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

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Abstract. Lake stratification controls the cycling of dissolved matter within the water body. This is of particular interest in the case of meromictic lakes, where permanent density stratification of the deep water limits vertical transport, and a chemically different (reducing) milieu can be established. As a consequence, the geochemical setting and the mixing regime of a lake can stabilize each other mutually. We attempt a quantitative approach to the contribution of chemical reactions sustaining the density stratification. As an example, we chose the prominent case of iron meromixis in Waldsee near Doebern, a small lake that originated from near-surface underground mining of lignite. From a data set covering 4 years of monthly measured electrical conductivity profiles, we calculated summed conductivity as a quantitative variable reflecting the amount of electro-active substances in the entire lake. Seasonal variations followed the changing of the chemocline height. Coinciding changes of electrical conductivities in the monimolimnion indicated that a considerable share of substances, precipitated by the advancing oxygenated epilimnion, re-dissolved in the remaining anoxic deep waters and contributed considerably to the density stratification. In addition, we designed a lab experiment, in which we removed iron compounds and organic material from monimolimnetic waters by introducing air bubbles. Precipitates could be identified by visual inspection. Eventually, the remaining solutes in the aerated water layer looked similar to mixolimnetic Waldsee water. Due to its reduced concentration of solutes, this water became less dense and remained floating on nearly unchanged monimolimnetic water. In conclusion, iron meromixis as seen in Waldsee did not require two different sources of incoming waters, but the inflow of iron-rich deep groundwater and the aeration through the lake surface were fully sufficient for the formation of iron meromixis.

1 Introduction

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

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

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

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

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

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

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

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

2 Site description

2.1 Study site

The demonstration site 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^2, has a volume of 6500 m^3 and reaches a maximum depth of 4.7 m (Boehrer et al., 2009). 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 that 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. Waldsee is the water filled depression of the former underground mining site Pflanzgartenmulde, which has been formed by the collapse of underground

mining structures after cessation of mining activities in 1948 (Schossig and Kulke, 2006).

The location of Waldsee shows an annual average precipitation between 500-600 mm and a potential open-water surface evaporation of 752 mm (Seebach et al., 2008). Waldsee does not have a surface inflow; hence, groundwater is the main source of recharge. Tracer experiments estimate a mean groundwater recharge to 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). A small, only occasionally filled drainage trench connects Waldsee with a mining lake (RL 0622/6) below. The resulting annual water level changes are in the range of a few decimetres.

2.2 Lake stratification and water chemistry

The physico-chemical profiles of 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).
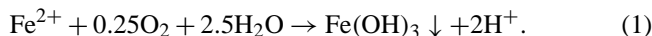
The mixolimnion was oxygenated (Fig. 2b) and had an electrical conductivity of about 0.4–$0.5 \, \text{mS cm}^{-1}$, which was approximately half of related values in the anoxic monimolimnion (Fig. 2c). Due to the absence of large pH differences (Diesing and Boehrer, 2010) this gradient in electrical 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–$400 \, \text{mg L}^{-1}$ between both water layers (Boehrer et al., 2009). The resulting density gradient across the chemocline overcompensated the destabilizing temperature gradient during wintertime (Fig. 2d) and in consequence no complete lake turnover was detected within more than 10 years of lake monitoring. However, both the mixolimnion and the monimolimnion could form two independent convection cells (Boehrer et al., 2009).

The depth of the chemocline, which could be marked as the point of inflection of the κ_{25} conductivity profiles and thus the volumetric ratio between mixolimnion and monimolimnion, varied seasonally by about 1 m (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 stratification of the two different water sections was maintained and stabilized by an internal iron-redox cycle and the outgassing of
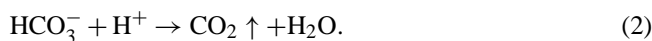
diffused bicarbonate from the mixolimnion counterbalanced by biological bicarbonate producing processes in the monimolimnion (Boehrer et al., 2009).

