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Can Chironomid Larvae Trigger the Formation of Vivianite in
Lake Sediments?

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Statutory Declaration

I, Dorothea Engl (Student-ID: 12032256), hereby declare that I have independently authored this master's thesis. I have used only the sources and literature explicitly cited in the thesis, and all verbatim or paraphrased content from these sources has been properly acknowledged and referenced.

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Kurzfassung

Die Eutrophierung von Seen, hervorgerufen durch die Anreicherung von Phosphor und Stickstoff aus anthropogenen Quellen, stellt weiterhin eine erhebliche Herausforderung für Süßwasserökosysteme weltweit dar. Phosphor spielt hierbei eine entscheidende Rolle, da es als limitierender Faktor für das Wachstum von Phytoplankton fungiert und somit den trophischen Zustand eines Sees maßgeblich beeinflusst. Trotz gezielter Maßnahmen zur Reduzierung der Nährstoffeinträge erweist sich die Umkehrung der Eutrophierung aufgrund der lang anhaltenden Präsenz von Phosphor im System als langwieriger Prozess. Die nachhaltige Bewirtschaftung von Seen erfordert daher einen integrativen Ansatz, um die Wasserqualität zu sichern und das ökologische Gleichgewicht aufrechtzuerhalten.

Die Freisetzung von Phosphor aus Seesedimenten steht in engem Zusammenhang mit den vorherrschenden Redoxbedingungen und beeinflusst maßgeblich den Eisen- und Schwefelkreislauf. Diese Studie untersucht die Rolle von Chironomidenlarven bei der Modifikation der Sedimentchemie und des Nährstoffkreislaufs in eutrophen Seen, mit einem besonderen Fokus auf die Bildung von Vivianit, einem Eisen-Phosphor-Mineral. Die Vivianitbildung könnte den Phosphorhaushalt in Seen direkt beeinflussen, insbesondere durch die langfristige Retention von Phosphor in den oberen Sedimentschichten, die in direktem Austausch mit dem überliegenden Wasser stehen und nach der Entstehung thermodynamisch stabil bleiben.

Röhrenbewohnende Chironomidenlarven, die in den oberen Sedimentschichten leben, sind von besonderer Bedeutung, da sie schwankende Redoxbedingungen erzeugen. Ihre Bewegungen fördern den Transport von Nährstoffen und Sauerstoff in ihre Röhren und beeinflussen dadurch die Phosphorbindung im Sediment. Die experimentellen Ergebnisse dieser Arbeit zeigen, dass Chironomidenlarven unter bestimmten Bedingungen tatsächlich die Bildung von Vivianit initiieren können. Ein zentraler Faktor ist dabei die durch bioturbative Aktivität vergrößerte oxidierte Sedimentoberfläche, die die Anreicherung von Phosphor und Eisen in Form von Eisenoxyhydroxidphosphaten ermöglicht. Nach dem Tod oder Schlüpfen der Larven können sich anaerobe Bedingungen wieder einstellen, welche die Reduktion von Eisen(III) zu Eisen(II) begünstigen und in Gegenwart von Phosphor zur Vivianitbildung führen können. Niedrige Sulfidkonzentrationen verhindern dabei die Bildung von Eisensulfiden, wodurch ausreichend Eisen(II) für die Vivianitbildung verfügbar bleibt. Allerdings zeigte sich, dass das Verhältnis von Eisen zu Phosphor und Eisen zu Schwefel allein nicht ausreicht, um die Vivianitbildung zuverlässig vorherzusagen. Im Sediment des Müggelsees, das moderate Konzentrationen von Eisen und Phosphor bei niedrigem Schwefelgehalt aufweist, konnte Vivianitbildung nachgewiesen werden. Im Gegensatz dazu führten die Sedimente des Arendsees, die niedrige Konzentrationen von Eisen und Phosphor, aber hohe Schwefelgehalte aufwiesen, nicht zur Vivianitbildung. Überraschenderweise wurde in den Sedimenten des Müggelsees, die zu Beginn des Ex-

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periments künstlich mit Eisen und Phosphor angereichert wurden, keine Vivianitbildung beobachtet, was auf die Komplexität der beteiligten Faktoren hinweist und ein tieferes Verständnis der Bedingungen zur Vivianitbildung erfordert.

Die wissenschaftliche Bedeutung der Untersuchung, ob Chironomidenlarven die Vivianitbildung in Seesedimenten fördern können, liegt in ihren potenziellen Auswirkungen auf die Wasserqualität und das Management aquatischer Ökosysteme. Die Vivianitbildung bietet eine potenzielle natürliche Methode zur Sanierung eutrophierter Gewässer, indem sie Phosphor langfristig in den Sedimenten bindet und somit eine nachhaltige Kontrolle der Phosphorfreisetzung ermöglicht. Ein besseres Verständnis der Rolle von Chironomidenlarven bei der Beeinflussung von Redoxbedingungen und Phosphorbindung könnte entscheidend für die Optimierung dieser Methoden sein. Insgesamt liefert diese Forschung wichtige Erkenntnisse für umweltfreundliche Ansätze im Management aquatischer Ökosysteme und zur Bewältigung von Herausforderungen der Wasserqualität.

