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

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Monitoring wetlands with field pH and EC

P. J. Gerla

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

[I◀](#)

[▶I](#)

[◀](#)

[▶](#)

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)



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 ground-water, (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

HSSD

10, 699–728, 2013

Monitoring wetlands with field pH and EC

P. J. Gerla

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



function. For example, climate variability leading to long-term changes in temperature and precipitation generally produces irreversible alteration in water budget or changes in biogeochemical processes (Burkett and Kusler, 2000; Erwin, 2009). Urbanization and expanding land use for agriculture practice can increase the transport of sediment, nutrients, and pesticides into wetlands (e.g., Davis and Froend, 1999; Gleason et al., 2003). Although these alterations can be manifest in many ways, perhaps the earliest and most evident changes occur in the wetland's water balance and water composition.

Carbonate reactions, controlled by the interaction of atmospheric, biologic, and soil/substrate processes in the presence of wetland waters, commonly buffers pH and moderates dissolved mineral concentration, thus creating the foundation on which wetland biogeochemical processes proceed (e.g., Almendinger and Leete, 1998; Grootjans et al., 2006). The spatial extent and zonation of these reactions can vary in scale from a single wetland (Almendinger and Leete, 1998) to sub-continental (Gorham et al., 1983).

In a carbonate-dominated geochemical system, the following processes exert significant control on water composition:

- a. dilution of evolved wetland and substrate water by meteoric water,
- b. reaction of calcite (CaCO_3) and other carbonate minerals with either evolved or meteoric water,
- c. loss of oxygen and chemical reduction by reaction with organic matter,
- d. buffering of the wetland water and saturated substrate by CO_2 gas that is generated through biological activity and the oxidation of organic matter,
- e. loss of water through evapotranspiration.

Therefore, in many wetlands, and especially calcareous wetlands characterized by carbonate-rich substrate and Ca-Mg- HCO_3 -type waters (Hem, 1985), geochemical processes and mechanisms can be revealed at various scales by observing pH, electrical conductivity, and oxidation-reduction potential (ORP). These processes indicate

Monitoring wetlands with field pH and EC

P. J. Gerla

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



the buffering capacity and the potential for the wetland to be affected by external factors such as climate variation and changes in nearby land cover. Furthermore, numerical models can provide a framework and convenient means to both characterize wetland water budgets and predict changes in hydrological regime (Šimůnek et al., 2008) and biogeochemical processes (Frei et al., 2012), but have been applied rarely in wetland research.

This report demonstrates how basic, easily obtained field measurements can be combined with numerical geochemical modeling to reveal hydrological processes occurring at local and landscape scale. Three years of routine field measurements at 48 wetland sites in the Tallgrass Aspen Parkland ecoregion of northwest Minnesota show how this monitoring and modeling framework can be applied and implemented in practice. Periodic measurement of pH, electrical conductivity (EC), temperature, and estimate of ORP at established monitoring points in wetlands are shown to define the controlling geochemical processes and the potential for alteration of these processes by changes in land use and wetland management. In many instances, low-cost water-quality measurements can help determine how land use and wetland management affect biogeochemical processes.

2 Methods

2.1 Description of the study site

To demonstrate these principles, wetlands spanning an area extending 60 km north-south by 30 km east-west and lying within the core of the Tallgrass Aspen Parkland (TAP) ecoregion of northwest Minnesota (Fig. 1) were monitored. The parkland is characterized by a humid continental climate, low relief (a few 10 s of meters), and a mosaic of habitat types, including tallgrass prairie, aspen woodland, sedge meadow wetlands, riparian woodland, and oak savanna (Winckler, 2004). In this 1800 km² region, wetlands vary between two end-members: small, isolated pothole wetlands in the former

Monitoring wetlands with field pH and EC

P. J. Gerla

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



**Monitoring wetlands
with field pH and EC**P. J. Gerla

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

sandy beach ridges of glacial Lake Agassiz and large wetlands developed on glacial-lake beds and wave-washed till plains (Fig. 2). The mineral soil substrate for these wetland basins consists of Wisconsinan-age Red Lake Falls Till (Harris et al., 1974). This pebble-loam diamicton contains about 20 % clay, 40 % silt, and 40 % sand and larger-sized clasts. Calcareous material comprises about 32 % of the fine-grained (minus 200 mesh) fraction. Limestone and dolomite make up approximately 66 % of sand and larger-sized particles. The remainder of the till is composed of siliceous fragments and matrix, along with a few percent shale (Harris et al., 1974).

