Dear Editor

We thank the editor for the constructive comments. We appreciated most of the proposed changes, see below. Only in very few cases, we refrained from the proposed change, as we thought a different solution would be better. For details see below.

We are looking forward to the final publication in HESS.

For both authors

Erik Nixdorf

Editor questions and remarks

Page 1 – Overall the front of the abstract is better but some recommended changes to the abstract are required as I was still left with some confusion after reading this version.
Lines 9-11 – needs rewording

Done, reads now: "From a data set covering four years of monthly measured electrical conductivity profiles, we calculated summed conductivity as a quantitative variable reflecting the amount of electro-active substances in the entire lake."

Line 12 – changing … the … chemocline height

Done

Line 15+ - The sentence " In addition, we constructed a lab experiment …" I think could be better worded to improve the flow:
"A lab experiment was undertaken to further demonstrate that …

We corrected the sentence. It reads now: "In addition, we designed a lab experiment, in which we removed iron compounds and organic material from monimolimnetic waters by introducing air bubbles."
Page 2 – lines 1-5. This ending I find confusing. The lab experiment is described without a purpose and instead a statement of result (ln 17, "iron was removed", see above comment), and then that result is repeated "precipitates were observed" – this is referring to the same thing and could be more concisely described. Also, organic material is introduced here, but it is not clear the relevance. Finally, the final abstract statement it is not clear. It should be better worded to link the field and lab observations and the significance. This sentence describes a finding about the sources of water and introduces the concept of iron rich groundwater for the first time. If understanding the importance of Fe rich groundwater is the purpose then should it not be an aim / knowledge gap identified at the beginning of the abstract?

We changed the text in the abstract: It reads now: "Lake stratification controls the cycling of dissolved matter within the water body. This is of particular interest in the case of meromictic lakes, where *permanent density stratification of the deep water limits the vertical transport, and a chemically different (reducing) milieu can establish. As a consequence, the geochemical setting and the mixing regime of a lake can stabilize each other mutually. We attempt a quantitative approach to the contribution of chemical reactions sustaining the density stratification. As a demonstration object, we chose the prominent case of iron meromixis in Waldsee near Doebern, a small lake that originated from near surface underground mining of lignite. From a data set covering four years of monthly measured electrical conductivity profiles, we calculated summed conductivity as a quantitative variable reflecting the amount of electro-active substances in the entire lake. Seasonal variations followed changing the chemocline height. Coinciding changes of electrical conductivities in the monimolimnion indicated that a considerable share of substances, precipitated by the advancing oxygenated epilimnion, re-dissolved in the remaining anoxic deep waters and contributed considerably to the density stratification. In addition, we designed a lab experiment, in which we removed iron compounds and organic material from monimolimnetic waters by introducing air bubbles. Precipitates could be identified by visual inspection. Eventually, the remaining solutes in the aerated water layer looked similar to mixolimnetic Waldsee water. Due to its reduced concentration of solutes, this water became less dense and remained floating on nearly unchanged monimolimnetic water. In conclusion, iron meromixis as seen in Waldsee did not require two different sources of incoming waters, but the inflow of iron rich deep groundwater and the aeration through the lake surface were fully sufficient for the formation of iron meromixis."*

Line 10 – with … the … atmosphere

Done

Line 20 – replace loads with release . ?

No, "gas load" is correct

Line 21 - which … are likely to … be exploited~~ …~~

Done

Line 25 - Meromictic lakes … have been … identified

Done

Page 3 , line 1 - where stratification … limits

Done

Line 4 - stratification … has even been …

Done

Line 11 – replace e.g. with ", for example by"

Done

Line 17 – needs a reference or to be stated more clearly as an unknown.

We added "Boehrer and Schultze 2008"

Line 19-20 - One prominent reactant is iron, which … precipitates within … the oxygenated mixolimnetic waters and dissolves in the anoxic (reducing) … conditions of the monimolimnion

Done

Line 21 – Exemplarily is not a good word. Also – is this sentence stated as fact or as a hypothesis?
Line 24-25 – It seems this question is answering the "proposed" question and bringing into question the need for this paper. Some rewording needed here

Done: "For the shallow mining lake Waldsee we hypothesize that changes in chemocline height trigger internal, trans-chemocline transport of iron species by oxidation, precipitation and re-dissolution, in combination with related CO_2 outgassing and regeneration."

Page 4 – Line 4-7, this paragraph seems to summarise the above paragraph, so I think they would be better together (not separated)

Done

Line 11-13 – the use of summed is not clear (what is nbeing summed?) – I think you need to point out the sum is over the vertical profile

Done: "We sum up electrical conductivity over the vertical profile and use the derived "summed conductivity" as a measure for the amount of solutes within Waldsee,..."

Line 12 - replace "give a rough" with "give an approximate"

Done

Page 5 – The section 2.2 is a mix of prior results and lit review on the lake. lines 16-19 is written more like results than "site description", and should be more clear this is historical data, not data collected as in Section 3.2 where the vertical profiles are described. Needs rewording like: "Prior monitoring has indicated …"

The data shown here are new data. However if a property of the lake had been known before, we cited the corresponding reference.

Methods – litres should be capital L (throughout)

Done

Eq (5) – maybe worth putting the full integral form before the summation as well?

We refrain from doing this: Our definition of summed conductivity is the sum over our layers.

Results

Page 12 – line 1 – “attributed to … the … expected”

Done

Line 4 : change to : “The precipitation of iron hydroxide flocks was visible.”

Done

Update the Figure 5 caption to be more useful

Done: “ Figure 5: Selected conductivity (κ25) profiles at different time steps of the lab experiment. The earliest profile shows the initial condition in the water column followed by two profiles during active aeration at a depth of 0.5 m and 1 m, respectively. Last two profiles show the conductivity distribution in the column a certain time after cessation of aeration.”

Lines 16-23 – this paragraph is crossing into discussion. Don't use the word “obviously”. Don't open a sentence with “In conclusion…” as you should not be making a conclusion in the results, just presenting the data and helping the reader with the interpretation. Please improve the wording of this paragraph.

Reads now : “Profiles of electrical conductivity (Figure 5) showed a distinct step similar to measured profiles in Waldsee. Elevated values of electric conductivity appeared towards the end of the experiment near the bottom. In conclusion, iron hydroxide flocks precipitated down to the bottom before reduction and re-dissolution could set in. However, this happened at a small rate and with temporal delay. This could be attributed to the limited bacterial presence in the beginning. The formation of a visible several centimeter thick iron hydroxide layer at the column bottom confirmed the quantitative removal of substances from the experimental water.”

Page 13 – line 2: replace lab with laboratory

Done

Line 3 – replace drastically with significantly

Done

Line 7 – word needed before DOC

We inserted “as”

Note: DFe DOC and TIC are being defined in the results – they need to be defined in the methods where the chemical analysis is described!

We added a sentence at the end of section "3.1"

Line 25-26 – is a discussion statement, not results.

Well, the reviewer is correct: this is more something of a discussion, though not really the topic of this study. Hence this sentence would appear disruptive in the discussion. Anyway the explanation would be too late, and the results would look incomprehensible. Hence we decided to leave things as they are.

Discussion

Page 15 Line 6 : doesn't make sense: "…of a closed system Lake Waldsee."

We changed the sentence to "For quantification of internal processes versus external sources, we compared measured values with the calculated values of a hypothetical situation, in which Waldsee did not experience matter fluxes with the ambient groundwater."

Line 12 – what graph?? Are you referring to lab or field? This para could be more specific than generically referring to graphs and curves.

We specified: "The graphical display (Fig. 9) of the calculated values showed that even in total absence of groundwater related ion exchange, the internal iron redox cycle alone was able to maintain the conductivity gradient."

Line 22 – subsequent rise … of the … chemocline

Done

Page 16 Line 5 – comma after However

Done

Line 14 Reword: "of the biochemically iron hydroxide reduction "

Done. we removed "biochemically" and "as a by-product"; reads now: "On the other hand, the closed model silently assumed that the loss of the bicarbonate conductivity by CO_2 escaping to the atmosphere (eq. 2) was entirely counterbalanced by CO_2 production from iron hydroxide reduction (eq. 3)."

Line 19: replace re-covering with recovery

Done

Line 22: replace “temporarily” with temporary

Done

Page 17 – fix up: “This is where our investigation our findings …”
Line 18 : “…for the parameterization”

we changed the sentence: “This is where our findings based on measurements and simple 1D algebraic mass balance equations may deliver new insight for the parametrization of numerical models for the prediction of stratification in meromictic lakes.”

Page 18 line 2: remove “in a 5 m high PVC pipe”

Done

Figure 4. Remove the “in” in the X-axis labek so it is Time [h]. Also put EC in brackets in the caption so it links to the Y-axis label (same in Fig 5)

Done

Manuscript

Main document changes and comments

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aeration of monimolimnetic waters

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from monimolimnetic waters by introducing air bubbles

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Eventually, the remaining solutes in the aerated water layer looked

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Introduced air bubbles ascended through the water column and formed a water

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Due to its reduced concentration of solutes, this water

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The remaining

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became

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for the formation of iron meromixis.

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(Boehrer and Schultze, 2008)

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sum up electrical conductivity over the vertical profile and use the derived

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to estimate the concentration of dissolved iron (DFe) and total iron (TFe) and total inorganic carbon (TIC) and dissolved organic carbon (DOC) as well as to estimate electrical conductivity and pH-value of the samples.

