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Can pH and electrical conductivity monitoring reveal spatial and temporal patterns in wetland geochemical processes?

P. J. Gerla

The Nature Conservancy – Minnesota, North Dakota, and South Dakota Chapter,
81 Cornell Street Stop 8358, Grand Forks, North Dakota 58202-8358, USA

Department of Geology and Geological Engineering, University of North Dakota,
81 Cornell Street Stop 8358, Grand Forks, North Dakota 58202-8358, USA

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Correspondence to: P. J. Gerla (phil.gerla@engr.und.edu)

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Abstract

Carbonate reactions and equilibria play a dominant role in the biogeochemical function of many wetlands. The US Geological Survey PHREEQC computer code was used to model geochemical reactions that may be typical for wetlands with water budgets characterized by: (a) input dominated by direct precipitation, (b) interaction with groundwater, (c) variable degrees of reaction with organic carbon, and (d) different rates of evapotranspiration. Rainfall with a typical composition was progressively reacted with calcite and organic carbon at various rates and proportions using PHREEQC. Contrasting patterns of the results suggest that basic water quality data collected in the field can reveal differences in the geochemical processes in wetlands. Given a temporal record, these can signal subtle changes in surrounding land cover and use. To demonstrate this, temperature, pH, and electrical conductivity (EC) were monitored for three years in five large wetlands comprising 48 sample sites in northwest Minnesota. EC and pH of samples ranged greatly – from 23 to 1300 μScm^{-1} and 5.5 to 9. The largest range in pH was observed in small beach ridge wetlands, where two clusters are apparent: (1) low EC and a wide range of pH and (2) higher pH and EC. Large marshes within a glacial lake – till plain have a broad range of pH and EC, but depend on the specific wetland. Outlying data typically occurred in altered or disturbed areas. The inter-annual and intra-wetland consistency of the results suggests that each wetland system hosts characteristic geochemical conditions.

1 Introduction

Wetland management often focuses on maintaining diverse natural vegetation and providing wildlife habitat, both of which are strongly influenced by water quality and chemistry (Houlahan and Findlay, 2003; McCormick et al., 2009). Successful management of wetlands, however, can be challenged by climate variability and changes in local land use, which may disrupt a wetland's hydrological and water-quality regime and

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result is consistent with their moderate pH and relatively low dissolved solid concentration.

2.4 Modeling

To characterize the relative importance and control of wetland water composition by landscape-related processes, numerical modeling was used to investigate the influence of the carbonate-system geochemical processes. Models were developed to explain more fully not only the process, but also to quantify the hydrogeochemical reactions occurring in the wetland waters. For this purpose, the US Geological Survey's PHREEQC version 2 code was used to model reaction of rainwater with organic carbon, carbonate, and CO₂ gas, and account for variable degrees of evapotranspiration (Parkhurst and Appelo, 1999). PHREEQC is a public-domain computer program, written in the C programming language, which performs a wide range of low-temperature aqueous geochemical calculations. PHREEQC is based on an ion-association aqueous model and has capabilities for both speciation and batch-reaction calculations involving both reversible and irreversible reactions, including aqueous, mineral, and gas reactions, which are the program's options used in the analysis of this report.

Hydrogeochemical modeling was used track the progression of basic geochemical processes in the wetlands, assuming:

- a. rainwater composition is the starting solution,
- b. organic carbon/oxidation-reduction and carbonate system reactions dominate the processes responsible for the composition and chemical properties of the wetland waters,
- c. other ions and reaction processes (such as ionic exchange) exert a minor effect on water composition, and
- d. the relationship between ionic strength and dissolved solid concentration can be approximated (Fig. 3).

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Reaction progress can be then traced by including sufficient reaction steps, with complicating factors such as reaction with humic acids, silicate minerals, and clay cation exchange not included.

