

Supporting Information

for

**“A Hydrous Manganese Oxide Doped Gel Probe Sampler for Measuring *In Situ* Reductive
Dissolution Rates: I. Field Deployment”**

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Contents: 9 pages including 4 figures, 3 tables, and 1 MATLAB m-file code

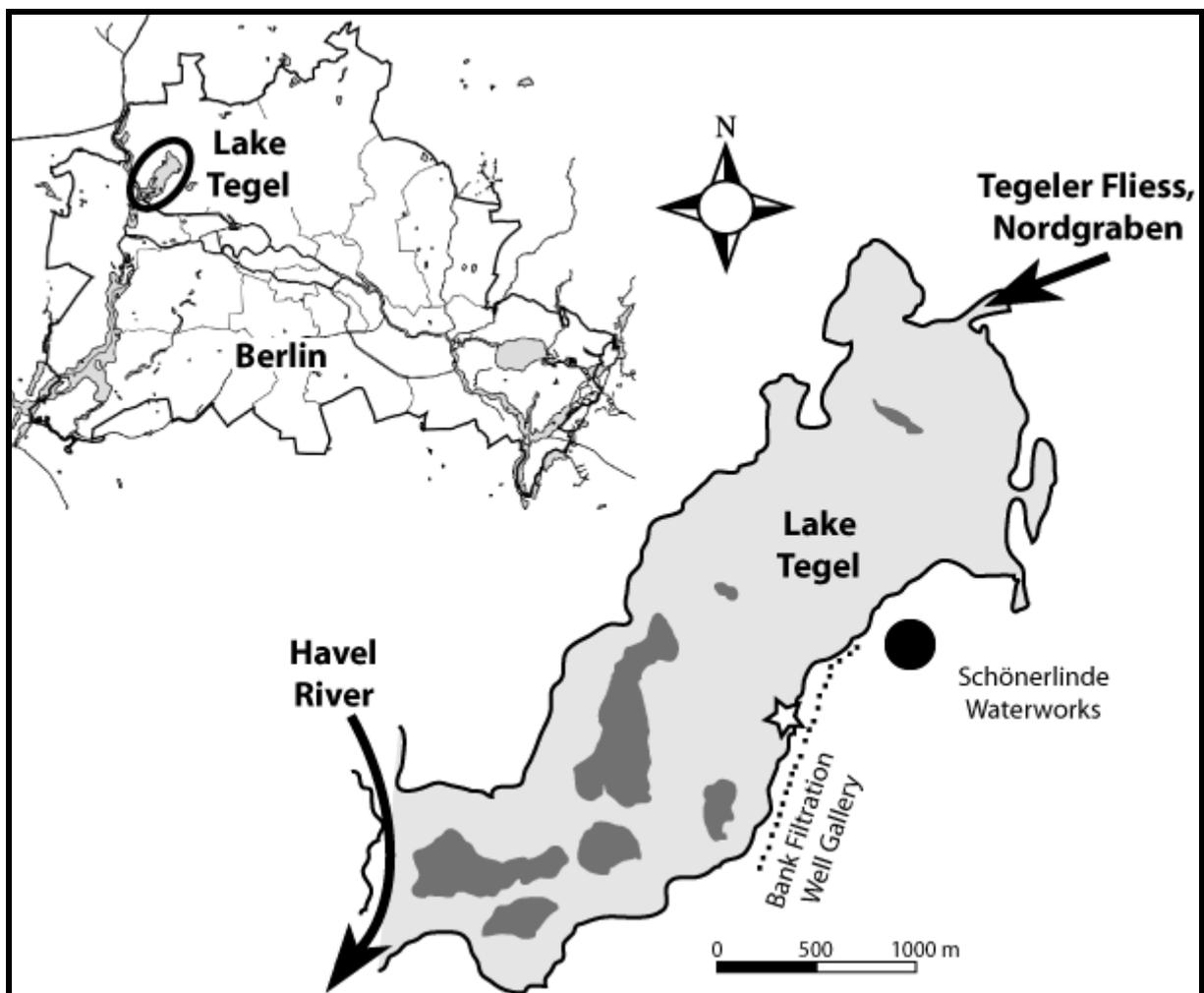


Figure S1. Location of Lake Tegel within Berlin city limits (upper left) and location of sampling site (star) within the lake (right; shaded regions indicate islands). Arrows indicate in- and outflows to the lake. Scale bar applies to right figure only.

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 $2.35 \text{ m}^3 \text{ s}^{-1}$. For a lake cross-section approximately 1000 m wide and 8 m deep [1], the average surface water velocity is $\sim 25 \text{ m d}^{-1}$ (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 $\sim 30 \text{ m}$ 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:

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

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 [2]. 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 $\gamma = 9.79 \text{ kN m}^{-3}$, $\rho = 1000 \text{ kg m}^{-3}$, $g = 9.8 \text{ m s}^{-2}$, $L = 4.5 \text{ m}$, 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 [3].