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a hypothetical situation, in which

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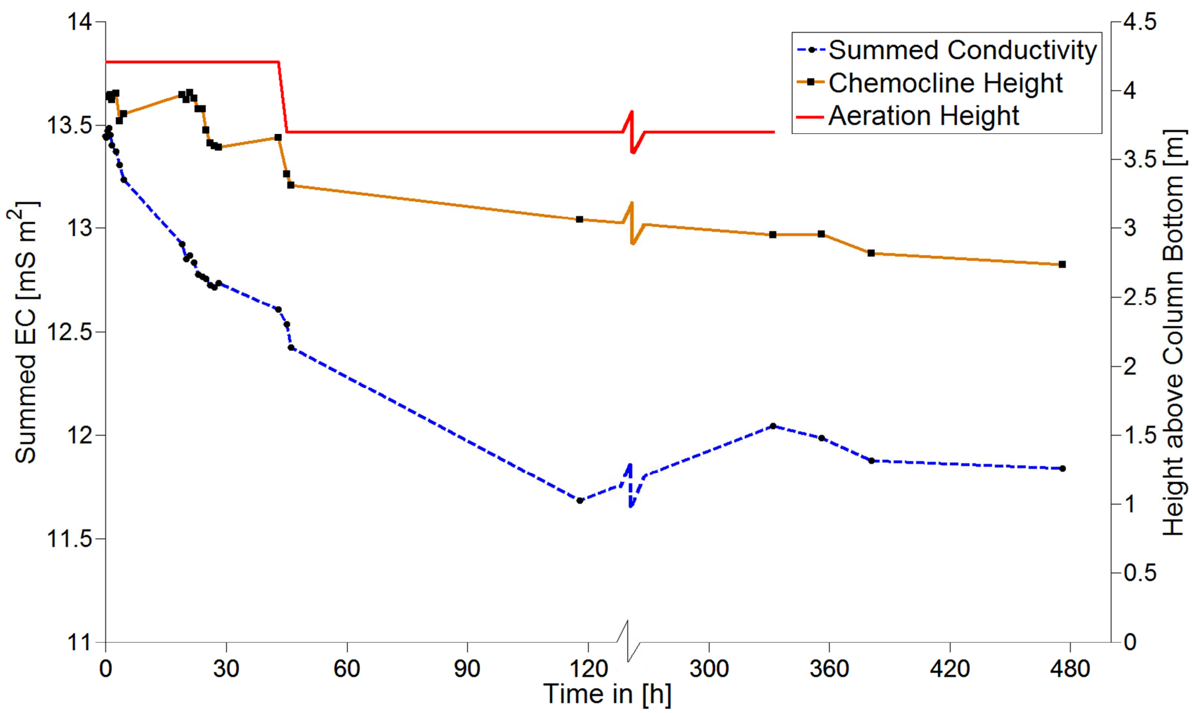

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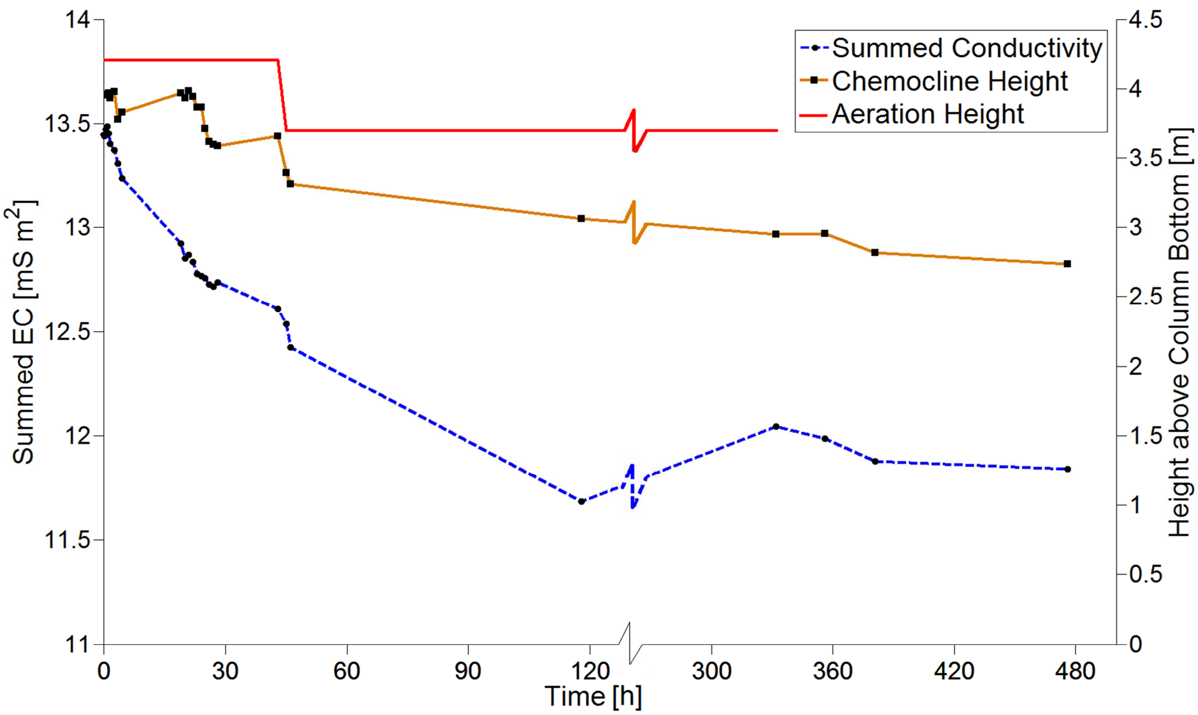

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(κ_{25}) profiles at different time steps of the lab experiment. The earliest profile shows the initial condition in the water column followed by two profiles during active aeration at a depth of 0.5 m and 1 m, respectively. Last two profiles show the conductivity distribution in the column a certain time after cessation of aeration.

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profiles in the lab experiment

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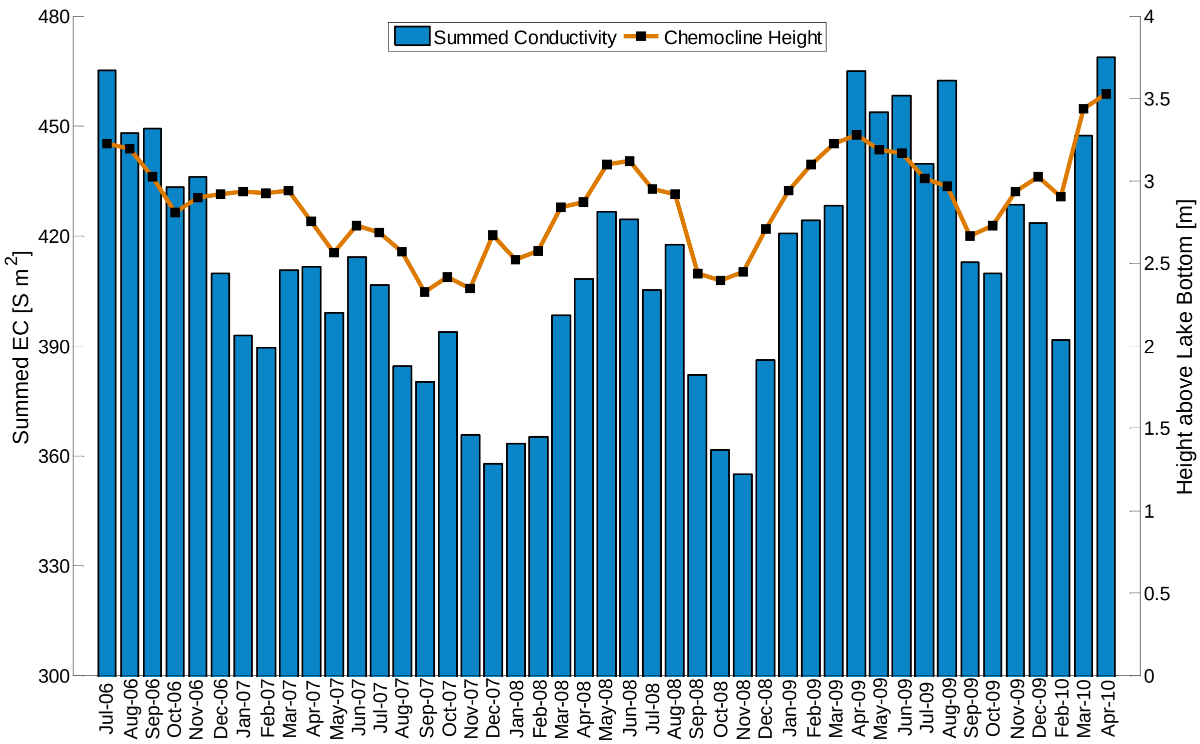

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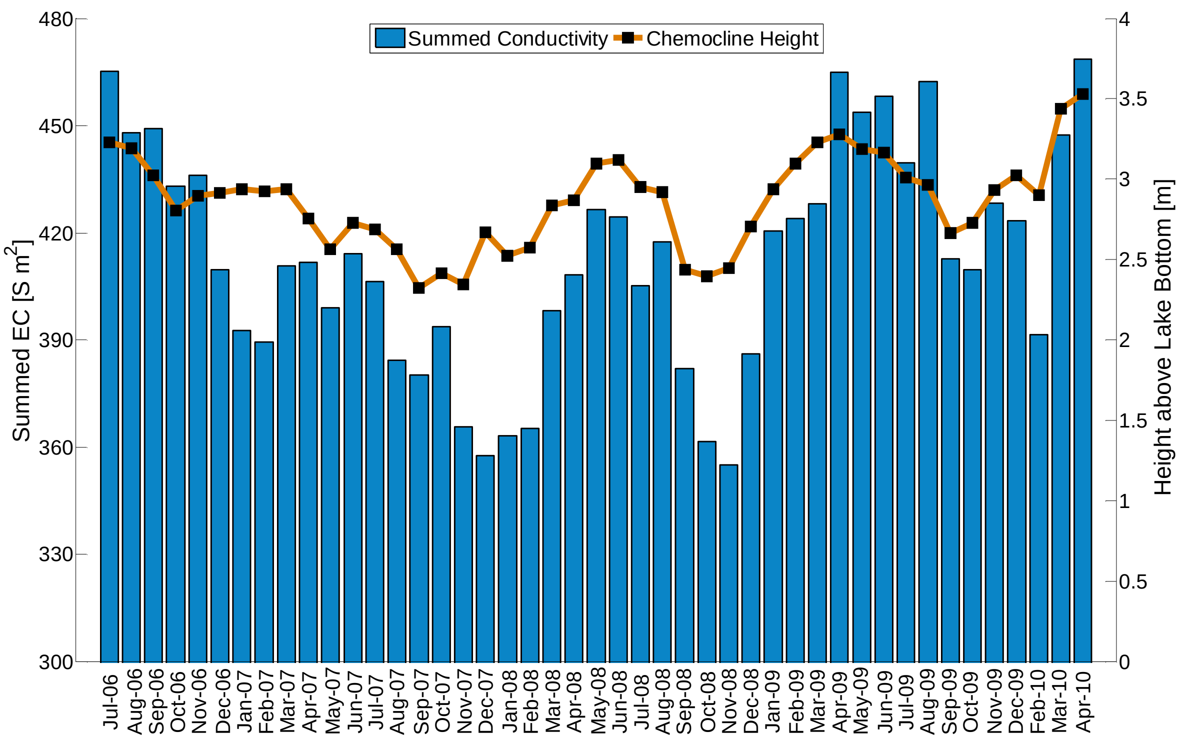