Abstract

This master's thesis investigates the role of tube-dwelling chironomid larvae in vivianite formation in lake sediments, with a particular focus on their impact on phosphorus binding and redox dynamics. Eutrophication of lakes, driven by phosphorus and nitrogen enrichment from human activities, remains a significant challenge for freshwater ecosystems. Phosphorus limits phytoplankton growth and significantly affects the trophic state of lakes. Despite nutrient reduction efforts, reversing eutrophication remains complex due to persistent phosphorus binding.

This study analyzes how chironomid larvae alter sediment chemistry and nutrient cycling in eutrophic lakes, particularly by forming vivianite, an iron-phosphorus mineral. Chironomid larvae, residing in the upper sediment layers, create fluctuating redox conditions that influence nutrient and oxygen transport, thereby affecting phosphorus binding. The findings indicate that chironomid larvae can initiate vivianite formation under certain conditions by enlarging the oxidized sediment surface and facilitating phosphorus and iron retention. Anaerobic conditions following the death of larvae promote the reduction of iron(III) to iron(II) and thus vivianite formation, especially when sulfide concentrations are low.

Vivianite formation was observed in sediments from Lake Müggelsee, which has moderate concentrations of iron and phosphorus with low sulfur content. In contrast, sediments from Lake Arendsee, characterized by low iron and phosphorus concentrations but high sulfur levels, did not lead to vivianite formation. Interestingly, vivianite was not formed in sediments from Lake Müggelsee that were artificially enriched with iron and phosphorus, highlighting the complexity of the conditions required for vivianite formation.

This research provides significant insights into phosphorus binding mechanisms and offers a foundation for future studies on sediment biogeochemistry and nutrient cycling in eutrophic waters. Understanding whether chironomid larvae can promote vivianite formation in lake sediments has important implications for water quality and aquatic ecosystem management. Vivianite formation presents a potential natural method for remediating eutrophic waters by sequestering phosphorus in sediments, thus enabling sustainable phosphorus release control. Improved knowledge of chironomid larvae's role in influencing redox conditions and phosphorus binding could be crucial for optimizing these methods.

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1. Introduction

1.1. Eutrophication and Lake Restoration Strategies

Eutrophication in lakes, driven by the accumulation of nutrients such as phosphorus (P) and nitrogen (N) primarily from human activities, remains a significant environmental challenge for freshwater systems globally (Meinikmann, 2017). The total phosphorus (TP) concentrations in lakes show considerable variation, ranging from oligotrophic conditions ($0\text{--}12\text{ g L}^{-1}$) to hypertrophic levels ($> 96\text{ g L}^{-1}$), according to Carlson (1977) Trophic State Index. In extreme cases, TP concentrations exceeding $1,000\text{ g L}^{-1}$ have been documented (Downing & McCauley, 1992).

The excessive nutrient load, originating from direct discharges, such as wastewater and agricultural effluents, as well as from diffuse sources via groundwater, leads to ecological disruptions, including harmful algal blooms and oxygen (O_2) depletion, threatening aquatic ecosystems (Schwoerbel & Brendelberger, 2022). P is particularly critical in freshwater environments as it often limits phytoplankton growth, thereby influencing the lake's ecosystem. Although P is abundant in eutrophic systems, much of it, such as P in bound or mineral forms, remains non-bioavailable, creating a paradox where nutrient richness does not necessarily equate to increased productivity. Consequently, water quality regulations focus heavily on managing bioavailable P to maintain the balance in these ecosystems (McMahon & Read, 2013; Schwoerbel & Brendelberger, 2022). Only sustained P input over extended periods leads to a significant impact. Microorganisms play a key role by assimilating P even at low concentrations, incorporating it into biomass, releasing it from organic matter (OM), and altering its solubility through redox reactions. These microbial activities can create persistent P reserves in sediments, supporting elevated levels of primary productivity for decades, even after external P inputs are reduced (McMahon & Read, 2013). Despite extensive efforts to reduce nutrient inputs from point sources such as sewage discharges and agricultural runoff, reversing eutrophication is a gradual process that can take several years, depending on the water body's residence time (Gulati & Van Donk, 2002; Sharpley et al., 2013). In natural systems, P predominantly resides in water, soil, and sediments, with low concentrations in undisturbed waters, often only a few micrograms per liter. These low levels are due to the slow release of P from mineral sources. P can be stored in rocks or sediments over long periods, and released into the environment gradually. Natural sources of inorganic P include precipitation, atmospheric deposition, and P-containing minerals such as apatite, which are introduced into lakes via inflows (Psenner, 1984). In natural soils, P is typically strongly adsorbed, making it less prone to runoff. However, excessive fertilization in agricultural areas can significantly increase P levels in the runoff, exacerbating lake eutrophication (Schindler,

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2012; Wang & Wang, 2009). P in lake sediments plays a vital role in both storing and releasing P, thus regulating nutrient cycles and significantly impacting ecological processes within aquatic systems (Hupfer & Lewandowski, 2008; Song et al., 2017).

