Biogeochemical processes controlling density stratification in an iron-meromictic lake

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Abstract

In many mining regions on earth, pit lakes have been indentified where a permanent stratification creates an anoxic reductive deep water layer, the monimolimnion, with increased concentrations of dissolved gases and undesired ionic substances, e.g. heavy metals. We investigate one of the processes responsible for permanent stratification formation, the cycle of precipitation and re-dissolution of iron species due to changing redox conditions in different water layers. Hence, evaluating the relevant processes in these so called iron-meromictic lakes on their impact on density stratification helps to predict future water quality and to forecast potential turnovers.

We present an approach of quantifying the impact of iron-redox reactions on lake stability of a small well documented iron meromictic Lake called *Waldsee* in the lower Lusatian Mining district by summing up in-situ measured vertical electrical conductivity profiles. We used the derived "summed conductivity" as a measure reflecting the amount and seasonal mass-balance dynamics of electro-active substances in the lake. Furthermore we conducted a unique aeration experiment to physically reproduce the assumed chemical reactions in the lake.

Our findings showed that calculating "summed conductivity" revealed a seasonal oscillation in phase with the chemocline depth which indicates the transition zone between the two water layers. However, induced stratification was sustained throughout the observation period of four years. Mass-balance calculations revealed that the internal iron redox cycle alone was able to maintain the conductivity gradient. However, an inflow of significant amounts of ion rich groundwater seemed to be needed for the recovery of summed conductivity during times of rising chemocline in Waldsee. Aeration of deep water from the lake by the experiment lead to a change in water properties close to surface water layer properties of *Waldsee* and hence confirmed the occurrence of internal geochemical processes: iron removal, pH depression, DOC removal and CO_2 loss.

Key words: physical limnology; meromixis; mining lake; chemocline; column experiment

Introduction

Mining lakes, showing meromictic which means that a part of the lake (called monimolimnion) is not involved in the seasonal overturns of the lake (Boehrer and Schultze 2008) could be identified in several metal or lignite mining regions of the world, such the Iberian Pyrite Belt, Spain (e.g. Lake San Telmo (Cánovas et al. 2012) and Lake Conception (Santofimia and López-Pamo 2013)), Vancouver Island, Canada (Island Copper Mine pit lake (Wilton et al. 1998)), the Central German Mining District (e.g. Lake Wallendorfer See and Lake Rassnitzer See (Boehrer et al. 2014) and the Lower Lusatian Mining District, Germany (e.g. Lake Moritzteich (von Rohden et al. 2009)).Typically meromictic conditions in mining lakes are sustained by a continuous inflow of denser groundwater and surface water via streams or precipitation and the very low diffusion rate of substances via the zone of sharp gradients, the chemoline (Rohden and Ilmberger 2001). In some cases, stratification has even been implemented to restrict the vertical transport (Island Copper Mine pit lake in Canada, (Wilton 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 (e.g. (Santofimia and

López-Pamo 2013)) as well as diffusive processes are able to cause a upward movement of the chemocline. Additionally chemical reactions such as trans-chemocline transport of iron species are able to sustain meromixis in mining lakes (Boehrer et al. 2009).

We use easily measurable vertical profiles of in-situ electrical conductivity as a quantitative bulk measure of solutes. similar to calculating salinity from electrical conductivity measurements in oceanography (e.g. Fofonoff and Millard (1983)). We sum up electrical conductivity over the vertical profile of *Waldsee* and use the derived "summed conductivity" as a measure for the amount of solutes within a pit lake, 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. For more detail on the study see Nixdorf and Boehrer (2015).