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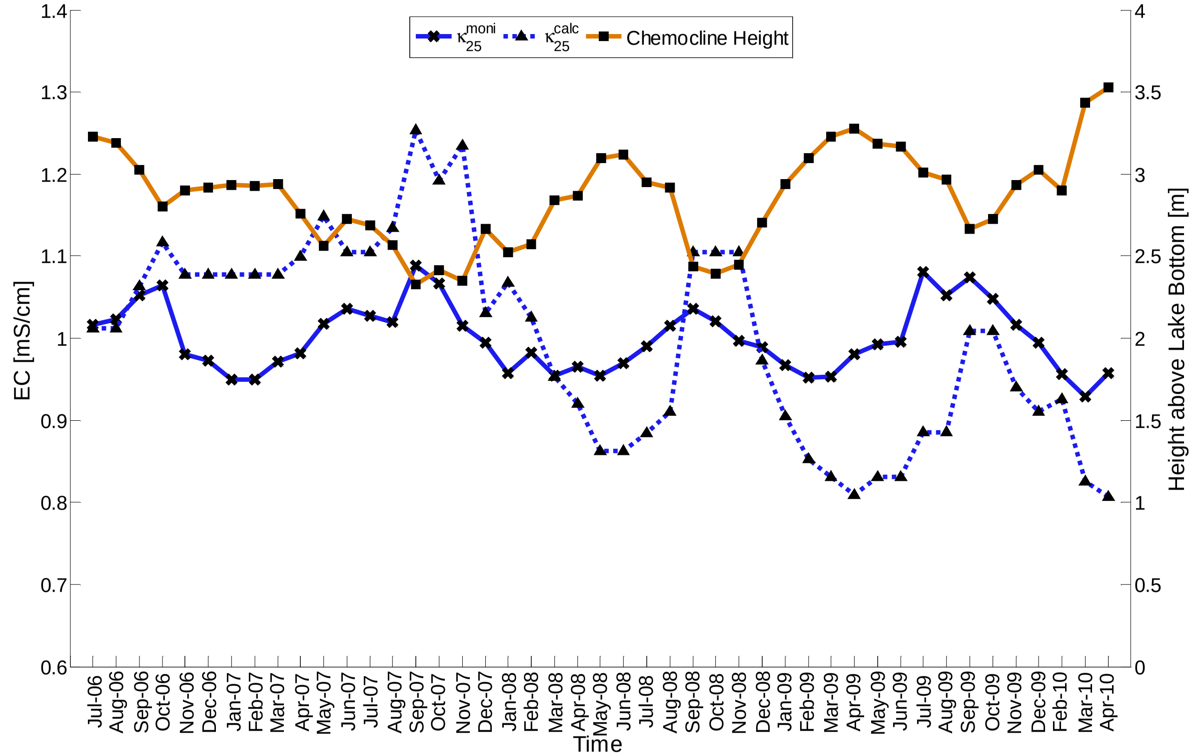

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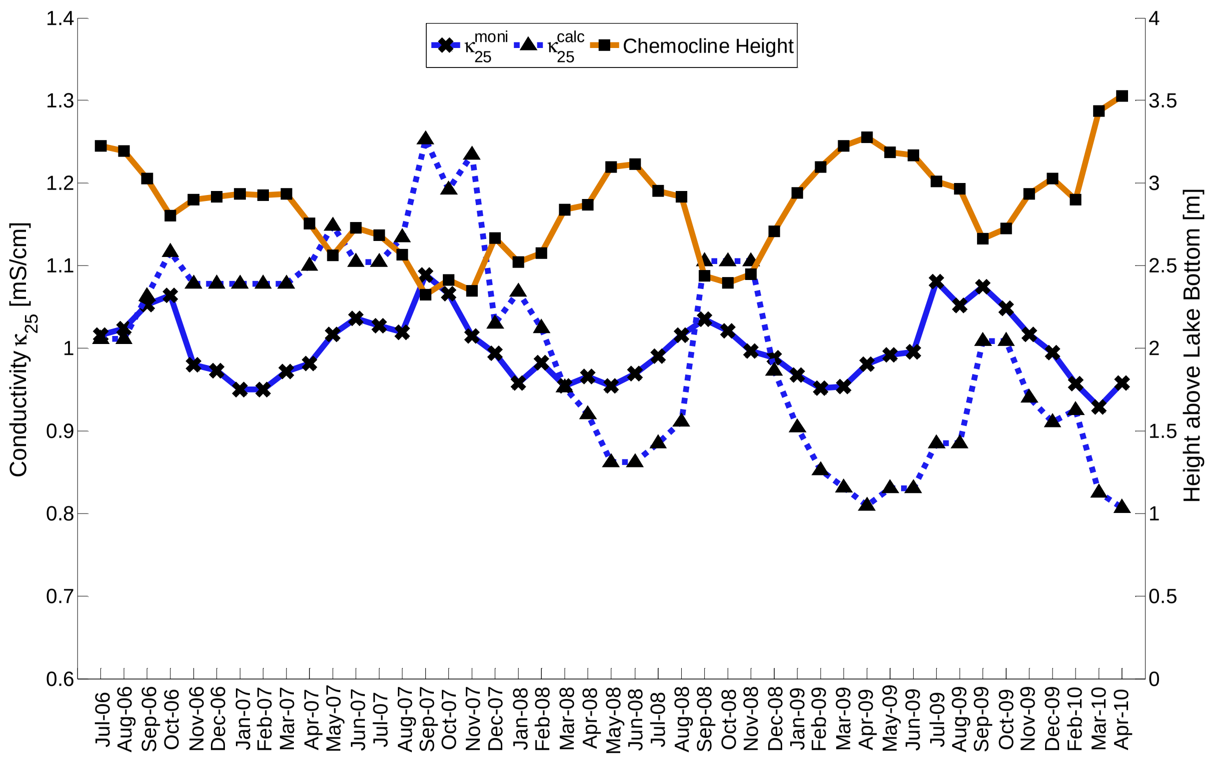

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Quantitative analysis of biogeochemically controlled density stratification in an iron-meromictic lake

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Abstract

Lake stratification controls the cycling of dissolved matter within the water body. This is of particular interest in the case of meromictic lakes, where permanent density stratification of the deep water limits the vertical transport, and a chemically different (reducing) milieu can establish. As a consequence, the geochemical setting and the mixing regime of a lake can stabilize each other mutually. We attempt a quantitative approach to the contribution of chemical reactions sustaining the density stratification. As a demonstration object, we chose the prominent case of iron meromixis in Waldsee near Doebern, a small lake that originated from near surface underground mining of lignite. From a four years data set covering four years of monthly measured electrical conductivity profiles, we calculated summed conductivity as a quantitative variable reflecting the amount of electro-active substances in the entire lake. Seasonal variations followed changing the chemocline height. Coinciding changes of electrical conductivities in the monimolimnion indicated that a considerable share of substances, precipitated by the advancing oxygenated epilimnion, re-dissolved in the remaining anoxic deep waters and contributed considerably to the density stratification. In addition, we designedconstructed a lab experiment, in which we aeration of monimolimnetic waters removed iron compounds and organic material from monimolimnetic waters by

introducing air bubbles. Precipitates could be identified by visual inspection. Eventually, the remaining solutes in the aerated water layer looked ~~Introduced air bubbles ascended through the water column and formed a water mass~~ similar to ~~the~~ mixolimnetic Waldsee water. Due to its reduced concentration of solutes, this water ~~The remaining~~became less dense and ~~water~~ remained floating on ~~the~~ nearly unchanged monimolimnetic water. In conclusion, iron meromixis as seen in Waldsee did not require two different sources of incoming waters, but the inflow of iron rich deep groundwater and the aeration through the lake surface were fully sufficient for the formation of iron meromixis.~~.~~

1. Introduction

Lakes are called meromictic, if a deep water layer, the monimolimnion, perennially shows pronounced chemical differences to the surface water due to incomplete recirculation during the deep mixing period (Boehrer and Schultze, 2008). The exclusion of the monimolimnia from gas exchange with the atmosphere creates anoxic, reducing conditions leading to an enrichment of dissolved gases and ionic substances in the deep water. Despite their worldwide occurrence, only a small number of internal and external processes can be responsible for the formation of density stratification (e.g. Walker and Likens, 1975; Hakala, 2004; Boehrer and Schultze, 2008).

There are good reasons for scientific interest in meromictic lakes: some of the largest lakes are meromictic (e.g. Lake Malawi/Nyasa, e.g. Vollmer et al., 2002). Chemical gradients in meromictic lakes form habitats for specialized organisms (e.g. sulfur bacteria performing anoxygenic photosynthesis (Camacho et al., 2001) or anammox (Hamersley et al., 2009)). Some meromictic lakes became famous through their dangerous gas loads (e.g. Lake Nyos and Lake Monoun in Cameroon, Halbwachs et al., 2004). The monimolimnion of Lake Kivu contains considerable methane deposits (Tietze, 1978), which are likely to be~~will be~~ exploited in near future. Sediments in some meromictic lakes have been undisturbed for thousands of years and hence the varved sediments represent excellent climate archives and fossil deposits (e.g. Walker and Likens, 1975; Lenz et al., 2011). Meromictic lakes ~~could be~~have been identified in many mining regions on earth where stratification ~~limited~~ limits the vertical transport of undesirable substances (e.g. Spain: Lake San Telmo, Cánovas et al., 2012, and Lake Conception, Santofimia and López-Pamo, 2013; Germany: Lake Wallendorfer See and Lake Rassnitzer See, Boehrer et al., 2014; Lake Moritzteich, von Rohden et al., 2009). In some cases, stratification ~~was~~ has eve~~n~~n been implemented to restrict the vertical transport (Island Copper Mine pit lake in Canada, Wilton et al., 1998; Stevens and Lawrence, 1998).

