Appendix B

Supporting Information for

Chapter 4: A Hydrous Manganese Oxide Doped Gel Probe

Sampler for Measuring *In Situ* Reductive Dissolution Rates: II.

Field Deployment

Contents: 6 figures, 6 tables, and 1 MATLAB m-file code

Advection at the Lake Tegel Shoreline

The calm weather during deployment implies that exchange of surface water and sediment porewater due to wind-driven waves perpendicular to the shoreline was negligible. The main input flow to Lake Tegel from Nordgraben and Tegeler Fliess is 2.35 m^3 s^{-1}. For a lake cross-section approximately 1000 m wide and 8 m deep (Schauser and Chorus 2009), the average surface water velocity is ~ 25 m d^{-1} (parallel to the shoreline). However, this value was almost certainly much lower in our specific sampling location, which was protected by a barrier perpendicular to the shoreline that extended ~ 10 m into the lake. Thus, surface water flow is unlikely to affect our interpretation of sediment porewater chemistry.

Water levels in groundwater monitoring wells adjacent to the shoreline confirmed the presence of an unsaturated zone, with the depth to the water table 4.5 m below the lake water surface elevation. Infiltrating lake water should then be flowing vertically down through the area in which samples were collected, and thus this setting can be described with a generalized form of Darcy's Law appropriate for vertical flow:

$$v = K \cdot \left(\frac{\gamma(h_1 - h_2)}{\rho g L} + 1 \right)$$
(B-1)

where v is flow velocity (cm s^{-1}), γ is the specific weight of water, h_1 and h_2 are the water depths (m) at the two points, and L is the length (m) of the infiltration flow path (Bear 1972). The water depth at the sediment-water interface is 0.18 m (h_1), and the water depth at the groundwater table is 0 (h_2; pressure is assumed to be atmospheric). Using $\gamma = 9.79$ kN m^{-3}, $\rho = 1000$ kg m^{-3}, $g = 9.8$ m s^{-2}, L = 4.5 m, and the mean value for K, we estimate that the downward velocity of the infiltrating lake water was 0.055 cm s^{-1}.

In light of such downward advection, upward diffusion of dissolved species has little influence on these sediments. We can consider porewater Fe and Mn, as well as any *in situ* reductants, to reflect steady-state, rather than equilibrium, concentrations with stable redox boundaries, as seen in column studies (von Gunten and Zobrist 1993).

**Table B.1.** Lake Tegel sediment characterization

depth (cm)	porosity	particle size		hydraulic conductivity (cm s^{-1})
		mean (μm)	mode (μm)	
0 - 5	0.43	303	302	5.6×10^{-2}
5 - 10	0.41	315	304	6.0×10^{-2}
10 - 15	0.50	266	321	6.4×10^{-2}
15 - 20	0.50	254	337	7.1×10^{-2}
20 - 27.5	0.55	333	382	6.7×10^{-2}

Because cores were collected so as to avoid compaction of sediment, porosity (ϕ) could be calculated as the volume of pore space in a core section (V_p) divided by the total volume of that core section (V_s). V_p was estimated as the dry mass of the sediment in a core section divided by an assumed density of 2.65 g cm^{-3} for sand (Bear 1972) and subtracted from V_s.

Particle size was measured with a Mastersizer 2000 (Malvern Instruments, Ltd., Worcestershire, U.K.) laser diffractometer following Sperazza et al. (2004) and Wildman (2009). Briefly, ~ 0.5 g of dry sediment was shaken in 5.5 g l^{-1} sodium hexametaphosphate for $\geq$ 4 h, and the sample-solution ratio was adjusted to give an obscuration of 20 ± 4%. Data were complied with the Mastersizer 2000 computer program (version 5.22, Malvern Instruments) using a particle absorbance index of 1.0 and a refractive index of 1.52. Five analytical replicates were averaged for each sample.

Table B.2. Porewater concentrations of detectable trace elements. Other elements tested, but below detection limits (in parentheses) were: As, Be, Cd, Mo, Sb, Tl, V ($0.2 \ \mu g \ l^{-1}$); Cr, Pb ($0.5 \ \mu g \ l^{-1}$); Se ($10 \ \mu g \ l^{-1}$); Zn ($5 \ \mu g \ l^{-1}$). Only Fe and Mn displayed trends with depth.

