



**Biogeochemical processes controlling density stratification**

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This discussion paper is/has been under review for the journal Hydrology and Earth System Sciences (HESS). Please refer to the corresponding final paper in HESS if available.

# Biogeochemical processes controlling density stratification in an iron-meromictic lake

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Received: 28 April 2015 – Accepted: 21 May 2015 – Published: 12 June 2015

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Published by Copernicus Publications on behalf of the European Geosciences Union.

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## Abstract

Biogeochemical processes and mixing regime of a lake can control each other mutually. The prominent case of iron meromixis is investigated in Waldsee near Doebern, a small lake that originated from surface mining of lignite. 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, redissolved 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.

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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). 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). 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 Concepcion, 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.

Subterranean iron 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). Addi-

tionally, chemical reactions are able to sustain meromixis in mining lakes. Exemplarily it is proposed for the shallow mining 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<sub>2</sub> 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).

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 and measurements

### 2.1 Study 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 south-east of Berlin (Fig. 1). The lake covers an area of about 2400 m<sup>2</sup>, has a volume of 6500 m<sup>3</sup> 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 de-

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pression 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). Tracer experiments estimate a mean groundwater recharge to Lake Waldsee of  $8.2 \text{ m}^3 \text{ d}^{-1}$  (mostly from southern direction) and a mean groundwater outflow of  $6 \text{ m}^3 \text{ s}^{-1}$  (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 and water 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 (Fig. 2a).

The mixolimnion was oxygenated (Fig. 2b) and had an electrical conductivity of about  $0.4\text{--}0.5 \text{ mS cm}^{-1}$  which was approximately half of related values in the anoxic monimolimnion (Fig. 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  $150 \text{ mg L}^{-1}$  and in bicarbonate concentration of about  $300\text{--}400 \text{ mg L}^{-1}$  between both water layers (Boehrer et al., 2009). The resulting density gradient across the chemocline over-compensated the destabilizing temperature gradient during winter time (Fig. 2d) and in consequence no complete lake turnover was detected within more than 10 years of lake monitoring.

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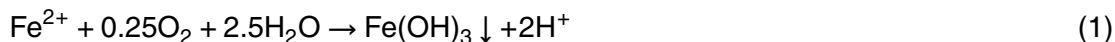
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However, both the mixolimnion and the monimolimnion could form two independent convection cells (Boehrer et al., 2009).

The depth of the chemocline, which could be marked as the point of inflection of the  $\kappa_{25}$  conductivity profiles and thus the volumetric ratio between mixolimnion and monimolimnion, varied seasonally by about 1 m (Fig. 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:



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

Similarly, bicarbonate ions transferred into oxygenated water layers could either be up-taken by photosynthetic organisms or outgas as  $\text{CO}_2$  through the carbonate equilibrium to the atmosphere:



Internally, dissolved ferrous iron and inorganic carbon were resupplied by the micro-bacterial anaerobic degradation of organic matter in the monimolimnion using precipi-

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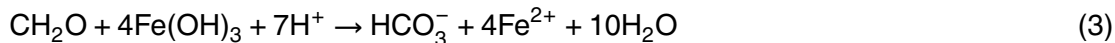
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tated iron hydroxide as an electron acceptor:



The increase of measured conductivity and pH in the monimolimnion near the lake bottom (Fig. 2a and c) 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  $\kappa_{25}$  at 25 °C (sometimes named as electrical conductance) by

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

where a lake specific  $\alpha_{25}$  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 18 May 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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### 3 Methodology

#### 3.1 Set-up of 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. The column was covered by PE-containing mattresses in order to thermally insulate the column and to avoid photo-chemical iron reduction (Herzprung et al., 1998). Prior to filling, the column was flushed with nitrogen gas to avoid initial oxidation of ferrous iron. The column was filled with 130 L of 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 May 2011 13:00 and the 14 June 2011 09:00 LT, 28 vertical profiles of temperature, pressure, turbidity and electrical conductivity were sampled with the multi-parameter CTD-O<sub>2</sub> fast profiling probe with a sampling frequency of 4 Hz. The airflow was increased after 24 h of experiment time and additional 20 h 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 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 sub-

