Supplementary Information: Nitrate stimulated release of naturally occurring sedimentary uranium

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Supplementary Information

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Supplementary Information Table 1. Groundwater geochemical data collected from two different alluvial aquifer sites

Sample ID	Sample Depth (m)	pH	Eh (mV)	Dissolved Oxygen (mg/L)	Nitrate (mg/L-N)	Uranium (ICPMS; µg/L)	Alkalinity (mg/L as bicarbonate)	Dissolved Organic Carbon (mg/L-C)	Aqueous Fe(II) (mg/L)
Alda West- 33	10.0	7.2	-25.2	2.33	33.73 ± 0.18	12.2 ± 0.2	395.44	5.59 ± 0.09	0.000 ± 0.000
Alda West -40	12.2	7	2.1	2.49	27.50 ± 0.43	33.9 ± 0.8	385.67	4.17 ± 0.07	0.000 ± 0.000
Alda West -59	17.9	6.9	-22.1	1.64	26.58 ± 0.54	153.7 ± 1.9	331.98	3.705 ± 0.03	0.005 ± 0.003
Alda North- 32	9.7	7.2	-407	0.96	4.40 ± 0.03	2.47 ± 0.07	113.1	3.05 ±0.16	0.000 ± 0.000
Alda North -38	11.6	7.1	-520	1.1	0.59 ± 0.03	3.47 ± 0.53	142.4	2.97 ± 0.08	0.721 ± 0.055
Alda North -52	15.8	7.3	-434	1.26	0.0187 ± 0.02	4.93 ± 1.03	106.1	2.88 ±0.02	0.943 ± 0.000

Groundwater from the borehole was collected by bailing from two sites in Central Nebraska. Eh, pH, DO, and Alkalinity were measured in the field using calibrated electrodes. Additional samples were filtered and preserved before analysis back at the University of Nebraska-Lincoln.

Supplementary Information Table S2. Descriptive statistics including R-factor and chi^2 for XANES Linear Combination Fits

Alda North, 10.2 m bgs

U(VI) reference	fraction U(VI)	fraction UO$_2$	sum	R-value	chi^2
U(VI) adsorbed to ferrihydrite	0.60	0.47	1.072	0.0053	0.18
Andersonite	0.51	0.64	1.15	0.0065	0.22
Autunite	0.55	0.51	1.06	0.0054	0.18
U(VI) Nitrate	0.68	0.41	1.09	0.0074	0.25
U(VI) acetate	0.57	0.49	1.06	0.0062	0.21
average f_U(VI)	0.58	**avareage f_U(VI)**	0.50		
average f_U(IV)	0.06	**standard dev f_U(IV)**	0.085		

Alda West, 11.7 m bgs

U(VI) reference	fraction U(VI)	fraction UO2	sum	R-value	chi2
U(VI) adosorbed to ferrihdrite	0.90	0.12	1.02	0.0013	0.05

Supplementary Information Table S3. Measured geochemical parameters within the batch adsorption experiments

| Sample ID	pH	DIC Average (mol/L CO2 dissolved)	Fe(II) (mg L^{-1} or kg)	Fe(II) (mmol L^{-1} or kg)	Total Sed Fe (mg L^{-1} or kg)	Total Sed Fe (mmol L^{-1} or kg)	% Sediment Fe(II)
Anoxic 1	7.2	0.009	101.74	1.82	138.06	2.47	73.69
Anoxic 2	7.2	0.01	91.62	1.64	100.18	1.79	91.45
Anoxic 3	7.2	0.009	92.92	1.66	204.17	3.66	45.51
Anoxic 4	7.2	0.009	64.57	1.16	83.30	1.49	77.52
Anoxic 5	7.2	0.009	59.72	1.07	118.91	2.13	50.22
Anoxic 6	7.2	0.009	92.06	1.65	179.97	3.22	51.15
Oxic 1	7.2	0.005	62.39	1.12	221.05	3.96	28.22
Oxic 2	7.2	0.005	6.22	0.11	162.28	2.91	3.84
Oxic 3	7.2	0.007	7.73	0.14	108.64	1.95	7.11
Oxic 4	7.2	0.01	35.67	0.64	212.28	3.80	16.8
Oxic 5	7.2	0.006	15.62	0.28	94.77	1.70	16.49
Oxic 6	7.2	0.008	3.58	0.06	183.93	3.29	1.95

