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Article

Supporting Information

Transport and speciation of uranium in groundwater-surface water systems impacted by legacy milling operations

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Number of figures: 2

Number of tables: 2

Methodological Approach

Calculation of DGT solute concentrations

Diffusive gradients in thin-film (DGT) is a method of measuring potentially bioavailable or labile metal species in stream water and sediment pore waters. The commercially available DGT probes (DGT Research Ltd., Lancaster, UK) comprise a plastic holder containing three separate layers: an outer filter (0.45 µm) layer, a hydrogel diffusive layer, and a resin or binding layer. Specific properties of the resin layer bind solutes of interest. At the resin layer, the concentration of solutes is effectively zero so this induces a gradient from the stream water or sediment pore water across the diffusive layer and into the resin. After deployment, the resin layer from each probe is eluted in 10 mL 1M nitric acid (trace metal grade) and analyzed by ICP-MS. The DGT solute (metal) concentrations, C_{DGT}, are calculated as:

$$C_{DGT} = M \times \Delta_{MDL} / D_{MDL} \times A_p \times t \tag{1}$$

where M = the mass of solute accumulated in the resin gel [ng]; Δ_{MDL} = the thickness of the material diffusion layer [cm]; D_{MDL} = the diffusion coefficient of the specific solute in the diffusive gel [cm^2 s^{-1}]; A_p = the sample exposure window [cm^2]; and t = the deployment time [s]. The diffusion coefficients used in the present study (3.11 x 10^{-6} cm^2 s^{-1} for sediment pore waters and 4.44 x 10^{-6} cm^2 s^{-1} for stream water) are derived from the experimental study of Hutchins et al. (2012) for uranium diffusion at different pH values.

The mass of solute accumulated in the resin gel [ng] is calculated as:

$$M = C_e \times (V_e + V_{bl}) / f_e \tag{2}$$

where C_e = the solute (metal) concentration in the eluted solution, determined by ICP-MS [µg L^{-1}]; V_e = the volume of acid used in the elution step [mL]; V_{bl} = the volume of the resin layer [cm^3]; and f_e = the elution factor, derived from Hutchins et al. (2012).

Surface water grab sampling using the Equal Discharge Increments method

Bank operated cableways were established across the Little Wind River at three transects along the study reach (aligned with Riv – U/S, Riv-Mid and Riv-D/S in Figure 1) during August 2016 and August 2017. River discharge was measured multiple times at each transect using an Acoustic Doppler Current Profiler (ADCP) according to established U.S. Geological Survey methods (Turnipseed and Sauer, 2010). River discharge data from each transect were used to define three equal discharge increments (EDI), with the left, center, and right increments each representing one-third of the transect river discharge. The EDI sampling scheme was designed to detect both the longitudinal changes in concentration as the Little Wind River passes by the contaminant plume as well as changes in the transverse direction (perpendicular to streamflow) at each transect. Overall longitudinal changes in concentration are assessed by averaging concentrations from the left, center, and right increments at each transect; changes in the transverse direction are assessed by plotting the left, center, and right concentrations for each transect (Figure S1). Water-quality samples were collected at the midpoint of each EDI at each transect on August 11, 2016, and August 27, 2017, according to established U.S. Geological Survey methods (U.S. Geological Survey, 2012). Samples were filtered (0.45 µm) and acidified with trace metal grade concentrated nitric acid to 1 percent (volume to volume).

PHREEQC modelling

Dissolved U(VI) speciation was calculated using PHREEQC for the pore water chemistry measured at 15 cm depth in streambed adjacent to DGT deployment sites, and for mean surface

water chemistry from transect samples. Major ion chemistry is shown in Table S1 with sampling and analysis methods described in Naftz et al. (2019). Uranium aqueous speciation was calculated assuming oxic conditions based on measured dissolved oxygen of 0.4 mg L^{-1} or higher at depth of 30 cm in the streambed. See methods section of main text for further description. Speciation results are shown in Table S2 both as concentration of each species and as the fraction of the total dissolved uranium for key species.