Lake management strategies encompass a variety of integrated approaches aimed at preserving and enhancing water quality, as well as maintaining the ecological balance in lakes through targeted interventions in nutrient cycles, biological structures, and physical processes (Kelly Vargas & Qi, 2019).

This master thesis focuses on Lake Müggelsee in Berlin and Lake Arendsee in Saxony-Anhalt, both affected by eutrophication. Long-term studies by Shatwell and Köhler (2019) on Lake Müggelsee reveal that reductions in total nitrogen (TN) and TP inputs by 79 % and 69 %, respectively since the late 1970s led to a rapid decline in N concentrations in the lake by 2016 (see Figure 1.1). The nutrient concentrations in the lake responded immediately to these reductions, a response attributed to the combination of decreased water volume from the inflowing Spree River and lower nutrient concentrations in the inflows. However, P concentrations remained elevated for approximately 20 years. Seasonal variations indicated that P was the limiting factor for growth in spring, while N became limiting in summer due to high P release from the sediments.

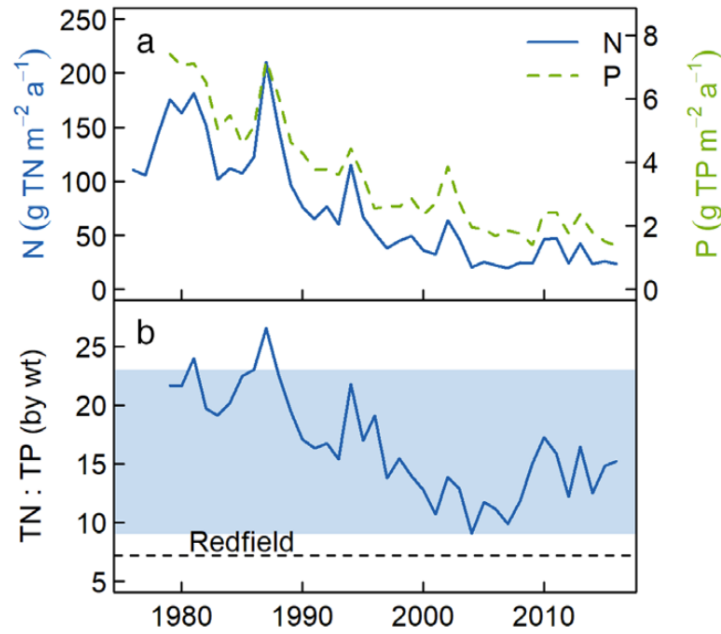


Figure 1.1.: Annual inputs of TN and TP and their corresponding TP/TN ratios by weight in incoming flows in Lake Müggelsee. The dashed line represents the Redfield ratio, while the shaded zone signifies the range of co-limitation by N and P ($9 \leq \text{TN}/\text{TP} \leq 23$) with strict P or N limitations beyond this range (Guildford & Hecky, 2000; Shatwell & Köhler, 2019).

1.2. Research Question and its Significance

Over the years, various lake restoration strategies have been implemented in Lake Arendsee to reduce P concentrations and mitigate associated eutrophication. Earlier restoration efforts, including hypolimnetic withdrawal (Klapper, 1992; Klapper, 1991) and mechanical resuspension of calcareous sludge from the shore zone (Roenicke et al., 1995), did not result in a significant reduction of P concentrations. In 1995, an artificial calcite layer was applied during a restoration attempt to control the internal P cycle by covering the natural bottom sediments with calcareous sludge. However, this intervention did not yield the expected reduction in P levels in the water as well. Laboratory tests indicated that the sorption properties and P uptake mechanisms were inadequate under field conditions. The resuspension and subsequent deposition of the calcareous sludge did not lead to a significant reduction in P levels. After deposition, anaerobic conditions in the sediment further hindered potential P binding, rendering the large-scale intervention ineffective (Hupfer et al., 2000). Management strategies in Arendsee now aim to lower the TP concentration to 60-80 $\mu\text{g L}^{-1}$, creating P-limited conditions during the growth period. A critical component of these strategies is the analysis of internal P sources and their binding within the sediment, as these factors are crucial for the success of restoration efforts (Hupfer et al., 2016).

1.2. Research Question and its Significance

The dynamics of P release in lake sediments are closely linked to redox conditions and have significant implications for the cycling of iron (Fe) and sulfur (S). Traditionally, it has been understood that the presence of O_2 or NO_3^- in sediments prevents P release by maintaining an oxidized surface layer, while anaerobic conditions promote the release of P. However, recent studies challenge this conventional view, suggesting a more nuanced regulation of sedimentary processes (Hupfer & Lewandowski, 2008). New research highlights the role of ferrous iron Fe(II) in binding P and forming vivianite ($\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$) (Heinrich et al., 2021, 2022). The accumulation of P in surface sediments (Rothe et al., 2016) can affect the availability of orthophosphate (PO_4^{3-}) to primary producers in the overlying water, potentially altering the N/P stoichiometric ratio and shifting algal community composition. The formation of vivianite could have immediate implications for the P balance in lakes, particularly if the formation contributes significantly to benthic P retention, occurs in the uppermost sediment layers that interact closely with overlying water, and remains stable after deposition (Kubeneck, 2024).

