Dear Editor

Thank you very much for handling out manuscript. Thanks for the comments and thanks to the reviewers. We have considered all their comments and hope we managed to include all improvements they have hoped to see. Some of the questions have been answered in the comments during the discussion period of this manuscript. Here we refer in detail to the remaining questions and technical corrections that have been listed in separate, see below.

Thanks very much for considering our manuscript for HESS

For both authors

Erik Nixdorf

<u>**Editor questions and remarks**</u>

<u>E1.) I agree with Reviewer 2 that the abstract could be sharpened, in particular make the clear the novel methodological approach adopted here and highlight the broader significance of the research (bearing in mind the general nature of HESS and broad readership). I think it is a bit confusing at the moment for some non-experts in this field.</u>

We modified the abstract. Especially the first few sentences are used to introduce meromixis and stratification to direct the reader more towards the core considerations of the paper. We have also changed the title: „Quantitative analysis of biogeochemically controlled density stratification in an iron-meromictic lake". In addition we included two more fundamental references on iron meromixis (Kjensmo 1967, Hongve 1997) to connect the new investigation with the previous knowledge. Also the structure of the introduction has been changed: it starts with the topic of meromixis then moves to the special case of iron meromixis, in mine lakes and especially in Lake Waldsee. Now also clearly showing what is known about the chemical contributions to the density stratification and what is missing (the quantification of redissolution of iron).

<u>E2.) I would also ask that in the revision you review the headings and sub-headings to ensure the logical progression is clear (for example methodology is used for Section 3 heading, but plenty of methodology is described also in Section 2).</u>

We have done this; we clearly separated methods from measurements and results, and included subheadings in the methods section as well as in the discussion.

E3.) Similarly, the first sentence of the discussion is a results statement – it would be beneficial in my view to open the paragraphs with a clear statement on finding or opinion, that is then developed within the paragraph, in order to ensure readers clear follow the "story" of the research work.

We removed the first sentence. The "Discussion" 5.1 now starts appropriately, with a clear statement followed by the interpretation of the measurements.

E4.) I also like the discussion you had with reviewer 2 to link to the work to geochemical modelling prior results, and in particular in the latter part of the discussion it would be ideal if some lines are added to make clear the broader implications of this study (beyond Waldsee) – for example can this be a cost-saving method others could use in other lakes? also, are our current lake mixing models that focus on surface heating adequate, and/or does this approach open a new opportunity for exploring new numerical model approaches?

We condensed the discussion with reviewer #2 to a subsection „5.3 Consequences for Lake Stratification Modelling". In addition – as mentioned above – we have put our work more in the perspective of previous investigations. We hope that the extension of knowledge presented in this publication can be seen more clearly bedded into the wider limnological perspective.

E5.) A final suggestion – since the overall paper is not very long and given the discussion in particular is relatively short, it seems possible to potentially merge the discussion and "summary"(/conclusions), and then introduce 2 or 3 sub-headings to help guide the reader. This may help address the issues I raised above since the clear statements of your findings in the discussion can help put the technical discussion in context, helping the overall readability.

We included subheadings in the discussion section and we changed the final section from „Conclusions" to „Summary". We hope that the main conclusions are easily found by the reader.

Reply on specific remarks and technical corrections of reviewer 1 (Hydrol. Earth Syst. Sci. Discuss., 12, C2599–C2601, 2015)

R1_1.) From biological point of view, authors should add to Chapter 2.2. important parameter: visibility of Secchi disk. This parameter allow to estimate depth of light penetration and possibility of oxygen production by phytoplankton. It is important for iron oxidation

We provided Secchi-depth data to the reviewer. As outlined in our reply, a quantitative approach for oxygen production cannot be based on these data and would require considerable space and would distract from the main purpose of the study.

R1_2.) In the chapter 4.3, page 5613 line 5): Authors discussed correlation coefficient 0.71 whereas on fig 8 this value is has coefficient of determination R2. See comment to fig 8.

We corrected and used correlation coefficients in the text (p.14 line 17 and figure (figure 8), only.

R1_3.) In the Chapter 5 (page 5613line 15). Is: “this result confirmed that the permanent stratification of Lake Waldsee was preserved by the presence of conductivity gradients”. Comment: shorthand, slang. Rather dissolved compounds.

We replaced the expression “conductivity gradients” by “dissolved compounds” (p.14 line 25)

R1_4.) Figure 1. Right map, Change colour of letters “Waldsee” suggestion: white.

Changed to white (figure 1)

R1_5.) Fig 2,Rearrange drawings and increase the size of letters and add identification by letters a,b, c, d, e

We rearranged the drawings, increased the size of the letters and numbered the subplots of figure 2

R1_6.) Figure 3.lack of citation in the text

Citation was added (p.8 line 9)

R1_7.) Figure 5. letters of legend and axis tags should be greater

Letters of legend and axis tags were enlarged

Reply on specific remarks and technical corrections by Reviewer 2 (Hydrol. Earth Syst. Sci. Discuss., 12, C2647–C2649, 2015

R2_1) The title of the paper seems to reflect the content not adequately. The research did not focus on the understanding of the (already known) biogeochemical processes but on the effects of these processes on electrical conductivity as an expression of water density in the different layers of meromictic lakes. The prominent part of the title should address this aspect. The same discrepancy is also felt when comparing the abstract with the main paper.

We changed the title, and the abstract. Further explanations see above (reply on comment E1)

R2_2) The introduction is not well structured. The contents of the first paragraph is repeated in the following paragraphs. It can be deleted without loss of information. The second paragraph starts to describe the formation of meromictic lakes followed by a paragraph referred to the distribution of meromictic lakes and returning to the background of their formation in the fourth and fifth paragraph.

The structure of the introduction has been changed: it starts with the topic of meromixis then moves to the special case of iron meromixis, in mine lakes and especially in Lake Waldsee. Now *also clearly showing what is known about the chemical contributions to the density stratification and what is missing (the quantification of redissolution of iron).*

R2_3) Chapter 2 should be arranged in another way. Whereas subchapters 1 and 2 can form the description of the study site, subchapter 2.3 should become part of the following methodology chapter (chapter 3). Table 1 does not provide significant information. It may be not necessary. Some of the information can be added to the text. It does not become clear if the authors considered different species of iron.

Subchapter 2.3 was shifted to the methodology part (chapter 3.2) Table 1 was deleted and import information were included in the text (chapter 3.1). Information were added in chapter 3.1 that the authors considered ferrous and ferric iron for the chemical analysis of water compounds

R2_4.) In the result chapter (chapter 4), some data could be presented more precisely. Especially figure 4 seems to need a revision. The figure would be more clearly with a real time scale on the x-axis. The breaks in the measurements should become visible. Furthermore, it would be useful to compare the rates of the decrease in conductivity in certain periods of the experiment to evaluate if the formation of iron precipitates is a steady process or if different steps occur.

We revised fig.4 by using a real time scale on the x-axis. This makes it much easier to evaluate the changes in degradation rate with time in dependence of the experiment progress and the aeration depth.

R2_5.) In the last paragraph of chapter 4.1 the authors describe "elevated values of electrical conductivity towards the end of the experiment near the bottom" by referring to figure 5. This does not become visible from the figure that shows a permanent slight decrease in the whole lower water layer during the experiment.

We decided to replace one profile in fig. 5 (see appendix) and changed the scaling of the y-axis that it aligns with figure 4, increased the font size as suggested and add lines to increase the visibility of the increased conductivity values close to the bottom. We hope that this facilitates an easier perception of increased EC-values in the range up to 1.2 mS/cm at the bottom of the column

R2_6.) It would be interesting to test if the assumptions drawn from the experiment results and lake measurements could be confirmed by geochemical modelling. This would also allow a more reliable assumption for the interpretation of the carbon data (chapter 4.2).

There has been a geochemical simulation of Waldsee by Moreira et al. (2011). Thank you for this comment, we should cite this publication in our paper. However, they provided no quantification of the partial re-dissolution of the precipitated iron. This is where our investigation delivers new parametrizations. Running a geochemical model is far outside the scope of this paper, but definitely an interesting challenge. We added a new subchapter "5.3 Consequences for Lake Stratification Modelling". We hope that the extension of knowledge presented in this publication can be seen more clearly bedded into the wider limnological perspective

R2_7.) The conclusions expressed in the first paragraph of chapter 4.3 have to be proved by statistical analyses.

We decided to calculate the statistical moments mean and standard deviation for our results in the first paragraph of chapter 4.3 in order to justify our statements and conclusions.

R2_8.) The chapter entitled "Conclusions" more resembles a "Summary" than what can be expected from conclusions. It should be renamed or be revised.

Changed to "Summary"

R2_9.) The authors should call their research lake always "Waldsee" as in the abstract and not "Lake Waldsee" (due to doubling of the term "lake").

We replaced all terms "Lake Waldsee" by "Waldsee"

R2_10.) Does the lake originate from surface (abstract) or underground mining (chapter 2.1)?

The lake originated from underground mining. We changed the wrong expression in the abstract (line 9)

R2_11.) Figure 2 is far too small. It is not possible to read the different legends.

We increased the font size and the axis scaling of Figure 2 in order to increase readability

R2_12.) Figure 4: 06/25 measurement has to be placed as third bar instead of sixths

Figure 4 was changed completely (see reply on comment R2_4)

R2_13.) Figure 5: Same depth scale from bottom to surface should be used as in figure 4.

Y-axis was reversed and font size increased

R2_13.) Figure 6: enlarge for better readability.

Font size was increased to improve readability

Quantitative analysis of b~~B~~iogeochemically ~~processes~~ ~~control~~controlled ~~ling~~ 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 ~~Bio~~geochemical setting and the ~~processes and~~ mixing regime of a lake can stabilize ~~control~~ each other mutually. We attempt a quantitative approach to the contribution of chemical reactions sustaining the density stratification. As a demonstration object, ~~W~~we chose t~~T~~he prominent case of iron meromixis ~~is investigated~~ in Waldsee near Doebern, a small lake that originated from near surface underground mining of lignite~~, as a demonstration object~~. From a four years data set 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 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 constructed a lab experiment, in which aeration of monimolimnetic waters removed iron compounds and organic material. Precipitates could be

identified by visual inspection. Introduced air bubbles ascended through the water column and formed a water mass similar to the mixolimnetic Waldsee water. The remaining less dense 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.