The small pothole wetlands vary from less than 0.1 hectare to several tens of hectares (Fig. 2). Their connection to groundwater is often very good; the potholes create “windows” to groundwater and have a large range of geochemical characteristics depending on their position within the beach-dune landscape, with some on groundwater divides, others at flow-through locations, and a few at discharge sites (e.g. Winter, 1998). In contrast, the much larger glacial lake-bed wetlands (> 1000 ha) generally overlie a meter or less of peat with a few cm of carbonate-rich gravel at the base, which is underlain by clay till with low permeability. These wetlands, except near their margins, rely on precipitation as their source of water. Seasonal evapotranspiration constitutes the main loss of water.

2.2 Sampling and analysis

Water-quality measurements were collected in the field at least five times per year over the course of three years at 48 wetland sites, comprising five broad wetland areas (Fig. 1): (1) Skull Lake Wildlife Management Area (WMA), (2) Caribou WMA, (3) TNC Caribou Township Tract, (4) Twistal Marsh, and (5) Deerwood Marsh. Glacial beach ridge deposits are best developed in Skull Lake and Caribou WMAs, whereas the latter three areas are characterized by lake-plain sediments of glacial Lake Agassiz. Except for a state highway, rural homes, and some pasture along the southeastern margin of Twistal Marsh, none of the wetlands or their surrounding areas have been developed.

Sites were sampled for pH, EC, and temperature using an Extech EC500 portable combination meter and oxidation-reduction potential with an Extech RE300 ORP meter, which were calibrated daily. Measurements were made directly in saturated soils (Faulkner et al., 1989) or much more often in undisturbed water, consistently close to the sediment- water interface during the ice-free seasons of 2005–2007. At each location and for each visit, measurements were made at least five times to test reproducibility and provide for statistical evaluation of variability at each site. EC was corrected for differences in temperature.

Precipitation and weather data were obtained from the North Dakota Agricultural Weather Network, which includes a station 12 km west of Greenbush, Minnesota. It lies near the south-central portion of the area described in this report (Fig. 1) and provides seasonal trends of precipitation and Penman evapotranspiration (Penman, 1948).

2.3 Laboratory analysis

In October 2008, water samples from sites revealing some of the greatest contrast in field parameters were collected and transported on ice to the University of North Dakota's Environmental Analytical Research Laboratory, where the samples were analyzed for major ions, phosphorus, nitrate, ammonium, and carbon (organic, inorganic, and total). While in the field, water sampled for the analysis of major ions was passed through a 0.45 μm filter and acidified for cation analysis. Samples for carbon analysis were similarly filtered and filled without head-space in brown glass bottles. Cations were analyzed by flame atomic absorption spectrometry and anions by ion chromatography. Organic, inorganic, and total organic carbon were determined using an automated carbon analyzer.

These more complete chemical analyses of ten samples (Table 1), selected to represent the variability across the study area, shows that all the waters are of Ca-Mg-HCO₃-type (Hem, 1985) and likely dominated by natural reactions in the carbonate system. Regression of EC and estimated total dissolved solids indicated that EC, when multiplied by 0.6, can be used to estimate total dissolved solid concentration, which

Monitoring wetlands with field pH and EC

P. J. Gerla

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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).