This phenomenon has been observed at the sediment-water interface (SWI) in natural settings, where factors such as stratification, mixing in deep waters, diurnal shifts in redox conditions in macrophyte-dominated areas or tube-dwelling Chironomid larvae play a role. Chironomid larvae are particularly important, as they induce fluctuating redox conditions (Hölker et al., 2015). The movement of these larvae facilitates the transport of nutrients and O_2 into their tubes, thereby influencing P binding processes (Lewandowski & Hupfer, 2005). A key factor is the oxidized sediment surface area expansion due to high larval density, which enhances P binding to oxidized Fe (Hupfer et al., 2019). After the larvae die or emerge from their tubes, anaerobic conditions may

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return, potentially leading to vivianite formation. Vivianite is an effective P sink in lake sediments due to its stability under anaerobic and fluctuating redox conditions (Rothe et al., 2016). This hypothesis lacks definitive structural evidence, and this Master's thesis aims to provide such evidence through qualitative analysis. The scientific relevance of studying whether Chironomid larvae trigger vivianite formation in lake sediments lies in its potential impact on water quality and ecosystem management. If confirmed, vivianite formation could represent a natural remediation strategy to address issues related to anthropogenic eutrophication in freshwater ecosystems (Welch & Cooke, 2005; Zamparas & Zacharias, 2014). This process, which involves the sequestration of P in sediments through vivianite, may offer a long-term solution for controlling P release (Gunnars et al., 2002). Understanding how Chironomid larvae influence redox conditions and P binding could inform the development of sustainable water quality improvement strategies, particularly in lakes affected by excessive nutrient inputs (Hölker et al., 2015; Hupfer et al., 2019). Moreover, these findings could have broader applications, such as enhancing P immobilization in constructed wetlands designed for wastewater treatment under specific conditions (Vymazal, 2007). Overall, this research contributes valuable insights into environmentally sustainable approaches for managing aquatic ecosystems and addressing water quality challenges.

1.3. Research Gaps

The potential role of Chironomid larvae in promoting vivianite formation and contributing to long-term P retention in lake sediments is a critical, yet underexplored, area of research. Key gaps include the lack of long-term studies on the sustained impact of Chironomid larvae on sediment and water layers. Current research, largely focused on short-term effects, may not fully capture the long-term implications of Chironomid activity on nutrient cycling and redox dynamics and may overestimate their effectiveness (Hupfer et al., 2019; Lewandowski et al., 2007).

While vivianite plays a crucial role in the P cycle, the mechanisms of its formation, especially under varying redox conditions, remain poorly understood. The interaction between Fe(II) and P under anoxic conditions, particularly with S dynamics, is not fully elucidated and requires further investigation (Hupfer et al., 2019; Rothe et al., 2016). Chironomid larvae significantly influence nutrient cycles at the SWI, yet their broader effects on redox gradients in lake ecosystems are underinvestigated (Kristensen et al., 2012; Xing et al., 2018). Understanding their role in facilitating vivianite formation could lead to natural remediation strategies for eutrophication in freshwater systems (Hupfer et al., 2019; Welch & Cooke, 2005).

1.4. Hypothesis and Objectives

This master's thesis investigates how tube-dwelling Chironomid larvae may promote the formation of vivianite in lake sediments by inducing fluctuating redox conditions, thereby

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contributing to the long-term retention of P. The study focuses on examining the mechanisms of P binding and release in sediments from Lake Müggelsee and Lake Arendsee, which are characterized by different Fe/P and Fe/S ratios. Particular attention is given to the role of vivianite and the influence of redox conditions. Through a detailed analysis of sediment properties and biogeochemical processes at the sediment-water interface, the research aims to deepen the understanding of P availability. The ultimate goal is to develop lake management strategies to improve water quality through targeted P retention measures in sediments.

Hypothesis 1: Chironomid larvae increase the oxidized surface area in sediment, promoting the oxidation of Fe(II) to Fe(III). The resulting redox-active microzones could, upon reduction, release Fe(II), potentially leading to vivianite formation.

Hypothesis 2: The bioturbation activities of Chironomid larvae enhance P transport and accumulation onto Fe(III) within the sediment tubes. This increased P availability, combined with reduced Fe(II) in anoxic zones, could facilitate the formation of vivianite.

Hypothesis 3: Chironomid larvae promote the formation of vivianite in sediments with a Fe/P ratio of 1.5 to 2.5 and a Fe/S ratio greater than 1 following the transition from oxic to anoxic conditions.

In the context of this experiment, the hypotheses translate to the following specific scenarios: (i) Sediment from Lake Müggelsee, characterized by moderate concentrations of Fe and P and low S content, is likely to support vivianite formation. (ii) Sediment from Lake Arendsee, which is low in Fe and P but high in S, is unlikely to promote vivianite formation. (iii) Sediment from Lake Müggelsee that is rich in Fe and P but poor in S has a high probability of facilitating vivianite formation.