1. Introduction

~~In meromictic lakes (see below), transport of matter differs from other lakes fundamentally. Oxygen supply to the deep water, recycling of nutrients from the sediments and deep recirculation during winter do not happen as in holomictic lakes. As a consequence, entirely different chemical milieus can establish, with all consequences for water quality and the food web. The permanent stratification can be imposed from outside by inflows, but lake intrinsic processes, which create meromixis or contribute essentially to the creation of meromixis, are of particular interest.~~

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 atmosphere creates anoxic, reducing conditions leading to an enrichment of dissolved gases and ionic substances in the deep water~~ (Boehrer and Schultze, 2008)~~.

~~Meromictic lakes show a global distribution. Meromictic lakes could be identified in mining regions on Earth, such as the Iberian Pyrite Belt, Spain (e.g. Lake San Telmo, Cánovas et al.,~~

~~2012, and Lake Conception, Santofimia and López-Pamo, 2013), Vancouver Island, Canada (Island Copper Mine pit lake, Wilton et al., 1998; Stevens and Lawrence, 1998), the Central German Mining District (e.g. Lake Wallendorfer See and Lake Rassnitzer See, Boehrer et al., 2014) and the Lower Lusatian Mining District, Germany (e.g. Lake Moritzteich, von Rohden et al, 2009) to name just a few~~Despite their worldwide occurrence, only ~~A~~a small number of internal and external processes can be responsible for the formation of density stratification (e.g. ~~Hakala, 2004;~~ Walker and Likens, 1975; Hakala, 2004; Boehrer and Schultze, 2008).

There are good reasons for scientific interest in meromictic lakes: ~~S~~some of the largest lakes are meromictic (~~Tanganyika,~~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 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 identified in many mining regions on ~~E~~earth where stratification limited 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 even implemented to restrict the vertical transport (Island Copper Mine pit lake in Canada, Wilton et al., 1998; Stevens and Lawrence, 1998).

Meromictic conditions ca~~in mining lakes are~~n be sustained by a continuous inflow of high density groundwater ~~formed by weathering processes of exposed sulfide-bearing material (Geller et al., 1998)~~ 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 chemocline~~. The dense water ~~can~~ may also be formed within the lake e.g.~~(~~ by weathering processes of exposed sulfide-bearing material (Geller et al., 1998).~~von Rohden and Ilmberger, 2001). In case of mining lakes, establishing stable meromictic conditions might be favorable as it allows the confinement of water quality problems (e.g. heavy metals) from the surface water into the deep water layers (Jöhnk, 1999; Nixdorf et al., 2001; Wiessner et al., 2014). The exclusion of the monimolimnia from gas exchange with atmosphere creates anoxic, reducing conditions leading to an enrichment of dissolved gases and ionic substances in the deep water (Boehrer and Schultze, 2008).~~

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~~Subterranean ion rich acid mining drainage (AMD) can be formed by weathering processes of exposed sulfide-bearing material (Geller et al., 1998). Meromictic conditions in mining lakes are 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, the chemocline (von Rohden and Ilmberger, 2001). In case of mining lakes, establishing stable meromictic conditions might be favorable as it allows the confinement of water quality problems (e.g. heavy metals) from the surface water into the deep water layers (Jöhnk, 1999; Nixdorf et al., 2001; Wiessner et al., 2014).~~

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 ~~mining~~ lakes.

One prominent reactant is iron, which gets precipitated from the oxygenated mixolimnetic waters and dissolves in the anoxic (reducing) chemical conditions of the monimolimnion (Kjensmo, 1967; Hongve, 1997). Exemplarily it is proposed for the shallow mining ~~L~~lake Waldsee 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 ~~are able to~~ 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 calculate “summed conductivity" as a measure for the amount of solutes within Lake Waldsee, and give a 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~~ description ~~and Measurements~~

2.1 Study ~~Site~~site

The demonstration site Lake 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 m², has a volume of 6500 m³ and reaches a maximum depth of 4.7 m (Boehrer et al., 2009). Lake 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 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 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 does not have a surface inflow. Hence groundwater is the main source of recharge. Tracer experiments estimate a mean groundwater recharge to Lake Waldsee of 8.2 m³/d (mostly from southern direction) and a mean groundwater outflow of 6 m³/s (von Rohden et al., 2009).~~ Lake Waldsee does not have a surface inflow, which makes groundwater the main source of recharge.~~ A small only occasionally filled drainage trench connects Lake 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~~ stratification and ~~Water~~ water ~~Chemistry~~chemistry

The physico-chemical profiles of Lake 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 ~~driven~~ 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:

$$HCO_3^- + H^+ \rightarrow CO_2\uparrow + H_2O \tag{2}$$

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:

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

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.

~~2.3 Field and lab measurements~~

~~45 monthly field measurements have been conducted in Lake Waldsee between July 2006 and April 2010. Vertical profiles of temperature, pressure, pH, turbidity and in-situ electrical conductivity were collected in Lake 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~~

~~$\kappa_{25} = \frac{C}{\alpha_{25}\cdot(T-25°C)+1}$ (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). On May 18th 2011, mixolimnion and monimolimnion water were collected for chemical analysis (Table 1). In addition, 150 l of monimolimnion were sampled and air-tightly and opaquely stored at a temperature of 4°C for later use in a column experiment.~~

3. Methodology

3.1 Sampling and ~~Set~~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. ~~(Table 1).~~ In addition, 150 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~~ the column was subsequently filled with 130 l of this monimolimnetic lake water to reproduce the maximum water depth of 4.7 m in Lake 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 ~~the~~ 25.05.2011 13:00 and ~~the~~ 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.

3.2 ~~Calculating summed e~~Electrical conductivity

45 monthly field measurements have been conducted in Lake Waldsee between July 2006 and April 2010. Vertical profiles of temperature, pressure, pH, turbidity and in-situ electrical conductivity were collected in Lake 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

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

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 ~~former~~ 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:

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

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, 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:

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

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 $\kappa_{25}^{moni}(j, t_{i-1}) - \overline{\kappa}_{25}^{mixo}(t_i)$ and that the entire amount of conductivity was transferred to the remaining monimolimnion volume:

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

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 ~~the~~ 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 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 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 ~~is~~ was beyond the scope of this experiment.

Profiles of electrical conductivity (Figure 5) showed a distinct step similar to measured profiles in Lake 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. The temporal delay could be 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 lab analysis showed that the aeration of the column's upper water changed the water characteristics drastically (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, 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

The height of the chemocline varied seasonally over ~~4~~ four years of monthly observation (see also von Rohden et al., 2009). From April to October, the chemocline ~~rose~~sank, while it ~~sank~~ 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 ~~showing a slightly rising trend~~. 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 ~~significantly~~ about three times higher than the observed variations in lake water level.~~.~~

The summed conductivity of ~~Lake Waldsee~~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 ~~421~~ 412±31.3 $S\cdot m^2$, meaning that about ~~20~~ 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.~~71~~ 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

~~The measured averaged electrical conductivity of the monimolimnion in Lake Waldsee was in a range between 0.93 mS/cm and 1.09 mS/cm within the observation period, having a temporal mean of 1.00 mS/cm (Figure 9) and a standard deviation of 0.041 mS/cm. Considering that the averaged electrical conductivity of the mixolimnion never exceeded 0.54 mS/cm, this result confirmed that the~~ Ppermanent stratification of Lake Waldsee was preserved over the observation period by the presence of ~~conductivity gradients~~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 Waldsee 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. ~~Assuming that groundwater showed fairly constant chemical properties, this indicated that internal physico-chemical processes were potential drivers of the monimolimnetic electrical conductivity variations.~~

For quantification of internal processes versus external sources, we compared measured values with the calculated values of our simplified model of a closed system Lake Waldsee. Based on eq. 7 and 8, the average monimolimnion conductivity $\bar{\kappa}_{25}^{calc}(t_i)$ 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 ~~of deviations~~ between the calculated and the measured average electrical conductivity of the monimolimnion.

The graph 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 ~~increase~~ rise of 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, the area of the sidewalls ~~is~~ was only about 1-3% of the total area of each lake layer. Hence, the potential storage capacity ~~efficiency~~ 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 itself.

~~Furthermore~~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 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 ~~As this was taking place in a chemically similar setting, it is justified to use summed conductivity as a quantitative measure to draw conclusions about relevant processes involved in the stratification of Lake Waldsee~~.

5.2 Impact of groundwater recharge on permanent stratification

A less pronounced re-covering 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 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 parametrization of numerical models for the prediction of stratification in meromictic lakes.

6. ~~Conclusions~~Summary

Regular measurements of electrical conductivity could confirm that the induced stratification of Lake 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. 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. A sharp conductivity (and hence density) gradient formed as had been observed in Lake 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: iron removal, pH depression, DOC removal and CO_2 loss. This confirmed previous research that the density-gradient in meromictic Lake 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.

Acknowledgement

This work was funded in part by Deutsche Forschungsgemeinschaft DFG. The authors thank Uwe Kiwel and Karsten Rahn for great support during field and lab-work. Measurement data are available from the authors upon request (erik.nixdorf@ufz.de). The data are archived at the Helmholtz Centre for Environmental Research (UFZ).

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~~Tables~~

~~Table 1: Analyzed physical and chemical water parameters and used lab measurement methods~~

~~Measured variable~~	~~Measurement procedure~~
~~Electrical conductivity~~	~~7-pole platinum cell conductivity sensor~~
~~pH-value~~	~~pH meter~~
~~Carbon species (DOC, TIC, TOC)~~	~~Thermal-catalytic oxidation with subsequent infrared spectroscopy~~
~~Iron~~	~~Atomic emission spectroscopy~~