Element	Average (μM)
Co	0.03
Cu	0.9
Fe	24.8
Mn	2.5
Ni	0.1
Sr	2.5
Ti	6.2
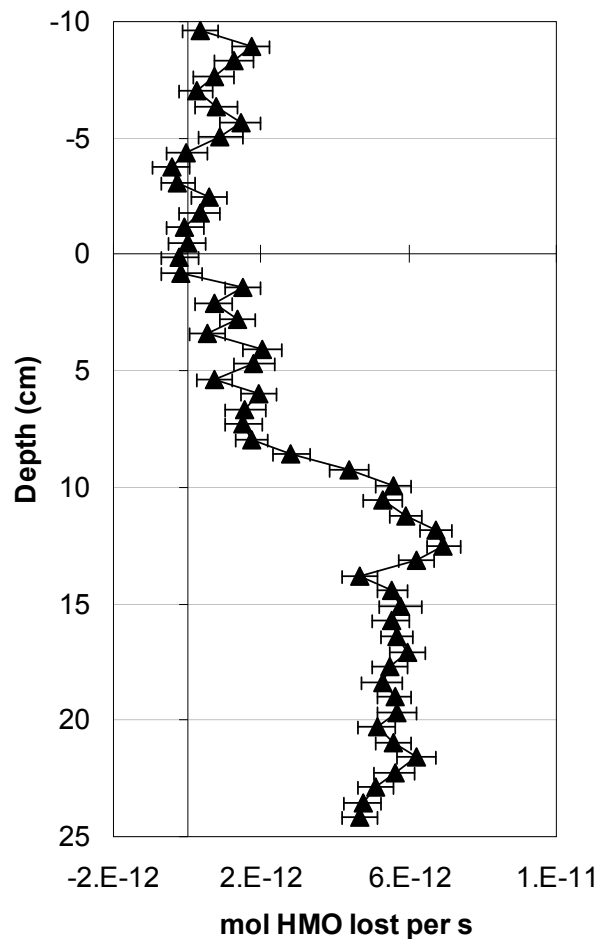
Figure B.1. Moles of HMO lost in each gel per s of deployment time. Error bars represent the variation from the 95% confidence interval in Mn_T. The R_{meas} data input to the MATLAB code is this data array divided by the mass of each gel.
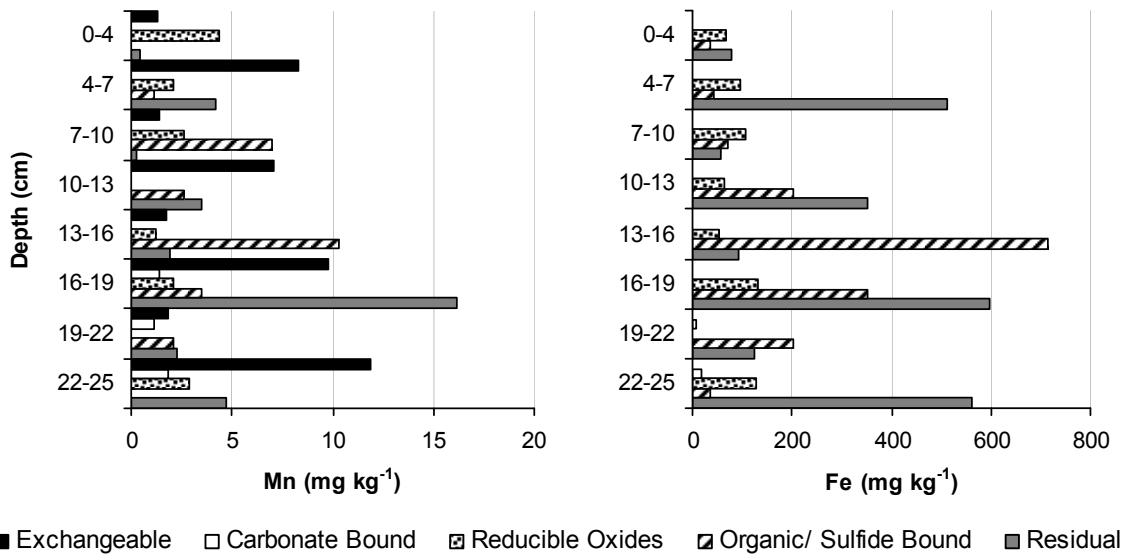
Figure B.2. Extracted manganese (left) and iron (right) concentrations per kg dry sediment, as determined by sequential extraction. Note the different scales of the two x-axes. Bars are averages of 3 subsamples for each core section.
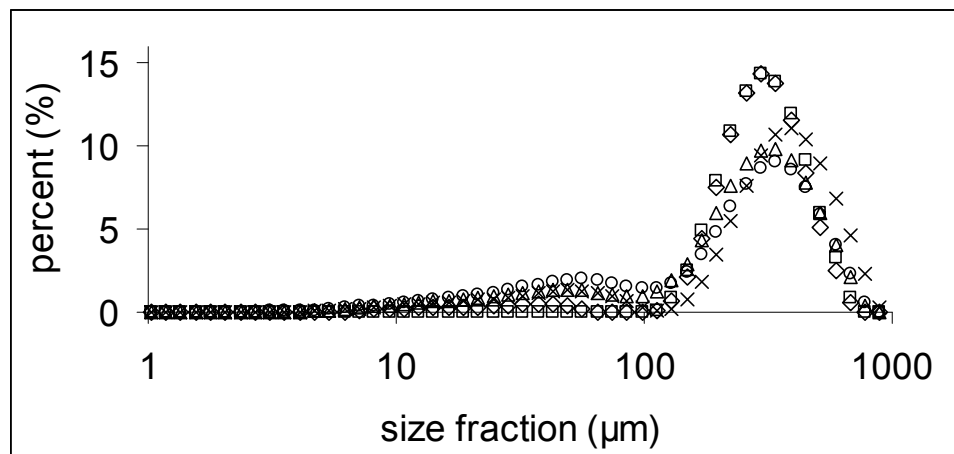
Figure B.3. Particle size in Lake Tegel shoreline sediment for 0–5 cm (◇), 5–10 cm (□), 10–15 cm (△), 15–20 cm (○), and 20–27.5 cm (×) core sections. Mode particle size values range from 301 to 382 μm (mean = 329 μm) and increase with depth.

