Biogeosciences Discuss., 6, S78–S89, 2009
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Biogeosciences Discussions

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

R. F. Krachler et al.

Received and published: 8 February 2009

We thank anonymous referee #1 for comments and criticism. We'll try to answer to the comments.

General comments:

(1) ". . . apparently assumed to be composed of humics." These substances have been identified as humics. Reference: Reitner, B., Herndl, G. J. and Herzig, A.: Role of ultraviolet-B radiation on photochemical and microbial oxygen consumption in a humic-rich shallow lake. Limnol. Oceanogr. 42 (5), 1997, 950-960.

". . . the authors conclude that the humics are exported by wind driven circulations and are then incorporated into the lake foodweb. No data are presented to support these conclusions." The fate of humic substances in Lake Neusiedler See has been described earlier. Reference: Reitner, B., Herzig, A., and Herndl, G. J.: Dynamics in bacterioplankton production in a shallow, temperate lake (Lake Neusiedl, Austria):

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Evidence for dependence on macrophyte production rather than on phytoplankton. Aquatic Microbial Ecology 19 (3), 245-254, 1999.

"There is no measurement pertaining to, and not even any discussion of, wind-driven circulation of the lake." This phenomenon in Lake Neusiedler See has been studied extensively. References: Jungwirth, M.: Currents, p. 85. In H. Löffler [ed.], Neusiedlersee, Limnology of a shallow lake in Central Europe. Dr. W. Junk bv Publishers, The Hague, 1979.

Stalzer, W. and Spatzierer, G.: Wind- und Strömungsverhältnisse im See, Wissenschaftlichen Nachrichten aus dem Burgenland, issue 77, pp. 165-177, Eisenstadt, 1987.

(2) ". . .original salinity and alkalinity": Before Hansag Channel was constructed (before 1900) Reference: Weisser, P.: Die Verschilfung des Neusiedler Sees. Umschau 73, 440 - 441, 1973.

(3) "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." The change in organic matter deposition rate is the topic discussed in the present paper. In Lake Neusiedler See, nutrient availability increased during 1950 through 1980, and since then declined due to a better wastewater management. There seems to be no correlation between nutrient availability and the observed continuous progression of the reed belt. Infill due to physical transport is negligible.

(4) "A quick search on Web of Science yields many references" ... however, to the best of our knowledge, none regarding pH dependent mineralization in aquatic environments. Please cite references.

(5) "Although a large amount of data seems to have been collected, hardly any is shown in the paper." On demand the authors will submit the complete data set (about 50000 single measured values).

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Specific comments: Pg. 492, Line 2: We'll try to find a better term

Pg. 492, Line 16: "When did abrupt shrinkage of the lake begin?" The abrupt shrinkage of Lake Neusiedl started with the installation of Hansag Channel at the beginning of 20th century. Reference: Weisser, P.: Die Verschilfung des Neusiedler Sees. Umschau 73, 440 - 441, 1973.

Pg. 493, Line 2: "Is it necessarily true that decreasing pH will inhibit organic matter mineralization?" Reference: Curtin, D.; Campbell, C.A.; Jalil, A.: Effects of acidity on mineralization: pH-dependence of organic matter mineralization in weakly acidic soils, Soil Biology & Biochemistry, Volume: 30, Issue: 1, Pages: 57-64, 1998.

Pg. 493, Line 8: 'salt-affected' will be replaced with 'saline'.

Pg. 493, Line 9-10: pH range: 6.0-10.0

Pg. 493, Line 18: "Replace 'at present' with information regarding when shrinkage began." Shrinkage began when Hansag Channel was built at the beginning of 20th century. During 1901-1995 the lake (at water level 115.5 m MSL) lost 29.2% of its volume. Reference: Bacsatyai, L., Csaplovics, E., Márkus, I., and Sindhuber, A.: Digitales Geländemodell des Neusiedler See-Beckens. Wissenschaftliche Arbeiten aus dem Burgenland 97. Burgenländisches Landesmuseum, Eisenstadt, Austria, 1997.

Pg. 493, Line 16: REM means "Rasterelektronenmikroskop" and will be replaced by "SEM".

Pg. 495, Line 17: "Can you safely assume that nothing else is contributing to the total alkalinity, e.g. organic matter?" Other components can be ignored since they are present in negligible quantities, as has been shown by Berger and Neuhuber (1979). Reference: Berger F, Neuhuber F. (1979) The hydrochemical problem, p. 89. In H. Löffler [ed.], Neusiedlersee, Limnology of a shallow lake in Central Europe. Dr. W. Junk bv Publishers, The Hague, 1979.

Pg. 495, Line 24-25: Samples in general were collected and analyzed monthly around

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the year at all stations.

