

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

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## 1 Abstract

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

1 identified by visual inspection. Eventually, the remaining solutes in the aerated water layer  
2 looked similar to mixolimnetic Waldsee water. Due to its reduced concentration of solutes,  
3 this water became less dense and remained floating on nearly unchanged monimolimnetic  
4 water. In conclusion, iron meromixis as seen in Waldsee did not require two different sources  
5 of incoming waters, but the inflow of iron rich deep groundwater and the aeration through the  
6 lake surface were fully sufficient for the formation of iron meromixis.

## 7 **1. Introduction**

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

16

17 There are good reasons for scientific interest in meromictic lakes: some of the largest lakes  
18 are meromictic (e.g. Lake Malawi/Nyasa, e.g. Vollmer et al., 2002). Chemical gradients in  
19 meromictic lakes form habitats for specialized organisms (e.g. sulfur bacteria performing  
20 anoxygenic photosynthesis (Camacho et al., 2001) or anammox (Hamersley et al., 2009)).  
21 Some meromictic lakes became famous through their dangerous gas loads (e.g. Lake Nyos  
22 and Lake Monoun in Cameroon, Halbwegs et al., 2004). The monimolimnion of Lake Kivu  
23 contains considerable methane deposits (Tietze, 1978), which are likely to be exploited in  
24 near future. Sediments in some meromictic lakes have been undisturbed for thousands of  
25 years and hence the varved sediments represent excellent climate archives and fossil deposits

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

1 (e.g. Walker and Likens, 1975; Lenz et al., 2011). Meromictic lakes have been identified in  
2 many mining regions on earth where stratification limits the vertical transport of undesirable  
3 substances (e.g. Spain: Lake San Telmo, Cánovas et al., 2012, and Lake Concepcion,  
4 Santofimia and López-Pamo, 2013; Germany: Lake Wallendorfer See and Lake Rassnitzer  
5 See, Boehrer et al., 2014; Lake Moritzteich, von Rohden et al., 2009). In some cases,  
6 stratification has even been implemented to restrict the vertical transport (Island Copper Mine  
7 pit lake in Canada, Wilton et al., 1998; Stevens and Lawrence, 1998).

8  
9 Meromictic conditions can be sustained by a continuous inflow of high density groundwater  
10 and low density surface water via streams or precipitation and the very low diffusion rate of  
11 substances over sharp gradients (e.g. von Rohden and Ilmberger, 2001; Wiessner et al., 2014).  
12 The dense water may also be formed within the lake e.g. by weathering processes of exposed  
13 sulfide-bearing material (Geller et al., 1998). The volume ratio between the monimolimnion  
14 and the mixolimnion can show seasonal changes due to chemocline erosion by mixolimnion  
15 turnover (e.g. von Rohden et al., 2009) or by increased surface runoff, whereas increased  
16 groundwater inflow and higher surface evaporation as well as diffusive processes are able to  
17 cause an upward movement of the chemocline (e.g. Santofimia and López-Pamo, 2013).  
18 Additionally, chemical reactions are able to sustain meromixis in lakes (Boehrer and Schultze,  
19 2008)

20  
21 One prominent reactant is iron, which precipitates within the oxygenated mixolimnetic waters  
22 and dissolves in the anoxic (reducing) conditions of the monimolimnion (Kjensmo, 1967;  
23 Hongve, 1997). For the shallow mining lake Waldsee, we hypothesize that changes in  
24 chemocline height trigger internal, trans-chemocline transport of iron species by oxidation,  
25 precipitation and re-dissolution, in combination with related CO<sub>2</sub> outgassing and regeneration.  
26 Both processes maintain density gradients between both water layers and inhibit a complete

1 mixing of this shallow lake (Boehrer et al., 2009). For Waldsee, Dietz et al. (2012) showed  
2 that dissolved iron and carbon species ( $\text{CO}_2$ , bicarbonate and DOC) contribute the same  
3 amount to the density gradient and all other substances contribute a much subordinate portion.  
4 From previous investigations, it is clear that both precipitation of iron out of the mixolimnion  
5 and gas exchange with the atmosphere are important contributors to the permanent  
6 stratification. It is also known that re-dissolution of iron happens in the monimolimnion, but  
7 there has not been any quantitative approach to determine its role in sustaining meromixis.

8

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

## 19 **2. Site description**

### 20 **2.1 Study site**

21 The demonstration site Waldsee ( $51^\circ37'14.1''\text{N}$ ,  $14^\circ34'16.7''\text{E}$ ) is a former mining site  
22 located in a forested area in the Lower Lusatian Mining District 130 km southeast of Berlin  
23 (Figure 1). The lake covers an area of about  $2400 \text{ m}^2$ , has a volume of  $6500 \text{ m}^3$  and reaches a  
24 maximum depth of 4.7 m (Boehrer et al., 2009). Waldsee is embedded in The Muskau Arch,  
25 which represents an Elsterian push moraine cut by deep erosion. This geological deformation

1 process folded up the horizontal geological layers which caused the crop out of Miocene  
2 lignite layers in conjunction with later glacier advances (Kozma and Kupetz, 2008). The near-  
3 surface coal was exploited by both underground mining and surface mining. Waldsee is the  
4 water filled depression of the former underground mining site “Pflanzgartenmulde”, which  
5 has been formed by the collapse of the underground mining structures after cessation of  
6 mining activities in 1948 (Schossig and Kulke, 2006).

