

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

**R. F. Krachler et al.**

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We thank anonymous referee #2 for her or his constructive criticism that helped to improve the manuscript substantially.

S339. We will rewrite the manuscript thereby including plots of seasonal variations and across-lake gradients of measured chemical components in addition to the trends of overall annual mean values.

a) S342. We agree that the thermodynamic constants used in the pH model should take the salinity variation due to dilution/concentration into account, and we will re-calculate the pH model considering ion pairing constants and free species activity coefficients as suggested by the referee.

2. S341. "While the data seem to be unpublished (or has it been published by Maracek, see caption of Fig. 6?)". From caption of Fig. 6 one can see that K. Maracek, Hydrographic Agency of Burgenland, Austria, measured the water discharge volumes.

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Hydrographisches Jahrbuch von Österreich, 103 (1995)-116 (2008), published by Federal Ministry of Agriculture, Forestry, Environment and Water Management, Republic of Austria. The hydro-chemical data presented in the discussion paper have been measured by one of the authors (A. Herzig) and are unpublished so far.

b) S343: "Their pH model is ill-determined: 7 unknown variable ( $H^+$ ,  $H_2CO_3$ ,  $HCO_3^-$ ,  $CO_3^{2-}$ ,  $OH^-$ ,  $Ca^{2+}$ ), but only 6 equations. This leads to an infinite number of solutions." We do not agree with this comment. The number of unknown variables included in brackets by the referee is 6 (not 7 as has been claimed by the referee). 6 equilibrium equations incorporate 6 unknowns. The theoretical curves in Fig. 5 of the manuscript have been calculated using this pH model.

b) S343. "Instead the authors use the salt ions which are not pH relevant and connect them to the pH model via a charge balance equation." These salt ions show in the first approximation a linear dependence on the degree of dilution and have therefore been chosen as input parameters.

Fig. R1 of the referee report: The referee used the carbonate alkalinity (CA) as input parameter, assuming a linear dependence of the carbonate alkalinity on the degree of dilution. However, in the turbid water column of Neusiedler See, calcium carbonate particles are permanently present (see Fig. 3 of the manuscript). Depending on dilution/concentration, these small particles dissolve rapidly or provide nuclei for carbonate crystallization, respectively. Metastable states of  $CaCO_3$  over-saturation or under-saturation are extremely short-lived in Neusiedler See. Thus the effect of carbonate dissolution/precipitation on the alkalinity and hence pH is substantial and cannot be neglected. The referee's model calculation is therefore inadequate.

Table R1, S342. The referee calculated  $KC_2$  for pure water:  $KC_2=1.7 \times 10^{-11}$ . This is a wrong value. The correct value is  $KC_2=4.68 \times 10^{-11}$ .

c) S344. We agree that natural fulvic and humic acids anions contribute to the alkalinity, and may give rise to deviations of the pH model.

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e) S344. "The shifted response in the alkalinity data can potentially be explained by e.g., carbonate dissolution and the DOC buffering capacity." We think the shifted alkalinity response is more likely connected to low groundwater tables 2001 to 2005 in the catchment area east of the lake which reduced the inflow rates of soda-rich and MgCO<sub>3</sub>-rich springs to the lake, the more so because higher ground water tables 2006 to 2008 are correlated with higher alkalinity values.

