

Supplement of

Numerical modeling of physical and biochemical processes and their impacts on the self-potential signature

Xin Liu et al.

Correspondence to: Xin Liu (lucyliu0908@outlook.com) and Alex Furman (afurman@technion.ac.il)

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S.1 Exchange current derivation

Following Section 2.2.2, when the redox electrode is in contact with the electrolyte, it tends to electrochemically equilibrate with dissolved electroactive species (Peiffer et al., 1992). This causes the counterbalance of electron transfer for the forward and backward reactions. At equilibrium, the net current becomes zero, and the balanced Faradaic activity is usually expressed in terms of the exchange current, which is equal to either component current (Peiffer et al., 1992).

$$|i_{o_j}| = |i_{a_j}| = |i_{c_j}| \quad (\text{S.1})$$

where i_{a_j} and i_{c_j} are the anodic and cathodic currents of redox couple j , respectively (positive for anodic current and negative for cathodic current) (A).

The anodic and cathodic currents can be calculated as

$$i_{a_j} = k_{f_j}^{\text{el}} C_{\text{Ox}_j} n_j F A \quad (\text{S.2})$$

$$i_{c_j} = k_{b_j}^{\text{el}} C_{\text{Red}_j} n_j F A \quad (\text{S.3})$$

where $k_{f_j}^{\text{el}}$ and $k_{b_j}^{\text{el}}$ are the heterogeneous rate constants for redox couple j forward and backward reactions (m s^{-1}).

The heterogeneous rate constants strongly depend on the difference of electrode voltage and standard potential of redox couple j , which can be described as

$$k_{f_j}^{\text{el}} = k_{0_j}^{\text{el}} \exp \left[-\alpha_j \frac{n_j F}{RT} (E_{\text{eq}_j} - E_{\text{eq}_j}^0) \right] \quad (\text{S.4})$$

$$k_{b_j}^{\text{el}} = k_{0_j}^{\text{el}} \exp \left[(1 - \alpha_j) \frac{n_j F}{RT} (E_{\text{eq}_j} - E_{\text{eq}_j}^0) \right] \quad (\text{S.5})$$

where $E_{\text{eq}_j}^0$ is the standard potential of redox couple j (V)

Then, the Nernst equation is used to describe the redox potential of redox couple j (Eq. 29) at equilibrium condition, and it is shown as

$$E_{\text{eq}_j} = E_{\text{eq}_j}^0 - \frac{RT}{n_j F} \ln \frac{[\text{Red}_j]}{[\text{Ox}_j]} \quad (\text{S.6})$$

After that, we use C_{Ox_j} and C_{Red_j} to represent $[\text{Ox}_j]$ and $[\text{Red}_j]$, and change the Nernst equation into another form.

$$\frac{C_{\text{Red}_j}}{C_{\text{Ox}_j}} = \exp \left[-\frac{n_j F}{RT} (E_{\text{eq}_j} - E_{\text{eq}_j}^0) \right] \quad (\text{S.7})$$

Taking Eq. S.7 into Eqs. S.4 and S.5, we get

$$k_{f_j}^{\text{el}} = k_{0_j}^{\text{el}} \left(\frac{C_{\text{Red}_j}}{C_{\text{Ox}_j}} \right)^{\alpha_j} \quad (\text{S.8})$$

$$k_{b_j}^{\text{el}} = k_{0_j}^{\text{el}} \left(\frac{C_{\text{Red}_j}}{C_{\text{Ox}_j}} \right)^{\alpha_j - 1} \quad (\text{S.9})$$

Continuously, we introduce Eqs. S.8 and S.9 into Eqs. S.2 and S.3 and combine the results with Eq. S.1, and finally get the exchange current.

$$i_{0_j} = k_{0_j}^{\text{el}} C_{\text{Red}_j}^{\alpha} C_{\text{Ox}_j}^{1-\alpha} n_j F A \quad (\text{S.10})$$

S.2 Supplement figures

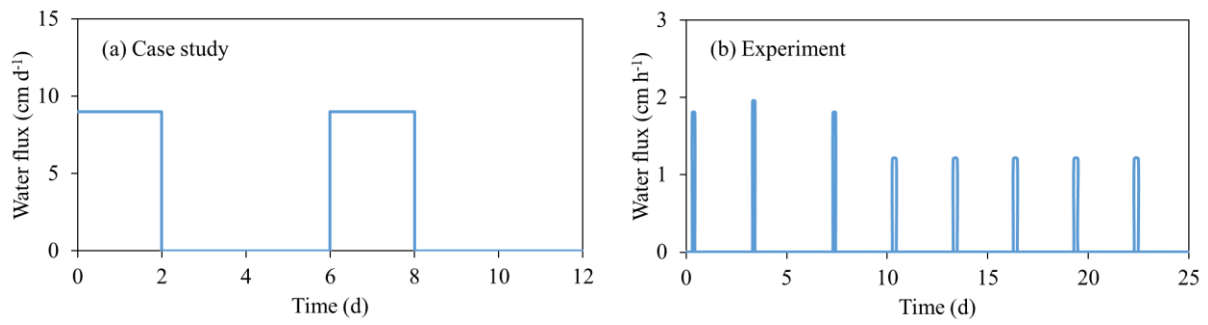


Figure S.1 Water flux from soil top in the case study and experiment.