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sequently integrating results over the complete water depth. Therefore the lake was vertically portioned into  $j = 1 \dots n$  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  $S\ m^{-2}$ , could be calculated for each time of measurement  $t_j$  by

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

For the column experiment, the area of each layer was  $0.028\ m^2$  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  $\bar{\kappa}_{25}^{\text{moni}}(t_j)$  could be derived from measurements by solving Eq. (5) for  $\kappa_{25}$  and summing up all layers from the lake bottom up to layer  $j_c$  where the chemocline was located:

$$\bar{\kappa}_{25}^{\text{moni}}(t_j) = \frac{S_{\kappa_{25}}^{\text{moni}}(t_j)}{V^{\text{moni}}(t_j)} = \frac{\sum_{j=1}^{j=j_c(t_j)} \kappa_{25}(j, t_j) \cdot A(j) \cdot h_j}{\sum_{j=1}^{j=j_c(t_j)} A(j) \cdot h_j} \quad (6)$$

The average mixolimnion conductivity  $\bar{\kappa}_{25}^{\text{mixo}}(t_j)$  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 ( $j_c(t_j) > j_c(t_{j-1})$ ) would be connected to a decrease of the calculated average electrical conductivity in the monimolimnion  $\bar{\kappa}_{25}^{\text{calc}}(t_j)$ . Mathematically this could be written as

inclusion of less conductive mixolimnic water layers into the expanding monimolimnion:

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

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

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

## 4 Results

### 4.1 Development of summed conductivity in the column experiment

During the aeration period from 25 to 27 May, the summed conductivity decreased continuously (Fig. 4). This decline continued after cessation of the aeration with the exception of the measurement on the 30 May. Over all, the summed conductivity dropped by about 12 % from 13.44 to 11.84 S m<sup>2</sup> 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  $1 \text{ mm s}^{-1}$ . 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 26 May 13:00 and the change of aeration depth 20 h later shifted the chemocline in the vertical by 20 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 beyond the scope of this experiment.

Profiles of electrical conductivity (Fig. 5) show 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 (Fig. 6). Dissolved iron (DFe) was removed almost entirely from the upper water. Resulting concentrations of  $5 \text{ mg L}^{-1}$  concurred with mixolimnic lake water ( $2 \text{ mg L}^{-1}$ ). In parallel, electrical conductivity fell from 1.0 to  $0.77 \text{ mScm}^{-1}$  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 to  $10 \text{ mg L}^{-1}$ . The aeration also stripped  $\text{CO}_2$  from the water resulting in a measurable drop in TIC (Total Inorganic Carbon) concentration from 122 to  $17.5 \text{ mg L}^{-1}$ , which were

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in the range of the mixolimnion water ( $13.1 \text{ mg L}^{-1}$ ). 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 ( $177 \text{ mg L}^{-1}$ ) compared to the initial concentration ( $148 \text{ mg L}^{-1}$ ). The supplementary measured TFe in the bottom water  $313 \text{ mg L}^{-1}$  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 Fig. 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  $75 \text{ mg L}^{-1}$  were lower than monimolimnic water ( $122 \text{ mg L}^{-1}$ ) reflecting losses during sampling, transport and filling process. DOC in the deeper column of  $54 \text{ mg L}^{-1}$  was higher than the initial value of  $48 \text{ mg L}^{-1}$ . 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 years of monthly observation (see also von Rohden et al., 2009). From April to October, the chemocline rose, while it sank during winter months (Fig. 7). The height above the deepest point varied between 2.3 and 3.5 m showing a slightly rising trend. This meant that the amplitude of the chemocline changes were significantly higher than the observed variations in lake water level.

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

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of  $421 \text{ S m}^2$ , meaning that about 20% 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  $465.18 \text{ S m}^2$  was only slightly different from the last measurement of  $468.72 \text{ S m}^2$  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 indicating a connection between electrical conductivity of the monimolimnion and chemocline location (Fig. 8).

