

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

Anonymous Referee #1

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This manuscript reports electrical conductivity (EC) and pH measured in a large number of wetlands in Minnesota, USA, and attempts to relate the variability of these parameters to the hydrological condition of wetlands based on physiographical setting. The author uses geochemical simulation of hypothetical scenarios to interpret the data. I agree with the author that EC and pH are readily measured in the field and can provide useful tool for characterizing hydrological condition of wetlands and detecting changes. The ideas pursued in this study are interesting and potentially useful. However, I think that the current manuscript has some fundamental issues that need to be addressed before it is considered for publication.

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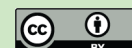
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1. The main result of this study is contained in Figure 4 showing the relation between pH and EC. The author attempts to explain the pH-EC trends based on the location of wetlands shown in Figures 1 and 2, and conceptual sketches shown in Figure 6. However, the manuscript does not show any field evidence indicating how a particular wetland fits one of the settings in Figure 6. I understand that the intent of the paper is to examine the overall pattern, not the detailed hydrology of individual wetlands. However, without seeing the field evidences linking pH and EC to hydrological setting, the reader has no way of knowing how reliable the information is. The manuscript needs to clearly establish the link between pH-EC and hydrological settings supported by field data and observation.

2. It is a good idea to use PHREEQC to simulate hypothetical geochemical scenarios and guide the interpretation of field data. However, the approach used in this manuscript appears to be overly simplified and unrealistic, even for hypothetical simulations. For example, a pure Ca-carbonate system is assumed in simulations, but the data clearly indicate that high-EC wetlands (TNC Caribou 2 and 3, Table 1) are strongly influenced by sulfate dissolution. How does the presence of other ions affect pH-EC relation? Calcite dissolution is modeled by specified mass input rates without consideration of equilibrium with mineral phases. It appears (Page 703, Line 5-7) that the sediments in contact with water have plenty of carbonates. As more mass is added, does the system reach saturation with respect to calcite? How does the modeled CO₂ partial pressure compare with the values calculated from the data shown in Table 1? Reaction rate for CO₂ input is arbitrarily set as the same as calcite dissolution or four times higher than calcite dissolution. Are these CO₂ input rates realistic in comparison to net primary production (photosynthesis minus respiration) in similar wetland systems reported in the literature? These questions need to be carefully examined and discussed.

3. A large body of literature exists on the geochemistry of prairie pothole wetlands, which likely share common features with many of the wetlands in this study. They

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have identified the effects of hydrological setting on wetland chemistry and its inter-annual variability (e.g. Rozkowski, 1967; LaBaugh, 1989; Euliss et al., 2004), and examined key geochemical processes (e.g. Heagle et al., 2007). In a more general scope, combined effects of geochemical processes and evaporation have been studied by numerous researchers (see Drever, 1988, p.232). I think that the current manuscript is missing the review of relevant literature. It will be useful to review key concepts and place this study in context of existing knowledge and gaps.

I also have more specific comments.

4. Page 703, line 10. "Connection to groundwater is often very good". What does this mean? Can it be more specific?
5. Page 704, line 3. How was the ORP meter calibrated?
6. Page 704, line 3. "Directly in saturated soils". What does this mean? Was the probe in direct contact with soil?
7. Page 704, line 24. Where are these sampling points? Please show the location in Figure 1 or 2.
8. Page 704, line 25. Some of the samples have high SO₄ concentration, and are not of Ca-Mg-HCO₃ type.
9. Figure 3. This is not a figure. Please explain this procedure in the texts.
10. Page 705, line 25. I do not think the procedure in Figure 3 accurately indicates what PHREEQC does. The program performs the speciation of carbonate species and ion coupling using a more sophisticated algorithm.
11. Page 706, line 26. Were field measurements "replicated" on the same day, or different days during 2005-2007?
12. Page 707, line 5-12. How were these conceptual models developed? Were these based on field measurements? Which of the ten wetlands listed in Table 1 belong to

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each setting? How was that verified?

13. Page 708, line 15. As I understand, CO₂ is added to the system at a specified rate in this simulation. Therefore, it is a bit misleading to state this as organic carbon. Organic carbon input would be added as a product of redox reaction involving an organic carbon species such as CH₂O (see PHREEQC documentation).

14. Page 710, line 6-7. How were the redox reactions modelled in PHREEQC?

15. Page 712, line 16. Which points in Figure 4 does this refer to? I do not see gradually decreasing pH with increasing EC in Figure 4.

References

Drever, J.I., 1988. The geochemistry of natural waters, 2nd ed. Prentice-Hall.

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