +10. Ore and weathered sediment below the ore were sampled at sites A and B respectively.

U from these ores. Dissolution of U(VI)-bearing minerals such as meta-schoepite $[(\text{UO}_2)_4\text{O}(\text{OH})_6 \cdot (\text{H}_2\text{O})_5]$, carnotite $[\text{K}_2(\text{UO}_2)_2\text{V}_2\text{O}_8]$ or tyuyamunite $[\text{Ca}(\text{UO}_2)_2\text{V}_2\text{O}_8 \cdot (5-8)\text{H}_2\text{O}]$ will cause the release of soluble U(VI) into solution.^{25–27} However, uranium phosphates such as meta-autunite $[\text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 6\text{H}_2\text{O}]$ have low solubilities. The presence of U-bearing mineral phases was reported by Moench and Schlee⁹ at the Jackpile Mine, identifying the minerals uraninite, meta-autunite $[\text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 6\text{H}_2\text{O}]$, tyuyamunite $[\text{Ca}(\text{UO}_2)_2\text{V}_2\text{O}_8 \cdot (5-8)\text{H}_2\text{O}]$, and coffinite $[\text{U}(\text{SiO}_4)_{1-x}(\text{OH})_{4x}]$. These minerals are found in subsurface deposits of the Morrison Formation at the Jackpile Mine. Uranium can undergo adsorption, redox, and desorption reactions with iron oxides such as goethite and ferrihydrite under environmentally relevant conditions.^{16,28,29} Additionally, U has an affinity for ternary complexes with alkaline earth metals and carbonates, which lowers the potential for adsorption and immobilization.^{30,31} The charge of these complexes under circumneutral pH conditions typical of natural waters is often neutral or negative and therefore the surface charge and types of sediments play an important role in mobility and accumulation. Finally, under reducing conditions, microbial activity can cause U(VI) reduction to U(IV) producing UO_2 , monomeric U(IV), or other U(IV) species.^{22,32–35} These processes need to be considered to investigate metal mobility and accumulation in abandoned uranium mine sites.

The primary objective of this paper is to investigate U mobility in water and accumulation in sediments of the Rio Paguate. We performed aqueous chemistry measurements as well as electron microprobe, X-ray diffraction and spectroscopy analyses to determine relevant geochemical interactions. The

specific objectives are: (a) determine the chemical composition of abandoned ores at the Jackpile Mine and adjacent areas in the Rio Pagate; (b) assess the fluctuations of U and co-occurring metal concentrations in aqueous and sediment samples along a reach of the Rio Pagate; and, (c) investigate the accumulation and distribution of U in sediments along the Rio Pagate. This interdisciplinary work seeks to better understand how the complex interaction between mine waste solids, surface water quality, and river sediments affects the fate of U. The findings from this study provide new insights about how hydrologic events may affect the reactivity of U present in mine waste solids exposed to surface oxidizing conditions, and the influence of organic-rich sediments on U accumulation in the Rio Pagate. This information has relevant implications for the development of risk assessment and remediation strategies relevant to decision makers and communities dealing with mining legacy issues.

2. Study area

The Jackpile Mine is located in the Grants-Laguna District, where U deposits are present in Jurassic and Cretaceous strata. The Jackpile Sandstone, found in the uppermost part of the Brushy Basin Shale Member of the Jurassic Morrison Formation, is the dominant ore bearing unit.^{9,36,37} The source of the uranium could be volcanic glasses which were altered after deposition.³⁸ Roughly

20 km wide, 50 km long and up to 70 m thick, the Jackpile sandstone is a fine- to medium-grained cross-stratified sandstone deposited by a system of northeastward flowing streams.⁹ The U ore deposits in the Jackpile sandstone are semi-tabular layers that are not generally thicker than 5 m. The combined U ore in the Jackpile deposit is 2 km long and 600 m wide.^{9,36,37}

The Rio Pagate flows from its headwaters in the Miocene basalt and andesite flows of Mount Taylor southeast towards the village of Pagate through the Cretaceous Mancos Shale and Dakota Sandstone until flowing through the Jurassic Morrison Formation and the abandoned Jackpile Mine.^{8,39} It then continues southward into the Pagate/Mesita dam and periodically overflows into a drainage that leads to the Rio San Jose.

Fig. 1 shows sampling sites along the Rio Pagate, with sites numbered –6 to +10 and additional details about these sites are in the ESI, Table S1.† Sites –6 to –2 in the Rio Pagate are upstream from the occurrence of mining activity, site –1 is in the Rio Moquino, an ephemeral tributary to the Rio Pagate, site 0 is just below the confluence of the Rio Moquino and Rio Pagate (both site –1 and 0 are within the mining region though upstream of the main mine location), and sites 1 to 10 are in the Rio Pagate within and downstream of the former mining area. An outcrop of exposed ore and weathered sediment below the ore are located to the east of the Rio Pagate labeled A and B. Between this outcrop and the Rio Pagate are numerous mine waste piles covered with alluvium or topsoil.

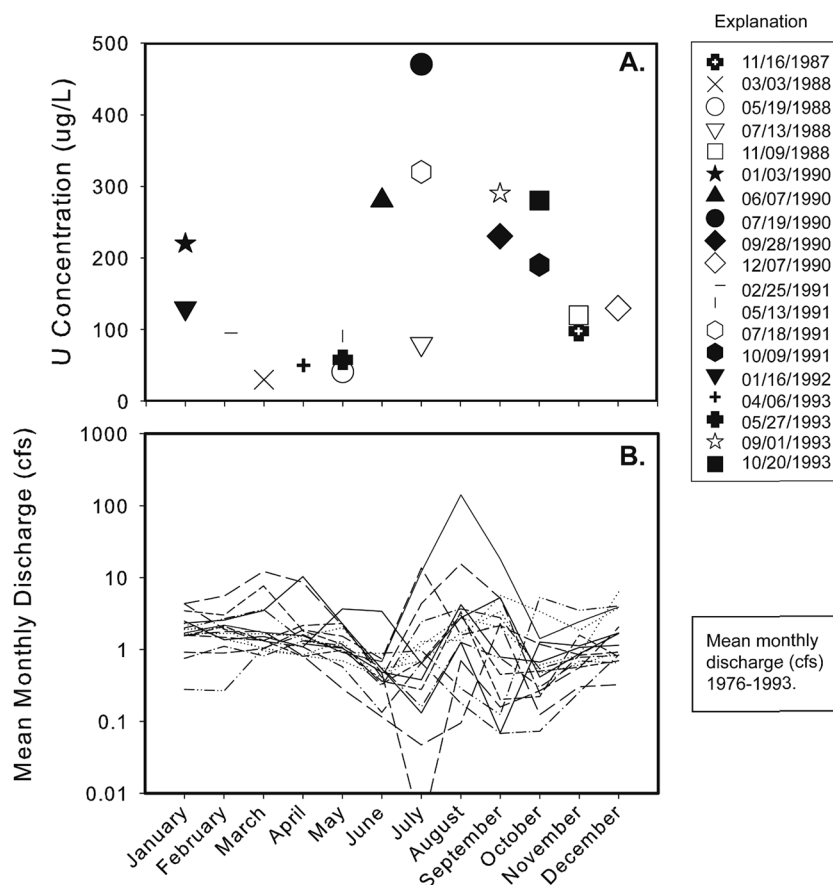


Fig. 2 USGS U concentration (A) and mean monthly discharge (B) data from 1976 to 1993 from a former USGS gaging station.

The United States Geological Survey (USGS) maintained a discharge gaging station along the Rio Paguete (35°07'09", -107°19'57") (Fig. 1) from 1976 to 1993, measuring discharge and U concentrations (as well as other constituents). As a reference, Fig. 2a illustrates the U concentration reported by USGS from the gaging station site (located near site 1 and 2, this study) and Fig. 2b shows the discharge data from the Rio Paguete from 1976 to 1993.⁴⁰ The Jackpile Mine was in operation from 1953 to 1982; therefore the data collected from the gaging station report 6 years of active mining followed by 11 years of mining closure. The gage was not in operation during the reclamation of the site which started in 1995. The lowest U concentrations measured by the USGS were sampled in March 1988 (30 µg L⁻¹) and May 1988 (41 µg L⁻¹) while the highest U concentrations measured by the USGS were sampled in July 1990 (470 µg L⁻¹) and July 1991 (320 µg L⁻¹). These data have similar variation in concentration during the year compared to the data collected in this study. Additionally, the U concentrations from these historic data appear to have a relationship with discharge, an observation that is seen in this study and will be discussed later in the manuscript. The USGS U concentrations were measured by extraction or direct fluorimetry, neutron activation, or ICP-MS.

3. Materials and methods

3.1 Water and sediment sampling

Forty-three surface water samples were collected at a total of 17 locations at various dates along the Rio Paguete from the headwaters to the Paguete/Mesita dam (Fig. 1 and Table S1†). One sample was collected in September 2014, 11 samples in November 2014, 10 samples in February 2015, 4 samples in March 2015, 1 sample in June 2015, 4 samples in August 2015, 4 samples in September 2015, 3 samples in May, 2016, 2 samples in June and July 2016, and only one sample in August 2016 due to the low water level along the river. The authors were required to have an escort from Laguna Pueblo Environmental and Natural Resources Department while conducting sampling. Staff escort time constraints reduced the number of possible sampling locations during certain sampling events; therefore efforts were made to sample across a reasonable distribution of sites at each sampling event. Two hundred and fifty milliliters were collected for each sample using trace metal grade nitric acid (HNO₃, 67–70% by mass) cleaned polypropylene (PP) Nalgene bottles. Each bottle was rinsed with surface water three times before the final sample was collected with zero head space when possible. The width of the Rio Paguete and Rio Moquino ranges from 1.5 m to 6 m across and therefore grab samples were collected rather than integrated samples. Hyporheic zone waters were sampled 8 cm and 15 cm below the sediment–water interface at site 1 using a polyvinyl chloride (PVC) pipe, PP tubing, and 50 mL syringes. Field parameters were measured with a Thermo Scientific Orion Star A329 pH/temp/conductivity probe. Samples were placed on ice in a cooler for transport to the laboratory for immediate processing and preservation. All water samples were filtered with 0.45 µm Whatman filters and a subset of waters was filtered with 0.22 µm filters in the

laboratory. Samples for analysis by Inductively Coupled Plasma were preserved to a pH ≤ 2 with ultrapure nitric acid by adding between 0.5 and 1 mL to each sample. The hyporheic zone waters and related surface waters were analyzed as total water (unfiltered and digested with ultrapure nitric acid), less than 0.45 µm, and less than 0.22 µm. Lab blanks and two quality control (QC) standards were used during analysis, one at a concentration of 25% of the highest calibration standard and one at a concentration of 75% of the highest calibration standard. The latter QC standard (75% of the highest calibration standard) was checked every 15 samples to monitor potential instrument drift.