7

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

## 15 **2.2 Lake stratification and water chemistry**

16 The physico-chemical profiles of Waldsee clearly showed pronounced differences in water  
17 parameters between the upper 1-1.5 m thick mixolimnic water layer and the monimolimnion  
18 below. pH in both mixolimnion and monimolimnion was slightly acidic with values between  
19 5.5 and 7.0 having lower values during spring time (Figure 2a).

20

21 The mixolimnion was oxygenated (Figure 2b) and had an electrical conductivity of about 0.4-  
22 0.5 mS/cm which was approximately half of related values in the anoxic monimolimnion  
23 (Figure 2c). Due to the absence of large pH differences (Diesing and Boehrer, 2010) this  
24 gradient in electrical conductivity could be related to gradients in the concentrations of

1 electro-active water constituents, mainly ferrous iron and bicarbonate also being the major  
2 contributors to the density difference (Dietz et al., 2012).

3

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

12

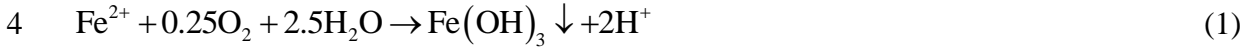
13 The depth of the chemocline, which could be marked as the point of inflection of the  $\kappa_{25}$   
14 conductivity profiles and thus the volumetric ratio between mixolimnion and monimolimnion,  
15 varied seasonally by about 1 m (Figure 2c). During the warm season, the erosion (lowering)  
16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

23

24 Ferrous iron transported into the oxygenated water layers, either by convective transport due  
25 to chemocline erosion or by molecular diffusion was oxidized to ferric iron and was

1 subsequently transported back to the monimolimnion as rust-colored, voluminous iron  
2 hydroxide precipitate:

3



5

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

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

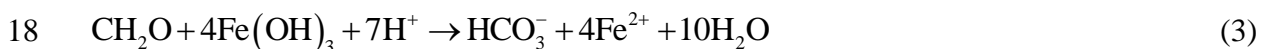
11



13

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

17



19

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

## 22 **3. Methodology**

### 23 **3.1 Sampling and set-up of column experiment**

24 On May 18th 2011, mixolimnion and monimolimnion water were collected for chemical  
25 analysis. This included the measurement of electrical conductivity using a 7-pole platinum

1 cell conductivity sensor and pH with a pH-meter as well as determining concentration of  
2 carbon species (DOC; TIC, TOC) by infrared spectroscopy following thermal-catalytic  
3 oxidation and iron species (ferrous and ferric iron) by atomic emission spectroscopy. In  
4 addition, 150 L of monimolimnion were sampled and air-tightly and opaquely stored at a  
5 temperature of 4°C for later use in a column experiment.

6

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

16

17 The aeration was accomplished with pressurized air at a water depth of 50 cm. Between  
18 25.05.2011 13:00 and 14.06.2011 09:00 o'clock, 28 vertical profiles of temperature, pressure,  
19 turbidity and electrical conductivity were sampled with the multi-parameter CTD-O<sub>2</sub> fast  
20 profiling probe with a sampling frequency of 4 Hz. The airflow was increased after 24 h of  
21 experiment time and additional 20 hours later the aeration depth was changed to 1 m for a  
22 time span of three additional days in order to see the response of chemocline height in the  
23 water. Finally the aeration was stopped and four further profiles were measured during the  
24 next 14 days. At the end of the experiment, water samples were taken from the aerated top  
25 water layer and the bottom water and analyzed in the lab together with collected mixolimnion  
26 and monimolimnion water from the lake to estimate the concentration of dissolved iron (DFe)



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

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

### 3 **3.2 Electrical conductivity**

4 45 monthly field measurements have been conducted in Waldsee between July 2006 and April  
5 2010. Vertical profiles of temperature, pressure, pH, turbidity and in-situ electrical  
6 conductivity were collected in Waldsee using the multi-parameter probes *Ocean Seven*  
7 *316CTD* (Idronaut, Italy) and *CTD90M* (Sea & Sun, Germany). The sampling rate was  
8 between 1 and 4 Hz and the small offset between the sensors of the two different probes was  
9 compensated. Measured electrical conductivity  $C$  was converted into electrical conductivity  
10  $\kappa_{25}$  at 25°C (sometimes named as electrical conductance) by

11

$$12 \quad \kappa_{25} = \frac{C}{\alpha_{25} \cdot (T - 25^\circ\text{C}) + 1} \quad (4)$$

13

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

15

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

### 19 **3.3 Calculating summed electrical conductivity**

20 The summed conductivity  $S_{\kappa_{25}}$  could be interpreted as a value representing the total amount of  
21 electro-active constituents in the water. It was calculated by multiplying the measured  
22 electrical conductivity with the corresponding water volume and subsequently integrating  
23 results over the complete water depth. Therefore the lake was vertically portioned into  $j=1 \dots n$   
24 layers of volumina  $V_j$  where layer  $j=1$  represented the bottom water layer. In the lake, the

1 number of layers varied between 40 and 45 due to changes in water level whereas in the  
 2 column experiment a constant value of 47 layers could be used in each time step. Each layer  $j$   
 3 had a respective height  $h_j$  of 10 cm. Furthermore, it was assumed that conductivity gradients  
 4 in the planar directions were negligible. The summed conductivity, given in  $S \cdot m^2$ , could be  
 5 calculated for each time of measurement  $t_i$  by

$$7 \quad S_{\kappa_{25}}(t_i) = \sum_{j=1}^n \kappa_{25}(j, t_i) \cdot V_j = \sum_{j=1}^n \kappa_{25}(j, t_i) \cdot A(j) \cdot h_j \quad (5)$$

8  
 9 For the column experiment, the area of each layer was  $0.028 \text{ m}^2$  according to the geometry. In  
 10 the lake the specific size of each layer was derived from a bathymetric study (Brandenburg  
 11 University of Technology, 1998).

