

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 four years data set of monthly
10 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 chemocline height. Coinciding changes of electrical
13 conductivities in the monimolimnion indicated that a considerable share of substances,
14 precipitated by the advancing oxygenated epilimnion, re-dissolved in the remaining anoxic
15 deep waters and contributed considerably to the density stratification. In addition, we
16 constructed a lab experiment, in which aeration of monimolimnetic waters removed iron
17 compounds and organic material. Precipitates could be identified by visual inspection.

1 Introduced air bubbles ascended through the water column and formed a water mass similar to
2 the mixolimnetic Waldsee water. The remaining less dense water remained floating on the
3 nearly unchanged monimolimnetic water. In conclusion, iron meromixis as seen in Waldsee
4 did not require two different sources of incoming waters, but the inflow of iron rich deep
5 groundwater and the aeration through the lake surface were fully sufficient.

6 **1. Introduction**

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

15

16 There are good reasons for scientific interest in meromictic lakes: some of the largest lakes
17 are meromictic (e.g. Lake Malawi/Nyasa, e.g. Vollmer et al., 2002). Chemical gradients in
18 meromictic lakes form habitats for specialized organisms (e.g. sulfur bacteria performing
19 anoxygenic photosynthesis (Camacho et al., 2001) or anammox (Hamersley et al., 2009)).
20 Some meromictic lakes became famous through their dangerous gas loads (e.g. Lake Nyos
21 and Lake Monoun in Cameroon, Halbwegs et al., 2004). The monimolimnion of Lake Kivu
22 contains considerable methane deposits (Tietze, 1978), which will be exploited in near future.
23 Sediments in some meromictic lakes have been undisturbed for thousands of years and hence
24 the varved sediments represent excellent climate archives and fossil deposits (e.g. Walker and
25 Likens, 1975; Lenz et al., 2011). Meromictic lakes could be identified in many mining regions

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1 on earth where stratification limited the vertical transport of undesirable substances (e.g.
2 Spain: Lake San Telmo, Cánovas et al., 2012, and Lake Conception, Santofimia and López-
3 Pamo, 2013; Germany: Lake Wallendorfer See and Lake Rassnitzer See, Boehrer et al., 2014;
4 Lake Moritzteich, von Rohden et al., 2009). In some cases, stratification was even
5 implemented to restrict the vertical transport (Island Copper Mine pit lake in Canada, Wilton
6 et al., 1998; Stevens and Lawrence, 1998).

7

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

18

19 One prominent reactant is iron, which gets precipitated from the oxygenated mixolimnetic
20 waters and dissolves in the anoxic (reducing) chemical conditions of the monimolimnion
21 (Kjensmo, 1967; Hongve, 1997). Exemplarily it is proposed for the shallow mining lake
22 Waldsee that changes in chemocline height trigger internal, trans-chemocline transport of iron
23 species by oxidation, precipitation and re-dissolution, in combination with related CO₂
24 outgassing and regeneration. Both processes maintain density gradients between both water
25 layers and inhibit a complete mixing of this shallow lake (Boehrer et al., 2009). For Waldsee,
26 Dietz et al. (2012) showed that dissolved iron and carbon species (CO₂, bicarbonate and

1 DOC) contribute the same amount to the density gradient and all other substances contribute a
2 much subordinate portion.

3
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 calculate “summed
12 conductivity” as a measure for the amount of solutes within Lake Waldsee, and give a rough
13 quantitative estimate for the re-dissolution of precipitated iron. Furthermore a lab experiment
14 was conducted to physically reproduce the assumed chemical reactions in the lake in order to
15 get evidence about the origin of the two different water types in the lake and the production of
16 mixolimnetic water from monimolimnetic waters during periods of vertical chemocline
17 propagation.

18 **2. Site description**

19 **2.1 Study site**

20 The demonstration site Lake Waldsee (51°37'14.1''N, 14°34'16.7''E) is a former mining site
21 located in a forested area in the Lower Lusatian Mining District 130 km southeast of Berlin
22 (Figure 1). The lake covers an area of about 2400 m², has a volume of 6500 m³ and reaches a
23 maximum depth of 4.7 m (Boehrer et al., 2009). Lake Waldsee is embedded in The Muskau
24 Arch which represents an Elsterian push moraine cut by deep erosion. This geological
25 deformation process folded up the horizontal geological layers which caused the crop out of

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

6

7 The location of Lake Waldsee shows an annual average precipitation between 500-600 mm
8 and a potential open water surface evaporation of 752 mm (Seebach et al., 2008). Lake
9 Waldsee does not have a surface inflow. Hence groundwater is the main source of recharge.
10 Tracer experiments estimate a mean groundwater recharge to Lake Waldsee of 8.2 m³/d
11 (mostly from southern direction) and a mean groundwater outflow of 6 m³/s (von Rohden et
12 al., 2009). A small only occasionally filled drainage trench connects Lake Waldsee with a
13 mining lake (RL 0622/6) below. The resulting annual water level changes are in the range of a
14 few decimeters.