A total of eighty sediment samples were collected with a hand trowel (cleaned between each use with DI water) and placed in gallon plastic bags for transport to the laboratory at: an ore outcrop (site A, Fig. 1); weathered sediment below the ore (site B, Fig. 1); and, in the stream bank and stream bed at sites -6 to 10 with repeat sediments collected at sites 1 to 10. Sediment cores of the hyporheic zone were collected in 1 1/4 inch PVC pipes at site 1. Sediments were dried overnight in an oven at 80 °C prior to use. Homogenized sediment samples were digested in duplicate for analysis using 1 gram of sediment and *aqua regia* [2 mL HNO₃ and 6 mL hydrochloric acid (HCl, 34–37% by mass, trace metal grade)]. The extracted solution from the sediment digestion was measured as described in the next subsection to determine extractable elemental concentration amenable to reaction with *aqua regia*. The grain size in the stream bank and bed ranged from silt/clay to sand.

3.2 Solution chemistry analyses

Major elemental contents of filtered and acidified water samples and acid digested sediments were analyzed using a PerkinElmer Optima 5300DV Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES). A PerkinElmer NexION 300D (Dynamic Reaction Cell) Inductively Coupled Plasma-Mass Spectrometer (ICP-MS) was used for trace element (U, Cr, Pb, As) analysis. A ThermoFisher Scientific Ion Chromatogram (ICS-1100) was used to analyze 0.45 µm filtered, un-acidified water samples for anion concentration. Total Organic Carbon (TOC) was measured on a subset of 0.45 µm filtered, un-acidified water samples using a Tekmar-Dohrmann Phoenix 8000 TOC analyzer, which uses the UV-persulfate method.

3.3 Solid characterization analyses

Bulk sediment analysis was performed using X-ray fluorescence with a Rigaku ZSX with a rhodium X-ray tube that can be operated from 200 to 4000 watts (End window, Rh-anode, 4 kW, 60 kV) that delivers rapid quantitative determination of major and minor atomic elements, from beryllium (Be) through uranium (U), in a wide variety of sample types with minimal standards. The software is ZSX Primus II that performs both qualitative and quantitative analysis. X-ray diffraction (XRD) was performed on the ore sample (location A), stream bed sediments from site 1 and site 9 using a Rigaku Smart Lab X-ray diffraction (XRD) using Cu Kα radiation with a scintillation detector and a graphite monochromator, to obtain information

on the crystallinity, mineral structure, and normalized approximate percent amount of mineral phases present in the sediment samples. The XRD data were analyzed using Jade® software. An X-ray Photoelectron Spectrometer (XPS) was used to acquire the near surface (<10 nm) elemental composition and oxidation states. A monochromatic Al source was used at 150 W power to obtain Fe 3p high resolution spectra from top ~4 nm of the surface. Au reference powder was used to calibrate the spectra. Shirley background was used to process the spectra. Quantification utilized sensitivity factors that were provided by the manufacturer. A 70% Gaussian/30% Lorentzian (GL (30)) line shape was used for the curve fittings. Constraints used in curve fitting were in correspondence with our previous study.² Qualitative X-ray mapping of epoxy-mounted polished ore samples was performed on a JEOL 8200 electron microprobe. Maps were acquired at 20 kV accelerating voltage and 30 nA beam current utilizing stage mapping at 2 µm steps (pixel) and 100 ms dwell time per pixel. The K-α X-ray lines for Mg, P, S, K, Ca, Ti, V, and Fe; the L-α line of As; and the M-α line of U were mapped on 5 separate wavelength dispersive spectrometers (2 passes per map area) simultaneously with the K-α lines for Al and Si on an energy dispersive spectrometer. A backscattered electron image was also acquired on each map area. The JEOL software utilizes a “free shape map” process in which undesirable areas, such as epoxy, may be excluded from the overall map; therefore map sizes varied according to the size of particles mapped. Loss on ignition was performed to determine the organic matter content in sediments by heating porcelain crucibles in a muffle furnace at 550 °C for one hour, cooling, and weighing empty crucibles.

3.4 Laboratory batch experiments

These experiments were performed to evaluate the reaction of U in sediments from site 9 with bicarbonate (a natural complexant) at pH and alkalinity values relevant to those observed in the Rio Paguete. Other investigations have performed bicarbonate extractions to evaluate U amenable to complexation.^{2,41,42} Sediments were dried overnight in an oven at 80 °C prior to use. These wetland samples (site 9) from February 2015 were sieved with a US Standard #230 mesh (63 µm) to analyze the mobility of U in fine sediments. Triplicate sediment samples (2 g each) were weighed in 50 mL centrifuge tubes for reaction at pH 8.3 with: (a) 50 mL 1 mM HCO₃⁻; and, (b) 50 mL 18 MΩ DI water. Centrifuge tubes were placed on a rotator, with 6 mL subsampled each time at times 0.5, 1, 2, 4, 6, and 24 h. Samples were then filtered and diluted for analysis of U and other metal concentrations using ICP-MS. The final calculations of concentration took into account the change in volume over time.

3.5 Extraction and amplification of DNA, and analysis of sequencing data

Sediment and water samples collected from site 1 during the March sampling event were processed for microbial community analysis. Sediment was scooped into a sterile centrifuge tube using a flame sterilized spatula. Microorganisms in water were

concentrated by filtering the water sample through a sterile mixed cellulose-ester filter membrane with 0.22 µm pores. Samples were stored in the field on ice in a cooler and were immediately frozen (−20 °C) in the lab within 8 hours after collection, which is acceptable as per the results in Lauber *et al.* (2010).⁴³ Total community DNA was extracted from the sediment and the water filter using an UltraClean® Soil DNA Isolation Kit (MO BIO).⁴⁴ We contracted MR DNA® laboratory to amplify and sequence 16S rRNA genes in the samples. The laboratory amplified DNA over 30 cycles of PCR using the Hot-StarTaq Plus Master Mix Kit (Qiagen) under the following conditions: 94 °C for 3 minutes, followed by 28 cycles of 94 °C for 30 seconds, 53 °C for 40 seconds and 72 °C for 1 minute. Following the final cycle, the reaction sequence included an elongation step at 72 °C for 5 minutes. Reaction mixtures used universal primers 519F (GTGCCAGCMGCCGCGGTAA) and 806R (GGACTACVSGGGTATCTAAT) to cover the variable region V4 of the 16S rRNA gene.⁴⁵

After amplification, the laboratory verified amplification success using electrophoresis, pooled samples together in equal proportions, and purified using calibrated Ampure XP beads. The pooled and purified PCR product was used to prepare a DNA library by following the Illumina TruSeq DNA library preparation protocol. Paired-end 2 × 250 sequencing was performed on an Illumina MiSeq system following manufacturer guidelines.

We processed sequencing data using QIIME v. 1.8.0.⁴⁶ We first split samples according to barcodes and filtered the sequences to remove low-quality reads (script: split_libraries.py). Next, we generated operational taxonomic unit (OTU) tables at 97% similarity and evaluated taxonomy with uclust (script: pick_de_novo_otus.py). The method used the Greengenes reference dataset release 13.8;⁴⁷ and assigned the most detailed lineage description shared by at least 90% of the sequences within each OTU. Lastly, we removed singletons and created taxonomy tables (scripts: filter_otus_from_otu_table.py, summarize_taxa_through_plots.py).

4. Results and discussion

4.1 Solid analysis

Elevated concentrations of U were observed in the ore collected from the Jackpile Mine (Table 1). The ore (location A, Fig. 1) has the highest concentration of U (9300 mg kg⁻¹ or ~1 wt%) measured by XRF, followed by the two sediment samples below the ore (location B, Fig. 1) (1400 and 320 mg kg⁻¹). These samples below the ore are weathered deposits with variable sediment distribution and geochemical concentrations, but provide insight into the concentrations of U from these types of deposits. However, U concentrations were below detection limit (BDL) of the XRF (60 mg kg⁻¹) in stream bed and bank sediments collected from the Rio Paguete.

The presence of other co-occurring elements such as iron (Fe), phosphorus (P), sulfur (S), and vanadium (V) was also determined within these samples. These elements are important considering their ability to form secondary minerals that could be associated with U, and a summary of their

Table 1 XRF data from an ore lens, sediment below the ore lens, and the stream bed and stream bank from sites 1 and 9. Note that the XRF detection limit is 60 mg kg⁻¹ for U, 100 mg kg⁻¹ for Fe, 30 mg kg⁻¹ for P, 40 mg kg⁻¹ for S, 100 mg kg⁻¹ for V, 100 mg kg⁻¹ for Cr, 100 mg kg⁻¹ for Pb, and 40 mg kg⁻¹ for As

Sample location	U (mg kg ⁻¹)	Fe (mg kg ⁻¹)	P (mg kg ⁻¹)	S (mg kg ⁻¹)	V (mg kg ⁻¹)	Cr (mg kg ⁻¹)	Pb (mg kg ⁻¹)	As (mg kg ⁻¹)
Laguna ore lens (A on Fig. 1)	9300	109 000	2700	4900	660	270	340	BDL
Sediment below ore lens (B on Fig. 1)	1400	13 000	380	3000	140	BDL	BDL	58.0
Sediment below ore lens (B on Fig. 1)	320	18 000	370	2800	150	140	BDL	BDL
Site -6 stream bank	BDL	42 000	1400	1000	BDL	180	BDL	BDL
Site -6 stream bed	BDL	42 000	1300	900	BDL	190	BDL	BDL
Site -1 stream bank	BDL	61 000	990	2900	BDL	160	BDL	53
Site -1 stream bed	BDL	103 000	2300	950	BDL	300	BDL	BDL
Site 1 stream bank	BDL	106 000	2800	700	BDL	880	BDL	BDL
Site 1 stream bed	BDL	30 000	790	1600	BDL	190	BDL	BDL
Site 9 stream bank	BDL	38 000	1100	4500	BDL	1200	BDL	BDL
Site 9 stream bed	BDL	33 000	990	2900	BDL	700	BDL	BDL

concentration in the sediments is presented in Table 1. The concentration of Fe in the ore was 109 000 mg kg⁻¹, and in the sediment below the ore it is 13 000 and 18 000 mg kg⁻¹. The stream bank sediment Fe concentration at site 1 ranges from 61 000 mg kg⁻¹ to 106 000 mg kg⁻¹ and site 1 stream bed ranges from 30 000 to 103 000 mg kg⁻¹, showing the inherent variability of elemental concentrations in stream deposits. Both samples from site 9 range from 30 000 to 38 000 mg kg⁻¹. The P concentrations vary, with the largest concentrations from the ore (location A, Fig. 1) (2700 mg kg⁻¹ P), site 1 stream bank (2800 mg kg⁻¹ P), and site 9 stream bank (1100 mg kg⁻¹ P). Sulfur concentrations are largest in the ore and site 9 stream bank, 4900 and 4500 mg kg⁻¹, respectively. The V concentration in the ore is 660 mg kg⁻¹ and the average in the sediment below the ore is 140 mg kg⁻¹. Concentrations of these elements in site -6 and site -1 vary and are listed in Table 1. These XRF results provide information about the bulk elemental concentrations regardless of sediment size, which provides an understanding of the samples as a whole. The sediment samples were also analyzed for the presence of other metals of concern due to their negative effect on human health such as arsenic (As), chromium (Cr), and lead (Pb). The concentrations of As, Cr, and Pb were detected at lower concentrations than U. Additional XRF results are provided in the ESI, Table S2.†