12  
 13 The spatially averaged monimolimnion conductivity  $\bar{\kappa}_{25}^{\text{moni}}(t_i)$  could be derived from  
 14 measurements by solving eq.5 for  $\kappa_{25}$  and summing up all layers from the lake bottom up to  
 15 layer  $j_c$  where the chemocline was located:

$$17 \quad \bar{\kappa}_{25}^{\text{moni}}(t_i) = \frac{S_{\kappa_{25}}^{\text{moni}}(t_i)}{V^{\text{moni}}(t_i)} = \frac{\sum_{j=1}^{j=j_c(t_i)} \kappa_{25}(j, t_i) \cdot A(j) \cdot h_j}{\sum_{j=1}^{j=j_c(t_i)} A(j) \cdot h_j} \quad (6)$$

18  
 19 The average mixolimnion conductivity  $\bar{\kappa}_{25}^{\text{mixo}}(t_i)$  could be calculated similarly to the approach  
 20 shown in eq. 6.

21

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

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

5

$$6 \quad \bar{\kappa}_{25}^{\text{calc}}(t_i) = \frac{V^{\text{moni}}(t_{i-1}) \cdot \bar{\kappa}_{25}^{\text{calc}}(t_{i-1}) + \sum_{j=j_c(t_{i-1})+1}^{j_c(t_i)} A_j \cdot h_j \cdot \kappa_{25}(j, t_{i-1})}{V^{\text{moni}}(t_i)} \quad (7)$$

7

8 In contrast in our model during seasonal observed chemocline erosion ( $j_c(t_i) < j_c(t_{i-1})$ ), the  
 9 iron redox-cycle was able to restore the gradient between monimolimnion and mixolimnion.  
 10 Mathematically, the corresponding increase in electrical conductivity could be calculated  
 11 assuming that previous monimolimnic water (time step  $t_{i-1}$ ) affected by the chemocline  
 12 erosion was changed to mixolimnic water (time step  $t_i$ ) with a complete loss of excess  
 13 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  
 14 to the remaining monimolimnion volume:

15

$$16 \quad \bar{\kappa}_{25}^{\text{calc}}(t_i) = \frac{V^{\text{moni}}(t_{i-1}) \cdot \bar{\kappa}_{25}^{\text{calc}}(t_i) + \sum_{j=j_c(t_i)+1}^{j_c(t_{i-1})} A_j \cdot (\kappa_{25}(j, t_{i-1}) - \bar{\kappa}_{25}^{\text{mixo}}(t_i)) \cdot h_j}{V^{\text{moni}}(t_i)} \quad (8)$$

17

## 18 **4. Results**

### 19 **4.1 Development of summed conductivity in the column experiment**

20 During the aeration period from 25<sup>th</sup> to 27<sup>th</sup> of May, the summed conductivity decreased  
 21 continuously (Figure 4). This decline continued after cessation of the aeration with the

1 exception of the measurement on 30<sup>th</sup> of May. Over all, the summed conductivity dropped by  
2 about 12 % from 13.44 S·m<sup>2</sup> to 11.84 S·m<sup>2</sup> over the complete experiment time. This could be  
3 attributed to the expected oxidation and subsequent precipitation of iron hydroxide from the  
4 aerated part of the column. The precipitation process could be visually verified by a water  
5 discoloration to reddish brown and a measured increase in the turbidity NTU of the surface  
6 water by a factor of 26.5 in comparison to the deep column water value. The precipitation of  
7 iron hydroxide flocks was visible. The flocks sank at a settling speed of about 1 mm/s. The  
8 decline of summed conductivity decelerated during the experiment due to the limited amount  
9 of ferrous iron ions remaining in the aerated part of the column.

10

11 A distinct chemocline was formed in a water depth of about 0.5 m similar to the aeration  
12 depth after an initial phase of about 1 h. The increase of airflow on the 26<sup>th</sup> of May 13:00 and  
13 the change of aeration depth 20 hours later shifted the chemocline in the vertical by 20 cm and  
14 50 cm, respectively. The chemocline height continued declining after the cessation of the  
15 aeration due to the diffusion of oxygen into deeper water layers. However the quantitative  
16 analysis was beyond the scope of this experiment.

17

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

## 1 **4.2 Comparison of column experiment samples with lake samples properties**

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

12  
13 Similarly, changes of lower water properties during the experiment could be attributed to the  
14 impact of the iron hydroxide reduction and re-dissolution process. The re-dissolution process  
15 of precipitated iron caused a measurable increase of dissolved iron (177 mg/l) compared to  
16 the initial concentration (148 mg/l). The supplementary measured TFe in the bottom water  
17 313 mg/l indicated that not all precipitated iron had been re-dissolved during the experiment.  
18 The determination of a plausible TFe value for the monimolimnion failed and was therefore  
19 excluded from Figure 6. On the other hand, the partial reduction and re-dissolution of iron  
20 caused only a slight increase in both electrical conductivity and pH in the bottom water.