Figures

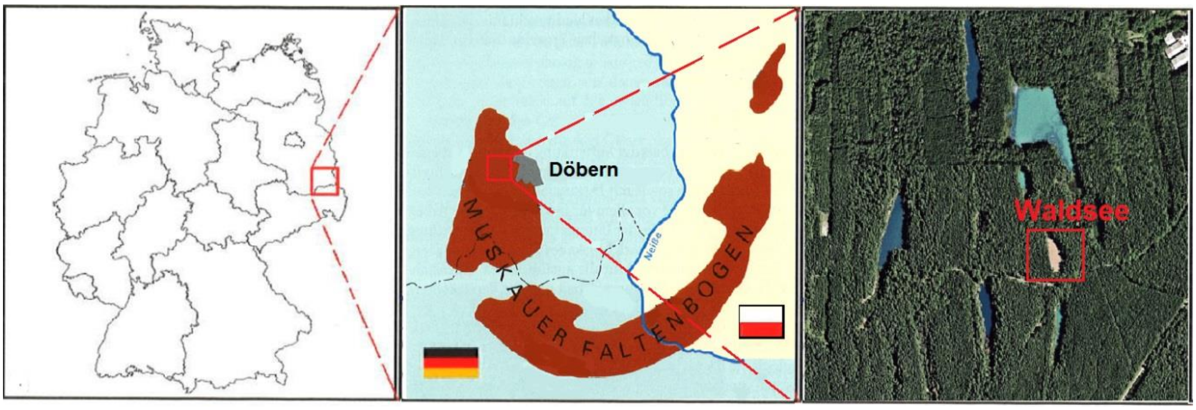
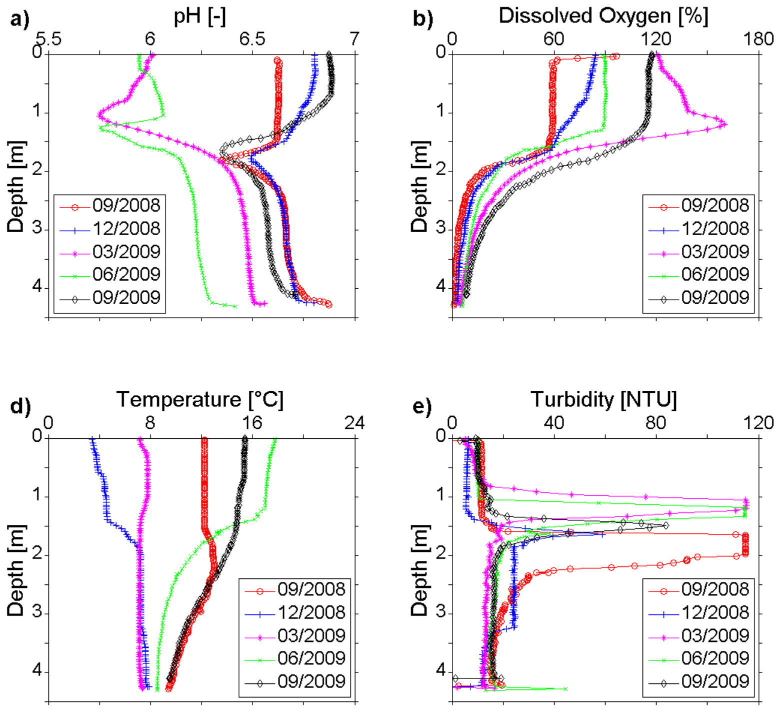


Figure 1: Geographical location of Lake Waldsee within the Muskau Arch in Eastern Germany [after *Kozma and Kupetz*, 2008]



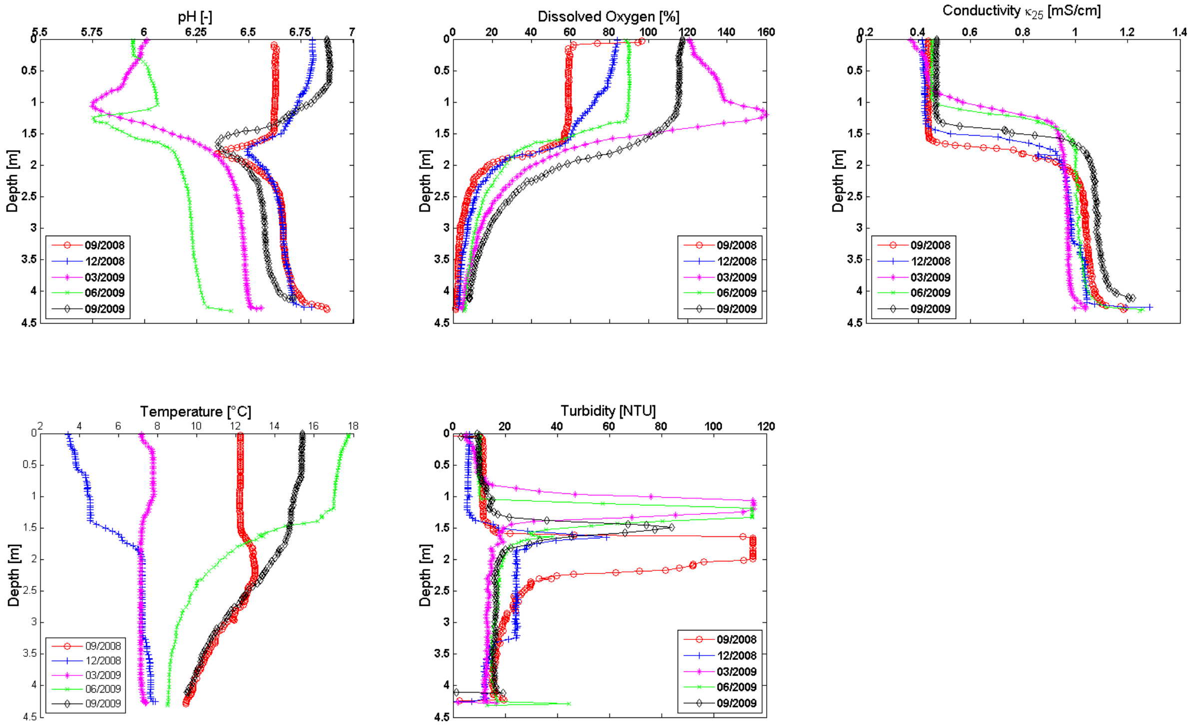


Figure 2: Physico-chemical profiles in Lake Waldsee between September 2008 and September 2009

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.

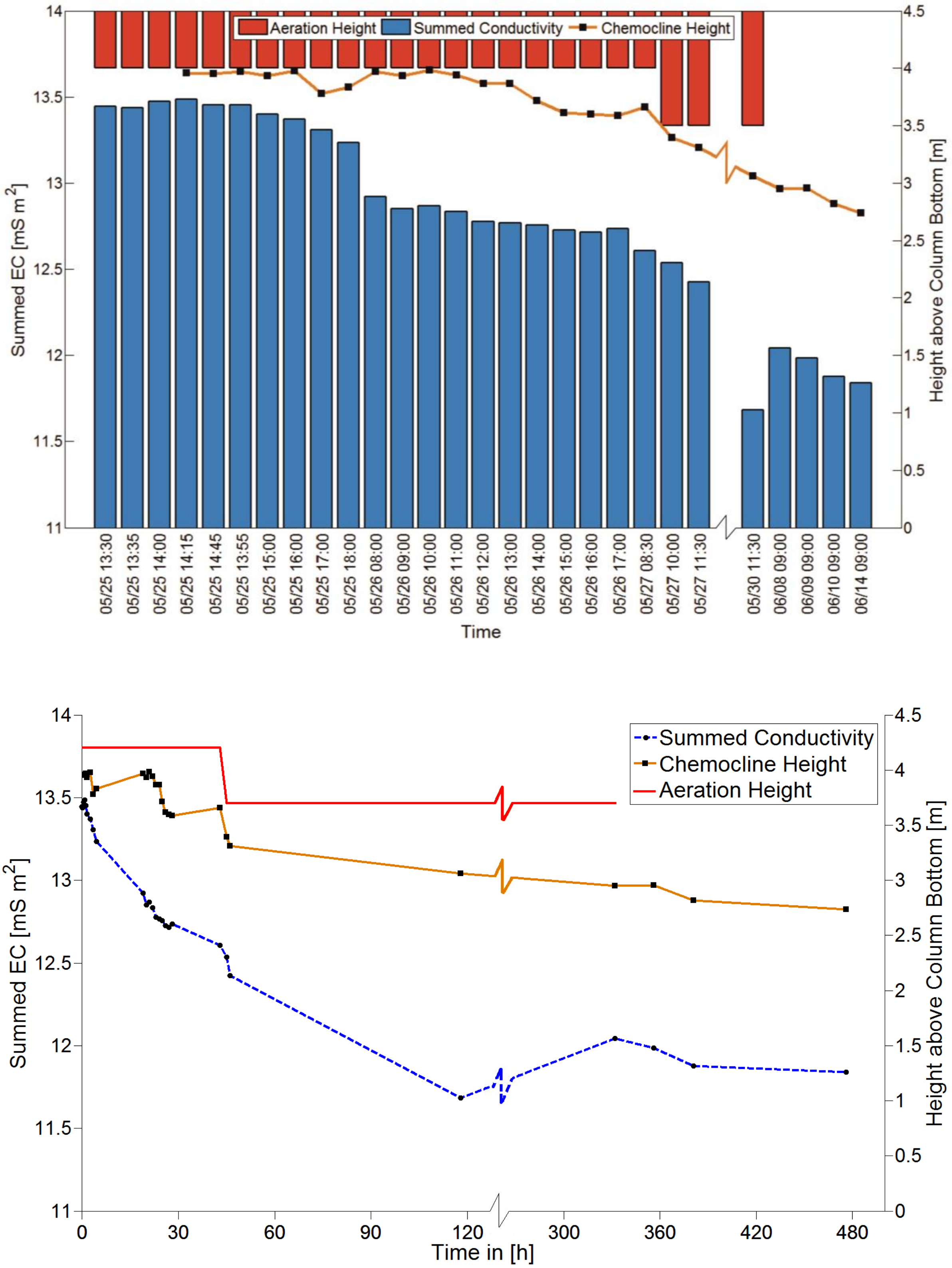


Figure 4: Temporal dynamics of chemocline height and summed conductivity during the column experiment. The scale breakage indicates the end of the hourly range sampling period of the experiment.