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-coloured, voluminous iron hydroxide precipitate:

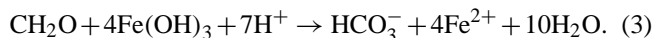$$Fe^{2+} + 0.25O_2 + 2.5H_2O \rightarrow Fe(OH)_3 \downarrow + 2H^+. \tag{1}$$

Thus, the zone of iron hydroxide formation was traceable by its increase in turbidity, measured in NTU (Nephelometric Turbidity Unit) 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 CO_2 through the carbonate equilibrium to the atmosphere:

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

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

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

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

3 Methodology

3.1 Sampling and set-up of column experiment

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

A 5 m high bluish-transparent PVC column with an outer diameter of 20 cm and a wall thickness of 0.5 cm was installed and fastened at the technical hangar of UFZ Magdeburg (Fig. 3). The column was covered by PE-containing mattresses in order to thermally insulate the column and to avoid photo-chemical iron reduction (Herzsprung et al., 1998). Prior to filling, the column was flushed with nitrogen gas to avoid initial oxidation of ferrous iron. On 25 May
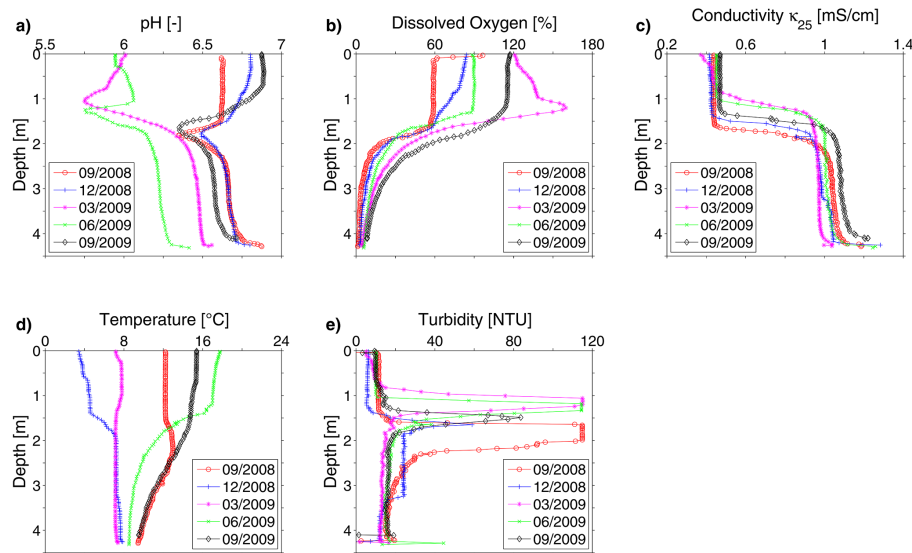
Figure 2. Physico-chemical profiles in Waldsee between September 2008 and September 2009.

2011, the column was subsequently filled with 130 L of this monimolimnetic lake water to reproduce the maximum water depth of 4.7 m in Waldsee. The water was filled in slowly from below. We implemented a thermal-stratification to prevent vertical circulation at the beginning of the experiment.

The aeration was accomplished with pressurized air at a water depth of 50 cm. Between 25 May 2011, 13:00 and 14 June 2011, 09:00 (UTC+02:00), 28 vertical profiles of temperature, pressure, turbidity and electrical conductivity were sampled with the multi-parameter CTD-O$_2$ fast profiling probe with a sampling frequency of 4 Hz. The airflow was increased after 24 h of experiment time and additional 20 h later the aeration depth was changed to 1 m for a time span of 3 additional days in order to see the response of chemocline height in the water. Finally the aeration was stopped and four further profiles were measured during the next 14 days. At the end of the experiment, water samples were taken from the aerated top water layer and the bottom water and analyzed in the lab together with collected mixolimnion and monimolimnion water from the lake to estimate the concentration of dissolved iron (DFe) and total iron (TFe) and total inorganic carbon (TIC) and DOC as well as to estimate electrical conductivity and pH value of the samples.

3.2 Electrical conductivity

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

cal conductivity C was converted into electrical conductivity κ_{25} at 25°C (sometimes named as electrical conductance) by