## 5 Discussion

The measured averaged electrical conductivity of the monimolimnion in Lake Waldsee was in a range between  $0.93$  and  $1.09 \text{ mS cm}^{-1}$  within the observation period, having a temporal mean of  $1.00 \text{ mS cm}^{-1}$  (Fig. 9) and a standard deviation of  $0.041 \text{ mS cm}^{-1}$ . Considering that the averaged electrical conductivity of the mixolimnion never exceeded  $0.54 \text{ mS cm}^{-1}$ , this result confirmed that the permanent stratification of Lake Waldsee was preserved by the presence of conductivity gradients. 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 vs. external sources, we compared measured values with the calculated values of our simplified model of a closed system Lake Waldsee. Based on Eqs. (7) and (8), the average monimolimnion conductivity  $\bar{\kappa}_{25}^{\text{calc}}(t_i)$  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

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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 and 1.25 mS cm<sup>-1</sup> and a corresponding standard deviation of 0.12 mS cm<sup>-1</sup>, 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 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 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, the closed model silently assumed that the loss of the bicarbonate conductivity by CO<sub>2</sub> escaping to the atmosphere (Eq. 2) was entirely counterbalanced by CO<sub>2</sub> production as a by-product of the biochemically iron hydroxide reduction (Eq. 3).

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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.

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.

## 6 Conclusions

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 monimolimnic 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<sub>2</sub> loss. This

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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 redissolution 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).

*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).

The article processing charges for this open-access publication were covered by a Research Centre of the Helmholtz Association.

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

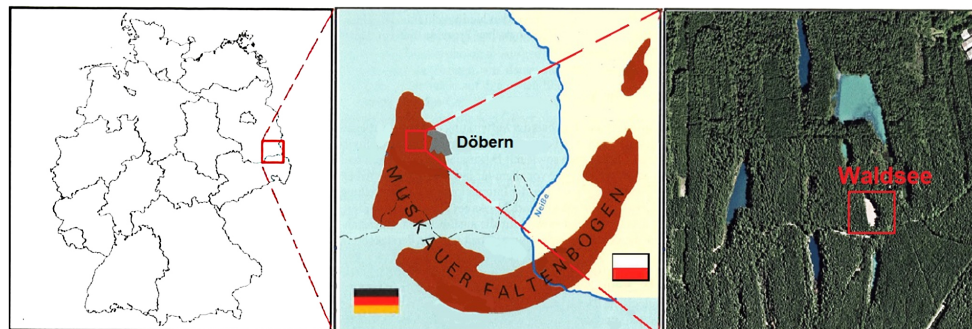
Measured variable	Measurement procedure
Electrical conductivity	7-pole platinum cell conductivity sensor
pH-value	pH meter
Carbon species (DOC, TIC, TOC)	Thermal-catalytic oxidation with subsequent infrared spectroscopy
Iron	Atomic emission spectroscopy

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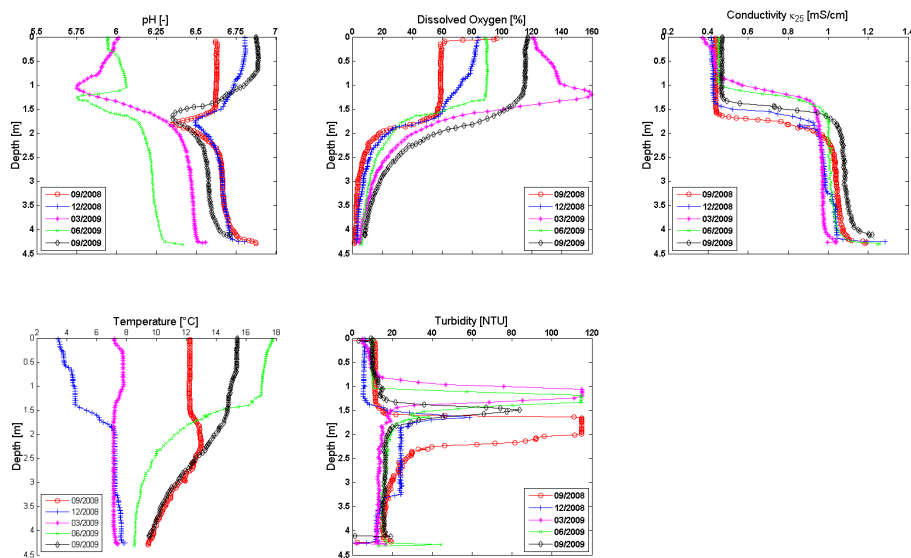


**Figure 1.** Geographical location of Lake Waldsee within the Muskau Arch in Eastern Germany (after Kozma and Kupetz, 2008).

