

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

### **Anonymous Referee #2**

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The manuscript presents the changes in chemical composition of the water body of the Neusiedler See in Austria from 2000-2007 that result from man-made lake water discharge until the year 2000. Presented are the annual means of the major dissolved salt components as well as the total alkalinity. The basis is a tremendous data set consisting of 500 measurements per year at 37 locations across the lake over 8 consecutive years. In addition, one experiment was conducted investigating the decomposition of reed litter in natural (i.e., unfiltered) lake water at different pH values (between 8.5 and 9.2).

### **Recommendation**

After reading the interesting and well-written abstract, I was really looking forward to this manuscript. Unfortunately, the manuscript dramatically loses its quality from this

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point on. The problems of this manuscript are severe and manifold: scope scientific output, structure of the manuscript, and technical/methodological performance. Overall, it does not fulfill what I would regard as minimum requirements for scientific publications. At best, the manuscript could serve as a data report after some revision.

I, therefore, have to recommend rejection of this manuscript. The rationale of my decision is given below.

Nevertheless, I would like to encourage the authors to either substantially rewrite the manuscript (this requires thorough and comprehensive data analysis, however) or resubmit as data report after some improvements. It would be sad if such an enormous and valuable data set is lost to the scientific community. As a data report it should include the entire data set (or a link/reference where to get the data) together with additional plots of the seasonal variations and across-lake gradients of the measured chemical components, in addition to the trends of overall annual means presented here (see below for detailed comments).

## Major problems

### 1. Acclaimed scope of the manuscript

The title and the abstract are completely misleading:

a) The effects of pH on reed litter decomposition are only presented in 1 very short paragraph (3.3) and in the Discussion section the authors finally reveal that all this has been studied previously (Hietz et al.) and nothing new has been found.

The major part (~90 %) of the paper is about the change in salt/alkalinity change of the lake water after the water discharges through a channel at the south end of the lake have been stopped in 2000.

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b) While most of the acclaimed "conclusions" in the abstract sound logically, none is substantiated and proof is missing in the manuscript. These include: "observation of a 2-step degradation mechanism", "increasing pH accelerated leaching of humics", "2-step mechanism controls carbon flux since large quantity of humics are currently released in the reed belt", "lake is shrinking due to peat formation and has been resistant to silting-up in the past", "substantially lower pH in the present lake", "pH dependence of reed decomposition points at causal connection of low pH and peat formation", "pH stimulated OM remineralization play major role for long-term integrity of saline lake/wetland systems". In the Discussion section, the reader learns that some of these "conclusions" were originally derived by other authors.

## 2. Novelty of presented concepts/ideas/tools/data

Only the annual means of an extremely comprehensive and unique data set are presented. While the data seem to be unpublished (or has it been published by Maracek, see caption of Fig. 6?), no new interpretations and ideas are delivered. Particularly, the discussion only reproduces and summarizes the findings of other previously published papers. As outlined in detail below, the data interpretation by the authors is also inaccurate and, at least in my view, meaningless.

In addition, the experiment on the pH dependence of reed litter decomposition is also not new. Similar experiments have been conducted by other groups, even with similar material from the Neusiedler See (Hietz et al.) as finally stated by the authors in the Discussion section, 4.2). The results presented in this manuscript do not exhibit any new insights into this process, but fall in line with previously published studies.

## 3. pH model

The pH model seems to be inaccurate in several aspects.

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a) The thermodynamic constants used by the authors are approximated (rounded) values for pure water (i.e., infinitely dilute aqueous solutions). While the error on the resulting pH introduced by this rounding is small and negligible (the rounding errors luckily cancel each other out), the effect of salinity on the pH is quite substantial and cannot be neglected. For demonstration purposes, I have re-plotted Fig. 5 of the manuscript using the analytical solution for the pH as a function of  $p\text{CO}_2$  and carbonate alkalinity. Hence, I ignore any effects due to other acid-base systems (e.g, humic + fulvic acids) and calcium carbonate. The result is that the authors choice of thermodynamic constants agrees with the result of pure water ( $S=0$ ), because the rounding errors cancel each other out, but predicts higher pH with respect to the data (taken from their Fig.5). The pH calculated with constants for  $S=1.9$  gives an accurate prediction up to  $\text{EC}=3$  mS/cm. For higher values it predicts a too low pH. Since I used algorithms that are derived for seawater, I also ignore effects of the somewhat different salt composition of the Neusiedler See. This might explain the deviation from the data points at higher salt concentrations.