The initial day is the 4th day of the experiment.

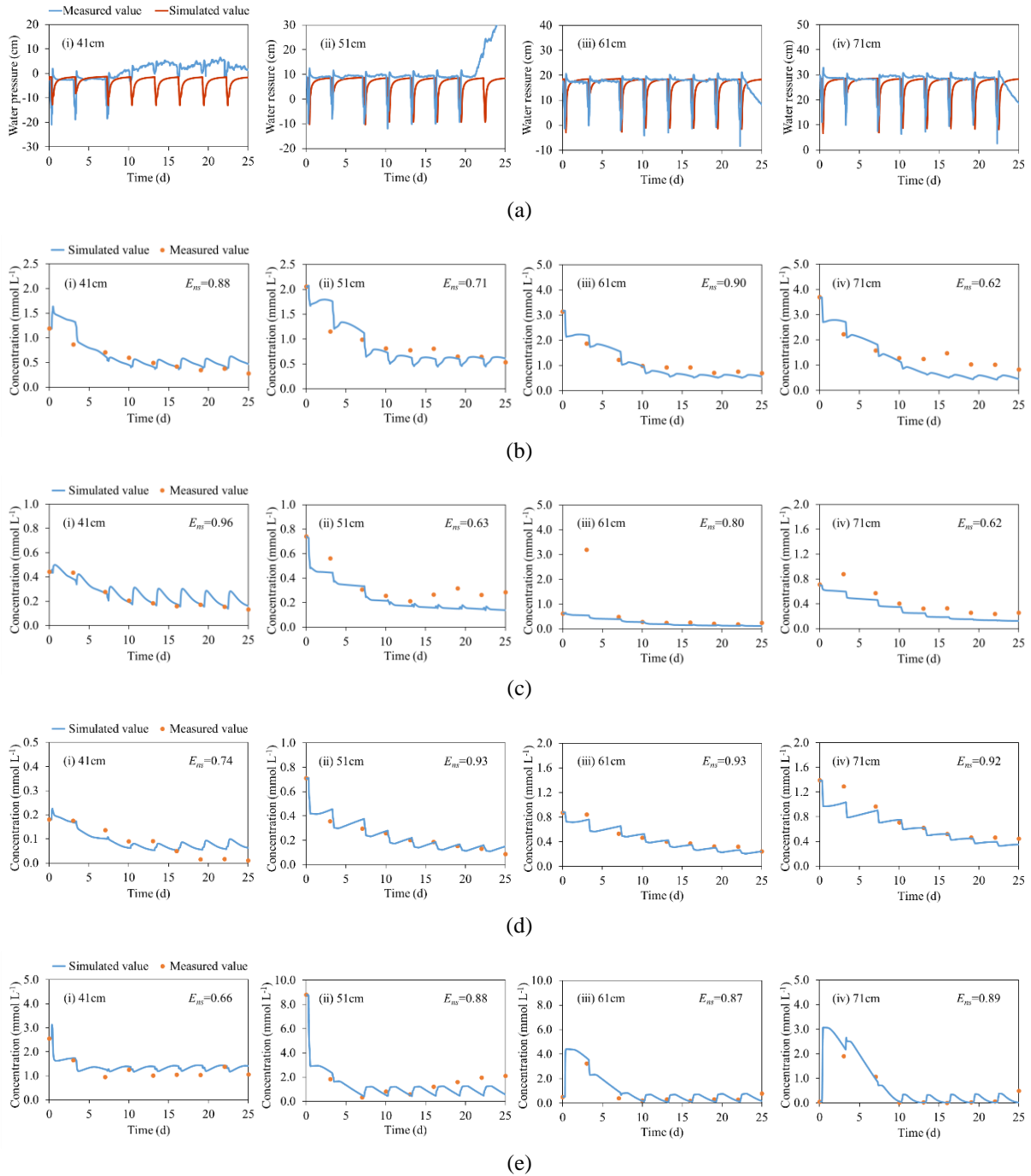


Figure S.2 Measured and simulated values of water pressure, DOC, DON, ammonium, and nitrate concentrations for model calibration and verification. Panes (a), (b), (c), (d), and (e) represent calibrated and verified results for water pressure, DOC, DON, ammonium, and nitrate respectively. Sub-panes (i), (ii), (iii), and (iv) indicate the calibrated and verified results at 41cm, 51cm, 61cm, and 71cm depths, respectively.