Acid digested stream bed sediments contain U concentrations ranging from 0.20 mg kg⁻¹ to 5.20 mg kg⁻¹ in sites -6 to -1 and 1 through 8. U concentrations increase above 5.20 mg kg⁻¹ in sites 9 and 10 located in the wetland and reservoir downstream (Fig. 3). In February the wetland sediment collected at site 9 had a concentration of 20.0 mg kg⁻¹ U and the reservoir sediment at site 10 had a concentration of 7.30 mg kg⁻¹. The crustal average concentration of U is 2.78 mg kg⁻¹ (ref. 4) and sites -6 to -1 U concentrations range from 0.20 mg kg⁻¹ to 1.90 mg kg⁻¹, seemingly due to the surrounding geology. Since these sites are all upstream of the main mining occurrences, U concentrations from these areas may be considered a local background. Uranium concentrations in

sites 1 to 8 are in general higher than the sediments sampled upstream of the mine, in some cases twice the crustal average. This difference is potentially due to the transport of U bearing sediments from the mine area downstream. The elevated concentrations found in sediments from sites 9 and 10 in February 2015 may be due to the ability of U to associate with particulate organic matter such as what exists in the wetland. This relationship is explained in more detail later in the manuscript.

Electron microprobe mapping of an ore (location A, Fig. 1) grain reveals heterogeneous areas of elevated uranium deposits and other metals (Fig. 4), suggesting that U co-occurs with P, Fe, and V in ore samples from the Jackpile Mine. In this image, a part of the mapped grain shows distinct associations between U, V, and Fe. Additionally, some intermediate concentrations of U are detected at discrete points where P is present. The association of U with Fe and S in Fe oxides or Fe-S mineral solids has been reported in other studies.³⁵ Locations where U and V are not associated may suggest the role of other U minerals in the ore. To complement electron microprobe analyses (for

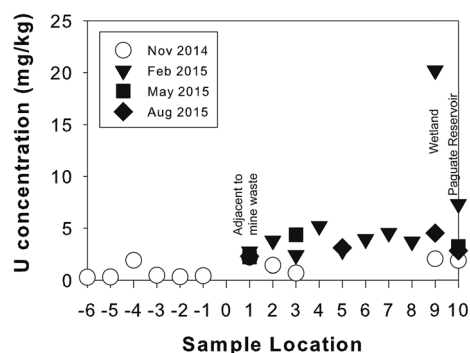


Fig. 3 Stream bed sediment U chemistry by sample location and month. The majority of samples are 2 times the local background U concentration of 1–2 mg kg⁻¹. Sites 9 and 10 (the wetland and reservoir) have the highest U concentrations in the sediments.

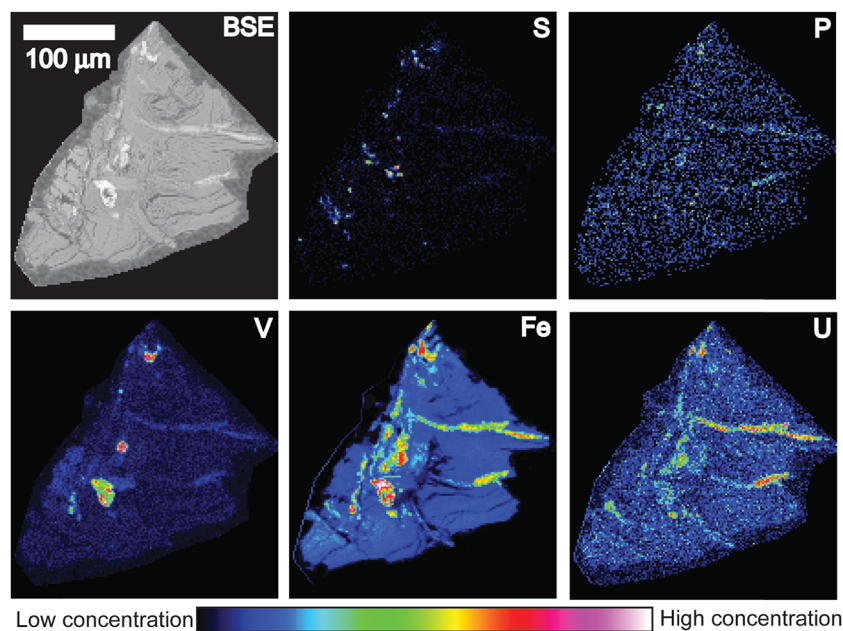


Fig. 4 Electron microprobe maps of ore deposit collected from site A. Yellow, red, pink and white colors represent higher concentration of elements.

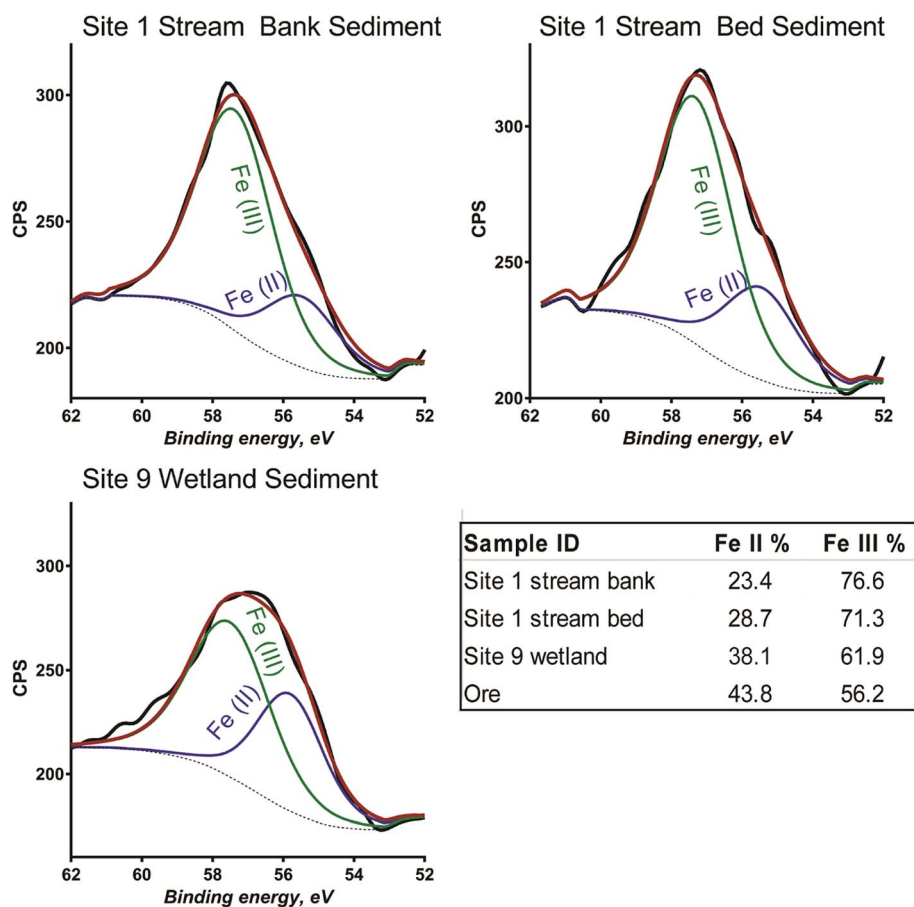


Fig. 5 XPS Fe 3p fits for Fe II and Fe III from three sediments, site 1 stream bank, site 1 stream bed, and site 9 wetland sediment. Quantified % of Fe oxidation state is shown in the table.

which the signal corresponds to the top 1–10 μm of sample), XPS analyses were performed to investigate the chemical composition in the “near surface” (top 5 nm of the sample).

The oxidation state of Fe in sediments is relevant given that Fe(II) and Fe(III) minerals play an important role in adsorption and redox reactions, including those that affect the biogeochemical cycle of metals in the Rio Paguete. Curve fitting analysis of XPS Fe 3p spectra from the top 5 nm of stream bank and stream bed sediments from site 1 (September 2014 sampling event) indicates that Fe(III), 72–77%, and Fe(II), 23–28%, contents are similar in the two samples (Fig. 5). Site 9 (the wetland) has 61.9% Fe(III) and 38.1% Fe(II) (Fig. 5). The higher percentage of Fe(III) in the sediments may affect the adsorption of U to these solids. The distribution of Fe(III) and Fe(II) from a weathered sediment collected below the exposed ore outcrop is 63.6% and 30.5%, respectively, whereas the distribution in the ore lens itself is 56.2% Fe(III) and 43.8% Fe(II). The predominance of Fe(III) in all sediments detected by XPS analyses also suggests that Fe(III)-oxides could serve as a major sink for U and other metals in this system.^{28,29} In contrast, the

existence of Fe(II) in the sediments may play a role. Additional XRD analyses were performed to learn more about the bulk mineralogy of sediment samples.

