

Supplementary material

In situ oxalic acid injection to accelerate arsenic remediation at a superfund site in New Jersey

Karen Wovkulich,^{A,B,E} Martin Stute,^{B,C} Brian J. Mailloux,^C Alison R. Keimowitz,^D James Ross,^B Benjamin Bostick,^B Jing Sun^{A,B} and Steven N. Chillrud^B

^ADepartment of Earth and Environmental Sciences, Columbia University, New York, NY 10027, USA.

^BLamont-Doherty Earth Observatory, Palisades, NY 10964, USA.

^CDepartment of Environmental Sciences, Barnard College, New York, NY 10027, USA.

^DDepartment of Chemistry, Vassar College, Poughkeepsie, NY 12604, USA.

^ECorresponding author. Present address: Department of Chemistry, Vassar College, Poughkeepsie, NY 12604, USA. Email: kawovkulich@vassar.edu

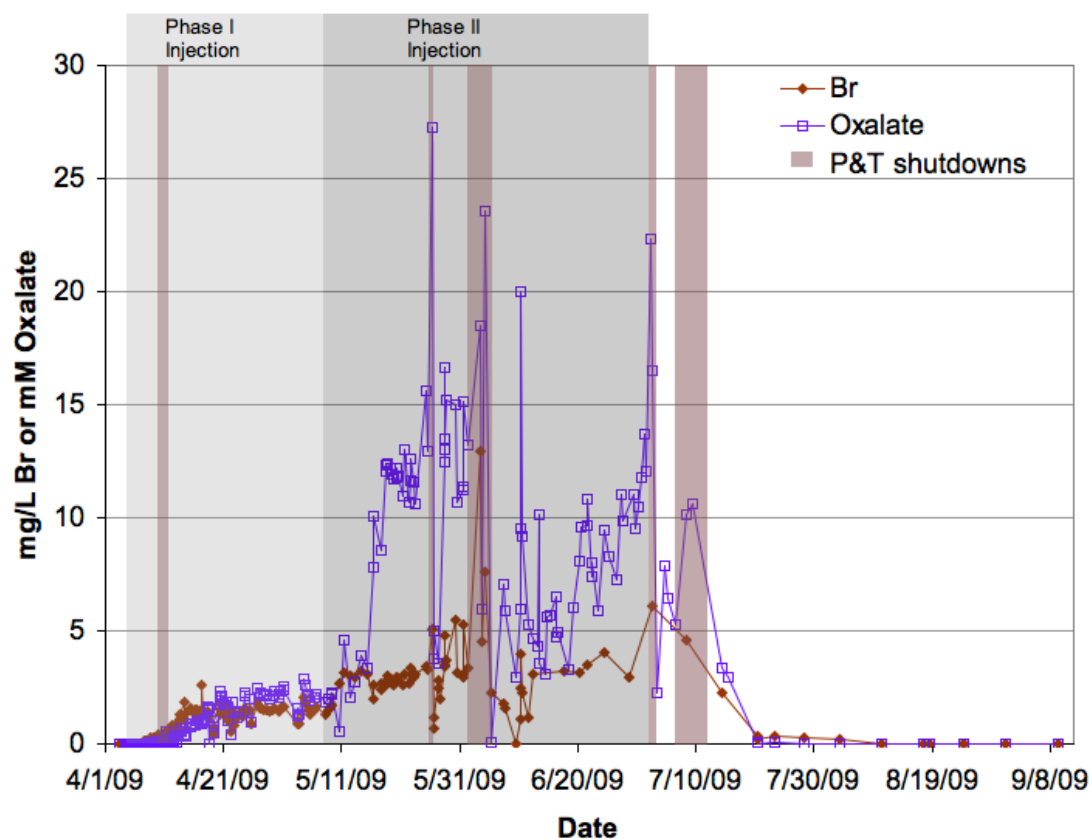


Fig. S1. Concentrations of bromide and oxalate over the course of the oxalic acid injection experiment at the monitoring well, CW 1, above the packer (and therefore excluding the coarser layer). Average influent oxalic acid concentrations were 93 ± 11 mM during Phase I and 351 ± 30 mM during Phase II. Average influent bromide concentrations were 48 ± 5 mM during Phase I and 92 ± 10 mM during Phase II.

