SUPPLEMENTAL APPENDIX

GWB Input Files

The thermodynamic calculations in this paper were performed with The Geochemist's Workbench® software package (Bethke, 2008), release 8.0.10, as described below.

Thermodynamic dataset. — To facilitate the calculations, a version of the LLNL thermodynamic database "thermo.dat" (Delany and Lundeen, 1989) was modified and named "thermo_ladder.dat". The database is prepared as follows.

1. Import the entry for Mn^{3+} from the Version 8, Release 6 version of the LLNL dataset and set it as a redox couple

```
Mn+++
     charge=  3.0      ion size=  5.0 A      mole wt.=   54.9380 g
     4 species in reaction
      -0.5000 H2O                0.2500 O2(aq)              1.0000 H+
       1.0000 Mn++
         3.0256    4.0811    5.2722    6.3335
         7.3364    8.0646    8.5874    8.9360
```

2. Create a fictive Mn^{IV} species MnO_2(aq) and list it as a redox couple. Set the species' stability such that its activity in equilibrium with pyrolusite is 10^{-9}. To wit:

$$\text{Pyrolusite} + 2\,\text{H}^+ \rightleftarrows \text{Mn}^{2+} + \tfrac{1}{2}\text{O}_2(\text{aq}) + \text{H}_2\text{O} \qquad \log K = 1.4378$$

and

$$\text{Pyrolusite} \rightleftarrows \text{MnO}_2(\text{aq}) \qquad \log K = -9$$

giving the coupling reaction

$$\text{MnO}_2(\text{aq}) + 2\,\text{H}^+ \rightleftarrows \text{Mn}^{2+} + \tfrac{1}{2}\text{O}_2(\text{aq}) + \text{H}_2\text{O} \qquad \log K = 7.5622$$

The entry for the redox couple is

```
MnO2(aq)
     charge=  0.0      ion size=  0.0 A      mole wt.=  86.9368 g
     4 species in reaction
      -2.000 H+              1.000 Mn++            1.000 H2O
       0.500 O2(aq)
       500.0000    7.5622  500.0000  500.0000
       500.0000  500.0000  500.0000  500.0000
```

3. Create a fictive mixed Mn^{III}-Mn^{IV} species Birn(aq) with the oxidation state of birnessite, to use as a redox species. The species' activity in equilibrium with birnessite is 10^{-9}. Since from the database

$$\text{Birnessite} + 16\ H^+ \rightleftarrows 8\ Mn^{2+} + 3\ O_2(aq) + 13\ H_2O \qquad \log K = 11.6975$$

and

$$\text{Birnessite} \rightleftarrows \text{Birn(aq)} \qquad \log K = -9$$

the coupling reaction is

$$\text{Birn(aq)} + 16\ H^+ \rightleftarrows 8\ Mn^{2+} + 3\ O_2(aq) + 13\ H_2O \qquad \log K = 22.6975$$

The redox couple is entered

```
Birn(aq)
*     formula= Mn8O14:5H2O
     charge=  0.0      ion size=  0.0 A      mole wt.= 753.5724 g
     4 species in reaction
     -16.000 H+              8.000 Mn++           13.000 H2O
       3.000 O2(aq)
       500.0000   22.6975  500.0000  500.0000
       500.0000  500.0000  500.0000  500.0000
```

4. Include among the minerals a new entry for soil ferrihydrite, from Lindsay (1979)

```
Fe(OH)3(soil)                   type=
     formula=
     mole vol.=    0.000 cc      mole wt.=  106.8689 g
     3 species in reaction
      -3.000 H+              1.000 Fe+++           3.000 H2O
       500.0000     2.700  500.0000  500.0000
       500.0000  500.0000  500.0000  500.0000
```

5. Set the log *K* for Goethite at 25°C to reflect the solubility reported by Bigham and others (1996)

```
Goethite                        type= hydroxide
     formula= FeOOH
     mole vol.=   20.820 cc      mole wt.=   88.8537 g
     3 species in reaction
      -3.000 H+              1.000 Fe+++           2.000 H2O
       500.0000    1.4000  500.0000  500.0000
       500.0000  500.0000  500.0000  500.0000
```