The presence of the U(IV)-bearing mineral coffinite (USiO_4) was identified using XRD analyses in ore sediment (location A) from the Jackpile Mine. This is a relevant finding given that the ore sediments have been exposed to surface oxidizing conditions for several decades, while Moench and Schlee⁹ found coffinite in subsurface ore deposits exposed to reducing conditions prior to mining activities. The ore sample contains 1.3 weight percent coffinite (USiO_4); the presence of U-bearing minerals was not detected in the stream bed sediments from site 1 and site 9. It is probable that the mineral coffinite is coated by other phases in the surface of ore solids that are more exposed to ambient oxidized conditions. Additionally, sediments from site 1 and site 9 contain halloysite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$) and albite ($\text{Na,CaAl}(\text{Si,Al})_3\text{O}_8$), which are not detected in the ore sample. These minerals are byproducts of feldspar weathering and feldspar was identified in the Jackpile ore by Adams *et al.* (1978). All three samples contain varying weight percentages of

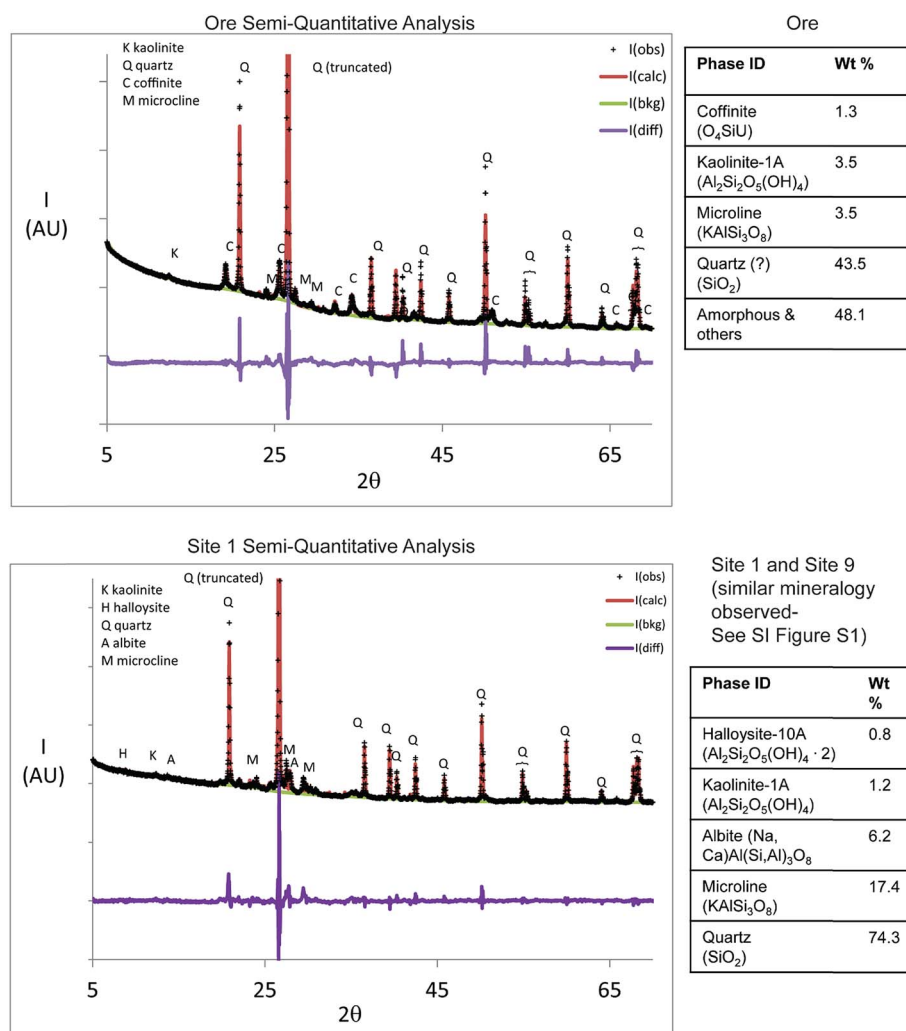


Fig. 6 XRD analysis of ore (location A), stream bed sediments from site 1 using Cu $K\alpha$ radiation. Weight percent values of phases are shown in adjacent tables.

quartz, microcline, and kaolinite (Fig. 6). Site 1 and site 9 have similar mineralogy (ESI, Fig. S1†). The identification of clay minerals such as halloysite by XRD analyses suggests that sediments from site 1 have a negative charge at pH 6.8–8.2 observed in the Rio Paguete. Thus, despite the high aqueous U concentrations in site 1, the negative charge of sediments in site 1 and the negative/neutral charge of aqueous U–Ca–CO₃(aq) complexes (predominant due to the water chemistry of the Rio Paguete at pH 6.8–8.2) inhibit accumulation of U in these sediments. More extensive sampling and analyses need to be performed to further determine the presence of various mineral phases within the mine waste samples.

Analyses of surface water samples collected at different locations along the Rio Paguete at various times of the year were conducted to further understand the mobility and accumulation of uranium and other co-occurring elements.

4.2 Aqueous uranium and total organic carbon concentrations along the Rio Paguete

The concentrations of U in surface water samples ($N = 43$) collected from the Rio Paguete are highest at site 1 and decrease downstream (Fig. 7 and Table 2) during each sampling event. Decreases in U concentration from site 1 to sites 9 and 10 range from 27 to 96%. Similar to the historic USGS data (Fig. 2), the highest U concentrations are generally measured from May through September. For instance, the two highest U concentrations measured in surface water (711 and 772 $\mu\text{g L}^{-1}$) in this

study were measured on September 12, 2014, and on July 25, 2016 at site 1, respectively, while the highest concentrations measured historically were in July 1990 and July 1991. The lowest U concentrations in this study were measured in November 2014 and in the USGS data are March and May 1988. The November 2014 data include seven samples upstream of the confluence of the Rio Paguete and Rio Moquino (U concentrations from sites –6 to 0 ranging from 0.403 to 7.97 $\mu\text{g L}^{-1}$). Sites –6 to –2 are upstream/upgradient of the mine site

Table 2 Results for chromium and lead in some samples are below detection limit (BDL) (for Cr 0.01 mg L⁻¹; for Pb 0.0004 mg L⁻¹)

Date	Site #	pH	U ($\mu\text{g L}^{-1}$)	Cr ($\mu\text{g L}^{-1}$)	Pb ($\mu\text{g L}^{-1}$)	As ($\mu\text{g L}^{-1}$)
9/17/2014	1	8.17	711	9.95	BDL	1.30
11/13/2014	–6	8.33	0.784	0.069	BDL	1.33
	–5	8.21	0.796	0.097	BDL	1.21
	–4	—	0.921	0.149	BDL	1.40
	–3	—	0.404	0.116	BDL	1.36
	–2	—	0.651	0.154	BDL	1.45
	–1	8.58	7.97	5.46	BDL	0.56
	1	8.27	131	2.30	BDL	1.41
	2	6.81	128	2.37	BDL	1.59
	3	7.80	123	2.32	BDL	1.45
	9	—	5.77	1.76	BDL	0.997
	10	—	6.40	3.02	BDL	1.77
2/23/2015	1	7.56	35.3	0.200	2.34	2.33
	2	7.56	35.9	BDL	1.80	2.56
	3	7.58	38.6	BDL	1.66	2.50
	4	7.21	39.7	BDL	1.74	2.55
	5	6.83	39.8	3.77	2.14	2.35
	6	7.19	39.0	BDL	3.49	2.23
	7	7.07	36.9	BDL	2.15	2.58
	8	7.50	36.6	BDL	2.32	2.70
	9	6.99	27.0	BDL	1.74	2.16
	10	7.91	5.46	BDL	1.86	2.44
3/11/2015	0	7.71	7.28	BDL	BDL	—
	1	7.73	68.8	2.57	1.56	—
	5	7.50	83.1	BDL	BDL	—
	7	8.33	72.1	BDL	BDL	—
5/11/2015	1	8.05	148	—	—	9.25
	3	8.46	132	—	—	11.6
	10	8.29	76.5	—	—	12.0
6/17/2015	1	8.08	170	—	—	1.95
8/14/2015	1	8.08	341	—	—	3.41
	5	8.16	301	—	—	2.40
	9	7.72	110	—	—	3.51
	10	7.34	13.9	—	—	1.85
9/23/2015	1	7.78	75.3	—	—	32.1
	5	8.08	41.3	—	—	24.5
	9	8.03	23.6	—	—	17.1
	10	7.06	7.36	—	—	24.1
5/11/2016	1	8.02	290	0.33	4.55	7.18
	–1	8.30	7.76	7.78	4.45	5.20
	10	8.10	28.4	1.41	5.36	2.01
6/03/2016	1	8.08	373	14.4	5.66	3.82
	10	7.78	24.1	1.97	9.96	5.99
7/25/2016	1	8.16	772	5.12	5.80	14.4
	10	7.93	21.9	0.28	2.30	4.05
8/18/2016	1	8.06	286	1.28	4.52	7.04

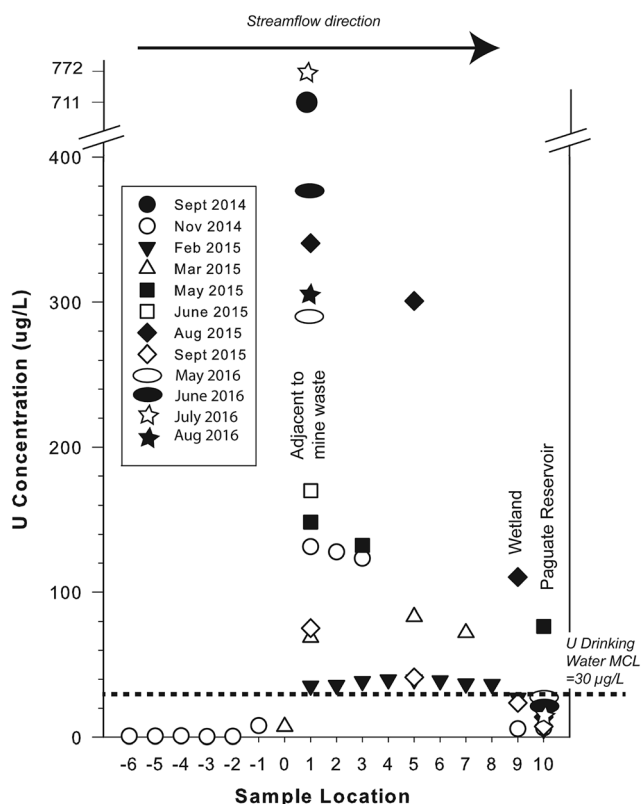


Fig. 7 Concentration of U ($\mu\text{g L}^{-1}$) in surface water by sample location and month.

(Fig. 1) and flow through different geology than the ore bearing Jackpile Sandstone. Therefore, these sites were not sampled again for the duration of the study. Sites -1 and 0 have low U concentrations of $7.97 \mu\text{g L}^{-1}$ and $7.28 \mu\text{g L}^{-1}$ and are upstream of the highest U concentrations measured. The focus of this study was on the locations where U concentrations tended to exceed the USEPA maximum contaminant level (MCL) of $30 \mu\text{g L}^{-1}$ (ref. 48) and subsequent behavior downstream; therefore, sites -1 and 0 were not sampled again until May 11, 2016, where site -1 was sampled again and U concentration was $7.76 \mu\text{g L}^{-1}$. Given the overall trend of higher U concentrations at site 1 from May through September, there may be seasonal processes such as increased rainfall or conversely increased drought that effect the U concentrations in the Rio Paguete. Summers 2014 and 2015 were reasonably wet for the southwest and rain events may have played a role in mobilizing U to the surface water. Summer 2016 was a dry season and river flowrate decreased considerably, surface water at site 1 was in stagnant pools, site 9 was completely dry since May, and by September 2016, there was no water at site 10.

The concentrations of co-occurring metals As, Cr, and Pb were detected at lower concentrations than U (Table 2). Given that U concentrations higher than the USEPA MCL of $30 \mu\text{g L}^{-1}$ (ref. 48) have been detected in several locations in the Rio Paguete, the community does not use this water source for drinking water purposes. Additional water chemistry can be found in the ESI, Table S3.† The community has access to aquifers in the area for drinking water. However, water from the Rio Paguete is consumed by livestock and other animals in the area and used for irrigation in portions of the community.