3 Results

3.1 Field observations

Soon after field data began to be collected, consistency in the relationship between pH and EC was observed for groups of wetlands that shared either a spatial or physiographic relationship (Fig. 4). The sample standard deviation for replicated field measurements each time a site was sampled (Fig. 5) showed some scatter, but a small pooled standard deviation (IUPAC, 1997) suggests good reproducibility using this field measurement technique. It further indicates that variation would not affect significantly the observed pH-EC trends. Pooled standard deviation for pH, EC, and temperature was 0.11, 19.4, and 0.46, respectively ($n = 498$). For individual measurements, there was no correlation between pH and standard deviation and only a slight positive correlation between EC and standard deviation (Fig. 5).

The large range and distinctive patterns of pH and EC revealed by the field analyses suggest that hydrogeochemistry is related to processes affecting the water budget, including: (a) degree of meteoric-groundwater interaction, (b) extent of evapotranspiration, (c) reaction of wetland waters with organic carbon near the water-soil interface, and (d) reaction of wetland waters with carbonate minerals in the underlying substrate.

3.2 Hydrological regime – surface water and groundwater interaction

In the context of the glacial Lake Agassiz beach ridges in the Tallgrass Aspen Parkland, wetlands interact with groundwater and surface water in various patterns and with different magnitudes. A map of wetlands at the northern end of the Skull Lake WMA (US Fish and Wildlife Service National Wetlands Inventory, 2012) shows the typical spatial

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small wetlands formed within permeable glacial-lake beach sediments, and in large wetlands with deeper groundwater interaction.

The small proportion of calcite available for reaction strongly inhibits the rise of pH (Fig. 7, cc : oc = 1 : 4). Furthermore, the extent of the reaction limits the generation of cations and bicarbonate, thereby mitigating increases in ionic strength and dissolved mineral concentration. In contrast, reaction of the initial water with larger amounts of carbonate leads to a rise in pH and greater dissolution of solids (Fig. 7, cc : oc = 1 : 1). The break in slope shown for both paths results from the onset of methanogenesis as organic carbon is progressively added to the system.

Continued increase dissolution of solids and evolution of the wetland waters requires that the model consist of a two-step process, where water reacts with CaCO_3 and organic carbon, as described, and undergoes reaction with CO_2 . Interaction of the wetland waters with abundant dissolved CO_2 gas will buffer the increase of pH due to the reaction of the water with calcite (Fig. 7). Model results show that early in the reaction progress both processes lead to increasing ionic strength and pH, although the system with limited calcite reaction shows significantly less increase in pH and ionic strength, which may be anticipated for isolated, precipitation-dependent wetlands. Reaction with CO_2 buffers pH; because pH appears to rise to as high as nine in natural wetland waters (Fig. 4), kinetics associated with calcite and organic carbon reactions may be more rapid than buffering by CO_2 gas.

Following the initial reaction of one kg of meteoric water with 1 : 1 calcite and organic carbon, the model water undergoes reaction with CO_2 and evaporation in various proportions, as shown by paths A, B, C, and D on Fig. 6. Path A and B have only a very small amount of water lost to evapotranspiration (total 10^{-2} moles per initial kg of water, in seven steps) (Table 2). Path A reacts with a total of 10^{-4} moles of CO_2 in seven steps; path B reacts with 10^{-2} moles. Paths C and D react with the same amount of CO_2 as A and B, respectively, but with 100 times more water lost. By the final step, the original 1 kg of water in paths C and D is reduced to 0.82 kg (1 mole of H_2O is evaporated). This reaction will reduce pH, with greater CO_2 interaction leading to a lower pH.

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Further increase in dissolved solids requires additional evapotranspiration, which also leads to small increase in pH (Fig. 7, dashed line), with the path of further pH changes depending on the degree of interaction with CO_2 .

3.4 Oxidation-reduction potential

Field ORP measurements ranged from -70 to $+260$ mV and varied both temporally for individual sites and spatially. Results from the PHREEQC models (all run at 15°C) showed a maximum range from -340 to greater than $+500$ mV. ORP and EC revealed a weak, statistically insignificant correlation and not considered further in this report. No apparent relationship was found between ORP and the other field parameters, perhaps revealing the difficulties in making reproducible field measurements of ORP using reference/sensor electrodes (Fiedler et al., 2007). ORP is complicated to measure for a variety of other reasons (e.g. Lindberg and Runnells, 1984; Runnells and Lindberg, 1990; Kolka and Thompson, 2006) and is strongly controlled seasonally and by site-specific conditions, such as microbiological activity, presence and absence of common oxidation-reduction couples, and interaction of soils with processes related to plant physiology.