6. Rebalance the reactions for the various Mn^{III} and Mn^{IV} minerals in the dataset as follows:

```
Birnessite                      type=
     formula= Mn8O19H10
     mole vol.= 1128.300 cc      mole wt.=  753.5716 g
     1 species in reaction
       1.000 Birn(aq)
```

```
       500.0000   -9.0000  500.0000  500.0000
       500.0000  500.0000  500.0000  500.0000

Bixbyite                        type= oxide
     formula= Mn2O3
     mole vol.=   31.370 cc      mole wt.=  157.8742 g
     3 species in reaction
      -6.000 H+             2.000 Mn+++           3.000 H2O
         2.1087   -0.9684   -4.3898   -7.3267
        -9.9536  -11.7923  -13.1366  -14.3679

Hausmannite                     type= oxide
     formula= Mn3O4
     mole vol.=   46.950 cc      mole wt.=  228.8116 g
     4 species in reaction
      -8.000 H+             1.000 Mn++            4.000 H2O
       2.000 Mn+++
        14.4659   10.1554    5.3205    1.1380
        -2.6589   -5.3919   -7.4870   -9.4911

Manganite                       type= hydroxide
     formula= MnOOH
     mole vol.=   20.450 cc      mole wt.=   87.9447 g
     3 species in reaction
      -3.000 H+             2.000 H2O             1.000 Mn+++
         0.9482   -0.1668  500.0000  500.0000
       500.0000  500.0000  500.0000  500.0000

Mn(OH)3(c)                      type=
     formula=
     mole vol.=    0.000 cc      mole wt.=  105.9599 g
     3 species in reaction
      -3.000 H+             3.000 H2O             1.000 Mn+++
         8.3786    6.3465    4.1591    2.3582
         0.8397   -0.1330  500.0000  500.0000

MnO2(gamma)                     type=
     formula=
     mole vol.=   17.890 cc      mole wt.=   86.9368 g
     1 species in reaction
       1.000 MnO2(aq)
       500.0000   -7.4832  500.0000  500.0000
       500.0000  500.0000  500.0000  500.0000

Pyrolusite                      type= oxide
     formula= MnO2
     mole vol.=   16.610 cc      mole wt.=   86.9368 g
     1 species in reaction
       1.000 MnO2(aq)
       500.0000   -9.0000  500.0000  500.0000
       500.0000  500.0000  500.0000  500.0000

Todorokite                      type= oxide
```

```
formula= Mn7O12:3H2O
mole vol.=  163.800 cc      mole wt.=  630.6044 g
4 species in reaction
-12.000 H+              4.000 Mn+++           9.000 H2O
  3.000 MnO2(aq)
  500.0000  -27.9486  500.0000  500.0000
  500.0000  500.0000  500.0000  500.0000
```

7. Update the header lines showing the number of redox couples and minerals.

Input scripts. — File “Nominal.sp8” was used with SpecE8 to calculate the redox potentials needed to calculate the free energies reported in tables 1 and 2

```
data thermo_ladder.dat verify
decouple Carbon, Iron, Manganese, Sulfur, Nitrogen, H2(aq)

swap Goethite for Fe+++
1 free g Goethite

swap Manganite for Mn+++
swap MnO2(gamma) for MnO2(aq)
swap Birnessite for Birn(aq)
1 free g Manganite
1 free g MnO2(gamma)
1 free g Birnessite

swap N2(g) for N2(aq)
fugacity N2(g)  = .8

pH = 7

Ca++    = 1 mmolal
HCO3-   = 1 mmolal
SO4--   = 1 mmolal
NO3-    = 1 mmolal
Fe++    = 1 mmolal
Mn++    = 1 mmolal

CH3COO- = 1 umolal
CH4(aq) = 1 umolal
HS-     = 1 umolal
NH4+    = 1 umolal

H2(aq)  = 1 free nmolal

balance off
```

File “pH_scan.rea” was used in React to calculate the redox potentials as a function of pH, to provide for the results shown in figures 3, 4, and 10

```
read Nominal.sp8
pH = 4
precip off
delxi = 1/30
slide pH to 10
suffix _pHscan
```

File “H2_scan.rea” was used to prepare the plot of usable energy vs. dihydrogen concentration shown in figure 5

```
read Nominal.sp8
precip off
delxi = 1/40
log activity H2(aq) = -11
slide log activity H2(aq) to -7
suffix _H2scan
```

File “SO4_scan.rea” was used to prepare the plot of usable energy vs. sulfate concentration shown in figure 5

```
read Nominal.sp8
precip off
delxi = 1/40
log a SO4-- = -6.259
slide log a SO4-- to -2.2665
suffix _SO4scan
```

File “Ac_scan.rea” was used to prepare the plot of usable energy vs. acetate concentration shown in figure 5

```
read Nominal.sp8
precip off
delxi = 1/40
log activity CH3COO- = -9.107
slide log activity CH3COO- to -5.107
suffix _Acscan
```

File “CH4_scan.rea” was used to prepare the plot of usable energy vs. methane concentration shown in figure 5

```
read Nominal.sp8
precip off
delxi = 1/40
log activity CH4(aq) = -9.0045
slide log activity CH4(aq) to -5.0045
suffix _CH4scan
```

Bioreactor Experiments

The SO4-only, FeOOH-only, FeOOH+SO4, and sterile control experiments were presented by Kirk (2008) and, except for the results of the FeOOH-only reactor, published by Kirk and others (2010). Complete results of the four experiments are given below.