Table B.3. Calculation of surface-area-normalized Mn reduction rates from field studies

Source	Location	Rate	Units	[MnOx] (M)	Notes
[1]	equatorial Atlantic Ocean	2.0×10^{-3}	yr^{-1}		a
	Chesapeake Bay	1.73×10^{-2}	yr^{-1}		a
	Long Island Sound	2.5×10^{1}	yr^{-1}		a
[2]	AMD wetland: shallow	5.2×10^{-10}	$M\ s^{-1}$	5.24×10^{-3}	a,b
	AMD wetland: maximum	1.04×10^{-9}	$M\ s^{-1}$	5.24×10^{-3}	a,b
[3]	Lake Michigan	7.0×10^{-6}	$g\ cm^{-2}\ yr^{-1}$		c
[4]	North Sea: Skagerrak Basin	$2.0\text{-}10\times10^{-4}$	$M\ d^{-1}$	6.14×10^{-4}	a,d
This	Lake Tegel: shallow	3.9×10^{-3}	h^{-1}		a
Study	Lake Tegel: deep	3.1×10^{-2}	h^{-1}		a
	Lake Tegel: maximum	1.0×10^{-1}	h^{-1}		a
[5]	eastern Danish coast	$3.6\text{-}11.7\times10^{-4}$	$mol\ m^{-2}\ d^{-1}$		e
[6]	Gulf of St. Lawrence	$3.1\text{-}46.2\times10^{-4}$	$mol\ m^{-2}\ d^{-1}$		e

[a] Rate divided by Mn oxide surface area of 49 $m^2\ g^{-1}$ and molecular weight of 86.94 g mol^{-1} (chemical formula MnO_2) for conversion

[b] Rate divided by the concentration of Mn oxide in the study's gel slabs, calculated from 1.1×10^{-6} mol Mn per unit length of gel and gel volume of 2.1×10^{-4} l per unit length

[c] Rate divided by Mn oxide molecular weight of 86.94 g mol^{-1} for conversion

[d] Rate divided by the concentration of Mn oxide in the sediment columns, 3×10^{-6} mol cm^{-3} of sediment, and $(1-\phi)\cdot\phi^{-1}$ (where ϕ is sediment porosity, 0.83) to convert the sediment volume to porewater volume (consistent with rate volume units)

[e] Only unit conversion needed

Sources: 1 Burdige and Gieskes (1983); 2 Edenborn and Brickett (2002); 3 Robbins and Callender (1975); 4 Canfield et al. (1993); 5 Balzer (1982); 6 Sundby and Silverberg (1985)