4 Discussion

The difference in the relationship to groundwater regime suggests that EC and pH will vary significantly between the beach-ridge and lake-plain wetlands (Figs. 2 and 6), which was observed in the field measurements (Fig. 4). Water composition in the beach-ridge wetlands is controlled largely by processes related to shallow groundwater interaction with meteoric water. In contrast, evapotranspiration and the natural cycling of organic carbon influences the composition of shallow water in the larger lake-plain wetlands. In both wetland types, the soil substrate contains varying amounts of carbonate minerals, which plays an important role in determining the buffering capacity of

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- e. For a few samples, relatively low pH (< 7) and increased EC (~ 600) may suggest longer time in contact with organic carbon. These waters were apparently separated from contact with mineral substrate, perhaps by low permeability layers or by an isolated, shallow groundwater flow system lying entirely within organic-rich sediments.

4.2 Application

Wetland management issues and questions often relate to water budget. For example, land stewards and wetland managers in the Tallgrass Aspen Parkland and nearby ecoregions have asked the following questions concerning management options and choices:

- a. Do wetlands of different size and landscape setting have a significantly different hydrological function? If so, then do wetland types need to be classified and distinguished for more effective management?
- b. Are some wetland types more vulnerable to land-use changes than others?
- c. How does climate variability influence wetland hydrology and what efforts need to be taken to adapt to future climate change?

Although determining even approximate wetland water budgets requires extensive field measurement and monitoring (e.g., Lent et al., 1997; Drexler et al., 1999), the results reported here suggest that the pH–EC composition of wetland waters can provide an indication of the processes that control the water budget. For example, a relatively larger EC may reveal that groundwater input occurs as a major component of a wetland water budget (Almendinger and Leete, 1998). Evapotranspiration may further increase the EC. In contrast, a small isolated wetland may have a water budget that lacks interaction with groundwater and receives most its input from direct precipitation, such as occurs in raised bogs (e.g. Bragg and Tallis, 2001). Some of the beach ridge wetlands in the TAP, characterized by pH < 6 and EC $< 100 \mu\text{S cm}^{-1}$, may fall into this category.

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These will be particularly vulnerable to even small changes to the surrounding physical environment, such as subtle, long-term changes in recharge or either a rise or fall of the water table, which can be caused by climate variability or the alteration of land cover. In contrast, the range in geochemical character exhibited by larger, more complex wetlands, such as TAP's lake-plain wetlands will likely have capacity to buffer new hydrogeochemical conditions brought about by changes in land use and climate. Finally, human interaction with wetlands, such as drainage, peat mining, and grazing, among others, can often disrupt the natural function and therefore the chemical processes of wetlands (e.g., Marsalek, 2003; Dillon and Merritt, 2005), which will be reflected early in the transition by changing pH and EC.

Ideally, periodic complete geochemical analysis of wetland waters and monitoring of water budgets would provide the best assurance for predicting and then avoiding ecosystem damage brought about by changes in land use. By recognizing the position of the wetland on the landscape and routinely monitoring pH and EC, however, wetland managers can better judge if alteration to the wetland environs will pose a significant threat or not. By monitoring pH and EC, these data may signal the early effects of climate change, thus enabling adaptation to the alteration.

