Electronic supplementary information

Cr(VI) Uptake and Reduction by Biogenic Iron (Oxyhydr)oxides

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- 8 pages, 4 figures, 4 tables -

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Figure S1. The BIOS collected at Rocky Branch Creek (35°46’49”N 78°40’01”W; Raleigh, North Carolina).[1-3]

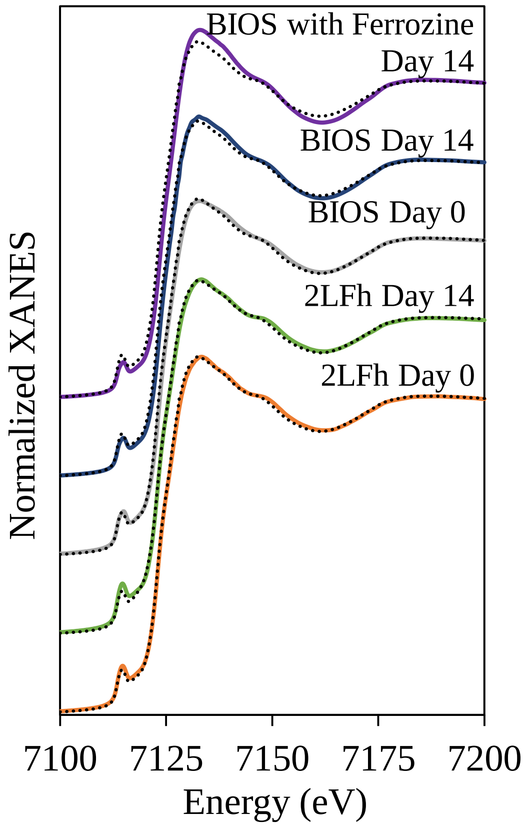

Figure S2. Fe K-edge XANES spectra and pre-Cr sorption (Day 0) and post-Cr sorption (Day 14) 2LFh, BIOS, and BIOS with 0.135 M ferrozine. Spectra are fit with ferrihydrite, an Fe(III) standard, and pyrite, an Fe(II) standard. In all cases, LCFs (black dotted lines) indicate 100% Fe(III).

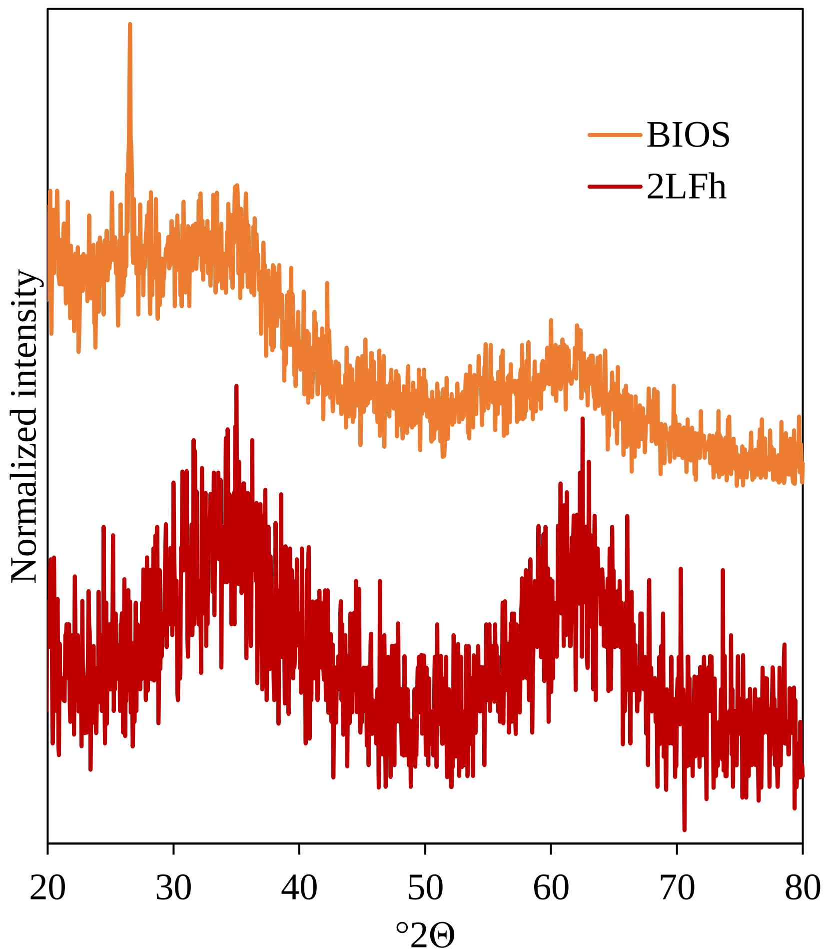

Figure S3. X-ray diffractograms of BIOS and 2LFh collected with Rigaku SmartLab X-ray diffractometer with graphite monochromated Cu K-α radiation. The sharp peak at 26.65 °2Θ in the BIOS diffraction pattern is due to minor amounts of quartz that make up less than 10% of the BIOS.