15 **2.2 Lake stratification and water chemistry**

16 The physico-chemical profiles of Lake Waldsee clearly showed pronounced differences in
17 water parameters between the upper 1-1.5 m thick mixolimnic water layer and the
18 monimolimnion below. pH in both mixolimnion and monimolimnion was slightly acidic with
19 values between 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).

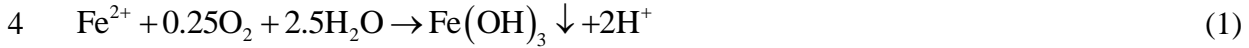
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13 The depth of the chemocline, which could be marked as the point of inflection of the κ_{25}
14 conductivity profiles and thus the volumetric ratio between mixolimnion and monimolimnion,
15 varied seasonally by about 1 m (Figure 2c). During the warm season the erosion (lowering) of
16 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:

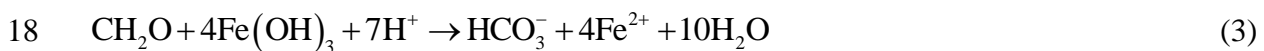


5
6 Thus the zone of iron hydroxide formation was traceable by its increase in turbidity and was
7 located slightly below the current chemocline height (Figure 2e).

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



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:



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 (Herzsprung et al., 1998).
11 Prior to filling, the column was flushed with nitrogen gas to avoid initial oxidation of ferrous
12 iron. On May 25th 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 Lake
14 Waldsee. The water was filled in slowly from below. We implemented a thermal stratification
15 to prevent 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-O₂ 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.

1 **3.2 Electrical conductivity**

2 45 monthly field measurements have been conducted in Lake Waldsee between July 2006 and
3 April 2010. Vertical profiles of temperature, pressure, pH, turbidity and in-situ electrical
4 conductivity were collected in Lake Waldsee using the multi-parameter probes *Ocean Seven*
5 *316CTD* (Idronaut, Italy) and *CTD90M* (Sea & Sun, Germany). The sampling rate was
6 between 1 and 4 Hz and the small offset between the sensors of the two different probes was
7 compensated. Measured electrical conductivity C was converted into electrical conductivity
8 κ_{25} at 25°C (sometimes named as electrical conductance) by

$$10 \quad \kappa_{25} = \frac{C}{\alpha_{25} \cdot (T - 25^{\circ}\text{C}) + 1} \quad (4)$$

11

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

13

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

17 **3.3 Calculating summed electrical conductivity**

18 The summed conductivity $S_{\kappa_{25}}$ could be interpreted as a value representing the total amount of
19 electro-active constituents in the water. It was calculated by multiplying the measured
20 electrical conductivity with the corresponding water volume and subsequently integrating
21 results over the complete water depth. Therefore the lake was vertically portioned into $j=1 \dots n$
22 layers of volumina V_j where layer $j=1$ represented the bottom water layer. In the lake, the
23 number of layers varied between 40 and 45 due to changes in water level whereas in the
24 column experiment a constant value of 47 layers could be used in each time step. Each layer j

1 had a respective height h_j of 10 cm. Furthermore, it was assumed that conductivity gradients
 2 in the planar directions were negligible. The summed conductivity, given in $S \cdot m^2$, could be
 3 calculated for each time of measurement t_i by

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

6
 7 For the column experiment, the area of each layer was 0.028 m^2 according to the geometry. In
 8 the lake the specific size of each layer was derived from a bathymetric study (Brandenburg
 9 University of Technology, 1998).

10
 11 The spatially averaged monimolimnion conductivity $\bar{\kappa}_{25}^{\text{moni}}(t_i)$ could be derived from
 12 measurements by solving eq.5 for κ_{25} and summing up all layers from the lake bottom up to
 13 layer j_c where the chemocline was located:

$$15 \quad \bar{\kappa}_{25}^{\text{moni}}(t_i) = \frac{S_{\kappa_{25}}^{\text{moni}}(t_i)}{V^{\text{moni}}(t_i)} = \frac{\sum_{j=1}^{j_c(t_i)} \kappa_{25}(j, t_i) \cdot A(j) \cdot h_j}{\sum_{j=1}^{j_c(t_i)} A(j) \cdot h_j} \quad (6)$$

16
 17 The average mixolimnion conductivity $\bar{\kappa}_{25}^{\text{mixo}}(t_i)$ could be calculated similarly to the approach
 18 shown in eq. 6.