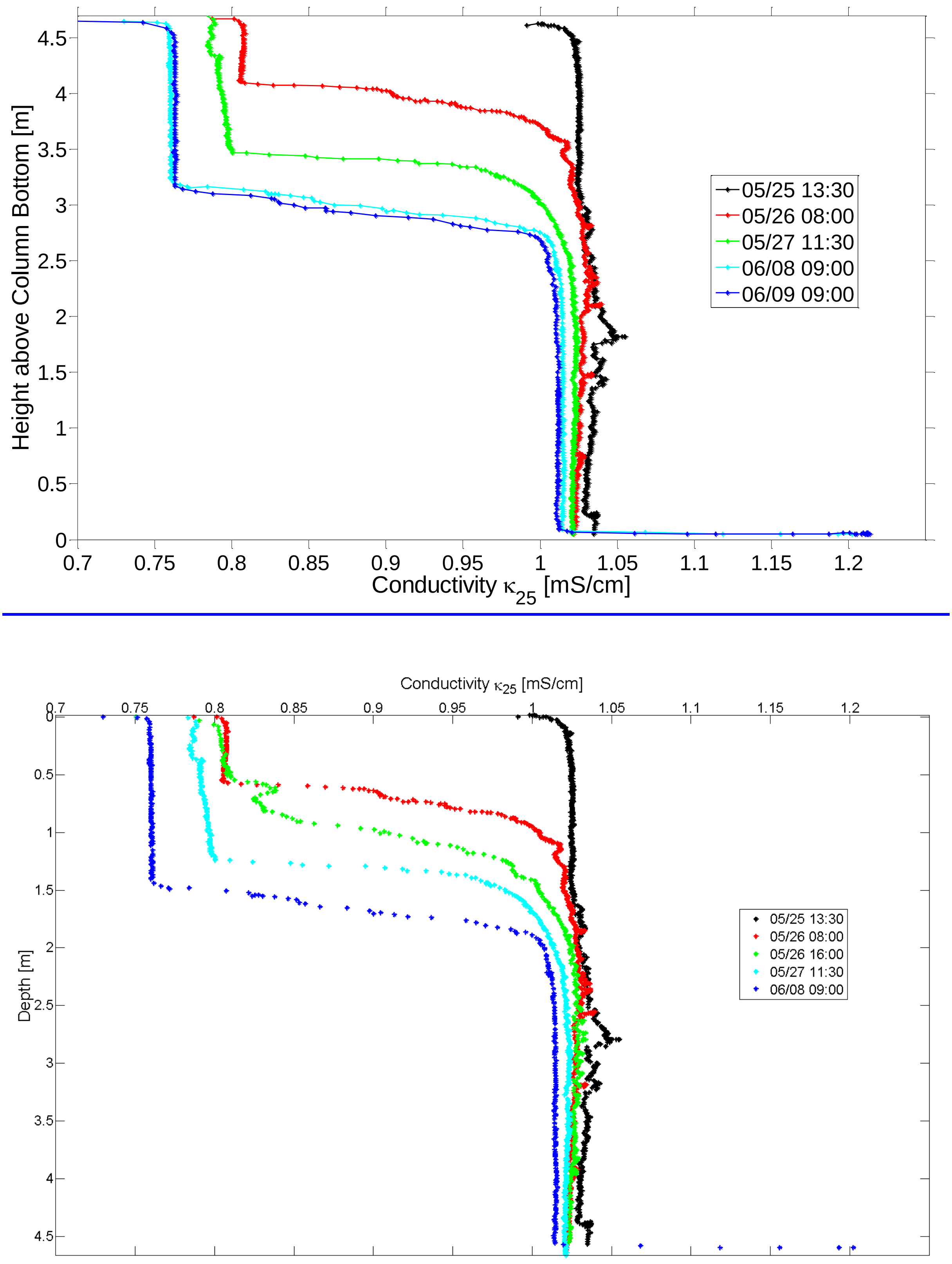
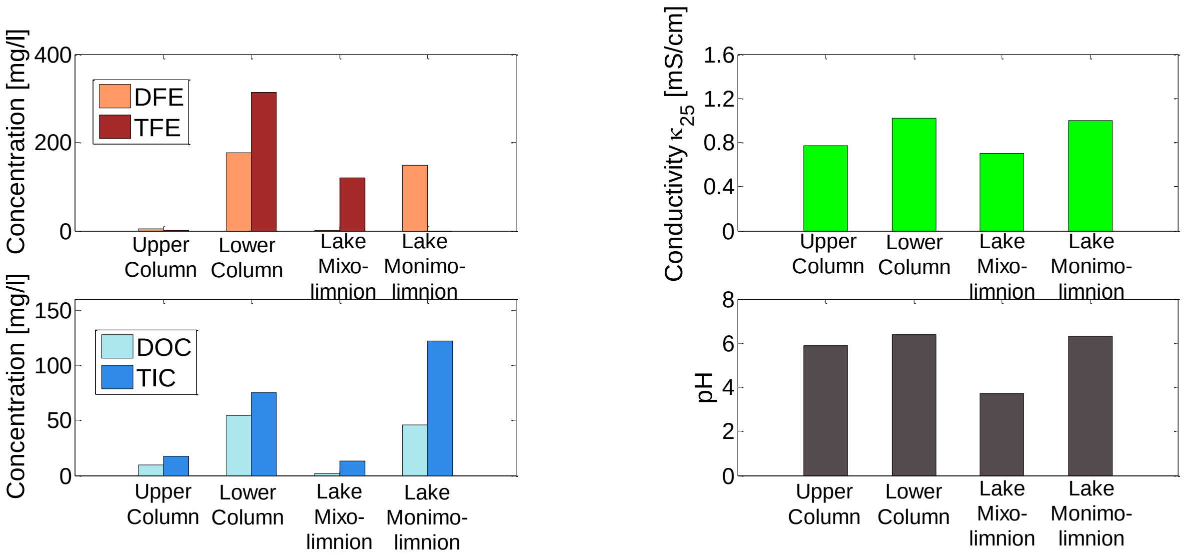


Figure 5: Selected conductivity profiles in the lab experiment~~water column~~



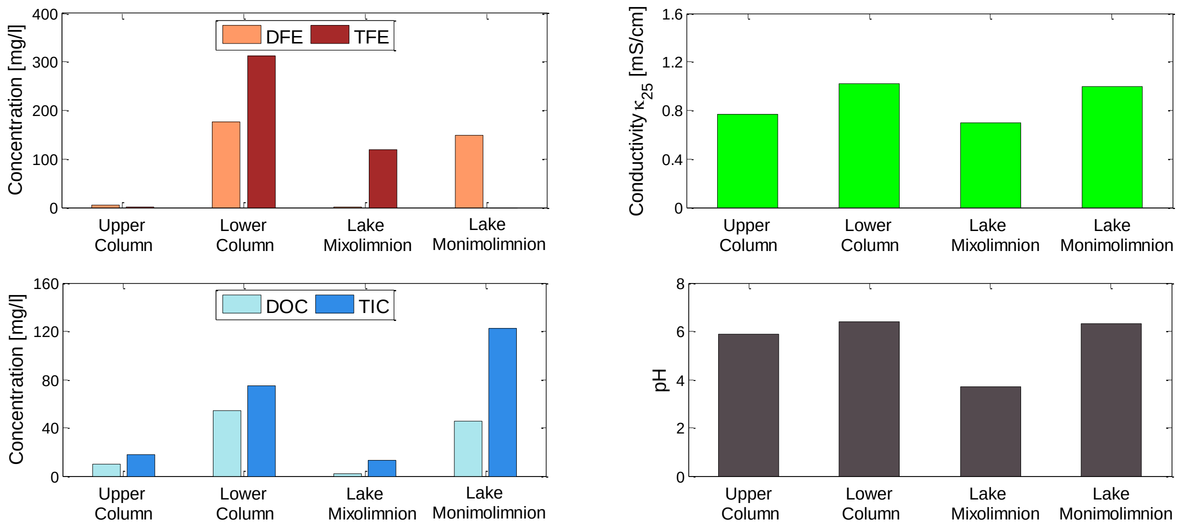


Figure 6: Iron species content (DFE and TFE), electrical conductivity, carbon species content (DOC and TIC) and pH-value of samples from different water layers in Lake Waldsee and the water column

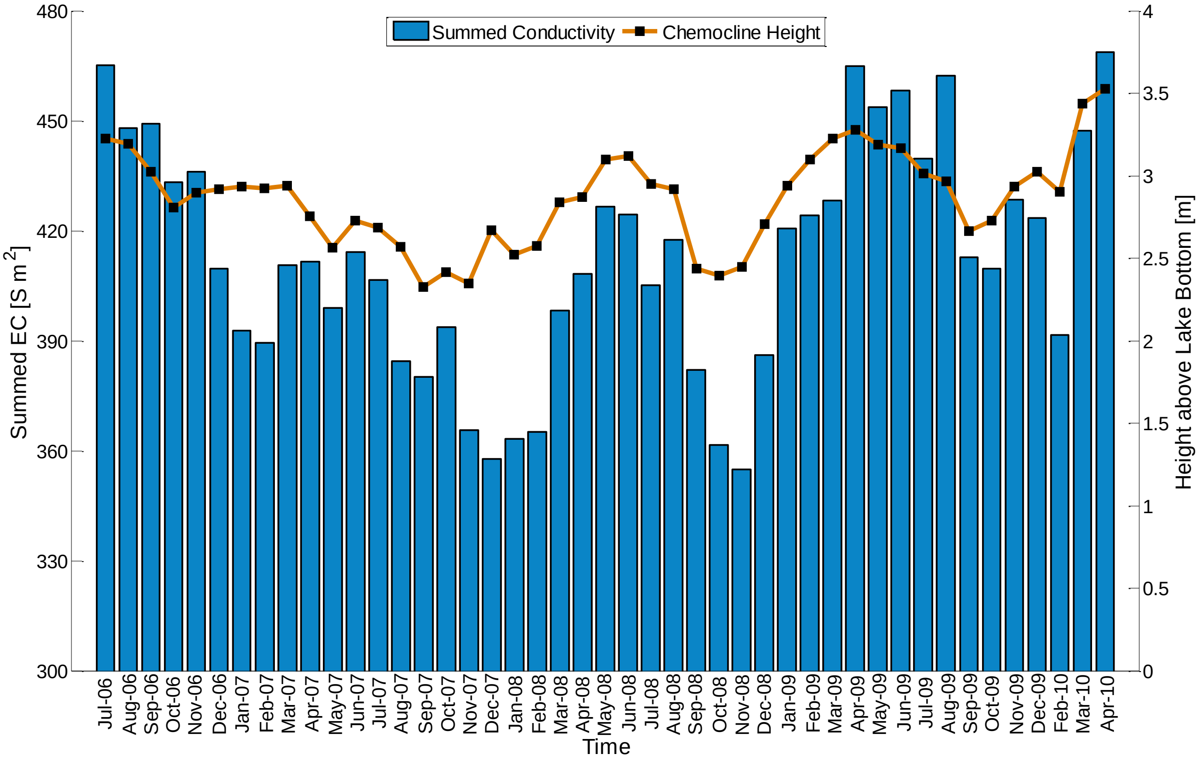
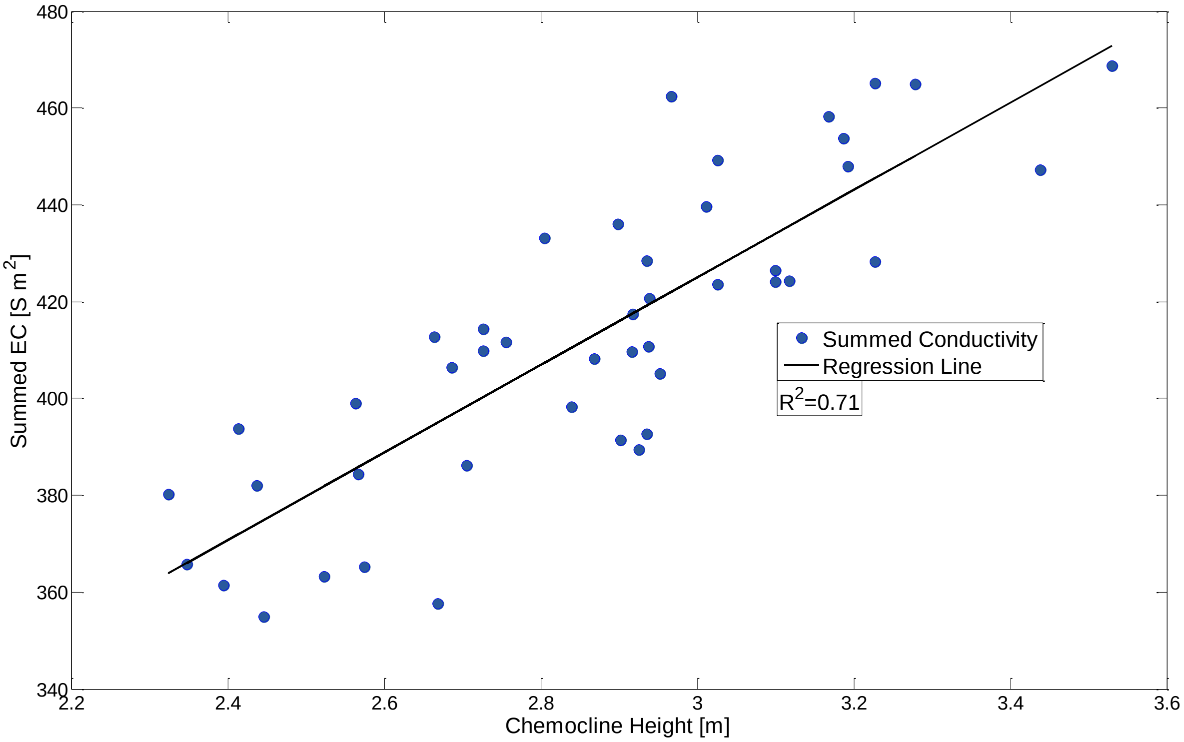


