

THE FORMATION, PERSISTENCE, AND CONSEQUENCES
OF PELAGIC OXYCLINES IN LAKES

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ABSTRACT

Pelagic oxyclines, the transition zone between oxygen rich surface waters and oxygen depleted deep waters, are a common characteristic of eutrophic lakes during summer stratification. They can have tremendous effects on the biodiversity and the ecosystem functioning of lakes and, to add insult to injury, are expected to become more frequent and more pronounced as climate warming progresses. On these grounds, this thesis endeavors to advance the understanding of formation, persistence, and consequences of pelagic oxyclines: We test, whether the formation of metalimnetic oxygen minima is intrinsically tied to a locally enhanced oxygen consuming process, investigate the relative importance of vertical physical oxygen transport and biochemical oxygen consumption for the persistence of pelagic oxyclines, and finally assess their potential consequences for whole lake cycling. To pursue these objectives, the present thesis nearly exclusively resorts to *in situ* measurements. Field campaigns were conducted at three lakes in Germany featuring different types of oxyclines and resolved either a short (hours to days) or a long (weeks to months) time scale. Measurements comprised temperature, current velocity, and concentrations of oxygen and reduced substances in high temporal and vertical resolution. Additionally, vertical transport was estimated by applying the eddy correlation technique within the pelagic region for the first time. The thesis revealed, that the formation of metalimnetic oxygen minima does not necessarily depend on locally enhanced oxygen depletion, but can solely result from gradients and curvatures of oxygen concentration and depletion and their relative position to each other. Physical oxygen transport was found to be relevant for oxycline persistence when it considerably postponed anoxia on a long time scale. However, its influence on oxygen dynamics was minor on short time scales, although mixing and transport were highly variable. Biochemical consumption always dominated the fate of oxygen in pelagic oxyclines. It was primarily determined by the oxidative breakdown of organic matter originating from the epilimnion, whereas in meromictic lakes, the oxidation of reduced substances dominated. Beyond that, the results of the thesis emphasize that pelagic oxyclines can be a hotspot of mineralization and, hence, short-circuit carbon and nutrient cycling in the upper part of the water column. Overall, the present thesis highlights the importance of considering physical transport as well as biochemical cycling in future studies.

1 INTRODUCTION

1.1 Pelagic oxyclines in lakes

The density stratification of lakes limits the vertical exchange between surface and bottom waters and thereby divides the water column: While the epilimnion experiences an input of oxygen by gas exchange with the atmosphere as well as photosynthetic activity, the hypolimnion is mostly isolated from oxygen replenishment and oxygen depleting processes dominate. The transition zone between the oxygen rich epilimnion and oxygen depleted hypolimnion, characterized by a decline in dissolved oxygen with depth, is the so called pelagic oxycline (also referred to as clinograde oxygen profile; Figure 1). Depending on the characteristics of stratification, pelagic oxyclines can either be a temporary or permanent feature of lakes (Boehrer and Schultze, 2008). Lakes with a density stratification arising in the seasonal cycle of surface warming develop a temporary oxycline (Turner and Erskine, 2005), whereas in meromictic lakes the stratification due to high concentrations of dissolved and suspended substances results in permanent persistence of the oxycline throughout the year (Rodrigo et al., 2001).

It is the most drastic variation of pelagic oxyclines, when they become the transition zone between oxic surface and anoxic deep waters. Anoxic conditions usually characterize meromictic lakes but can also arise during seasonal stratification, whenever the oxygen consumption outbalances the hypolimnetic oxygen content, i.e., the sum of oxygen stored on the onset of seasonal stratification and replenished by vertical transport. During seasonal stratification, anoxia evolves at the sediment and rise in the water column as reduced substances diffuse upward and become oxidized. Thus these oxic-anoxic interfaces feature gradients in reduced and oxidized forms of redox sensitive elements, namely N, Fe, Mn, S, and CH₄ (Kirf et al., 2015) and are hotspots of biogeochemical cycling and transformations (Casamayor et al., 2008; Reiche et al., 2011).

A special variation of pelagic oxyclines is the occurrence of a metalimnetic oxygen minimum (also referred to as negative heterograde oxygen profile; Figure 1). It is characterized by an increase in oxygen concentration with depth following the initial decline and is a well-known but less investigated phenomenon in stratified lakes. So far, most studies exploring the formation of metalimnetic oxygen minima implicitly assumed that it is caused by locally enhanced oxygen depletion. This can be induced externally by irregularities in lake morphometry (Shapiro, 1960) or interflows of oxygen depleted or

depleting water (Nix, 1981), but can also occur *in situ* in the water column due to the respiration of phytoplankton (Effler et al., 1998), zooplankton (Shapiro, 1960), and microbial mineralization of organic matter (Mitchell and Burns, 1979; Schram and Marzolf, 1994). Even though many studies which dealt with the *in situ* processes struggled to sufficiently elucidate the formation of metalimnetic oxygen minima, the implicit assumption was never questioned.

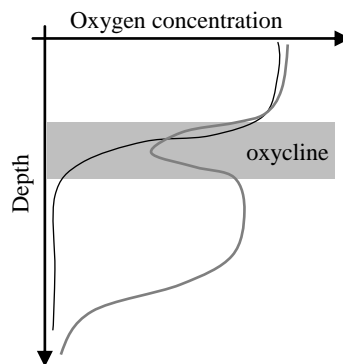


Figure 1: Schematic drawing of the oxycline layer (lightgray rectangle) in a clinograde (black line) and a negative heterograde oxygen profile (metalimnetic oxygen minimum, gray line).

1.2 The significance of pelagic oxyclines

The persistence of pelagic oxyclines, most often tied to oxygen depleted bottom waters, has profound influence on the lake as an ecosystem: They drastically alter the habitat of aerobic organisms and thereby strongly influence biodiversity (Vaquer-Sunyer and Duarte, 2008; Zhang et al., 2009). The lack of oxygen entails changes in chemical cycling with profound effects on water quality. All in all the persistence of pelagic oxyclines can come along with impaired lake ecosystem services such as drinking water supply, fishery, or recreational purposes (e.g., Rabotyagov et al., 2014; Watson et al., 2016). These scenarios will become an even more urgent thread for lakes in future: Climate warming not only increases lake temperature and the duration of the stratification period (Livingstone, 2003), but also affects plankton dynamics (Shimoda et al., 2011) and the input of nutrients (Jeppesen et al., 2010a). All together promoting deoxygenation and making the formation and persistence of oxyclines and anoxic conditions in lakes more frequent in future (Jeppesen et al., 2010b; Moss, 2010). A similar fate looms in the oceans, where the

combined effects of eutrophication and climate warming promote marine oxycline formation and threaten estuarine and coastal zones (Diaz and Rosenberg, 2008; Rabalais et al., 2009). Thus improving our understanding of the processes acting at pelagic oxyclines during their formation and persistence becomes increasingly important.

1.3 Oxygen transport and consumption at pelagic oxyclines

The formation and persistence of pelagic oxyclines results from an imbalance in the opposing processes of net oxygen consumption and vertical downward oxygen transport. Oxygen consumption describes the net effect of all oxygen producing and depleting processes and generally comprises of the oxidation of reduced substances (produced by anaerobe breakdown of organic matter in the hypolimnion or the sediment), the organismic respiration and mineralization (i.e., the aerobic break down of organic carbon), and photosynthetic primary production. It is equivalent to the term net production often used in literature but is considered more intuitive. In the search for the causes of hypoxia and anoxia in lake bottom waters, oxygen consumption has been in the focus of research and especially the relative importance of the oxygen uptake of the sediment and the hypolimnetic water body has been subject to scientific debate (e.g., Cornett and Rigler, 1979; Livingstone and Imboden, 1996; Müller et al., 2012). Matzinger et al. (2010) found the oxidation of reduced substances to considerably contribute to the oxygen depletion in the hypolimnia of eutrophic lakes. Additionally, oxygen consumption in the epilimnion has been studied intensively with respect to community respiration (Berman et al., 2004; Carignan et al., 2000) and net ecosystem production (Hanson et al., 2003; Solomon et al., 2013). However, not much attention has been paid to oxygen consumption in the oxycline itself. Only where it separates oxic from anoxic waters, the oxycline has been studied with a focus on the diverse microbial community and the related productivity and intense cycling of redox-sensitive compounds (Camacho et al., 2001; Casamayor et al., 2012; Massana et al., 1996). In sulfide rich lakes with anoxic bottom waters, the microbial oxidation of reduced substances can dominate local carbon cycling (dark carbon fixation by chemolithoautotrophs; Camacho et al., 2001; Casamayor et al., 2012; Massana et al., 1996). The role of pelagic oxyclines in carbon cycling also attracted notice, when differences in lake metabolism with depth recently were taken into account (Coloso et al., 2008; Dunalska et al., 2014). Staehr et al.

(2012) found the metalimnion including the oxycline to contribute about one fourth to the whole lake's respiration which is also supported by Obrador et al. (2014).