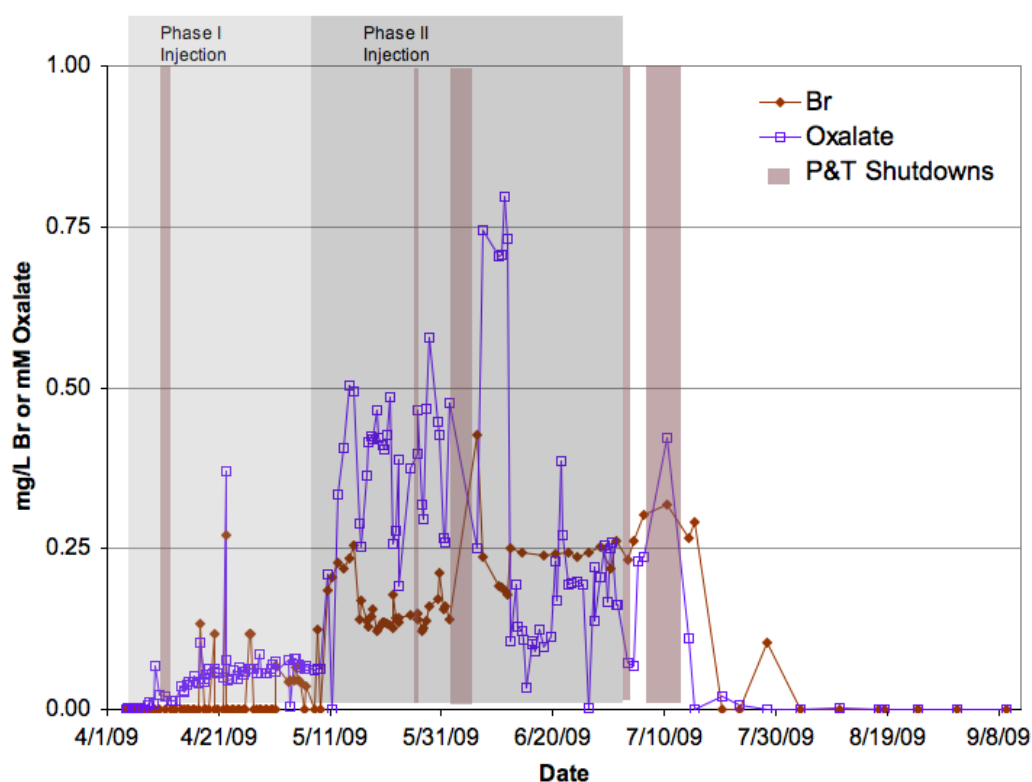


Fig. S2. Concentrations of bromide and oxalic acid at the pump and treat recovery well, RW 2a, over the course of the oxalic acid injection experiment. Average influent oxalic acid concentrations were 93 ± 11 mM during Phase I and 351 ± 30 mM during Phase II. Average influent bromide concentrations were 48 ± 5 mM during Phase I and 92 ± 10 mM during Phase II.