Meromictic conditions can be sustained by a continuous inflow of high density groundwater and low density surface water via streams or precipitation and the very low diffusion rate of substances over sharp gradients (e.g. von Rohden and Ilmberger, 2001; Wiessner et al., 2014). The dense water may also be formed within the lake e.g. by weathering processes of exposed sulfide-bearing material (Geller et al., 1998). The volume ratio between the monimolimnion and the mixolimnion can show seasonal changes due to chemocline erosion by mixolimnion turnover (e.g. von Rohden et al., 2009) or by increased surface runoff, whereas increased groundwater inflow and higher surface evaporation as well as diffusive processes are able to cause an upward movement of the chemocline (e.g. Santofimia and López-Pamo, 2013). Additionally, chemical reactions are able to sustain meromixis in lakes (Boehrer and Schultze, 2008)~~.~~

One prominent reactant is iron, which ~~gets precipitated~~ precipitates ~~from~~ within the oxygenated mixolimnetic waters and dissolves in the anoxic (reducing) ~~chemical~~ conditions of the monimolimnion (Kjensmo, 1967; Hongve, 1997). ~~Exemplarily it is proposed f~~For the shallow mining lake Waldsee, we hypothesize that changes in chemocline height trigger internal, trans-chemocline transport of iron species by oxidation, precipitation and re-dissolution, in combination with related CO_2 outgassing and regeneration. Both processes maintain density gradients between both water layers and inhibit a complete mixing of this shallow lake (Boehrer et al., 2009). For Waldsee, Dietz et al. (2012) showed that dissolved iron and carbon species (CO_2, bicarbonate and DOC) contribute the same amount to the density gradient and all other substances contribute a much subordinate portion.

From previous investigations, it is clear that both precipitation of iron out of the mixolimnion and gas exchange with the atmosphere are important contributors to the permanent stratification. It is also known that re-dissolution of iron happens in the monimolimnion, but there has not been any quantitative approach to determine its role in sustaining meromixis.

In this paper, we use easily measurable vertical profiles of in-situ electrical conductivity as a quantitative bulk measure of solutes like calculating salinity from electrical conductivity measurements in oceanography (e.g. Fofonoff and Millard, 1983). We sum up electrical conductivity over the vertical profile and use the derived~~calculate~~ "summed conductivity" as a measure for the amount of solutes within ~~Lake Waldsee~~Waldsee, and give an approximate rough quantitative estimate for the re-dissolution of precipitated iron. Furthermore a lab experiment was conducted to physically reproduce the assumed chemical reactions in the lake in order to get evidence about the origin of the two different water types in the lake and the production of mixolimnetic water from monimolimnetic waters during periods of vertical chemocline propagation.

2. Site description

2.1 Study site

The demonstration site ~~Lake Waldsee~~Waldsee (51°37’14.1’’N, 14°34’16.7’’E) is a former mining site located in a forested area in the Lower Lusatian Mining District 130 km southeast of Berlin (Figure 1). The lake covers an area of about 2400 m^2, has a volume of 6500 m^3 and reaches a maximum depth of 4.7 m (Boehrer et al., 2009). ~~Lake Waldsee~~Waldsee is embedded in The Muskau Arch, which represents an Elsterian push moraine cut by deep erosion. This geological deformation process folded up the horizontal geological layers which caused the crop out of Miocene lignite layers in conjunction with later glacier advances (Kozma and Kupetz, 2008). The near-surface coal was exploited by both underground mining and surface mining. ~~Lake Waldsee~~Waldsee is the water filled depression of the former underground mining site “Pflanzgartenmulde”, which has been formed by the collapse of the underground mining structures after cessation of mining activities in 1948 (Schossig and Kulke, 2006).

The location of ~~Lake Waldsee~~Waldsee shows an annual average precipitation between 500-600 mm and a potential open water surface evaporation of 752 mm (Seebach et al., 2008). ~~Lake Waldsee~~Waldsee does not have a surface inflow. Hence groundwater is the main source of recharge. Tracer experiments estimate a mean groundwater recharge to ~~Lake Waldsee~~Waldsee of 8.2 m^3/d (mostly from southern direction) and a mean groundwater outflow of 6 m^3/s (von Rohden et al., 2009). A small only occasionally filled drainage trench connects ~~Lake Waldsee~~Waldsee with a mining lake (RL 0622/6) below. The resulting annual water level changes are in the range of a few decimeters.

2.2 Lake stratification and water chemistry

The physico-chemical profiles of ~~Lake Waldsee~~Waldsee clearly showed pronounced differences in water parameters between the upper 1-1.5 m thick mixolimnic water layer and the monimolimnion below. pH in both mixolimnion and monimolimnion was slightly acidic with values between 5.5 and 7.0 having lower values during spring time (Figure 2a).

The mixolimnion was oxygenated (Figure 2b) and had an electrical conductivity of about 0.4-0.5 mS/cm which was approximately half of related values in the anoxic monimolimnion (Figure 2c). Due to the absence of large pH differences (Diesing and Boehrer, 2010) this gradient in electrical conductivity could be related to gradients in the concentrations of electro-active water constituents, mainly ferrous iron and bicarbonate also being the major contributors to the density difference (Dietz et al., 2012).

Constituent concentration measurements in the mixolimnion and the monimolimnion had shown a difference in ferrous iron concentration of about 150 mg/l and in bicarbonate concentration of about 300-400 mg/l between both water layers (Boehrer et al., 2009). The resulting density gradient across the chemocline over-compensated the destabilizing temperature gradient during winter time (Figure 2d) and in consequence no complete lake turnover was detected within more than 10 years of lake monitoring. However, both the mixolimnion and the monimolimnion could form two independent convection cells (Boehrer et al., 2009).

The depth of the chemocline, which could be marked as the point of inflection of the κ_{25} conductivity profiles and thus the volumetric ratio between mixolimnion and monimolimnion, varied seasonally by about 1 m (Figure 2c). During the warm season, the erosion (lowering) of the chemocline was caused by wind driven nocturnal mixolimnetic convection currents. On the other hand in winter, the monimolimnetic water section volume increased due to the weakened erosive forces and significant net groundwater inflow (von Rohden et al., 2009). Additionally the density stratification of the two different water sections was maintained and stabilized by an internal iron redox cycle and the outgassing of diffused bicarbonate from the mixolimnion counterbalanced by biological bicarbonate producing processes in the monimolimnion (Boehrer et al., 2009).

Ferrous iron transported into the oxygenated water layers, either by convective transport due to chemocline erosion or by molecular diffusion was oxidized to ferric iron and was subsequently transported back to the monimolimnion as rust-colored, voluminous iron hydroxide precipitate:

$$Fe^{2+} + 0.25O_2 + 2.5H_2O \rightarrow Fe(OH)_3 \downarrow + 2H^+ \qquad (1)$$

Thus the zone of iron hydroxide formation was traceable by its increase in turbidity and was located slightly below the current chemocline height (Figure 2e).

Similarly, bicarbonate ions transferred into oxygenated water layers could either be up-taken by photosynthetic organisms or outgas as CO_2 through the carbonate equilibrium to the atmosphere:

$$HCO_3^- + H^+ \rightarrow CO_2 \uparrow + H_2O \qquad (2)$$

Internally, dissolved ferrous iron and inorganic carbon were resupplied by the micro-bacterial anaerobic degradation of organic matter in the monimolimnion using precipitated iron hydroxide as an electron acceptor:

$$CH_2O + 4Fe(OH)_3 + 7H^+ \rightarrow HCO_3^- + 4Fe^{2+} + 10H_2O \qquad (3)$$

The increase of measured conductivity and pH in the monimolimnion near the lake bottom (Figure 2a and 2c) might be interpreted as evidence for this reduction process.

3. Methodology

3.1 Sampling and set-up of column experiment

On May 18th 2011, mixolimnion and monimolimnion water were collected for chemical analysis. This included the measurement of electrical conductivity using a 7-pole platinum cell conductivity sensor and pH with a pH-meter as well as determining concentration of carbon species (DOC; TIC, TOC) by infrared spectroscopy following thermal-catalytic oxidation and iron species (ferrous and ferric iron) by atomic emission spectroscopy. In addition, 150 ~~l~~ L of monimolimnion were sampled and air-tightly and opaquely stored at a temperature of 4°C for later use in a column experiment.

A 5 m high bluish-transparent PVC-column with an outer diameter of 20 cm and a wall thickness of 0.5 cm was installed and fastened at the technical hangar of UFZ Magdeburg (Figure 3). The column was covered by PE-containing mattresses in order to thermally insulate the column and to avoid photo-chemical iron reduction (Herzsprung et al., 1998). Prior to filling, the column was flushed with nitrogen gas to avoid initial oxidation of ferrous iron. On May 25th 2011, the column was subsequently filled with 130 ~~l~~ L of this monimolimnetic lake water to reproduce the maximum water depth of 4.7 m in ~~Lake Waldsee~~Waldsee. The water was filled in slowly from below. We implemented a thermal stratification to prevent vertical circulation at the beginning of the experiment.

The aeration was accomplished with pressurized air at a water depth of 50 cm. Between 25.05.2011 13:00 and 14.06.2011 09:00 o'clock, 28 vertical profiles of temperature, pressure, turbidity and electrical conductivity were sampled with the multi-parameter CTD-O_2 fast profiling probe with a sampling frequency of 4 Hz. The airflow was increased after 24 h of experiment time and additional 20 hours later the aeration depth was changed to 1 m for a time span of three additional days in order to see the response of chemocline height in the water. Finally the aeration was stopped and four further profiles were measured during the next 14 days. At the end of the experiment, water samples were taken from the aerated top water layer and the bottom water and analyzed in the lab together with collected mixolimnion and monimolimnion water from the lake~~.~~ to estimate the concentration of dissolved iron (DFe) and total iron (TFe) and total inorganic carbon (TIC) and dissolved organic carbon (DOC) as well as to estimate electrical conductivity and pH-value of the samples.

3.2 Electrical conductivity

45 monthly field measurements have been conducted in ~~Lake Waldsee~~Waldsee between July 2006 and April 2010. Vertical profiles of temperature, pressure, pH, turbidity and in-situ electrical conductivity were collected in ~~Lake Waldsee~~Waldsee using the multi-parameter probes *Ocean Seven 316CTD* (Idronaut, Italy) and *CTD90M* (Sea & Sun, Germany). The sampling rate was between 1 and 4 Hz and the small offset between the sensors of the two different probes was compensated. Measured electrical conductivity C was converted into electrical conductivity κ_{25} at 25°C (sometimes named as electrical conductance) by

$$\kappa_{25} = \frac{C}{\alpha_{25} \cdot (T - 25°C) + 1} \qquad (4)$$

where a lake specific α_{25} value of 0.0194 (Boehrer et al., 2009) was used.

Water depth was estimated by the hydrostatic pressure equation taking into account a lake specific empirical density function, which allowed calculating density profiles based on temperature and electrical conductivity measurements (Boehrer et al., 2009).