21  
22 TIC concentrations of the water at the column bottom of 75 mg/l were lower than  
23 monimolimnetic water (122 mg/l) reflecting losses during sampling, transport and filling  
24 process. DOC in the deeper column of 54 mg/l was higher than the initial value of 48 mg/l.  
25 Possibly, precipitating iron hydroxide flocks could include DOC but released some into the  
26 ambient water on the way to the column bottom (Duan and Gregory, 2003).

### 1 **4.3 Dynamics of chemocline height and summed conductivity in Waldsee**

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

9  
10 The summed conductivity of Waldsee underwent seasonal variations, similar to the behavior  
11 of the chemocline, within a range of  $354 \text{ S}\cdot\text{m}^2$  and  $468 \text{ S}\cdot\text{m}^2$  with an average of  
12  $412 \pm 31.3 \text{ S}\cdot\text{m}^2$ , meaning that about 25% of the summed conductivity disappeared over  
13 summer when the chemocline was moved downwards, but recovered again when the  
14 chemocline rose during winter months.

15  
16 The initial summed conductivity of  $465.18 \text{ S}\cdot\text{m}^2$  was only slightly different from the last  
17 measurement of  $468.72 \text{ S}\cdot\text{m}^2$  indicating a similar amount of electro-active substances at the  
18 beginning and at the end of the observation period. The linear correlation coefficient between  
19 the variations in summed conductivity and chemocline height was calculated to 0.84  
20 indicating a connection between electrical conductivity of the monimolimnion and  
21 chemocline location (Figure 8).

## 22 **5. Discussion**

### 23 **5.1 Preservation of permanent stratification by the iron-redox cycle**

24 Permanent stratification of Waldsee was preserved over the observation period by the  
25 presence of dissolved compounds considering that the averaged electrical conductivity of the

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

1 mixolimnion never exceeded 0.54 mS/cm and the electrical conductivity of the  
2 monimolimnion in Waldsee was in a range between 0.93 mS/cm and 1.09 mS/cm (Figure 9).  
3 The variations of the average monimolimnion conductivity showed an inverse relationship to  
4 the variations of the chemocline height. For quantification of internal processes versus  
5 external sources, we compared measured values with the calculated values of a hypothetical  
6 situation, in which Waldsee did not experience matter fluxes with the ambient groundwater.  
7 Based on eq. 7 and 8, the average monimolimnion conductivity  $\bar{\kappa}_{25}^{\text{calc}}(t_i)$  depending on the  
8 chemocline location could be calculated for each time step. For each time step the calculated  
9 value of the previous time step was used in the equations in order to see the development  
10 between the calculated and the measured average electrical conductivity of the  
11 monimolimnion.

12

13 The graphical display (Fig. 9) of the calculated values showed that even in total absence of  
14 groundwater related ion exchange, the internal iron redox cycle alone was able to maintain the  
15 conductivity gradient. Although the curves resembled each other in terms of mean value and  
16 location of maxima and minima, the graph of the calculated values showed, with values in a  
17 range between 0.81 mS/cm and 1.25 mS/cm and a corresponding standard deviation of  
18 0.12 mS/cm, a much larger excursion than the graph of the measured monimolimnetic  
19 electrical conductivities.

20

21 One potential reason for the discrepancy in the excursions of both curves is the precipitation  
22 of iron hydroxide flocks on oxic sediments close to the side walls following a decrease in  
23 chemocline height (Schultze et al., 2011). A subsequent rise of the chemocline would lead to  
24 a delayed re-dissolution of these flocks which meant that this mechanism would be able to  
25 buffer fluctuations in the electrical conductivity. However, due to the morphology of

1 Waldsee, the area of the sidewalls was only about 1-3% of the total area of each lake layer.  
2 Hence, the potential storage capacity of this process was limited.

3

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

## 17 **5.2 Impact of groundwater recharge on permanent stratification**

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



1 decrease of the measured monimolimnion conductivity in comparison to the results of the  
2 model.

### 3 **5.3 Consequences for lake stratification modelling**

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

### 19 **6. Summary**

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

25

1 An aeration experiment filled with monimolimnetic lake water replicated the stratification  
2 features in Waldsee. The immediate precipitation of iron hydroxide flocks after the beginning  
3 of the aeration from the upper part of the column led to an approximation of electrical  
4 conductivity towards the mixolimnion value of Waldsee. A sharp conductivity (and hence  
5 density) gradient formed as had been observed in Waldsee. The deep water basically retained  
6 its properties, while the upper water layer was changed to chemical conditions close to  
7 mixolimnion properties of Waldsee: iron removal, pH depression, DOC removal and CO<sub>2</sub>  
8 loss. This confirmed previous research that the density-gradient in meromictic Waldsee was  
9 sustained by internal geochemical processes and that mixolimnion and monimolimnion could  
10 both originate from the same groundwater source.

11  
12 Calculating “summed conductivity” as a quantitative bulk value for the dissolved ionic solutes  
13 revealed an oscillation in phase with the chemocline depth. However a comparison with an  
14 idealized model of complete retention of conductivity in the water body revealed that not all  
15 conductivity removed by chemocline erosion was lost, but a considerable part of it reappeared  
16 in the monimolimnion. Numerically we found 47 %. Though this number was affected by  
17 rough assumptions, it clearly indicated that re-dissolution was taking place, and this process  
18 must be considered as a factor for sustaining the density stratification. A groundwater inflow  
19 however was still required to balance the conductivity over the years in agreement with von  
20 Rohden et al. (2009).