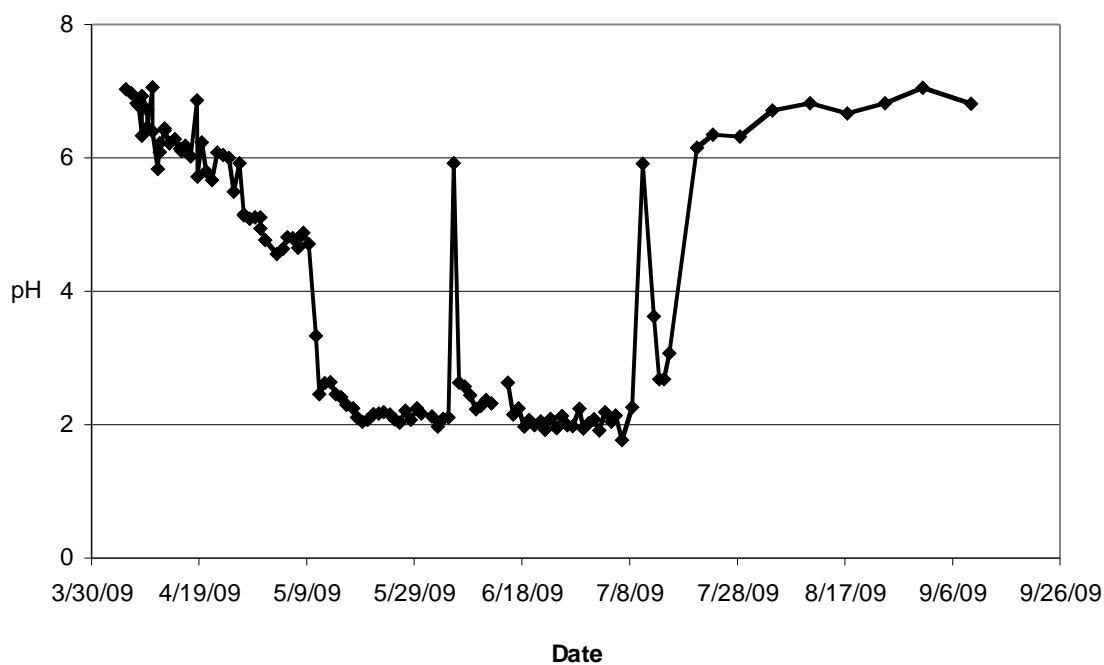


Fig. S3. Values for pH over time at the monitoring well (CW 1).

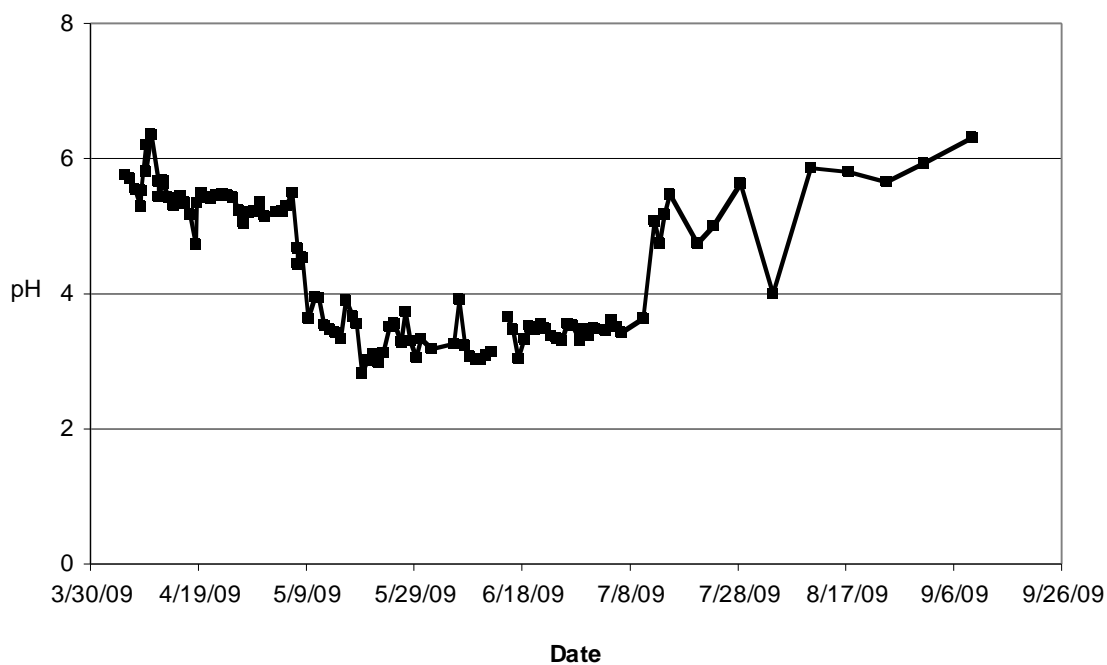


Fig. S4. Values for pH over time at the pump and treat recovery well (RW2a).

Table S1. Water quality parameters before effects of oxalic acid

Data are averages of first 2 days at the monitoring well (CW 1) and 3 days at pump and treat well RW 2a, before there should be any effect from oxalic acid

Well	Conductivity (mS cm ⁻¹)	Dissolved oxygen (mg L ⁻¹)	pH	Oxidation–reduction potential (mV)
CW 1	0.19	1.4	7	5.9
RW 2a	0.18	5.6	5.7	142

During the oxalic acid injection experiment, conductivity generally increased with oxalic acid concentration at the monitoring well (CW1). Dissolved oxygen concentrations (DO) did not show a trend at either well during the 2009 oxalic acid injection experiment. The DO values remained near 6 mg L⁻¹ for the P&T well (RW 2a) and near 1–2 mg L⁻¹ (with substantial scatter) at the monitoring well (CW 1). The oxidation–reduction potential (ORP) stayed high (>+100) at both wells during oxalic acid injection (possibly artificially high because of the presence of oxalic acid) but decreased after injection was stopped and even went negative at the monitoring well (CW 1). However, we don't have ORP measurements from a similar time period from previous years to know if some or all of this decrease could be attributed to seasonal variations in ORP at these wells.