Supplementary Information Table S4. Uranium geochemical data collected from batch adsorption experiments

| Sample ID	Labile[1] Adsorbed (ug/L)	Labile[1] Adsorbed (mol/L)	U (ug/L) Added[2]	U (mol/L) Added[2]	Final[3] U concentration (ug/L)	Final[3] U concentration (mol/L)	U adsorbed (ug/g)	U adsorbed (mol/g)	% U adsorbed
Anoxic 1	1.86	7.81E-09	10.00	4.20E-08	9.93	4.17E-08	0.02	8.09E-11	0.7
Anoxic 2	1.86	7.81E-09	60.94	2.56E-07	31.27	1.31E-07	0.32	1.33E-09	48.7
Anoxic 3	1.86	7.81E-09	99.02	4.16E-07	86.79	3.65E-07	0.14	5.91E-10	12.3
Anoxic 4	1.86	7.81E-09	149.96	6.30E-07	118.98	5.00E-07	0.33	1.38E-09	20.7
Anoxic 5	1.86	7.81E-09	219.94	9.24E-07	159.81	6.71E-07	0.62	2.61E-09	27.4
Anoxic 6	1.86	7.81E-09	285.63	1.20E-06	192.79	8.10E-07	0.95	3.99E-09	32.6
Oxic 1	4.05	1.70E-08	10.00	4.20E-08	7.93	3.33E-08	0.06	2.57E-10	20.7
Oxic 2	4.05	1.70E-08	60.94	2.56E-07	32.10	1.35E-07	0.33	1.38E-09	47.4
Oxic 3	4.05	1.70E-08	99.02	4.16E-07	58.38	2.45E-07	0.45	1.88E-09	41.0
Oxic 4	4.05	1.70E-08	149.96	6.30E-07	57.43	2.41E-07	0.97	4.06E-09	61.7
Oxic 5	4.05	1.70E-08	219.94	9.24E-07	86.46	3.63E-07	1.38	5.78E-09	60.7
Oxic 6	4.05	1.70E-08	285.63	1.20E-06	114.40	4.81E-07	1.76	7.38E-09	60.0