The concentration of U in water decreases as the TOC concentrations increase closer to the wetland area in the Rio Paguete (Fig. 8). The data presented in Fig. 8 are non-parametric and therefore a Spearman's rank order correlation coefficient was chosen to calculate the relationship between U and TOC from November [Rho = -0.939 ($P < 0.0001$)] and February [Rho = -0.800 ($P = 0.133$)]. The November correlation is statistically significant. The highest concentrations of U in water are found closer to the Jackpile Mine. In contrast, the highest TOC concentrations are found closer to the wetland downstream of the mine. An increase in total organic carbon (TOC) concentrations was observed in samples collected in November and February, when comparing site 1 ($2\text{--}4 \text{ mg L}^{-1}$) which is close to the Jackpile Mine, to downstream locations sites 9 and 10 ($6\text{--}15 \text{ mg L}^{-1}$) at the wetland and reservoir (Fig. 8a). In March, only 3 points were measured and have an average U concentration of $74.6 \pm 6.12 \mu\text{g L}^{-1}$ and an average TOC concentration of $2.62 \pm 0.246 \text{ mg L}^{-1}$ (Fig. 8b). Laboratory experiments have shown the affinity of U to form complexes with dissolved organic matter in water at pH values of 4.0 or 5.0 (Wang *et al.*, 2014¹¹). Additionally, other experiments performed at pH 7–8 have shown U association with solid organic matter at Rifle, CO.^{34,49,50} The Rio Paguete pH values range from 6.81 to 8.58 so it is likely that U is sorbing to particulate organic matter in the sediments rather than forming aqueous complexes with dissolved organic matter in the stream water. Given that the highest concentrations of U in sediments were detected at the wetland (20 mg kg^{-1} U),

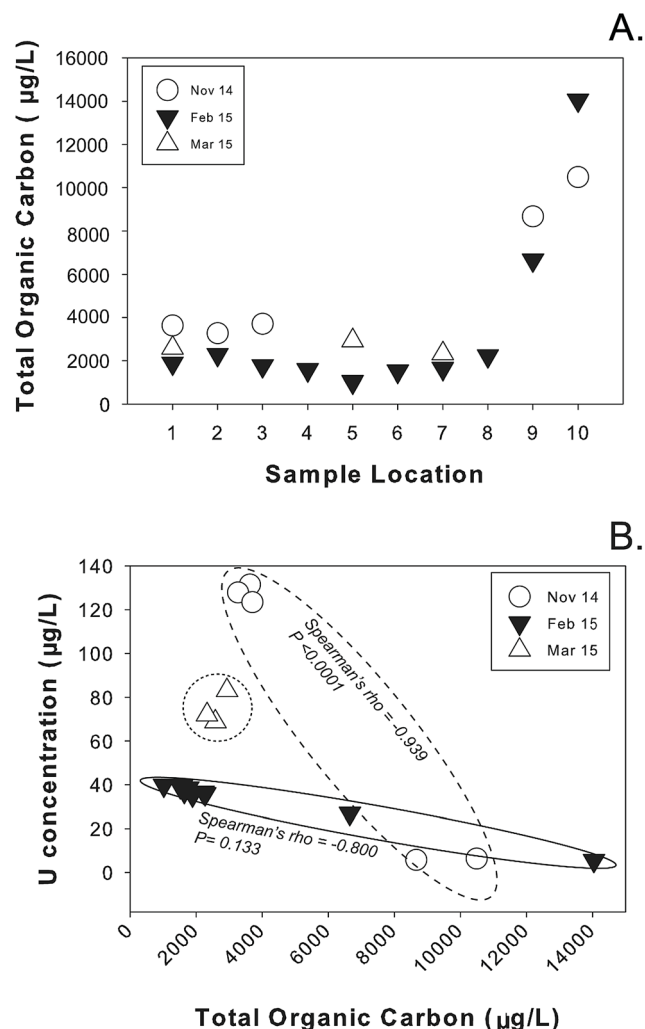


Fig. 8 (A) Total organic carbon (TOC) concentrations by sample location and month. Concentrations increase at sites 9 and 10. (B) U concentration vs. TOC concentration.

further experiments were pursued to better understand the association of U with organic-containing sediments (range 14% to 17% determined by loss of ignition) in the wetland and adsorption/desorption processes that could affect the accumulation/mobility of U in site 9.

4.3 Batch experiment assessing the reactivity of wetland sediments with bicarbonate

The release of U from $<63 \mu\text{m}$ wetland sediments under aerobic conditions reacted with 1 mM HCO_3^- is $11.3 \pm 0.583 \text{ mg kg}^{-1}$ after 30 minutes, and decreases to $4.88 \text{ mg kg}^{-1} \pm 0.045$ after 6 hours of reaction (Fig. 9). These results suggest that U is released in the first 30 minutes of reaction, but is then re-associated with the sediments at later times during the experiment causing the decrease of U concentrations in solution (decrease observed from 1 hour to 6 hours of reaction). Thus, the re-association of U with wetland sediments over time in these experiments is likely due to re-adsorption or surface heterogeneous precipitation. Uranium is known to have an

affinity for complexation, adsorption and/or precipitation to organic matter and therefore, natural and artificial wetlands have been used to immobilize U in surface waters.^{51–54} Enrichments of U in organic-rich sediments have been reported up to 3000 mg kg^{−1}, due to the formation of urano-organic complexes.⁵⁴ However, U can also desorb or dissolve from sediments in the presence of bicarbonate due to complexation reactions that result in the formation of neutrally or negatively charged carbonate complexes.^{14,30,55,56} Wetland sediments reacted with 18 MΩ DI water release 2.59 ± 0.193 mg kg^{−1} U from time zero to 6 hours (Fig. 9). After reacting each sediment with *aqua regia*, 165 mg kg^{−1} ± 11.6 U is released. This experiment focused on the fine grained sediments as U is often associated with smaller particle sizes. The homogenous sediment sample from this site reacted with *aqua regia* had a concentration of 20 mg kg^{−1}, seemingly due to the particle size distribution. The batch experiment performed on wetland sediments suggest that ~10% of the total U is weakly bound and can be readily released at bicarbonate concentrations that are representative of the Rio Pague and wetland waters. Given that only ~10% of the total U was amenable to complexation with 1 mM HCO₃[−] after 24 hours of reaction, most of the U is tightly bound to the wetland sediments. Although the total U concentrations of these sediments is 165 mg kg^{−1}, it was not possible to detect the oxidation state of U with XPS analyses. The limited release of U in the 18 MΩ DI water suggests that complexation with bicarbonate is an important mechanism in the release of U to solution observed in the first 30 minutes of the experiment.

The total organic matter content of sediments from the wetland area of the stream reach determined by loss of ignition is 14.8 ± 0.43% and 17.7 ± 0.90% from August 2015 and February 2015, respectively. Organic matter and clays tend to have a negative surface charge at the pH measured in the Rio Pague (pH range from 6.81 to 8.58), and therefore will not adsorb negatively charged complexes, such as the ternary calcium–uranyl–carbonate complexes predominant in the

system. This could explain why U accumulation in stream sediments along the reach of the Rio Pague is limited. However, it is possible that water retention (due to the slower water velocity compared to regular stream conditions) and interactions with organic matter or microbial processes in the wetland area could contribute to the accumulation of U. These interactions may increase accumulation of U in the wetland compared to the stream sediments.

Our results suggest that U is associated with organic-rich sediments (~14–15% as determined by LOI) in the wetland. Sediments from site 1 are not organic-rich (~2–4% as determined by LOI). Thus, at this point it is not clear if the interaction of U with organic-rich sediments contributed to the reductive precipitation of U. Future work is necessary to gain more specific information about the oxidation state and molecular coordination of U with organic matter in sediments from the wetland area. The impact of organic matter on the immobilization of U through the reduction of U(vi) to U(iv) in solids is still an unresolved subject, which has been attributed to a series of abiotic and biotic pathways.^{57–59} Microbial analyses were further pursued in water and solid samples collected from the Rio Pague to assess the potential for biotic processes on metal accumulation.

4.4 Microbial analyses

After processing data for each sample, 56 352 and 63 678 sequences remained in the sediment and water sample datasets, respectively. The total number of OTUs was greater for the sediment sample (4575) than the water sample (3063). Correspondingly, Chao1 estimates of species richness were 4621 and 3234, respectively. Sequences classified as Bacteria were far more abundant (>97%) than those classified as Archaea (<0.5%). Among Bacteria, sequences classified within the phylum *Proteobacteria* were the most abundant both in water and sediment samples, accounting for about half of the sequences overall (ESI Table S4†). However, the taxonomic distribution of sequences differed between the sediment and water sample. Compared to the water sample, the sediment sample had a higher relative abundance of sequences classified in classes *Deltaproteobacteria*, *Chloroplast*, and *Saprospirae* but a lower relative abundance of sequences classified in classes *Betaproteobacteria*, *Sphingobacteria*, *Verrucomicrobiae*, *Flavobacteriia*, and *Actinobacteria* (ESI Fig. S2 and ESI Table S4†).

Results of our sequencing analysis indicate the presence of metal reducing bacteria in sediments collected from the field area. Many of the sequences in our samples that were classified within the *Deltaproteobacteria* were further classified within groups that contain species capable of catalyzing Fe(III) and/or SO₄^{2−} reduction, including *Desulfarculales*, *Desulfobacterales*, *Desulfovibrionales*, *Desulfurellales*, *Desulfuromonadales*, *Myxococcales*, and *Syntrophobacterales* (ESI, Table S4†).^{60–63} Sequences classified within these orders made up 83% and 35% of the *Deltaproteobacterial* sequences from our sediment and water sample, respectively. Importantly, many microbes that are capable of Fe(III) and/or SO₄^{2−} reduction can also directly or indirectly reduce U(vi) to U(iv), causing U immobilization.^{35,64–66}

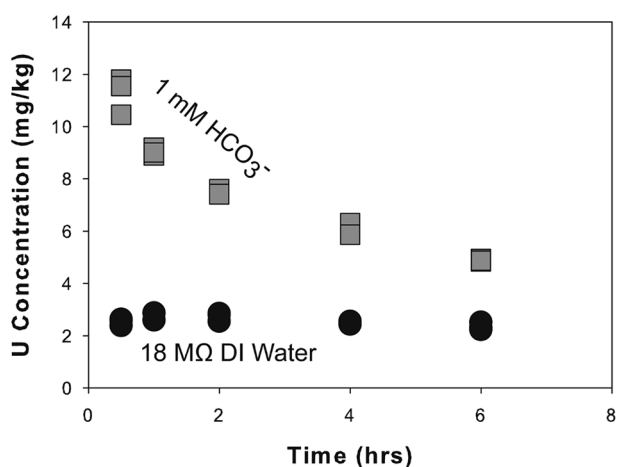


Fig. 9 Batch experiment results of U concentration (mg kg^{−1}) over time for reaction of sediment samples collected from the wetland (initial total U concentration is 160 mg kg^{−1}) reacted with 1 mM HCO₃[−] and 18 MΩ DI water.