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

"Why convert to a reference water level:" Fig. 4 gives the relation between average water level above MSL (Adriatic Sea) and water volume of the lake. For exact investigations an average water level has to be computed of a total of 7 experimentally measured levels as very frequently wind driven shifts of lake water (seiges) give rise to water level deviations up to several decimetres at different sites of the lake at the same time. Generally during a one-year period mean water levels vary between a high water level in spring to a low water level during autumn. E.g. in 2007 maximum water level extended to 115.60m MSL in March 2007, whereas minimum water level (during August 2007) was as low as 115.30m MSL. According to the relation given by Bacsatyai et al. (1997) (Fig. 4) these water levels refer to a maximum water volume of 244.18 millions m3 in March 2007 and a minimum water volume of 167.98 millions m3 in August 2007. It is now easy to understand, that without any change of the salt load of the lake solely due to evaporation starting from March 2007 up to August 2007 concentrations of sodium Na+ or chloride Cl- have increased by the factor 1.45. On the other hand, during autumn and wintertime, declining of concentration values by rising water levels due to precipitation (snow- and rainwater) occurs on the same order. What we want to show is that regardless of these changes in concentration due to changes of volume by precipitation and evaporation, salinity of Lake Neusiedler See increases by long-term accumulation as Lake Neusiedler See primordially is an endorheic system. This is why we had to convert all measured concentration data to a reference water level. As a reference level we have chosen 115.40m MSL (Adriatic Sea).

"How convert concentrations measured at level xm MSL (Adriatic Sea) to the reference water level of 115.40m MSL (Adriatic Sea):" Just calculate the ratio of the lake's water volume at water level xm MSL (Adriatic Sea) and the lake's water volume at reference water level 115.40m MSL (Adriatic Sea) (=191.26 millions m3) and apply as a conversion factor to concentrations at water level xm MSL (Adriatic Sea).

Pg. 496, Line 8: "The phrase 'ionic relationships and concentrations' is rather vague" will be replaced by 'ionic relationships and concentrations particularly of homogenous and heterogenous carbonate buffer systems'.

Pg. 496, Line 8-10: "What about the role of precipitation and dissolution reactions?" Every pH control by heterogenous buffering implies dissolution and precipitation reactions.

Pg. 496, Line 8-10: "How do you know that the main controls on dissolved CO2 are respiration, photosynthesis and wind turbulence?" Please consult e.g. the following reference: Loewenthal, R.E. and Marais, G.v.R. (1976), Carbonate Chemisty of Aquatic Systems: Theory and Application. Ann Arbor Science Publishers Inc., Michigan., pp 3-8.

Pg. 496, Line 21: "How much error will be introduced by using 25°C data? What is the actual average lake temperature? How much does it fluctuate?" Water temperatures in Lake Neusiedler See are influenced by its shallowness and by the high frequency of strong winds, which thoroughly mix the water. The mean water temperature during the summer months (May-September) (measured in 20-30 cm depth) is 20°C. Water temperatures fluctuate between 4°C and 32°C throughout the whole year. Reference: Dobesch, H., and Neuwirth, F., Climatic Conditions, p. 60. In H. Löffler [ed.], Neusiedlersee, Limnology of a shallow lake in Central Europe. Dr. W. Junk bv Publishers, The Hague, 1979.

Pg. 496-497, Equations (1): "I am not sure it's really necessary to reproduce the equations here." These equations contain the key information about the equilibria and charge balance considered in our simplified model.

Pg. 496-497, Equations (1): "Are you sure that these are the only ions contributing significantly to charge balance?" The accordance of the calculated curve with experi-

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mental data (Fig. 5) seems to justify our approach.

Pg. 497, Line 6: "You should explicitly state what you are solving for: H+, OH-, Ca2+, HCO3-, CO32- and H2CO3, I assume?" Yes, you are right. "Why do you solve for Ca2+ concentration when this was measured?" The concentration of Ca2+ is controlled by the carbonate concentration and therefore serves as a variable and cannot be used as an input parameter.

Pg. 497, Line 7: "How far from unity are the activity coefficients actually going to be? What kind of uncertainty will this introduce into your calculations?" Calculated activity coefficients (using Debye-Hückel theory) are fm(monovalent cation)=0.9, fd(divalent cation)=0.7. However, the effect on the species distribution of the carbonate system is rather small, and we decided to use activity coefficients fi=1 in this simplified model. References: Loewenthal, R.E. and Marais, G.v.R. (1976), Carbonate Chemisty of Aquatic Systems: Theory and Application. Ann Arbor Science Publishers Inc., Michigan., p. 93. Stumm, W. and Morgan, J. (1995): Aquatic Chemistry, Chemical Equilibria and Rates in Natural Waters. Environmental Science and Technology: Wiley-Interscience Series of Texts and Monographs.