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

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

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

3.3 Calculating summed electrical conductivity

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

$$S_{\kappa 25}(t_i) = \sum_{j=1}^{n} \kappa_{25}(j, t_i) \cdot V_j = \sum_{j=1}^{n} \kappa_{25}(j, t_i) \cdot A(j) \cdot h_j. \tag{5}$$
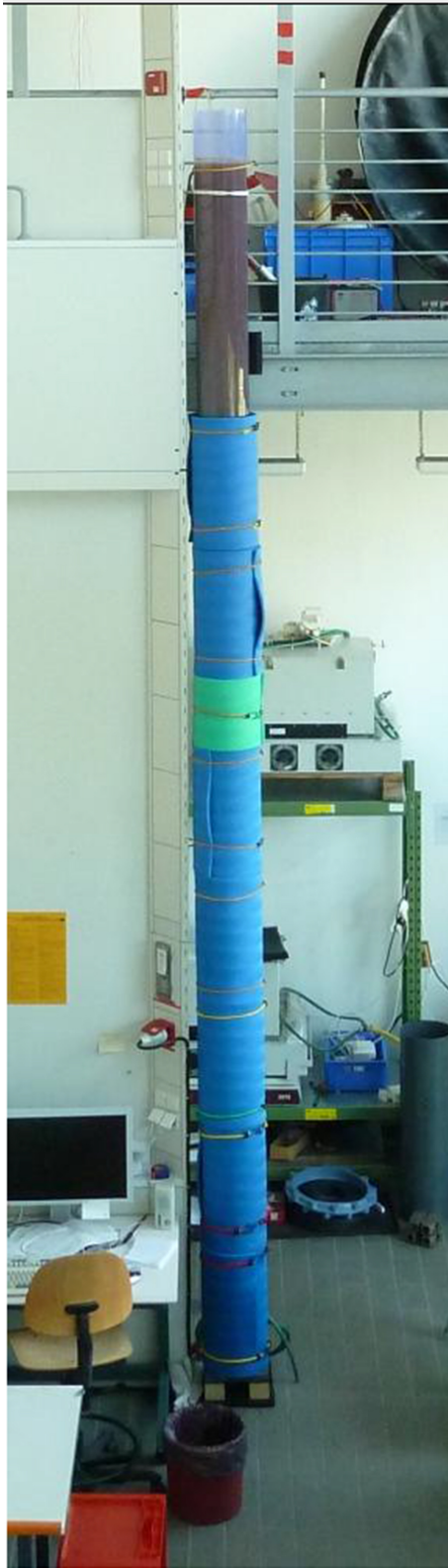
Figure 3. Initial conditions of the water column experiment: brownish monimolimnion water in a PVC pipe, thermally insulated by PE matrasses. Uppermost matrasses were removed for the purpose of this photograph.

For the column experiment, the area of each layer was $0.028\,\mathrm{m^2}$ according to the geometry. In the lake the specific size of each layer was derived from a bathymetric study (Dietz et al., 2012).

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

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

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

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

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

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

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

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 30 May. Over all, the summed conductivity dropped by about 12 % from 13.44 to 11.84 S m^2 over the complete experiment time. This could be attributed to the expected oxidation and subsequent precipitation of iron hydroxide from the aerated part of the column. The precipita-
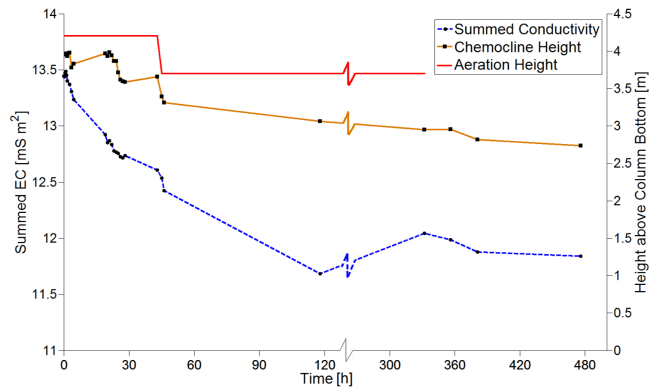
Figure 4. Temporal dynamics of chemocline height and summed conductivity (EC) during the column experiment. The scale breakage indicates the end of the hourly range sampling period of the experiment.

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

tion process could be visually verified by a water discolouration to reddish brown and a measured increase in the turbidity NTU of the surface water by a factor of 26.5 in comparison to the deep column water value. The precipitation of iron hydroxide flocks 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 was beyond the scope of this experiment.