Given the finding of these species, the populations likely have an effect on the interaction of U between sediments and water in the environment at this site. These data provide initial information about microbial populations of the Rio Pagate, which is valuable in understanding this complex system. By identifying the microbial species present, we learn about the potential processes that attribute to the mobility or accumulation of U in the Rio Pagate. Further study of the biological component in this system will enable the understanding of microbial interactions coupled with geochemical processes. Additional research needs to be conducted to investigate the distribution and function of these microbial populations to assess the effect of microbial activity on U mobility in this site. The mobility and accumulation of U was further investigated by analyzing sediment and water samples obtained from the hyporheic zone.

4.5 Analyses of water and sediment samples from the hyporheic zone in the Rio Pagate and the role of local geology

The U concentrations of hyporheic zone water collected in June 2015 are 2–3 times ($449 \mu\text{g L}^{-1} \pm 34.3$) higher than the surface water concentrations ($213 \mu\text{g L}^{-1} \pm 97.1$) at the same location and time (Fig. 10a). Additionally, the majority of the U is found in the $<0.22 \mu\text{m}$ fraction of water in the hyporheic zone suggesting a mobile form of U that is present as colloidal or nanoparticulate phases, or as a totally dissolved aqueous phase. The total uranium concentrations average $449 \pm 34.2 \mu\text{g L}^{-1}$ (including all the filtrates) and 95–100% is found in the <0.22

μm filtrate for the 8 cm and 15 cm samples. The range of total U present in the particulate form obtained from surface water samples is 179 to $354 \mu\text{g L}^{-1}$ U.

Six of the eight sediment core samples at site 1 have U concentrations within 2 times the local background of 0.20 – 2 mg kg^{-1} , while two samples have concentrations 10–15 times higher than the background (Fig. 10b). The average U concentration at 8 cm depth is $11.5 \pm 13.9 \text{ mg kg}^{-1}$ U and $7.60 \pm 7.84 \text{ mg kg}^{-1}$ U for 15 cm depth samples. Core 2, 8 cm depth has a U concentration of 35.5 mg kg^{-1} and core 3, 15 cm depth has a concentration of 21.1 mg kg^{-1} . In comparison to the stream bed sediment and stream bank sediment U concentration range at site 1 (0.20 mg kg^{-1} to 5.20 mg kg^{-1}), some sediments from the hyporheic zone are higher suggesting that U bearing sediments are found beneath the stream bed. The hyporheic zone has two samples with slightly higher concentrations compared to the wetland sediments (maximum U concentration of 20 mg kg^{-1}). This could be due to the proximity of the hyporheic zone samples to the mine site and depositional processes at this location. It is unknown how old the stream or wetland sediments are, which could also be a factor in U concentration. Particle sizes in general are smaller in the wetland (silt to clay) *versus* the hyporheic zone (pebble to silt). The solid analyses conducted in this study suggest that surficial ore and hyporheic zone sediments from the Jackpile Mine area are potential sources of U and other metals which could be released into the Rio Pagate. Dissolution of U phases from ore solids by flow events contributes to the transport of soluble U to the Rio Pagate. Our data suggest that U-bearing mineral phases in

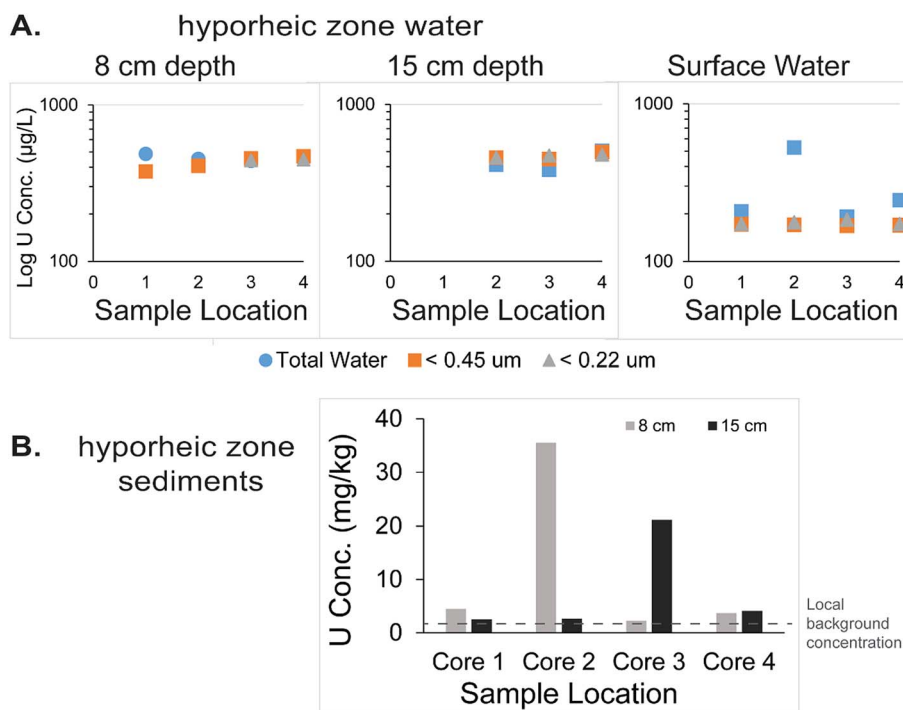


Fig. 10 (A) U concentrations from 8 cm and 15 cm below the sediment–water interface and surface water separated by total water (blue circles), $<0.45 \mu\text{m}$ (orange squares), and $<0.22 \mu\text{m}$ (gray triangles). (B) Concentration of U in hyporheic zone sediments from 8 cm (gray bars) and 15 cm (black bars).

abandoned mine wastes from the Jackpile Mine, identified in this study using electron microprobe and XRD analyses, are amenable to dissolution during rain events.

The local geology seems to play an important role in the mobility of U in the Rio Paguete. The relationship between U concentration and rain events at site 1 (Fig. 11) implies that surface water concentrations increase potentially due to desorption and dissolution of U from alluvium along the stream

banks or within the hyporheic zone. A similar relationship is seen between discharge and U concentration from historic USGS data (Fig. 2). Quaternary alluvium fills the shallow basin between a mine waste pile and the Rio Paguete. The southwestern edge of the stream abuts an outcrop of the Jurassic Morrison Formation, the majority being the Brushy Basin Member, with the top 5 meters of Jackpile Sandstone outcropping. The Lower Brushy Basin Member is a 60 m thick mudstone, has low permeability⁶⁷ and dips 27° to 33° to the northeast under the streambed. The Upper Brushy Basin Member, or Jackpile Sandstone, has a hydraulic conductivity of 0.09 m per day and the Quaternary alluvium has a hydraulic conductivity of 7 m per day.⁶⁸ The local flow pattern to the Rio Paguete is through Quaternary alluvium to the east and through alluvium, and Jackpile Sandstone to the west (Fig. 12).⁶⁸ Therefore, the mine waste covered with alluvium located 200 m east of the Rio Paguete has the potential for rain water to infiltrate and travel to the river as throughflow or recharge groundwater and, ultimately, enter the river through the hyporheic zone. The elevated U concentrations in the hyporheic zone water compared to the surface water further support this hypothesis. The U concentration of 75 $\mu\text{g L}^{-1}$ at site 1 in September 2015 is nearly 10% of what was measured in 2014 (711 $\mu\text{g L}^{-1}$) which was after a wet season in the area. This observation suggests that there may be mechanisms such as hydrology, large scale groundwater to surface water flow or local geochemical conditions controlling the U concentration in the stream. Future research should study the variation in U concentration in the days following a rain event in order to pinpoint the lag time between dilution and increase in U concentration from the hyporheic zone.

4.6 Uranium in surface water and the relationship with rain events

The data presented in this study report the occurrence of U in surface waters of the Rio Paguete adjacent to the Jackpile Mine. The highest U concentrations in the river were observed after rain events as well as during dry periods when evaporation may have occurred. The differences in U concentrations observed at each site and sampling event suggest that water chemistry in the Rio Paguete is affected by hydrogeological and geochemical processes at different times of the year. Snowmelt from nearby mountain peaks, dry seasons, or monsoonal rains could affect the mobility of U and other co-occurring elements in the system by means of dissolution, dilution, adsorption, chemical precipitation or other geochemical processes. Daily precipitation sum values from June 1, 2014 through September 30, 2016 for weather stations in Albuquerque, NM and Grants, NM are shown in Fig. 11. There are no long term weather data from Laguna, NM where the Jackpile Mine is located, therefore data from Albuquerque, NM (80 km east of Laguna, NM) and Grants, NM (55 km west of Laguna, NM) were used. This area of NM is arid and prone to variable precipitation. The rainy season is generally during late summer to early fall monsoons. Of particular note is the summer of 2014 where precipitation was low from the end of July until mid-September, which may have

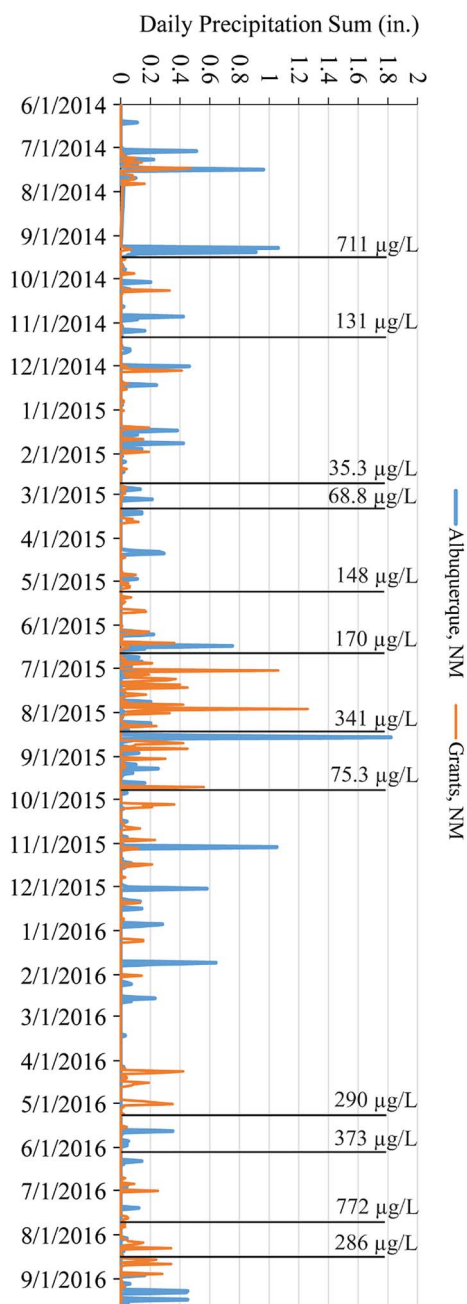


Fig. 11 Daily precipitation sum from Grants, NM (orange curve) and Albuquerque, NM (blue curve). Laguna, NM is located 80 km west of Albuquerque, NM and 55 km east of Grants, NM. Black lines indicate dates of sampling the Rio Paguete. Dissolved uranium concentrations at site 1 are shown adjacent to the black line. Precipitation data from <http://wunderground.com>.