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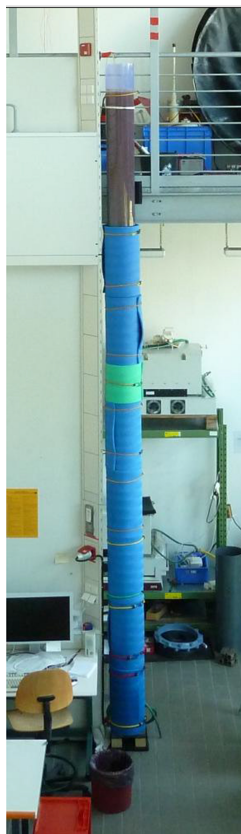
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**Figure 2.** Physico-chemical profiles in Lake Waldsee between September 2008 and September 2009.

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

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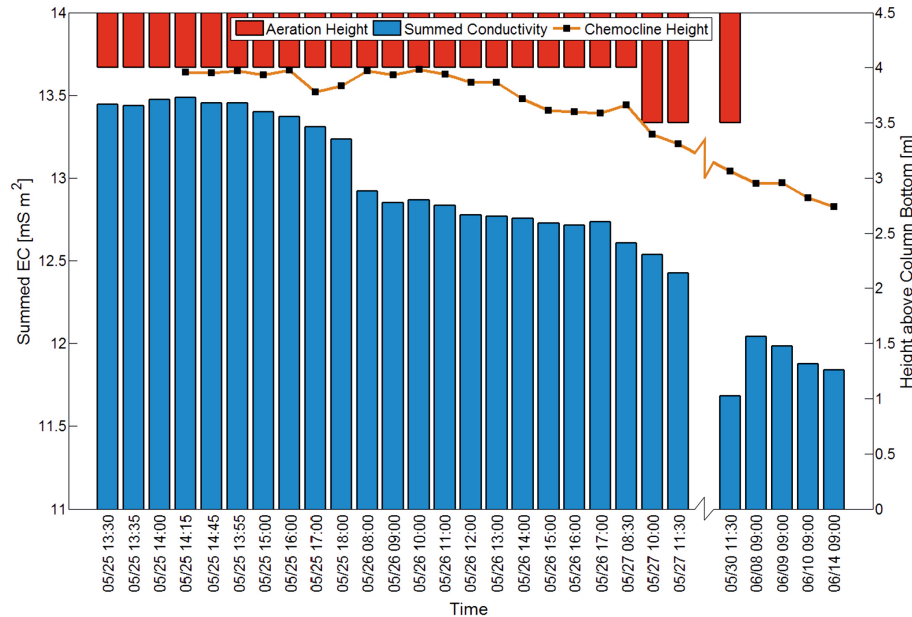
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**Figure 4.** Temporal dynamics of chemocline height and summed conductivity during the column experiment. The scale breakage indicates the end of the hourly range sampling period of the experiment.