Figure 7: Time series of chemocline height and summed conductivity at Lake Waldsee between July 2006 and April 2010.



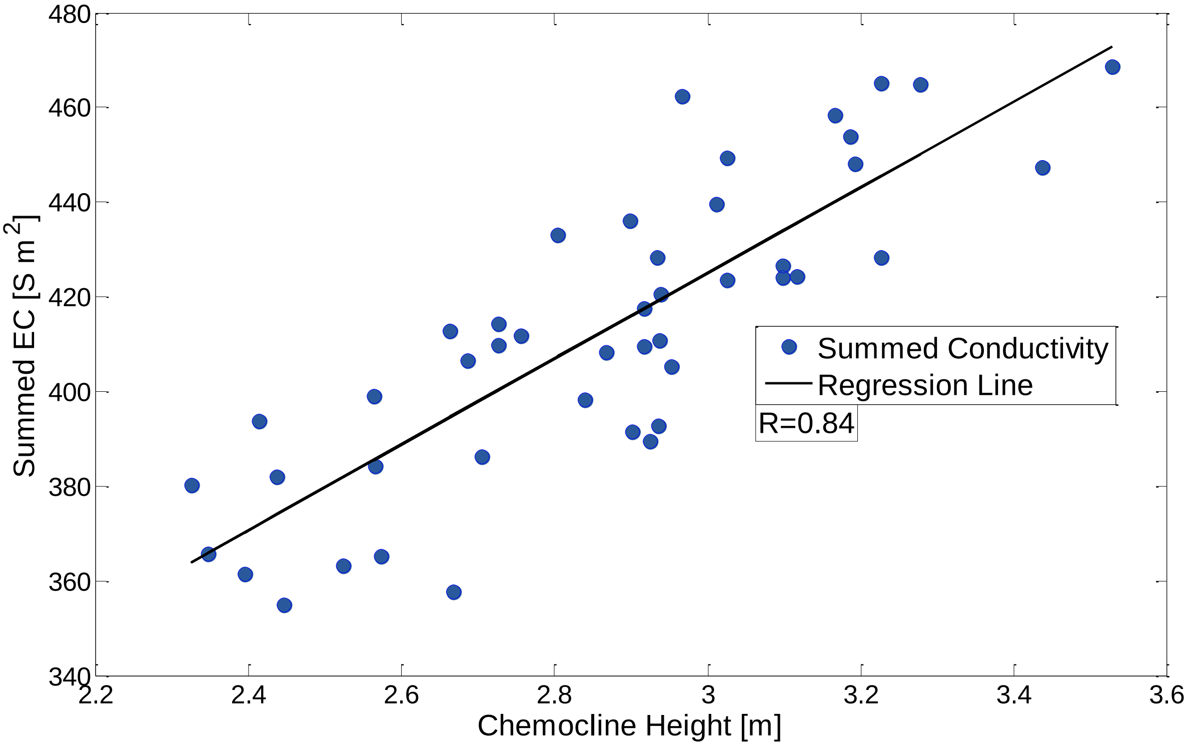


Figure 8: Correlation between summed conductivity and chemocline height. A linear regression results in a correlation coefficient of 0.~~7~~84~~1~~.

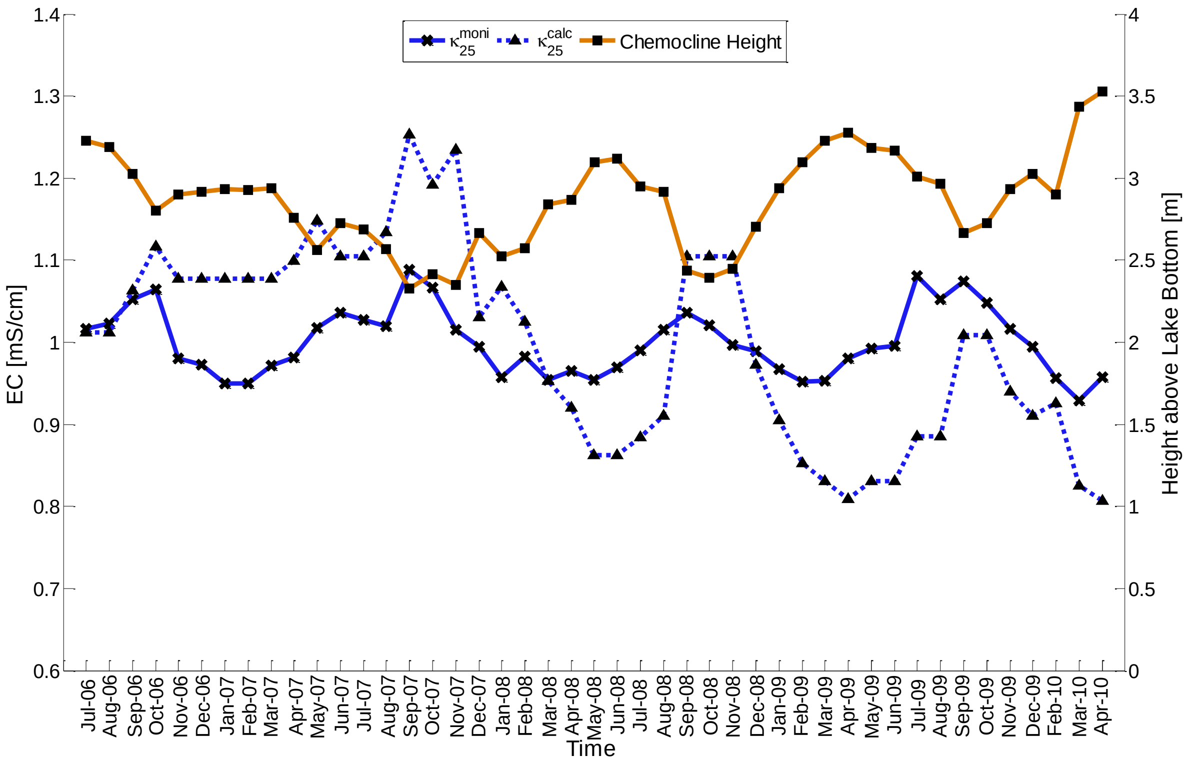


Figure 9: Comparison of time series of measured and calculated average electrical conductivity in the monimolimnion.

List of changes made in the manuscript

Main document changes and comments

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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

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setting and the

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We attempt a quantitative approach to the contribution of chemical reactions sustaining the density stratification.

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As a demonstration object,

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is investigated

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near surface underground

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, as a demonstration object

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, as a demonstration object

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In meromictic lakes (see below), transport of matter differs from other lakes fundamentally. Oxygen supply to the deep water, recycling of nutrients from the sediments and deep recirculation during winter do not happen as in holomictic lakes. As a consequence, entirely different chemical milieus can establish, with all consequences for water quality and the food web. The permanent stratification can be imposed from outside by inflows, but lake intrinsic processes, which create meromixis or contribute essentially to the creation of meromixis, are of particular interest.

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The exclusion of the monimolimnia from gas exchange with atmosphere creates anoxic, reducing conditions leading to an enrichment of dissolved gases and ionic substances in the deep water (Boehrer and Schultze, 2008).

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(Boehrer and Schultze, 2008)

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Meromictic lakes show a global distribution. Meromictic lakes could be identified in mining regions on Earth, such as the Iberian Pyrite Belt, Spain (e.g. Lake San Telmo, Cánovas et al., 2012, and Lake Conception, Santofimia and López-Pamo, 2013), Vancouver Island, Canada (Island Copper Mine pit lake, Wilton et al., 1998; Stevens and Lawrence, 1998), the Central German Mining District (e.g. Lake Wallendorfer See and Lake Rassnitzer See, Boehrer et al., 2014) and the Lower Lusatian Mining District, Germany (e.g. Lake Moritzteich, von Rohden et al, 2009) to name just a few

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Despite their worldwide occurrence, only

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Hakala, 2004;

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; Hakala, 2004; Boehrer and Schultze

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2008

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There are good reasons for scientific interest in meromictic lakes:

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ome of the largest lakes are meromictic (Tanganyika,

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Tanganyika,

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e.g. Lake

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Malawi / Nyasa, e.g. Vollmer et al.

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2002).

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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)).