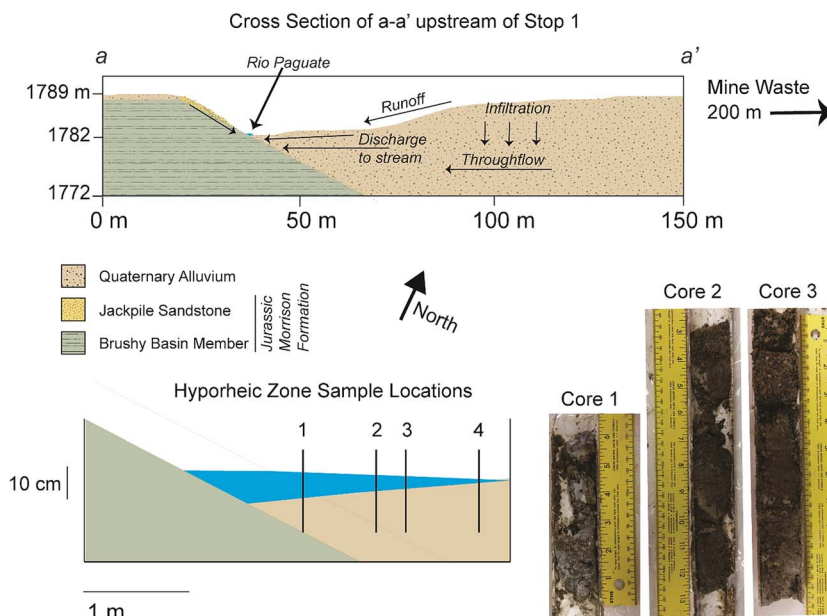


Fig. 12 Schematic cross-section 10 meters upstream of site 1.

had an effect on the mobility of U from the sediments surrounding the Jackpile Mine. Uranium concentrations in February and March 2015 may be lower due to reduced precipitation or precipitation in the form of snow. Persistent rain events during the monsoon season of 2015 may explain the U concentrations in June, and August. By September 2015 rain has been prevalent and available U in the sediment may have been flushed into the river by previous storm events therefore resulting in lower U concentrations at site 1. The spring and summer of 2016 were very dry compared to 2015, however, we observe similar high U concentrations in the Rio Pague water. The decrease in rainfall reduces the inflow to the Rio Pague, allowing time for evaporation to occur, which creates more mass per unit volume or $\mu\text{g L}^{-1}$ in a water body. In general, the U concentrations collected in water from sites 9 and 10 are lower than upstream concentrations observed on the same sampling date. The surface water at sites 9 and 10 is retained in the wetland and reservoir in 2014 and 2015, which may allow time for uranium to adsorb or precipitate, facilitating U deposition in sediments. In 2016, the wetland and reservoir were dry during the sampling events reported in this study. Additional sediment analyses sampled in 2016 from these two locations may elucidate the geochemical mechanisms occurring; future studies will pursue this effort.

The surface water chemistry analyses conducted in this study provide valuable information towards understanding the geochemical interactions between the Jackpile Mine and the Rio Pague and the mobility of U and other constituents in the system. Of particular interest is the relationship between U concentration and rain events or droughts, which needs further study. Literature related to this site is limited, outdated, and does not focus on the geochemical mechanisms related to U mobility in this system.^{8,10,36,67} While other studies have evaluated the effect of U mining on surface water chemistry,^{68–70} the

focus of this study site is unique due to the variability of water and sediment chemistry along the stream reach. Additionally, the geology and sediments of the area may play an important role in the change in U concentrations found in the surface water. The geochemical processes are complex and need further assessment to fully understand the system. Due to our constraints in resources and escorting, we were not able to take more periodic samples representative of seasons. However, the data suggest that seasons may play a role in the changes in surface water U concentrations observed. Future research should further address the seasonality of U concentrations in water and sediments.

5. Summary and conclusions

This investigation identified geochemical interactions between the Jackpile Mine and the Rio Pague which have relevant implications to communities located near mine wastes. For instance, U mobility from sediments, due to mineral dissolution, was observed in the surface water of the Rio Pague under varying hydrologic conditions. High flow events caused by rain and snowmelt could play an important role in the mobility of U from these ore sediments containing U-bearing minerals. The mineral coffinite was identified in ore samples from the Jackpile Mine by XRD analyses, which is an interesting finding given that the presence of U(IV) was identified even after exposure of these mine wastes to oxidizing conditions for several decades. Additionally, the increase in U concentrations measured in the hyporheic zone waters compared with surface water sampled on the same date suggests that U is transported through hyporheic zone interactions.

The accumulation of U on organic-rich sediments under oxidizing conditions provides insight into the complex geochemical interactions that occur between U and organic

matter. The increase in hydraulic retention combined with the lower sediment particle sizes and the organic content in the wetland potentially enhances U accumulation. It is worth noting that the stream discharge and sediment characteristics differ from the main channel of the stream to the wetland area where flow rate is lower, facilitating the contact time between water and sediments due to the hydraulic retention in the wetland. The presence of metal reducing bacteria identified in water and sediments collected near the Jackpile Mine provides a dataset to build upon for further understanding of the role microbial activity plays in U mobility.

Through the integration of tools from different disciplines, this study contributes new insights about how the complex interaction between mine wastes, stream sediments, and surface water of the Rio Paguete affects U mobility and accumulation. The knowledge gained in this study has relevant implications for stakeholders and land managers dealing with mining legacy issues. Future studies are needed to answer unresolved questions about hyporheic zone interactions, microbial activity, and the larger role of organic-rich sediments in systems affected by mining activities.

Acknowledgements

The authors thank the members of the Laguna Pueblo, former Governor Richard Luarkie, current Governor Virgil Siow, and the Pueblo Council for their support. The authors would like to acknowledge the existing partnership with the Pueblo of Laguna Environment and Natural Resources Department. Special thanks to Loren Arkie, Vince Rodriguez, Sabin Chavez, Deborah Anyaibe, Dorothy Beecher, Cherylin Atcity, and Gregory Jojola for their assistance in the field and knowledge of the area. Additionally, we thank Paul Robinson and Chris Shuey from the Southwest Research and Information Center. Funding for this research was provided by the National Science Foundation under New Mexico EPSCoR (Grant Number #IIA-1301346) and CREST (Grant Number 1345169). Any opinions, findings, and conclusions or recommendations expressed in this publication are those of the author(s) and do not necessarily reflect the views of the National Science Foundation.

References

- 1 US Bureau of Land Management, *Abandoned Mine Lands: A New Legacy*, US Dept. of the Interior, Bureau of Land Management, 2013, Publication Number BLM/WO/GI-13/007-3720.
- 2 J. M. Blake, S. Avsarala, K. Artyushkova, A.-M. S. Ali, A. J. Brearley, C. Shuey, W. P. Robinson, C. Nez, S. ill, J. Lewis, C. Hirani, J. S. L. Pacheco and J. M. Cerrato, *Environ. Sci. Technol.*, 2015, **49**, 8506–8514.
- 3 S. D. Kamp and S. J. Morrison, *Groundwater Monit. Rem.*, 2014, **34**, 68–78.
- 4 USEPA, *Technical Report on Technologically Enhanced Naturally Occurring Radioactive Materials from Uranium Mining Volume 1: Mining and Reclamation Background*, U.S. Environmental Protection Agency, Office of Radiation and Indoor Air, 2008, EPA 402-R-08-005.
- 5 R. Seager, M. Ting, C. Li, N. Naik, B. Cook, J. Nakamura and H. Liu, *Nat. Clim. Change*, 2013, **3**, 482–486.
- 6 L. Hund, E. J. Bedrick, C. Miller, G. Huerta, T. Nez, S. Ramone, C. Shuey, M. Cajero and J. Lewis, *J. Roy. Stat. Soc.*, 2015, **178**(4), 1069–1091.
- 7 USEPA, NPL Site narrative for Jackpile-Paguete Uranium Mine, <http://semspub.epa.gov/work/06/300064.pdf>, last updated 12/6/2013.
- 8 J. T. Nash, *Econ. Geol.*, 1968, **63**, 737–750.
- 9 R. H. Moench and J. S. Schlee, *Geology and uranium deposits of the Laguna district*, US Government Printing Office, New Mexico, 1967.
- 10 US Bureau of Land Management, *Jackpile Paguate uranium mine reclamation project: environmental impact statement*, US Dept. of the Interior, Bureau of Land Management, Albuquerque District Office: Bureau of Indian Affairs, Albuquerque Area Office, 1985.
- 11 Y. Wang, A. Bagnoud, E. Suvorova, E. McGivney, L. Chesaux, V. Phrommavanh, M. Descostes and R. Bernier-Latmani, *Environ. Sci. Technol.*, 2014, **48**, 10062–10070.
- 12 J. M. Zachara, P. E. Long, J. Bargar, J. A. Davis, P. Fox, J. K. Fredrickson, M. D. Freshley, A. E. Konopka, C. Liu, J. P. McKinley, M. L. Rockhold, K. H. Williams and S. B. Yabusaki, *J. Contam. Hydrol.*, 2013, **147**, 45–72.
- 13 B. D. Stewart, M. A. Mayes and S. Fendorf, *Environ. Sci. Technol.*, 2010, **44**, 928–934.
- 14 K. U. Ulrich, E. S. Ilton, H. Veeramani, J. O. Sharp, R. Bernier-Latmani, E. J. Schofield, J. R. Bargar and D. E. Giammar, *Geochim. Cosmochim. Acta*, 2009, **73**, 6065–6083.
- 15 N. P. Qafoku, J. M. Zachara, C. X. Liu, P. L. Gassman, O. S. Qafoku and S. C. Smith, *Environ. Sci. Technol.*, 2005, **39**, 3157–3165.
- 16 D. E. Giammar and J. G. Hering, *Environ. Sci. Technol.*, 2001, **35**, 3332–3337.
- 17 P. Byrne, I. Reid and P. J. Wood, *Environ. Monit. Assess.*, 2013, **185**, 2817–2832.
- 18 G. Olivie-Lauquet, G. Gruau, A. Dia, C. Riou, A. Jaffrezic and O. Henin, *Water Res.*, 2001, **35**, 943–952.
- 19 M. C. Moncur, C. J. Ptacek, M. Hayashi, D. W. Blowes and S. J. Birks, *Appl. Geochem.*, 2014, **41**, 176–188.
- 20 L. Newsome, K. Morris and J. R. Lloyd, *Chem. Geol.*, 2014, **363**, 164–184.
- 21 G. M. Gadd, *Geoderma*, 2004, **122**, 109–119.
- 22 R. T. Anderson, H. A. Vronis, I. Ortiz-Bernad, C. T. Resch, P. E. Long, R. Dayvault, K. Karp, S. Marutzky, D. R. Metzler, A. Peacock, D. C. White, M. Lowe and D. R. Lovley, *Appl. Environ. Microbiol.*, 2003, **69**, 5884–5891.
- 23 R. Schueneman, A. Khaskelis, D. Eastwood, W. Van Ooij and L. Burggraf, *J. Nucl. Mater.*, 2003, **323**, 8–17.
- 24 R. J. Finch and R. C. Ewing, *J. Nucl. Mater.*, 1992, **190**, 133–156.
- 25 P. C. Burns, *Can. Mineral.*, 2005, **43**, 1839–1894.
- 26 D. Gorman-Lewis, P. C. Burns and J. B. Fein, *J. Chem. Thermodyn.*, 2008, **40**, 335–352.