21  
22 Contributing to the aim of making reliable predictions of future water quality in meromictic  
23 lakes our findings imply that additional effects such as the limited re-dissolution of iron  
24 hydroxide in the monimolimnion and the buffering of mixing processes by ion-rich  
25 groundwater inflow have to be considered for the setup of numerical geochemical models  
26 predicting permanent stratification in iron-meromictic lakes.

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5 the Helmholtz Centre for Environmental Research (UFZ).

6

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

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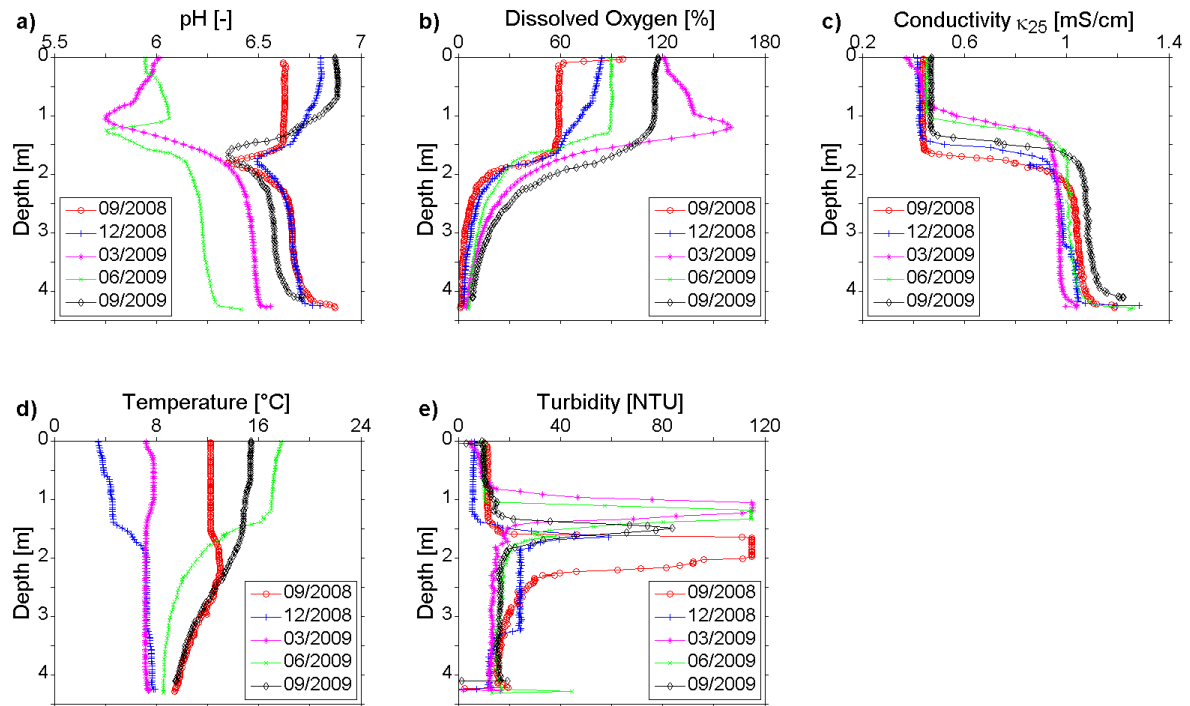
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- 26

## Figures



**Figure 1:** Geographical location of Waldsee within the Muskau Arch in Eastern Germany

[after *Kozma and Kupetz, 2008*]