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

4.2 Comparison of column experiment samples with lake samples properties

The results of the laboratory analysis showed that the aeration of the column's upper water changed the water characteristics significantly (Fig. 6). Dissolved iron was removed almost entirely from the upper water. Resulting concentra-
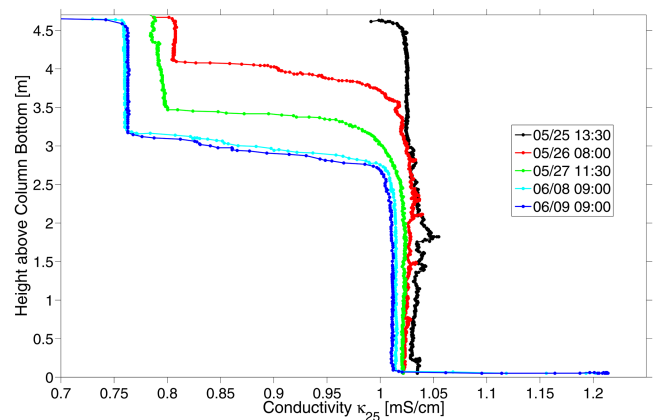
tions of $5 \, \text{mg L}^{-1}$ concurred with mixolimnic lake water ($2 \, \text{mg L}^{-1}$). In parallel, electrical conductivity fell from 1.0 to $0.77 \, \text{mS cm}^{-1}$ close to the mixolimnetic value of the lake. Most of the dissolved organic carbon was removed from the aerated water as DOC concentration fell from 46 to $10 \, \text{mg L}^{-1}$. The aeration also stripped CO_2 from the water resulting in a measurable drop in TIC concentration from 122 to $17.5 \, \text{mg L}^{-1}$, which were 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 ($313 \, \text{mg L}^{-1}$) in the bottom water 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 monimolimnetic 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).
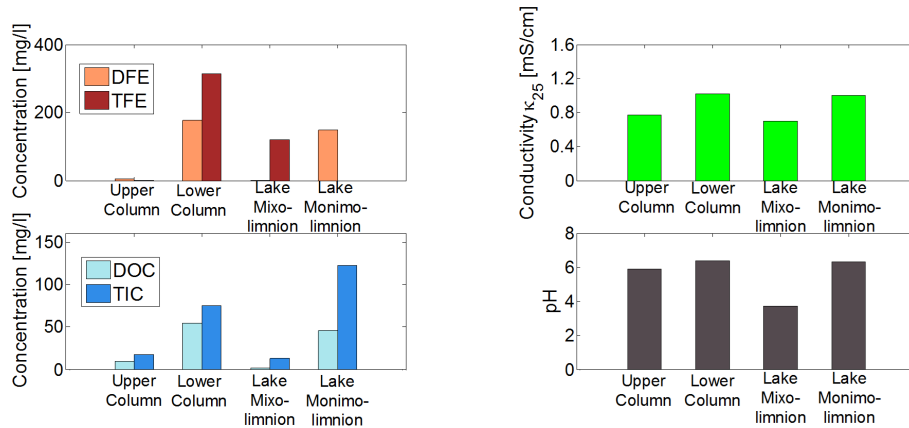
Figure 6. Iron species content (DFe and TFe), electrical conductivity, carbon species content (DOC and TIC) and pH value of samples from different water layers in Waldsee and the water column.
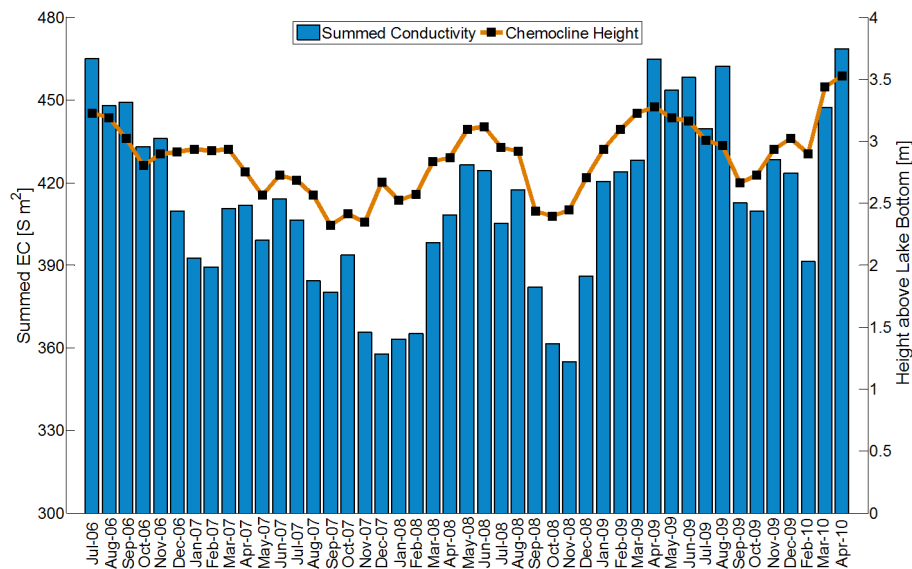

Figure 7. Time series of chemocline height and summed conductivity at Waldsee between July 2006 and April 2010.

