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Biogeosciences Discussions

Interactive comment on "Effects of pH on aquatic biodegradation processes" *by* R. F. Krachler et al.

Anonymous Referee #1

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The overall aim of this paper is to study Lake Neusiedler See, a large alkaline lake that is shrinking due to infilling with peat. The authors aim to investigate the causes of the infilling by measuring the dependence of leaf detritus mineralization on pH and by examining changes in water chemistry (pH, alkalinity, salinity). They suggest that changes in pH, related to changes in carbonate alkalinity and salinity, are responsible for the increased infill of the lake. Unfortunately, I cannot recommend publication of this paper because I do not believe that this hypothesis can be tested with the data presented, and I do not believe that the conclusions are adequately justified by the data and analyses presented in this paper.

General comments:

(1) The authors state in the abstract (Pg. 492, Lines 9-16) that the plant litter was dissolved in a two-step processes, first forming humics, which are then mineralized

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Interactive Discussion
Discussion Paper

to CO2 in the water column. However, no data is presented to justify this conclusion other than discoloration of the aqueous solutions with degrading leaf litter, which is apparently assumed to be composed of humics. Further, the authors conclude that the humics are exported by wind-driven circulations and are then incorporated into the lake foodweb. Again, no data are presented to support these conclusions. All of the data presented is averaged over spatial (and temporal) scales. There is no measurement pertaining to, and not even any discussion of, wind-driven circulation of the lake.

(2) Another conclusion of this paper (Pg. 492, Lines 21-23) is that the lake had an 'original' (and it is not at all clear what this means: preanthropogenic? 10 years ago? 100 years ago? 1000 years ago?) salinity and alkalinity 70-90% higher than present conditions. Again, I do not believe that this statement can be justified by the data and arguments presented in the paper.

(3) The authors further conclude in the abstract (Pg. 492, Lines 23-25) that there is a causal connection between low pH, slower litter biodegradation rates and increased accumulation of peat in the basin. This is a remarkably naïve interpretation of their scanty experimental data. They do not consider any of the myriad possible reasons for changing infill rates, including changes in organic matter deposition rates, nutrient chemistry, physical transport changes, etc.

(4) The authors do not adequately cite relevant literature. The first line of the abstract (Pg. 492, Line 2) states that 'little is known' about the pH-dependence of organic matter mineralization in aquatic environments. No references are cited discussing pH dependence of organic matter degradation. This is hardly an area of no research - just a quick search using terms like 'organic matter mineralization'and 'pH dependence' on Web of Science yields many references.

(5) Although a large amount of data seems to have been collected, hardly any is shown in the paper.

Specific Comments: Pg. 492, Line 2: pH-stimulated is a strange term. Do you mean

BGD

6, S55–S60, 2009

pH-dependent? Or are you specifically referring to do you mean high pH, low pH, oscillating pH? Just pH-stimulated doesn't have any meaning

Pg. 492, Line 16: When did abrupt shrinkage of the lake begin?

Pg. 493, Line 2: Is it necessarily true that decreasing pH will inhibit organic matter mineralization? Can you cite references to support this statement?

Pg. 493, Line 8: 'salt-affected' is a strange term - replace with 'saline'

Pg. 493, Line 9-10: over what pH range?

Pg. 493, Line 18: Replace 'At present' with information regarding when shrinkage began

Pg. 494, Line 16: What is REM? It looks like an SEM image (scanning electron microscope)? Please define acronym.

Pg. 495, Line 17: Can you safely assume that nothing else is contributing to the total alkalinity, e.g. organic matter?

Pg. 495, Lines 24-25: Can you provide information on the sampling times? Were these measurements made monthly at each station? Were measurements concentrated in certain seasons or spread evenly through the year?

Pg. 496, Line 2-4: I'm not sure how (or why) you convert to a reference water level? This needs to be clarified.

Pg. 496, Line 8: The phrase 'ionic relationships and concentrations' is rather vague

Pg. 496, Lines 8-10: What about the role of precipitation and dissolution reactions?

Pg. 496, Lines 8-10: How do you know that the main controls on dissolved CO2 are respiration, photosynthesis and wind turbulence? Can you cite a reference to back this statement up?

Pg. 496, Line 21: Why do you say the values are approximate? Are these standard

BGD

6, S55–S60, 2009

Interactive Comment

state values for 25°C and 1 bar? This should be stated. How much error will be introduced by using 25°C data? What is the actual average lake temperature? How much does it fluctuate?