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Some meromictic lakes became famous through their dangerous gas loads (e.g. Lake Nyos

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and

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, Lake Monoun

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, Cameroon, Halbwachs et al.

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2004). The monimolimnion of Lake Kivu contains considerable methane deposits (Tietze

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1978), which 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

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, Lenz et al.

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2011). Meromictic lakes could be identified in many mining regions on E

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arth where stratification limited the vertical transport of undesirable substances (e.g.

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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

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, 2009). In some cases, stratification was even implemented to restrict the vertical transport (Island Copper Mine pit lake in Canada, Wilton et al., 1998; Stevens and Lawrence, 1998).

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Meromictic conditions cain mining lakes aren be sustained by a continuous inflow of high density groundwater formed by weathering processes of exposed sulfide-bearing material (Geller et al., 1998) 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 chemocline . The dense water can may also be formed within the lake e.g.(by weathering processes of exposed sulfide-bearing material (Geller et al., 1998).von Rohden and Ilmberger, 2001). In case of mining lakes, establishing stable meromictic conditions might be favorable as it allows the confinement of water quality problems (e.g. heavy metals) from the surface water into the deep water layers (Jöhnk, 1999; Nixdorf et al., 2001; Wiessner et al., 2014).

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in mining lakes are

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formed by weathering processes of exposed sulfide-bearing material (Geller et al., 1998)

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formed by weathering processes of exposed sulfide-bearing material (Geller et al., 1998)

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(e.g. von Rohden and Ilmberger, 2001; Wiessner et al., 2014)

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, the chemocline

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. The dense water can

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within the lake e.g.

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by weathering processes of exposed sulfide-bearing material (Geller et al., 1998).

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von Rohden and Ilmberger, 2001). In case of mining lakes, establishing stable meromictic conditions might be favorable as it allows the confinement of water quality problems (e.g. heavy metals) from the surface water into the deep water layers (Jöhnk, 1999; Nixdorf et al., 2001; Wiessner et al., 2014). The exclusion of the monimolimnia from gas exchange with atmosphere creates anoxic, reducing conditions leading to an enrichment of dissolved gases and ionic substances in the deep water (Boehrer and Schultze, 2008).

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The exclusion of the monimolimnia from gas exchange with atmosphere creates anoxic, reducing conditions leading to an enrichment of dissolved gases and ionic substances in the deep water (Boehrer and Schultze, 2008).

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Subterranean ion rich acid mining drainage (AMD) can be formed by weathering processes of exposed sulfide-bearing material (Geller et al., 1998).

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Meromictic conditions in mining lakes are 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, the chemocline (von Rohden and Ilmberger, 2001). In case of mining lakes, establishing stable meromictic conditions might be favorable as it allows the confinement of water quality problems (e.g. heavy metals) from the surface water into the deep water layers (Jöhnk, 1999; Nixdorf et al., 2001; Wiessner et al., 2014).

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mining

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One prominent reactant is iron, which gets precipitated from the oxygenated mixolimnetic waters and dissolves in the anoxic (reducing) chemical conditions of the monimolimnion (Kjensmo, 1967; Hongve, 1997).

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are able to

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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

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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.

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Description

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Lake Waldsee does not have a surface inflow. Hence groundwater is the main source of recharge.

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Lake Waldsee does not have a surface inflow, which makes groundwater the main source of recharge.

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Stratification

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stratification

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Water

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water

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Chemistry

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chemistry

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2.3 Field and lab measurements

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45 monthly field measurements have been conducted in Lake Waldsee between July 2006 and April 2010. Vertical profiles of temperature, pressure, pH, turbidity and in-situ electrical conductivity were collected in Lake 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).

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

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On May 18th 2011, mixolimnion and monimolimnion water were collected for chemical analysis (Table 1). In addition, 150 l of monimolimnion were sampled and air-tightly and opaquely stored at a temperature of 4°C for later use in a column experiment.

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Sampling and

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On May 18th 2011, mixolimnion and monimolimnion water were collected for chemical analysis

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. 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.

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(Table 1). In addition, 150 l of monimolimnion were sampled and air-tightly and opaquely stored at a temperature of 4°C for later use in a column experiment

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(Table 1).

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(Figure 3)

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. On May 25th 2011,

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On May 25th 2011,

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Calculating

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45 monthly field measurements have been conducted in Lake Waldsee between July 2006 and April 2010. Vertical profiles of temperature, pressure, pH, turbidity and in-situ electrical conductivity were collected in Lake 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

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

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).

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3.3 Calculating summed electrical conductivity

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four

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rose

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sank

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sank

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rose

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showing a mean of 2.86±0.29 m

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showing a slightly rising trend

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In contrast, water level in Waldsee was on average at 4.18 ±0.10 m.

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, expressed by standard deviation,

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significantly

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about three times

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Lake Waldsee

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412±31.3

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5.1 Preservation of permanent stratification by the iron-redox cycle

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The measured averaged electrical conductivity of the monimolimnion in Lake Waldsee was in a range between 0.93 mS/cm and 1.09 mS/cm within the observation period, having a temporal mean of 1.00 mS/cm (Figure 9) and a standard deviation of 0.041 mS/cm. Considering that the averaged electrical conductivity of the mixolimnion never exceeded 0.54 mS/cm, this result confirmed that the

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over the observation period

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conductivity gradients

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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 Waldsee was in a range between 0.93 mS/cm and 1.09 mS/cm (Figure 9)

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Assuming that groundwater showed fairly constant chemical properties, this indicated that internal physico-chemical processes were potential drivers of the monimolimnetic electrical conductivity variations.

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of deviations

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increase

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rise

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is

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was

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efficiency

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Furthermore

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On the other hand

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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

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As this was taking place in a chemically similar setting, it is justified to use summed conductivity as a quantitative measure to draw conclusions about relevant processes involved in the stratification of Lake Waldsee

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5.2 Impact of groundwater recharge on permanent stratification

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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.

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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 parametrization of numerical models for the prediction of stratification in meromictic lakes.

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Conclusions

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Summary

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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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Tables

Table 1: Analyzed physical and chemical water parameters and used lab measurement methods

Measured variable	Measurement procedure
Electrical conductivity	7-pole platinum cell conductivity sensor
pH-value	pH meter
Carbon species (DOC, TIC, TOC)	Thermal-catalytic oxidation with subsequent infrared spectroscopy
Iron	Atomic emission spectroscopy

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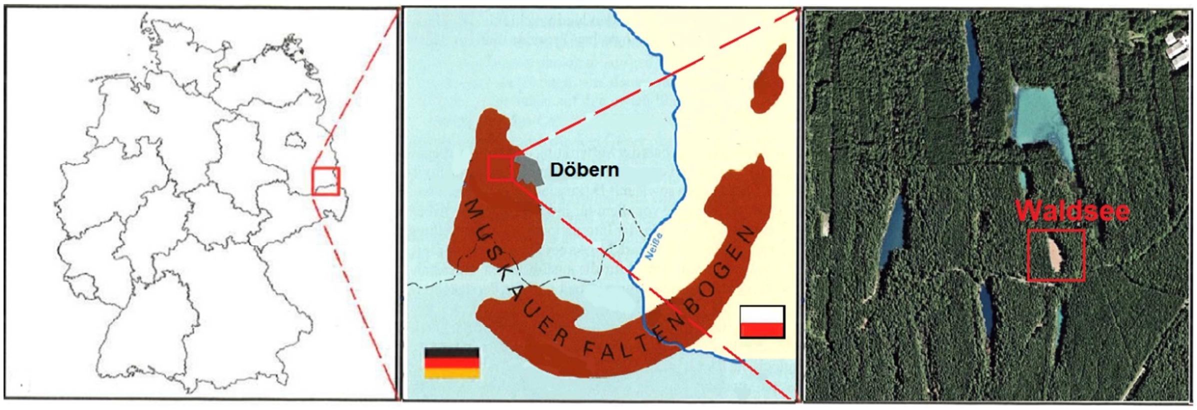

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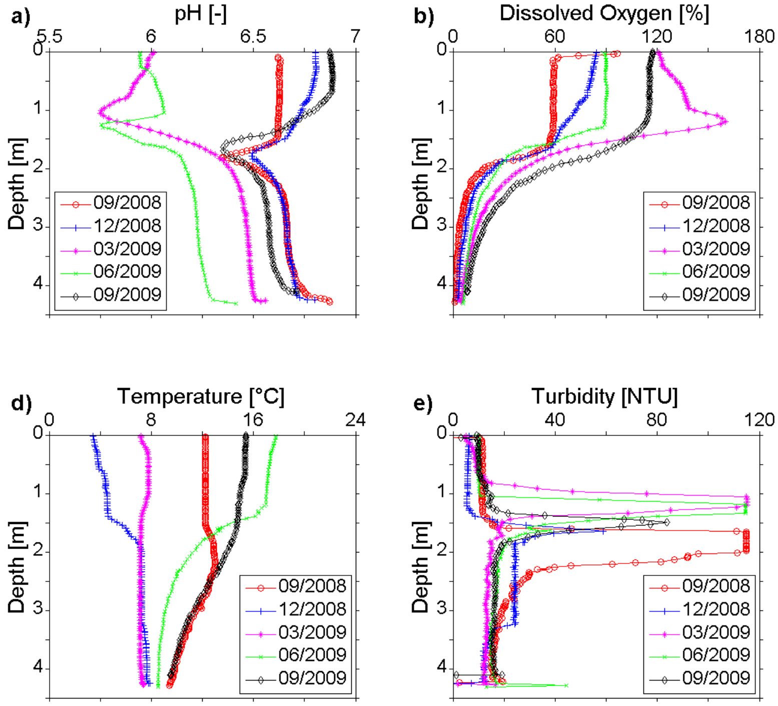