Methods

Site Description

Lake Waldsee is a shallow pit lake which has been formed by the collapse of underground mining structures after cessation of mining activities in 1948 (Schossig and Kulke 2006) (fig.1a). The lake has an area of about 2400 m² and fills a volume of 6500 m³. The maximum water depth is 4.7 m (Boehrer et al. 2009). *Waldsee* has no surface water inflow and is mainly supplied by local groundwater (von Rohden et al. 2009).
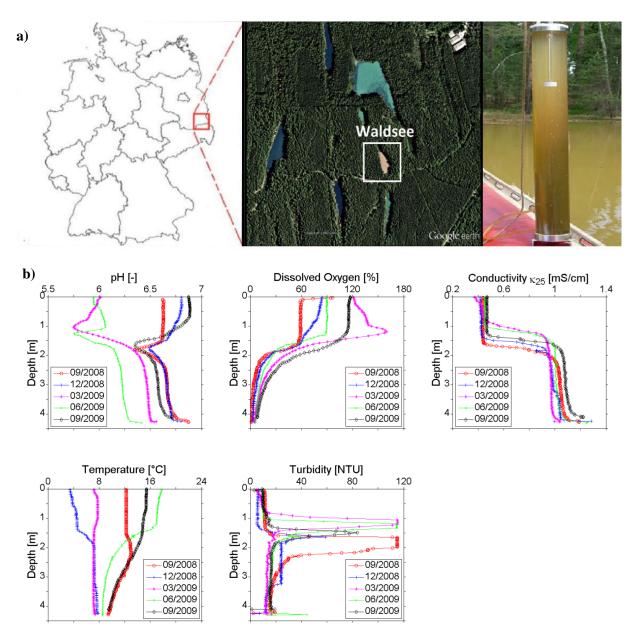
The physico-chemical profiles of *Waldsee* show a strong discrepancy in water parameters between the upper 1-1.5 m thick mixolimnic water layer and the monimolimnion below which additionally vary over the seasons (fig. 1b).

The mixolimnion is oxygenated and has an electrical conductivity which is approximately half of the related values for the anoxic monimolimnion (0.9-1.1 mS/cm). Due to the absent of large differences in pH value (Diesing and Boehrer 2010) this gradient can be mainly related to gradients in the concentrations of ferrous iron and bicarbonate (Dietz et al. 2012). Constituent concentration measurements in the mixolimnion and the monimolimnion have shown a difference in ferrous iron concentration of about 150 mg/l and in bicarbonate concentration of about 300-400 mg/l between both water sections (Boehrer et al. 2009).

The depth of the chemocline, which can be marked as the point of inflection of the κ_{25} conductivity profiles (figure 1b), varies with an amplitude up to 1 m due to seasonal changes. The lowering of the chemocline during the warm season is caused by wind driven nocturnal mixolimnic convection currents. On the other hand in winter, weakened erosive forces and significant net groundwater inflow lead to an increase of the monimolimnic water (von Rohden et al. 2009).

Additionally the density driven stratification of the two different water sections is maintained and stabilized by an internal iron redox cycle (Boehrer et al. 2009). The zone of iron hydroxide production is traceable by its increase in turbidity and is located slightly below the current chemocline height.

It is proposed that internal, trans-chemocline transport of iron species by oxidation, precipitation and re-dissolution, in combination with diffusive CO2 loss and regeneration, both triggered by changes in chemocline height, are able to maintain the density gradients between the two water layers and inhibit a complete mixing of this shallow lake (Boehrer et al. 2009).

Figure 1: *a) from left to right: Location of the study site within Germany and within the local mining district, water sample containing both mixolimnion (yellowish color) and monimolimnion (darker colored) water. b) Hydrochemical profiles in Waldsee between 09/2008 and 09/2009 (from Nixdorf and Boehrer, 2015)*

Measurements and experimental set-up

45 monthly field measurements have been conducted in *Waldsee* between July 2006 and April 2010. Vertical profiles of temperature, pressure, pH, turbidity and in-situ electrical conductivity (κ_{25}) were collected in *Waldsee* with a sampling rate between 1 and 4 Hz.

On May 18th 2011, mixolimnion and monimolimnion water were collected for chemical analysis in the laboratory including the determination of carbon (DOC; TIC, TOC) and iron species (ferrous and ferric iron) concentration.

For the 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. Prior to filling, the column was flushed with nitrogen gas to avoid initial oxidation of ferrous iron. The column was subsequently filled with 130 L of previously sampled monimolimnetic lake water to reproduce the maximum water depth of 4.7 m in *Waldsee*. We implemented an initial

thermal stratification of the water and covered the column by PE-containing madrassas to prevent vertical circulation at the beginning of the experiment.