Vertical oxygen transport in lakes is coupled to turbulence, generally created by a multitude of physical drivers like surface waves, currents, internal waves, or differential heating and cooling, all ultimately caused by wind, inflows, or density differences (Wüest and Lorke, 2003). The variety of drivers causes turbulence to occur on all spatial and temporal scales, from lake width to the smallest turbulent eddies in the size of millimeters and from seasonal dynamics to seconds (Imboden and Wüest, 1995). Furthermore, turbulence is attenuated by density stratification and only a small portion of the kinetic energy is finally used for mixing and thus results in vertical transport of e.g. oxygen. This portion, the so-called mixing efficiency, links turbulence and transport and is known to vary with turbulence intensity (Bouffard and Boegman, 2013; Osborn, 1980; Shih et al., 2005). The interactions between driving forces and transport have been studied intensively in the benthic zone of lakes (Bryant et al., 2010; Lorke et al., 2003) where the influence of stratification is weak and energetic turbulence prevails. In the benthic zone, the eddy correlation technique (EC) enables direct, noninvasive flux measurements (Berg et al., 2003). Its general measurement principle is described in *Box 1* (next page). An increasing usage of the method revealed a high temporal variability in boundary layer transport, driven by shoaling of internal waves and seiche-induced flow (Brand et al., 2008; McGinnis et al., 2008). In contrast, transport in the interior of lakes and therefore at pelagic oxyclines is much stronger affected by stratification and therefore is considerably smaller. This finding is mainly based on basin wide budgets or tracer experiments (Maiss et al., 1994; Quay et al., 1980; Wüest and Lorke, 2005) which provide bulk indirect estimates and neither take the variability of transport nor of its driving forces into account. Nevertheless, a few studies investigated pelagic transport directly but likewise the used methods did not allow to resolve the statistical characteristics of turbulence and transport but rather provided snapshots of the instantaneous turbulence field (Etemad-Shahidi and Imberger, 2001; Etemad-Shahidi and Imberger, 2002; Saggio and Imberger, 2001). However, Saggio and Imberger (2001) found turbulence in the metalimnion to be patchy and to cover on average only 35% of its vertical extent. Thus the knowledge on pelagic vertical transport and its drivers, including mixing and transport in oxyclines, is small (Ivey et al., 2008) and especially a mechanistic understanding is lacking.

Box 1: The eddy correlation technique

The eddy correlation technique (EC), originally established to quantify gaseous exchange between atmosphere and terrestrial environments (Baldocchi et al., 1988), enables direct and noninvasive measurements of turbulent fluxes in aquatic environments. Therefore, time series of vertical velocity (w) and e.g. oxygen concentration or temperature (C) are measured simultaneously and with high frequency in a small sampling volume. Recorded data usually becomes de-spiked, coordinate rotated, de-trended to derive fluctuation components, and corrected for a time shift (Lorrai et al., 2010; McGinnis et al., 2008) before the vertical turbulent flux is finally calculated as the temporal mean (denoted with overbar) of the product of the two fluctuation components (denoted by prime): $F = \overline{w' \cdot C'}$. Final flux calculation, however, can also be achieved by integrating the co-spectral variance of the two fluctuation components. Since its first application in aquatic systems by Berg et al. (2003), the EC technique is still improving with regard to technical requirements and data processing (Donis et al., 2015; Holtappels et al., 2015).

Beyond that, the role of vertical oxygen transport has rarely been considered in research on deep water oxygen depletion and oxycline persistence. Only for Lake Erie, Canada, the influence of vertical and horizontal transport and mixing processes on hypolimnetic oxygen conditions has been documented (Rao et al., 2008). Bouffard et al. (2013) assessed that ~18% of the oxygen depleted in the hypolimnion of Lake Erie originated from a vertical oxygen flux through the thermocline related to hourly patterns of Poincaré wave activity. Only recently, physical transport was considered when estimating net ecosystem production based on observed changes in oxygen concentrations (Antenucci et al., 2012; Sadro et al., 2011; Staehr et al., 2012), however, transport serves just as a means to the end of optimizing estimates of lake metabolism. Hence, a comprehensive understanding of the role of vertical oxygen transport at pelagic oxyclines and its relation to oxygen consumption is lacking.

2 OBJECTIVES

This thesis endeavors to advance the understanding of pelagic oxyclines in lakes with special emphasis on their formation, the relative contributions of physical oxygen transport and biochemical oxygen consumption during their persistence, and their consequences for lake cycling. Based on the gaps in the current state of scientific knowledge outlined above, the present thesis addresses five research questions visualized in Figure 2 (*Objective 1* to *Objective 5*).

In detail, this thesis aims to understand the formation of pelagic oxyclines, namely how metalimnetic oxygen minima evolve (*Objective 1*). We therefore test whether a locally enhanced oxygen consumption causes the occurrence of metalimnetic oxygen minima as traditionally assumed (*Hypothesis 1*). Further this thesis aims to understand the relative importance of physical oxygen transport and biochemical oxygen consumption during the persistence of pelagic oxyclines with special respect to the time scales on which the two processes act (*Objective 4*). To test the hypothesis that physical transport is a relevant and so far overlooked process in the occurrence of pelagic oxyclines (*Hypothesis 4*) we first look at the two processes separately. Thus, on the one hand, we want to elucidate the magnitude, variability, and driving forces of physical oxygen transport at pelagic oxyclines on short as well as long time scale (*Objective 2*) and state that it is, similar to its characteristics in the bottom boundary layer, highly variable on short time scales (*Hypothesis 2*). To test this hypothesis, we apply the eddy correlation technique within the water column (*New method*). On the other hand, we aim to understand to what extent the oxidation of reduced substances and of organic carbon determine the overall oxygen consumption at pelagic oxyclines (*Objective 3*). Therefore we test whether the oxidation of reduced substances considerably contributes to oxygen consumption like it does in meromictic lakes and lake hypolimnia (*Hypothesis 3*). Finally, the thesis aims to elucidate the consequences of pelagic oxyclines with a focus on their effect on lake's internal cycling (*Objective 5*). We hypothesize that a significant share of the whole lake's respiration and mineralization can occur at pelagic oxyclines (*Hypothesis 5*) like it was recently shown for the metalimnion of two lakes.

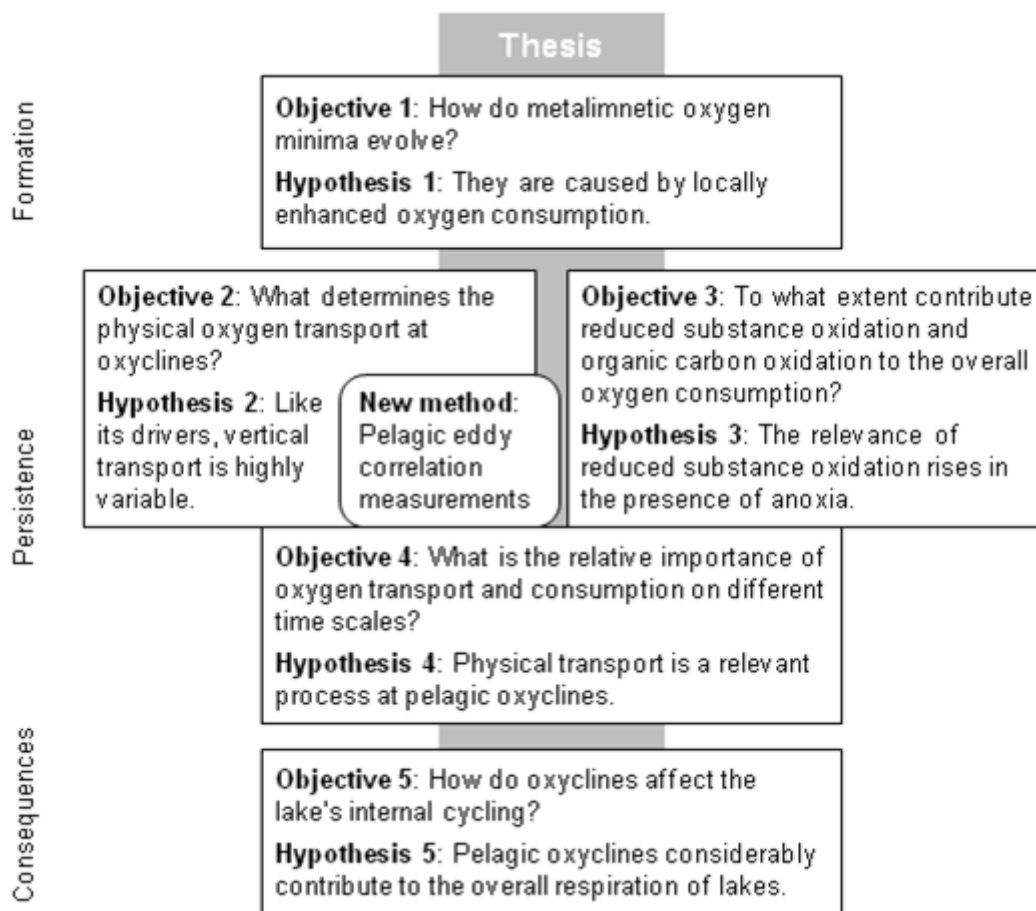
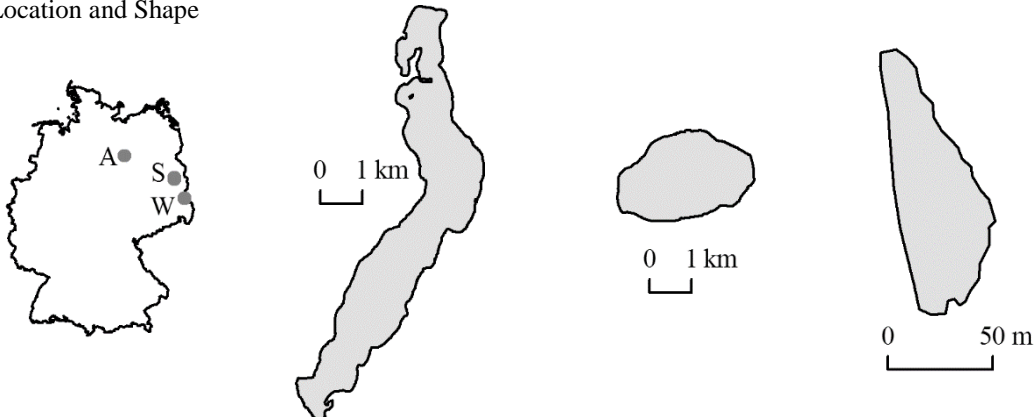
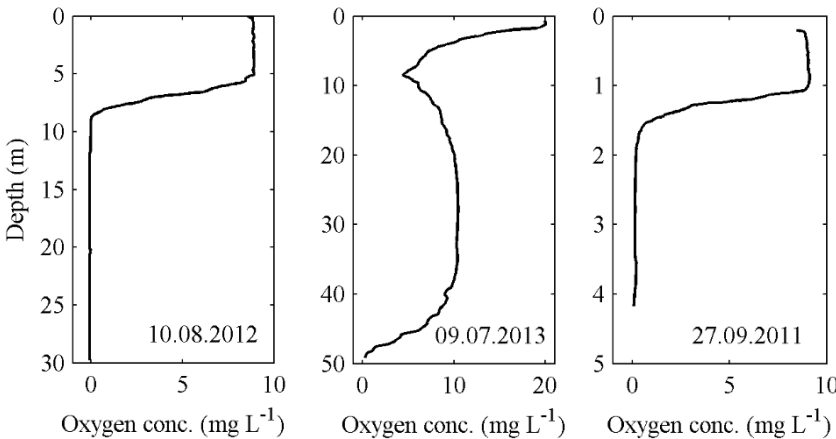