Figure S1. Concentration of filtered uranium in three equal discharge increments representing one-third of the transect river flow at the left, center, and right locations at the upper, middle, and downstream transects during August 2016 [a] and August 2017 [b]. Locations of the river transects (Riv-U/S, Riv-Mid, Riv-D/S) along the Little Wind River study reach are shown in Figure 1.
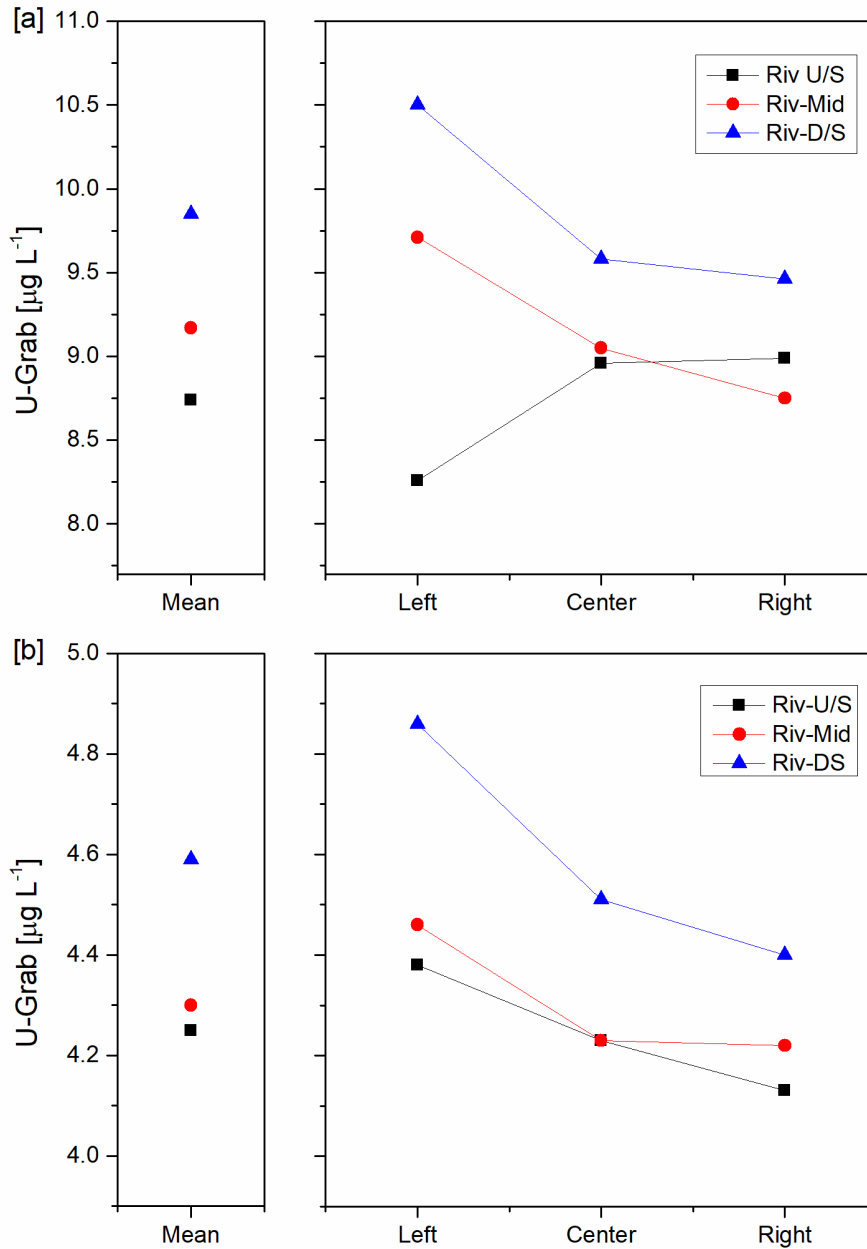
Figure S2. Sediment pore water uranium (U) concentrations from three diffusive equilibrium in thin-film (DET) sediment probes deployed at site WR17-6 in August 2018. Probes were deployed within 30 cm of each other and retrieved after 24 hours (0700), 31 hours (1400) and 38 hours (2100).
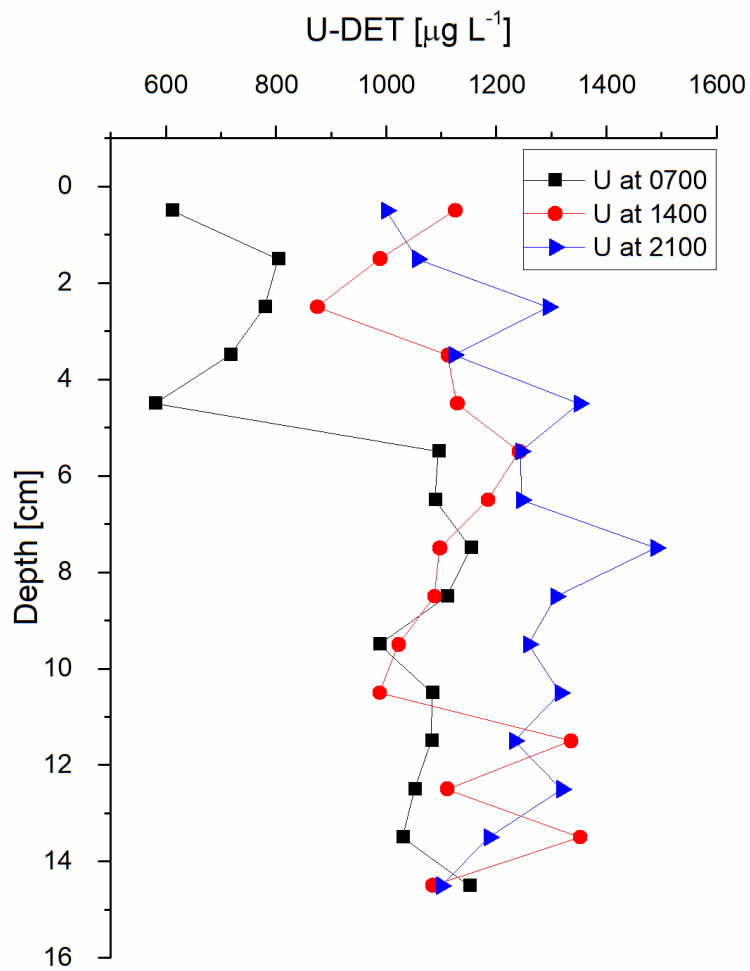
Table S1. Pore water chemistry at 15 cm depth from minipiezometer array (all WR sites) and mean of surface water from transect samples (SW). ALK is total alkalinity in milli-equivalents per liter. Dissolved inorganic constituents in units of moles per liter. Data from Naftz et al (2019).