Table S1. 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 [2] 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. [4] and Wildman [5]. Briefly, $\sim 0.5 \text{ g}$ of dry sediment was shaken in 5.5 g L^{-1} sodium hexametaphosphate for $\geq 4 \text{ h}$, and the sample-solution ration was adjusted to give an obscuration of $20 \pm 4\%$. Data were compiled 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 S2. Porewater concentrations of detectable trace elements. Other elements tested, but below detection limits (in parentheses) were: As, Be, Cd, Mo, Sb, Tl, V ($0.2 \mu\text{g l}^{-1}$); Cr, Pb ($0.5 \mu\text{g l}^{-1}$); Se ($10 \mu\text{g l}^{-1}$); Zn ($5 \mu\text{g l}^{-1}$). 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

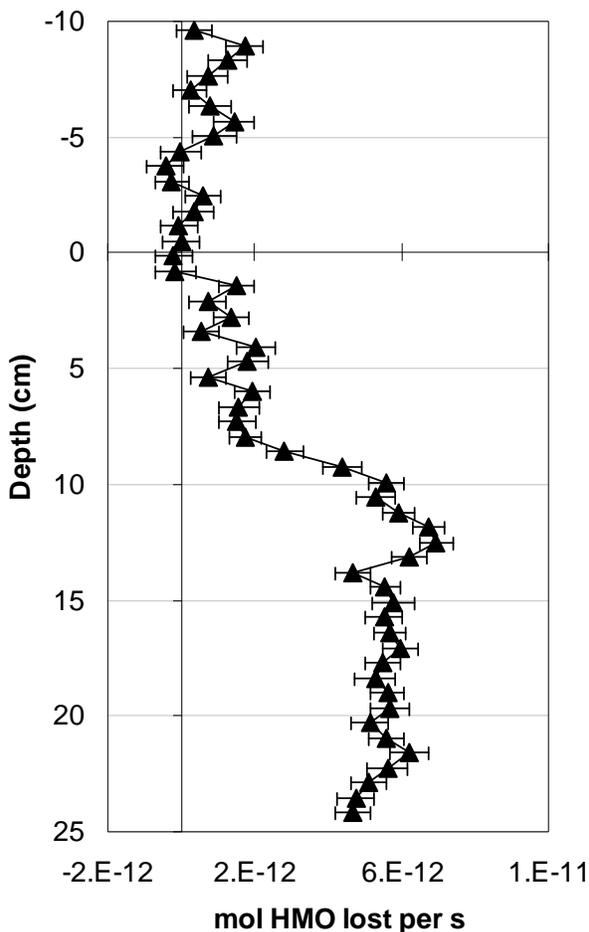


Figure S2. Moles of HMO lost in each gel per s of deployment time. Error bars represent the variation from the 95% confidence interval in Mn_T . The R_{meas} data input to the MATLAB code is this data array divided by the mass of each gel.