2. Theoretical Background

2.1. Lake Zonation and Definitions

Lakes are characterized by distinct zones that create different habitats, as Figure 2.1 illustrates. The primary divisions are the open water zone, the limnetic or pelagic zone, and the bottom zone, or benthic zone. Organisms inhabiting the benthic zone, including microorganisms, protists, and higher organisms such as Chironomid larvae, are collectively referred to as benthos. The benthic zone is further subdivided into the littoral zone, the nearshore area, and the profundal zone, the deep open-water region. The littoral zone encompasses the shallow, sunlit region near the shoreline, extending to the depth

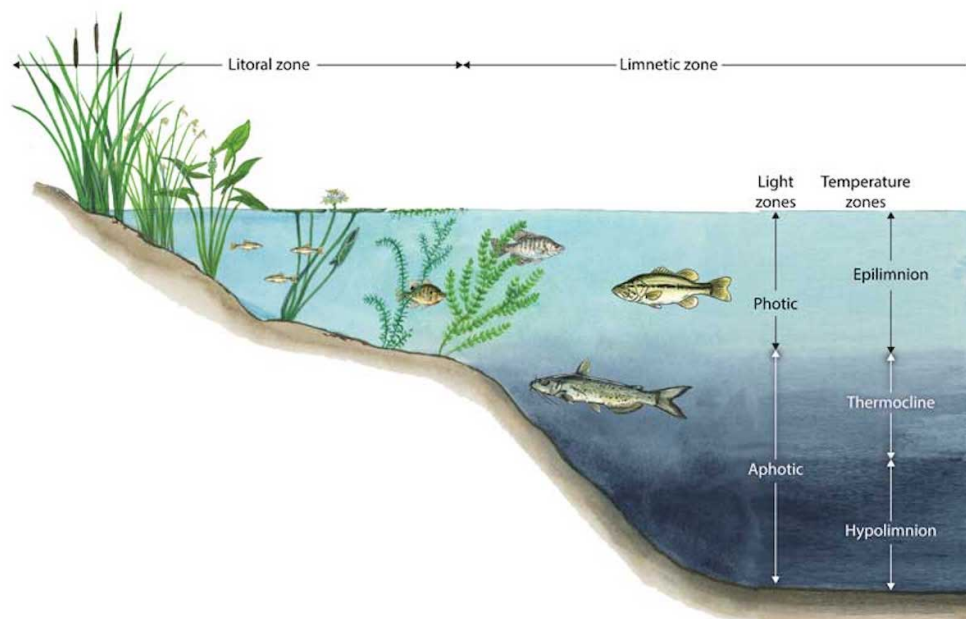


Figure 2.1.: Lakes comprise distinct zones: the littoral and limnetic zones demarcate the shoreline area from the free-water zone. The boundary layer where the light intensity in the spectrum usable by plants is reduced to 1 % of its original intensity delineates the euphotic zone from the aphotic zone. The thermocline separates a thermally homogeneous surface layer, the epilimnion, from the hypolimnion, where the temperature corresponds to the greatest density of water (Holz, 2016).

2.1. Lake Zonation and Definitions

at which sunlight no longer supports photosynthesis. Within the littoral zone, there are two subzones: the emergent zone, where plants extend above the water surface, and the submerged zone, where plants are entirely below the water. As a result, O_2 levels in the littoral zone tend to be relatively higher due to the photosynthetic activity of organisms. In contrast, the profundal zone is typically located below the depth where sunlight can penetrate. This zone is characterized by low O_2 levels and limited primary production through photosynthesis, making the profundal suitable for organisms adapted to these conditions (Schönborn & Risse-Buhl, 2013; Schwoerbel & Brendelberger, 2022). The community in this bottom water layer is purely consumer-based, depending on biomass generated in the littoral and pelagic zones (Hupfer & Lewandowski, 2008). The compensation level defines the boundary between these zones, a theoretical depth where photoautotrophs can no longer maintain a positive photosynthetic balance over 24 h. However, the actual compensation depth varies among photoautotrophic organisms (Figuerola et al., 1997).

This compensation level definition also applies to the pelagic zone, which is divided into the sunlit upper pelagic zone (euphotic zone) and the deeper pelagic zone without adequate sunlight (aphotic zone). According to Lambert-Beer's law, light intensity decreases exponentially with increasing depth. The euphotic zone, which approximately corresponds to the trophogenic zone, ends where the light intensity in the spectrum usable by plants is reduced to 1 % of its original intensity. Below this boundary lies the aphotic zone. In lakes without allochthonous (external) turbidity substances, light absorption by phytoplankton constitutes the largest contribution to light extinction. The intrinsic color of the water is therefore influenced by dissolved substances such as yellow-brown humic substances and particles (Schönborn & Risse-Buhl, 2013).

The water layer above the compensation level is known as the trophogenic zone, encompassing the littoral and epipelagic zones, where predominant photoautotrophic production occurs. In contrast, the underlying tropholytic zone, which includes the profundal and bathypelagic zones, lacks photoautotrophic production (Schwoerbel & Brendelberger, 2022).

Additionally, the thermocline serves as a boundary between the distinct thermal layers in a stratified lake. The epilimnion is the uppermost, warm, and well-mixed layer. Below this lies the metalimnion, which contains the thermocline, marked by a steep temperature and density gradient inhibiting mixing between the epilimnion and the underlying hypolimnion. The hypolimnion, being the deepest and coldest layer, has minimal light and O_2 in eutrophic lakes and serves as a repository for OM and nutrients.