3.3 Calculating summed electrical conductivity

The summed conductivity $S_{\kappa 25}$ could be interpreted as a value representing the total amount of electro-active constituents in the water. It was calculated by multiplying the measured electrical conductivity with the corresponding water volume and subsequently integrating results over the complete water depth. Therefore the lake was vertically portioned into j=1…n layers of volumina V_j where layer j=1 represented the bottom water layer. In the lake, the number of layers varied between 40 and 45 due to changes in water level whereas in the column experiment a constant value of 47 layers could be used in each time step. Each layer j had a respective height h_j of 10 cm. Furthermore, it was assumed that conductivity gradients in the planar directions were negligible. The summed conductivity, given in $S \cdot m^2$, could be calculated for each time of measurement t_i by

$$S_{\kappa_{25}}(t_i) = \sum_{j=1}^{n} \kappa_{25}(j, t_i) \cdot V_j = \sum_{j=1}^{n} \kappa_{25}(j, t_i) \cdot A(j) \cdot h_j \tag{5}$$

For the column experiment, the area of each layer was 0.028 m² according to the geometry. In the lake the specific size of each layer was derived from a bathymetric study (Brandenburg University of Technology, 1998).

The spatially averaged monimolimnion conductivity $\overline{\kappa}_{25}^{moni}(t_i)$ could be derived from measurements by solving eq.5 for κ_{25} and summing up all layers from the lake bottom up to layer j_c where the chemocline was located:

$$\overline{\kappa}_{25}^{moni}(t_i) = \frac{S_{\kappa 25}^{moni}(t_i)}{V^{moni}(t_i)} = \frac{\sum_{j=1}^{j=j_c(t_i)} \kappa_{25}(j,t_i)\cdot A(j)\cdot h_j}{\sum_{j=1}^{j=j_c(t_i)} A(j)\cdot h_j} \tag{6}$$

The average mixolimnion conductivity $\overline{\kappa}_{25}^{mixo}(t_i)$ could be calculated similarly to the approach shown in eq. 6.

In the hypothetical scenario of a closed ~~Lake Waldsee~~Waldsee, a rise in the chemocline ($j_c(t_i) > j_c(t_{i-1})$) would be connected to a decrease of the calculated average electrical conductivity in the monimolimnion $\overline{\kappa}_{25}^{calc}(t_i)$. Mathematically this could be written as inclusion of less conductive mixolimnic water layers into the expanding monimolimnion:

$$\overline{\kappa}_{25}^{calc}(t_i) = \frac{V^{moni}(t_{i-1})\cdot \overline{\kappa}_{25}^{calc}(t_{i-1}) + \sum_{j=j_c(t_{i-1})+1}^{j=j_c(t_i)} A_j \cdot h_j \cdot \kappa_{25}(j,t_{i-1})}{V^{moni}(t_i)} \tag{7}$$

In contrast in our model during seasonal observed chemocline erosion ($j_c(t_i) < j_c(t_{i-1})$), the iron redox-cycle was able to restore the gradient between monimolimnion and mixolimnion. Mathematically, the corresponding increase in electrical conductivity could be calculated assuming that previous monimolimnic water (time step t_{i-1}) affected by the chemocline erosion was changed to mixolimnic water (time step t_i) with a complete loss of excess conductivity $\kappa_{25}^{moni}\left(j, t_{i-1}\right) - \overline{\kappa}_{25}^{mixo}\left(t_i\right)$ and that the entire amount of conductivity was transferred to the remaining monimolimnion volume:

$$\overline{\kappa}_{25}^{calc}\left(t_i\right) = \frac{V^{moni}\left(t_{i-1}\right)\cdot\overline{\kappa}_{25}^{calc}\left(t_i\right) + \sum_{j=j_c(t_i)+1}^{j_c(t_i-1)} A_j\cdot\left(\kappa_{25}\left(j, t_{i-1}\right) - \overline{\kappa}_{25}^{mixo}\left(t_i\right)\right)\cdot h_j}{V^{moni}\left(t_i\right)} \quad (8)$$

4. Results

4.1 Development of summed conductivity in the column experiment

During the aeration period from 25th to 27th of May, the summed conductivity decreased continuously (Figure 4). This decline continued after cessation of the aeration with the exception of the measurement on 30th of May. Over all, the summed conductivity dropped by about 12 % from 13.44 S·m² to 11.84 S·m² over the complete experiment time. This could be attributed to the expected oxidation and subsequent precipitation of iron hydroxide from the aerated part of the column. The precipitation process could be visually verified by a water discoloration to reddish brown and a measured increase in the turbidity NTU of the surface water by a factor of 26.5 in comparison to the deep column water value. The precipitation of iron hydroxide flocks ~~precipitation~~ was visible. The flocks sank at a settling speed of about 1 mm/s. The decline of summed conductivity decelerated during the experiment due to the limited amount of ferrous iron ions remaining in the aerated part of the column.

A distinct chemocline was formed in a water depth of about 0.5 m similar to the aeration depth after an initial phase of about 1 h. The increase of airflow on the 26th of May 13:00 and the change of aeration depth 20 hours later shifted the chemocline in the vertical by 20 cm and 50 cm, respectively. The chemocline height continued declining after the cessation of the aeration due to the diffusion of oxygen into deeper water layers. However the quantitative analysis was beyond the scope of this experiment.

Profiles of electrical conductivity (Figure 5) showed a distinct step similar to measured profiles in ~~Lake Waldsee~~Waldsee. Elevated values of electric conductivity appeared towards the end of the experiment near the bottom. In conclusion, iron hydroxide flocks precipitated down to the bottom before reduction and re-dissolution could set in. However, this ~~obviously~~ happened at a small rate and with~~. The~~ temporal delay. This ~~which~~ could be attributed to the ~~a consequence of~~ limited bacterial presence in the beginning. The formation of a visible several centimeter thick iron hydroxide layer at the column bottom confirmed the quantitative removal of substances from the experimental water.

4.2 Comparison of column experiment samples with lake samples properties

The results of the laboratory analysis showed that the aeration of the column's upper water changed the water characteristics ~~drastically~~ significantly (Figure 6). Dissolved iron ~~(DFe)~~ was removed almost entirely from the upper water. Resulting concentrations of 5 mg/l concurred with mixolimnic lake water (2 mg/l). In parallel, electrical conductivity fell from 1.0 mS/cm to 0.77 mS/cm close to the mixolimnetic value of the lake. Most of the dissolved organic carbon was removed from the aerated water~~,~~ as DOC concentration fell from 46 mg/l to 10 mg/l. The aeration also stripped CO_2 from the water resulting in a measurable drop in TIC ~~(Total Inorganic Carbon)~~ concentration from 122 mg/l to 17.5 mg/l, which were in the range of the mixolimnion water (13.1 mg/l). pH of the surface water has decreased slightly from 6.3 to 5.9 probably due to the acidifying process of ferrous iron oxidation and precipitation.

Similarly, changes of lower water properties during the experiment could be attributed to the impact of the iron hydroxide reduction and re-dissolution process. The re-dissolution process of precipitated iron caused a measurable increase of dissolved iron (177 mg/l) compared to the initial concentration (148 mg/l). The supplementary measured TFe in the bottom water 313 mg/l indicated that not all precipitated iron had been re-dissolved during the experiment. The determination of a plausible TFe value for the monimolimnion failed and was therefore excluded from Figure 6. On the other hand, the partial reduction and re-dissolution of iron caused only a slight increase in both electrical conductivity and pH in the bottom water.

TIC concentrations of the water at the column bottom of 75 mg/l were lower than monimolimnetic water (122 mg/l) reflecting losses during sampling, transport and filling process. DOC in the deeper column of 54 mg/l was higher than the initial value of 48 mg/l. Possibly, precipitating iron hydroxide flocks could include DOC but released some into the ambient water on the way to the column bottom (Duan and Gregory, 2003).

4.3 Dynamics of chemocline height and summed conductivity in ~~Lake Waldsee~~Waldsee

The height of the chemocline varied seasonally over four years of monthly observation (see also von Rohden et al., 2009). From April to October, the chemocline sank, while it rose during winter months (Figure 7). The height above the deepest point varied between 2.3 m and 3.5 m showing a mean of 2.86±0.29 m. In contrast, water level in Waldsee was on average at 4.18 ±0.10 m. This meant that the amplitude of the chemocline changes, expressed by standard deviation, were about three times higher than the observed variations in lake water level.

The summed conductivity of Waldsee underwent seasonal variations, similar to the behavior of the chemocline, within a range of 354 $S\cdot m^2$ and 468 $S\cdot m^2$ with an average of

412±31.3 S·m², meaning that about 25% of the summed conductivity disappeared over summer when the chemocline was moved downwards, but recovered again when the chemocline rose during winter months.

The initial summed conductivity of 465.18 S·m² was only slightly different from the last measurement of 468.72 S·m² indicating a similar amount of electro-active substances at the beginning and at the end of the observation period. The linear correlation coefficient between the variations in summed conductivity and chemocline height was calculated to 0.84 indicating a connection between electrical conductivity of the monimolimnion and chemocline location (Figure 8).

5. Discussion

5.1 Preservation of permanent stratification by the iron-redox cycle

Permanent stratification of Lake WaldseeWaldsee was preserved over the observation period by the presence of dissolved compounds considering that the averaged electrical conductivity of the mixolimnion never exceeded 0.54 mS/cm and the electrical conductivity of the monimolimnion in Lake WaldseeWaldsee was in a range between 0.93 mS/cm and 1.09 mS/cm (Figure 9). The variations of the average monimolimnion conductivity showed an inverse relationship to the variations of the chemocline height. For quantification of internal processes versus external sources, we compared measured values with the calculated values of a hypothetical situation, in whichour simplified model of a closed system Lake WaldseeWaldsee which did not experienceallow matter fluxes with the ambient groundwater. Based on eq. 7 and 8, the average monimolimnion conductivity $\overline{\kappa}_{25}^{calc}(t_i)$ depending on the chemocline location could be calculated for each time step. For each time step the calculated value of the previous time step was used in the equations in order to see the development between the calculated and the measured average electrical conductivity of the monimolimnion.

The graphical display (Fig. 9) of the calculated values showed that even in total absence of groundwater related ion exchange, the internal iron redox cycle alone was able to maintain the conductivity gradient. Although the curves resembled each other in terms of mean value and location of maxima and minima, the graph of the calculated values showed, with values in a range between 0.81 mS/cm and 1.25 mS/cm and a corresponding standard deviation of 0.12 mS/cm, a much larger excursion than the graph of the measured monimolimnetic electrical conductivities.