4.3 Dynamics of chemocline height and summed conductivity in 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 sank, while it rose during winter months (Fig. 7). The height above the deepest point varied between 2.3 and 3.5 m showing a mean of 2.86 ± 0.29 m. In contrast, water level in Waldsee was on average at 4.18 ± 0.10 m. This meant that the amplitude of the chemocline changes, expressed by standard deviation, were about 3 times higher than the observed variations in lake water level.

The summed conductivity of Waldsee underwent seasonal variations, similar to the behaviour of the chemocline, within a range of 354 and 468 S m^2 with an average of 412 ± 31.3 S m^2, meaning that about 25 % of the summed conductivity disappeared over summer when the chemocline was moved downwards, but recovered again when the chemocline rose during winter months.

The initial summed conductivity of 465.18 S m^2 was only slightly different from the last measurement of 468.72 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 0.84 indicating a connection between electrical conductivity of the monimolimnion and chemocline location (Fig. 8).
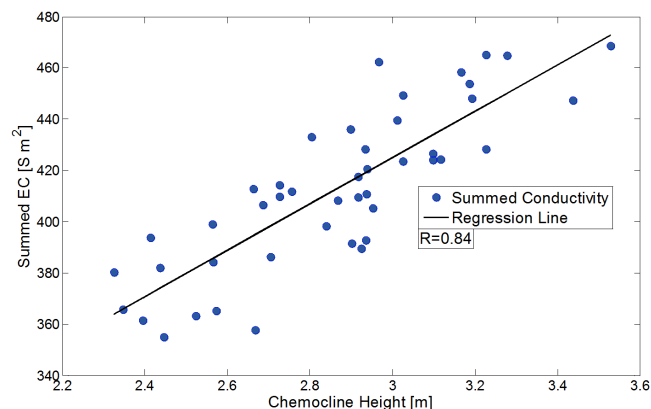
Figure 8. Correlation between summed conductivity and chemocline height. A linear regression results in a correlation coefficient of 0.84.

5   Discussion

5.1   Preservation of permanent stratification by the iron-redox cycle

Permanent stratification of Waldsee was preserved over the observation period by the presence of dissolved compounds considering that the averaged electrical conductivity of the mixolimnion never exceeded $0.54\,\text{mS}\,\text{cm}^{-1}$ and the electrical conductivity of the monimolimnion in Waldsee was in a range between 0.93 and $1.09\,\text{mS}\,\text{cm}^{-1}$ (Fig. 9). The variations of the average monimolimnion conductivity showed an inverse relationship to the variations of the chemocline height. For quantification of internal processes versus external sources, we compared measured values with the calculated values of a hypothetical situation, in which Waldsee did not experience matter fluxes with the ambient groundwater. 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 order to see the development between the calculated and the measured average electrical conductivity of the monimolimnion.

The graphical display (Fig. 9) of the calculated values showed that even in total absence of groundwater related ion exchange, the internal iron-redox cycle alone was able to maintain the conductivity gradient. Although the curves resembled each other in terms of mean value and location of maxima and minima, the graph of the calculated values showed, with values in a range between 0.81 and $1.25\,\text{mS}\,\text{cm}^{-1}$ and a corresponding standard deviation of $0.12\,\text{mS}\,\text{cm}^{-1}$, a much larger excursion than the graph of the measured monimolimnetic electrical conductivities.

One potential reason for the discrepancy in the excursions of both curves is the precipitation of iron hydroxide flocks on oxic sediments close to the side walls following a decrease in

chemocline height (Schultze et al., 2011). A subsequent rise of the chemocline would lead to a delayed re-dissolution of these flocks, which meant that this mechanism would be able to buffer fluctuations in the electrical conductivity. However, due to the morphology of Waldsee, the area of the sidewalls was only about 1–3 % of the total area of each lake layer. Hence, the potential storage capacity of this process was limited.

As a consequence, we had to conclude that not all electrical conductivity came back into solution. However, the synchronous variation indicated that a considerable portion remained in or returned quickly into the water body. Focusing on the three periods of chemocline erosion between spring and autumn in the years 2007 to 2009, measured excursions were in a range between 26 and 66 % of the closed model, showing a mean of 47 %. In conclusion, the electrical conductivity of precipitated ions from chemocline erosion reappeared 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 also be valid in Waldsee itself. On the other hand, the closed model silently assumed that the loss of the bicarbonate conductivity by CO_2 escaping to the atmosphere (Eq. 2) was entirely counterbalanced by CO_2 production from iron hydroxide reduction (Eq. 3). The additional impact of a potential disequilibrium in the CO_2 balance on the changes in monimolimnion conductivity could not be delineated by our simple quantitative analysis.