Figure 2: Thesis' objectives and related hypotheses

To test the hypotheses (Figure 2), intensive field campaigns were conducted at three lakes in Germany which differ in their type of stratification and oxygen profile. An overview on the characteristics of the lakes is provided in Table 1. Lake Scharmützelsee and Lake Arendsee both are eutrophic and dimictic, but the former features a clinograde oxygen profile during summer stratification with an anoxic hypolimnion, while the latter develops a negative heterograde oxygen profile with both eventually turning anoxic, the oxycline as well as the bottom waters. Lake Waldsee, in contrast, is meromictic and exhibits an oxycline throughout the year which features anoxic deep waters and is accompanied by a strong gradient in dissolved iron. Field campaigns were designed to illuminate two different time scales, a short time scale covering hours to days and a long time scale covering weeks to months. They further included a novel and innovative approach: For the first time, we applied the EC technique in the pelagic water column which so far was proved and tested only in the benthic region. This enabled direct measurements of vertical oxygen and heat fluxes above pelagic oxyclines and provided estimates of the transport coefficient.

Table 1: Overview on the characteristics of the three lakes investigated in this thesis. A, S, and W indicate the locations of Lake Arendsee, Lake Scharmützelsee, and Lake Waldsee within Germany, respectively. (Shape files of Lake Arendsee and Lake Scharmützelsee were provided by K. Meinikmann (Leibniz-Institute of Freshwater Ecology and Inland Fisheries, Berlin) and B. Grüneberg (Brandenburg University of Technology Cottbus-Senftenberg), respectively.)

	Lake Scharmützelsee	Lake Arendsee	Lake Waldsee
Mixis	dimictic	dimictic	meromictic
Maximum depth (m)	29.5	49.5	4.7
Mean depth (m)	8.9	29	2.7
Surface area (ha)	1209	514	0.24
Location and Shape			
Vertical oxygen profile			

3 OUTLINE

The present thesis comprises of four parts which are either published in or submitted to peer-reviewed journals and are provided in Appendix I-IV. They all investigate oxygen transport, consumption, or both at pelagic oxyclines, however, each with a special main emphasis concentrating on either the short or the long time scale. The contribution of each part of the thesis to the verification of the stated hypotheses and the understanding of the overall objectives is described in the following.

Part 1

The first part of the thesis resolves the short term variability of transport and mixing at pelagic oxyclines statistically (*Objective 2*). Therefore it combines pelagic EC measurements from Lake Scharmützelsee and Lake Arendsee. Necessary methodical improvements in data analysis are suggested with regard to the application of the EC technique in a stratified, low turbulent environment (*New method*).

To contribute to the verification of *Hypothesis 2*, transport of oxygen and heat (measured as vertical turbulent fluxes), the respective vertical gradients, and turbulence (measured as dissipation rates of turbulent kinetic energy) were quantified to estimate transport coefficients and mixing efficiencies. Transport coefficients were qualitatively linked to its forcing parameters: Density stratification (measured as buoyancy frequency), current velocity, and wave intensity (quantified as spectral variance of vertical velocity fluctuations).

Weck, Julika and A. Lorke (2017), Mixing efficiency in the thermocline of lakes observed from eddy correlation flux measurements, Journal of Geophysical Research - Oceans, doi:10.1002/2016JC012188. (Appendix I)

Part 2

In the second part of the thesis, oxygen transport and consumption are investigated on the short time scale of hours to days in Lake Scharmützelsee which features a pelagic oxycline with anoxic bottom waters (*Objective 2 to Objective 5*). In this study, the EC technique was applied in the water column and the prevalence of internal waves necessitated adjustments in data processing (*New method*).

To test *Hypothesis 2*, we measured time series of transport, i.e. oxygen fluxes, into the pelagic as well as benthic oxycline of the lake using the EC technique and related them to time series of turbulence (quantified as dissipation rate of turbulent kinetic energy), wave intensity (quantified as spectral variance of vertical velocity fluctuations), and current velocity. To test *Hypothesis 3*, depth profiles of water samples were analyzed for redox sensitive compounds and were used together with transport coefficients (derived from temperature microstructure profiling) to estimate the contribution of the oxidation of reduced substances to the overall oxygen consumption in the oxycline. Using a one-dimensional oxygen mass balance, the resulting oxygen consumption due to respiration and mineralization was determined and *Hypothesis 4* was tested by comparing the different oxygen flux paths. Finally, derived results were interpreted in respect to *Hypothesis 5*.

Kreling, Julika, J. Bravidor, D. F. McGinnis, M. Koschorreck, and A. Lorke (2014), Physical controls of oxygen fluxes at pelagic and benthic oxyclines in a lake, Limnology and Oceanography, 59(5), 1637-1650, doi:10.4319/lo.2014.59.5.1637. (Appendix II)

Part 3

The third part of the thesis investigates the effects of varying oxygen transport on a single oxygen consuming process, namely the oxidation of reduced iron, on a short time scale of hours and days (*Objective 2* to *Objective 4*). To focus on oxygen consumption in detail, measurements were conducted in the small and sheltered meromictic Lake Waldsee which is characterized by a minimum of hydrodynamic forcing. The lakes features high concentrations of ferrous iron and therefore iron oxidation is suitable to exemplarily elucidate the response of oxygen consumption to varying oxygen transport.

Continuous measurements of oxygen concentration at various depths throughout the pelagic oxycline were conducted to detect events of oxygen transport and thus contributed to the verification of *Hypothesis 2*. To test *Hypothesis 3*, the oxidation of reduced substances (here ferrous iron) was quantified with laboratory measurements of iron oxidation rates and its occurrence *in situ* was surveyed with depth profiles of water samples conducted each 6 to 12 hours and analyzed for their iron content. To test *Hypothesis 4* with special emphasis on the requirements for interaction of oxygen transport and consumption, we investigated the time needed for the two processes to occur and compared it with the actual duration of oxygenation events.

Bravidor, Jenny, J. Kreling, A. Lorke, and M. Koschorreck (2015), Effect of fluctuating oxygen concentration on iron oxidation at the pelagic ferrocline of a meromictic lake, Environmental Chemistry, 12, 723-730, doi:10.1071/EN14215. (Appendix III)

Part 4

Similar to part 2 of the thesis, the last part deals with oxygen transport and consumption (*Objective 2 to Objective 5*), however, it focuses on the processes on a long time scale of weeks to months in Lake Arendsee. Field measurements covered the whole stratification period and thereby enabled insight into oxycline formation (*Objective 1*).

To test *Hypothesis 1*, we initially undertook theoretical considerations on potential combinations of oxygen profiles and profiles of oxygen depletion which can lead to the formation of metalimnetic oxygen minima and then compared them to the actual situation in the lake. *Hypothesis 2*, here, was tested on long time scale: Based on long term continuous measurements of temperature, transport coefficients were determined via a heat balance approach and were correlated to the intensity of stratification, wind forcing, and waves (quantified as buoyancy frequency, wind speed at the lake's surface, and wave displacement variance, respectively). Continuous measurements of oxygen concentration further enabled the estimation of the long term averaged net oxygen transport and, in addition with a one dimensional oxygen mass balance, the determination of the magnitude and temporal variation of the biochemical oxygen consumption. Both processes were compared to test *Hypothesis 4* on long time scale. To test *Hypothesis 3*, drivers of oxygen consumption were further investigated using depth profiles of turbidity. Finally, the findings are discussed in respect to *Hypothesis 5*.