One potential reason for the discrepancy in the excursions of both curves is the precipitation of iron hydroxide flocks on oxic sediments close to the side walls following a decrease in chemocline height (Schultze et al., 2011). A subsequent rise of the chemocline would lead to a delayed re-dissolution of these flocks which meant that this mechanism would be able to buffer fluctuations in the electrical conductivity. However, due to the morphology of ~~the Lake Waldsee~~Waldsee, the area of the sidewalls was only about 1-3% of the total area of each lake layer. Hence, the potential storage capacity of this process was limited.

As a consequence, we had to conclude that not all electrical conductivity came back into solution. However, the synchronous variation indicated that a considerable portion remained in or returned quickly into the water body. Focusing on the three periods of chemocline erosion between spring and autumn in the years 2007 to 2009, measured excursions were in a range between 26 % and 66% of the closed model, showing a mean of 47 %. In conclusion, the electrical conductivity of precipitated ions from chemocline erosion re-appeared in the monimolimnion, but some iron was deposited in the sediment. High iron mass concentrations of about 20 % in a sediment depth of more than 10 cm (Friese, 2004) indicated that this could be also valid in ~~Lake Waldsee~~Waldsee itself. On the other hand, the closed model silently assumed that the loss of the bicarbonate conductivity by CO_2 escaping to the atmosphere (eq. 2) was entirely counterbalanced by CO_2 production~~ as a by-product~~ ~~of the~~from ~~biochemically~~ iron hydroxide reduction (eq. 3). The additional impact of a potential disequilibrium in the CO_2 balance on the changes in monimolimnion conductivity could not be delineated by our simple quantitative analysis.

5.2 Impact of groundwater recharge on permanent stratification

A less pronounced r~~e-covering~~ ecovery of electrical conductivity losses in the monimolimnion, as discussed above, would lead to a further decrease in monimolimnion conductivity. Even for the chosen model, the calculated conductivity values dropped below the measured values significantly. Excluding the ~~temporarily~~ temporary storage of iron flocks on the side walls of being an efficient storage mechanism, the inflow of significant amounts of ion rich groundwater was the only remaining mechanism for the recovery of summed conductivity during times of rising chemocline in Waldsee. Finally, a net outflow of groundwater during periods of chemocline erosion (von Rohden et al., 2009) could also contribute to the less pronounced decrease of the measured monimolimnion conductivity in comparison to the results of the model.

5.3 Consequences for lake stratification modelling

Modelling lake stratification in meromictic lakes allows forecasting future stability of the density gradients. In particular, this is of high importance for many pit lakes, as undesired substances such as heavy metals are typically trapped in enriched concentrations within the monimolimnion. Hence, an unexpected turnover of a meromictic lake could produce serious environmental problems. Early numerical models for meromictic lakes such as Böhrer et al. (1998) did not include the effect of chemical reactions on the permanent density stratification. There has been a geochemical simulation of Waldsee by Moreira et al. (2011) including geochemical equilibrium based chemical equations for the iron-redox system but provided no quantification of the partial re-dissolution of the precipitated iron in the sediments. Furthermore, as their geochemical model ran entirely during a time of chemocline decline, the proposed effect of gradient stabilization by the inflow of significant amounts of ion rich groundwater was not included in their model. This is where ~~our investigation~~ our findings based on measurements and simple 1D algebraic mass balance equations may deliver new insight ~~in the~~for the parametrization of numerical models for the prediction of stratification in meromictic lakes.

6. Summary

Regular measurements of electrical conductivity could confirm that the induced stratification of ~~Lake Waldsee~~Waldsee in two water sections was sustained throughout the observation period of four years. Both layers, mixolimnion and monimolimnion, experienced volume changes, which followed a seasonal pattern with an increase of monimolimnion volume in winter and early spring and a decrease in the remaining months.

An aeration experiment ~~in a 5 m high PVC pipe~~ filled with monimolimnetic lake water replicated the stratification features in ~~Lake Waldsee~~Waldsee. The immediate precipitation of iron hydroxide flocks after the beginning of the aeration from the upper part of the column led to an approximation of electrical conductivity towards the mixolimnion value of ~~Lake Waldsee~~Waldsee. A sharp conductivity (and hence density) gradient formed as had been observed in ~~Lake Waldsee~~Waldsee. The deep water basically retained its properties, while the upper water layer was changed to chemical conditions close to mixolimnion properties of ~~Lake Waldsee~~Waldsee: iron removal, pH depression, DOC removal and CO_2 loss. This confirmed previous research that the density-gradient in meromictic ~~Lake Waldsee~~Waldsee was sustained by internal geochemical processes and that mixolimnion and monimolimnion could both originate from the same groundwater source.

Calculating "summed conductivity" as a quantitative bulk value for the dissolved ionic solutes revealed an oscillation in phase with the chemocline depth. However a comparison with an idealized model of complete retention of conductivity in the water body revealed that not all conductivity removed by chemocline erosion was lost, but a considerable part of it reappeared in the monimolimnion. Numerically we found 47 %. Though this number was affected by rough assumptions, it clearly indicated that re-dissolution was taking place, and this process must be considered as a factor for sustaining the density stratification. A groundwater inflow however was still required to balance the conductivity over the years in agreement with von Rohden et al. (2009).

Contributing to the aim of making reliable predictions of future water quality in meromictic lakes our findings imply that additional effects such as the limited re-dissolution of iron hydroxide in the monimolimnion and the buffering of mixing processes by ion-rich groundwater inflow have to be considered for the setup of numerical geochemical models predicting permanent stratification in iron-meromictic lakes.

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Figures

Figure 1: Geographical location of ~~Lake Waldsee~~Waldsee within the Muskau Arch in Eastern Germany [after *Kozma and Kupetz*, 2008]

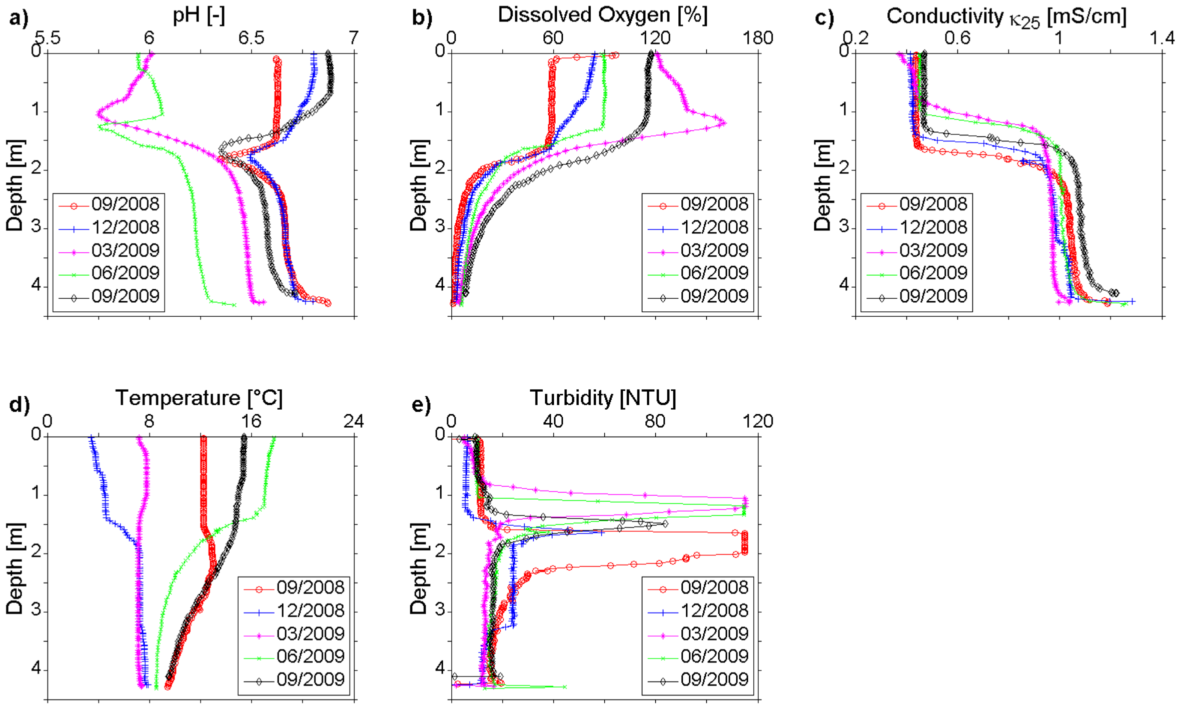


Figure 2: Physico-chemical profiles in ~~Lake Waldsee~~Waldsee between September 2008 and September 2009

Figure 3: Initial conditions of the water column experiment: brownish monimolimnion water in a PVC pipe, thermally insulated by PE matrasses. Uppermost matrasses were removed for the purpose of this photograph.