S.3 Supplement tables

Table S.1 Chemical species concentrations in the TWW.

Chemical species	Case study (mmol L ⁻¹)	Experiment (mmol L ⁻¹)
DOC	1.071	0.920
DON	0.11	0.608
NH ₄ ⁺	0.152	0.606
NO ₂ ⁻	0.022	0.055
NO ₃ ⁻	0.13	0.741
Mn ²⁺	0.0015	5.955×10 ⁻⁵
Fe ²⁺	0.0006	0
SO ₄ ²⁻	1.021	1.063
Na ⁺	7.783	7.032
K ⁺	0.564	0.674
Ca ²⁺	1.825	1.822
Mg ²⁺	0.958	0.883
O _{2 (g)}	16.96 (%)	16.96 (%)

Oxygen concentration is the volume percentage in the gas phase.

Table S.2 Parameters for soil properties.

Parameter	Value
θ_r	0.045 ^(a)
θ_s	0.43 ^(a)
K_s (cm d ⁻¹)	712.8 ^(a)
D_L (cm)	5
D_w (cm ² d ⁻¹)	2
D_g (cm ² d ⁻¹)	17798.4 ^(b)
ρ_s (g dm ⁻³)	1600

Parameters with superscript marks (a) are from Carsel and Parrish (1988), while parameters with marks (b) are from Alfnes et al. (2004).

Table S.3 Parameters for multiple-Monod kinetics and microbial dynamics.

Biochemical reaction	μ_{\max}^p (mmol C or N / mg cell d ⁻¹)	$K_{C_1}^p$ (mmol L ⁻¹)	$K_{C_2}^p$ (mmol L ⁻¹)	k_{I,O_2}^p (mmol L ⁻¹)	$k_{I,NO_3^-}^p$ (mmol L ⁻¹)	k_{I,MnO_2}^p (mmol L ⁻¹)	$k_{I,Fe(OH)_3}^p$ (mmol L ⁻¹)	k_b (mg L ⁻¹)	Y_m (mg cells/ mmol C or N)	d_m (d ⁻¹)
RD _y -NH ₂ $\xrightarrow[\text{NO}_3^-]{\text{O}_2(\text{aq})}$	0.3214	0.1429	0.0241	-	-	-	-	0.5	7	0.02
	0.025	0.1429	0.1857	7.8125×10 ⁻³	-	-	-	0.5	7	0.02
DOC + O _{2(aq)}	0.4167 ^(e)	0.1667 ^(a)	0.0241 ^(b)	-	-	-	-	0.5 ^(b)	6 ^(b)	0.02 ^(b)
DOC + NO ₃ ⁻	0.625 ^(e)	0.1667 ^(a)	0.1857 ^(b)	3.125×10 ⁻⁴ ^(b)	-	-	-			
DOC + NO ₂ ⁻	0.625 ^(e)	0.1667 ^(a)	0.1857 ^(e)	3.125×10 ⁻⁴ ^(b)	-	-	-	0.5 ^(b)	6 ^(b)	0.02 ^(b)
DOC + NO _(aq)	0.3125 ^(e)	0.1667 ^(a)	0.1857 ^(e)	3.125×10 ⁻⁴ ^(b)	-	-	-			
DOC + N ₂ O _(aq)	0.3125 ^(e)	0.1667 ^(a)	0.1857 ^(e)	3.125×10 ⁻⁴ ^(b)	-	-	-			
DOC + MnO _{2(s)}	0.0054 ^(c)	0.1667	0.2727 ^(c)	3.125×10 ⁻⁴	0.1857 ^(d)	-	-	0.53	2.52 ^(c)	0.0002 ^(c)
DOC + Fe(OH) _{3(s)}	0.0054 ^(c)	0.1667	0.8929 ^(c)	3.125×10 ⁻⁴	0.1857 ^(d)	0.2727 ^(d)	-	0.5	0.756 ^(c)	0.0002 ^(c)
DOC + SO ₄ ²⁻	0.0167	0.1667	0.15625	3.125×10 ⁻⁴	0.1857 ^(d)	0.2727 ^(d)	0.8929 ^(d)	0.5	0.36	0.0002
NH ₄ ⁺ + O _{2(aq)}	0.3571 ^(e)	0.0714 ^(b)	0.0241 ^(b)	-	-	-	-	1 ^(b)	6.3 ^(b)	0.02 ^(b)
NO ₂ ⁻ + O _{2(aq)}	0.3571 ^(e)	0.1286 ^(b)	0.0241 ^(b)	-	-	-	-	1 ^(b)	6.3 ^(b)	0.02 ^(b)

(1) Parameters with superscript marks (a), (b), and (c) are from Lee et al. (2009), Lee et al. (2006), and Essaid et al. (1995), respectively.