Tables A1–A4 show analyses of the fluids extracted from the four experiments weekly, at the end of each reaction interval. Analyses were conducted on samples filtered through 0.45 µm membranes, unless designated “NF”. Table A5 shows dissolved methane concentration in the reactors at each gas sampling event, as calculated from the composition of gas in the reactor headspace. Table A6 summarizes precision and detection limits of the analytical techniques.

Table A1. Composition of effluent from SO_4-only reactor

Date	Time	pH	Fe(II)	S(-II)	HCO_3^-	CH_3COO^-	Cl^-	PO_4^{3-}	SO_4^{2-}	As(t) NF	As(t)	As(III)	As(V)
	days		µM	µM	mM	mM	mM	µM	mM	µM	µM	µM	µM
2/7/2007	7	7.43	5.9	< 1.5	2.09	0.76	5.80	< 5	1.09	8.68	8.61	6.77	1.84
2/14/2007	14	7.44	6.3	4.6	2.07	0.79	5.83	< 5	1.07	8.11	8.44	6.51	1.94
2/21/2007	21	7.41	4.0	26.6	2.16	0.69	4.32	< 5	1.02	8.91	8.51	7.91	0.60
2/28/2007	28	7.41	< 1.8	108.4	2.30	0.51	3.24	< 5	0.85	6.87	6.64	5.61	1.03
3/7/2007	35	7.44	< 1.8	303.2	2.94	0.09	2.50	< 5	0.47	7.38	7.18	5.81	1.37
3/14/2007	42	7.43	< 1.8	312.2	3.09	< 0.05	1.96	< 5	0.43	7.18	7.14	6.14	1.00
3/21/2007	49	7.41	< 1.8	326.3	3.07	< 0.05	1.67	< 5	0.41	6.87	6.67	6.24	0.43
3/28/2007	56	7.41	< 1.8	340.4	3.02	< 0.05	1.45	< 5	0.40	7.18	7.01	6.24	0.77
4/4/2007	63	7.47	< 1.8	320.4	2.31	< 0.05	1.35	< 5	0.39	6.91	7.08	5.87	1.20
4/11/2007	70	7.42	< 1.8	349.8	2.91	< 0.05	1.28	< 5	0.38	6.44	6.71	6.01	0.70
4/18/2007	77	7.41	< 1.8	355.7	2.99	< 0.05	1.19	< 5	0.36	7.28	7.01	6.41	0.60
4/25/2007	84	7.44	< 1.8	360.4	2.94	< 0.05	1.16	< 5	0.37	7.28	6.94	6.24	0.70
5/2/2007	91	7.41	< 1.8	360.4	3.03	< 0.05	1.12	< 5	0.36	6.44	6.27	5.37	0.90
5/9/2007	98	7.43	< 1.8	373.3	3.02	< 0.05	1.11	< 5	0.35	6.14	6.01	5.31	0.70
5/16/2007	105	7.44	< 1.8	442.7	2.97	< 0.05	1.10	< 5	0.34	6.51	6.34	5.61	0.73
5/23/2007	112	7.39	< 1.8	381.6	3.08	< 0.05	1.07	< 5	0.33	6.51	6.34	5.81	0.53
5/30/2007	119	7.44	< 1.8	389.8	3.02	< 0.05	1.07	< 5	0.33	6.51	6.17	5.57	0.60
6/6/2007	126	7.43	< 1.8	332.2	3.07	< 0.05	1.07	< 5	0.33	6.24	6.07	5.34	0.73
6/13/2007	133	7.43	< 1.8	383.9	3.03	< 0.05	1.06	< 5	0.33	6.11	5.91	5.14	0.77
6/20/2007	140	7.44	< 1.8	387.4	2.95	< 0.05	1.06	< 5	0.33	6.69	6.57	5.63	0.94
6/27/2007	147	7.42	< 1.8	402.7	3.01	< 0.05	1.08	< 5	0.33	7.23	7.28	6.38	0.90
7/4/2007	154	7.43	< 1.8	383.9	2.97	< 0.05	1.08	< 5	0.33	7.38	7.58	6.53	1.05
7/11/2007	161	7.44	< 1.8	418.0	2.91	< 0.05	1.08	< 5	0.34	7.54	7.58	6.32	1.26
7/18/2007	168	7.45	< 1.8	395.7	2.85	< 0.05	1.10	< 5	0.34	7.35	7.91	6.83	1.08
7/25/2007	175	7.43	< 1.8	401.6	2.98	< 0.05	1.08	< 5	0.34	7.83	7.64	6.38	1.26
8/1/2007	182	7.43	< 1.8	320.4	3.04	< 0.05	1.07	< 5	0.34	6.62	6.70	5.60	1.10
8/8/2007	189	7.43	< 1.8	394.5	2.96	< 0.05	1.10	< 5	0.34	6.84	6.82	5.72	1.09
8/15/2007	196	7.44	< 1.8	354.5	2.93	< 0.05	1.11	< 5	0.34	7.72	7.78	6.59	1.19
8/21/2007	202	7.42	< 1.8	440.4	2.98	< 0.05	1.12	< 5	0.33	7.39	7.25	5.94	1.31
8/28/2007	209	7.43	< 1.8	409.8	2.91	< 0.05	1.13	< 5	0.32	6.25	6.16	5.54	0.61
9/4/2007	216	7.44	< 1.8	396.9	2.89	< 0.05	1.13	< 5	0.32	7.08	6.87	5.17	1.70
9/11/2007	223	7.42	< 1.8	387.4	2.95	< 0.05	1.13	< 5	0.32	7.04	6.98	5.51	1.47
9/18/2007	230	7.42	< 1.8	411.0	2.96	< 0.05	1.07	< 5	0.33	6.44	6.61	5.54	1.07
9/25/2007	237	7.42	< 1.8	422.7	2.97	< 0.05	1.09	< 5	0.32	7.38	7.38	5.87	1.50
10/2/2007	244	7.42	< 1.8	408.6	2.85	< 0.05	1.13	< 5	0.31	7.54	7.48	5.94	1.54
10/9/2007	251	7.43	< 1.8	401.6	2.90	< 0.05	1.14	< 5	0.32	6.81	6.61	5.31	1.30
10/16/2007	258	7.43	< 1.8	416.9	2.89	< 0.05	1.19	< 5	0.36	6.54	6.37	4.84	1.54
10/23/2007	265	7.43	< 1.8	439.2	2.86	< 0.05	1.17	< 5	0.33	6.27	6.27	5.31	0.97
10/30/2007	272	7.43	< 1.8	412.2	2.78	< 0.05	1.27	< 5	0.34	7.01	7.21	5.34	1.87
11/6/2007	279	7.44	< 1.8	445.1	2.69	< 0.05	1.56	< 5	0.36	7.18	7.18	6.11	1.07
11/13/2007	286	7.43	< 1.8	380.4	2.82	< 0.05	1.39	< 5	0.34	6.34	6.61	5.77	0.83
11/20/2007	293	7.44	< 1.8	407.4	2.76	< 0.05	1.23	< 5	0.37	7.24	7.41	6.14	1.27