Pg. 496-7, Equations 1: This is pretty basic textbook geochemistry. I'm not sure it's really necessary to reproduce the equations here.

Equations 1: Are you sure that these are the only ions contributing significantly to charge balance (i.e., you are assuming negligible DOC, phosphate, nitrate, etc.?)?

Pg. 497, Line 6: You should explicitly state what you are solving for: H+, OH-, Ca+2, HCO3-, CO3-2 and H2CO3, I assume? Why do you solve for Ca+2 concentration when this was measured (Pg. 495, Line 16)?

Pg. 497, Line 7: What is the actual ionic strength of this alkaline lake? How far from unity are the activity coefficients actually going to be? What kind of uncertainty will this introduce into your calculations?

Pg. 498, Lines 2-9: The point of this experiment is not clearly explained. I don't understand how this is relevant to averaged changes in the lake chemistry with time. Do you have evidence that the only processes influencing the lake are evaporation and dilution? This seems very unlikely, since you also have changes in discharge to the lake. What about runoff of nutrients in the lake?

Pg. 498, Line 17-18: How much water is lost during evaporation? How does replacing this water with ultraclean water change the solute concentrations? How does the nutrient chemistry change as the experiment progresses over the 5 week period? Are these experimental conditions really relevant to the lake? I assume that changes in the lake chemistry will reflect more than simple evaporation and dilution with ultrapure water.

Pg. 498, Line 17: Why do you now choose 15 C when above you were using 25 C to do calculations?

BGD

6, S55–S60, 2009

Pg. 499, Lines 3-6: How do you know that pH changes in the lake are due to dilution? You have only shown that this is true (as it must be) in a laboratory experiment where you subject lake water only to dilution/evaporation. Furthermore, comparing Figure 4 and table 2 shows that the actual change in EC of the lake is much less than in the experiment (corresponding to a pH shift of at most 0.2 units). It also appears that a 'typical lake' pH of $>$9 corresponds (on Figure 4) to an EC that is not in good agreement with the measured EC for the lake.

Pg. 499, Line 7-8: Again, I don't understand what is meant by converting Na+ concentration to a common reference water level.

Pg. 499, Line 24: The inference regarding controls on K+ concentration is quite speculative (at a minimum, some citations should be provided to justify this inference).

Pg. 499, Line 26-27: What evidence is there that this trend can be extrapolated into the future?

Pg. 500, Line 2: sensitivity, not sensibility

Pg. 500, Lines 3-7: What would cause these dramatic shifts in sodium carbonate/sodium sulphate levels?

Pg. 500 Lines 9-17: What justification can you provide for this scenario?! This is much too speculative.

Pg. 500, Lines 25-1: How do you know they are humics? Why don't you show the DOC values? Why not show the molecular weight data?

Pg. 501, Lines 2-3: Is this surprising? Presumably, your other experiments included the indigenous bacteria, but this was likely a sterile solution.

Pg. 501, Lines 9-10: You have not shown any rain or snowmelt data to back this inference up.

Pg. 501, Line 13-15: Again, I see no justification for the extrapolation of the trends

BGD

6, S55–S60, 2009

Interactive Comment

which was apparently used to come to this conclusion.

Pg. 501, Lines 16-17: What do you mean by 'chronically over-diluted' Relative to what? I also do not see sufficient evidence here to suggest that the pH is controlled by dilution.

Pg. 502, Lines 1-8: I don't believe it follows that because a microbe has been isolated from this lake which has optimal growth at higher pH and salinity necessarily means that the lake used to be more alkaline and saline.

Pg. 502, Lines 9-14: I do not understand why none of the DOC data is shown, and furthermore, I don't understand how you can make inferences about humics in the laboratory experiment (let alone in the lake) just by looking at the color of the water.

Pg. 502, Lines 18-27: There is no data shown in this paper that can be used to draw conclusions regarding wind driven transport of solutes.

Figures: Figure 1: Is dark grey area reed belt and light grey open water? Needs to be stated in figure caption (looks like it is labeled as such in Figure 2, just not in Figure 1).

Figure 3: This figure does not contribute much to the paper and should be deleted.

Figure 5. There are many less datapoints on this graph then were actually measured according to methods, so which are these? How were they chosen? Caption hypothetical', not hypothetic.

Figure 6: Should state in the caption that there are no discharges after 2000.

Interactive comment on Biogeosciences Discuss., 6, 491, 2009.