5 Conclusions

This case study shows that significantly different hydrogeochemical processes and functions occur in wetlands across the Tallgrass Aspen Parkland ecoregion landscape, based on observations of field pH and EC. Wetlands function differently, depending greatly on the relative magnitude of water budget components, degree of interaction with groundwater, the typical extent of evapotranspiration, and hydrological disturbances. With their small-size coupled with a direct meteoric source for water, even small changes in climate or other physical disturbance will alter the condition of beach-ridge wetlands within the Tallgrass Aspen Parkland ecoregion. Larger wetlands developed on former glacial lake plains tend to have greater variability in their

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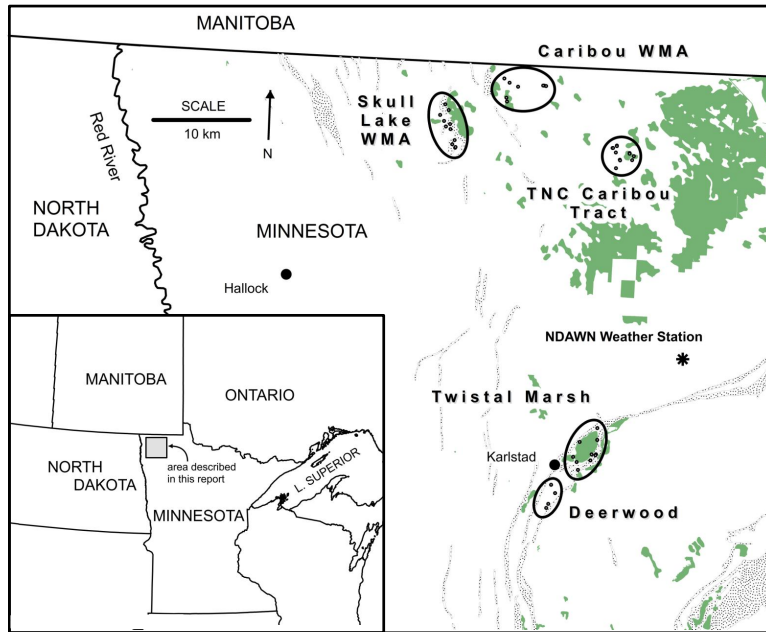


Fig. 1. Map showing northwest Minnesota, US (insert) and the location of wetland sampling sites (ovals and small circles). Beaches associated with glacial Lake Agassiz are stippled; extensive wetland areas are shaded.

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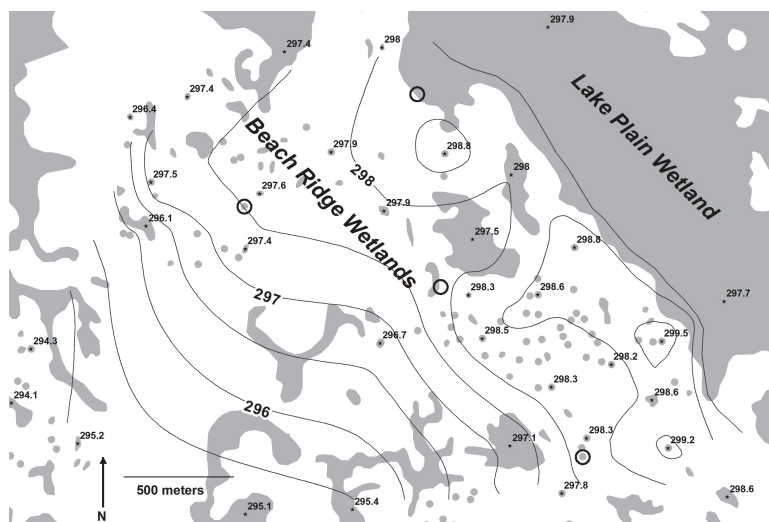


Fig. 2. Detailed map of the north end Skull Lake WMA wetland sample area (Fig. 1). Gray pattern shows all wetlands delineated in the US Fish and Wildlife Service National Wetlands Inventory (2012). Spot elevations (star symbol) in meters are shown for selected wetlands. All wetland surface elevations (based on LiDAR data from the International Water Institute, 2012) are contoured using a 0.5 m interval. Circles indicate wetlands sampled for this study.