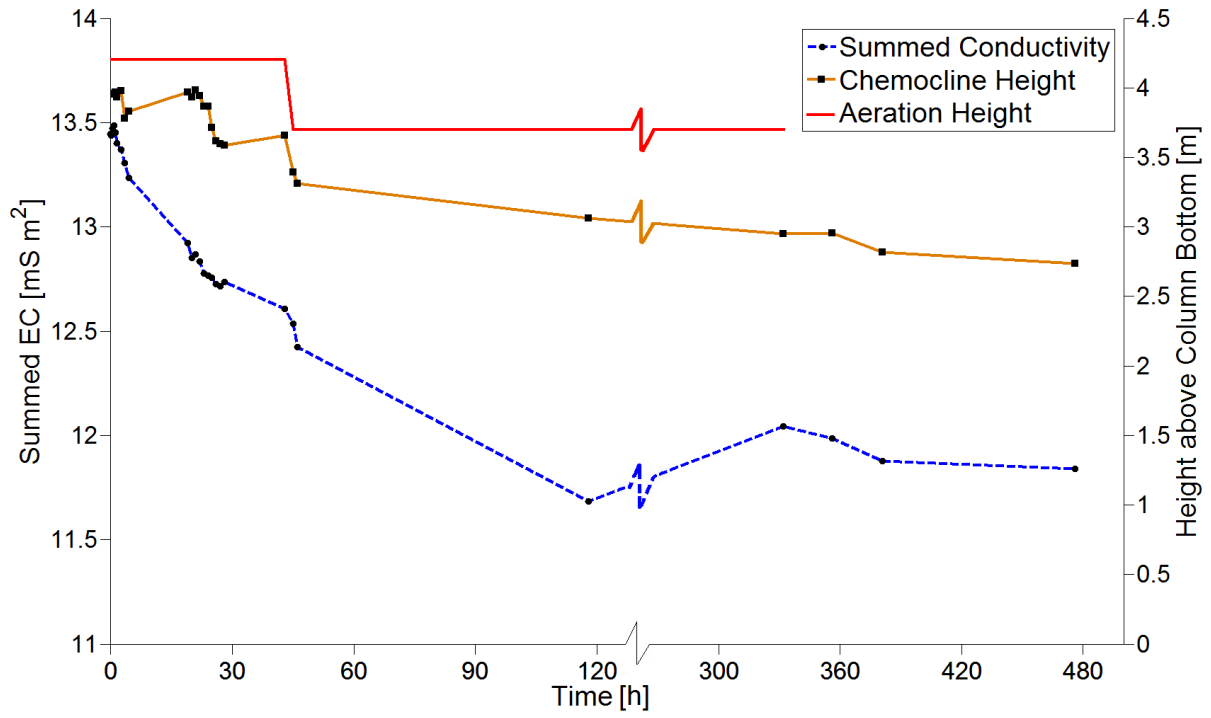


**Figure 2:** Physico-chemical profiles in Waldsee between September 2008 and September 2009

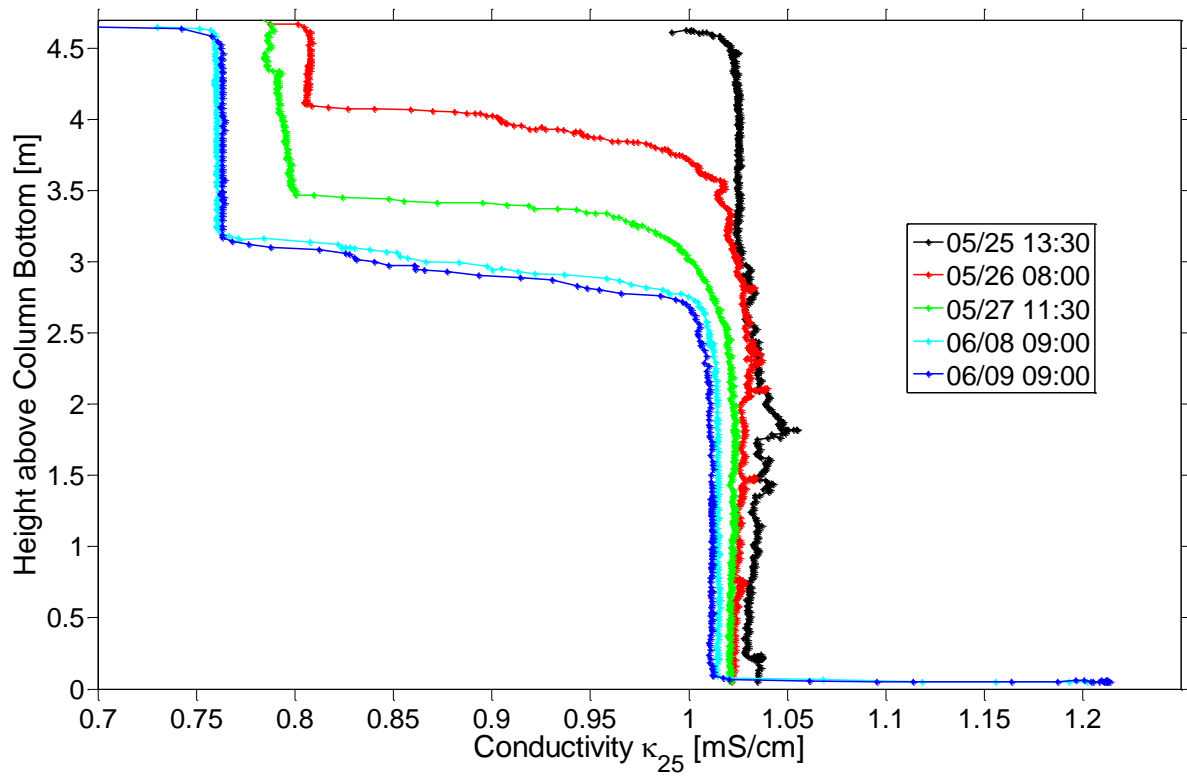




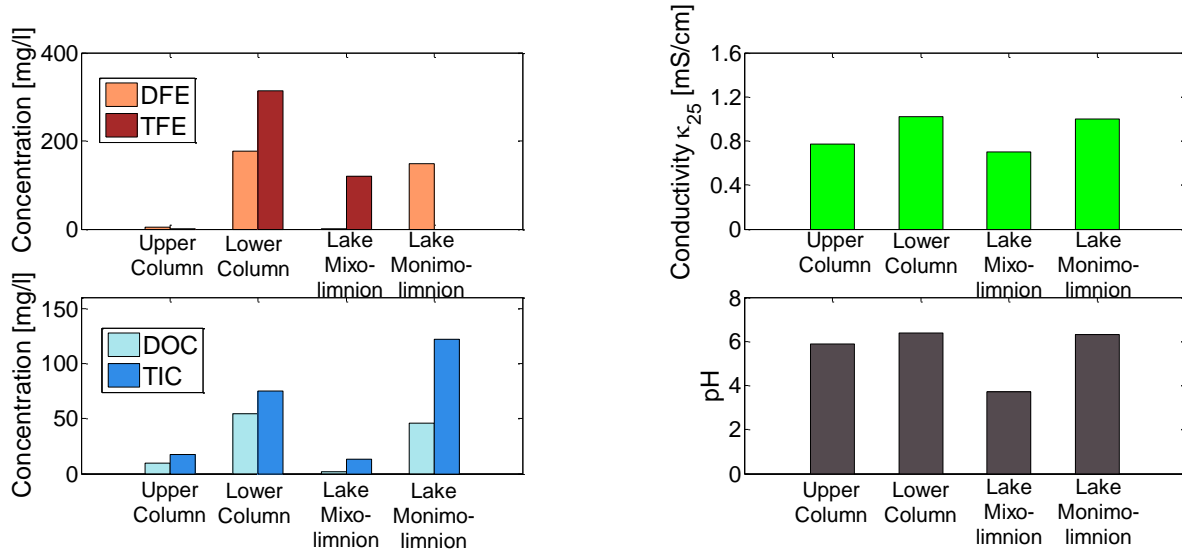
**Figure 3:** Initial conditions of the water column experiment: brownish monimolimnion water in a PVC pipe, thermally insulated by PE mattresses. Uppermost mattresses were removed for the purpose of this photograph.



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