Monitoring wetlands with field pH and EC

P. J. Gerla

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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

Monitoring wetlands with field pH and EC

P. J. Gerla

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

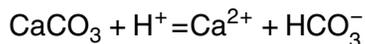
Printer-friendly Version

Interactive Discussion



distribution and scale of wetland types in the ecoregion (Fig. 2). Contours and spot elevations on Fig. 2 are derived from bare ground LiDAR data (International Water Institute, 2012) in wetlands. During periods of normal precipitation and soil moisture, these wetlands are coincident with the surface-water or groundwater saturation elevation, and reveal the pattern of the water table across the terrain. Schematically, Fig. 6a shows a small, isolated beach-ridge wetland receiving groundwater flow from nearby recharge within underlying organic-rich substrate, in addition to a contribution from meteoric water. In Fig. 6b, the wetland interacts with groundwater in a similar way, but the substrate consists of predominantly mineral soil. Finally, the hydrological regime of a large inter-beach wetland developed on sediments of former lake plains may be characterized by shallow, internally circulating groundwater (Fig. 6c) with variable degrees of interaction between underlying organic matter and mineral substrate. Note that the hydraulic gradient diminishes greatly inward from the margin of the wetland (Fig. 2); only the margins of the large wetland receive flow from adjoining uplands, and in some cases these areas have been influenced by human development and activity.

This relationship of the wetland's landscape position to the shallow groundwater flow regime creates a generally characteristic dissolved mineral content, pH, and reduction-oxidation potential for wetland waters. For example, dissolution of calcite in the substrate in the absence of buffers quickly raises the pH of infiltrating soil water through the following reaction:



Thus, wetlands with aerobic, oxygen-rich waters and thin organic horizons can develop an elevated pH with little increase in dissolved solid concentration. In contrast, large wetlands with little groundwater influence (Fig. 6c) are poorly flushed and the water composition develops in response to primarily precipitation and evapotranspiration with minimal, but long-term interaction with substrate. This can create wetland waters with variable pH (depending on the substrate and organic matter content) and elevated concentration of dissolved minerals.

**Monitoring wetlands
with field pH and EC**

P. J. Gerla

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



3.3 Modeling

For wetlands where the substrate is calcareous and carbonate-rich, such as those in the Tallgrass Aspen Parkland, the following processes likely control the pH and dissolved mineral concentration:

- 5 a. Rainwater reacts with various amounts and proportions of (a) organic carbon, (b) carbonate (limestone fragments in till and sediment), and (c) CO₂ gas in wetland sediments.
- b. Periodic flooding and saturation lower the pH through increasing interaction with CO₂ gas (Ponnamperuma, 1972).
- 10 c. Evapotranspiration increases the total dissolved concentration of wetland waters through the loss of essentially pure water to the atmosphere.

Table 2 provides a summary of the input data for the PHREEQC simulation of main reactions likely to occur in the TAP wetlands. Rainfall composition (Table 2) is based on the average of results obtained in Minnesota by Krupa and Nosal (1999). A large range of calcite (cc) to organic carbon (oc) ratios were used initially in the model, with the best correlation to observed pH and oxidation-reduction values for ratios ranging from 1 : 1 to 1 : 4 calcite to organic carbon. Beyond this range, either pH increased far beyond observed values or reduction fell below the measured mV (Table 1).

Initially in the PHREEQC model, 1 kg of rainwater reacts with calcite (cc) and organic carbon (oc) in a 1 : 4 molar ratio, which may represent a condition where a large fraction of the water budget remains out of contact with mineral soil substrate (i.e. Fig. 6a). The wetland functions as a bog with little groundwater interaction (Fig. 6b). A similar but alternate model provides a 1 : 1 ratio of cc and oc in the reaction (Table 2), simulating greater interaction of rainwater with mineral soils and glacial tills in wetlands. For the TAP wetlands, the first model represents processes occurring in small, more isolated beach-ridge wetlands, and to a lesser extent, lake-plain wetlands that have a thick underlying zone of organic matter. The alternate model fits the conditions found in

Monitoring wetlands with field pH and EC

P. J. Gerla

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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.