Trophic status refers to the intensity of organic photoautotrophic production (Elster, 1958). Eutrophic lakes are distinguished by elevated concentrations of nutrients, particularly P and N, which stimulate excessive plant and algal growth. This heightened productivity increases OM accumulation, potentially leading to O_2 depletion in deeper waters as decomposers break down organic material. Conversely, oligotrophic lakes have low nutrient concentrations, supporting lower levels of primary productivity. These lakes are typically characterized by clear waters with high O_2 levels throughout, including in the deeper regions. Lakes with such a trophic status are generally found in regions with

2. Theoretical Background

minimal human impact and their limited nutrient availability restricts the growth of algae and other plants, resulting in less OM and a more stable aquatic environment (Schönborn & Risse-Buhl, 2013).

2.2. Temperature and Mixing of Lakes

Temperature plays a crucial role in shaping the ecosystem of a lake, primarily through its effect on water circulation and subsequent substance exchange across the entire lake (Schönborn & Risse-Buhl, 2013). Lakes that undergo seasonal transitions between periods of circulation and stagnation are considered either meromictic or holomictic, based on whether at least one mixing event involves the entire water column. The pattern of circulation and stagnation in a lake is determined by the climatic conditions of its region.

2.2.1. Dimictic Lakes

Dimictic lakes, which mix twice a year as illustrated in Figure 2.2, are commonly found in northern Eurasia, North America, and other regions with similar climates in the Southern Hemisphere (Hutchinson & Löffler, 1956). In dimictic lakes that are deeper than 20 meters, wind patterns significantly impact the heat balance. In spring, the temperature is homogenous, and the lake mixes completely (Tomczak, 1963). In summer, heat transport is limited to a warm, thermally more or less homogeneous surface layer, the epilimnion. Beyond the thermocline, there is little heat transport into the depths, so that the temperature of the hypolimnion is close to the temperature of the maximal density of water (Birge & Juday, 1911). This state of stable thermal stratification in the lake is known as summer stagnation. As autumn progresses and surface water cools, wind-driven mixing and thermal convection can reintroduce deeper water mixing. Once temperatures drop to 4°C, the lake's entire water column may undergo circulation, replacing thermal stratification with uniform temperature distribution. This state is known as autumn turnover, which, as temperatures continue to drop in winter, leads to thermal stratification or winter stagnation. During winter stagnation period, the lake exhibits two distinct temperature zones: cold surface water and deeper water at 4°C. The winter stratification lacks a true epilimnion, and the vertical temperature profile starts with an inverse thermocline. In spring, after the ice cover melts, the lake experiences homothermy again, resulting in spring turnover, which is followed by the gradual development of thermal summer stratification (Welch, 1968; Wells & Troy, 2022).

2.2.2. Polymictic Lakes

Polymictic lakes undergo complete mixing multiple times per year or even daily, allowing warmer surface waters to reach the lake bottom through various transport processes (Welch, 1968; Wells & Troy, 2022). This mixing can occur without wind, driven solely by the sinking of slightly cooled surface water. Unlike dimictic lakes, polymictic mixing events do not follow a regular periodic pattern, except in specific geographical regions. In temperate zones, for example, ponds or shallow lakes such as Lake Müggelsee can exhibit polymictic