MATLAB m-file: "ksolver.m"

```
function [k,err,output] = ksolver(mn_f, MnT, var, Cpw, top, T)
% File ksolver.m
%  This function will solve the following partial differential equation
%  for k, the rate constant for Mn oxide reduction in sediments:
%    (dC/dt) = R_reductive_dissolution - R_diffusion
%    (dC/dt) = (k*(Mn_gel_total - C)) - (d/dx(dC/dx))
%   where C = C(t,x) and subject to boundary conditions:
%    C(0,x) = 0;
%    C(t,pw) = Cpw; pw = porewater outside of gel
%   The program will iterate upon various k values until (dC/dt)_gel at the
%   final t is equal to the dC/dt measured in the gel, within the
%   permissible error.
%   The rows in the mn_f matrix are considered separate "gels".  The
%   program will continue through each row until every gel has a k value.
%  The following variables must be entered:
%  mn_f = final amount of Mn recovered in each gel, given as mols
%    Mn/gel volume.  [vector; umol/mL]
%  MnT = total amount of Mn initially in gel, given as mols Mn/gel
%    volume.  Units must match mn_f. [single number; umol/mL]
%  var = 95% confidence interval bound for MnT batch.  Units must match
%    MnT. [single number; umol/mL]
%  Cpw = porewater Mn concentration for each depth, given as mols
%    Mn/porewater volume.  Assume porewater is an infinite sink for Mn,
%    with constant concentration Cpw. Units must match mn_f and MnT; size
%    must match mn_f. [vector; umol/mL]
%  top = distance from the top of the probe to the sediment-water
%    interface [cm]
%  T = total time of deployment [hrs]
%  The following output variables are possible:
%  k = rate coefficient for each gel, beginning at the top.  Columns list
%  k for MnT_lower, MnT, MnT_upper respectively. [1/hrs]
%  err = approximate relative error for each k [fractional]
%  output = code describing the solution of each k [0 = ok; 1 = error, k =
%    NaN; 2 = max iterations (100) reached before solution found]

%****************************************************************
% First define parameters needed for calculations in all gels:
%
% Set dz step = vertical distance between gels = 0.65 cm.
dz = 0.65;
% Set number of gels = maximum number of z steps.
Z = max(size(mn_f));
% Define depth axis:
depth = top - dz*(0:(Z-1));
% Set dx step = gel thickness/5 "cells"
dx = 0.2/5;
% Set Dmn, the diffusion coefficient for Mn(2+) in gel [cm*cm/hr]. At 18C,
% Dmn = 5.75e-6 cm*cm/s (Li+Gregory 1974).
dmn = 0.0207;
B = dmn/dx/dx;
% Set initial dt step for stability: (1/(2B))>>dt
```

```
dt = dx*dx/(20*dmn);
% Define maximum number of time steps.
P = round(T/dt);
% Set limits of MnT; solving for k at each MnT gives an approximation of
% the k "error bounds".
Mn=[MnT-var;MnT;MnT+var];
% Begin at top of probe and run following code on each gel.
k=zeros(Z,3);
err=zeros(Z,3);
output=zeros(Z,3);
% Begin with MnT_lower, then MnT, finally MnT_upper.
for m=1:3
for z=1:Z
%****************************************************************
% Next define parameters that apply only to one gel at a time:
%
% Set initial values of k equal to upper and lower guesses.
K=zeros(101,1);
K(1)=1e-4;
K(2)=2e-2;
% Calculate the measured dC/dt:
X=(Mn(m)-mn_f(z))/T;
% Acceptable error: [(k(i+1) - k(i))/k(i+1)] = 0.0005 = 0.05% for 3
% significant digits.
E=0.0005;
% Residual difference between X and X_t; solve for Resid(k)=0.
Resid=zeros(101,1);
Resid(1)=X;
%****************************************************************
% Iterate on k until Resid is approximately 0.
%
for n=2:101
% Define concentration matrix: # columns = 5 cells.  Set boundary
% conditions: by default, C(0,x)=0 and C(t,pw)=Cpw.
% **Needs to be redefined for each iteration of code**
   C=zeros(P,5);
   HMO=Mn(m)*ones(P,1);
% Calculate C(t,x) for all t and x; keep track of HMO(t) [umols Mn/mL]
% for each time step.  HMO(t) is equivalent for all 5 cells.  When t = P (=
% approx. T), calculate dC [delta C (as in dC/dt); umols Mn/mL] and assess
% dC/T.
   for t=2:P
      HMO(t)=HMO(t-1)-dt*(K(n)*HMO(t-1));
      C(t,1)=C(t-1,1)+dt*(K(n)*(HMO(t-1))+B*(C(t-1,2)-C(t-1,1)));
      for x=2:4
         C(t,x)=C(t-1,x)+dt*(K(n)*HMO(t-1)+B*(C(t-1,x-1)-2*C(t-1,x)+C(t-1,x+1)));
      end
      C(t,5)=C(t-1,5)+dt*(K(n)*HMO(t-1)+B*((C(t-1,4)-C(t-1,5))+2*(Cpw(z)-C(t-1,5))));
   end
   dC=Mn(m)-HMO(P)-sum(C(P,1:5));
   X_t=dC/T;
   Resid(n)=X-X_t;
% Calculate new k value via the secant method.
   K(n+1)=K(n)-Resid(n)*(K(n)-K(n-1))/(Resid(n)-Resid(n-1));
% Compare k to previous k value; if less than acceptable error, return k.
   if abs((K(n+1)-K(n))/K(n+1))<=E
```

```
        k(z,m)=K(n+1);
        err(z,m)=abs((K(n+1)-K(n))/K(n+1));
        output(z,m)=0;
        break
      end
      % Break if k is not a number.
      if isnan(K(n+1))==1
        k(z,m)=K(n);
        err(z,m)=NaN;
        output(z,m)=1;
        break
      end
      % Maximum # of iterations is 100.
      if n+1==102
        k(z,m)=K(n);
        err(z,m)=NaN;
        output(z,m)=2;
      end
    end
    end
    plot(k(1:Z,2),depth,'-ok')
    hold on
    plot(k(1:Z,1),depth,'>b')
    plot(k(1:Z,3),depth,'<b')
    xlabel('k [1/hrs]')
    ylabel('Depth [cm]')
    title('Apparent MnOxide rate coefficient vs. sediment depth')
    hold off
    end
```