5.2   Impact of groundwater recharge on permanent stratification

A less pronounced recovery 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 temporary storage of iron flocks on the side walls of being an efficient storage mechanism, the inflow of significant amounts of ion-rich groundwater was the only remaining mechanism for the recovery of summed conductivity during times of rising chemocline in Waldsee. Finally, a net outflow of groundwater during periods of chemocline erosion (von Rohden et al., 2009) could also contribute to the less pronounced decrease of the measured monimolimnion conductivity in comparison to the results of the model.

5.3   Consequences for lake stratification modelling

Modelling lake stratification in meromictic lakes allows for forecasting future stability of the density gradients. In particular, this is of high importance for many pit lakes, as undesired substances such as heavy metals are typically trapped in enriched concentrations within the monimolimnion (e.g Jöhnk, 1999; Nixdorf et al., 2001). Hence, an unexpected
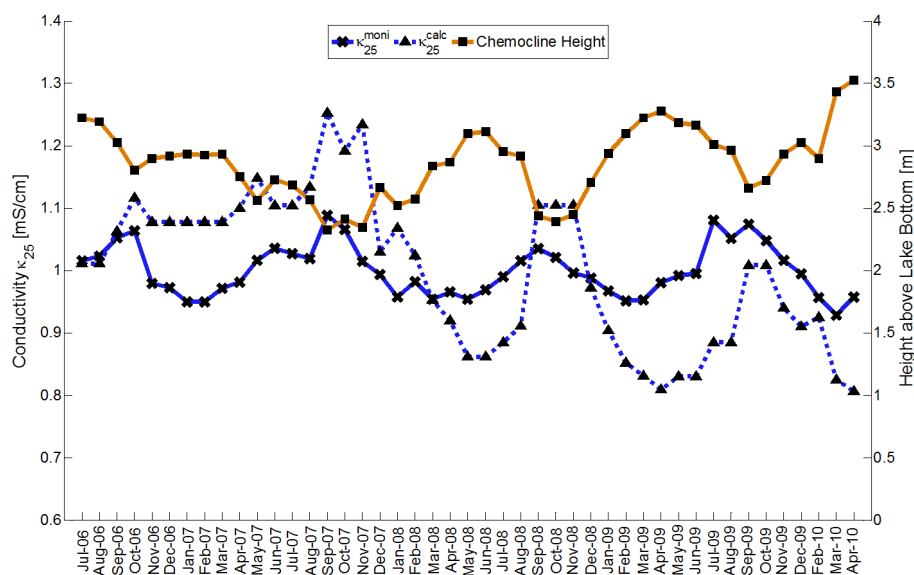
Figure 9. Comparison of time series of measured and calculated average electrical conductivity (κ_{25}) in the monimolimnion.

turnover of a meromictic lake could produce serious environmental problems. Early numerical models for meromictic lakes, such as Böhrer et al. (1998), did not include the effect of chemical reactions on the permanent density stratification. There has been a geochemical simulation of Waldsee by Moreira et al. (2011) including geochemical equilibrium based chemical equations for the iron-redox system but it provided no quantification of the partial re-dissolution of the precipitated iron in the sediments. Furthermore, as their geochemical model ran entirely during a time of chemocline decline, the proposed effect of gradient stabilization by the inflow of significant amounts of ion-rich groundwater was not included in their model. This is where our findings based on measurements and simple 1-D algebraic mass balance equations may deliver new insight for the parametrization of numerical models for the prediction of stratification in meromictic lakes.

6   Summary

Regular measurements of electrical conductivity could confirm that the induced stratification of Waldsee in two water sections was sustained throughout the observation period of 4 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 filled with monimolimnetic lake water replicated the stratification features in 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 Waldsee. A sharp conduc-

tivity (and hence density) gradient formed as had been observed in Waldsee. The deep water basically retained its properties, while the upper water layer was changed to chemical conditions close to mixolimnion properties of Waldsee: iron removal, pH depression, DOC removal and CO_2 loss. This confirmed previous research that the density gradient in meromictic Waldsee was sustained by internal geochemical processes and that mixolimnion and monimolimnion could both originate from the same groundwater source.

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

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

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

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