Table A2. Composition of effluent from FeOOH-only reactor

Date	Time	pH	Fe(II)	S(-II)	HCO_3^-	CH_3COO^-	Cl^-	PO_4^{3-}	SO_4^{2-}	As(t) NF	As(t)	As(III)	As(V)
	days		μM	μM	mM	mM	mM	μM	μM	μM	μM	μM	μM
2/7/2007	7	7.49	< 1.8	1.7	2.30	0.79	6.49	< 5	28	< 0.01	< 0.01	< 0.01	< 0.01
2/14/2007	14	7.5	52.1	< 1.5	2.32	0.76	6.56	< 5	< 20	< 0.01	< 0.01	< 0.01	< 0.01
2/21/2007	21	7.44	146.4	< 1.5	2.26	0.60	4.72	< 5	< 20	< 0.01	< 0.01	< 0.01	< 0.01
2/28/2007	28	7.4	180.5	< 1.5	2.03	0.77	3.52	< 5	< 20	0.03	0.01	0.02	< 0.01
3/7/2007	35	7.36	198.5	< 1.5	1.91	0.75	2.67	< 5	< 20	0.01	< 0.01	< 0.01	< 0.01
3/14/2007	42	7.35	185.6	< 1.5	2.03	0.62	2.07	< 5	< 20	0.02	< 0.01	< 0.01	< 0.01
3/21/2007	49	7.35	184.6	< 1.5	1.93	0.72	1.74	< 5	< 20	0.02	< 0.01	< 0.01	< 0.01
3/28/2007	56	7.35	178.8	< 1.5	1.95	0.68	1.50	< 5	< 20	0.02	0.01	0.01	< 0.01
4/4/2007	63	7.36	171.5	< 1.5	1.94	0.61	1.37	< 5	< 20	0.03	0.01	0.01	< 0.01
4/11/2007	70	7.33	164.9	< 1.5	1.94	0.69	1.27	< 5	< 20	0.04	< 0.01	< 0.01	< 0.01
4/18/2007	77	7.34	183.8	< 1.5	1.89	0.73	1.21	< 5	< 20	0.05	0.02	0.02	< 0.01
4/25/2007	84	7.33	194.6	< 1.5	1.87	0.71	1.19	< 5	< 20	0.07	0.03	0.03	< 0.01
5/2/2007	91	7.33	198.6	< 1.5	1.96	0.62	1.15	< 5	< 20	0.09	0.03	0.05	< 0.01
5/9/2007	98	7.34	197.3	< 1.5	1.88	0.69	1.14	< 5	< 20	0.12	0.08	0.09	< 0.01
5/16/2007	105	7.31	189.4	< 1.5	1.99	0.61	1.12	< 5	< 20	0.06	0.05	0.05	< 0.01
5/23/2007	112	7.31	176.1	< 1.5	2.06	0.45	1.10	< 5	< 20	0.20	0.13	0.15	< 0.01
5/30/2007	119	7.34	172.5	< 1.5	2.25	0.23	1.09	< 5	< 20	0.49	0.25	0.20	0.05
6/6/2007	126	7.26	143.7	< 1.5	2.58	0.06	1.08	< 5	< 20	0.49	0.35	0.23	0.12
6/13/2007	133	7.36	117.2	< 1.5	2.36	0.06	1.03	< 5	< 20	0.85	0.45	0.35	0.09
6/20/2007	140	7.35	100.0	< 1.5	2.40	0.05	1.09	< 5	< 20	1.18	0.92	0.80	0.12
6/27/2007	147	7.31	82.8	< 1.5	2.54	< 0.05	1.10	< 5	< 20	1.23	1.09	0.91	0.18
7/4/2007	154	7.35	70.9	< 1.5	2.44	< 0.05	1.10	< 5	< 20	1.59	1.49	1.09	0.40
7/11/2007	161	7.35	68.9	< 1.5	2.47	< 0.05	1.11	< 5	< 20	2.39	2.08	1.61	0.47
7/18/2007	168	7.37	52.1	< 1.5	2.38	< 0.05	1.15	< 5	< 20	2.43	1.96	1.47	0.49
7/25/2007	175	7.35	55.2	< 1.5	2.47	< 0.05	1.11	< 5	< 20	2.68	2.62	2.08	0.54
8/1/2007	182	7.35	47.3	< 1.5	2.45	< 0.05	1.08	< 5	< 20	2.97	2.55	1.93	0.62
8/8/2007	189	7.35	55.2	< 1.5	2.40	< 0.05	1.14	< 5	< 20	4.01	3.69	2.55	1.15
8/15/2007	196	7.36	44.0	< 1.5	2.31	< 0.05	1.16	< 5	< 20	4.55	3.59	2.63	0.96
8/21/2007	202	7.34	52.0	< 1.5	2.34	< 0.05	1.17	< 5	< 20	4.95	4.60	4.01	0.59
8/28/2007	209	7.33	49.0	< 1.5	2.32	< 0.05	1.19	< 5	< 20	5.07	4.74	3.69	1.06
9/4/2007	216	7.33	49.7	< 1.5	2.33	< 0.05	1.18	< 5	< 20	5.15	4.53	3.64	0.90
9/11/2007	223	7.33	51.7	< 1.5	2.31	< 0.05	1.18	< 5	< 20	6.13	5.44	4.41	1.03
9/18/2007	230	7.33	50.1	< 1.5	2.28	< 0.05	1.14	< 5	< 20	5.57	4.97	4.22	0.75
9/25/2007	237	7.34	59.0	< 1.5	2.25	< 0.05	1.67	< 5	< 20	6.16	5.62	4.90	0.73
10/2/2007	244	7.33	60.0	< 1.5	2.16	< 0.05	1.17	< 5	< 20	5.83	5.49	4.57	0.93
10/9/2007	251	7.32	60.0	< 1.5	2.20	< 0.05	1.18	< 5	< 20	6.57	6.15	5.09	1.05
10/16/2007	258	7.33	57.9	< 1.5	2.19	< 0.05	1.19	< 5	< 20	6.26	5.91	4.88	1.03
10/23/2007	265	7.32	58.5	< 1.5	2.24	< 0.05	1.20	< 5	< 20	5.31	5.27	5.08	0.19
10/30/2007	272	7.31	56.4	< 1.5	2.19	< 0.05	1.21	< 5	< 20	6.15	5.61	5.51	0.11
11/6/2007	279	7.32	47.8	< 1.5	2.11	< 0.05	1.35	< 5	< 20	6.47	5.42	4.90	0.52
11/13/2007	286	7.33	48.3	< 1.5	2.21	< 0.05	1.22	< 5	< 20	5.88	6.05	5.06	0.99
11/20/2007	293	7.33	50.3	< 1.5	2.18	< 0.05	1.05	< 5	< 20	6.43	6.39	4.59	1.80