Monitoring wetlands with field pH and EC

P. J. Gerla

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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 CO₂.

3.4 Oxidation-reduction potential

5 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, per-
10 haps 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
15 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),
20 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
25

Monitoring wetlands with field pH and EC

P. J. Gerla

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



the soil, and therefore the differences in pH, dissolved carbonate species, and cation concentrations of the wetland waters.

4.1 Comparison of monitoring and modeling results

Trends of pH-conductivity measured in the field (Fig. 4) can be related to patterns revealed by PHREEQC models (Fig. 7). Results of repeated measurements at each site during the monitoring period show significant pH and EC clustering within wetland groups across the landscape (Fig. 4):

- a. Although fields of EC and pH data for various wetlands overlap, most analyses fall within a discrete range of values and have maintained their general position (Fig. 2), even under widely varying weather conditions (Fig. 8). For example, both the 2005 and 2007 ice-free seasons were characterized by above normal precipitation, but 2006 experienced below normal rainfall. In addition, Penman evapotranspiration in 2006 was high relative to 2007, and especially so compared to 2005.
- b. Beach-ridge and lake-plain wetlands at Skull Lake WMA show a strong bimodal pattern between very low and moderate EC (< 200 and $250\text{--}700 \mu\text{S cm}^{-1}$).
- c. The small, isolated beach-ridge wetlands at Skull Lake WMA reveal a wide range in pH (5.4–7.6), but have a consistently low EC ($< 150 \mu\text{S cm}^{-1}$).
- d. Unusually large EC occurs in wetlands that show hydrological disruption, alteration, and proximity to potential sources of soluble minerals (Caribou Tract and Twistal Marsh samples with $> 500 \mu\text{S cm}^{-1}$).

By comparing the field monitoring data (Fig. 4) with model output (Fig. 7), the following are possible interpretations for the patterns of pH and EC within the wetlands that were monitored:

Monitoring wetlands with field pH and EC

P. J. Gerla

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



**Monitoring wetlands
with field pH and EC**

P. J. Gerla

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



- a. Small, isolated wetlands at Skull Lake WMA show a large range of pH and conductivity, varying from precipitation-dominated bogs with a low pH and EC (Fig. 6a), to groundwater “windows” characterized by higher pH and EC that developed by significant interaction with soils and mineral substrates (Fig. 6b, c).
- 5 b. Large wetlands at Skull Lake show greater influence of evapotranspiration or perhaps they occur at the more distant end of longer groundwater flow lines. Distinction between these would require more thorough chemical analysis of wetland water samples. Processes related to evapotranspiration would show effects of water loss and fewer changes in the relative abundance of ions. Groundwater interaction with soil and underlying geological materials leads to patterns that show a progressive reaction and trends in the ratios of ions.
- 10 c. The high pH of some of the sample sites in the TNC Caribou Tract (Fig. 4) may suggest early and rapid interaction of infiltration and groundwater with carbonate-rich gravels that lie at shallow depth below the lake-plain wetlands within the tract (Fig. 6c).
- 15 d. Lake-plain wetland waters reveal gradually decreasing pH with increasing conductance, perhaps indicating coupling between greater evapotranspiration and longer interaction with CO₂. The elevated Na and Cl concentration of water sampled at Twistal Marsh (Table 1) strongly suggests road salt/winter deicing on wetland waters because chloride is not found naturally in such large concentrations in the area. (The Twistal Marsh sample site lies within a few hundred meters of state-owned land where snow plows and other equipment are parked). In contrast, sample 2 from the TNC Caribou Tract (Table 1), has almost double the dissolved solid content, but about one-half the concentration of Na and Cl. This sample was
- 20 collected from a wetland site near a ditch, where water accumulates and undergoes evapotranspiration, leading to increased EC.
- 25

**Monitoring wetlands
with field pH and EC**

P. J. Gerla

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

- 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:

- 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?
- Are some wetland types more vulnerable to land-use changes than others?
- 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 $\text{pH} < 6$ and $\text{EC} < 100 \mu\text{Scm}^{-1}$, may fall into this category.