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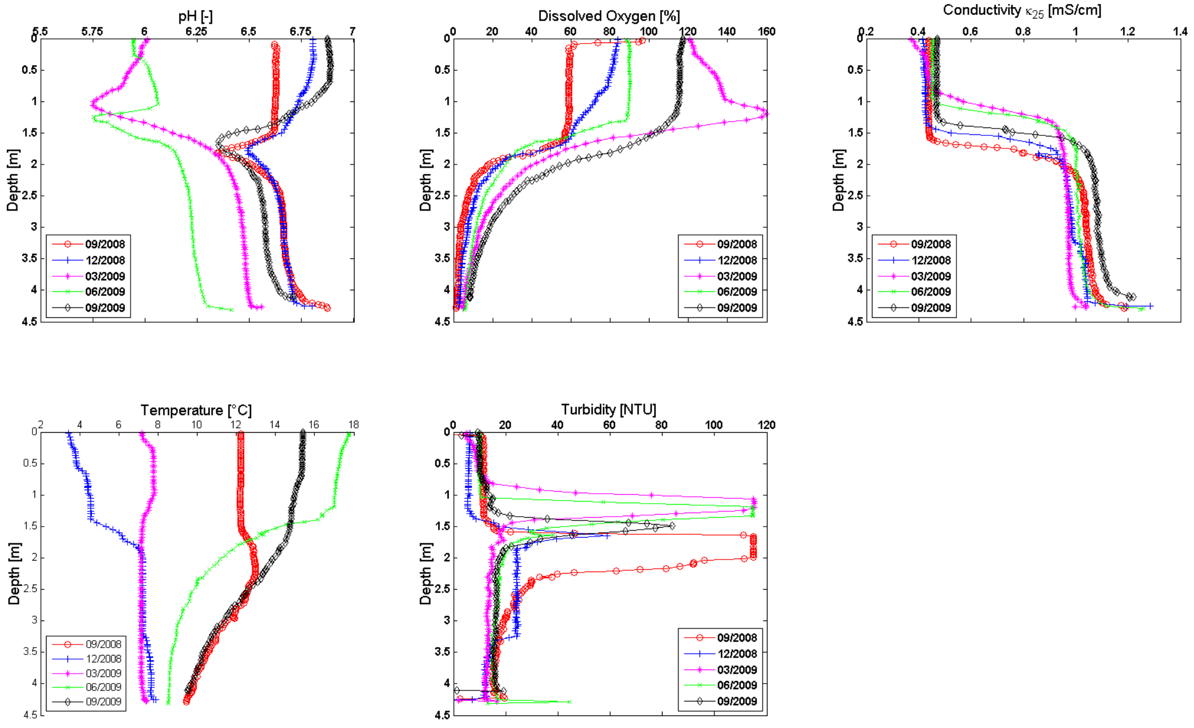

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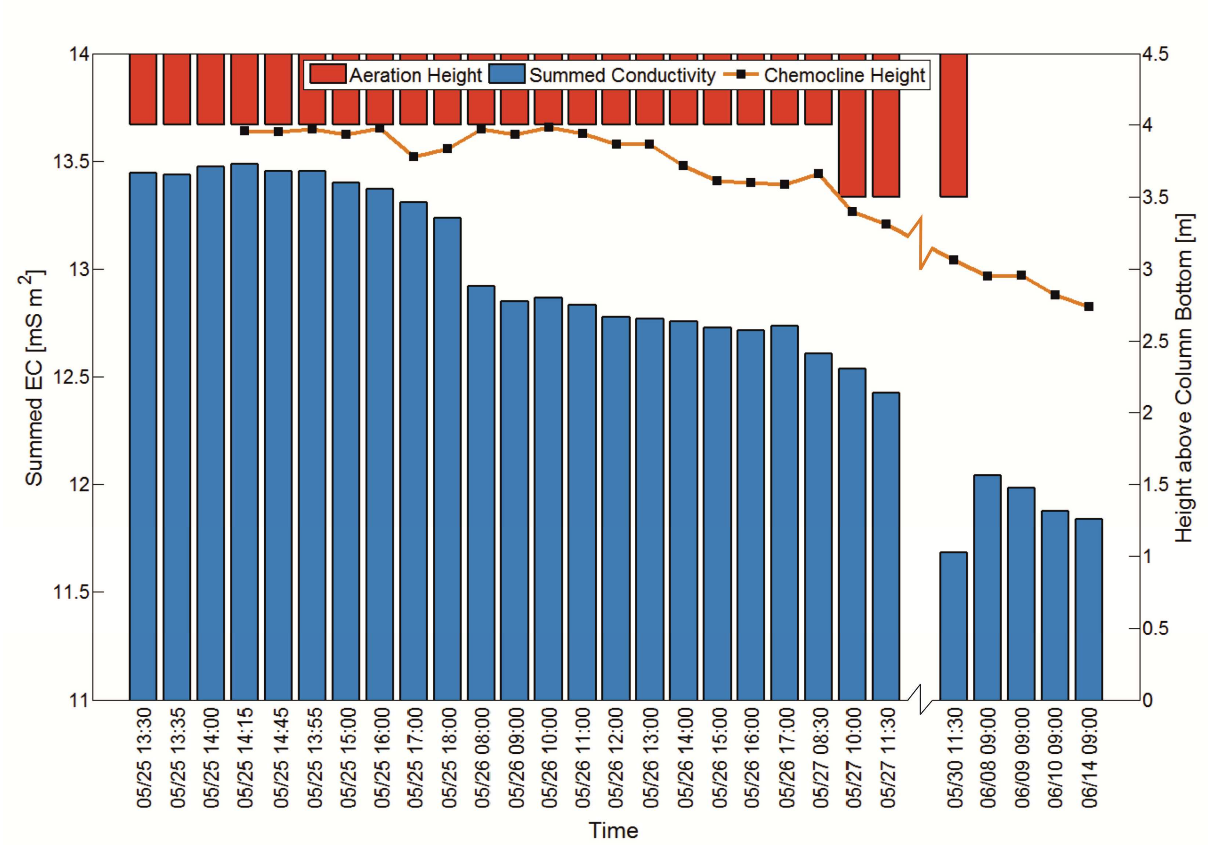

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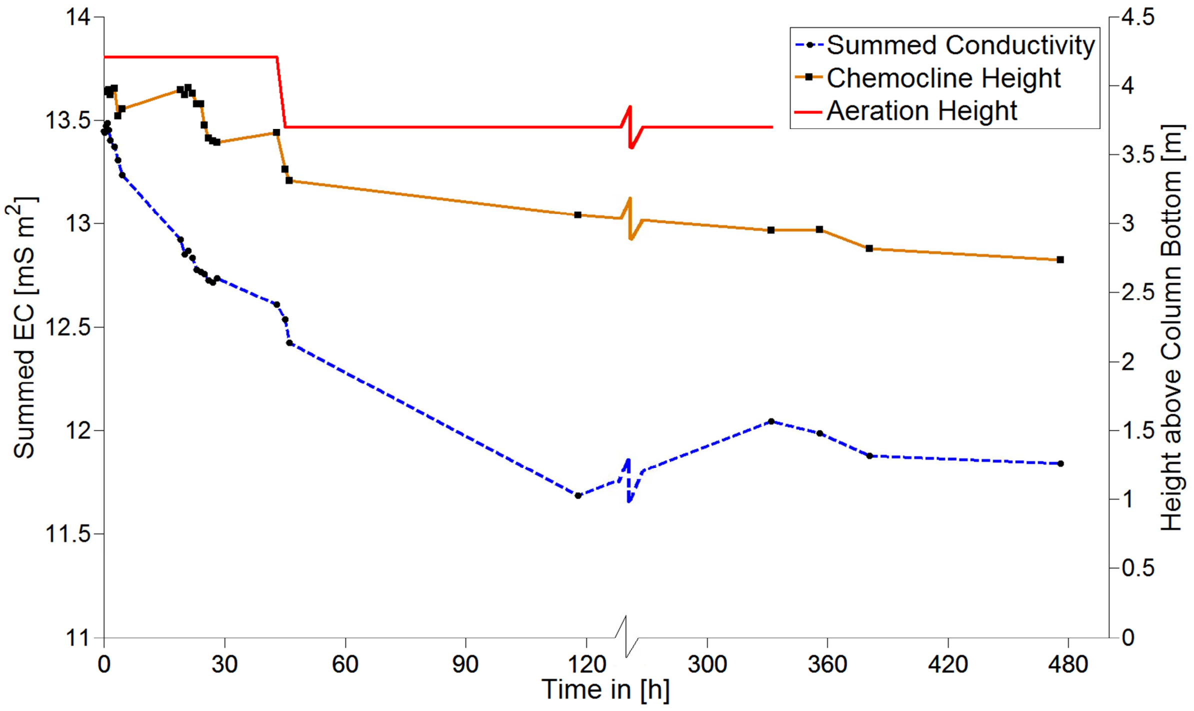

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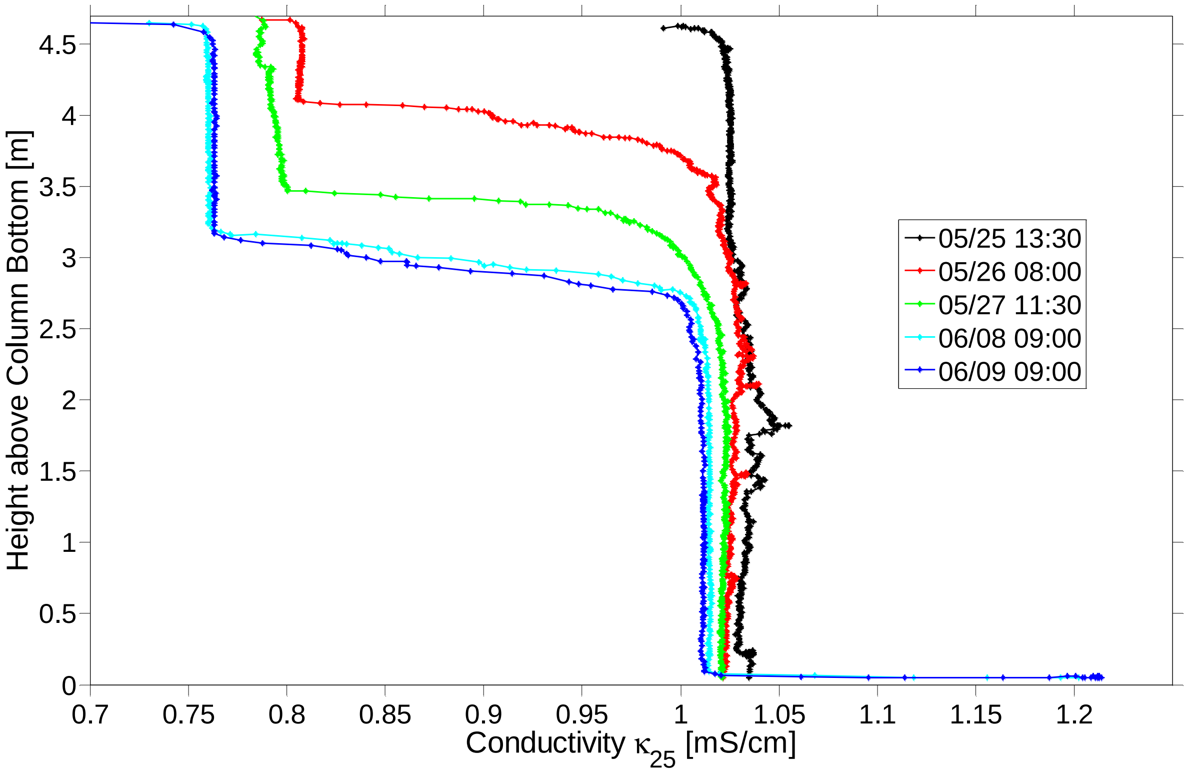