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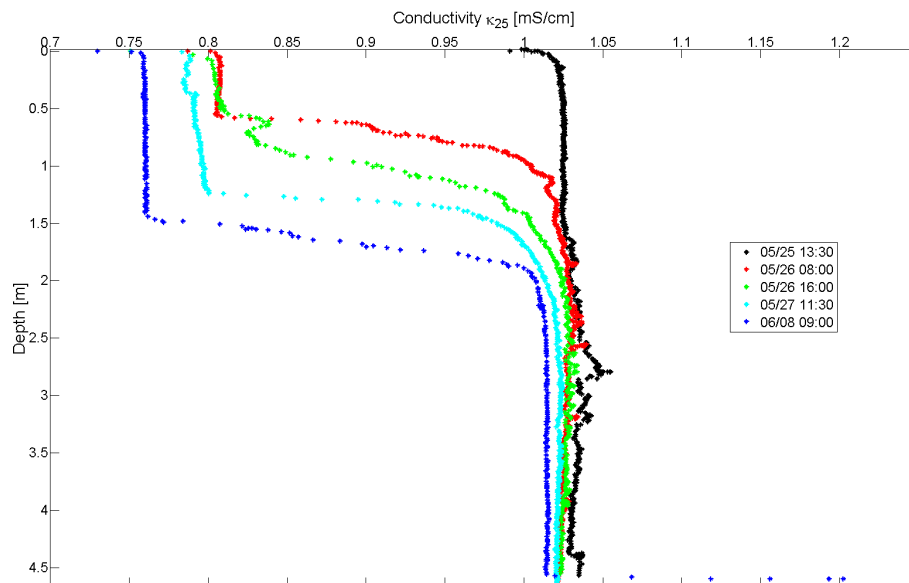
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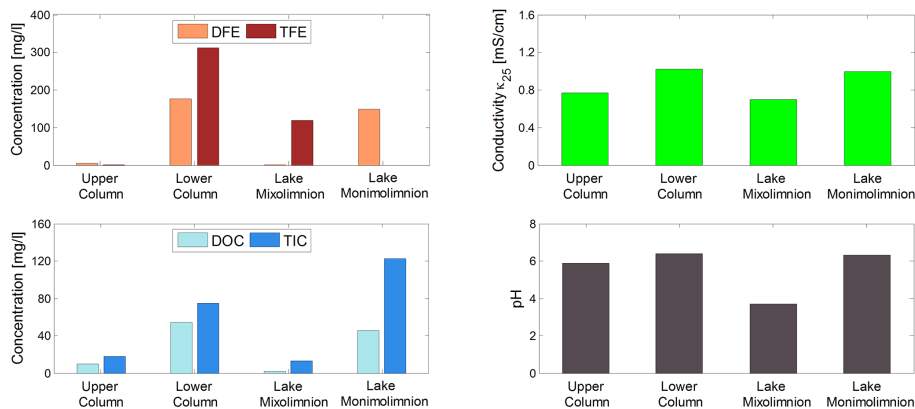
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**Figure 5.** Selected conductivity profiles in the water column.[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)



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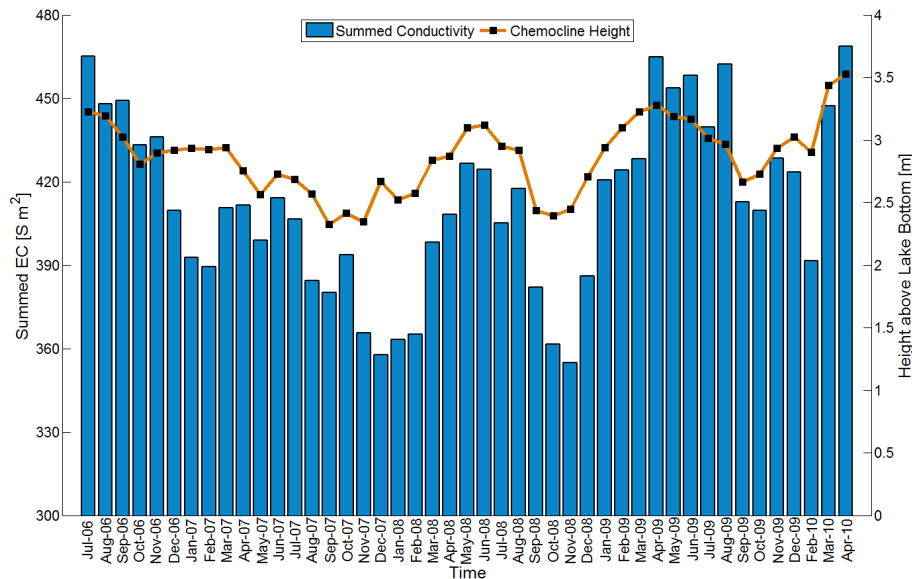
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**Figure 6.** Iron species content (DFE and TFE), electrical conductivity, carbon species content (DOC and TIC) and pH-value of samples from different water layers in Lake Waldsee and the water column.