Table A3. Composition of effluent from $FeOOH+SO_4$ reactor

Date	Time	pH	Fe(II)	S(-II)	HCO_3^-	CH_3COO^-	Cl^-	PO_4^{3-}	SO_4^{2-}	As(t) NF	As(t)	As(III)	As(V)
	days		μM	μM	mM	mM	mM	μM	mM	μM	μM	μM	μM
2/7/2007	7	7.47	< 1.8	< 1.5	2.15	0.77	5.77	< 5	1.08	0.00	< 0.01	< 0.01	< 0.01
2/14/2007	14	7.44	52.3	< 1.5	2.14	0.70	5.83	< 5	1.07	0.00	< 0.01	< 0.01	< 0.01
2/21/2007	21	7.38	60.5	< 1.5	2.15	0.60	4.28	< 5	1.05	0.01	0.02	0.01	< 0.01
2/28/2007	28	7.33	47.6	< 1.5	2.22	0.51	3.21	< 5	1.02	0.01	< 0.01	< 0.01	< 0.01
3/7/2007	35	7.33	57.0	< 1.5	2.29	0.36	2.45	< 5	0.95	0.02	0.01	0.01	< 0.01
3/14/2007	42	7.32	70.3	< 1.5	2.60	0.11	1.95	< 5	0.86	0.02	0.01	0.01	< 0.01
3/21/2007	49	7.30	101.3	< 1.5	2.82	< 0.05	1.67	< 5	0.78	0.04	0.03	0.02	< 0.01
3/28/2007	56	7.33	106.7	< 1.5	2.82	< 0.05	1.46	< 5	0.71	0.05	0.04	0.03	< 0.01
4/4/2007	63	7.36	109.2	< 1.5	2.73	< 0.05	1.35	< 5	0.67	0.06	0.07	0.04	0.02
4/11/2007	70	7.36	107.7	< 1.5	2.73	< 0.05	1.28	< 5	0.64	0.13	0.07	0.05	0.02
4/18/2007	77	7.36	117.2	< 1.5	2.80	< 0.05	1.20	< 5	0.61	0.17	0.13	0.12	0.02
4/25/2007	84	7.37	127.8	< 1.5	2.86	< 0.05	1.16	< 5	0.59	0.26	0.17	0.15	0.02
5/2/2007	91	7.39	105.9	< 1.5	2.87	< 0.05	1.13	< 5	0.56	0.29	0.21	0.15	0.06
5/9/2007	98	7.41	109.5	< 1.5	2.88	< 0.05	1.11	< 5	0.53	0.62	0.43	0.38	0.05
5/16/2007	105	7.40	63.8	< 1.5	2.93	< 0.05	1.10	< 5	0.52	0.66	0.23	0.18	0.05
5/23/2007	112	7.39	37.2	< 1.5	2.94	< 0.05	1.07	< 5	0.49	1.18	0.69	0.51	0.18
5/30/2007	119	7.42	92.0	< 1.5	2.96	< 0.05	1.07	< 5	0.48	1.26	0.82	0.62	0.19
6/6/2007	126	7.38	73.9	< 1.5	3.00	< 0.05	1.06	< 5	0.47	1.18	1.00	0.77	0.22
6/13/2007	133	7.44	21.6	< 1.5	2.84	< 0.05	1.07	< 5	0.50	1.01	0.82	0.71	0.11
6/20/2007	140	7.43	23.3	< 1.5	2.79	< 0.05	1.06	< 5	0.52	1.16	1.03	0.90	0.14
6/27/2007	147	7.41	9.9	< 1.5	2.80	< 0.05	1.07	< 5	0.53	1.66	1.24	1.05	0.19
7/4/2007	154	7.42	44.4	< 1.5	2.81	< 0.05	1.08	< 5	0.51	2.30	1.84	1.48	0.36
7/11/2007	161	7.43	44.0	< 1.5	2.87	< 0.05	1.08	< 5	0.49	3.70	2.82	2.34	0.48
7/18/2007	168	7.44	53.4	< 1.5	2.78	< 0.05	1.11	< 5	0.50	4.61	3.84	3.16	0.68
7/25/2007	175	7.45	24.8	< 1.5	2.87	< 0.05	1.07	< 5	0.48	5.32	3.85	2.66	1.19
8/1/2007	182	7.43	32.8	< 1.5	2.94	< 0.05	1.06	< 5	0.47	5.66	5.28	3.65	1.64
8/8/2007	189	7.45	12.2	< 1.5	2.91	< 0.05	1.09	< 5	0.45	7.21	6.01	4.71	1.30
8/15/2007	196	7.46	11.6	< 1.5	2.80	< 0.05	1.11	< 5	0.45	8.85	7.47	5.80	1.67
8/21/2007	202	7.45	27.2	< 1.5	2.83	< 0.05	1.12	< 5	0.45	8.93	8.11	6.64	1.47
8/28/2007	209	7.45	27.2	< 1.5	2.83	< 0.05	1.14	< 5	0.42	10.20	9.51	7.41	2.10
9/4/2007	216	7.46	25.9	< 1.5	2.74	< 0.05	1.14	< 5	0.46	10.62	8.83	6.50	2.33