19
 20 In the hypothetical scenario of a closed Lake Waldsee, a rise in the chemocline (
 21 $j_c(t_i) > j_c(t_{i-1})$) would be connected to a decrease of the calculated average electrical

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1 conductivity in the monimolimnion $\bar{\kappa}_{25}^{\text{calc}}(t_i)$. Mathematically this could be written as
 2 inclusion of less conductive mixolimnic water layers into the expanding monimolimnion:

3

$$4 \quad \bar{\kappa}_{25}^{\text{calc}}(t_i) = \frac{V^{\text{moni}}(t_{i-1}) \cdot \bar{\kappa}_{25}^{\text{calc}}(t_{i-1}) + \sum_{j=j_c(t_{i-1})+1}^{j_c(t_i)} A_j \cdot h_j \cdot \kappa_{25}(j, t_{i-1})}{V^{\text{moni}}(t_i)} \quad (7)$$

5

6 In contrast in our model during seasonal observed chemocline erosion ($j_c(t_i) < j_c(t_{i-1})$), the

7 iron redox-cycle was able to restore the gradient between monimolimnion and mixolimnion.

8 Mathematically, the corresponding increase in electrical conductivity could be calculated

9 assuming that previous monimolimnic water (time step t_{i-1}) affected by the chemocline

10 erosion was changed to mixolimnic water (time step t_i) with a complete loss of excess

11 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

12 to the remaining monimolimnion volume:

13

$$14 \quad \bar{\kappa}_{25}^{\text{calc}}(t_i) = \frac{V^{\text{moni}}(t_{i-1}) \cdot \bar{\kappa}_{25}^{\text{calc}}(t_i) + \sum_{j=j_c(t_i)+1}^{j_c(t_{i-1})} A_j \cdot (\kappa_{25}(j, t_{i-1}) - \bar{\kappa}_{25}^{\text{mixo}}(t_i)) \cdot h_j}{V^{\text{moni}}(t_i)} \quad (8)$$

15

16 **4. Results**

17 **4.1 Development of summed conductivity in the column experiment**

18 During the aeration period from 25th to 27th of May, the summed conductivity decreased

19 continuously (Figure 4). This decline continued after cessation of the aeration with the

20 exception of the measurement on 30th of May. Over all, the summed conductivity dropped by

21 about 12 % from 13.44 S·m² to 11.84 S·m² over the complete experiment time. This could be

1 attributed to expected oxidation and subsequent precipitation of iron hydroxide from the
2 aerated part of the column. The precipitation process could be visually verified by a water
3 discoloration to reddish brown and a measured increase in the turbidity NTU of the surface
4 water by a factor of 26.5 in comparison to the deep column water value. The iron hydroxide
5 flocks precipitation was visible. The flocks sank at a settling speed of about 1 mm/s. The
6 decline of summed conductivity decelerated during the experiment due to the limited amount
7 of ferrous iron ions remaining in the aerated part of the column.

8
9 A distinct chemocline was formed in a water depth of about 0.5 m similar to the aeration
10 depth after an initial phase of about 1 h. The increase of airflow on the 26th of May 13:00 and
11 the change of aeration depth 20 hours later shifted the chemocline in the vertical by 20 cm and
12 50 cm, respectively. The chemocline height continued declining after the cessation of the
13 aeration due to the diffusion of oxygen into deeper water layers. However the quantitative
14 analysis was beyond the scope of this experiment.

15
16 Profiles of electrical conductivity (Figure 5) showed a distinct step similar to measured
17 profiles in Lake Waldsee. Elevated values of electric conductivity appeared towards the end
18 of the experiment near the bottom. In conclusion, iron hydroxide flocks precipitated down to
19 the bottom before reduction and re-dissolution could set in. However, this obviously
20 happened at a small rate. The temporal delay could be a consequence of limited bacterial
21 presence in the beginning. The formation of a visible several centimeter thick iron hydroxide
22 layer at the column bottom confirmed the quantitative removal of substances from the
23 experimental water.

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

2 The results of the lab analysis showed that the aeration of the column's upper water changed
3 the water characteristics drastically (Figure 6). Dissolved iron (DFe) 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, DOC concentration fell from 46 mg/l to 10 mg/l. The
8 aeration also stripped CO₂ from the water resulting in a measurable drop in TIC (Total
9 Inorganic Carbon) concentration from 122 mg/l to 17.5 mg/l, which were in the range of the
10 mixolimnion water (13.1 mg/l). pH of the surface water has decreased slightly from 6.3 to 5.9
11 probably due to the acidifying 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 Lake 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 ± 0.29 m. In contrast, water level in Waldsee was on
6 average at 4.18 ± 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 Lake Waldsee was preserved over the observation period by the
25 presence of dissolved compounds considering that the averaged electrical conductivity of the

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1 mixolimnion never exceeded 0.54 mS/cm and the electrical conductivity of the
2 monimolimnion in Lake Waldsee was in a range between 0.93 mS/cm and 1.09 mS/cm
3 (Figure 9). The variations of the average monimolimnion conductivity showed an inverse
4 relationship to the variations of the chemocline height. For quantification of internal processes
5 versus external sources, we compared measured values with the calculated values of our
6 simplified model of a closed system Lake Waldsee. Based on eq. 7 and 8, the average
7 monimolimnion conductivity $\bar{\kappa}_{25}^{\text{calc}}(t_i)$ depending on the chemocline location could be
8 calculated for each time step. For each time step the calculated value of the previous time step
9 was used in the equations in order to see the development between the calculated and the
10 measured average electrical conductivity of the monimolimnion.