	WR17-1	WR17-2	WR17-3	WR17-4	WR17-5	WR17-6	WR17-7	WR17-8	WR17-9	SW
pH	7.15	7.52	7.27	7.27	7.09	7.20	6.94	6.94	7.07	8.40
ALK	7.39	10.3	12.9	11.8	13.5	11.3	10.4	9.17	11.8	3.23
Na	2.18E-02	4.75E-02	9.09E-02	8.04E-02	7.52E-02	8.82E-02	6.21E-02	5.95E-02	4.59E-02	1.89E-03
Ca	8.26E-03	1.63E-02	1.81E-02	1.66E-02	1.18E-02	1.25E-02	2.15E-02	1.63E-02	1.95E-02	1.79E-03
Mg	4.81E-03	7.76E-03	1.55E-02	1.65E-02	1.29E-02	1.45E-02	1.06E-02	1.16E-02	1.03E-02	1.13E-03
K	1.95E-04	7.10E-04	8.57E-04	3.83E-04	3.68E-04	4.20E-04	5.16E-04	4.69E-04	5.85E-04	6.84E-05
Sr	2.59E-05	6.84E-05	9.74E-05	6.51E-05	5.29E-05	4.91E-05	7.55E-05	4.89E-05	7.05E-05	9.11E-06
Mn	1.07E-04	7.46E-04	6.94E-04	1.38E-04	1.41E-04	6.03E-05	7.15E-04	3.47E-04	6.12E-04	2.62E-07
SO4	1.95E-02	3.94E-02	6.62E-02	6.12E-02	5.23E-02	6.07E-02	5.43E-02	5.14E-02	4.35E-02	2.13E-03
Cl	2.85E-03	8.73E-03	1.65E-02	1.54E-02	1.21E-02	1.38E-02	8.97E-03	6.28E-03	1.04E-02	1.99E-04
F	1.22E-05	7.03E-06	6.30E-06	1.24E-05	2.81E-05	5.14E-05	6.63E-06	4.36E-05	5.26E-06	1.38E-05
U	9.21E-08	5.55E-07	2.28E-06	2.91E-06	2.69E-06	5.48E-06	9.35E-07	1.11E-06	5.00E-07	2.04E-08