The aeration was accomplished with pressurized air at a water depth of 50 cm. The airflow was increased after 24 h of experiment time and additional 20 hours later the aeration depth was doubled in order to see the response of chemocline height in the water. 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.

Conceptual electro-active species mass balance model

The total amount of electro-active constituents in the lake could be quantified by a parameter called summed conductivity $S_{\kappa 25}$. For each time of measurement it was calculated by multiplying the measured electrical conductivity κ_{25} with the corresponding water volume and subsequently integrating results over the complete water depth.

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

Therefore the lake was vertically portioned into $j=1\ldots n$ layers of volumina V_j where layer $j=1$ represented the bottom water layer. In the lake, the number of layers varied between 40 and 45 due to changes in water level whereas in the column experiment a constant value of 47 layers could be used in each time step. Each layer j had a respective height h_j of 10 cm. Furthermore, it was assumed that conductivity gradients in the planar directions were negligible.

Beside the assessment of the dynamics of the mass balance in the entire water body, calculating the spatially averaged conductivity of mixolimnion and monimolimnion for each time step allows to quantify changes in stratification stability.
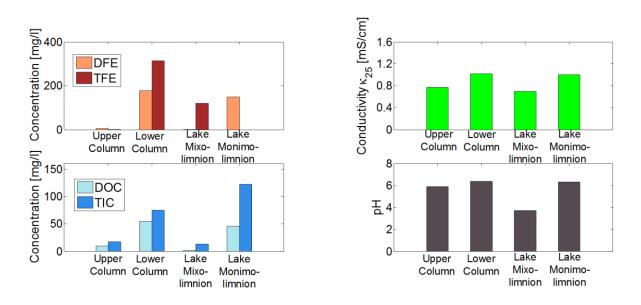
Discrepancies between the measured dynamics of monimolimnion and mixolimnion conductivities and values calculated using a hypothetical scenario of a closed *Waldsee* represent the impact of cross-boundary mass fluxes on the electro-active species mass balance of *Waldsee*. For detail in the calculation see Nixdorf and Boehrer (2015).

Results

Column Experiment

Over the complete experiment time summed conductivity dropped by about 12 % from 13.44 S·m² to 11.84 S·m². This could be attributed to the expected oxidation and subsequent precipitation of iron hydroxide from the aerated part of the column. The precipitation process could be visually verified by a water discoloration to reddish brown and a settling of flocks within the column.

The results of the laboratory analysis showed that the aeration of the column's upper water changed the water characteristics significantly (fig. 2). Resulting upper water parameters approach in the direction of mixolimnetic water properties in *Waldsee* indicating the efficiency of the proposed iron hydroxide formation process. Similarly, changes of lower water properties during the experiment could be attributed to the impact of iron hydroxide reduction and re-dissolution process.

Figure 2: *Water properties of samples from different water layers in Waldsee and the water column. The determination of a plausible TFe value for the monimolimnion failed and was therefore excluded (from Nixdorf and Boehrer, 2015)*

Dynamics of chemocline height and summed conductivity in Waldsee

Over four years of monthly observation, a seasonal variation of the chemocline could be observed. (see also von Rohden et al. 2009). From April to October, the chemocline sank, while it rose during winter months (fig. 3a). The mean height above the lake bed was 2.86±0.29 m showing variations between 2.3 m and 3.5 m. Compared with the water level in *Waldsee* which was on average at 4.18 ±0.10 m this meant that the amplitude of the chemocline changes, expressed by standard deviation, were about three times higher than the observed variations in lake water level.

Similar to the behavior of the chemocline, summed conductivity of *Waldsee* underwent seasonal variations, within a range of 354 S·m² and 468 S·m². This means 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·m² was only slightly different from the last measurement of 468.72 S·m² indicating a similar amount of electro-active substances at the beginning and at the end of the observation period.