11

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

19

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

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 in
6 or returned quickly into the water body. Focusing on the three periods of chemocline erosion
7 between spring and autumn in the years 2007 to 2009, measured excursions were in a range
8 between 26 % and 66% of the closed model, showing a mean of 47 %. In conclusion, the
9 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 Lake Waldsee itself. On the other hand, the closed model silently assumed
13 that the loss of the bicarbonate conductivity by CO₂ escaping to the atmosphere (eq. 2) was
14 entirely counterbalanced by CO₂ production as a by-product of the biochemically iron
15 hydroxide reduction (eq. 3). The additional impact of a potential disequilibrium in the CO₂
16 balance on the changes in monimolimnion conductivity could not be delineated by our simple
17 quantitative analysis.

18 **5.2 Impact of groundwater recharge on permanent stratification**

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

1 chemocline erosion (von Rohden et al., 2009) could also contribute to the less pronounced
2 decrease of the measured monimolimnion conductivity in comparison to the results of the
3 model.

4 **5.3 Consequences for lake stratification modelling**

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

20 **6. Summary**

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

1

2 An aeration experiment in a 5 m high PVC pipe filled with monimolimnetic lake water
3 replicated the stratification features in Lake Waldsee. The immediate precipitation of iron
4 hydroxide flocks after the beginning of the aeration from the upper part of the column led to
5 an approximation of electrical conductivity towards the mixolimnion value of Lake Waldsee.
6 A sharp conductivity (and hence density) gradient formed as had been observed in Lake
7 Waldsee. The deep water basically retained its properties, while the upper water layer was
8 changed to chemical conditions close to mixolimnion properties of Lake Waldsee: iron
9 removal, pH depression, DOC removal and CO₂ loss. This confirmed previous research that
10 the density-gradient in meromictic Lake Waldsee was sustained by internal geochemical
11 processes and that mixolimnion and monimolimnion could both originate from the same
12 groundwater source.

13

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

23

24 Contributing to the aim of making reliable predictions of future water quality in meromictic
25 lakes our findings imply that additional effects such as the limited re-dissolution of iron
26 hydroxide in the monimolimnion and the buffering of mixing processes by ion-rich

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1 groundwater inflow have to be considered for the setup of numerical geochemical models
2 predicting permanent stratification in iron-meromictic lakes.

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6 are available from the authors upon request (erik.nixdorf@ufz.de). The data are archived at
7 the Helmholtz Centre for Environmental Research (UFZ).