Table A4. Composition of effluent from sterile control reactor

Date	Time days	pH	Fe(II) µM	S(-II) µM	HCO_3^- mM	CH_3COO^- mM	Cl^- mM	PO_4^{3-} µM	SO_4^{2-} mM	As(t) NF µM	As(t) µM	As(III) µM	As(V) µM
2/7/2007	7	7.48	< 1.8	< 1.5	2.38	< 0.05	5.94	< 5	1.09	0.01	< 0.01	< 0.01	< 0.01
2/14/2007	14	7.51	< 1.8	< 1.5	2.47	< 0.05	6.09	< 5	1.10	< 0.01	< 0.01	< 0.01	< 0.01
2/21/2007	21	7.49	< 1.8	< 1.5	2.40	< 0.05	4.47	< 5	1.11	0.01	0.01	< 0.01	0.01
2/28/2007	28	7.44	< 1.8	< 1.5	2.31	< 0.05	3.33	< 5	1.10	< 0.01	< 0.01	< 0.01	< 0.01
3/7/2007	35	7.39	< 1.8	< 1.5	2.16	< 0.05	2.52	< 5	1.08	0.01	< 0.01	< 0.01	< 0.01
3/14/2007	42	7.36	< 1.8	< 1.5	2.07	< 0.05	1.99	< 5	1.07	0.01	< 0.01	< 0.01	< 0.01
3/21/2007	49	7.31	< 1.8	< 1.5	2.03	< 0.05	1.68	< 5	1.08	< 0.01	< 0.01	< 0.01	< 0.01
3/28/2007	56	7.3	< 1.8	< 1.5	1.96	< 0.05	1.47	< 5	1.07	0.01	< 0.01	< 0.01	< 0.01
4/4/2007	63	7.32	< 1.8	< 1.5	1.81	< 0.05	1.35	< 5	1.08	0.01	< 0.01	< 0.01	< 0.01
4/11/2007	70	7.3	< 1.8	< 1.5	1.88	< 0.05	1.26	< 5	1.08	0.01	< 0.01	< 0.01	< 0.01
4/18/2007	77	7.29	< 1.8	< 1.5	2.09	< 0.05	1.20	< 5	1.09	0.02	< 0.01	< 0.01	< 0.01
4/25/2007	84	7.28	< 1.8	< 1.5	1.85	< 0.05	1.16	< 5	1.08	0.01	< 0.01	< 0.01	< 0.01
5/2/2007	91	7.28	< 1.8	< 1.5	1.84	< 0.05	1.14	< 5	1.08	0.01	< 0.01	< 0.01	< 0.01
5/9/2007	98	7.29	< 1.8	< 1.5	1.79	< 0.05	1.13	< 5	1.08	0.03	< 0.01	< 0.01	< 0.01
5/16/2007	105	7.27	< 1.8	< 1.5	1.84	< 0.05	1.11	< 5	1.08	0.02	< 0.01	< 0.01	< 0.01
5/23/2007	112	7.22	< 1.8	< 1.5	1.92	< 0.05	1.09	< 5	1.08	0.03	0.01	< 0.01	0.01
5/30/2007	119	7.29	< 1.8	< 1.5	1.89	< 0.05	1.09	< 5	1.08	0.02	0.01	< 0.01	0.01
6/6/2007	126	7.25	< 1.8	< 1.5	1.78	< 0.05	1.08	< 5	1.08	0.02	< 0.01	< 0.01	< 0.01
6/13/2007	133	7.28	< 1.8	< 1.5	1.73	< 0.05	1.09	< 5	1.08	0.02	< 0.01	< 0.01	< 0.01
6/20/2007	140	7.29	< 1.8	< 1.5	1.66	< 0.05	1.10	< 5	1.08	0.02	0.01	< 0.01	0.01