(a)

(b)
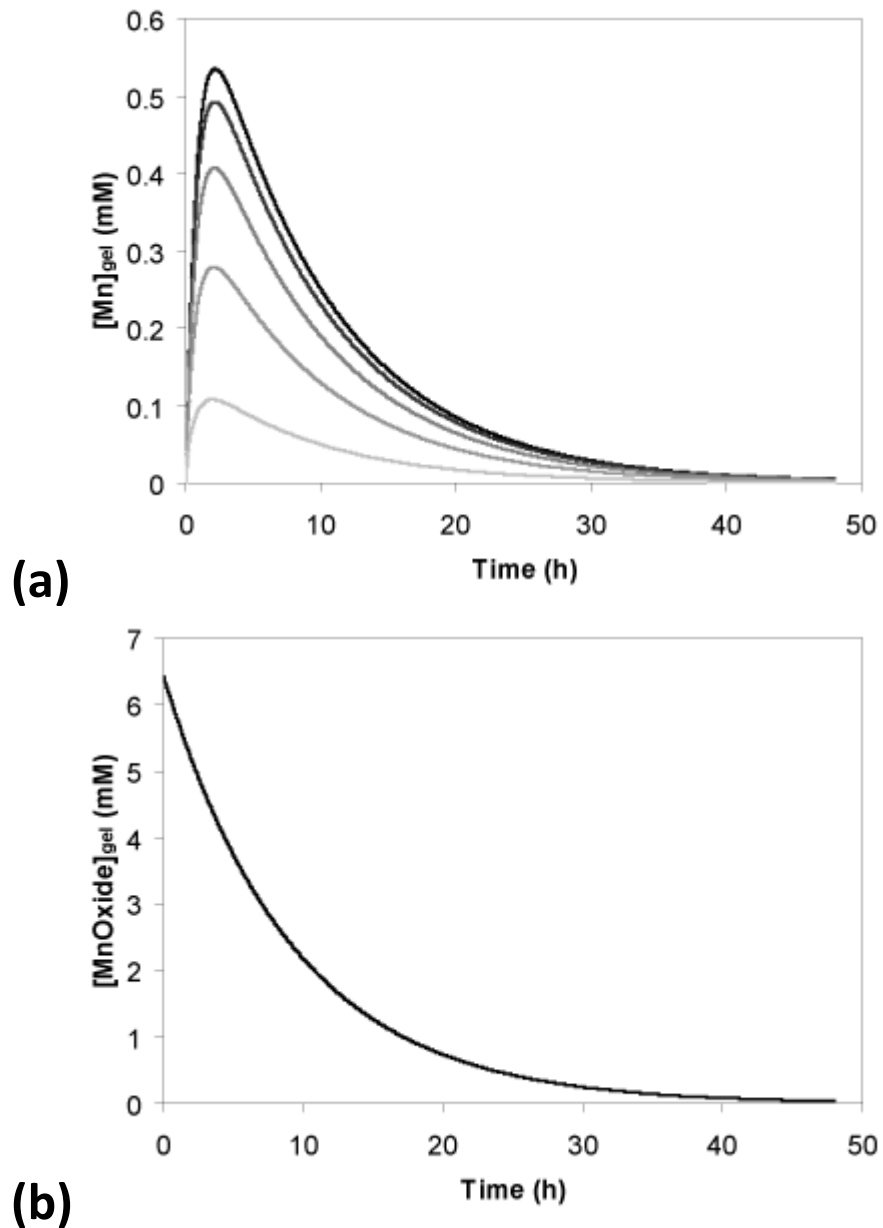
Figure B.4. Buildup of dissolved Mn ("C"; a) and decline of Mn oxide ("HMO"; b) inside of a gel, as calculated by the above Matlab m-file "ksolver". Dissolved Mn is plotted for each of the 5 cells, with darkest lines for the cells furthest from the porewater. This output was generated with the data for the maximum observed rate of Mn reduction in Figure 4.2b.
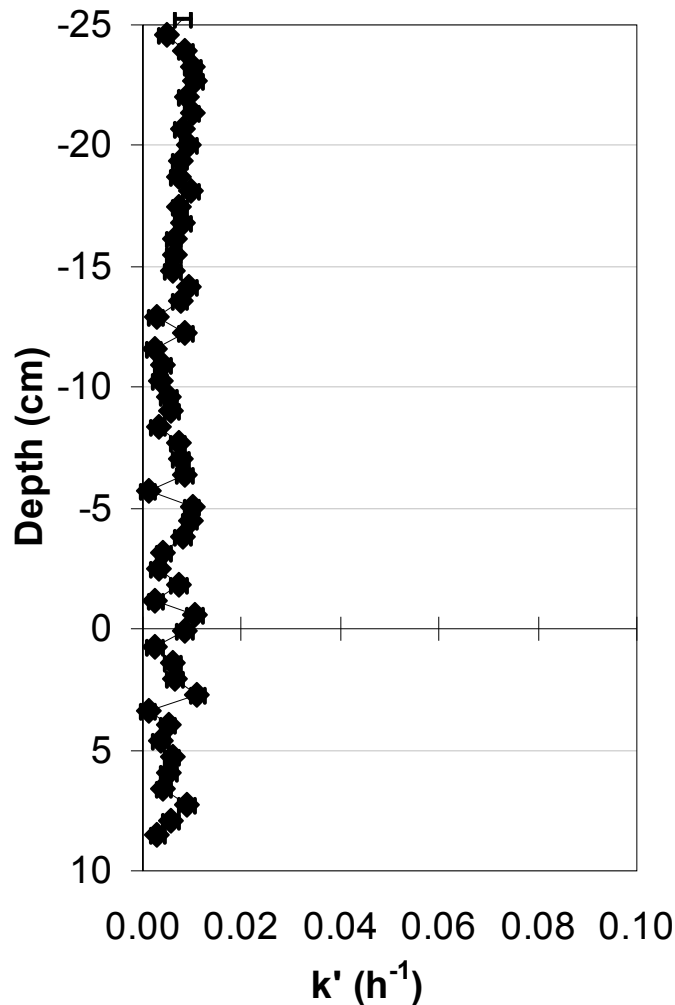
Figure B.5. Apparent pseudo-first-order rate coefficient k′ from HMO-doped gel probe deployed 20 m from the shoreline of Lake Tegel, Berlin, Germany (water depth = 89 cm). Porewater Mn was input as a constant 0.49 μM. This probe and a probe for clear gels were deployed, back-to-back, simultaneously with the probes presented in Chapter 4. However, sediments were quite hard, and both probes had to be hammered to reach just 10 cm depth (HMO-doped gel probe) and 20 cm depth (clear gel probe). The membrane of the clear gel probe ripped during deployment, so its data were