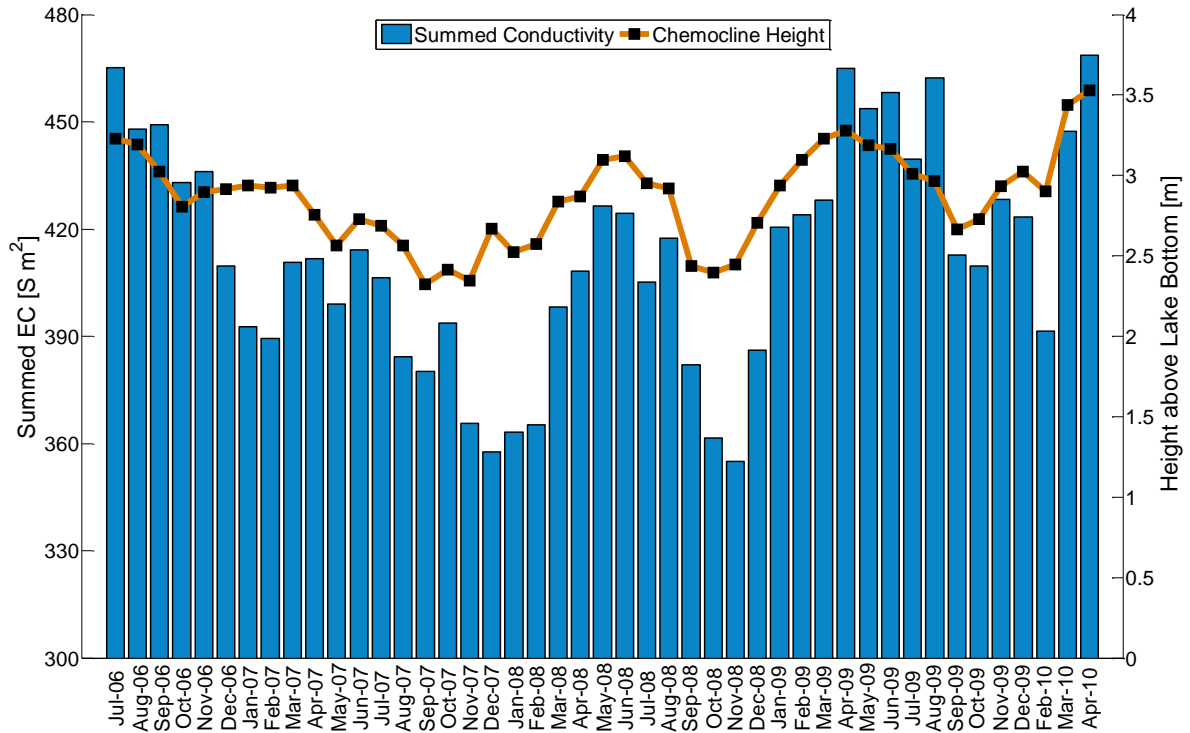


**Figure 5:** Selected conductivity ( $\kappa_{25}$ ) profiles at different time steps of the lab experiment. The earliest profile shows the initial condition in the water column followed by two profiles during active aeration at a depth of 0.5 m and 1 m, respectively. Last two profiles show the conductivity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