Table S2. Aqueous uranium speciation in pore water at 15 cm depth and river water. See Table S1 and Naftz et al. (2019) for major ion concentrations used in speciation calculations.

	WR17-1	WR17-2	WR17-3	WR17-4	WR17-5	WR17-6	WR17-7	WR17-8	WR17-9	River Water	Notes
pH	7.15	7.52	7.27	7.27	7.09	7.20	6.94	6.94	7.07	8.40	
U total	9.21E-08	5.55E-07	2.28E-06	2.91E-06	2.69E-06	5.48E-06	9.35E-07	1.11E-06	5.00E-07	2.04E-08	
UO_2^{+2}	1.12E-16	1.55E-17	2.70E-16	4.43E-16	1.40E-15	2.46E-15	1.12E-15	2.85E-15	1.57E-16	1.44E-19	
$CaUO_2(CO_3)_3^{-2}$	2.11E-08	1.09E-07	5.33E-07	6.90E-07	7.63E-07	1.59E-06	1.71E-07	2.44E-07	8.83E-08	6.43E-09	
$Ca_2UO_2(CO_3)_3$	6.94E-08	4.39E-07	1.68E-06	2.13E-06	1.81E-06	3.64E-06	7.51E-07	8.42E-07	4.05E-07	1.35E-08	
$MgUO_2(CO_3)_3^{-2}$	1.00E-09	4.23E-09	3.73E-08	5.60E-08	6.79E-08	1.49E-07	6.88E-09	1.41E-08	3.82E-09	3.43E-10	
$UO_2(CO_3)_2^{-2}$	6.46E-11	7.63E-11	6.12E-10	8.85E-10	1.69E-09	3.33E-09	3.87E-10	7.99E-10	1.30E-10	5.68E-12	
UO_2CO_3	1.56E-12	5.19E-13	5.34E-12	8.40E-12	2.14E-11	3.85E-11	9.20E-12	2.16E-11	2.09E-12	2.53E-14	
$UO_2(CO_3)_3^{-4}$	5.13E-10	3.08E-09	2.43E-08	3.12E-08	4.21E-08	9.61E-08	5.10E-09	8.93E-09	2.31E-09	1.09E-10	
$(UO_2)_2CO_3(OH)_3^-$	4.28E-18	2.22E-18	6.52E-17	1.70E-16	4.02E-16	2.67E-15	4.93E-17	2.98E-16	3.97E-18	6.73E-19	
$(UO_2)_3(CO_3)_6^{-6}$	6.19E-25	3.08E-24	3.34E-21	8.99E-21	5.17E-20	4.74E-19	6.09E-22	4.75E-21	1.74E-23	3.56E-29	
UO_2OH^+	4.75E-15	1.34E-15	1.19E-14	1.98E-14	4.23E-14	9.38E-14	2.41E-14	6.23E-14	4.70E-15	1.47E-16	
$UO_2(OH)_2$	6.74E-15	4.20E-15	2.00E-14	3.36E-14	4.80E-14	1.35E-13	1.94E-14	5.05E-14	5.19E-15	4.17E-15	
$UO_2(OH)_3^-$	9.46E-16	1.46E-15	4.11E-15	6.83E-15	6.37E-15	2.34E-14	1.82E-15	4.70E-15	6.47E-16	9.29E-15	
$(UO_2)_2(OH)_2^{+2}$	2.61E-24	2.27E-25	1.91E-23	5.24E-23	2.35E-22	1.17E-21	7.59E-23	5.03E-22	2.84E-24	2.04E-27	
$UO_2(OH)_4^{-2}$	1.77E-20	7.38E-20	1.28E-19	2.09E-19	1.26E-19	6.10E-19	2.54E-20	6.47E-20	1.18E-20	2.28E-18	
