

Interactive comment on “Can pH and electrical conductivity monitoring reveal spatial and temporal patterns in wetland geochemical processes?” by P. J. Gerla

Anonymous Referee #2

Received and published: 25 March 2013

General Comments: This manuscript attempts to infer the main controls on hydrochemical/hydrologic conditions in a study area in Minnesota from pH and EC measurements. This is a laudable goal given that field electrochemistry allows large surveys of pH and EC to be performed relatively quickly and affordably in contrast to many other types of analyses. The methods draw from simple reaction stoichiometry and some hypothetical equilibrium reaction models. While a reasonable approach in general, the current manuscript is unconvincing because it includes some weak assumptions and poor supporting evidence at critical junctures, and it arrives at rather equivocal conclusions. And while I understand the motivation to keep the analysis as simple as possible, there is a missed opportunity to use the scarce available ion data to their greatest possible

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extent. My main points of suggestion follow:

1. Further develop the hydrochemical conceptual model. The introduction lists five processes that undoubtedly can exert strong influence on distributions of pH and major ions in wetlands, but no information is provided to help rule out the influence of other processes (which are conceptually grouped together as “complicating factors”). Before reducing the discussion to the highly simplified conceptual model based on carbonate minerals, CO₂ and organic carbon, the authors should address whether other processes affecting pH/EC relationships in fact can be safely dismissed. There is contrary evidence in several places. For example, it is assumed that ion exchange does not play a large role on water composition, but the mineral substrate given in the paper lists clay at 20%, and Na/Cl ratios seem elevated for some samples. Also, sulfate is high in some samples and not attributable to carbonates (gypsum? Sulfide oxidation?). Silica measurements are not available but certainly silicate mineral and clay weathering can play a role as well.

2. Explore the reliability of the inferred carbonate/EC relationship. I have several reservations about the current approach based mainly on the steps listed in Fig 3. (The contents of Fig 3 should be embedded in the text rather than a figure). For one, the charge balance considers the carbonate system only, whereas it is clear from Table 1 that other ions will affect it in this settings (SO₄²⁻ and Mg²⁺ especially; possibly organic acids; K⁺ not reported; also possibly CO₃²⁻ could become relevant at the higher range of pH values found in the study area). Second, EC/TDS relationships can vary significantly with water type and need to be confirmed locally.

3. Better constrain the numerical model. It appears that several important parameterization decisions were not well substantiated by field data. Perhaps it would help to discuss the previous results referred to in text (Krupa and Nosal 1999) but at present it appears that the model is both highly idealized and poorly constrained. Can availability of various carbon sources be constrained with mass balance? Can saturation indices of field data help to constrain the role of inorganic weathering processes (especially

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calcite)?

Specific comments: p. 703, lines 9-18, wetland characterization: This paragraph describes the differences between the 'pothole' wetlands and the larger lakebed wetlands, including differences in hydrologic regime. However, no references or supporting data collected by the author are provided.

p. 704, line 27, TDS estimation: EC/TDS regression slope should be established locally if possible. It is not clear from the text whether this was done.

P. 07, indicate the solution charge balance error on Table 1.

p. 705, line 21: The authors assume that rainwater is the starting composition in the hydrochemical progression of the wetland waters. However, the small wetlands are well connected to groundwater, which could be of a very different composition of rainfall. Therefore, precipitation as a starting composition probably is best suited only for the large, lake plain wetlands.

p. 705, line 25 and figure 3. The authors make an assumption that the relationship between ionic strength and dissolved solid concentration can be approximated, if all of the dissolved constituents are Ca^{++} or HCO_3^- . This is true but does not accurately reflect the measured ion concentrations presented in Table 1.

p. 708, line 10: The author states that evapotranspiration impacts water quality in the wetlands, but there is no attempt to constrain the degree of evapoconcentration outside of the model. Evaporation can strongly affect model results, and so should be constrained. Options might include review of energy balance data, using Cl or Br as an index variable, etc.

Figure 7: The author states that the Phreeqc model uses seven steps to react with CO_2 . However, the figure only illustrates a few of these data points from each run. Perhaps a smaller step size, or showing the ionic strength from each of the 7 steps would make the figure more clear.

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p. 710, like 19: I disagree that the EC and pH from the two types of wetlands vary significantly. There is moderate overlap between the Caribous WMA and the Lake plain wetland results, such that it seems to fit just as closely with the lake plain wetlands as it does with the Skull Lake results.

p. 712, paragraph d, explanation of pH and increasing conductance: The language used (increasing, decreasing) in the first sentence suggests that pH and conductance exhibit a temporal or spatial trend, but temporal trends are not discussed anywhere else in the paper. It would be helpful to see figures illustrating these changes. It would be helpful to know if the increasing conductance is driven by increases in one ion, a few ions, or all ions. Under circumstances of calcite saturation, pCO₂ increase can cause an increase in bicarbonate, and subsequently increase conductance.

Interactive comment on Hydrol. Earth Syst. Sci. Discuss., 10, 699, 2013.

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