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- by definition $I_{\text{solution}} = 0.5 \sum (z_i^2 m_i)$
 - assume all dissolved constituents are Ca^{2+} and HCO_3^-
 - charge balance requires $2 m_{(\text{HCO}_3)} = m_{(\text{Ca})}$
 - $m_{(\text{Ca})} = m_x$ and $m_{(\text{HCO}_3)} = 0.5 m_x$
- combining gives $I = 0.5 * [(4 * m_x) + (1 * 0.5 * m_x)] = 2.25 m_x$
- $I / 2.25 = m_{(\text{Ca})}$ and $I / 4.5 = m_{(\text{HCO}_3)}$
- converting to concentration (conc) in mg L^{-1} :
- $\text{conc}_{\text{total}} = (1000 \text{ mg g}^{-1}) (40.08 \text{ g mole}^{-1}) (I / 2.25) + (1000 \text{ mg g}^{-1}) (61.01 \text{ g mole}^{-1}) (I / 4.5)$
- or
- $31,371 * I = \text{approximate concentration in mg L}^{-1}$

Fig. 3. Computational steps relating ionic strength to approximate total dissolved solid concentration for systems dominated by carbonate reactions. The variable z represents ionic charge and m ionic molality.

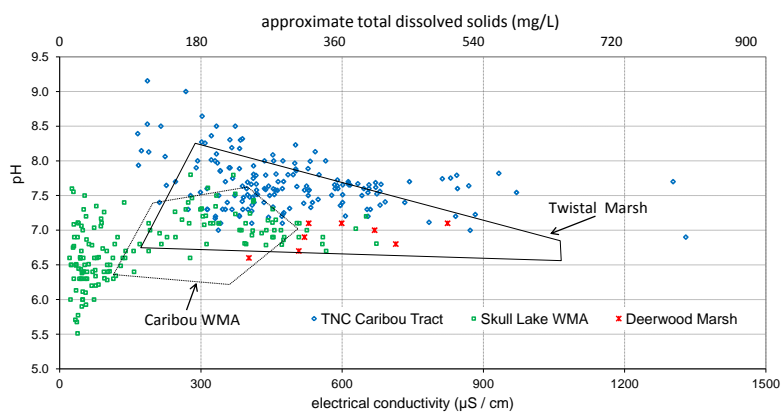


Fig. 4. Scatterplot showing results of pH–EC measurements for the five wetland sampling clusters during the 2005–2007 ice-free seasons. To make the plot easier to read, values for Twistal Marsh (86 measurements) and Caribou WMA (88 measurements) are not shown individually, but delimited by a solid and dash outline box, respectively.

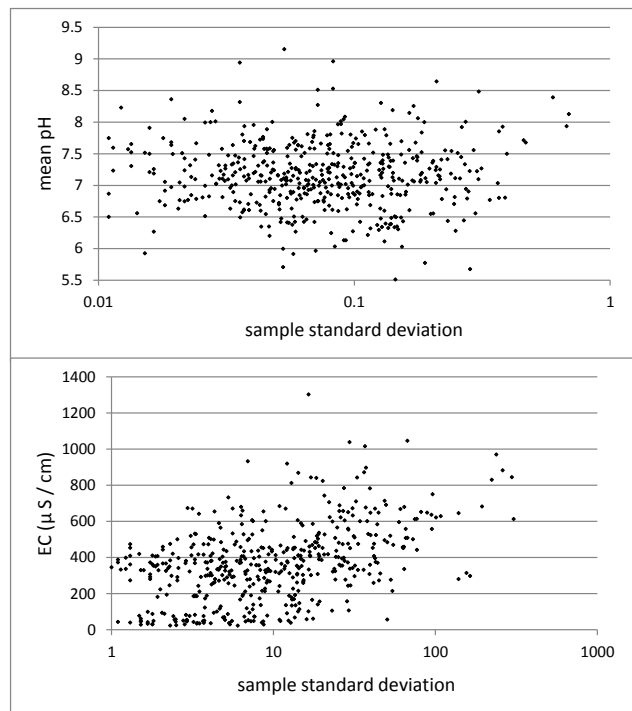


Fig. 5. Scatterplots of sample standard deviation (log scale) versus mean pH and EC. Standard deviation is based on field measurements replicated at least five times for each sample. The standard deviation for pH is based on the log of hydrogen ion concentration.