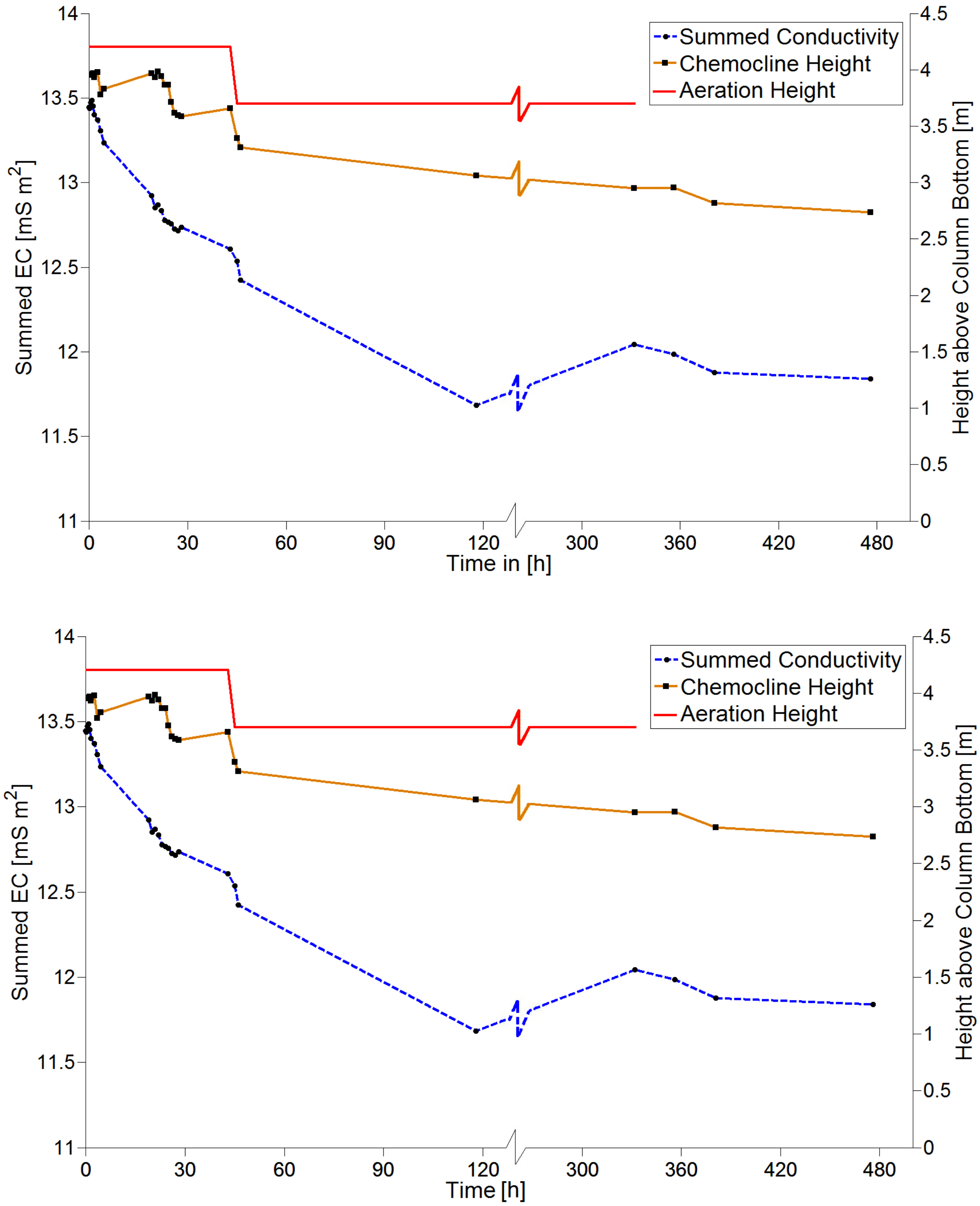


Figure 4: Temporal dynamics of chemocline height and summed conductivity (EC) during the column experiment. The scale breakage indicates the end of the hourly range sampling period of the experiment.

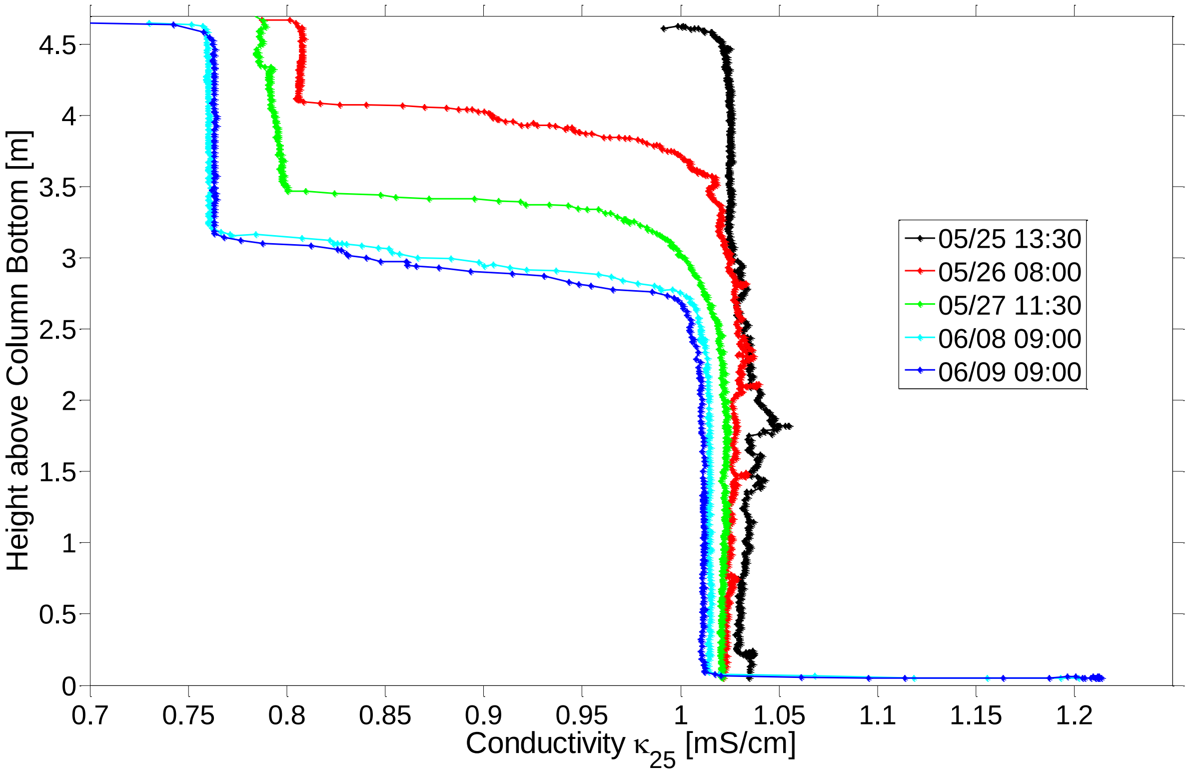


Figure 5: Selected conductivity (κ_{25}) profiles at different time steps of the lab experiment. The earliest profile shows the initial condition in the water column followed by two profiles during active aeration at a depth of 0.5 m and 1 m, respectively. Last two profiles show the conductivity distribution in the column a certain time after cessation of aeration. ~~profiles in the lab experiment~~

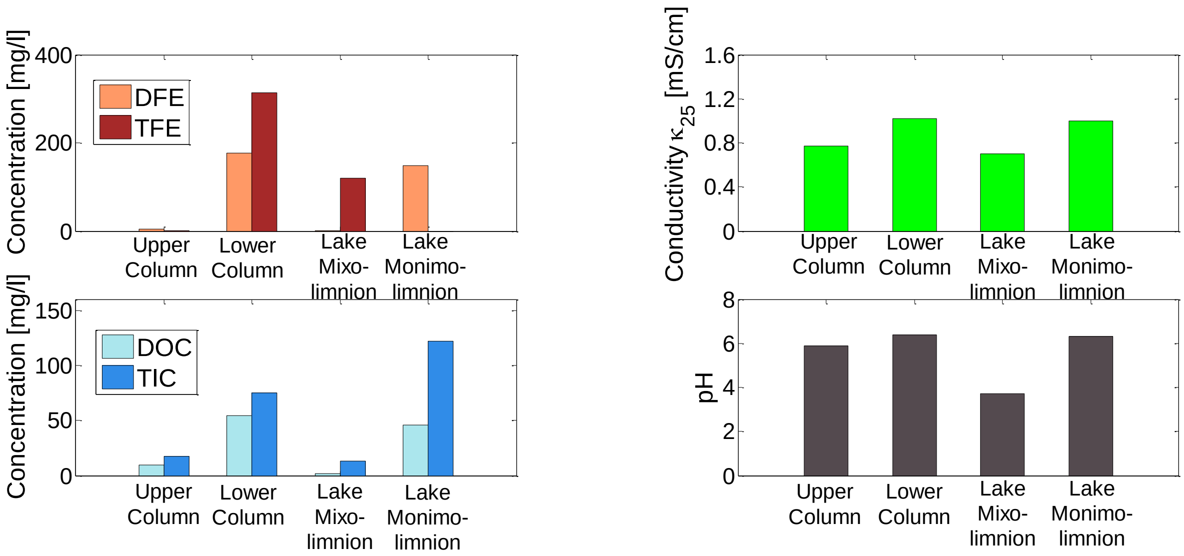
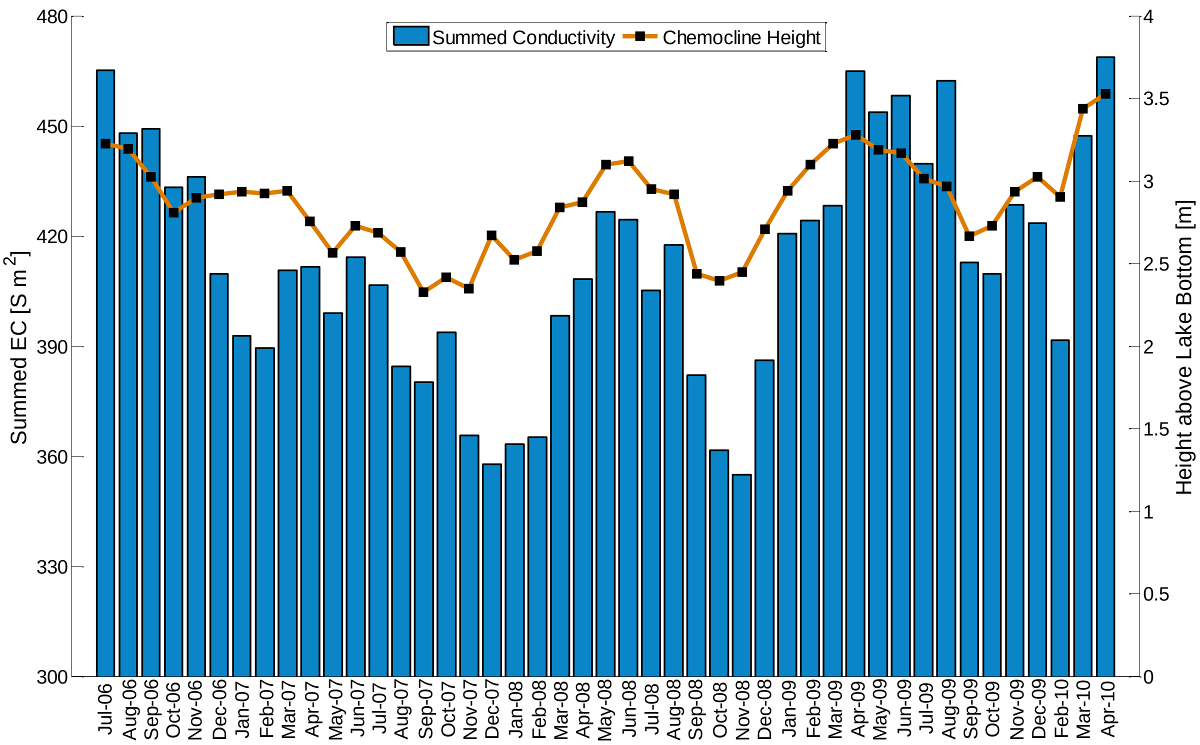