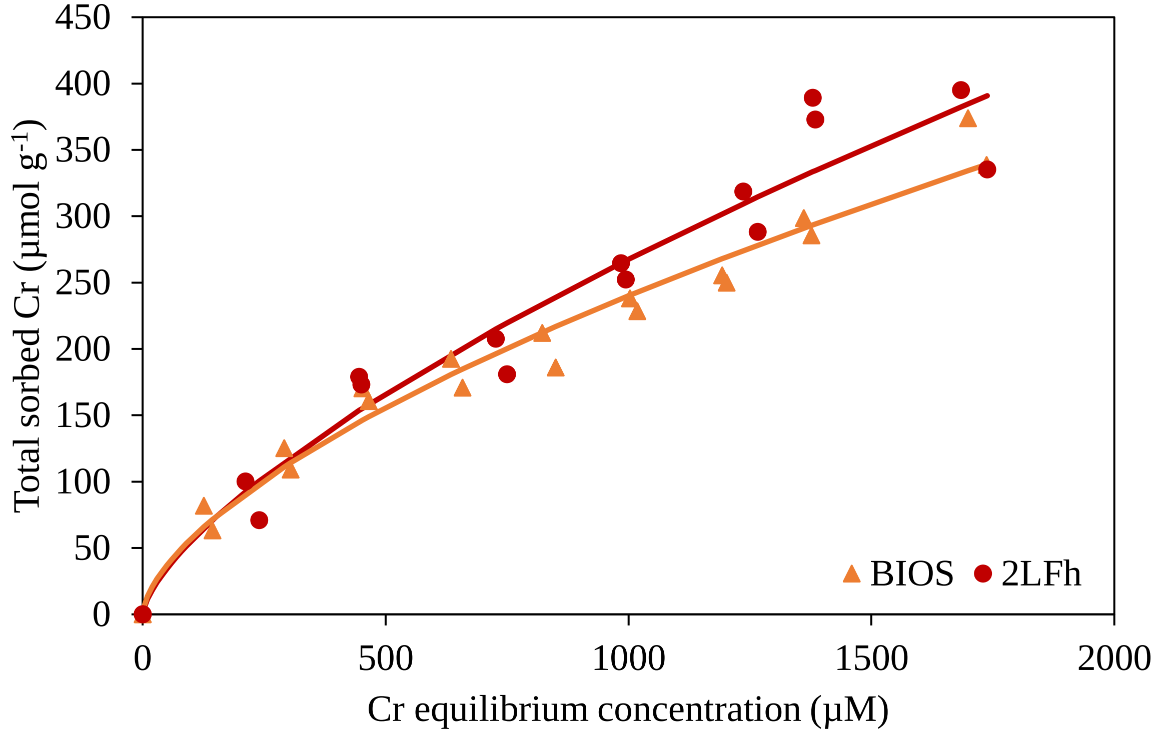

Figure S4. Mass normalized sorption of Cr onto 2LFh (red circles) and BIOS (orange triangles) as a function of dissolved Cr. All sorption data were modeled with a Freundlich fit (solid lines). Initial experimental conditions: 1 g L^{-1} sorbent (dry weight basis), Cr(VI) = 0.96 mM, I = 0.01 M NaCl, pH = 7.0 ± 0.2. The Freundlich sorption constant (K_f) and exponential constant (n) for 2LFh was 2 ± 1 µmol Cr g^{-1} solid and 0.69 ± 0.07, respectively, whereas for BIOS they were 3.2 ± 0.8 µmol Cr g^{-1} solid and 0.63 ± 0.04, respectively.

Table S1. Standard spectra used in LCFs for BIOS and 2LFh K-edge XANES spectra on Day 0 and 14, and Cr K-edge XANES standard spectra used in BIOS LCFs. Standards in bold italics were used for the final fits.[4-9]

Fe EXAFS standards
Ferrihydrite
Hydrous ferric oxide w/Si
Hydrous ferric oxide
Goethite
Hematite
Lepidocrocite
Nano-goethite
Magnetite
Fe(III)-peat
Fe(III)-chloride
Fe(III)-phosphate
Fe(III)-rhizoferrin (carboxylate complex)
Fe(III)-protochelin (catecholate complex)
Pyrite
Siderite
Cr XANES standards
Cr(III)-DFOB (hydroxamate complex)
Cr(III)-rhizoferrin (carboxylate complex)
Cr(III)-protochelin (catecholate complex)
Cr(III)2Fe8 (mixed Cr(III)-Fe(III)-(oyxhydr)oxide)
Cr(VI) sorbed to 2LFh (day 14)

Table S2. Elemental composition of the BIOS in g kg^{-1} dry solid. Synthetic 2LFh contained 553.3 g Fe kg^{-1} sorbent. Fe(II) concentrations in the BIOS were < 0.5% of the total Fe. Water chemistry for the site is reported elsewhere.[1]

Sample	**Fe**	**Al**	**Mn**	**Si**	**Ca**	**K**	**Mg**	**Na**	**Cr**	**Pb**	**Zn**	**Cu**	**P**	**S**	**C**	**N**
BIOS	370.4	3.2	1.6	11.9	2.3	0.3	0.5	BDL	BDL	0.9	0.2	BDL	2.1	2.0	68.5	6.0

Table S3. Results of LCF fits for Cr sorbed to BIOS. Uncertainty from LCFs is reported as the software output but is estimated to be 10%.[10, 11]

days exposed	Cr(VI) sorbed to 2LFh	Cr(III)-Rhizoferrin	Cr2Fe8	R-value
1	85.0 ± 0.7	15.0 ± 0.1	0	0.00009
3	65.7 ± 0.4	9.6 ± 0.4	24.7 ± 0.5	0.00012
7	68.8 ± 0.1	0	31.2 ± 0.1	0.00017
14	51.9 ± 0.3	0	48.1 ± 0.2	0.0011

Table S4. Estimated mol% Cr(VI) sorbed to BIOS, as determined by pre-edge integration and LCFs. Uncertainty from the pre-edge integration is estimated to be 10% of the quantity; uncertainty from LCFs is reported as the software output but is estimated to be 10%.[10, 11]

days exposed	pre-edge integration mol % Cr(VI)	LCFs mol % Cr(VI)
1	73 ± 7	85.0 ± 0.7
3	54 ± 5	65.7 ± 0.4
7	61 ± 6	68.8 ± 0.1
14	55 ± 6	52.0 ± 0.2

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