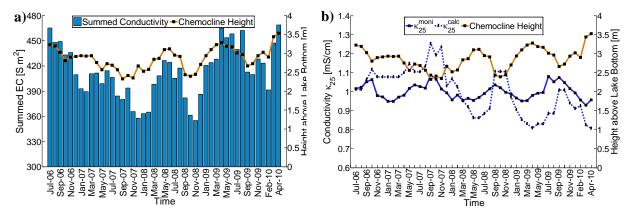### Impact of internal and external fluxes on stratification preservation

Within the observation period, measured averaged EC of the monimolimnion was in a range between 0.93 mS/cm and 1.09 mS/cm, having a temporal mean of 1.00 mS/cm and a standard deviation of 0.041 mS/cm (fig. 3b). In contrast average EC in the mixolimnion never exceeded 0.54 mS/cm. This confirmed that the permanent stratification of *Waldsee* was preserved during the entire observation period by the presence of conductivity gradients. An inverse relationship could be observed between variations of the average monimolimnion conductivity and variations of the chemocline. Assuming that groundwater showed fairly constant chemical properties, this indicated that internal physico-chemical processes were potential drivers of the monimolimnetic electrical conductivity variations.

We compared measured values with the calculated values of our simplified model of a closed system *Waldsee* in order to quantify the impact of internal processes versus external sources. The graph of the calculated values, which were in a range between 0.81 mS/cm and 1.25 mS/cm, 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 measured values showed, on average, only 47 % of the excursions found in the graph of the calculated monimolimnetic electrical conductivity values.

In conclusion, the electrical conductivity of precipitated ions from chemocline erosion partly re-appeared in the monimolimnion, but some iron was permanently deposited in the sediment. Correspondingly high iron mass concentrations of about 20 % could be measured in the sediment of *Waldsee* up to a depth of more than 10 cm (Friese 2004).

A less pronounced re-covering of electrical conductivity losses in the monimolimnion would lead to a continuous decrease in monimolimnion conductivity. For the chosen model, the calculated conductivity values dropped below the measured values significantly during periods of chemocline increase and additionally showed a long term decreasing trend. Excluding the temporarily storage of iron flocks on the side walls of being an efficient storage mechanism, the inflow of significant amounts of ion rich groundwater was the only remaining mechanism for the recovery of EC 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.

It should be taken into consideration that the closed model silently assumed that the loss of the bicarbonate conductivity by CO_2 escaping to the atmosphere was entirely counterbalanced by CO_2 production as a by-product of the biochemically iron hydroxide reduction. At this point further investigations, e.g. by numerical geochemical equilibrium models, are needed to quantify the impact of the carbonate system on the electrical conductivity dynamics in *Waldsee*.

Figure 3: *a) Time series of chemocline height and summed EC at Waldsee between July 2006 and April 2010. b) Comparison of measured and calculated average EC in the monimolimnion (from Nixdorf and Boehrer, 2015)*

Conclusions

The present study provides an easily applicable approach to delineate and quantify the impact of internal geochemical processes, partial intermixing processes and groundwater flow on the dynamics of mining lake water properties by using spatial high resolution electrical conductivity measurements and simple one-dimensional algebraic equations.

Regular measurements of electrical conductivity could confirm that the induced stratification of *Waldsee* in two water sections is permanent and that the volume of both sections undergoes changes which follow a seasonal pattern with an increase of monimolimnion volume in winter and early spring and a decrease in the remaining months. However, it could be shown that the total amount of electro-active substance in *Waldsee* correlates significantly with the volume of the monimolimnion with variations up to 25 % within the observation period.

An aeration experiment in a 5 m high PVC column filled with monimolimnic lake water replicated the proposed dominating geochemical processes in *Waldsee*, first and foremost the iron-redox-cycle. The immediate precipitation of iron hydroxide flocs after the beginning of the aeration of the upper part of the column led to an approximation in electrical conductivity to the mixolimnion of *Waldsee*. This could confirm the previous research that the density-gradient in meromictic *Waldsee* is sustained by internally geochemical process and that, on principle, the water of mixolimnion and monimolimnion could both originate from local groundwater.

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 about half of it reappeared in the monimolimnion. 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).

Acknowledgement

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