Figure 6: Iron species content (DFE and TFE), electrical conductivity, carbon species content (DOC and TIC) and pH-value of samples from different water layers in ~~Lake Waldsee~~Waldsee and the water column



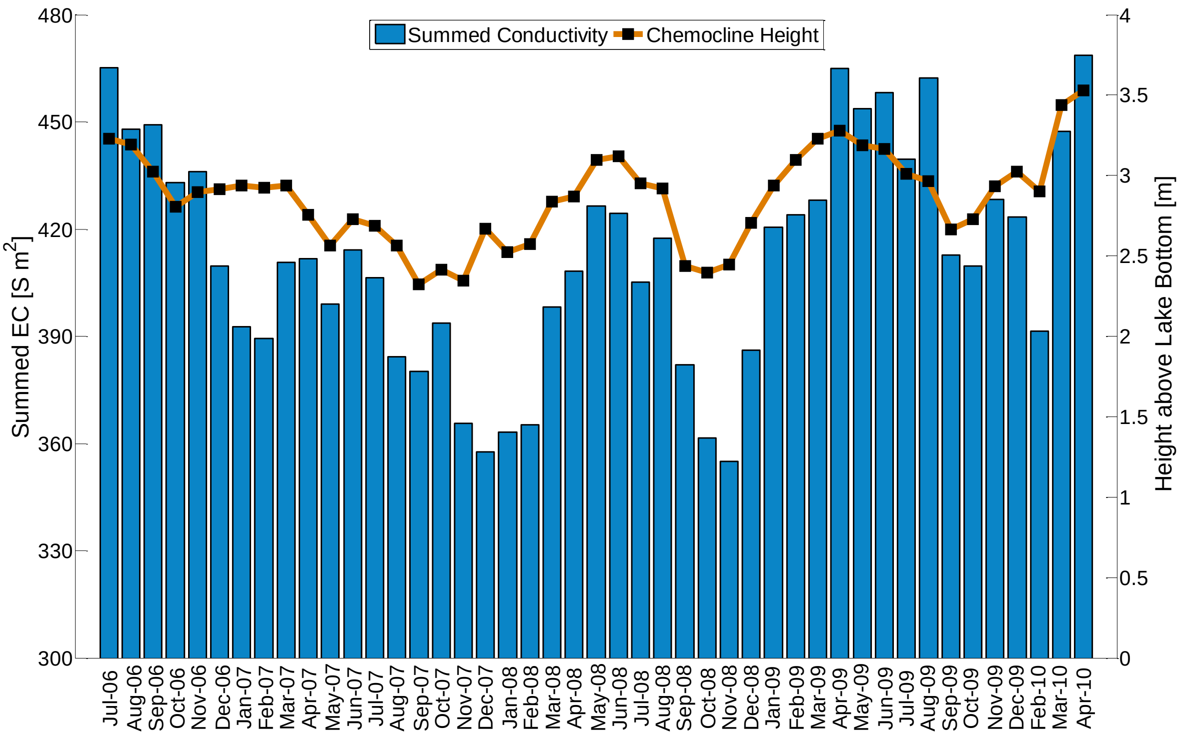


Figure 7: Time series of chemocline height and summed conductivity at ~~Lake Waldsee~~Waldsee between July 2006 and April 2010.

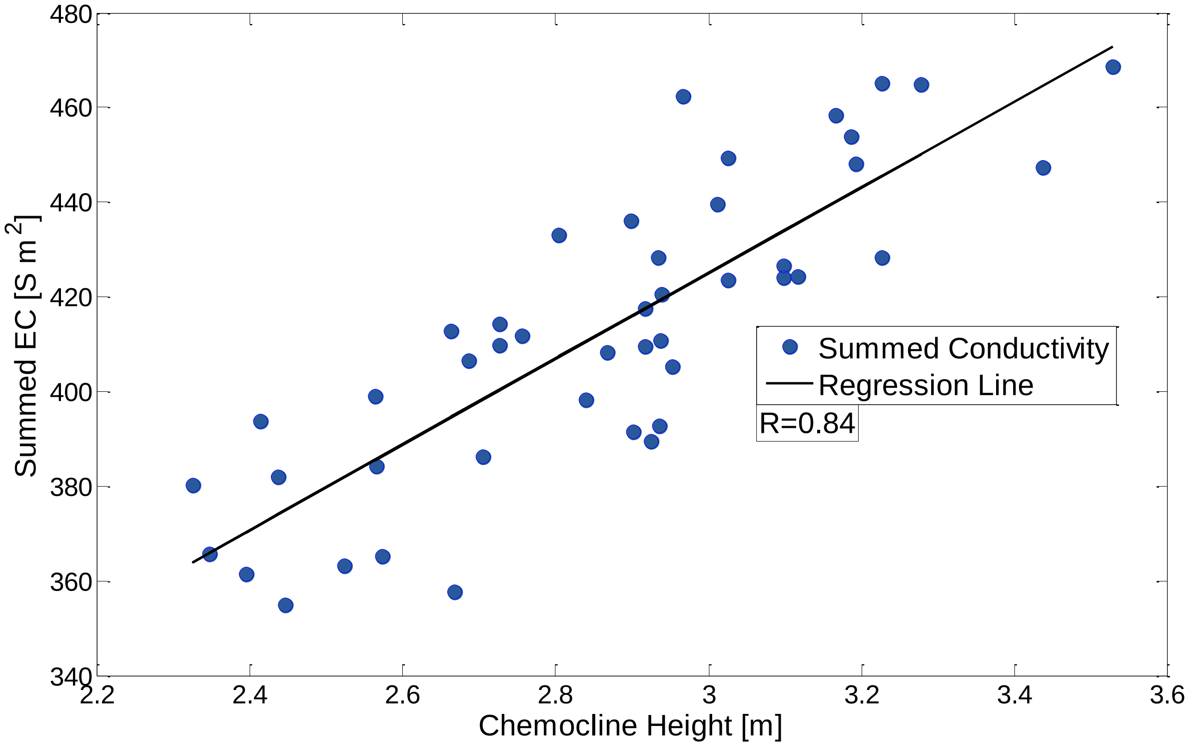


Figure 8: Correlation between summed conductivity and chemocline height. A linear regression results in a correlation coefficient of 0. 84.

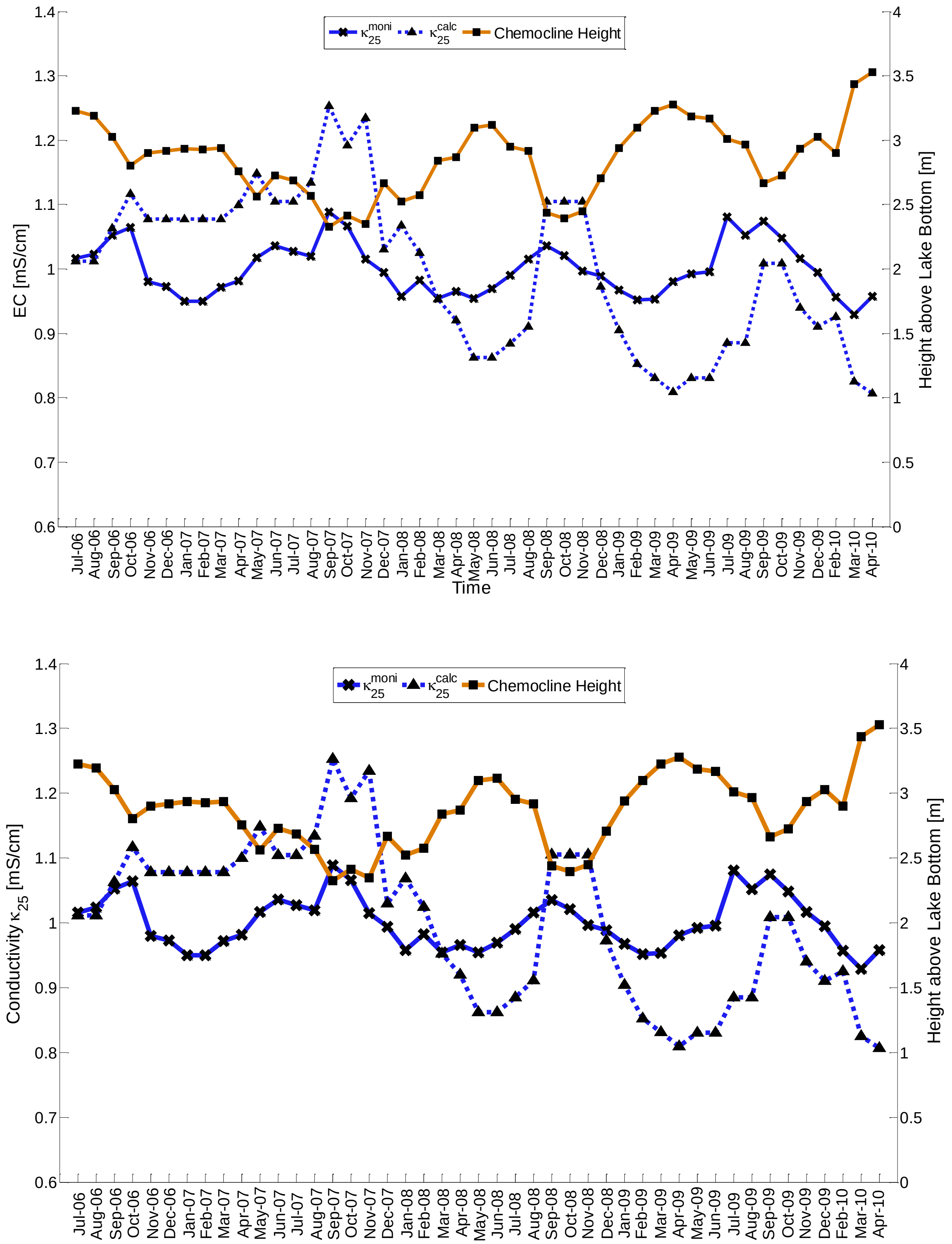


Figure 9: Comparison of time series of measured and calculated average electrical conductivity (κ_{25}) in the monimolimnion.