8

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Figures



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

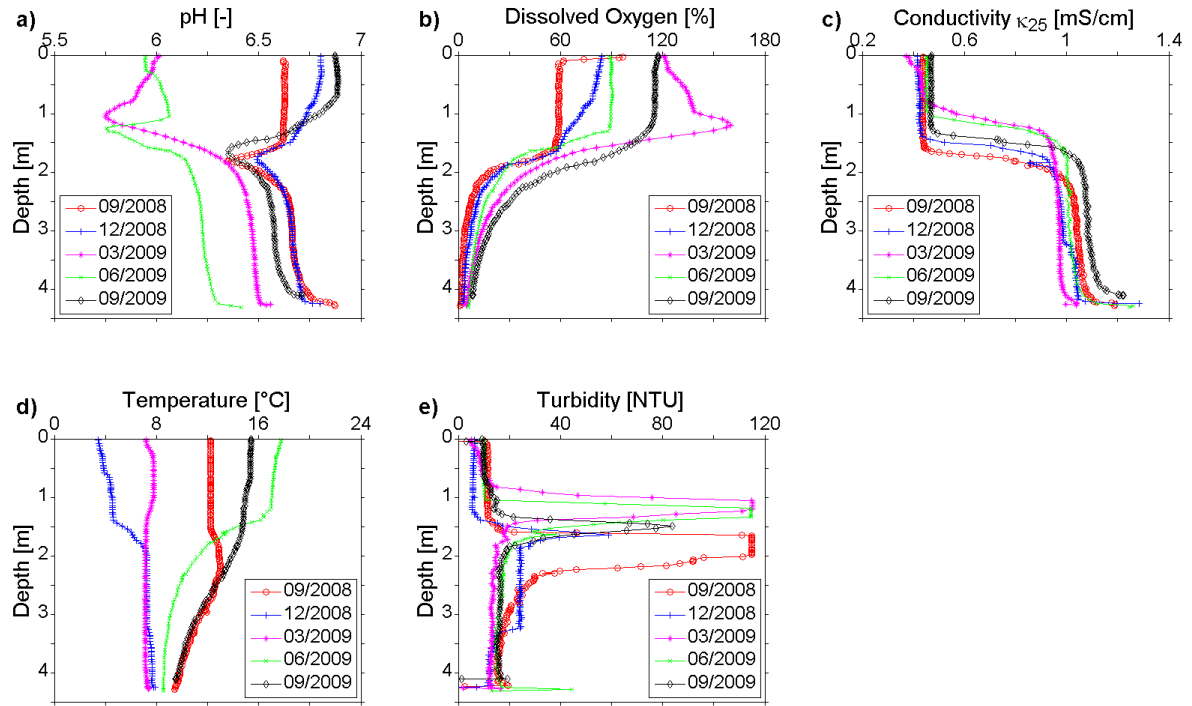


Figure 2: Physico-chemical profiles in Lake Waldsee between September 2008 and September 2009



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

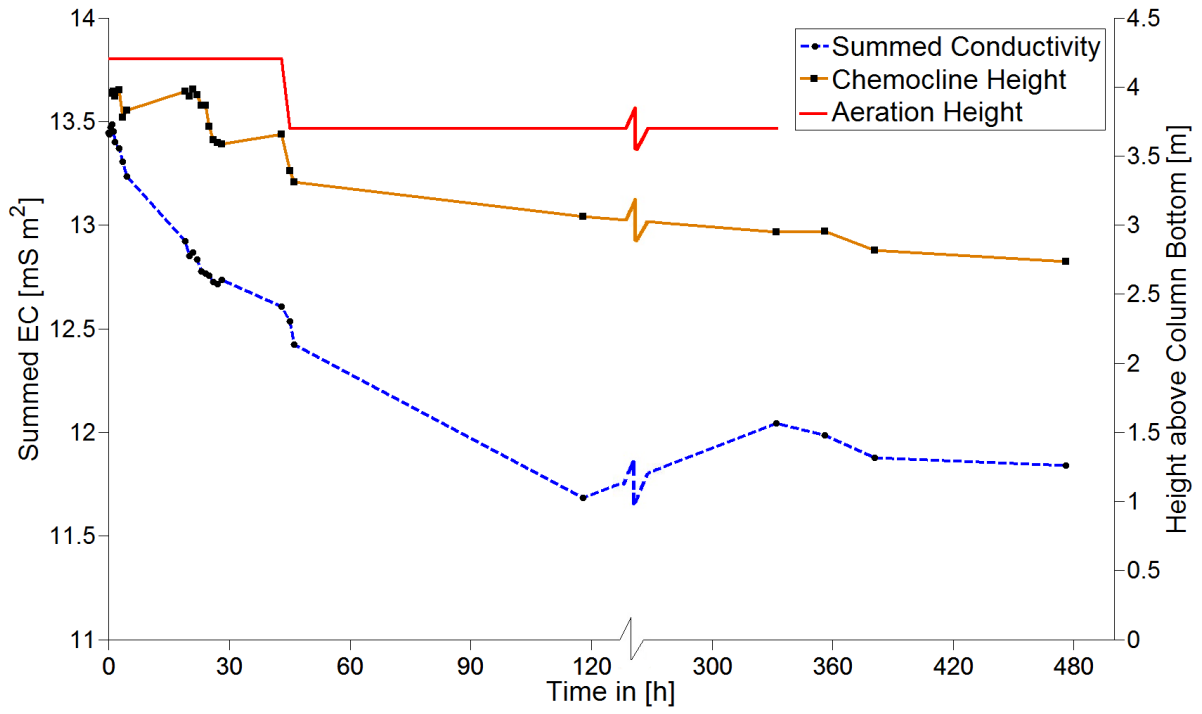


Figure 4: Temporal dynamics of chemocline height and summed conductivity during the column experiment. The scale breakage indicates the end of the hourly range sampling period of the experiment.