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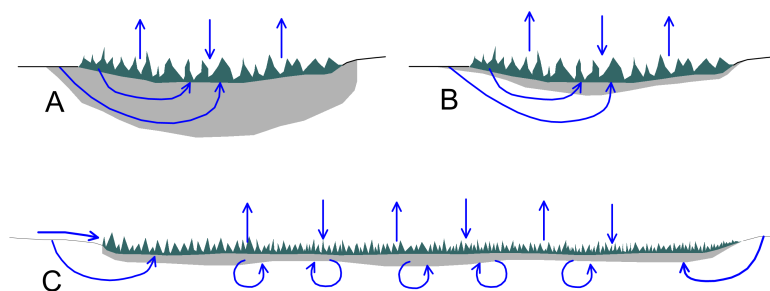


Fig. 6. Sketch showing the general groundwater flow pattern (arrows) in the beach-ridge (**A** – organic substrate and **B** – mineral substrate) and lake-plain (**C**) wetlands. Gray shading shows the distribution of organic-rich soils and peat.

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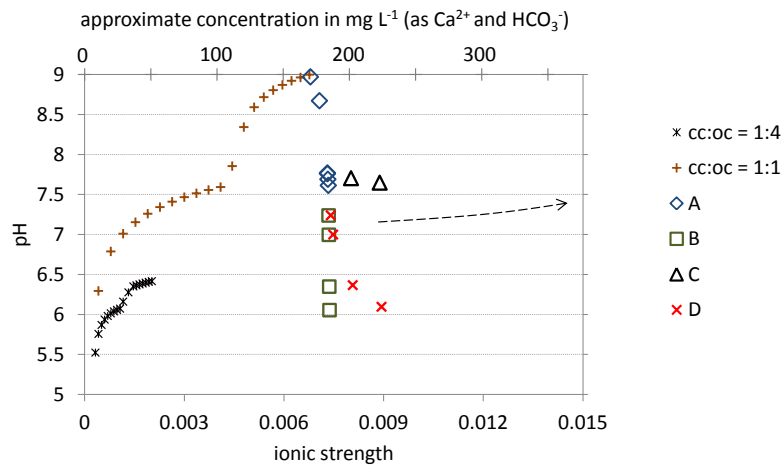


Fig. 7. Results of PHREEQC models using the input parameters given in Table 2. The dashed line on the right shows the general trend of water undergoing continued evaporation.

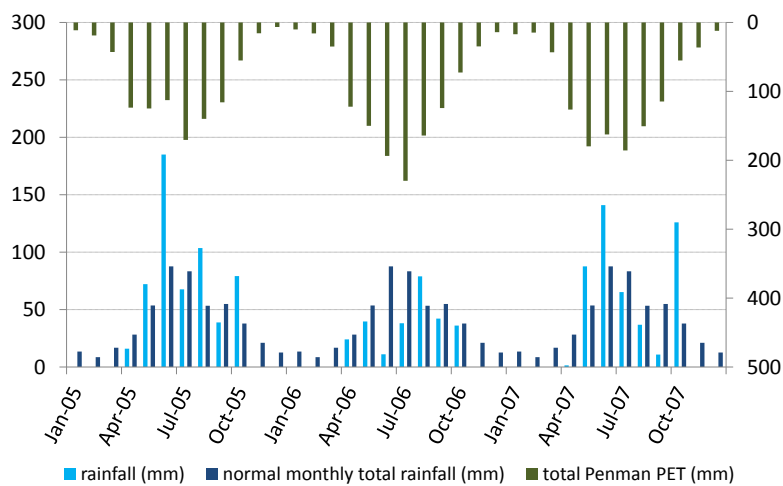


Fig. 8. Precipitation and Penman evapotranspiration records from the Greenbush NDAWN (North Dakota Agricultural Weather Network, 2012) weather station, approximately 11 km west of Greenbush, Minnesota (48.704°–96.325°, Fig. 1).