Kreling, Julika, J. Bravidor, C. Engelhardt, M. Hupfer, M. Koschorreck, and A. Lorke (2017), The importance of physical transport and oxygen consumption for the development of a metalimnetic oxygen minimum in a lake, Limnology and Oceanography, 62, 348-363, doi:10.1002/lno.10430. (Appendix IV)

4 DISCUSSION

4.1 The pelagic application of the eddy correlation technique

The to our knowledge first pelagic application of an EC system resulted in a unique dataset of direct flux measurements in the stratified interior of lakes. On the one hand, these data elucidated the temporal variability and the physical controls of oxygen fluxes into oxyclines (Appendix II) and, on the other hand, provided insights into vertical mixing (Appendix I). However, differences in the measured environment and the mounting of the instrument compared to the benthic application had to be considered to ensure the quality of results. Differences in the measured environment included a less confined sink, the absence of boundary conditions, and the prevalence of strong stratification entailing low turbulence, internal waves, and low current velocities. The mounting in the water column was subject to mooring motions and included a greater distance between the EC system and the sink than in benthic applications (~3 m in Appendix II and 0.1 – 0.2 m, respectively) because of the prevalence of internal waves. How these differences affect the underlying assumptions and the data analysis is described in the following.

The EC technique measures vertical turbulent transport only and for valid flux estimates vertical advection, diffusion, and horizontal transport have to be negligible (Burba, 2013). The latter implicates that no horizontal gradients prevail and changes in mean flow or concentration are small compared to the changes induced by eddies. The EC technique is generally used to quantify the transport into a sink, however, the measurement itself is separated from the sink. Thus, the measured flux F_{EC} only equates with the flux into the sink F_{sink} if they are in balance. Hence, if (i) no reaction of oxygen occurs, i.e., there are no sources or sinks in between the EC system and the actual sink, (ii) turbulence is homogenous and stationary, i.e., independent of position and time, and (iii) the mean oxygen concentration does not change with time (Lorrai et al., 2010). For benthic EC applications, Holtappels et al. (2013) estimate the error in F_{sink} if assumptions i and ii are not correct and give recommendations for validation. Regarding the pelagic EC application, oxygen is likely to become subject to reaction on its way from the EC system to the sink, since the sink is not as confined to a certain depth as the sediment in benthic applications and the great distance between F_{EC} and F_{sink} increases the risk of reaction to occur. Further turbulence in the stratified interior of lakes is strongly affected by stratification and its

stationarity and homogeneity is questionable. Horizontal changes in mean concentration can be expected to be small in proximity to pelagic oxyclines. However, the applicability of the assumptions has to be carefully considered with respect to the measured data. This is done in Chapter 4.3 of the thesis (page 20).

Besides its relevance for the fulfillment of the described assumptions, the greater distance between F_{EC} and F_{sink} entails that some time is needed for the balance to establish even if the assumptions are valid. This time is equal to the duration of transport between the EC system and the sink and can be estimated as $t_T = d^2/K$ (where d is the distance and K is the vertical transport coefficient) and, therefore, pelagic EC measurements have to last at least as long as t_T to be interpreted as measurements of the sink itself.

The pelagic mounting of the instrument and the stratified, low turbulent environment necessitated two adjustments in the data analysis compared to benthic applications:

- (1) Internal waves and mooring motions biased the measured signal. They detrimentally affect magnitude and direction of estimated fluxes if fluxes are not determined by integrating the co-spectral density of the fluctuation components. Integrating only a certain frequency range of the spectra assures that parts affected by waves or motions are excluded and the purely turbulent flux is obtained. However, restricting the frequency range generally entails the risk of underestimating the flux when turbulent flux-contributions are masked by waves. This approach further entails that time series of fluctuation components cannot be aligned using the maximum cross correlation, as recommended by Donis et al. (2015).
- (2) The prevalence of low turbulence and strong stratification strongly attenuates turbulent transport, bringing the measured signal close to the instrument noise or even preclude EC flux measurements when transport becomes molecular rather than turbulent. Part 1 of the thesis revealed that times of purely molecular transport covered as much as two thirds of the whole measurement time. Thereby the number of valid flux estimates is restricted in pelagic compared to benthic EC measurements. Times of molecular transport were separated from times of turbulent transport manually after visual inspection of the integrated co-spectra and an objective (at the best automated) identification of times when transport is not quantifiable with the EC technique still needs to be developed. This is necessary to derive complete time series of fluxes which include times of molecular as well as turbulent diffusion and to therewith avoid a systematic overestimation of average fluxes.

The first modification was implemented in Part 2 of this thesis (Appendix II) by using the same portion of the spectra in flux calculation for the entire measurement duration and thereby to allow for automated data processing. But determining the turbulent portion of the spectrum for each flux estimate individually accounts for potential changes in the frequency of internal waves with time and appeared to be more appropriate in Part 1 of the thesis (Appendix I, which in fact was conducted later than Part 2). The second modification was not yet considered in Part 2 of the thesis and probably lead to an overestimation of the fluxes. Nevertheless, the insufficient implementation of the modifications in Part 2 is considered not to affect the major outcomes of the study: Although the actual time series of oxygen fluxes might be affected, the relation to its physical controls and the results of the presented oxygen balance remain unaffected.

Overall, the data processing established for benthic EC applications cannot be simply copied to pelagic applications but has to be complemented and modified with respect to the prevailing wave field and stratification. Vice versa the biasing effects of internal waves and low turbulence conditions might also need to be considered in benthic EC applications. The presented modifications and the different ways of implementation generally underline the need for further standardization of the data processing to ensure the comparability of the results and should be subject to future research.

4.2 The formation of metalimnetic oxygen minima

This thesis initially approached the formation of metalimnetic oxygen minima theoretically by describing the observed oxygen profile C_1 as the sum of an initial profile C_0 and the change in oxygen concentration between the two profiles ΔC : $C_1(z, t_1) = C_0(z, t_0) + \Delta C(z, \Delta t)$ (where t_0 , t_1 , and $\Delta t = t_1 - t_0$ are the respective times and all profiles vary with depth z ; Appendix IV). Based on mathematical considerations, it could be shown that a local minimum in the oxygen profile (C_1) can solely result from the related gradients (first derivative) and curvatures (second derivatives) of oxygen concentration (C_0) and depletion (ΔC). Comparing these theoretical findings with the actual situation in a lake revealed agreement: While the observed magnitudes of C_0 and ΔC decreased monotonically with increasing depth, both profiles exhibited a concave curvature at the formation depth of the metalimnetic oxygen minimum (Figure 3). Hence, contrary to the traditional assumption (Effler et al., 1998; Shapiro, 1960), the present thesis revealed that a locally enhanced

oxygen depletion is not mandatory for the formation of metalimnetic oxygen minima. They can also develop if oxygen concentration and oxygen depletion both monotonically change with depth and, therefore, *Hypothesis 1* needs to be rejected.

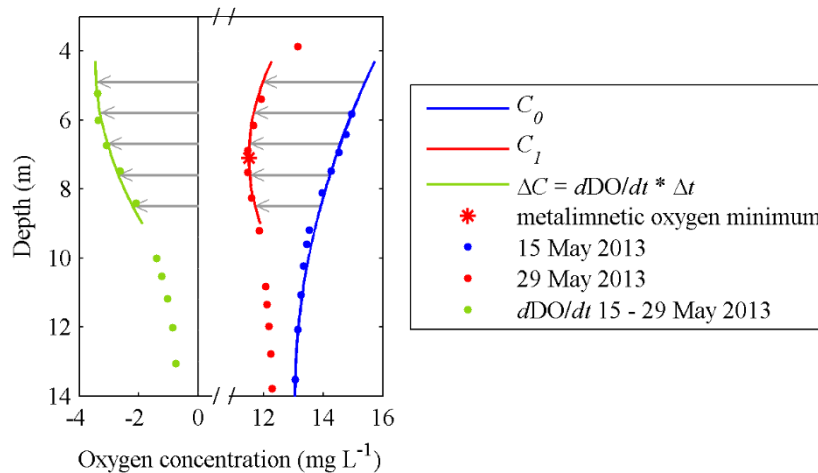


Figure 3: The formation of the metalimnetic oxygen minimum in Lake Arendsee. Oxygen concentrations at the depth of isotherms on 15 May 2013 (daily mean, blue dots), 29 May 2013 (daily mean, red dots), and the temporal change in oxygen (dDO/dt ; from linear fit between 15 and 29 May 2013, green dots). The initial oxygen profile C_0 (blue), the change in oxygen concentration $\Delta C = dDO/dt * \Delta t$ (green), and the resulting oxygen profile C_1 (red) are represented by power functions of depth. Gray arrows indicate the depth-dependent magnitude of ΔC . (This figure is equal to Figure 4 of Appendix IV.)

This new perspective is able to explain the formation of metalimnetic oxygen minima where previous explanations remained incomplete and has implications for future research. For future efforts in lake managing it would be necessary to know whether a systematic difference in the vertical distributions of C_0 and ΔC exists between lakes with and without a metalimnetic oxygen minimum. As long as this question is not answered, established efforts in lake restoration seeking to reduce nutrient loads with subsequent decrease in epilimnetic productivity seem to be advisable to face the formation of negative heterograde oxygen profiles. Nevertheless, it would be interesting to test whether actively changing the curvature of the oxygen profile by oxygenation of a certain water layer could prevent the formation of metalimnetic oxygen minima, however, this approach is not sustainable since it fights the symptom but not the cause.