suspect. Nevertheless, there was some evidence for a peak in dissolved Fe below 10 cm, which would be consistent with the probe deployed in more shallow water (Figure 4.2a). The rate coefficients for 0–9 cm depth in this figure (0.0056 ± 0.0026 h^{-1}) are comparable with those for the same sediment depth in Figure 4.2b (0.0039 ± 0.0025 h^{-1}).
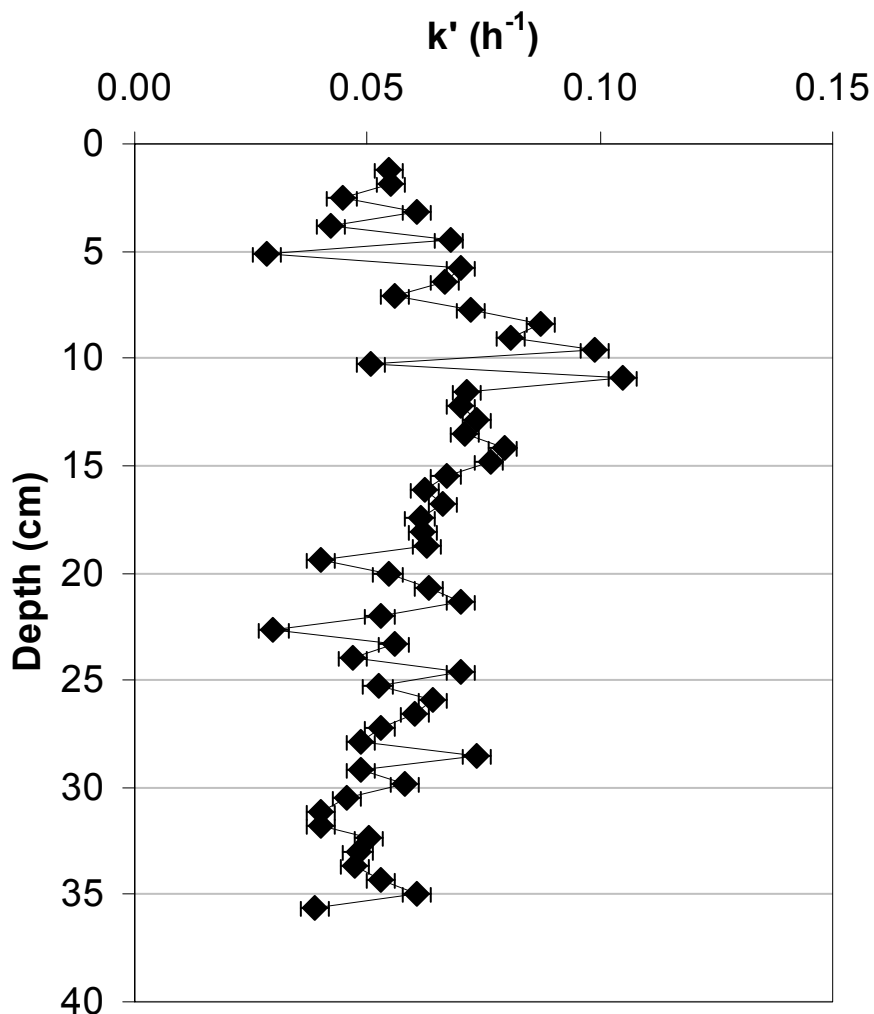
Figure B.6. Apparent pseudo-first-order rate coefficient k′ from HMO-doped gel probe deployed in the shallow sediments at Laguna Figueroa salt flats, Baja California, Mexico (12 h deployment; temperature 14–20°C). Porewater Mn was input as a constant 3.1 μM (average of porewater Mn from clear gel probe 85 cm away from HMO-doped gel probe), due to the contamination of many clear gels by sediment particles (Figure A8). The masses of the individual gels were not measured, and variation in these values may contribute significantly to the observed heterogeneities in the depth profile. Rate coefficients are comparable to the higher values in Figure 4.2b.