6/27/2007	147	7.25	< 1.8	< 1.5	1.74	< 0.05	1.11	< 5	1.08	0.03	0.02	< 0.01	0.01
7/4/2007	154	7.29	< 1.8	< 1.5	1.62	< 0.05	1.11	< 5	1.08	0.03	0.01	< 0.01	0.01
7/11/2007	161	7.27	< 1.8	< 1.5	1.75	< 0.05	1.11	< 5	1.09	0.01	0.01	< 0.01	0.01
7/18/2007	168	7.28	< 1.8	< 1.5	1.69	< 0.05	1.13	< 5	1.08	0.02	0.01	< 0.01	0.01
7/25/2007	175	7.28	< 1.8	< 1.5	1.71	< 0.05	1.10	< 5	1.08	0.02	0.01	< 0.01	0.01
8/1/2007	182	7.27	< 1.8	< 1.5	1.75	< 0.05	1.08	< 5	1.08	0.03	0.01	< 0.01	0.01
8/8/2007	189	7.27	< 1.8	< 1.5	1.68	< 0.05	1.11	< 5	1.07	0.02	0.02	< 0.01	0.02
8/15/2007	196	7.29	< 1.8	< 1.5	1.61	< 0.05	1.12	< 5	1.07	0.03	0.03	< 0.01	0.03
8/21/2007	202	7.28	< 1.8	< 1.5	1.65	< 0.05	1.13	< 5	1.05	0.03	0.03	< 0.01	0.03
8/28/2007	209	7.27	< 1.8	< 1.5	1.66	< 0.05	1.15	< 5	1.06	0.04	0.03	< 0.01	0.03
9/4/2007	216	7.28	< 1.8	< 1.5	1.65	< 0.05	1.17	< 5	1.07	0.04	< 0.01	< 0.01	< 0.01
9/11/2007	223	7.28	< 1.8	< 1.5	1.66	< 0.05	1.17	< 5	1.09	< 0.01	< 0.01	< 0.01	< 0.01
9/18/2007	230	7.28	< 1.8	< 1.5	1.65	< 0.05	1.15	< 5	1.07	0.01	< 0.01	< 0.01	< 0.01
9/25/2007	237	7.27	< 1.8	< 1.5	1.66	< 0.05	1.20	< 5	1.10	0.03	0.02	< 0.01	0.01
10/2/2007	244	7.27	< 1.8	< 1.5	1.58	< 0.05	1.18	< 5	1.09	0.03	0.03	< 0.01	0.03
10/9/2007	251	7.28	< 1.8	< 1.5	1.59	< 0.05	1.18	< 5	1.08	0.03	0.02	< 0.01	0.02
10/16/2007	258	7.28	< 1.8	< 1.5	1.62	< 0.05	1.20	< 5	1.14	0.04	0.03	< 0.01	0.02
10/23/2007	265	7.27	< 1.8	< 1.5	1.66	< 0.05	1.20	< 5	1.06	0.04	0.03	< 0.01	0.02
10/30/2007	272	7.27	< 1.8	< 1.5	1.61	< 0.05	1.09	< 5	1.08	0.04	0.04	< 0.01	0.03
11/6/2007	279	7.27	< 1.8	< 1.5	1.56	< 0.05	lost	< 5	1.06	0.11	0.03	< 0.01	0.03
11/13/2007	286	7.29	< 1.8	< 1.5	1.57	< 0.05	1.39	< 5	1.07	0.04	0.04	< 0.01	0.04
11/20/2007	293	7.28	< 1.8	< 1.5	1.62	< 0.05	1.10	< 5	1.06	0.08	0.05	< 0.01	0.04