[1]Labile U refers to the aqueous U concentration measured after a 36-hour pre-incubation period before a spike of U is added.
[2]U added is the amount of aqueous U added at the beginning of the experiment from a U stock solution (as uranyl chloride).
[3]Final U concentration is the concentration of aqueous U measured at the end of the experiment.
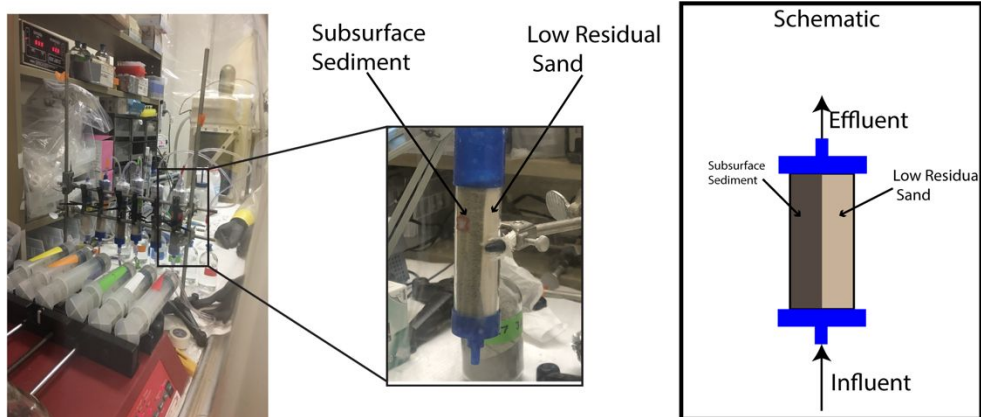
Supplementary Information Figure 1. Upflow-column reactor experimental design replicating the sand and silt lithologic interface. Image of the upflow column reactors within an anaerobic glove bag connected to syringe pump. Right, These columns contain a vertical interface between subsurface sediments collected from the Alda North site (11.7 m below ground surface) and acid-washed, combusted quartz sand. Photo credit: Jeffrey Westrop.
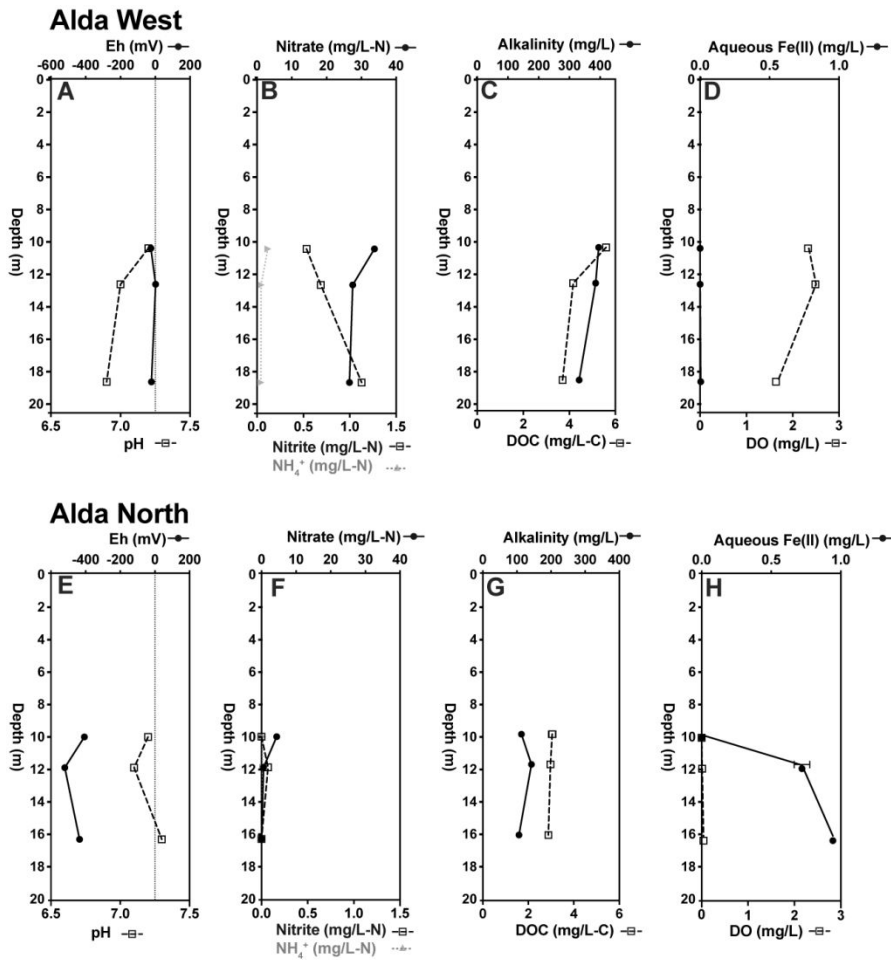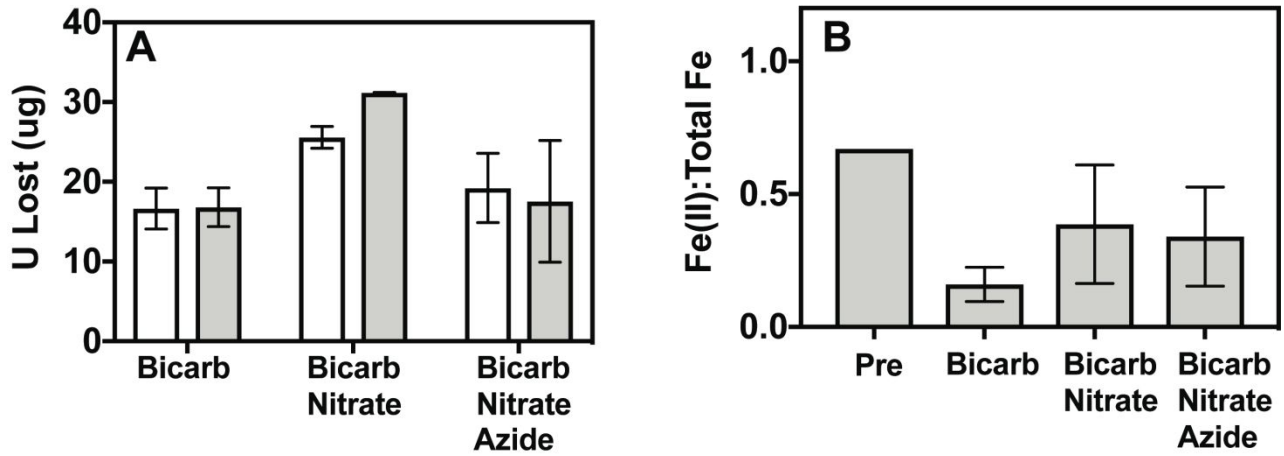
Supplementary Information Figure 2. Groundwater geochemical parameters collected from the boreholes at two coring sites. A. pH (solid) and Eh (dashed) from Alda