**Monitoring wetlands
with field pH and EC**P. J. Gerla

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

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 adaption 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

hydrogeochemical patterns. Results of modeling indicate that waters in these lake-plain wetlands have undergone greater evapotranspiration and interaction with CO₂. Because of their large size and geochemical heterogeneity, however, external environmental changes will likely cause changes that still fall within the previously existing geochemical range of conditions.

Observations and model results demonstrate that tracking, comparing, and modeling field pH and EC data can reveal wetland geochemical processes, and can also supplement and enhance interpretations based on water-balance observations alone. The measurements are easily done, reproducible, and require minimal equipment, thus providing low-cost information that can indicate a changing physical environment, whether that change results from a regional process such as climate variability or a local influence related to modifications of land cover or land use.

Although not providing a complete view of hydrogeochemical processes occurring in wetlands, simple field measurements, as suggested by the results of this case study, can indicate and reveal processes that may demand greater observation, monitoring, and scrutiny required for successfully managing and protecting wetland ecosystems.

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Monitoring wetlands with field pH and EC

P. J. Gerla

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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**Monitoring wetlands
with field pH and EC**P. J. Gerla

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

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HESSD

10, 699–728, 2013

Monitoring wetlands with field pH and EC

P. J. Gerla

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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HESSD

10, 699–728, 2013

Monitoring wetlands with field pH and EC

P. J. Gerla

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Monitoring wetlands with field pH and EC

P. J. Gerla

Table 1. Results of ion, nutrient, and dissolved carbon analyses of selected water sample sites.

	T °C	pH	EC	mV	Ca	Mg	Na	NH ₄	Cl	NO ₃ -N	SO ₄	IC	Tot P	Rctv P	OC
Caribou WMA	2.2	7.4	354	131	44.0	17.1	5.3	< 0.018	14	ND	ND	53	0.01	ND	18
Deerwood Marsh	2.7	7.1	599	118	79.0	37.1	2.4	0.05	3	< 0.1	8.6	101	0.02	0.02	31
Skull Lake WMA (1)	4.3	6.6	21	179	2.3	1.0	1.2	0.03	0.2	ND	ND	3	0.02	0.01	32
Skull Lake WMA (2)	5.1	6.6	44	143	3.0	1.7	2.0	< 0.018	0.5	ND	1	14	0.06	0.02	35
Skull Lake WMA (3)	6.0	7.3	299	137	43.9	12.2	3.2	< 0.018	7	0.12	1.7	48	0.03	0.01	21
Skull Lake WMA (4)	5.0	7.6	26	116	4.5	1.9	1.0	< 0.018	0.2	ND	2.4	6	0.01	ND	20
TNC Caribou Tract (1)	6.0	8.5	333	126	37.4	19.1	0.7	0.03	1.2	ND	0.3	49	0.12	0.09	11
TNC Caribou Tract (2)	8.5	6.9	2510	92	379	158	22.0	0.07	0.8	ND	1530	128	0.01	ND	19
TNC Caribou Tract (3)	9.4	6.9	1330	87	193	52.1	7.9	0.06	1	ND	433.2	95	0.01	ND	25
Twistal Marsh	2.6	7.3	832	130	107	29.0	57.2	0.05	121	< 0.1	5.1	96	0.08	0.06	26

EC in μScm^{-1} , mV = millivolts, remaining analytes are all in mg L^{-1} , ND – not detected, IC – inorganic carbon, Rctv P – reactive phosphorus, Tot P – total phosphorus, and OC – organic carbon.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Monitoring wetlands
with field pH and EC