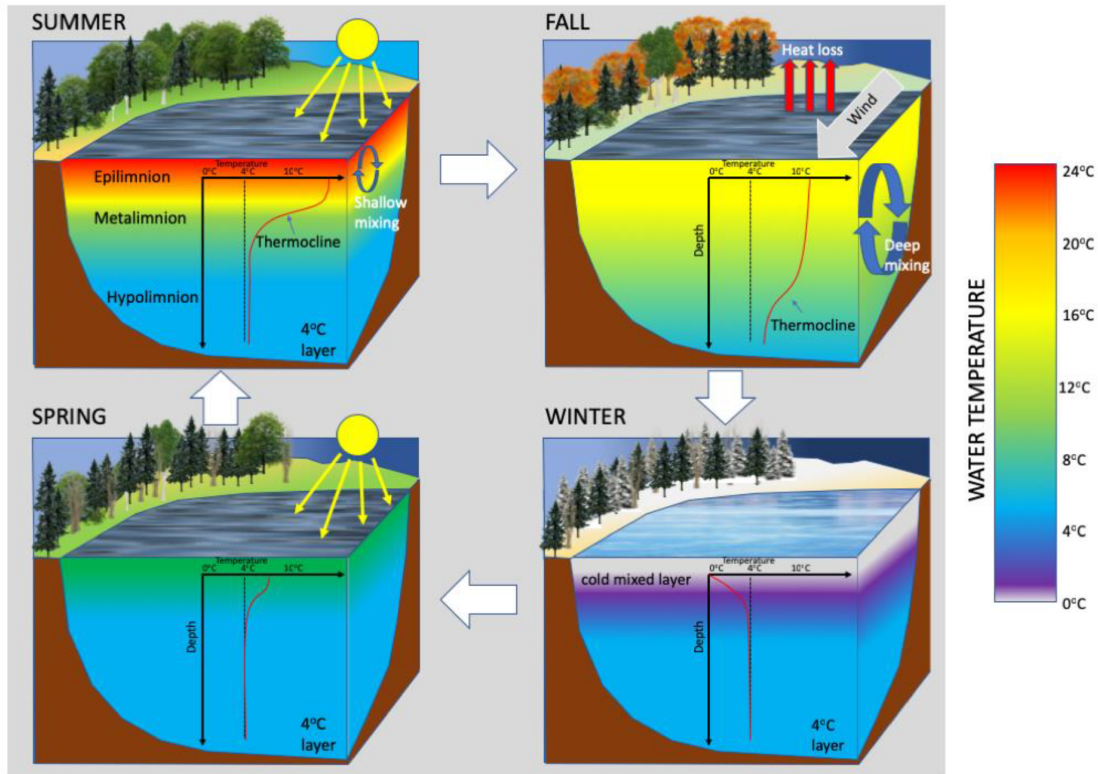


Figure 2.2.: Mixing and stratification processes in a dimictic lake with changing temperatures according to depth (Wells & Troy, 2022).

behavior. The circulation periods in these lakes are crucial for nutrient dynamics, as they facilitate the oxidation of substances and promote their even distribution throughout the water column (Hutchinson & Löffler, 1956; Schönborn & Risse-Buhl, 2013).

2.3. Nutrient Balance in Lakes

The nutrient dynamics of aquatic ecosystems are determined by several fundamental processes, as illustrated in Figure 2.3. The bioactivity of organisms (1), expressed through production, consumption, and decomposition, represents both nutrient cycling and energy flow. Equally important is the chemical and biologically mediated storage and release of substances and energy at the SWI (2, further information in Section 2.3.5). An additional significant factor is the rhythm of circulation and stagnation in lakes, which influences the distribution and availability of nutrients and other substances within the water body (3, not shown in the figure). Additionally, there is a continuous exchange with the atmosphere (4), including precipitation (5), and inflows, and outflows (7). Finally, the adsorption and desorption of substances on suspended particles (6) serve as a crucial mechanism

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for the transport and distribution of chemical compounds in the water (Schwoerbel & Brendelberger, 2022). Freshwaters are predominantly carbonate waters, in which

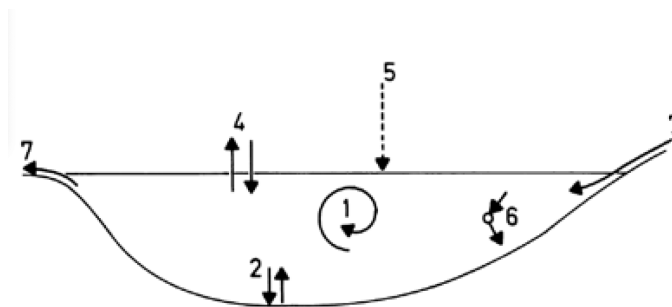


Figure 2.3.: Nutrient dynamics of lakes are driven by bioactivity of organisms (1), interactions between water and sediment (2), exchange with atmosphere (4), precipitation (5), adsorption and desorption on suspended particles (6) and inflows as well as outflows (7) (Schwoerbel & Brendelberger, 2022).

calcium carbonates dominate. Additionally, sodium chloride is often present in significant quantities. Nitrates and particularly silicates can also occur in substantial concentrations in inland waters, with their levels being strongly influenced by biological activity. Other chemical substances such as Fe, manganese (Mn), P, ammonium (NH_4^+), and nitrite (NO_2^-) are present in lower concentrations, while trace elements appear only in minimal amounts (Leppard, 2013).

In addition to these inorganic compounds, a wide variety of organic substances are dissolved in water, both in true and colloidal forms. These include amino acids, carbohydrates, humic substances, vitamins, enzymes, and other organic compounds. This complexity in chemical composition underscores the biogeochemical diversity of freshwater systems.

2.3.1. Oxygen Distribution

Lakes can experience both over- and undersaturation with O_2 . In oligotrophic lakes, O_2 levels remain fairly consistent year-round, typically around 10 mg L^{-1} , with even distribution throughout the water column. In contrast, dimictic eutrophic lakes like Lake Arendsee exhibit significant seasonal variations in O_2 distribution. During the summer stagnation phase, the hypolimnion becomes isolated, leading to substantial biogenic O_2 consumption and marked vertical differences in O_2 concentrations (Schönborn & Risse-Buhl, 2013).

In this period, the epilimnion continuously exchanges O_2 with the atmosphere, balancing O_2 consumption and production processes. High phytoplankton activity and vegetation growth in the littoral zone can cause O_2 supersaturation during the day, while at night, O_2 deficits may occur (Schwoerbel & Brendelberger, 2022). In the hypolimnion, however, O_2 consumption predominates, mainly due to microbial decomposition of OM, which settles in the profundal zone and accumulates on the upper sediment layers, where it contributes

to O₂ depletion. The OM accumulation plays a major factor in the hypolimnetic O₂ depletion commonly observed in the deeper water layers of eutrophic lakes (Fulthorpe & Paloheimo, 1985; Linsey & Lasenby, 1985). During the spring and autumn turnover, complete water column mixing occurs, allowing O₂-rich water to reach the lake bottom. The mixing results in nearly uniform O₂ concentrations throughout the water column, producing an O₂ profile similar to that found in oligotrophic lakes (Lambert et al., 1984).

