Electronic Supplementary Material (ESI) for Environmental Science: Processes & Impacts.

Supplementary Information

Characterization of manganese oxide amendments for *in situ* remediation of mercury-contaminated sediments

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Table S1. Sediment composition before amendment addition.

Table S2. Composition of surface water from the field site used in the mesocosm experiments.

Methods: Details of Mn X-ray absorption spectroscopy (XAS) analysis

Figure S1. Mn K-edge XANES spectra of reference compounds and aqueous solution (see text, Table 2 for the list of compounds).

Figure S2. Powder X-ray diffractograms of birnessite-amended sediment after (a) 4 months and (b) 15 months of reaction in mesocosm experiments. A: albite; Q: quartz; R: rhodochrosite. Note large increase in the primary reflection for rhodochrosite ($MnCO_3$) at 15 months.

Table S1. Sediment composition before amendment addition.

Analyte	Concentration[a]
Mercury (mg/kg)	124 (11)
Iron (mg/kg)	29,200 (6,400)
Manganese (mg/kg)	4,970 (970)
Sulfide (mg/kg)	609 (243)
Total Organic Carbon (wt. %)	6.3 (0.4)
Total Solids (wt. %)	31.3 (3.0)

[a] Average of three measurements; standard deviations given in parentheses.

Table S2. Composition of surface water from the field site used in the mesocosm experiments.

Analyte	Result	Unit	Method
pH	6.00	--	meter
ORP	240	mV	meter
Calcium	36.4	mg/L	EPA 6020 (ICPMS)
Magnesium	18.5	mg/L	EPA 6020 (ICPMS)
Potassium	12.1	mg/L	EPA 6020 (ICPMS)
Sodium	149	mg/L	EPA 6020 (ICPMS)
Chloride	239	mg/L	EPA 300.0/9056A (Ion Chromatography)
Sulfate	67.2	mg/L	EPA 300.0/9056A (Ion Chromatography)
Nitrate-N	0.695	mg/L	EPA 300.0/9056A (Ion Chromatography)
Phosphorus	0.082	mg/L	SM 4500P B
Iron, total	300	ug/L	EPA 6020 (ICPMS)
Iron, dissolved	188	ug/L	EPA 6020 (ICPMS)
Manganese, total	20.6	ug/L	EPA 6020 (ICPMS)
Manganese, dissolved	4.01	ug/L	EPA 6020 (ICPMS)
Mercury, total	60.1	ng/L	EPA 6020 (ICPMS)
Mercury, dissolved	ND	ng/L	EPA 6020 (ICPMS)
Total Organic Carbon	12.9	mg/L	SM 5310 B
Dissolved Organic Carbon	8.95	mg/L	SM 5310 B

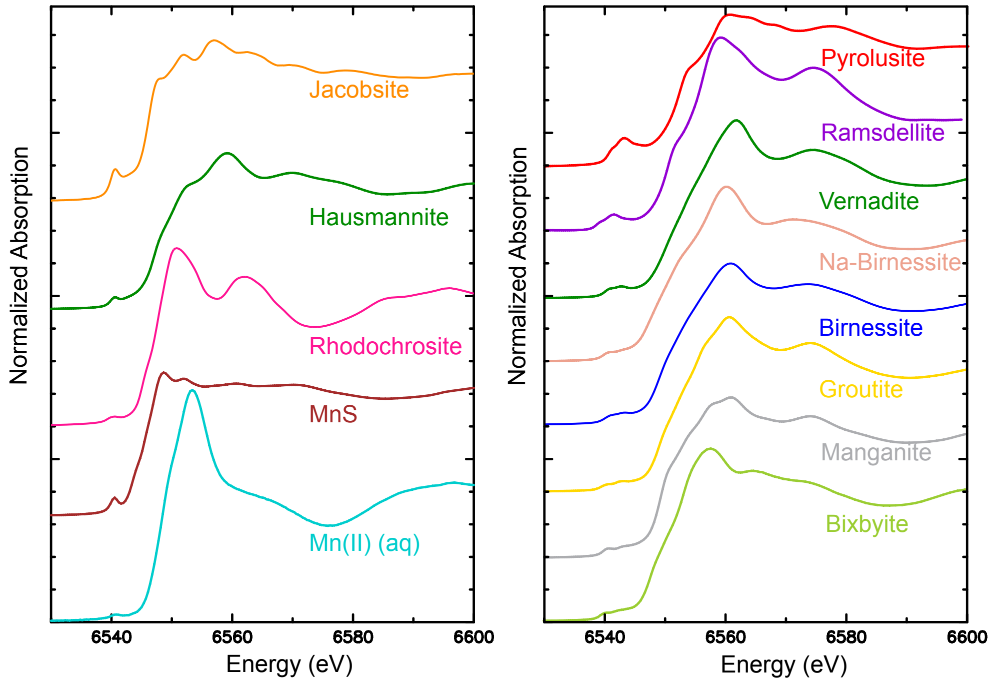
Methods: Details of Mn X-ray absorption spectroscopy (XAS) analysis