P. J. Gerla

Table 2. Model rainfall composition and PHREEQC input data.*Rainfall composition* (adapted from Krupa and Nosal 1999):

temperature = 15 °C, pH = 5.5

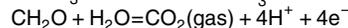
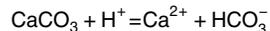
pe in equilibrium with the atmosphere

in equilibrium with CO₂ at 10^{-3.5} atmCa²⁺=0.233, Mg²⁺=0.043, Na⁺=0.038, K⁺=0.033,Cl⁻=0.053, C(4)=0.1, S(6)=1.097 (all in mg L⁻¹)*Initial reactions:*

(a) 1 : 4 molar ratio of calcite (cc) to organic carbon (oc)

(b) 1 : 1 molar ratio of calcite (cc) to organic carbon (oc)

react rainfall with the following reactions:

using 2.5 × 10⁻⁴ moles in 20 sequential steps, for a total of 5 × 10⁻³ moles*Later reactions:*

react the final solution composition from (b) above with –

CO₂(gas) + H₂O = HCO₃⁻ and evaporation of pure H₂O

in seven steps:

path A and C – CO₂ gas reacted: 1 × 10⁻⁸, 1 × 10⁻⁷, 1 × 10⁻⁶, 5 × 10⁻⁶, 1 × 10⁻⁵, 5 × 10⁻⁵, and 1 × 10⁻⁴ molespath B and D – CO₂ gas reacted: 1 × 10⁻⁶, 1 × 10⁻⁵, 1 × 10⁻⁴, 5 × 10⁻⁴, 1 × 10⁻³, 5 × 10⁻³, and 1 × 10⁻² molespath A and B – H₂O lost: 1 × 10⁻⁶, 1 × 10⁻⁵, 1 × 10⁻⁴, 5 × 10⁻⁴, 1 × 10⁻³, 5 × 10⁻³, and 1 × 10⁻² molespath C and D – H₂O lost: 1 × 10⁻⁴, 1 × 10⁻³, 1 × 10⁻², 5 × 10⁻², 1 × 10⁻¹, 5 × 10⁻¹, and 1 × 10⁰ moles

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

I◀

▶I

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



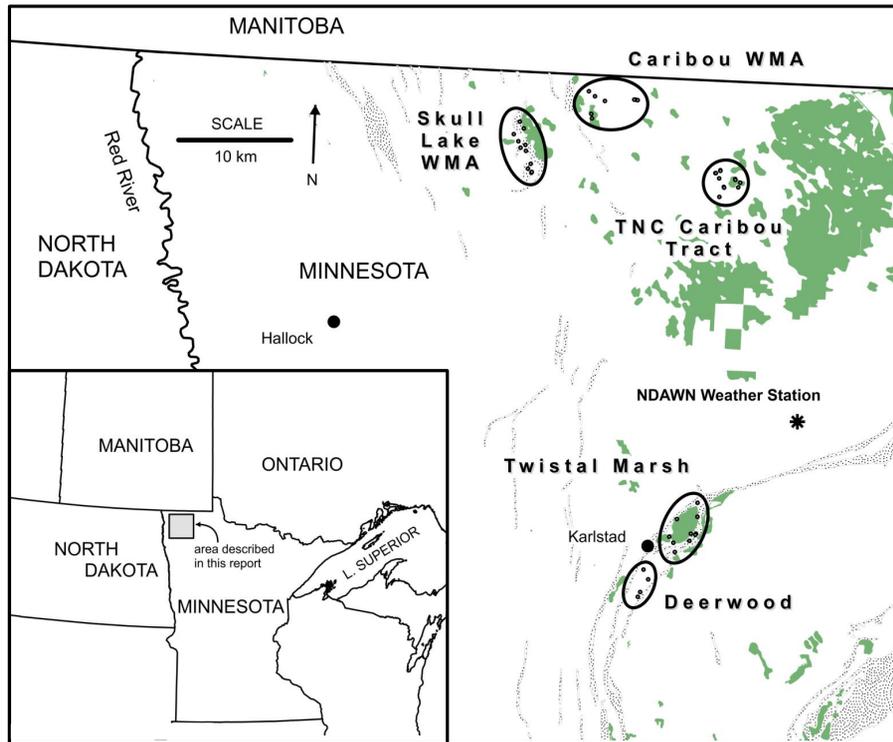


Fig. 1. Map showing northwest Minnesota, US (insert) and the location of wetland sampling sites (ovals and small circles). Beaches associated with glacial Lake Agassiz are stippled; extensive wetland areas are shaded.