4.3 The persistence of pelagic oxyclines as the result of oxygen transport and consumption

The opposing processes of vertical oxygen transport and biochemical oxygen consumption determine the persistence of pelagic oxyclines. In the following, we initially discuss the findings of the present thesis for each of the two processes separately. Subsequently, the relative importance of oxygen transport and consumption for oxycline persistence is discussed as well as the temporal and vertical separation of the two processes.

4.3.1 Physical oxygen transport

Observed oxygen transport above the pelagic oxycline was found to be highly variable on a short time scale and flux events in the order of hours contributed disproportionately to the overall flux. For example, oxygen transport ranged from -5.2 to $0.3 \text{ g m}^{-2} \text{ d}^{-1}$ (mean of $-0.5 \pm 0.7 \text{ g m}^{-2} \text{ d}^{-1}$) for most of the time, but as much as 56% of the total flux occurred during only 3 h of measurements (9.5% of total measurement time) (Appendix II and Figure 4 A). These characteristics were similar to those observed above a benthic oxycline, where time periods with extremely low oxygen fluxes covered about one third of the measurement time but contributed only 2% to the overall flux (Appendix II and Figure 4 A). Short term temporal variability of pelagic transport was also visible in transport coefficients which varied over several orders of magnitude (e.g. from 1.7×10^{-9} to $1.5 \times 10^{-4} \text{ m}^2 \text{ s}^{-1}$ (Appendix II) or from 8.2×10^{-8} to $3.8 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$ (for density, Appendix I)). Although transport coefficients in Part 1 of the thesis were derived for density instead of oxygen, it revealed that low turbulent conditions play a dominant role at pelagic oxyclines and therefore transport is mainly controlled by buoyancy and drops to molecular levels for up to two thirds of the time (Appendix I). Diurnal changes in oxygen profiles shown in Part 3 (Appendix III), which must be accompanied by changes in transport even though they were not quantified, emphasize the relevance of the daily time scale for the oxygen dynamics at pelagic oxyclines. Thus, corroborating *Hypothesis 2*, pelagic oxygen transport is characterized by a high temporal variability on a time scale of hours and times of molecular diffusion alternate with energetic turbulent transport. It can be assumed that these properties also apply to the depth of oxyclines, even though the temporal variability was not estimated there and the average observed transport and transport coefficient were considerably smaller than above the oxycline ($-16 \text{ mg m}^{-2} \text{ d}^{-1}$ and $7 \times 10^{-8} \text{ m}^2 \text{ s}^{-1}$, respectively, Appendix II).

In contrast, on a long time scale of weeks to months, oxygen transport was found to change rather smoothly. The biweekly-averaged transport coefficient in a metalimnetic oxygen minimum decreased only by a factor of 5 within two month (range from 4.4×10^{-6} to $8.9 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$, Appendix IV and Figure 4 C). It was found to exceed the transport coefficient in the oxycline determined at short time scale by about one order of magnitude. This difference might be related to the used heat budget method (Jassby and Powell, 1975) which includes the risk of overestimating pelagic transport by averaging it with benthic contributions (Goudsmit et al., 1997) and thereby would point to boundary mixing and horizontal transport processes. However, in Part 2 of the thesis no considerable differences between benthic and pelagic transport were observed.

The observed temporal variability in oxygen transport was controlled by turbulence (Appendix II) and this thesis covers a wide range of its physical driving forces. On short time scales, vertical transport at pelagic oxyclines was mainly driven by internal waves no matter if they featured periods in the order of minutes or hours (Appendix I, Appendix II, and Figure 4 B). But also current velocity was positively related to transport (Appendix I), however, current velocity in the pelagic region is known to be primarily caused by internal waves (Wain et al., 2013). At benthic oxyclines turbulence was induced by increased current velocities (Figure 4 B and Appendix II) which is in agreement with Lorke et al. (2003) who found it to control turbulence and transport in the bottom boundary layer. In sheltered lakes, oxygen transport is triggered by sunlight rather than by hydrodynamic forcing but acts on a similar, short time scale. The selective heating of a highly turbid water layer in the oxycline locally decreased its density and eventually resulted in convective mixing with overlying oxygen rich water (September data of Appendix III). Also on a long time scale of weeks to months, internal waves were found to drive vertical oxygen transport in pelagic oxyclines (Appendix IV). The seasonal weakening of the wind acting on the lake surface influenced the intensity of internal waves and the attenuating effect of stratification on turbulence was apparent, when the seasonal change in stratification was significantly, inversely correlated with estimated transport coefficients (Appendix IV). This relation, however, remained insignificant on short time scales (Appendix I). The described relationships are visualized on the left hand side of Figure 5 (page 27).

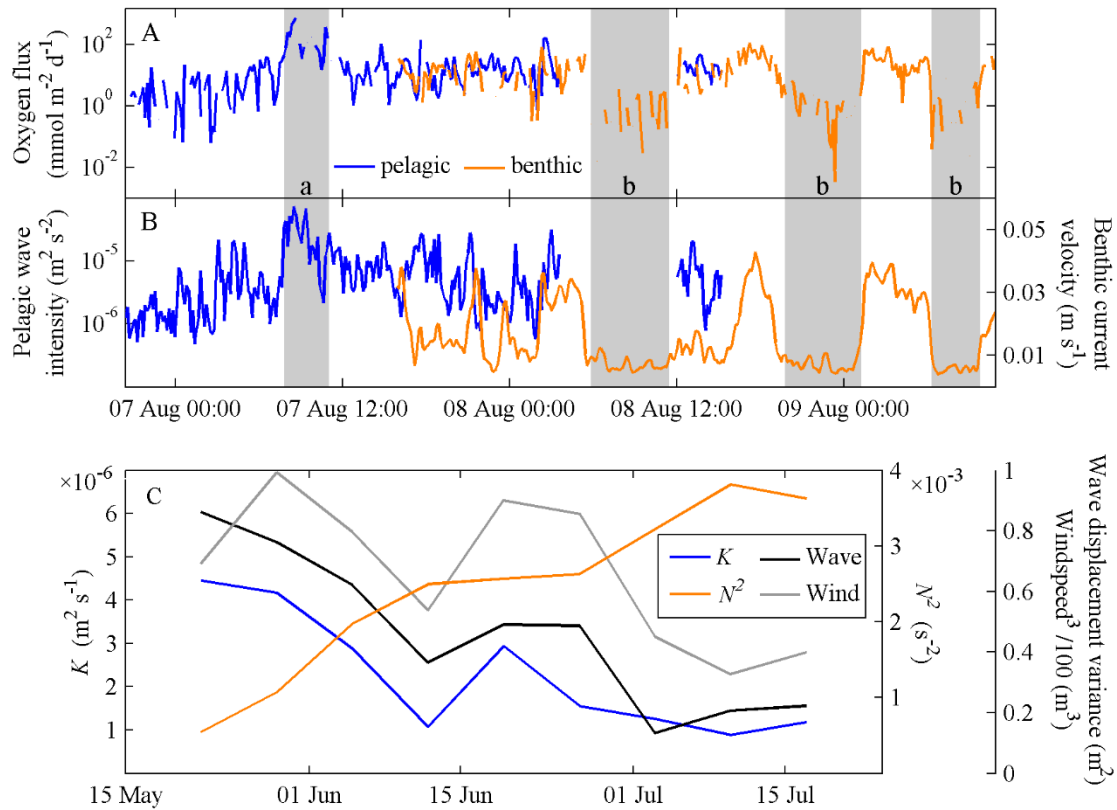


Figure 4: Temporal variability in transport (coefficient) and its driving forces on short (hours to days, A and B) and long time scale (weeks to months, C). (A) Downward directed oxygen fluxes measured above a pelagic (blue) and benthic (orange) oxycline in 2012. Shaded areas mark (a) the flux event and (b) periods of low flux discussed in the text. (B) Internal wave intensity above the pelagic oxycline (blue) and current velocity above the benthic oxycline (orange). (C) Bi-weekly averages of vertical transport coefficient K (blue), buoyancy frequency N^2 (orange), wave displacement variance (black) all at the depth of the metalimnetic oxygen minimum, and wind power (gray) measured in 2013. (Panel A and B depict data shown in Figure 3 and 4 of Appendix II. Panel C shows data depicted in Figure 5 of Appendix IV.)

Irrespective of its drivers, only a small fraction of the turbulent kinetic energy finally results in vertical transport. This fraction is described by the mixing efficiency which was determined directly from *in situ* flux measurements in Part 1 of the thesis. Observed results compared well with widely used parameterizations even though those were mainly based on laboratory measurements and numerical simulations (Appendix I). Thus, the maximum mixing efficiency of ~ 0.2 is reached at intermediate levels of turbulence and an even smaller fraction of the kinetic energy results in transport at lower and higher levels of turbulence (Bouffard and Boegman, 2013). Overall, the findings of the present thesis on mixing, transport, and its drivers support a mechanistic understanding of the physical processes in

the interior of stratified lakes which so far has been rarely investigated in field studies (Ivey et al., 2008).