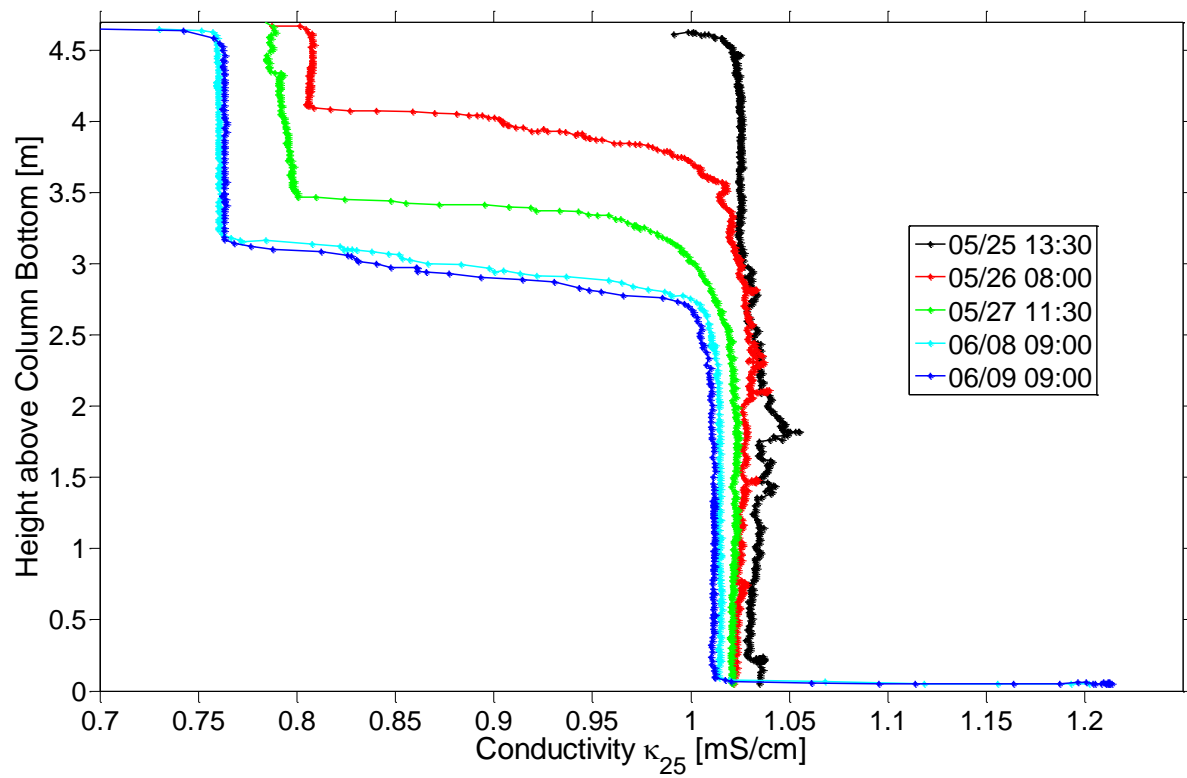


Figure 5: Selected conductivity profiles in the lab experiment

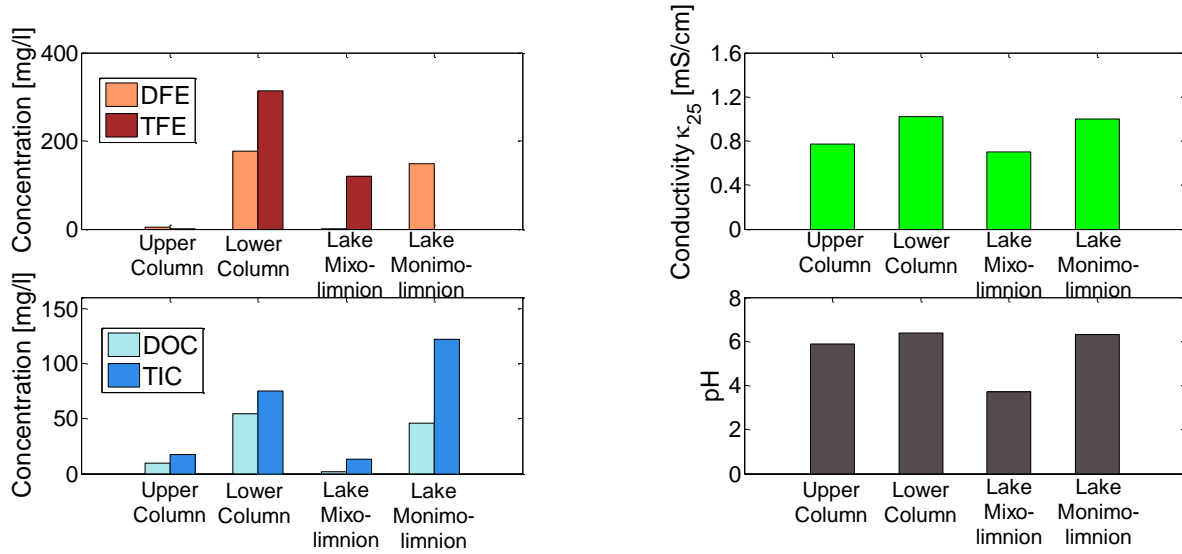


Figure 6: Iron species content (DFE and TFE), electrical conductivity, carbon species content (DOC and TIC) and pH-value of samples from different water layers in Lake Waldsee and the water column