Pg. 498, Lines 2-9: "The point of this experiment is not clearly explained. I don't understand how this is relevant to average 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?" The main processes influencing the lake on the time scale of weeks or months are evaporation and dilution. 116% of the lake's volume (at water level of 115.40m MSL) evaporate during one year (see water balance below). Inflows into the lake contribute dissolved salts and nutrients, but these inflows are small-sized and may influence the lake's chemical composition on the time scale of years. The present paper deals with the depletion or accumulation of salts, respectively, and shifts in the composition of salts in the lake basin on the time scale of years. In Lake Neusiedler See, nutrient concentrations increased during 1950 through

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1980, and since then declined due to a better wastewater management.

Water balance of Lake Neusiedler See, based on mean values in the time span 1967 - 1998. (millions m3 y-1):

Precipitation falling on the lake's surface: + 202.5

Surface + subterranean inflows: +45.7

Evaporation: -222.8

Discharge through Hansag Channel: -23.8

Subterranean outflow: -1.6

Volume of the lake at water level 115.40m MSL (millions m3): 191.26

Reference: Plattner, J.: Ökodynamische Rehabilitierung des Neusiedler Sees: Hydrologie-Quantität, Bericht. Landeswasserbaubezirksamt Schützen/Gebirge, Austria, 2004.

Pg. 498, Lines 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?" Approx. 60mL of water have been lost and replaced by ultraclean water during 5 weeks. There was no change in the solute concentrations since the total volume of 1000mL continuously was kept constant. The nutrient concentrations have been monitored and did not change substantially over the 5 week period: c(NO3-N) varied between 51μgL-1 - 82μgL-1 c(P-total) varied between 44μgL-1 - 148μgL-1

Pg. 498, Line 17: "Why do you now choose 15°C when above you were using 25°C to do calculations?" In order to minimize evaporation during the experiment.

Pg. 499, Lines 3-6: "How do you know that pH changes in the lake are due to dilution?" We never have claimed every change in the lake's pH being due to changes in dilution.

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But of course every change in dilution results in a corresponding change of equilibrium pH as is shown in Fig. 5.

"Furthermore, comparing Fig. 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)." We suppose you mean Fig. 5 instead of Fig. 4. Table 2 shows mean EC values converted to reference water level 115.40m MSL (Adriatic Sea). The raw data varied between 1.8-3.2 mS cm-1. In our experiments, the EC range 0.5- 6.0 mS cm-1 was chosen in order to model future conditions as well. In the past, the lake has survived through great climatic variability. In 1770-1790, extensive areas of the surrounding pastures and cultivated land were flooded. During the years 1866-1870, a period of reduced precipitation led to a complete drying up of the lake. Large amounts of crystalline soda and sodium sulphate accumulated on top of the dry sediment. 1880-1882 rapid refilling of the lake occurred leading to high water levels. One might imagine the wide range of EC the lake faced during its history. References: Dobesch , H. and Neuwirth, F., Water Balance, p. 79. In H. Löffler [ed.], Neusiedlersee, Limnology of a shallow lake in Central Europe. Dr. W. Junk bv Publishers, The Hague, 1979. Moser, I.: Der abgetrocknete Boden des Neusiedler Sees. Jahrb. Geol. Reichsanst., Vienna, 1866.

"It also appears that a 'typical lake' pH of >9 corresponds (on Fig. 4) to an EC that is not in good agreement with the measured EC of the lake." Again, we suppose you mean Fig. 5 instead of Fig. 4. This comment is erroneous. What you can read from the plot in Fig. 5 is that pH=9 corresponds to an EC of 2.3 mS cm-1 which is in excellent agreement with the measured EC of the lake.

Pg. 499, Lines 7-8: "Again, I don't understand what is meant by converting Na+ concentration to a common reference water level." Please see our answer Pg. 496, Line 2-4.

Pg. 499, Line 24: "The inference regarding controls on K+ concentration is quite spec-

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ulative (at a minimum, some citations should be provided to justify this inference)." Reference: Furquim, S.A.C., Graham, R.C., Barbiero, L., Neto J.P.D., Valles, V. (2008): Mineralogy and genesis of smectites in an alkaline-saline environment of Pantanal Wetland, Brazil. Clays and Clay Minerals 56 (5): 579-595.

Pg. 499, Lines 26-27: "What evidence is there that this trend can be extrapolated into the future?" Table 2 shows a delayed recovery of the alkalinity concentration with respect to the other parameters during the period 2000-2007. There is of course no evidence that this trend can be extrapolated into the future, but the actual shift as concentrations of sulphate and chloride increase more rapidly than those of carbonate points to a variability of the lake's chemical characteristics.

Pg. 500, Line 2: 'sensibility' will be replaced by 'sensitivity'.

Pg. 500, Lines 3-7: "What would cause these dramatic shifts in sodium carbonate/sodium sulphate levels?" These theoretical curves have been calculated in order to quantify the sensitivity of the pH to shifts in the ionic ratios.