In contrast to the assumption that the measured EC flux is equal to the flux into the studied sink, this thesis found transport measured above the oxycline to be considerably higher than in the oxycline (Appendix II). Evaluating the assumptions necessary for a steady state situation to develop, the pelagic EC application turned out to mostly fail in fulfilling of them: The oxycline was by far not as clearly confined as the sediment in benthic EC applications and oxygen consumption gradually changed with depth (Appendix IV). Thus oxygen concentrations in between EC system and oxycline likely were affected by consumption. Furthermore, turbulence above the oxycline was not homogenous and decreased with depth (Appendix II). Its strong temporal variability questions stationarity, but we cannot assess if measurements lasted long enough to sufficiently average statistical characteristics of turbulence, although the measurement duration exceeded the minimum time needed for a steady state to establish (Table 2 in Appendix V). Only the mean oxygen concentration conformed to the assumption and showed minor temporal changes above the oxycline (Appendix II). Altogether, it is suspected that measured oxygen fluxes above the oxycline do not describe the transport into the sink. While some effort could be put into minimizing the distance to the sink in future pelagic EC applications, the vertical spread of oxygen consumption and the low turbulent conditions would still hamper the system to achieve a steady state. Nevertheless the pelagic application of the EC technique proved to be a valuable tool to investigate the short term variability of mixing, transport, and its drivers and thereby contributed to the understanding of oxycline persistence indirectly.

4.3.2 Biochemical oxygen consumption

The observed oxygen decrease with time was found to be rather constant in the pelagic oxycline during a four day long time period (Appendix II) as well as over several weeks (Appendix IV). The overall oxygen consumption accounted for $-0.2 \text{ mg L}^{-1} \text{ d}^{-1}$ on the short time scale and ranged from -0.65 to $-0.28 \text{ mg L}^{-1} \text{ d}^{-1}$ on the long time scale. Hence, it was in the same order of magnitude and observed differences can be considered to be small in the light of different types of oxygen profiles, different months of sampling, and inter lake variability.

Primary production, oxidation of reduced substances, and uptake due to respiration and mineralization are possible sources and sinks of oxygen in pelagic oxyclines contributing to the overall oxygen consumption. A considerable influence of primary production on the metalimnetic oxygen dynamics was excluded in Part 1, 2, and 4 of the thesis with respect to the limited availability of light at the depth of the oxyclines. But Part 3 showed that oxygen concentrations can be substantially affected by diurnal changes in photosynthetic oxygen production when light penetrates to the depth of the oxycline (July data of Appendix III).

The relative contribution of reduced substance oxidation and respiration and mineralization to the overall oxygen consumption strongly depended on oxycline characteristics. The oxidation of reduced substances was assumed to have no influence as long as oxic conditions prevail in the oxycline (Appendix IV) and was estimated to account for at most ~2% of the total consumption in lakes where the oxycline separated oxic from anoxic waters ($-4.1 \mu\text{g L}^{-1} \text{d}^{-1}$, Appendix II). Therefore, the oxidation of reduced substances played only a minor role in overall oxygen consumption and *Hypothesis 3* has to be rejected. This is different to its role in lake hypolimnia (Matzinger et al., 2010; Müller et al., 2012) and other oxyclines with anoxic bottom waters (Casamayor et al., 2008; Hadas et al., 2001), however, the latter featured sulfide concentrations an order of magnitude higher than in the lake investigated in Part 2 of this thesis. Instead, overall oxygen consumption in non-meromictic lakes was almost exclusively determined by biological heterotroph respiration and mineralization (98% in Appendix II and 100% in Appendix IV), i.e., by the oxidation of organic carbon. Corresponding rates can be interpreted as an upper bound of heterotrophic microbial mineralization since the respiration of zooplankton contributed only insignificantly (Appendix IV) but a contribution of (autotrophic) phytoplankton respiration might exist. Oxygen consumption showed considerable temporal variability on the long time scale with smooth changes over months rather than weekly fluctuations (-0.65 to $-0.28 \text{ mg L}^{-1} \text{d}^{-1}$ with a mean value of $-0.40 \pm 0.12 \text{ mg L}^{-1} \text{d}^{-1}$, Appendix IV). While in Part 2 of the thesis (Appendix II) we could only deduce its relation to the input of organic matter originating from the photic zone, Part 4 (Appendix IV) exemplarily provided evidence. The observed relevance of the long time scale for variability in consumption therefore is induced by epilimnetic productivity, which is known to vary with development and break down of algal blooms, with seasonally changing temperature, and with the trophic status of the lake (Pace and Prairie, 2005). Furthermore, the decomposition of organic matter is a slow process with decay rates from ~ 0.02 to $\sim 0.2 \text{ d}^{-1}$ for the labile fractions (Hopkinson et al.,

2002; Koehler et al., 2012; Vähätalo et al., 2010) resulting in reaction times of ~5 to ~50 days (time needed for 63% of the molecules to react based on 1st order reaction kinetics). The relationships between oxygen consumption and its determinants are visualized on the right hand side of Figure 5 (page 27).

A different picture arose for the oxycline where anoxic bottom waters come along with peculiar water chemistry. In Part 3, the oxidation of ferrous iron accounted for -2.8 to -27.0 mg L⁻¹ d⁻¹ (depending on pH, Appendix III) and therefore exceeded mineralization in non-meromictic lakes by 1 to 2 orders of magnitude. The role of mineralization and respiration was not quantified in this Part of the thesis, but there are indications that iron oxidation was the main oxygen sink in the oxycline: Oxygen depletion could be described with 1st order reaction kinetics and the times needed for reaction were similar for iron oxidation and overall oxygen consumption (10 and 20 h, respectively, Appendix V). Therefore oxygen depletion dominated by the oxidation of reduced substances was faster than the decomposition of organic matter in non-meromictic lakes. This can be attributed to chemical iron oxidation which is faster than microbial oxidation and favored at the observed pH (Appendix III). However, oxidation reaction kinetics were also affected by the availability of oxygen (Appendix III). Temporal variability in the vertical distribution of reduced substances (ferrous iron) was small and bigger changes were observed on a time scale of month than on a time scale of days (Appendix III).

Except for the iron oxidation rates in Part 3 of the thesis, oxygen consumption was always determined indirectly as the resultant after estimating all other contributors in an oxygen mass balance. Although the derived consumption rates were comparable to literature values (del Giorgio and Williams, 2005; Solomon et al., 2013), future studies would benefit from a validation with direct measurements (e.g. from water sample incubation). Further the present thesis simplifies consumption by considering only chemolithoautotrophs (oxidizing reduced substances) and chemoorganoheterotrophs (oxidizing organic carbon) and thereby disregarding the vast diversity in microbial metabolisms. However, the present thesis does not aim for completeness but rather estimates the major contributors to oxygen consumption by considering the two groups of microbes mentioned above. Another simplification is the assumption that the oxidation of reduced substances is restricted to the transition zone between oxic and anoxic waters. This ignores the occurrence of ammonium and methane in the oxic parts of the water column where the former is excreted by heterotroph organisms and the latter can be produced by hydrogenotroph microbes (Grossart et al., 2011).

Concentrations of methane and ammonium were measured and included in estimates of the reduced substances oxidation in Part 2 of the thesis. In Lake Arendsee (Part 4), ammonium concentrations were reported to be small and also rates of nitrification were below the detection limit. Furthermore, measured methane concentrations did not indicate microbial methane production in the epilimnion of Lake Arendsee.

4.3.3 The relative importance of oxygen transport and consumption

Due to the presence of internal waves, oxygen concentrations at a certain depth in the oxycline showed a high temporal variability. But excluding the effect of internal waves (by regarding oxygen concentrations at isothermal depth) revealed that consumption dominated the fate of oxygen at pelagic oxyclines on the short as well as the long time scale (Appendix II and Appendix IV). However, the observed temporal variability on long but not on short time scales in conjunction with its dependence on the seasonal temperature indicate, that a time scale of weeks to months is the one relevant for the persistence of pelagic oxyclines (Figure 5). The relevant time scale might be shorter for meromictic lakes where the faster oxidation of reduced substances plays a major role in oxygen consumption (Appendix III). Thus, to evaluate the role of oxygen transport in oxycline persistence appropriately, its influence on oxygen dynamics has to be considered on a long time scale. There, downward directed transport (across the upper bound of the oxycline) increased the metalimnetic oxygen content considerably (27% of observed oxygen decrease, Appendix IV). This is in agreement with Bouffard et al. (2013) who estimated that ~18% of oxygen depleted in the hypolimnion originated from transport. Regarding the special case of a metalimnetic oxygen minimum, the net effect of oxygen transport even accounted for half the magnitude of consumption (Appendix IV). Although transport was not fast enough to balance consumption, it postponed the occurrence of anoxia considerably (for ~16 d in Appendix IV). Consequently, physical vertical transport of oxygen is a relevant process in oxycline persistence and *Hypothesis 4* is corroborated. Changes in oxygen transport and consumption on the relevant time scale were related to seasonal changes in temperature for both processes. While increasing temperature favors productivity and therewith consumption, it simultaneously intensifies stratification and therewith attenuates oxygen transport. Therefore, water temperature can be considered to be a crucial parameter for the oxygen dynamics in pelagic oxyclines and is known to rise in the face of climate warming

(Coats et al., 2006; Hampton et al., 2008; Straile et al., 2003). Thus pelagic oxyclines can be expected to occur more frequent and turn anoxic earlier in future which is in agreement with the current knowledge on climate change effects on lakes (Jeppesen et al., 2010b; Moss, 2010). From a methodical perspective, these results entail that the EC technique resolving a time scale of minutes to days is not suitable to reveal relevant long term trends in oxygen transport at pelagic oxyclines unless measurements cover at least several weeks or a whole stratification period at best. However, this seems, to date, unrealistic considering the technical complexity of the method and the associated maintenance effort.