Sediment extractions

Methods

Approximately 2 g of wet contaminated aquifer solids (~80 mg kg⁻¹ in As), equivalent to an average of ~1.7-g dry sediment, were combined with 10 mL of the desired extraction solution. The following solutions were used in separate extraction trials: 1, 10 and 100 mM HCl; 100 mM HNO₃; 10 and 100 mM ammonium oxalate; 1, 10 and 100 mM ethylenediaminetetraacetic acid (EDTA), disodium salt dihydrate (EDTA); 1 mM nitriloacetic acid (NTA). Extractions were performed in duplicate and averaged. These batch experiments were intended to investigate impacts of various extraction types on As mobilisation: efficacy of acidity alone (HCl and HNO₃), efficacy of an oxalate salt compared with oxalic acid (ammonium oxalate), and effect of chelating agents (EDTA and NTA). Extractions with 1, 10 and 100 mM oxalic acid have been reported elsewhere.^[1] The pH of the solutions was measured but not adjusted. Samples were extracted for 2 or 24 h (ammonium oxalate extractions were 2 h only) and were agitated on an adjustable rocker table (Cole-Parmer). Suspensions were centrifuged at 3000 rpm (Damon/IEC Division) for 10 min and the supernatants were decanted into acid washed bottles.

Results

Sediment characterisation

Sediments that were used for batch extractions have been described elsewhere.^[1] Briefly, complete digestion of the aquifer sediments collected for these experiments averaged (± 1 standard deviation): total As = $81 \pm 1 \text{ mg kg}^{-1}$ ($n = 5$), total Fe = $1050 \pm 180 \text{ mg kg}^{-1}$ ($n = 5$), total Al = $1070 \pm 110 \text{ mg kg}^{-1}$ ($n = 3$) and total Mn = $12 \pm 2 \text{ mg kg}^{-1}$ ($n = 5$).

Extraction experiments

Oxalic acid extractions have been reported elsewhere^[1] and reproduced in Fig. S4. Briefly, 1 mM oxalic acid (pH 3.1) mobilised 43–56 % of the As from the aquifer solids depending on extraction time (2 or 24 h), 10 mM oxalic acid (pH 2.3) mobilised 88–93 %, and 100 mM oxalic acid (pH 1.6) mobilised 89–99 %.

HCl and HNO₃ were used as extractants to test for effectiveness of acidity alone for mobilising As. Depending on extraction time (2 or 24 h), 1 mM HCl (pH 3.1) mobilised 5–6 % of the As from the aquifer sediments, 10 mM HCl (pH 2.2) mobilised 11–45 %, 100 mM HCl (pH 1.4) mobilised 53–72 %, and 100 mM HNO₃ (pH 1.4) mobilised 55–73 % of the As from the sediments (Fig. S5).

Ammonium oxalate extractions were performed at the 10- and 100-mM levels with only a 2-h extraction. The 10 mM ammonium oxalate extraction (pH 6.3) mobilised 14 % of the As from the aquifer solids and the 100-mM (pH 6.5) extraction mobilised 22 % in 2 h (Fig. S5).

Finally, the chelators EDTA and NTA were tested for their effect on As mobility. The 1 mM EDTA extraction (pH 5.1) mobilised 10–26 % of the As from the solids depending on extraction time (2 or 24 h), 10 mM EDTA (pH 4.7) mobilised 11–31 %, 100 mM EDTA (pH 4.5) mobilised 14–36 %. The 1 mM NTA extraction (pH 2.7) mobilised 22–66 % of the As from the solids (Fig. S5; 10- and 100-mM extractions were not possible with NTA due to limited solubility).