West site. B. Nitrate (Solid), Nitrite (Black dashed) and Ammonium (grey dashed) from Alda West site. C. Dissolved Organic Carbon, DOC, (solid) and Alkalinity (dashed) from Alda West site. D. Dissolved oxygen, DO, (solid) and aqueous Fe(II) (dashed) from Alda West site. E. pH (solid) and Eh (dashed) from Alda North site. F. Nitrate (Solid), Nitrite (Black dashed) and Ammonium (grey dashed) from Alda North site. G. Dissolved Organic Carbon, DOC, (solid) and Alkalinity (dashed) from Alda North site. H. Dissolved oxygen, DO, (solid) and aqueous Fe(II) (dashed) from Alda North site.
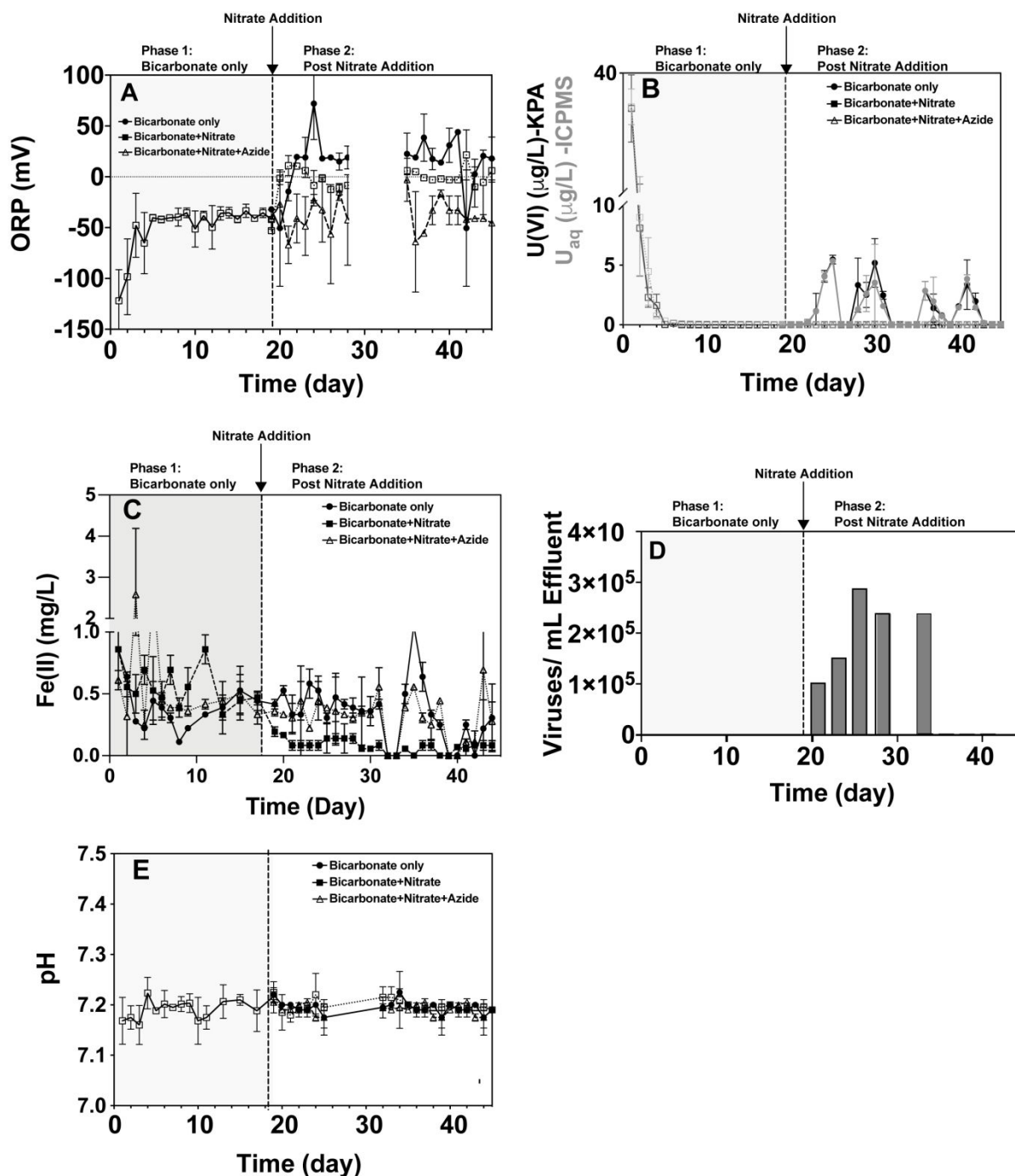
Supplementary Information Figure 3. Mobilization of naturally occurring uranium from upflow-column reactors in response to a nitrate amendment replicating the sand and silt lithologic interface. After 19 days of bicarbonate buffered artificial groundwater medium inflow two columns were amended with nitrate, two columns were amended with nitrate and sodium azide, and two columns remained unamended (denoted by arrow and dashed line). A, Measured