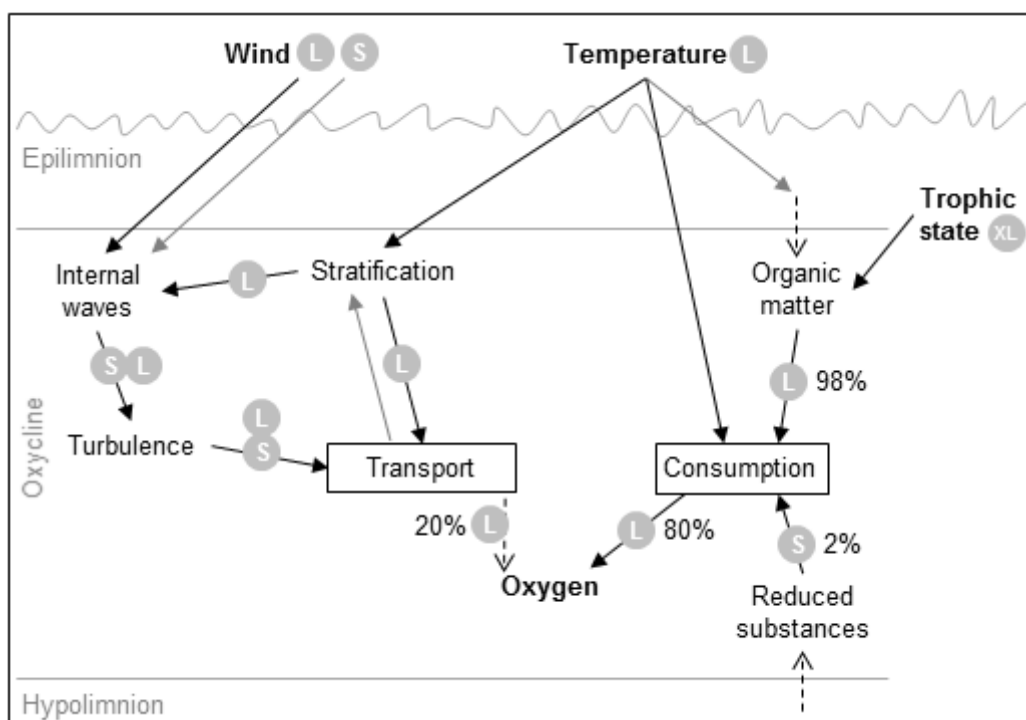


Figure 5: Schematic to visualize relations of oxygen transport and consumption and its drivers in pelagic oxyclines of non-meromictic lakes. Black arrows show dependencies discussed in the thesis with gray circles indicating the relevant time scale (S = short (hours to days), L = long (weeks to months), XL = years) and percentages quantifying the relative contribution of the respective dependency (relative contributions of organic matter oxidation and reduced substance oxidation to oxygen consumption (right) and of transport and consumption to the temporal change in oxygen (middle)). Gray arrows show existing dependencies not addressed in the thesis. Black dashed errors depict dependencies which are based on vertical transport from epi- or hypolimnion.

A different picture arose on a time scale of hours to days, when oxygen transport was found to be not relevant for oxygen dynamics (6% of observed oxygen decrease, Appendix II). As brought in earlier, this might be related to differences in the used methods

implicating an overlooked contribution of horizontal transport, however, it can also reflect differences among lakes as well as between the beginning and end of stratification. To rule out the former, additional near shore measurements to quantify benthic vertical transport and long term pelagic EC measurements would have been desirable, but future studies should involve horizontal transport. Nevertheless, the present thesis revealed that the duration of oxygenation events is critical for the effect of short-term fluctuating transport on the oxygen dynamics in the oxycline. On the one hand, observed oxygenation events did not last long enough to reach the oxycline. The time needed for transport to reach the oxycline, was estimated to last longer than the flux event observed in Part 2 (Appendix V). Consequently, at most a minor portion of the transported oxygen finally reached the oxycline whereas the rest might be accumulated, consumed, or transported horizontally. Note, that this favors the described non-steady state situation in EC measurements. Therefore short term changes in the oxycline might have been too small to be detected. On the other hand, observed oxygenation events did not last long enough for the oxygen consuming reactions in the oxycline to occur. Comparing the time needed for reaction with the observed event length revealed that this applies to the physically forced oxygen intrusions in Part 3 (September data of Appendix III). And also the oxygenation event in Part 2 would not have been answered by immediate consumption, since it lasted only 3 h while decomposition of organic matters needs days to occur. This might indicate a competition between different oxygen consuming processes - the fastest takes up the oxygen of short term events. Differently, oxygenation events driven by metalimnetic photosynthetic production lasted long enough for the oxidation of reduced substances (here the oxidation of ferrous iron) to happen and therewith a diurnal struggle between oxygen production and consumption became visible in the vertical distribution of iron and oxygen (July data of Appendix III).

The interplay of oxygen transport and consumption is not limited to the temporal aspect, but is also determined by the vertical zonation of the water column. Reduced substances as well as organic carbon both originate from surrounding water layers and have to be transported to the oxycline prior to oxidation. Thereby they are liable to different transport mechanisms, which might provide explanation for the different contributions of reduced substance oxidation and respiration and mineralization to the overall oxygen consumption observed in this thesis: The upward transport of reduced substances across the lower bound of the oxycline underlies strongly attenuated turbulent diffusion (e.g. 166 d for 1.5 m in Part

2, Appendix V). They therefore accumulate below the oxycline, where the limited transport allows for smallest vertical gradients in dissolved substances as well as microbe species to develop (Casamayor et al., 2012; Kirf et al., 2015; Rogozin et al., 2010) and the presence of submicromolar oxygen concentrations could sustain aerobic oxidation of reduced substances (Kirf et al., 2014; Stolper et al., 2010). This implicates, that most of the reduced substance oxidation takes place below the oxycline. In contrast, the transport of organic carbon is mostly accomplished by settling particles, while dissolved organic compounds play a minor role in eutrophic lakes (Biddanda et al., 2001). Thus, organic matter reaches the oxycline independent of limited mixing and becomes decelerated by density stratification resulting in a longer residence time and thereby promoting mineralization (Marsay et al., 2015). Therefore, future studies should not focus strictly on the depth of the oxycline but rather regard it as part of a continuous system, not only in temporal but also in spatial dimensions.

4.4 Consequences of pelagic oxyclines for lake internal cycling

The development and persistence of pelagic oxyclines is known to affect lake ecology (Zhang et al., 2009) and geochemical cycling (Reiche et al., 2011), however, our findings indicate that pelagic oxyclines additionally impact the turnover of carbon in lakes. The consumption of oxygen examined in this thesis can be used as a proxy for biogeochemical turnover (Gudasz et al., 2010) and is used to determine the metabolic state of lakes (Staehr et al., 2010). In Part 4 we showed that 26 % of the total loss of oxygen in a lake can occur in the metalimnion, hence, about one fourth of the lake's carbon mineralization. This is in agreement with the metalimnetic share of total lake respiration determined by Staehr et al. (2012) and Obrador et al. (2014). Turnover rates of oxygen and therewith of carbon in pelagic oxyclines were found to be as high as at the sediment water interface (Appendix II) and comparable to hypolimnetic oxygen depletion rates documented in literature (Müller et al., 2012). Thus pelagic oxyclines turned out to be another hotspot of carbon cycling in lakes besides the sediment. This corroborates *Hypothesis 5*. The enhanced decomposition of organic matter in pelagic oxyclines is opposed to the situation in meromictic lakes, where the autotroph oxidation of reduced substances can considerably contribute to the composition of organic matter, i.e., production (Camacho et al., 2001; Casamayor et al., 2008). While the latter is linked to hypolimnetic anoxia and high sulfide concentrations, the present thesis revealed that pelagic oxyclines can affect carbon cycling independent of water

chemistry or the presence of anoxia. However, this has strong consequences for the whole lake metabolism: High metalimnetic mineralization implicates a reduced loss of nutrients to the hypolimnion and their increased availability close to the photic zone. Thus pelagic oxyclines most likely entail a rapid circulation of carbon and nutrients in the upper part of the water column, a shift of major turnover from the benthic to the pelagic region and pelagic oxyclines therewith further amplify the decoupling of surface and deep waters in stratified lakes. Enhanced pelagic carbon turnover potentially reduces the sedimentation of organic carbon. This might affect the carbon burial in lakes which is a significant component in the global carbon cycle (Cole et al., 2007). The role of pelagic oxyclines in whole lake carbon cycling is a so far overlooked field of research (Staeher et al., 2012) and future studies should additionally consider vertical fluxes of nutrients, organic and inorganic carbon.