Discussion

Extraction experiments

A series of extractions were conducted to gain further insight into the mechanism by which oxalic acid can mobilise As. Three types of extractions were performed besides the oxalic acid extractions: acidity extractions (HCl and HNO₃), oxalate salt (ammonium oxalate) and chelating agents (EDTA and NTA). The acidity extractions were performed to evaluate whether low pH alone could explain the efficacy of the oxalic acid treatments. As seen in these extraction experiments, oxalic acid tended to be more effective at mobilising As than either HCl or HNO₃. At the 1- (pH 3) and 10-mM (pH 2) levels, oxalic

acid mobilised at least double the As as HCl. At the 100-mM (pH 1) level, oxalic acid still mobilised more As (89–99 %) than either HCl or HNO₃ (53–73 %), although the difference between the extractant efficacy was decreasing. However, it seems clear from these extractions that acidity alone cannot explain the As mobilisation by oxalic acid.

The oxalate salt extraction with ammonium oxalate showed mobilisation of 14–22 % of the As compared with 88–89 % with oxalic acid (10 and 100 mM with 2-h extraction). The ammonium oxalate extraction was meant to investigate whether an oxalate salt could be as effective as oxalic acid at mobilising As; these extractions suggest that ammonium oxalate is not as effective as oxalic acid. However, the pH values of the extraction solutions were not adjusted and this difference would play a role in effective mobilisation. Even though acidity alone does not seem to be the dominant mechanism for inducing As mobilisation, the pH will determine the level of protonation of the acid. The pK_a values for oxalic acid are 1.27 and 4.14. Therefore, the dominant form of oxalic acid in the extractions described is singly protonated. This may be an important feature in the oxalic acid mechanism. For instance, it has been suggested that optimal Fe release by oxalic acid occurs at pH 2–3, where oxalic acid is predominantly singly protonated. This optimal pH is in the range of observed pH for 1 and 10 mM oxalic acid extractions. However, the ammonium oxalate extractions took place at their unadjusted pH of ~6. The oxalate ions would likely be unprotonated at this pH and this may make them less effective for mobilising As.

Finally, because oxalic acid can act as a chelating agent, extractions were performed with other chelating agents (EDTA and NTA) to evaluate whether other chelators in similar molar amounts could be just as effective as oxalic acid. EDTA was not particularly effective at mobilising As, with a maximum of 36 % with 100 mM EDTA for 24 h, which is less effective than the 2-h extraction with 1 mM oxalic acid. Oxalic acid (1 mM) was more effective than 1 mM NTA for the 2-h extraction (43 v. 22 %). However, 1 mM NTA mobilised somewhat more As than 1 mM oxalic acid in the 24 h extraction (66 v. 56 %). Chelation, depending on the chelating agent, may be a useful mechanism for As removal. Although NTA may show promise for As mobilisation, low solubility makes it less useful for field applications. In these extractions, 3 % or less of the sediment Fe was mobilised by EDTA or NTA while oxalic acid mobilised somewhat more Fe, 3–27 %. It is possible that EDTA and NTA get used in this system to chelate ‘easier’ targets such as calcium or sodium and little is left to complex Fe. However, Fe mobilisation is still relatively low in the oxalic acid extractions as well. Mobilisation of 88 % of the sediment As was possible with a 2-h, 10 mM oxalic acid treatment, despite only 5 % Fe mobilisation. This may indicate re-

precipitation of Fe in the system or may indicate a role for competitive sorption between As and oxalic acid as part of the release mechanism.