Manganese X-ray absorption spectra were analyzed using the programs Sixpack[1] and Athena[2]. The XANES and EXAFS regions were treated separately for background subtraction in order to obtain uniform normalization and to better match reference spectra for linear combination (LC) fits. For XANES spectra, background was subtracted using a linear fit through the pre-edge region and extended through the post-edge region. The post-edge was fit with either a first or second order polynomial regression and spectra were normalized to the post-edge step height. Care was taken to match the post-edge normalized region between ~6580-6600 eV among unknown and reference spectra to minimize uncertainty in the LC fits. For EXAFS, background was subtracted using a linear fit through the pre-edge region and extended through the EXAFS region. The EXAFS region was normalized from ~6650-7050 eV. The Autobak routine in Athena was used to optimize the spline fit through the EXAFS region for the post-edge background function. Pre- and post-edge backgrounds were subtracted with E0 (where the photoelectron wave vector k equals 0) set to 6550 eV and the resulting EXAFS was weighted by k^3 for $k = 0\text{-}12$ Å^{-1}.

Both XANES and EXAFS spectra were fit independently by linear least-squares combination fits using a reference library of well-characterized compounds. In the initial XANES fits, 24 reference spectra were screened (using the automated LC fitting and statistical best-fit ranking functions in Athena) to determine combinations of reference spectra that best matched the unknown XANES spectra, which were fit between 6538-6590 eV to emphasize unique absorption features and energy shifts associated with the absorption edge. The full library included both natural and synthetic compounds of a variety of compositions (oxide, hydroxide, carbonate, phosphate, sulfide, Mn in reference clay minerals, and aqueous Mn). From the initial screening, obvious mismatches were discarded and the reference set was narrowed to the 13 spectra shown in Fig. S1 and listed in Table 2 (main text). Using this reference set, each spectrum was tested and ranked for the best LC fit using mixtures of 2 to 4 reference compounds. Note that some of the reference spectra in Fig. S1 are very similar, whereas others have unique adsorption features. The accuracy of LC fits of XANES spectra is limited to some extent by the richness of spectral features, i.e., spectra with multiple, unique absorption peaks are readily fit whereas spectra with similar, broad adsorption features may produce ambiguous or non-unique solutions. Furthermore, neo-formed phases in complex systems are often not pure and may form as surface coatings or small particles on other surfaces. As such, their absorption features will not necessarily match exactly those of pure, crystalline phases. These aspects and other experimental factors contribute to uncertainty in LC fits that are not easily captured by statistical methods (see [3] for an extended discussion of factors affecting quantification of component mixtures in natural materials for Fe XAS).

For this set of reference and unknown spectra, component fractions less than 5% were determined to be statistically insignificant and were not included. If component fractions between 5-10% statistically improved the fit, component uniqueness was critically evaluated to determine whether fit improvement was related to prominent absorption features in the XANES (reflecting differences in the Mn bonding environment), or simply improved a mismatch in amplitude or featureless parts of the spectrum. Sensitivity tests were done using spectra with similar features to determine fit uniqueness. In some cases with multiple components, tests with two similar spectra produced an equally good fit, but this typically occurred when the reference compounds were similar phases. For example, some unknown spectra could be fit with either groutite or managanite, but these are both polymorphs of $Mn^{III}OOH$ and thus confirmed the presence of a Mn(III) oxyhydroxide phase. Based on the sensitivity tests and our prior extensive experience with LC fits of XAS in the Mn [4] and Fe [3, 5, 6] K-edge systems, error in component fractions is estimated at ±5%. Components of the final fits, a statistical reduced χ^2 factor (equal to (F-factor) / (# of points - # of variables)), and a R-factor (equal to $\sum$ (data-fit)^2 / $\sum$ (data)^2)for the total fit from Athena are reported in Table 3 (main text). Normalized reference spectra were constrained to be between 0 and 1 (i.e., negative components were rejected), but total fits were not normalized to 100%. Because normalization was not forced during fitting, the deviation of sum of the reference components from 100% provides an additional indication of fit quality.