5 CONCLUSION

The present thesis advances the understanding of formation, persistence, and consequences of pelagic oxyclines in lakes. It revealed, that the formation of pelagic oxyclines featuring a negative heterograde oxygen profile can be solely determined by the vertical distribution of oxygen concentration and depletion. In contrast to the traditional assumption, a locally enhanced oxygen depleting process is not mandatory (*Hypothesis 1* rejected). During the persistence of pelagic oxyclines the considered time scale turned out to be important for the relative importance of physical oxygen transport and biochemical oxygen consumption: The thesis revealed a high temporal variability in mixing, transport, and its physical drivers near the pelagic oxycline (*Hypothesis 2* corroborated) which, however, did not affect the oxygen concentrations in the oxycline on a short time scale of days. Only on a long time scale of weeks to months, physical transport was a relevant process at pelagic oxyclines by considerably delaying the occurrence of anoxia (*Hypothesis 4* corroborated). Still, oxygen consumption was dominating the fate of oxygen in pelagic oxyclines on short and long time scales. Relevant seasonal changes in both transport and consumption were related to temperature, highlighting the sensitivity of pelagic oxyclines to climate warming. Different to the hypolimnion and benthic region of lakes, the oxidation of reduced substances was negligible in pelagic oxyclines and as long as no peculiar water chemistry prevailed, it was nearly exclusively determined by mineralization (*Hypothesis 3* rejected). Therefore, oxygen consumption in the oxycline was closely related to epilimnetic productivity. The intense oxygen consumption at pelagic oxyclines implicated strong consequences for the whole lake: A carbon turnover as high as at the sediment-water interface potentially leads to a short circuiting of the cycling of carbon and nutrients in the upper water layers and thereby promotes the decoupling of epi- and hypolimnion (*Hypothesis 5* corroborated).

Overall, it can be concluded that pelagic oxyclines are not just the upper end of hypolimnetic oxygen depletion but rather exhibit an immanent interplay of physical oxygen transport and biochemical consumption. Their role in whole lake carbon cycling was overlooked so far and, together with adjacent water layers, should be subject to future research. Generally, the present thesis highlights the importance of considering both, physical transport processes as well as the biochemical cycling, in limnological research.

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AUTHOR CONTRIBUTIONS

This thesis is based on four research articles provided in Appendix I-IV which were conceived by all of the authors. I was the lead author of three of the articles (Part 1, 2, and 4 of the thesis). The contributions of all authors are stated in the following using the author's initials.

Part 1: Weck, Julika and A. Lorke (submitted in 2016), Mixing efficiency in the thermocline of lakes observed from eddy correlation flux measurements, *Journal of Geophysical Research - Oceans*. (Appendix I)

Conception and design: AL, JW
Data acquisition: JW
Data analysis: JW
Interpretation of results: JW, AL
Writing the manuscript: JW
Revising the manuscript: AL

Part 2: Kreling, Julika, J. Bravidor, D. F. McGinnis, M. Koschorreck, and A. Lorke (2014), Physical controls of oxygen fluxes at pelagic and benthic oxyclines in a lake, *Limnology and Oceanography*, 59(5), 1637-1650, doi:10.4319/lo.2014.59.5.1637. (Appendix II)

Conception and design: JK, JB, MK, AL
Data acquisition: JK, JB, DFM, AL
Data analysis: JK
Interpretation of results: JK, AL
Writing the manuscript: JK, AL
Revising the manuscript: AL, JB, MK, DFM

Part 3: Bravidor, Jenny, J. Kreling, A. Lorke, and M. Koschorreck (2015), Effect of fluctuating oxygen concentration on iron oxidation at the pelagic ferrocline of a meromictic lake, *Environmental Chemistry*, 12, 723-730, doi:10.1071/EN14215. (Appendix III)

Conception and design: JB, JK, AL, MK
Data acquisition: JB, JK
Data analysis: JB, JK (estimates of turbulent diffusivities and transport time scales)
Interpretation of results: JB, MK
Writing the manuscript: JB
Revising the manuscript: MK, AL, JK

Part 4: Kreling, Julika, J. Bravidor, C. Engelhardt, M. Hupfer, M. Koschorreck, and A. Lorke (2016), The importance of physical transport and oxygen consumption for the development of a metalimnetic oxygen minimum in a lake, *Limnology and Oceanography*, doi:10.1002/lno.10430. (Appendix IV)

Conception and design: JK, AL, JB, MK, MH

Data acquisition: JK, JB, CE, MH

Data analysis: JK, CE (estimates of onset and breakdown of stratification)

Interpretation of results: JK, AL

Writing the manuscript: JK

Revising the manuscript: AL, CE, MH, MK

DECLARATION

I hereby declare that the thesis entitled “The formation, persistence, and consequences of pelagic oxyclines in lakes” is the result of my own work except where otherwise indicated. It has not been submitted for any other degree at another university or scientific institution.

Karlsruhe, 20th October 2016

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Background

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APPENDICES

APPENDIX I

Mixing efficiency in the thermocline of lakes observed from eddy correlation flux measurements

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<http://onlinelibrary.wiley.com/doi/10.1002/2016JC012188/abstract>

APPENDIX II

Physical controls of oxygen fluxes at pelagic and benthic oxyclines in a lake

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APPENDIX III

Effect of fluctuating oxygen concentration on iron oxidation at the pelagic ferrocline of a meromictic lake

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APPENDIX IV

The importance of physical transport and oxygen consumption for the development of a metalimnetic oxygen minimum in a lake

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APPENDIX V

The time needed for transport and reaction

The interactions of oxygen transport and its consumption via the oxidation of ferrous iron were elucidated in Part 3 of the thesis using the times needed for transport (t_T) and reaction (t_R) to occur and the N_E number (Appendix III). Here, these numbers are additionally applied to the results of Part 2 and 4 where possible and contribute to the discussion of the thesis.

The time needed for transport t_T depends on the distance to travel and the prevailing turbulent transport coefficient. Table 2 provides t_T as already calculated in Part 3 of the thesis and gives additional estimates for different water layers investigated in Part 2 and 4.

Table 2: Time needed for transport t_T to travel the distance d at a given turbulent transport coefficient K (with $t_T = d^2/K$) for the different water layers investigated in Part 2 to 4 of the thesis.

	Layer	Details	K ($\text{m}^2 \text{s}^{-1}$)	d (m)	t_T (h) (d)	
Part 2 (Appendix II)	oxycline		7.0E-08	1.5	8929	372.0
	above oxycline	from EC to oxycline with max. K	4.0E-04	3	6	0.3
	below oxycline		1.6E-07	1.5	7078	165.9
Part 3 (Appendix III)	mixolimnion	pH = 3.6	1.0E-06	0.5	69	2.9
	transition zone	pH = 4.5	1.0E-07	0.1	28	1.2
	monimolimnion	pH = 6	1.0E-09	0.1	2778	115.7
Part 4 (Appendix IV)	metalimn. oxygen min.	15–29 May 2013	4.4E-06	1.5	180	5.9
	metalimn. oxygen min.	22 May–05 June 2013	4.2E-06	1.5	193	6.2
	metalimn. oxygen min.	29 May–12 June 2013	2.9E-06	1.5	278	9.0
	metalimn. oxygen min.	05–19 June 2013	1.1E-06	1.5	751	24.4
	metalimn. oxygen min.	12–26 June 2013	2.9E-06	1.5	273	8.9
	metalimn. oxygen min.	19 June–03 July 2013	1.6E-06	1.5	516	16.7
	metalimn. oxygen min.	26 June–10 July 2013	1.3E-06	1.5	642	20.8
	metalimn. oxygen min.	03–17 July 2013	8.9E-07	1.5	905	29.4
	metalimn. oxygen min.	10–24 July 2013	1.2E-06	1.5	681	22.1
metalimn. oxygen min.	mean	2.3E-06			15.9	

For reactions which follow 1st order kinetics, the time needed for reaction t_R describes how long it takes for ~63% of the molecules to react. In the present thesis it is used to

compare iron oxidation (as determined in Appendix III) with the overall oxygen depletion (additional analysis, Table 3).

Table 3: Time needed for reaction t_R and decay coefficient k' (with t_R being equal to $1/k'$) for reactions with 1st order kinetics for the different water layers investigated in Part 3 of the thesis. Note that oxygen turnover rates in Part 2 and 4 were determined on the basis of 0th order kinetics.

	Layer	reaction	Details	k'	t_R	
				(d ⁻¹)	(h)	(d)
Part 3 (Appendix III)	mixolimnion	iron oxidation	pH = 3.6	0.01	2778	115.7
	mixolimnion	iron oxidation	pH = 3.6	0.26	93	3.9
	transition zone	iron oxidation	pH = 4.5	0.12	208	8.7
	monimolimnion	iron oxidation	pH = 6	2.45	10	0.4
	monimolimnion	oxygen depletion	September data, oxygen conc. at 13.6 and 13.8°C isotherms (~1.4 m depth)	1.20	20	0.8

The dimensionless number N_E relates the time needed for a reaction to occur to the actual duration of exposure (Oldham et al 2013). Assuming 1st order kinetics for the reaction, $N_E = 1$ implies that the exposure time (i.e., the observed duration of oxygenation events) is long enough for ~63% of the molecules to react. Consequently, a reaction happens completely if $N_E \gg 1$ and no reaction occurs if $N_E \ll 1$. The N_E number was used in Part 3 to test whether the conditions favoring iron oxidation lasted long enough for the reaction to occur. Here it is additionally applied to the flux event observed in Part 2 of the thesis (Table 4).

Table 4: The duration of oxygenation events t_E , the respective reaction times t_R , and the N_E numbers (with $N_E = t_E/t_R$). Values marked with * indicate highest decay coefficient, i.e., shortest t_R reported in literature (Hopkinson et al., 2002; Koehler et al., 2012; Vähätalo et al., 2010).

	Layer	Oxygenation event	k' (d ⁻¹)	t_R (h)	t_E (h)	N_E (-)
Part 2 (Appendix II)	oxycline	flux event a	0.20*	120*	3.2	0.0
Part 3 (Appendix III)	monimolimnion	July	2.45	10	12.0	1.2
	monimolimnion	July	2.45	10	16.0	1.6
	monimolimnion	September	2.45	10	8.5	0.9