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

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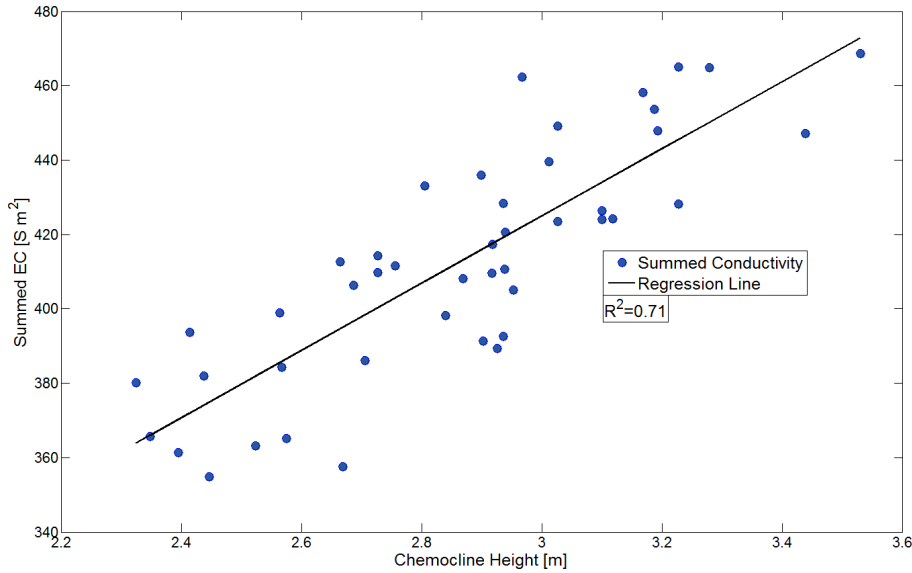


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**Figure 8.** Correlation between summed conductivity and chemocline height. A linear regression results in a correlation coefficient of 0.71.

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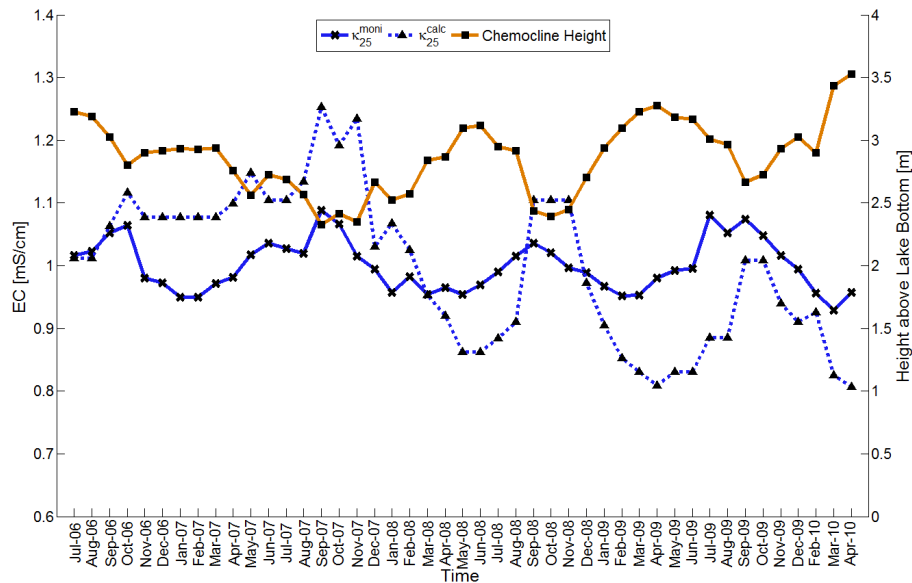
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**Figure 9.** Comparison of time series of measured and calculated average electrical conductivity in the monimolimnion.

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