(2) Parameters with superscript marks (d) are recommended by Roden (2008), who indicate that substrate half-saturation and inhibition constants can be assumed in the same values.

(3) Parameters with superscript marks (e) are within the range mentioned by Lee et al. (2006), Lee et al. (2009), Gu and Riley (2010), and Zheng and Doskey (2015). The relatively moderate values are considered.

(4) Others are the calibrated values.

Table S.4 Parameters for second-order reactions.

Second-order reaction	k^p (mmol ⁻¹ L ⁻¹ d ⁻¹)
$\text{Mn}^{2+} + \text{O}_{2(\text{aq})}$	1.26×10^{-5}
$\text{Fe}^{2+} + \text{O}_{2(\text{aq})}$	29.7
$\text{Fe}^{2+} + \text{MnO}_{2(\text{s})}$	0.0274
$\text{HS}^- + \text{O}_{2(\text{aq})}$	0.548
$\text{HS}^- + \text{MnO}_{2(\text{s})}$	2.19
$\text{HS}^- + \text{Fe}(\text{OH})_{3(\text{s})}$	0.00274
$\text{FeS}_{(\text{s})} + \text{O}_{2(\text{aq})}$	0.164 ^(a)

The parameter with superscript mark (a) is summarized from Wang and Van Cappellen (1996), while other parameters are collected from Xu et al. (2007).

Table S.5 Equilibrium constants for chemical equilibrium reactions, adsorption, and gas transfer

Complexation /hydrolysis	$\log K_i^h$	Precipitation /dissolution	$\log K_i^{SP}$	Adsorption	$\log K_i^S$	Gas transfer	$\log K_i^H$
HCO_3^-	-10.329	MnCO_3	-11.13	NH_4^+	0.6	O_2	-2.8983
H_2CO_3	-16.681	FeCO_3	-10.89	Mn^{2+}	0.52	CO_2	-1.468
NH_4^+	-9.252	FeS	-4.648	Fe^{2+}	0.44	NH_3	1.7966
HS^-	-12.918	CaCO_3	-8.48	Na^+	0	NO	-2.76 ^(a)
H_2S	-6.994	CaSO_4	-4.36	K^+	0.7	N_2O	-1.6 ^(a)
-	-	MgCO_3	-8.029	Ca^{2+}	0.8	N_2	-3.1864
-	-	-	-	Mg^{2+}	0.6	H_2S	-0.997

Parameters with superscript marks (a) are collected from Gu and Riley (2010), while other parameters are the recommended values in the PHREEQC database (i.e., phreeqc.dat and phreeqcU.dat), where data source can be found in Laudelout et al. (1968), Van Bladel and Gheyi (1980), Jardine and Sparks (1984), and Parkhurst and Appelo (1999).

Table S.6 Ionic mobility for different chemical species.

Species	β_i ($10^{-8} \text{ m}^2 \text{ s}^{-1} \text{ V}^{-1}$)
H^+	36.3 ^(a)
NH_4^+	7.60 ^(a)
Na^+	5.19 ^(a)
K^+	7.61 ^(a)
Ca^{2+}	6.16 ^(a)
Mg^{2+}	5.48 ^(a)
NO_3^-	7.38 ^(b)
HCO_3^-	4.59 ^(b)
Cl^-	8.47 ^(c)
OH^-	6.15
SO_4^{2-}	4.14 ^(c)

Parameters with superscript marks (a), (b), and (c) are from Revil et al. (1998), Mellage et al. (2018), and Vaudelet et al. (2011b), respectively.

Table S.7 Parameters for redox potential modeling.

Redox couple	$k_{0_j}^{el}$ (10^{-8} m s^{-1})	n_j	α_j
$\text{NH}_4^+ / \text{NO}_2^-$	10^{-9}	6	0.5
$\text{NO}_2^- / \text{NO}_3^-$	10^{-9}	2	0.5
$\text{NO} / \text{NO}_2^-$	$5 \times 10^{-16} \text{ (a)} / 4 \times 10^{-11} \text{ (b)}$	1	0.5
$\text{N}_2\text{O} / \text{NO}$	10^{-15}	1	0.5
$\text{N}_2 / \text{N}_2\text{O}$	10^{-15}	1	0.5
$\text{H}_2\text{O} / \text{O}_2$	10^{-9}	2	0.5
$\text{CH}_2\text{O} / \text{HCO}_3^-$	10^{-11}	4	0.5

The standard rate parameter for $\text{NO} / \text{NO}_2^-$ includes two values, (a) is for model calibration and verification, and (b) is for the case study.

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