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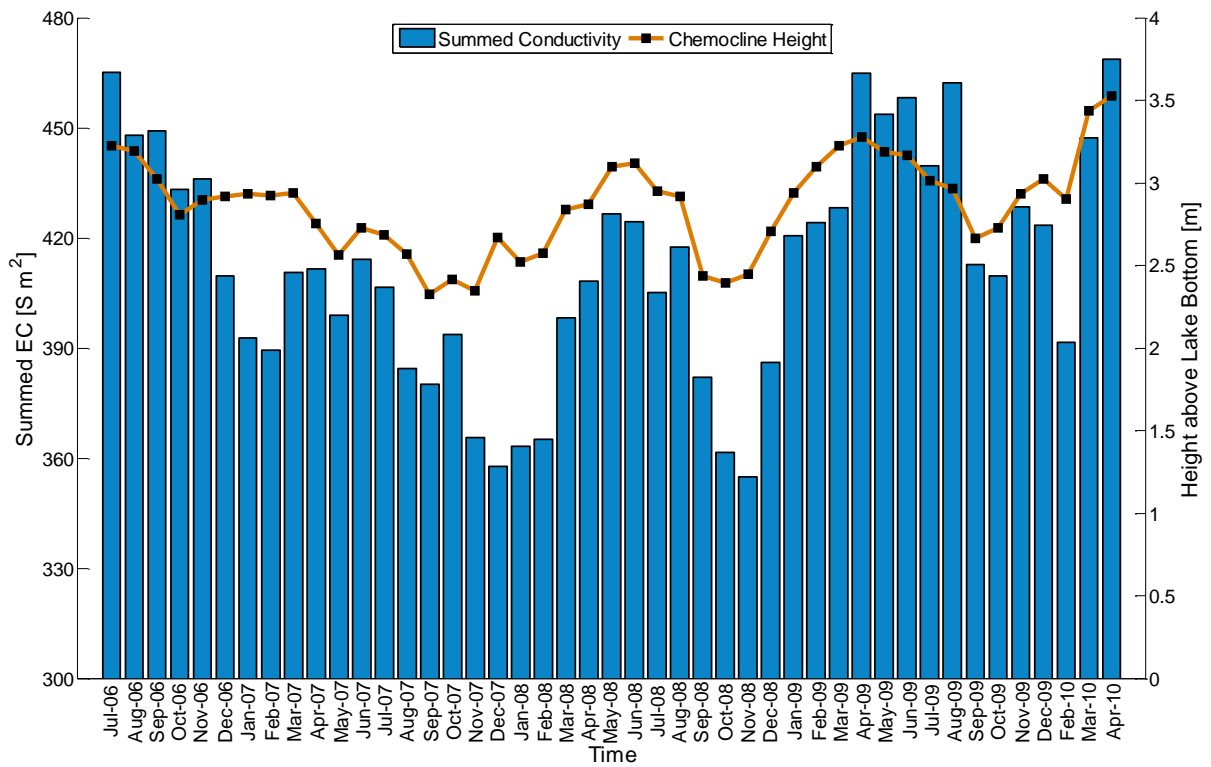


Figure 7: Time series of chemocline height and summed conductivity at Lake Waldsee between July 2006 and April 2010.