Oxidation Reduction Potential (ORP). B. Dissolved uranium eluted as quantified using KPA denoted in black and ICPMS denoted in grey. C, Daily measured Fe(II) concentration. D. Virus abundance above detection measured in the effluent. E. Measured pH within the column effluent.

Sediment Extraction Data

Supplementary Information Figure 4. Sediment geochemical data from nitrate addition column experiments. A. Total amount of U eluted from the column (white bars) and lost from sediments (U pre-experiment – U post experiment) (gray bars). B. Ratio of Sediment Fe(II) to Total Fe. **-f**. Error bars denote standard error of measure for duplicate treatments.

Supplementary Information: Surface Complexation Model

Multiple sorption equilibrium expressions were tested, including strong and weak sites, with only one reaction and formation constant required to provide the best fit for experimental data, likely due to only one experimental variable (U concentration). Surface site density was assumed to be 3.84 µmol/m [1,2], surface area was 1.92 m^2/ g (BET surface area analysis) and solid to solution ratio (SSR) was 100 g/L to match the SSR used in batch adsorption experiments. The surface adsorption reaction can be written as:

$$SOH + UO_2^{+2} = SOUO_2^+ + H^+$$ (equation 1)

where S denotes a generalized surface site. The optimized formation constant for equation 1 was log K = 3.507. Equation 1 and the associated formation constant were added to the PHREEQC calculation as SCM sediment adsorption reaction. The amount of U adsorbed under anoxic conditions were simulated over the experimental U concentration range. For the oxic condition, 50% of the Fe(II) was oxidized and assumed to precipitate as ferrihydrite with a surface area of 600 m^2/g and a site density of 0.016g/L [3]. A one-site ferrihydrite reaction was optimized:

$$FyOH + UO_2^{+2} = FYOUO_2^+ + H^+$$ (equation 2)

with an associated log K = 6.009. The oxic condition was modeled in PHREEQC using both equation 1 and 2 over the range of experimental U concentrations.

Supplemental Information References Cited

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