Constant | Krachler et al. | Pure water ( $S=0$ ) | Lake water ( $S=1.9$ )

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$K_H$ (M/bar)	$3 \times 10^{-2}$	$3.35 \times 10^{-2}$	$3.32 \times 10^{-2}$
$K_W$ ( $\text{M}^2$ )	$1 \times 10^{-14}$	$1.0 \times 10^{-14}$	$1.7 \times 10^{-14}$
$K_{C1}$ (M)	$5 \times 10^{-7}$	$4.4 \times 10^{-7}$	$6.8 \times 10^{-7}$
$K_{C2}$ (M)	$5 \times 10^{-11}$	$1.7 \times 10^{-11}$	$1.8 \times 10^{-10}$
$K_{CaCO_3}$ ( $\text{M}^2$ )	$4.8 \times 10^{-9}$	$3.3 \times 10^{-9}$	$2 \times 10^{-8}$

Table R1: Thermodynamic constants used by the authors compared to those calculated from analytical relations:  $K=f(P,T,S)$ . See Millero (1995, GCA 59(4), 661-677) and Millero (2007, Chem. Rev. 107, 308-341) for state-of-the-art reviews. Input temperature and pressure are  $T=25$  °C and  $P=1$  bar, respectively. The values given in

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Stumm Morgan (1996) are in good agreement with those above calculated for  $S=0$ .

(Figure not displayed: PDF sent to Editor)

Figure R1: Plot of pH vs electric conductivity similar to Fig.5 of the manuscript. The input values for the pH calculation are alkalinity (assumed as carbonate alkalinity, CA) and  $p\text{CO}_2=400$  ppm. The alkalinity of the diluted/concentrated lake water samples are calculated based on  $\text{CA}=12$  meq/L at  $\text{EC}=2.65$  mS/cm (see Tab.1 of the manuscript). The data points were visually taken from Fig.5 and, hence, might bear some inaccuracy. The thermodynamic constants used in the analytical pH model were calculated after Millero (1995+2007) and take the salinity variation due to dilution/concentration into account. Example values are given in Tab. R1 above.

b) Their pH model is ill-determined: 7 unknown variable ( $\text{H}^+$ ,  $\text{H}_2\text{CO}_3$ ,  $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{OH}^-$ ,  $\text{Ca}^{2+}$ ), but only 6 equations. This leads to an infinite number of solutions.

Why not include the definitions of DIC and CA in the model? This would provide 7 equations and they could have used the charge balance equation to independently check the pH model. In addition, the number of input parameters would have been reduced to 2 ( $p\text{CO}_2$  and CA), which are both pH relevant. Instead the authors use the salt ions which are not pH relevant and connect them to the pH model via a charge balance equation. This usually results in inaccurate pH prediction, mainly because  $\text{H}^+$  and  $\text{OH}^-$  concentrations are far below the measurement uncertainties of the salts. In addition, the charge imbalance in the measured salt composition is quite high:  $-2.2$  meq/l (= cations - anions). The authors close the charge balance with  $\text{Ca}^{2+}$  ( $\text{H}^+$  and  $\text{OH}^-$  are negligible in this respect). Why did they not measure  $\text{Ca}^{2+}$  in the lake water to verify/falsify their results?

c) What are the natural humic + fulvic acid concentrations in the lake water? Since the authors report about significant peat formation due to those DOC substances and release during reed decomposition, the concentrations could probably be quite high and thus significantly contribute to the total alkalinity. Hence, their pH buffering capacity is most likely not negligible at all. (This might also add to the deviation at higher salinities in my analytical pH model.)

d) Why did the authors not measure the salt concentrations in the diluted/concentrated water samples to validate and check their model?

e) How valid and meaningful is actually the pH experiment with diluted/concentrated lake water, since alkalinity does not seem to follow the salt trend in the lake, but shows a phase shift (see Fig.7 of the manuscript). The shifted response in the alkalinity data can potentially be explained by e.g., carbonate dissolution and the DOC buffering capacity.