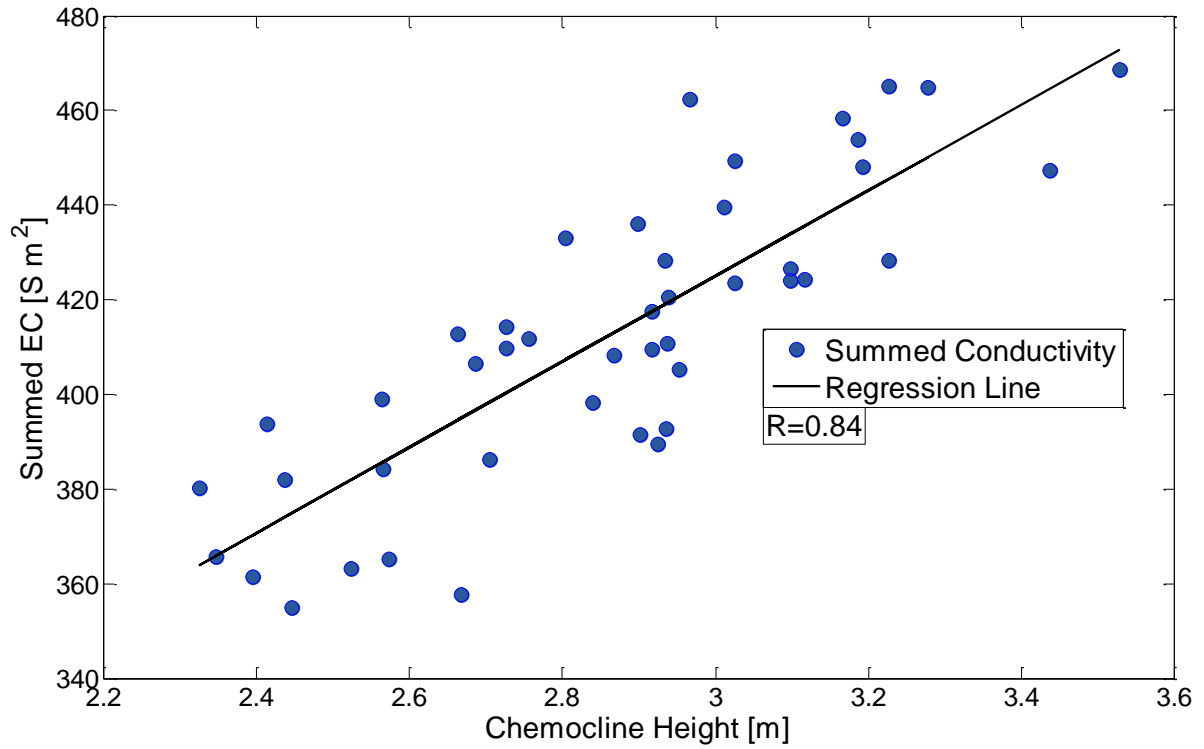


Figure 8: Correlation between summed conductivity and chemocline height. A linear regression results in a correlation coefficient of 0.84.

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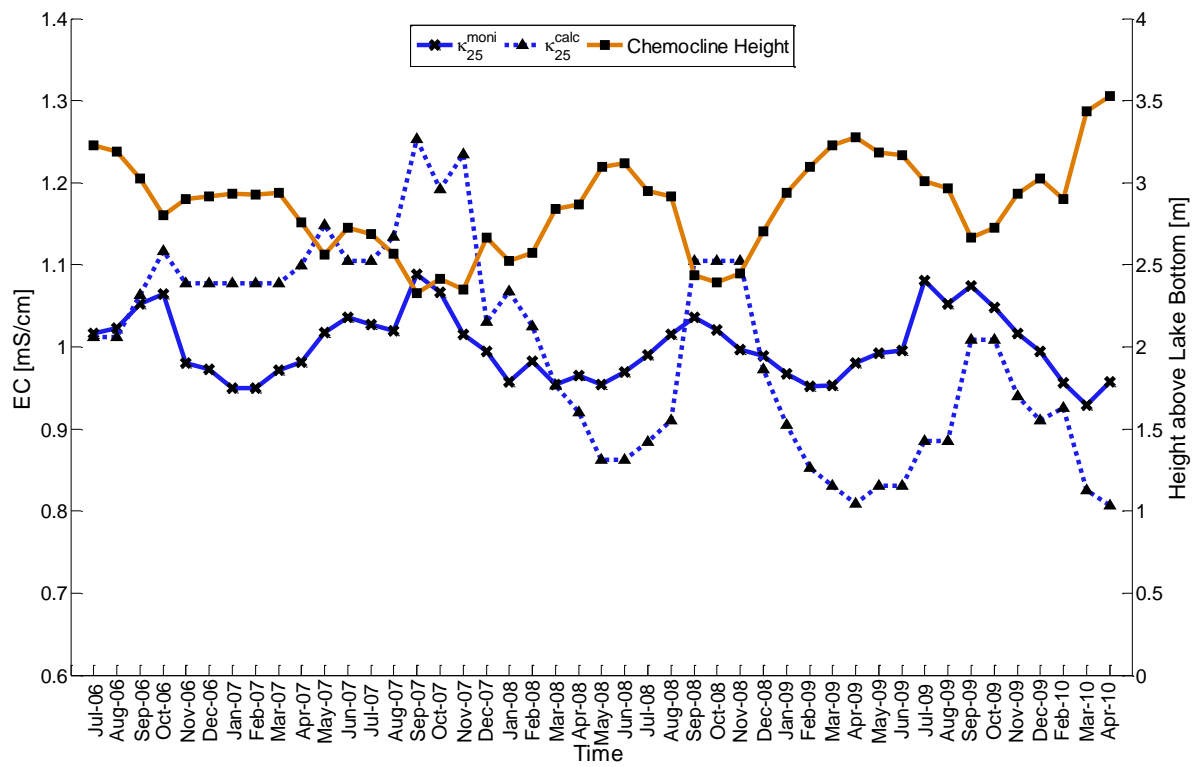


Figure 9: Comparison of time series of measured and calculated average electrical conductivity in the monimolimnion.