Table B.4. Gel probe data input to Matlab m-file "ksolver" and output k′ values. Total Mn for this batch was 6.03 ± 0.40 mM (95% confidence interval).

Sample:	Depth (cm)	C_{pw} (μM)	Mn recovered (mM)	k_lower	k (1/hr)	k_upper
a01	-10.25	2.445	5.61	8.80E-05	1.64E-03	3.09E-03
a02	-9.6	0.488	5.74	-4.48E-04	1.10E-03	2.55E-03
a03	-8.95	0.869	4.72	3.93E-03	5.48E-03	6.93E-03
a04	-8.3	0.007	5.09	2.23E-03	3.78E-03	5.23E-03
a05	-7.65	0.450	5.38	1.01E-03	2.56E-03	4.01E-03
a06	-7	1.252	5.85	-8.74E-04	6.76E-04	2.13E-03
a07	-6.35	0.358	5.44	7.58E-04	2.31E-03	3.76E-03
a08	-5.7	0.000	5.04	2.44E-03	3.99E-03	5.44E-03
a09	-5.05	0.000	5.36	1.05E-03	2.60E-03	4.05E-03
a10	-4.4	0.000	6.04	-1.60E-03	-4.95E-05	1.40E-03
a11	-3.75	0.000	6.42	-2.98E-03	-1.43E-03	1.96E-05
a12	-3.1	0.603	6.23	-2.30E-03	-7.51E-04	6.99E-04
a13	-2.45	0.000	5.59	1.29E-04	1.68E-03	3.13E-03
a14	-1.8	0.000	5.75	-5.21E-04	1.03E-03	2.48E-03
a15	-1.15	0.000	6.08	-1.75E-03	-2.01E-04	1.25E-03
a16	-0.5	0.791	6.03	-1.55E-03	5.03E-06	1.46E-03
a17	0.15	0.000	6.18	-2.11E-03	-5.60E-04	8.91E-04
a18	0.8	0.000	6.16	-2.04E-03	-4.94E-04	9.56E-04
a19	1.45	0.000	4.86	3.24E-03	4.79E-03	6.24E-03
a20	2.1	0.000	5.43	7.96E-04	2.35E-03	3.80E-03
a21	2.75	0.000	4.90	3.07E-03	4.62E-03	6.07E-03
a22	3.4	1.538	5.61	7.60E-05	1.63E-03	3.08E-03
a23	4.05	0.705	4.56	4.71E-03	6.26E-03	7.71E-03
a24	4.7	0.000	4.51	4.93E-03	6.48E-03	7.93E-03
a25	5.35	0.427	5.43	7.72E-04	2.32E-03	3.77E-03
a26	6	0.207	4.61	4.45E-03	6.00E-03	7.45E-03
a27	6.65	1.157	4.78	3.67E-03	5.22E-03	6.67E-03
a28	7.3	0.452	4.62	4.41E-03	5.96E-03	7.40E-03
a29	7.95	0.465	4.62	4.40E-03	5.94E-03	7.39E-03
a30	8.6	0.751	3.83	8.60E-03	1.01E-02	1.16E-02
a31	9.25	2.142	2.35	1.96E-02	2.11E-02	2.26E-02
a32	9.9	0.680	1.63	2.77E-02	2.93E-02	3.07E-02
a33	10.55	0.488	1.06	3.73E-02	3.89E-02	4.03E-02
a34	11.2	1.188	0.40	5.91E-02	6.06E-02	6.20E-02
a35	11.85	0.560	0.05	1.05E-01	1.07E-01	1.08E-01
a36	12.5	1.149	0.18	7.78E-02	7.94E-02	8.08E-02
a37	13.15	1.481	0.86	4.21E-02	4.36E-02	4.51E-02
a38	13.8	1.960	1.54	2.91E-02	3.06E-02	3.20E-02
a39	14.45	4.552	1.98	2.35E-02	2.51E-02	2.65E-02
a40	15.1	4.107	1.42	3.10E-02	3.25E-02	3.40E-02
a41	15.75	2.101	1.02	3.83E-02	3.99E-02	4.13E-02
a42	16.4	2.477	1.31	3.28E-02	3.43E-02	3.58E-02
a43	17.05	5.395	0.91	4.13E-02	4.28E-02	4.43E-02
a44	17.7	3.107	1.96	2.37E-02	2.53E-02	2.67E-02

