Can Conductivity, pH, and Temperature Measurements Reveal Spatial and Temporal Patterns and Trends in Wetland Geochemical Processes?

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Background:

Wetlands form an important component of The Nature Conservancy’s Northern Tallgrass Ecoregion preserves in western Minnesota and the eastern Dakotas:
Important wetland management issues in the Wallace C. Dayton Preserve include:

(1) Do wetland types need to be classified and distinguished?

(2) Do wetlands of different size and landscape setting function differently?

(3) Are some wetland types more vulnerable to land-use changes?

(4) Does climate variability influence wetland functions?

(5) If so, should management (establishing a fire regime, hydro-axe treatment, response to nearby drainage, etc.) be modified depending on the wetland type?
A continuum of wetlands between two end-members:

(1) Small, isolated pothole wetlands in the beach ridges of glacial Lake Agassiz

(2) Large wetlands that occur within large glacial lake plains

invasive weeds, illegal ditches

aspen encroachment & hydrological alteration
Can basic field data (pH, conductivity, temperature, ORP, and pH) can provide a significant indication of wetland geochemical processes?

Outline:

1. Physical Framework and Geomorphology
2. Methods and Sampling Sites
3. Summary of Field Measurement Results
4. Hydrochemical Modeling
5. Conclusions and Missing Information
Late Wisconsinan glacial lobes and advances (modified after Clayton & Moran, 1982 and Harris, 1995)
Wave-washed drumlin-like features in Caribou Township
Approach and Assumptions in Hydrochemical Modeling:

1. Rainwater reacts with various amounts and proportions of
   (a) Organic carbon
   (b) Carbonate (limestone fragments in till and sediment)
   (c) CO$_2$ gas in wetland sediments

2. Periodic flooding and saturation lower the pH through increasing interaction with CO$_2$ gas

3. Evapotranspiration mainly increases the total dissolved concentration of wetland waters

4. Other ions and reaction processes (such as ionic exchange) exert minimal control over overall water composition
• Four basic water quality parameters were measured in the field, close to the sediment – water interface:

   (1) pH
   (2) electrical conductivity
   (3) oxidation – reduction potential
   (4) temperature

• Sites were repeatedly visited and sampled during 2005, 2006, and 2007 during the ice-free season

• U.S. Geological Survey's PHREEQC code was used to model reaction of rainwater with organic carbon, carbonate, and CO$_2$ gas and account for variable degrees of evapotranspiration
Summary of Field Results –

(1) Water composition from different wetlands show consistent relationship between conductance and pH

(2) Although fields of conductivity and pH data overlap, all are discrete and have maintained their general position from 2005-2007

(3) Beach ridge and lake-plain wetlands at Skull Lake Wildlife Management area show a strong bimodal pattern

(4) Small, isolated beach ridge wetlands have a consistently low conductivity (<150 μS cm\(^{-1}\) ), but wide range in pH (5.4 – 7.6)

(5) The greatest conductivity occurs in hydrologically altered wetlands

(6) No apparent relationship exists with oxidation-reduction potential, except for possible increasing ORP with increasing conductance
Possible Interpretation:

(1) Small, isolated wetlands at Skull Lake range from bogs (low pH) to groundwater “windows” (higher pH)

(2) Large wetlands at Skull Lake show greater influence of evapotranspiration

(3) Lake-plain wetlands all show trends of decreasing pH with increasing conductance, perhaps indicating coupling between greater ET and longer interaction with CO₂

(4) For a few samples, a decreased pH and increased conductance may suggest longer time in contact with organic carbon, as revealed by ORP estimates
rain water composition

composition of water lost to ET

steps in the reaction process

definition of reactions and phases

etc.
Default output includes at each reaction step:

- solution composition
- solution description (pH, ORP, activity, etc.)
- distribution of species
- reaction progress
Converting ionic strength to an estimated total concentration in mg / L:

- assume all dissolved constituents are Ca\(^{2+}\) and HCO\(_3^-\)

- \[ I_{\text{solution}} = 0.5 \sum m_x z_x^2 \]

- and charge balance requires \( 2 \times m(\text{HCO}_3^-) = m(\text{Ca}^{2+}) \)

- setting \( m(\text{Ca}^{2+}) = m_x \) and combining gives \( I = 0.5 \times (4m_x + \frac{1}{2} m_x) = 2.25 m_x \)

- then \( I / 2.25 = m(\text{Ca}^{2+}) \) and \( I / 4.5 = m(\text{HCO}_3^-) \)

- converting to mg / L:

  \[ m_{\text{total}} = (1000 \text{ mg/g})(40.08 \text{ g/mole})(I / 2.25) + (1000 \text{ mg/g})(61.01 \text{ g/mole})(I / 4.5) = \]

  or

  \[ 31,371 \times I = \text{roughly approximate concentration in mg / L} \]
Run 1:

0.25 : 1.00 molar ratio of calcite to organic carbon with reactions

\[ \text{CaCO}_3 + \text{H}^+ = \text{Ca}^{2+} + \text{HCO}_3^- \]

\[ \text{CH}_2\text{O} + \text{H}_2\text{O} = \text{CO}_2 \text{(gas)} + 4\text{H}^+ + 4\text{e}^- \]

using 0.00025 moles in 20 steps

Run 2:

1.00 : 1.00 molar ratio of calcite to organic carbon (same reactions)

using 0.00025 moles in 20 steps, followed by

\[ \text{CO}_2 \text{(gas)} + \text{H}_2\text{O} = \text{HCO}_3^- \text{ & evaporation of pure H}_2\text{O} \]

In seven steps:

\[ 0.000001 \quad 0.0001 \quad 0.001 \quad 0.005 \quad 0.01 \quad 0.05 \quad 0.1 \]

(evaporation 100 x these amounts)
various combinations of CO$_2$ gas reaction and H$_2$O evaporation

reaction of 0.25:1 calcite:organic carbon

reaction of 1:1 calcite:organic carbon

decreasing oxidation potential

approx. concentration in mg/L (as Ca$_2^+$ and HCO$_3^-$)

ionic strength

pH
mg / L (about 0.6 x μS cm⁻¹)
Conclusions –

(1) Simple field hydrochemical measurements reveal variable wetland processes

(2) Application of this field measurement / modeling approach may be limited to systems dominated by carbonate equilibria

(3) Wetlands across the landscape function differently, depending greatly on:
   - relative water budget components
   - interaction with groundwater
   - typical extent of evapotranspiration
   - hydrological disturbance

(4) Beach ridge wetlands --- small-size coupled with meteoric source dependence --- suggests that even small changes in climate will alter their condition

(5) Land management and land use changes can greatly affect wetland function
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