Monitoring wetlands with field pH and EC

P. J. Gerla

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



- 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

$$31,371 * I = \textit{approximate concentration in mg L}^{-1}$$

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.

Monitoring wetlands with field pH and EC

P. J. Gerla

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Monitoring wetlands
with field pH and EC

P. J. Gerla

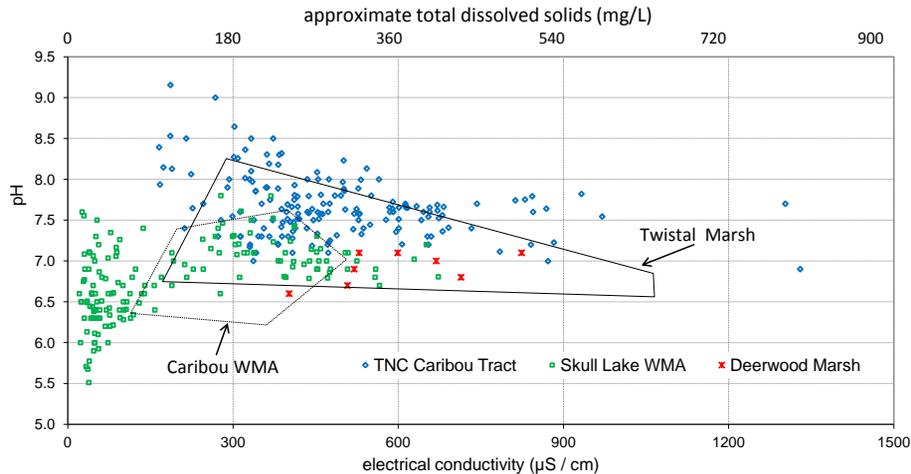


Fig. 4. Scatterplot showing results of pH–EC measurements for the five wetland sampling clusters during the 2005–2007 ice-free seasons. To make the plot easier to read, values for Twistel Marsh (86 measurements) and Caribou WMA (88 measurements) are not shown individually, but delimited by a solid and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

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

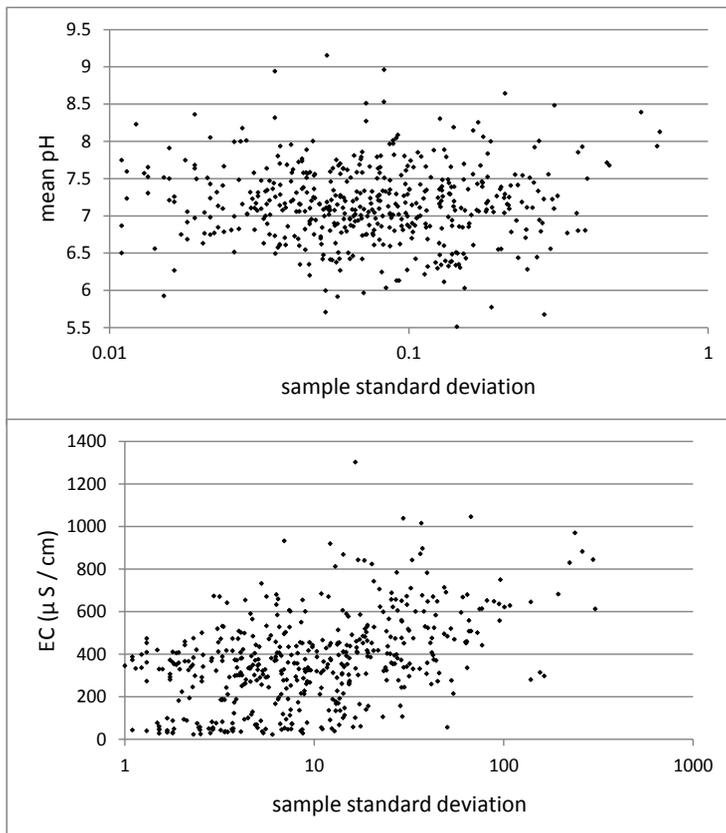


Fig. 5. Scatterplots of sample standard deviation (log scale) versus mean pH and EC. Standard deviation is based on field measurements replicated at least five times for each sample. The standard deviation for pH is based on the log of hydrogen ion concentration.