For spectra in which EXAFS data was collected, XANES fits were done first as described above. Linear combination fits with the full EXAFS were done using the reference compounds determined from the XANES fits to verify the presence and abundance of these phases or species. Sensitivity tests were then done to determine whether other reference spectra were permissible in the fit. Because only a limited number of EXAFS spectra were collected, the LC fits were used to confirm the XANES results and were not analyzed using shell-by-shell fitting.



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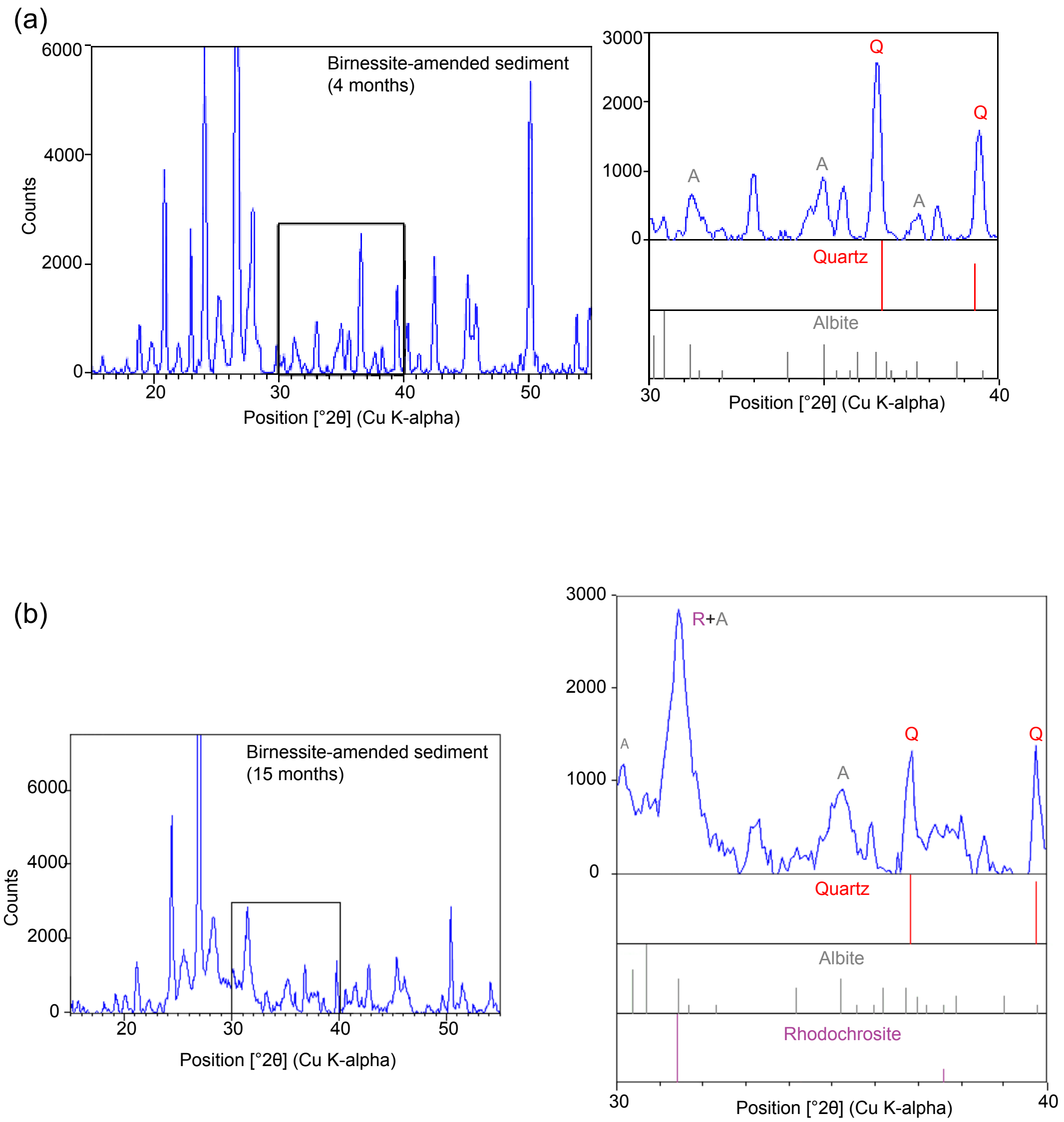

Figure S2

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