Table A5. Dissolved methane

Date	Time	SO_4-only	FeOOH-only	FeOOH+SO_4	Sterile
	days	µM	µM	µM	µM
2/5/2007	5	< 0.3	< 0.3	< 0.3	< 0.3
2/26/2007	26	2.6	0.9	0.4	< 0.3
3/12/2007	40	3.7	2.2	0.7	< 0.3
3/25/2007	53	3.8	4.6	1.0	< 0.3
4/9/2007	68	3.7	7.7	1.1	< 0.3
4/23/2007	82	3.6	9.9	1.1	< 0.3
5/7/2007	96	3.6	12.2	1.1	< 0.3
5/21/2007	110	3.4	18.2	1.1	< 0.3
6/4/2007	124	3.3	34.5	1.1	< 0.3
6/18/2007	138	3.4	53.9	1.0	< 0.3
7/2/2007	152	3.3	70.1	0.9	< 0.3
7/16/2007	166	3.3	83.1	1.1	< 0.3
8/6/2007	187	3.2	101.1	1.1	< 0.3
8/27/2007	208	2.6	141.1	0.5	< 0.3
9/24/2007	236	2.8	170.7		< 0.3
11/19/2007	292	2.6	186.8		< 0.3

Table A6. Precision and detection limits

Analyte	Method	Number	Concentration	Precision[a]	Source	Detection limit	Det. lim. description[b]
As	flame AA	40 QC samples	0.133 µM	0.008	Kirk and others (2010)	0.013 µM	low standard
CH_3COO^-	IC	25 QC samples	0.42 mM	0.05	Kirk and others (2010)	0.05 mM	estimated
Cl^-	IC	25 QC samples	0.71 mM	0.03	Kirk and others (2010)	0.04 mM	estimated
PO_4^{3-}	IC	24 QC samples	0.050 mM	0.005	Kirk and others (2010)	0.005 mM	estimated
SO_4^{2-}	IC	25 QC samples	0.52 mM	0.02	Kirk and others (2010)	0.03 mM	estimated
HCO_3^-	titration		2.44 mM	0.12	US EPA method 310.1	n/d	
S(-II)	methylene blue	34 sets of samples	6.0 to 45.0 µM	2.4	Eaton, Clesceri, and Greenberg (1995)	1.5 µM	low standard
Fe(II)	ferrozine	10 samples	19.1 µM	0.4	Stookey (1970)	1.8 µM	low standard
CH_4	GC			n/d		0.3 µM (aq)	estimated

[a]Precision estimated as twice the standard deviation.

[b]Detection limits for ion and gas chromatography were estimated based upon the ability to resolve peaks within specific retention-time windows; the detection limit for methane is expressed as the equivalent dissolved methane concentration in a solution at 25°C.

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