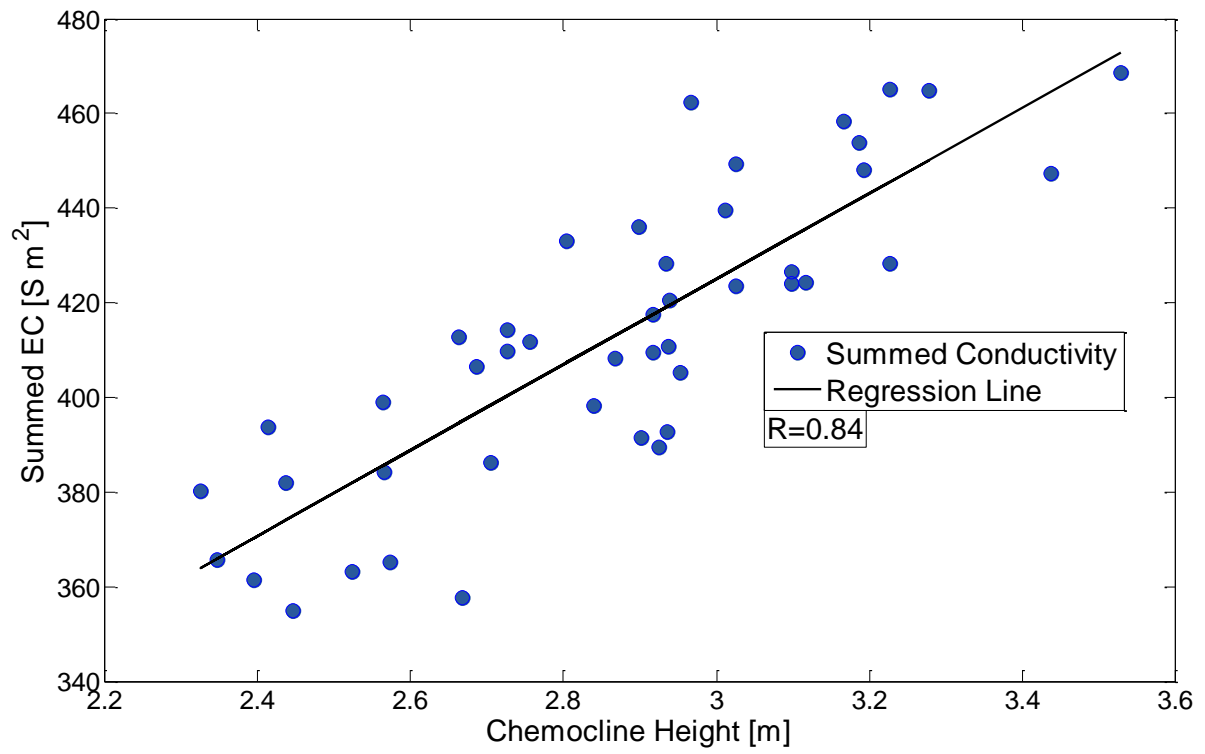


**Figure 6:** Iron species content (DFE and TFE), electrical conductivity, carbon species content (DOC and TIC) and pH-value of samples from different water layers in Waldsee and the water column

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

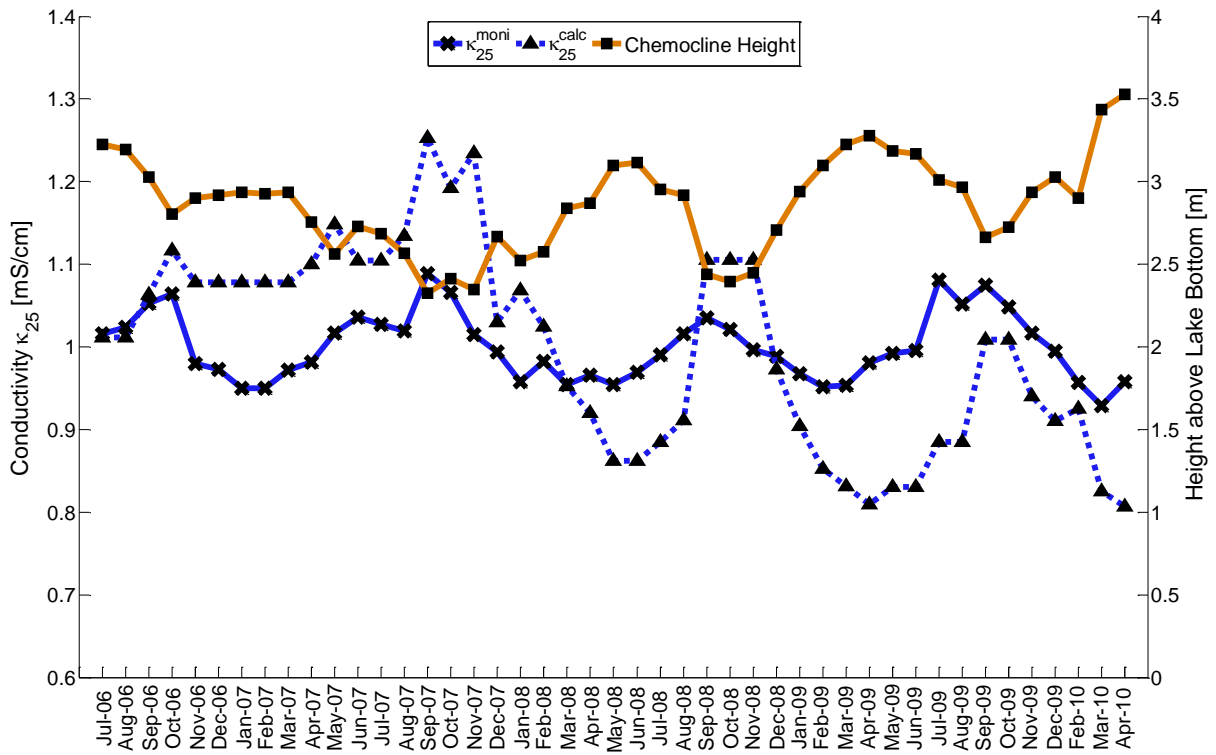


**Figure 7:** Time series of chemocline height and summed conductivity at Waldsee between July 2006 and April 2010.



**Figure 8:** Correlation between summed conductivity and chemocline height. A linear regression results in a correlation coefficient of 0.84.

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



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