#### 4. Data presentation interpretation

Why apply linear fits to the changes in annual mean concentrations? It is obviously not a linear trend, but an S-shape return to a (new) steady state. This shape is characteristic for non-steady state transport-dominated systems and here, the transport is diffusion of salts from the underlying marine sediments (+ dissolution of carbonates and release of humic substances from natural reed decomposition, which could potentially explain the response delay of alkalinity). 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. Here, information about the pore water and solid phase composition of the underlying marine sediments could have been helpful.

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Additional helpful information could come from the entire data set, including the seasonal variations and across-lake transects. What are the impacts of high evaporation in summer, rain falls, melt water input, the chemical composition and amount of river input from catchment area on the chemical composition of the lake water with respect to time and space? How did these parameters vary during the observation period (1995-2007)?

All these processes influence the annual means and their trends, particularly, since discharge by itself cannot change the salt/alkalinity content of the lake water at all! So, how important are these factors?

What is the gradient (N-S as stated by the authors) of the chemical composition in the lake? All this would help to understand the ongoing processes and enable reliable prediction of the evolution in the near future / new steady state. Looking at the annual means will not be sufficient to explain the observed dynamics in the data and I doubt the inferred linear trends provide any meaningful information.

#### 5. Scientific background structure of paper

The introduction is way too short and as reading of the entire manuscript reveals, far more background information is available, but hidden in different parts of the paper. In particular, the Discussion section finally provides most of the necessary and important background information with respect to the Neusiedler See and plant litter decomposition. Hence, the entire Discussion section belongs into the Introduction section. The Discussion does not present any findings of the authors anyways.

What is Fig.3 for? It provides a nice side information, but does not contribute anything to the story. The authors also do not analyse the figure in more detail.

#### 6. Methods explanation

The analytical methods need better description. Particularly, analytical accuracy and

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precision need to be stated. What kind of calibrations were done?

References are missing throughout this section.

7. Reference to average water volume of the lake Why use this awkward reference to 115.4 m above MSL? A more useful reference would be the respective water volume of the lake. This would make it easier to understand the data which are influenced by the water reservoir of the lake. By how much does the lake water volume actually change? This is difficult to conclude from Figs. 4+6.

What is the effect of peat formation on the 115.4 m MSL? Does this completely corrupt the chosen reference scale? I would doubt that the terrain model accounts for the change in lake bathymetry due to peat formation over the years.

Paragraph 3.2 on "pristine lake conditions": I cannot follow what has been done here and what the authors want to say. This section needs re-writing.

#### 8. Reed litter experiment

Besides the fact, that the experiments only reproduce the results of Hietz et al. (1991) and also cover the same pH range, as stated by the authors, no quantitative analyses has been attempted and several important information is missing.

Is there any correlation of DOC content and pH? Did the pH change during the experiment?

According to the description of the experimental setup, more parameters were measured, but the authors do not present those.

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. I would suspect that the rate will increase again at lower pH values.

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## Minor comments

- Skip Fig. 1 or combine with Fig. 2. Fig. 1 is missing necessary explanations (e.g., color coding) anyways.
- Fig. 2: y-axis should read "latitude" and x-axis "longitude".
- Fig. 2 caption: "Hydrologic catchment area".
- The English writing is generally good. Only a few phrases need correcting, particularly with respect to word order and awkward wording (e.g., p496/L5 "basis" instead of "base"; p498/L18 "immediately" instead of "currently").
- "MSL" is never explained in the text/figures/tables. MSL = Mediterranean sea level?
- Tab. 1: Use "standard deviation" instead of "standard error".
- Tab.1+2: Does the error of the statistical analysis refer to  $2\sigma$  standard deviation (SD) or something else? Please indicate.
- Methods section: The analytical procedures need to be described in more detail, particularly, the analytical precision and accuracy need to be stated to allow the reader to evaluate the meaning of the given standard deviation of the statistical data analysis (Results section). References to the analytical methods are completely missing.
- The units of the thermodynamic constants are missing (p496+470).
- Referencing: Original papers should be cited and not some secondary or later literature. An example is the reference made to Hofmann et al. (2008) for the pH treatment and thermodynamic constants. Hofmann et al. actually cite Stumm Morgan (1996) for the constants (as a general textbook on the topic) and provide a thorough overview on appropriate literature.
- The reference to Maracek (see Fig. 6) is missing.

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