Monitoring wetlands with field pH and EC

P. J. Gerla

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Monitoring wetlands
with field pH and EC

P. J. Gerla

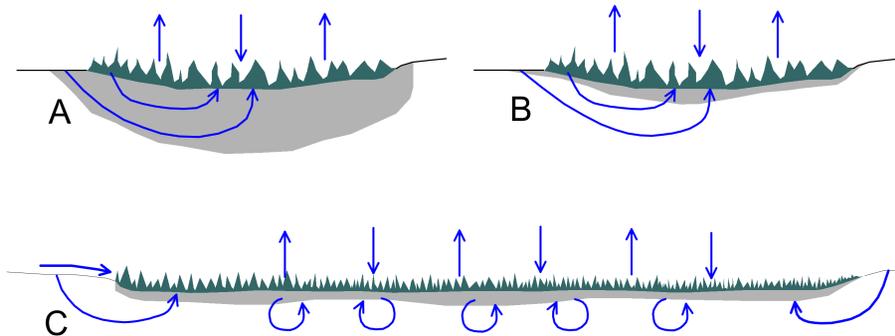


Fig. 6. Sketch showing the general groundwater flow pattern (arrows) in the beach-ridge (**A** – organic substrate and **B** – mineral substrate) and lake-plain (**C**) wetlands. Gray shading shows the distribution of organic-rich soils and peat.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[I◀](#)[▶I](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

Monitoring wetlands with field pH and EC

P. J. Gerla

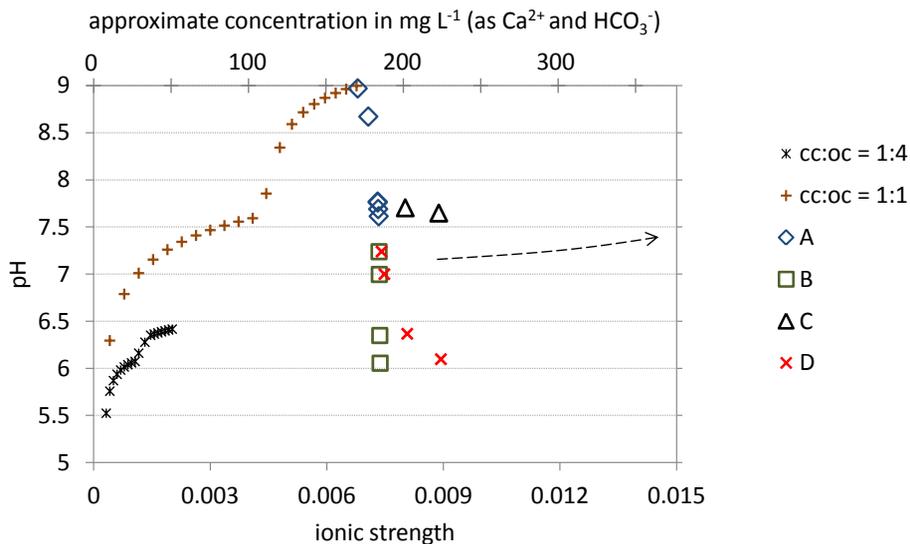


Fig. 7. Results of PHREEQC models using the input parameters given in Table 2. The dashed line on the right shows the general trend of water undergoing continued evaporation.

Title Page

Abstract Introduction

Conclusions References

Tables Figures

◀ ▶

◀ ▶

Back Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