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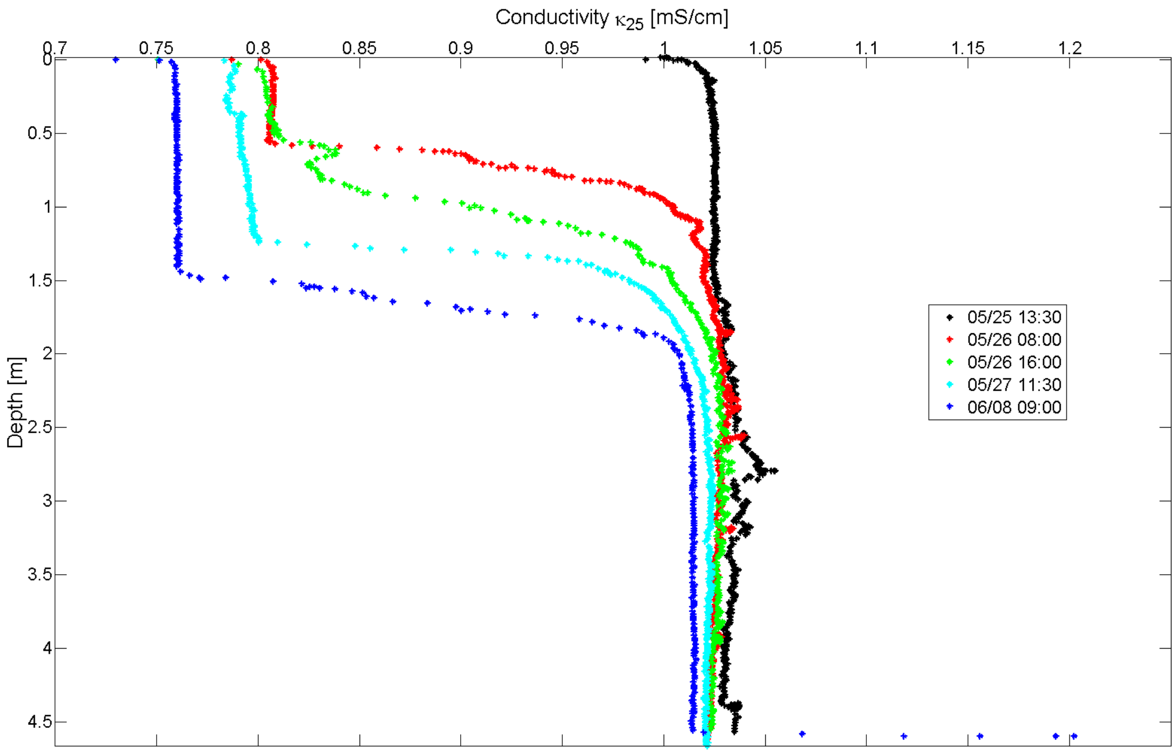

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lab experiment

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water column

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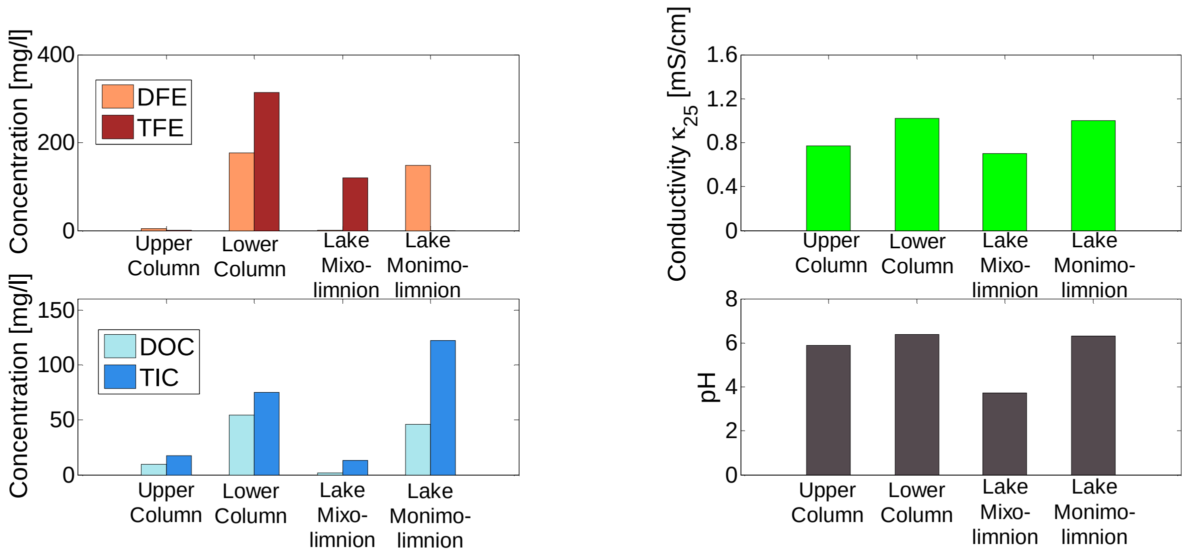

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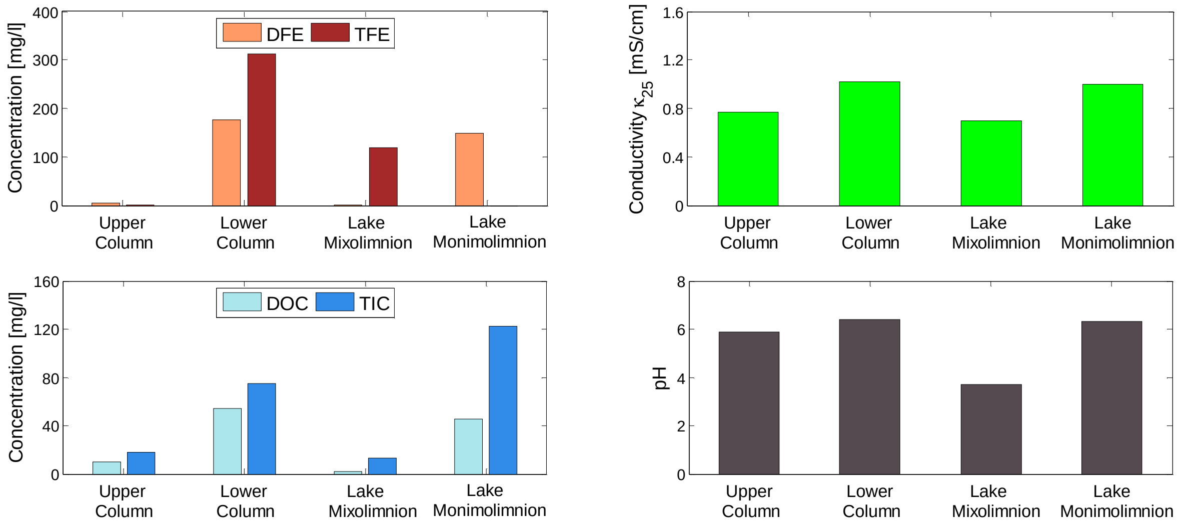

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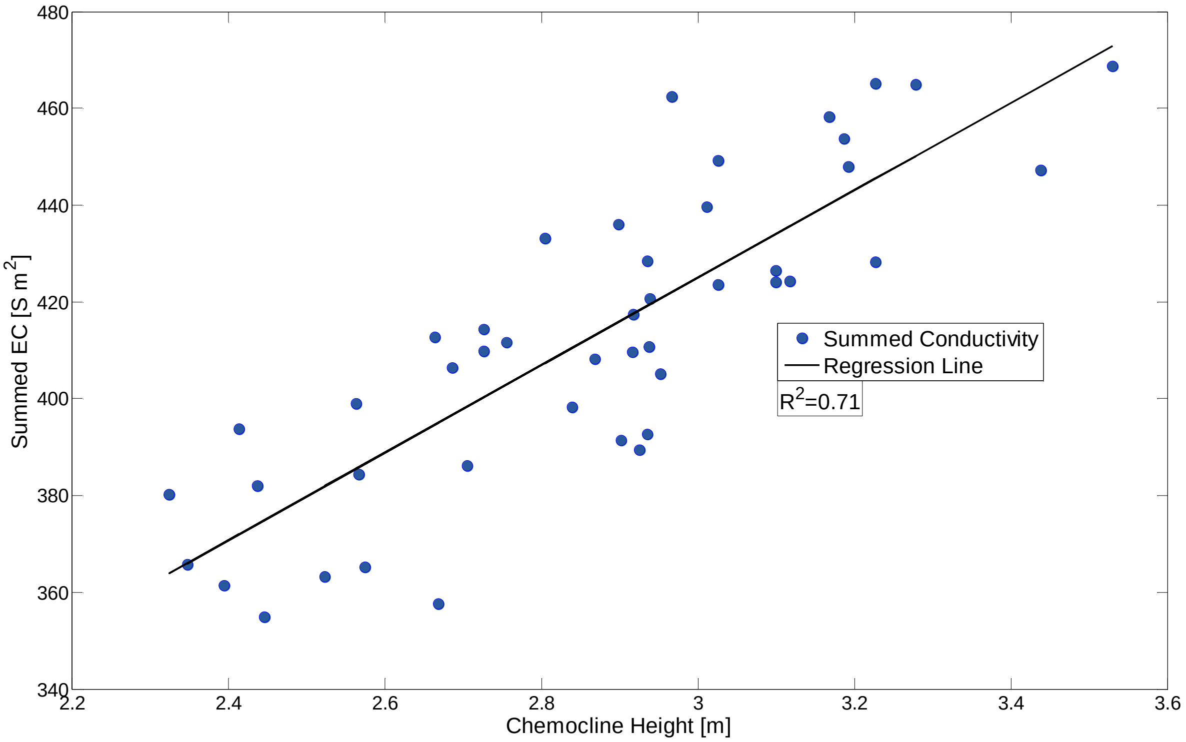

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Quantitative analysis of biogeochemically controlled stratification in an iron-meromictic lake

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Biogeochemical processes controlling density stratification in an iron-meromictic lake

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