Table B.4 (continued)

Sample:	Depth (cm)	C_{pw} (µM)	Mn recovered (mM)	k_lower	k (1/hr)	k_upper
a45	18.35	2.947	1.31	3.27E-02	3.43E-02	3.57E-02
a46	19	6.189	1.65	2.78E-02	2.94E-02	3.08E-02
a47	19.65	4.665	1.48	3.02E-02	3.18E-02	3.32E-02
a48	20.3	24.571	1.56	3.04E-02	3.20E-02	3.34E-02
a49	20.95	2.554	1.63	2.78E-02	2.94E-02	3.08E-02
a50	21.6	4.280	1.51	2.97E-02	3.12E-02	3.27E-02
a51	22.25	3.145	1.41	3.11E-02	3.26E-02	3.41E-02
a52	22.9	40.482	1.93	2.64E-02	2.80E-02	2.94E-02
a53	23.55	2.906	2.01	2.31E-02	2.46E-02	2.61E-02
a54	24.2	3.798	2.45	1.88E-02	2.03E-02	2.17E-02

Table B.5. Sequential extraction fractions of Mn (mg kg^{-1}). The detection limit was approximately 0.10 mg kg^{-1}.

	0-4 cm	4-7 cm	7-10 cm	10-13 cm	13-16 cm	16-19 cm	19-22 cm	22-25 cm
exchangeable	1.32	8.27	1.44	7.05	1.76	9.77	1.81	11.92
carbonate	>0.10	>0.10	>0.10	>0.10	0.10	1.42	1.16	1.80
reducible oxides	4.41	2.07	2.60	>0.10	1.22	2.13	>0.10	2.84
organics, sulfides	0.11	1.16	7.01	2.63	10.33	3.47	2.08	>0.10
residual (nonsilicate)	0.44	4.19	0.24	3.51	1.95	16.17	2.29	4.73

Table B.6. Sequential extraction fractions of Fe (mg kg^{-1}). The detection limit was approximately 0.10 mg kg^{-1}.

	0-4 cm	4-7 cm	7-10 cm	10-13 cm	13-16 cm	16-19 cm	19-22 cm	22-25 cm
exchangeable	1.1	>0.10	2.6	>0.10	>0.10	3.7	0.2	5.2
carbonate	>0.10	>0.10	>0.10	>0.10	>0.10	2.3	6.7	16.4
reducible oxides	67.9	97.5	105.6	62.4	53.8	131.7	3.5	128.0
organics, sulfides	33.8	41.8	71.7	201.6	714.5	353.4	201.4	36.4
residual (nonsilicate)	79.4	511.1	57.8	351.1	93.4	598.3	125.7	560.1