Pg. 500, Lines 9-17: "What justification can you provide for this scenario? This is much too speculative." The scenario is based on the measured salt accumulation rate during 2000-2007 assuming that the salt accumulation was on the same order of magnitude during the 20th century, and taking into account that, in the past, large floods have taken place which may have removed accumulated salts from the area. This is a conservative estimate.

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?" Please see our answer to 'general comments' (1). Measured DOC values varied between 20 mg L-1 and 40 mg L-1 and did not exceed 40 mg L-1. There was no correlation with pH. Molecular weights were up to 100 kDa. We are currently studying chemical structures and physical properties of aquatic humic substances in our laboratory, however, this is out of the scope of the present work, and will be reported on in the future.

Pg. 501, Lines 2-3: "Is this surprising? Presumably, your other experiments included the indigenous bacteria, but this was likely a sterile solution." We suppose that the reed litter granules contained indigenous bacteria and fungi. In preliminary experiments, where we used sterilized reed litter granules in contact with Lake Neusiedler See water, plant debris decomposition started much later and was slower than in the experiments where we used non-sterilized reed litter (Fig. 8).

Pg. 501, Lines 9-10: "You have not shown any rain or snowmelt data to back this inference up." Please see our answer Pg. 498, Lines 2-9 (water balance of Lake Neusiedler See).

Pg. 501, Line 13-15: "Again, I see no justification for the extrapolation of the trends which was apparently used to come to this conclusion." This comment is erroneous. We did not use any extrapolation of the trends. The mean annual salt accumulation of 14 900 tons per year results simply from our analytical data in the period 2000-2007. (Data fitting by application of linear least squares).

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." 'Over-diluted' means relative to the pristine lake. In Lake Neusiedler See, the pH is controlled by dilution which is a consequence of the presence of soda (sodium carbonate/bicarbonate). Please test and take natural water from the open lake and dilute with rainwater, ultra-clean water, or river water from the inflowing rivulet Wulka, respectively. You will observe a decrease in pH in any case.

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." Not necessarily, but it means that increasing pH would lead to increasing decomposition rates of reed litter which is in excellent accordance with our observations.

Pg. 502, Lines 9-14: "Humics" Please see our answer to Pg. 500, Lines 25-1.

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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." The frequent and well-developed currents in Lake Neusiedler See are primarily the result of wind action. The comparatively small inflows have practically no effect upon the currents in the open lake. Currents due to Coriolis forces and barometric pressure differences between the northern and southern part of the lake, or caused by seiches, can achieve velocities of up to several metres per second. The wind-driven currents in Lake Neusiedler See and the corresponding transport of solutes and erosion of sediments have been studied extensively. References: Jungwirth, M.: Currents, p. 85. In H. Löffler [ed.], Neusiedlersee, Limnology of a shallow lake in Central Europe. Dr. W. Junk bv Publishers, The Hague, 1979. Stalzer, W. and Spatzierer, G.: Wind- und Strömungsverhältnisse im See, Wissenschaftlichen Nachrichten aus dem Burgenland, issue 77, pp. 165-177, Eisenstadt, 1987.

Figures:

Figure 1: "Is dark grey area reed belt and light grey open water? Needs to be stated in figure caption." Will be stated in the figure caption.

Figure 3: "This figure does not contribute much to the paper and should be deleted." The SEM images show suspended carbonate particles in Lake Neusiedler See, providing information about their dimension and shape. The concentration of these small particles is very high, about 5-15 mg L-1, even under ice cover. The presence of these particles makes it possible to calculate the lake-water's pH, since we have to assume thermodynamic equilibrium between solid CaCO3 and the corresponding dissolved ions. In a lake without carbonate turbidity, the above thermodynamic equilibrium would not be established. The water column would either be under-saturated or over-saturated with calcium carbonate, depending on the conditions. In Lake Neusiedler See (as well as in other shallow dilute soda lakes), the suspended CaCO3 particles allow rapid dissolution of CaCO3 on the one hand and provide nuclei for the rapid crystallization of CaCO3 on the other hand. Therefore, due to the presence of the carbon-

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ate particles, we can assume thermodynamic equilibrium, which means that Equations (1) are valid. Reference: Dokulil M.: Optical Properties, Colour and Turbidity, p. 162. In H. Löffler [ed.], Neusiedlersee, Limnology of a shallow lake in Central Europe. Dr. W. Junk bv Publishers, The Hague, 1979.

Figure 5: "There are many less data points on this graph then were actually measured according to methods, so which are these? How were they chosen?" This comment is erroneous. We measured exactly 12 data points at 25°C according to the methods described in section 2.4.

"Caption: Hypothetical, not hypothetic." Thank you, this will be corrected.

Figure 6: "Should state in the caption that there are no discharges after 2000." Will be stated in the figure caption.

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