- 27 T. K. Tokunaga, Y. Kim, J. Wan and L. Yang, *Environ. Sci. Technol.*, 2012, **46**, 7471–7477.
- 28 M. S. Massey, J. S. Lezama-Pacheco, M. E. Jones, E. S. Ilton, J. M. Cerrato, J. R. Bargar and S. Fendorf, *Geochim. Cosmochim. Acta*, 2014, **142**, 166–185.
- 29 P. S. Nico, B. D. Stewart and S. Fendorf, *Environ. Sci. Technol.*, 2009, **43**, 7391–7396.
- 30 W. Dong and S. C. Brooks, *Environ. Sci. Technol.*, 2006, **40**, 4689–4695.
- 31 W. Dong and S. C. Brooks, *Environ. Sci. Technol.*, 2008, **42**, 1979–1983.
- 32 K. E. Fletcher, M. I. Boyanov, S. H. Thomas, Q. Z. Wu, K. M. Kemner and F. E. Löffler, *Environ. Sci. Technol.*, 2010, **44**, 4705–4709.
- 33 T. Borch, R. Kretzschmar, A. Kappler, P. V. Cappellen, M. Ginder-Vogel, A. Voegelin and K. Campbell, *Environ. Sci. Technol.*, 2010, **44**, 15–23.
- 34 K. M. Campbell, R. K. Kukkadapu, N. Qafoku, A. D. Peacock, E. Leshner, K. H. Williams, J. R. Bargar, M. J. Wilkins, L. Figueroa and J. Ranville, *Appl. Geochem.*, 2012, **27**, 1499–1511.
- 35 J. R. Bargar, K. H. Williams, K. M. Campbell, P. E. Long, J. E. Stubbs, E. I. Suvorova, J. S. Lezama-Pacheco, D. S. Alessi, M. Stylo, S. M. Webb, J. A. Davis, D. E. Giammar, L. Y. Blue and R. Bernier-Latmani, *Proc. Natl. Acad. Sci. U. S. A.*, 2013, **110**, 4506–4511.
- 36 D. W. Risser, P. A. Davis, J. A. Baldwin and D. P. McAda, *US Geological Survey Water Resources Investigation Report*, 1984, vol. 84, p. 26.
- 37 C. H. Maxwell, Mesozoic Stratigraphy of the Laguna-Grants Region, *New Mexico Geological Society Guidebook, 33rd Field Conference*, Albuquerque Country, 1982, vol. 2.
- 38 S. S. Adams, H. S. Curtis, P. L. Hafen and H. Salek-Nejad, *Econ. Geol.*, 1978, **73**, 1635–1654.
- 39 U. S. Geological Survey, Mineral Resource Online Data, <http://mrdata.usgs.gov/geology/state/map.html>, accessed November 10, 2016.
- 40 U. S. Geological Survey, 08349800 Rio Pagueate Below Jackpile Mine near Laguna, NM, https://waterdata.usgs.gov/nwis/inventory?agency_code=USGS&site_no=08349800, 2017, accessed January 14, 2017.
- 41 D. L. Stoliker, K. M. Campbell, P. M. Fox, D. M. Singer, N. Kaviani, M. Carey, N. E. Peck, J. R. Bargar, D. B. Kent and J. A. Davis, *Environ. Sci. Technol.*, 2013, **47**, 9225–9232.
- 42 D. S. Alessi, B. Uster, H. Veeramani, E. I. Suvorova, J. S. Lezama-Pacheco, J. E. Stubbs, J. R. Bargar and R. Bernier-Latmani, *Environ. Sci. Technol.*, 2012, **46**, 6150–6157.
- 43 C. L. Lauber, N. Zhou, J. I. Gordon, R. Knight and N. Fierer, *FEMS Microbiol. Lett.*, 2010, **307**, 80–86.
- 44 M. F. Kirk, B. H. Wilson, K. A. Marquart, L. H. Zeglin, D. S. Vinson and T. M. Flynn, *Front. Microbiol.*, 2015, **6**, DOI: 10.3389/fmicb.2015.01287.
- 45 C. Wuchter, E. Banning, T. J. Mincer, N. J. Drenzek and M. J. L. Coolen, *Front. Microbiol.*, 2013, **4**, DOI: 10.3389/fmicb.2013.00367.
- 46 J. G. Caporaso, J. Kuczynski, J. Stombaugh, K. Bittinger, F. D. Bushman, E. K. Costello, N. Fierer, A. G. Pena, J. K. Goodrich, J. I. Gordon, G. A. Huttley, S. T. Kelley, D. Knights, J. E. Koenig, R. E. Ley, C. A. Lozupone, D. McDonald, B. D. Muegge, M. Pirrung, J. Reeder, J. R. Sevinsky, P. J. Tumbaugh, W. A. Walters, J. Widmann, T. Yatsunenko, J. Zaneveld and R. Knight, *Nat. Methods*, 2010, **7**, 335–336.
- 47 D. McDonald, M. N. Price, J. Goodrich, E. P. Nawrocki, T. Z. DeSantis, A. Probst, G. L. Andersen, R. Knight and P. Hugenholtz, *ISME J.*, 2012, **6**, 610–618.
- 48 USEPA, *Radionuclides Rule: A Quick Reference Guide*, 2001, EPA 816-F-01-003.
- 49 N. Janot, J. S. Lezama Pacheco, D. Q. Pham, T. M. O'Brien, D. Hausladen, V. Noël, F. Lallier, K. Maher, S. Fendorf and K. H. Williams, *Environ. Sci. Technol.*, 2015, **50**, 46–53.
- 50 N. P. Qafoku, B. N. Gartman, R. K. Kukkadapu, B. W. Arey, K. H. Williams, P. J. Mouser, S. M. Heald, J. R. Bargar, N. Janot and S. Yabusaki, *Appl. Geochem.*, 2014, **42**, 77–85.
- 51 E. R. Gilson, S. Huang, P. G. Koster van Groos, K. G. Scheckel, O. Qafoku, A. D. Peacock, D. I. Kaplan and P. R. Jaffé, *Environ. Sci. Technol.*, 2015, **49**, 12214–12222.
- 52 D. Li, J. C. Seaman, H.-S. Chang, P. R. Jaffe, P. K. van Groos, D.-T. Jiang, N. Chen, J. Lin, Z. Arthur and Y. Pan, *J. Environ. Radioact.*, 2014, **131**, 40–46.
- 53 A. Schöner, C. Noubactep, G. Büchel and M. Sauter, *Chem. Erde-Geochem.*, 2009, **69**, 91–107.
- 54 J. Otton, *Surficial uranium deposits: summary and conclusions*, International Atomic Energy Agency, 1984.
- 55 P. E. Long, K. H. Williams, J. A. Davis, P. M. Fox, M. J. Wilkins, S. B. Yabusaki, Y. Fang, S. R. Waichler, E. S. Berman and M. Gupta, *Geochim. Cosmochim. Acta*, 2015, **150**, 106–124.
- 56 M. Duff and C. Amrhein, *Soil Sci. Soc. Am. J.*, 1996, **60**, 1393–1400.
- 57 S. A. Cumberland, G. Douglas, K. Grice and J. W. Moreau, *Earth-Sci. Rev.*, 2016, **159**, 160–185.
- 58 D. Li, D. I. Kaplan, H.-S. Chang, J. C. Seaman, P. R. Jaffé, P. Koster van Groos, K. G. Scheckel, C. U. Segre, N. Chen, D.-T. Jiang, M. Newville and A. Lanzirrotti, *Environ. Sci. Technol.*, 2015, **49**, 2823–2832.
- 59 A. E. Ray, J. R. Bargar, V. Sivaswamy, A. C. Dohnalkova, Y. Fujita, B. M. Peyton and T. S. Magnuson, *Geochim. Cosmochim. Acta*, 2011, **75**, 2684–2695.
- 60 E. Rosenberg, E. F. DeLong, S. Lory, E. Stackebrandt and F. Thompson, *The Prokaryotes: Actinobacteria*, Springer, Berlin Heidelberg, 2014.
- 61 G. Garrity, D. Brenner, N. Krieg and J. Staley, *Bergey's Manual of Systematic Bacteriology*, 2005, pp. 1059–1144.
- 62 N. Treude, D. Rosencrantz, W. Liesack and S. Schnell, *FEMS Microbiol. Ecol.*, 2003, **44**, 261–269.
- 63 D. J. Lonergan, H. L. Jenter, J. D. Coates, E. Phillips, T. M. Schmidt and D. R. Lovley, *J. Bacteriol.*, 1996, **178**, 2402–2408.

- 64 L. R. McGuinness, M. J. Wilkins, K. H. Williams, P. E. Long and L. J. Kerkhof, *PLoS One*, 2015, **10**, e0137270.
- 65 E. Cardenas, W.-M. Wu, M. B. Leigh, J. Carley, S. Carroll, T. Gentry, J. Luo, D. Watson, B. Gu and M. Ginder-Vogel, *Appl. Environ. Microbiol.*, 2010, **76**, 6778–6786.
- 66 J. D. Wall and L. R. Krumholz, *Annu. Rev. Microbiol.*, 2006, **60**, 149–166.
- 67 K. Maher, J. R. Bargar and G. E. Brown, *Inorg. Chem.*, 2013, **52**, 3510–3532.
- 68 H. H. Zehner, Hydrology and water-quality monitoring considerations, Jackpile uranium mine northwestern New Mexico, U.S. Geological Survey, Water-Resources Investigations Report 85-4226, 1985.
- 69 C. de Carvalho Filho, R. Moreira, B. Guimaraes, V. Ferreira, L. Auler, H. Palmieri, A. Oliveira and P. Dutra, *Environ. Earth Sci.*, 2016, **75**, 1–14.
- 70 A. Neiva, P. Carvalho, I. Antunes, M. Silva, A. Santos, M. C. Pinto and P. Cunha, *J. Geochem. Explor.*, 2014, **136**, 102–117.