Sediment extraction figures

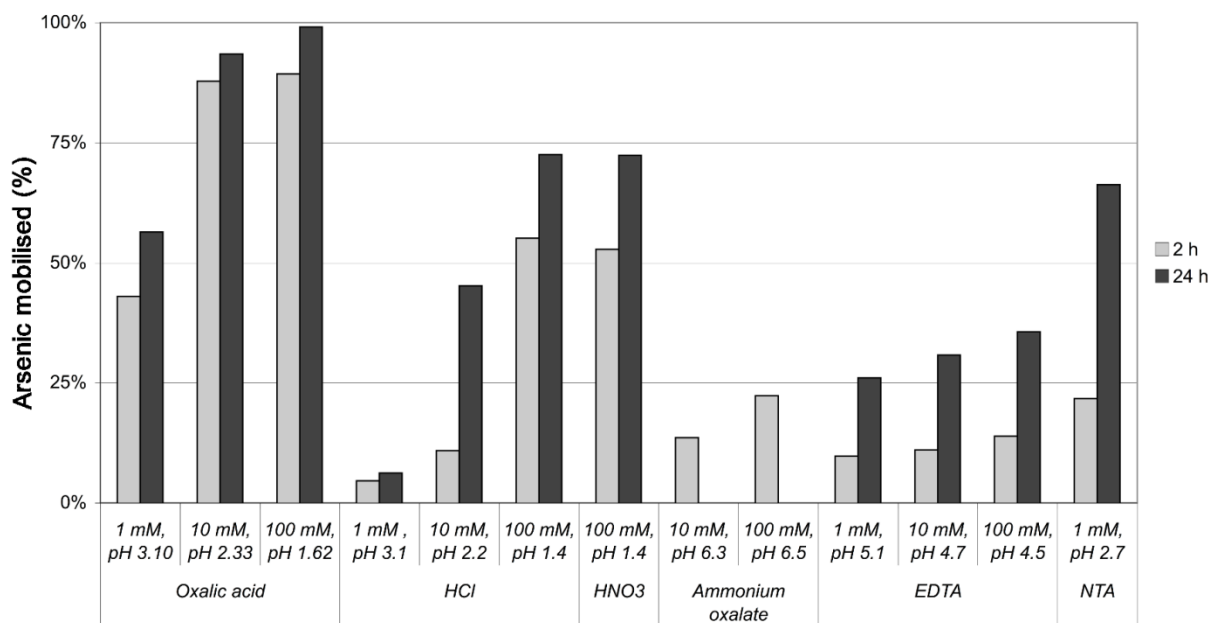


Fig. S5. Several types of batch extractions were performed. Extractants included oxalic acid, inorganic acids (HCl and HNO₃), an oxalate salt (ammonium oxalate) and chelating agents (ethylenediaminetetraacetic acid (EDTA) and nitriloacetic acid (NTA)). Other extractants typically did not perform as well as oxalic acid in terms of percentage As mobilised from the aquifer sediments except for 24-h NTA extraction.

X-Ray absorption spectroscopy

Analyses were performed at the Stanford Synchrotron Radiation Laboratory (SSRL) on beamline 4-1, which was equipped with a Si(220) monochromator and a phi angle of 90°. Fluorescence was measured with a 13-element Ge detector and the following filters: 6 µm Ge filter for As data and 6 µm Mn filter for Fe data. Arsenic and Fe spectra were averaged and normalised using *SIXpack* software (<http://ssrl.slac.stanford.edu/~swebb/sixpack.html>). Sample spectra were compared with standard spectra; linear combination fitting was performed with *SIXpack* software to determine the percentage of each reference in the samples. For arsenic X-ray absorption near edge structure (XANES), reference spectra were Na-arsenate, Na-arsenite and orpiment (As₂S₃). For Fe extended X-ray absorption fine-structure (EXAFS), the reference spectra included ferrihydrite, magnetite, mackinawite, crystalline Fe^{III} oxides (goethite and hematite) and other Fe^{II} minerals (siderite, biotite and hornblende). Errors from

linear combination fitting reported by *SIXpack* reflect error propagation from fitting, spectroscopic noise in sample and reference spectra, and similarities between reference spectra.

Table S2. Arsenic X-ray absorption near edge structure (XANES) data for core samples taken before and after oxalic acid injection

Poor spectroscopic quality data (–) for sample KW7-8b 100 cm are the result of low arsenic concentrations, which prevented reliable fits

Sample	Depth below ground surface (ft)	Location	Arsenate (%)	Arsenite (%)	Arsenic sulfides (%)
Before oxalic acid treatment (2008)					
KW3-8 40 cm	36.3	Near injection wells	99 ± 1	0 ± 2	1 ± 1
KW4-6 50 cm	26.6	Near monitoring well (CW1)	91 ± 1	0 ± 1	9 ± 1
KW4-8a 10 cm	38.1	Near monitoring well (CW1)	100 ± 2	0 ± 5	0 ± 3
KW5-7 10 cm	33.3	Between injection wells and monitoring well (CW1)	92 ± 1	0 ± 1	8 ± 1
After oxalic acid treatment (2009)					
KW7-8b 80 cm	37.6	Near monitoring well (CW1)	89 ± 1	11 ± 2	0 ± 1
KW7-8b 100 cm	38.3	Near monitoring well (CW1)	–	–	–
KW11-7 120 cm	33.9	Between injection wells and monitoring well (CW1) – off axis	91 ± 2%	3 ± 3	6 ± 2