4. S 344 "It is obviously not a linear trend, but an S-shape return to a (new) steady state. This shape is characteristic of non-steady state transport-dominated systems and here, the transport is diffusion of salts from the underlying marine sediments (+ dissolution of carbonates). It is uncertain if the values of 2006 + 2007 already reflect the approaching steady state or if the increases in salt concentrations will continue further." We do not agree with this comment. Salt accumulation in the lake basin is definitely not based on "diffusion of salts from the underlying marine sediments" since the underlying sediments are several hundred meters of tertiary freshwater sediments deposited by the Pannonian Lake. Below the open lake area these sediments directly cover the crystalline material which culminates west of the lake in the Leitha mountain range. It is of interest that between the crystalline and the Pannonian cover, sediments of the earlier stages of the Paratethys (brackish Sarmatian and marine Badian) are lacking, although they are present further west and east of the lake area. (A.F. Tauber, *Geologische Stratigraphie und Geschichte des Neusiedlerseegebietes*, Wissenschaftliche Arbeiten aus dem Burgenland 23 (1959), pp. 18-24. A.F. Tauber, *Zur Oberflächengeologie des Seewinkels*, Wissenschaftliche Arbeiten aus dem Burgenland 23 (1959), pp. 24-26. A.F. Tauber, *Grundzüge der Tektonik des Neusiedlerseegebietes*, Wissenschaftliche Arbeiten aus dem Burgenland 23 (1959), pp. 26-31. A.F. Tauber, K. Knie, H. Gams and E. Pescheck, *Die artesischen Brunnen des Seewinkels im Burgenland*, Wasser und Abwasser 1958 (1958), pp. 226-279. H. Löffler, *Neusiedler See*, Dr. W. Junk by Publishers The Hague-Boston-London 1979, p. 33) The main sources of soluble salts to the lake are inflows (e.g. creek Wulka). Provided the sluice gate to Hansag Channel is closed as it was during 2000 to 2008, the lake has no outlets and its most important

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feature is the salt accumulation within the lake basin by evaporation, which should follow a linear trend so long as the lake has no outlets and the inflows provide a nearly constant salt flux into the lake. Given the diluted state of the lake and provided that no precipitation occurs, it is clear that the soluble salt concentrations in the water column should more or less follow a linear trend. Fig. A1 (Figure not displayed: PDF sent to Editor) shows an update of Fig. 7 of the discussion paper including the new data of 2008. The new data do not support the supposed "S-shape".

4. S 345 line 8: "discharge by itself cannot change the salt/alkalinity content of the lake water at all!" We do not agree with this comment. It is widely accepted that endorheic drainage basins are a requirement of inland saline lakes. U.T. Hammer (Saline Lake Ecosystems of the World, 1986, Springer Netherland) pointed out that inland saline waters are very discrete in that they have no outlets. With an artificial outlet, the lake is no longer an endorheic system and its salts are lost in outflowing waters (discharge).

8. S346. "the experiments only reproduce the results of Hietz et al. (1991)." We do not agree with this comment. We measured (for the first time!) the dependence of reed litter biodegradation on dilution/concentration of the lake. In contrast, Hietz et al. (1991) measured reed litter biodegradation rates along a transect from the reed belt to the open lake.

7. S 346. "What is the effect of peat formation on the 115.4 m MSL?" Currently, a new investigation of the bottom of Neusiedler See is in progress and will be published by E. Csaplovics et al. in the future. These specific digital terrain data are of great value for a better understanding of the lake and will be used in the revised version of the present manuscript in order to evaluate the effect of peat formation on the lake volume at water level 115.4 m MSL.

8. S 346. "Is there any correlation of DOC content and pH? Did the pH change during the experiment?" The pH did not change during the experiment. Measured DOC values varied between 20 mg L<sup>-1</sup> and 40 mg L<sup>-1</sup>. There was no correlation of DOC and pH

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during these experiments (pH 8.6 to 9.2). However, DOC values increased as the pH was raised from 9.2 to 10.4 by adding Na<sub>2</sub>CO<sub>3</sub> (data not included in the discussion paper). DOC production at high pH is very likely due to abiotic depolymerisation of high molecular weight lignin. Accumulation of a water soluble lignin polymer (APPL, acid precipitable polymeric lignin) has been reported by Pometto A.L., Crawford D.L., 1986: Effects of pH on lignin and cellulose degradation by *Streptomyces viridosporus*, *Applied and Environmental Microbiology* 52(2): 246-250.

8. S 346. "The investigated pH range is quite limited, though it covers the natural range of Neusiedler See. Nevertheless, other scientists working in environments with lower pH (e.g., coastal areas) cannot extract much from the study." We agree with this comment. However, lower pH than 8.5 would cause considerable stress in the indigenous bacterial community of Neusiedler See and hence the results would not be applicable to other aquatic systems.

S 347 Minor comments: We would like to thank referee #2 for carefully reading and correcting the manuscript. We also thank for comments that made our manuscript more precise.

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

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