$(UO_2)_3(OH)_5^+$	2.22E-29	2.49E-30	5.21E-28	2.42E-27	1.04E-26	1.86E-25	9.65E-28	1.69E-26	1.34E-29	2.58E-31	
$(UO_2)_2OH^{+3}$	4.39E-28	2.06E-29	3.61E-27	9.63E-27	6.27E-26	2.53E-25	2.85E-26	1.85E-25	7.47E-28	1.16E-32	
$(UO_2)_3(OH)_4^{+2}$	1.32E-32	7.25E-34	2.97E-31	1.36E-30	8.64E-30	1.22E-28	1.13E-30	1.94E-29	1.12E-32	6.33E-36	
$(UO_2)_3(OH)_7^-$	9.90E-32	6.08E-32	4.02E-30	1.86E-29	3.51E-29	1.04E-27	1.63E-30	2.85E-29	4.13E-32	3.64E-31	
$(UO_2)_4(OH)_7^+$	9.58E-38	6.76E-39	6.87E-36	5.33E-35	3.27E-34	1.65E-32	1.22E-35	5.55E-34	4.52E-38	6.81E-40	
UO_2Cl^+	2.02E-19	7.01E-20	2.00E-18	3.13E-18	8.04E-18	1.56E-17	4.80E-18	8.77E-18	8.21E-19	2.75E-23	
UO_2Cl_2	1.98E-23	1.87E-23	9.13E-22	1.36E-21	2.81E-21	6.07E-21	1.25E-21	1.62E-21	2.56E-22	2.36E-28	
UO_2SO_4	4.17E-16	7.37E-17	1.56E-15	2.47E-15	7.58E-15	1.43E-14	6.03E-15	1.57E-14	7.47E-16	1.50E-19	
$UO_2(SO_4)_2^{-2}$	5.90E-17	1.98E-17	6.71E-16	9.87E-16	2.74E-15	5.90E-15	2.15E-15	5.44E-15	2.13E-16	2.57E-21	
	species fraction of total U concentration										
$f(UO_2^{+2})$	1.22E-09	2.80E-11	1.19E-10	1.52E-10	5.19E-10	4.49E-10	1.20E-09	2.57E-09	3.14E-10	7.05E-12	free uranyl ion
$f(UO_2(CO_3)_2^{-2})$	0.0007	0.0001	0.0003	0.0003	0.0006	0.0006	0.0004	0.0007	0.0003	0.0003	dicarbonato species
$f(U-CO_3)$	0.006	0.006	0.011	0.011	0.016	0.018	0.006	0.009	0.005	0.006	sum of all uranyl carbonate species
$f(Ca_2UO_2(CO_3)_3)$	0.754	0.791	0.739	0.732	0.675	0.665	0.803	0.758	0.811	0.662	uncharged ternary complex
$f(Ca-U-CO_3)$	0.983	0.987	0.973	0.970	0.958	0.955	0.987	0.978	0.987	0.977	sum of ternary Ca-U-CO3 species
$f(Mg-U-CO_3)$	0.011	0.008	0.016	0.019	0.025	0.027	0.007	0.013	0.008	0.017	ternary Mg-U-CO3 species
$f(Ca,Mg-U-CO_3)$	0.994	0.994	0.989	0.989	0.984	0.982	0.994	0.991	0.995	0.994	sum of all ternary (Ca+Mg)-U-CO3 species

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