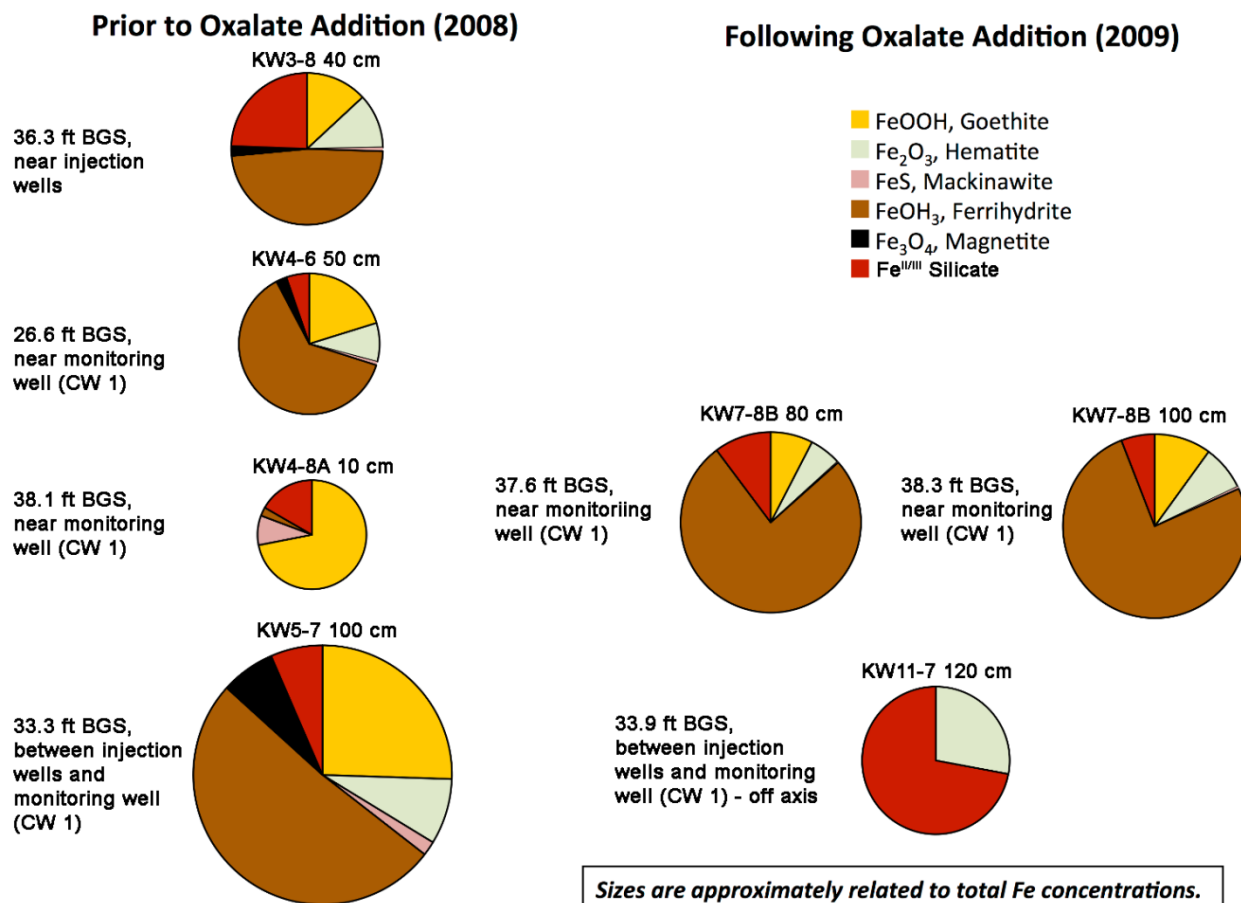


Fig. S6. Iron EXAFS (extended X-ray absorption fine-structure) data from core samples taken before and after oxalic acid injection.

Acknowledgement

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Reference

- [1] K. Wovkulich, B. J. Mailloux, A. Lacko, A. R. Keimowitz, M. Stute, H. J. Simpson, S. N. Chillrud, Chemical treatments for mobilizing arsenic from contaminated aquifer solids to accelerate remediation. *Appl. Geochem.* **2010**, 25, 1500. doi:10.1016/j.apgeochem.2010.08.001