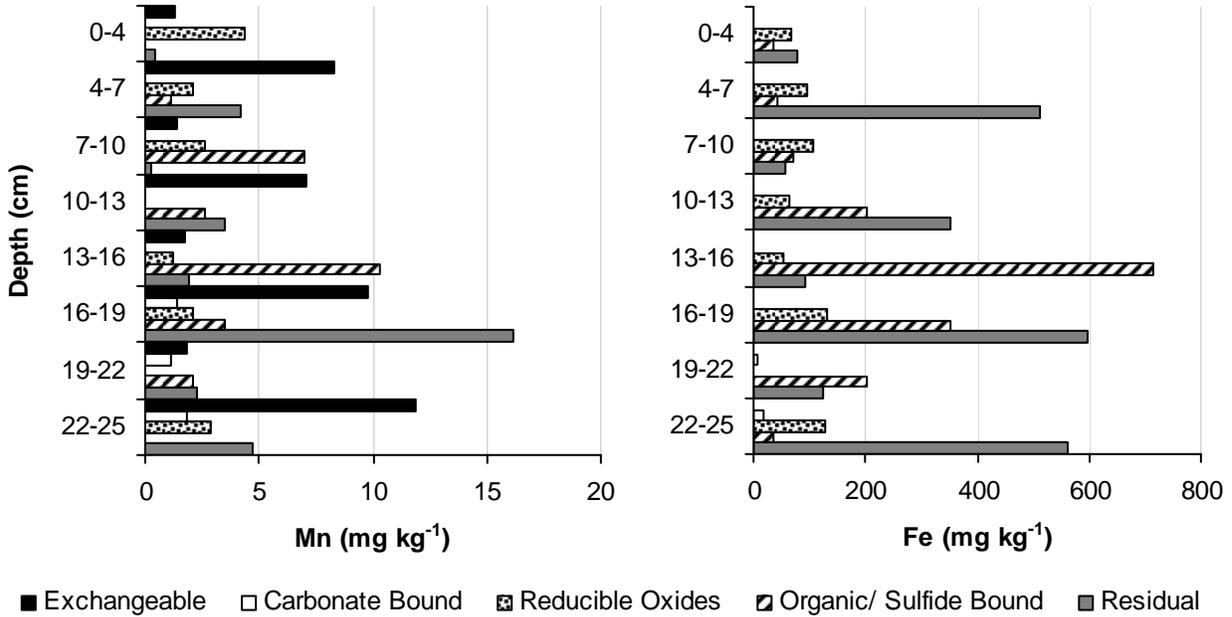


Figure S3. Extracted manganese (left) and iron (right) concentrations per kg dry sediment, as determined by sequential extraction. Note the different scales of the two x-axes. Bars are averages of 3 subsamples for each core section.

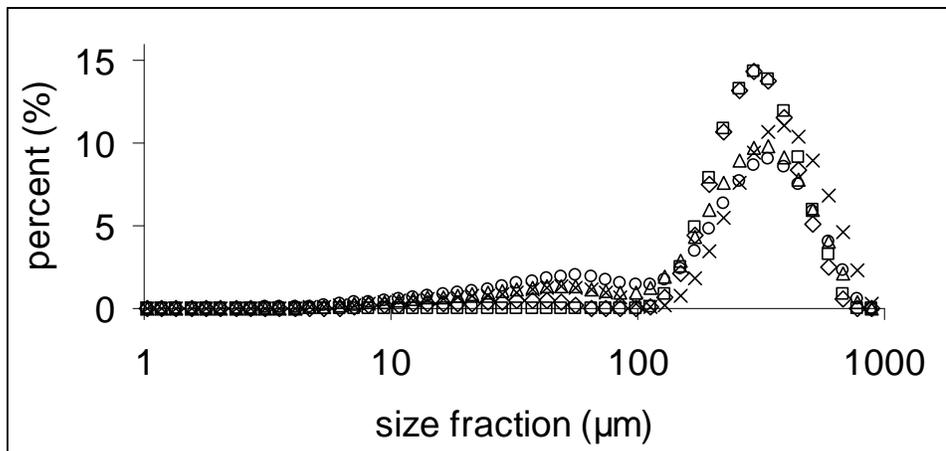


Figure S4. Particle size in Lake Tegel shoreline sediment for 0-5 cm (◇), 5-10 cm (□), 10-15 cm (Δ), 15-20 cm (○), and 20-27.5 cm (×) core sections. Mode particle size values range from 301 to 382 µm (mean = 329 µm) and increase with depth.

Table S3. Calculation of surface-area-normalized Mn reduction rates from field studies.

Source	Location	Rate	Units	[MnOx] (M)	Notes
[13]	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
[16]	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
[12]	Lake Michigan	7.0×10^{-6}	g cm ⁻² yr ⁻¹		c
[14]	North Sea: Skagerrak Basin	$2.0-10 \times 10^{-4}$	M d ⁻¹	6.14×10^{-4}	a, d
This Study	Lake Tegel: shallow	9.4×10^{-7}	h ⁻¹		a
	Lake Tegel: deep	7.3×10^{-6}	h ⁻¹		a
	Lake Tegel: maximum	2.4×10^{-5}	h ⁻¹		a
[15]	eastern Denmark coast	$3.6-11.7 \times 10^{-4}$	mol m ⁻² d ⁻¹		e
[11]	Gulf of St. Lawrence	$3.1-46.2 \times 10^{-4}$	mol m ⁻² d ⁻¹		e

^a Rate divided by Mn oxide surface area of 49 m² g⁻¹ and molecular weight of 86.94 g mol⁻¹ (chemical formula MnO₂) 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.

References Cited

- Schauser, I.; Chorus, I., Water and phosphorus mass balance of Lake Tegel and Schlachtensee - A modelling approach. *Water Res.* **2009**, *43*, (6), 1788.
- Bear, J., *Dynamics of Fluids in Porous Media*. Dover Pub.: Mineola, NY, 1972.
- von Gunten, U.; Zobrist, J., Biogeochemical Changes in Groundwater-Infiltration Systems - Column Studies. *Geochim. Cosmochim. Acta* **1993**, *57*, (16), 3895.
- Sperazza, M.; Moore, J. N.; Hendrix, M. S., High-Resolution Particle Size Analysis of Naturally Occurring Very Fine-Grained Sediment Through Laser Diffraction. *J. Sediment. Res.* **2004**, *74*, (5), 736-743.
- Wildman, R. A. Ph.D. Thesis. California Institute of Technology, 2009.

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);
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% 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);

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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

```