2.3.2. Phosphorus Cycle

Changes in P inputs and outputs shape the P cycle in eutrophic lakes. P enters lakes through surface runoff, hydrological inflows from rivers or streams, wet and dry atmospheric deposition, groundwater influx, and interactions with lake sediments. P is lost from the system via hydrological and groundwater outflows and through the sedimentation of particulate phosphorus (PP) (McMahon & Read, 2013). Various P fractions exist in lakes: dissolved inorganic phosphorus (DIP), which includes forms such as dihydrogen phosphate (H₂PO₄⁻), hydrogen phosphate (HPO₄²⁻), and PO₄³⁻ with concentrations that vary depending on pH; dissolved organic phosphorus (DOP), the bioavailable form of P; and PP, which includes particulate organic phosphorus (POP) found in organisms and detritus, as well as particulate inorganic phosphorus (PIP) that is adsorbed onto or incorporated within minerals. The sum of all these fractions is referred to as TP, and undergoes complex biological cycling within the water column (Schwoerbel & Brendelberger, 2022). In the trophogenic zone, phytoplankton and heterotrophic prokaryotes assimilate DIP and DOP, incorporating them into the food web (indicated by blue arrows in Figure 2.4). Higher trophic level organisms, such as zooplankton and fish, consume P through grazing, bacterivory, and predation (represented by black arrows in the upper part of the figure), leading to its integration into the higher food chain. The breakdown of biomass from living organisms releases DOP and POP (indicated by white arrows). While some of the PP settles with dead organisms and other materials, a significant portion is released back into the euphotic zone, particularly after resuspension, and is re-assimilated by organisms (McMahon & Read, 2013; Schwoerbel & Brendelberger, 2022). Within sediments, heterotrophic organisms play a crucial role in converting PIP to DIP and POP to DOP and then to DIP, as shown by the black arrows in the lower part of the diagram (McMahon & Read, 2013). P binding occurs through the transport of DOP and DIP between solid particles via adsorption and desorption, biological assimilation, and mineralization, which leads to the formation of PIP as iron and calcium phosphates, such as vivianite and apatite (Sondergaard et al., 2001). These processes involve the deposition, transformation, immobilization, and encapsulation of P, as well as its infiltration into deeper sediment layers (Boers et al., 1998), making the sediment both a significant source and a critical reservoir of P (Hupfer et al., 2019). In nutrient-rich systems, phytoplankton, particularly cyanobacteria, dominate and effectively compete with heterotrophic prokaryotes for DIP. During thermal stratification, P in the O₂-rich epilimnion is primarily bound within biomass, while DIP is present only in minimal concentrations (McMahon & Read, 2013; Schwoerbel & Brendelberger, 2022).

2. Theoretical Background

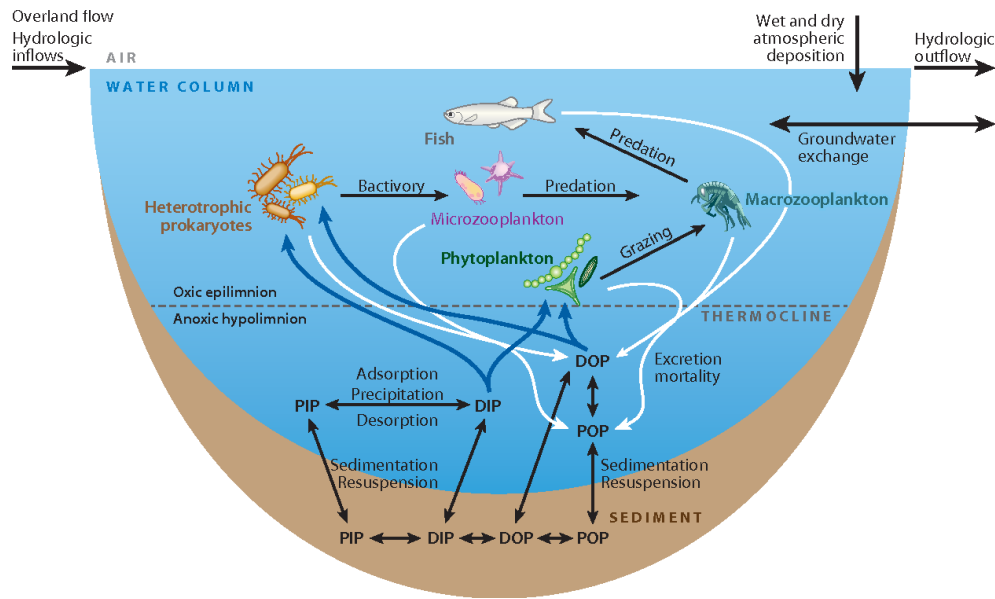


Figure 2.4.: P cycle in an idealized thermally stratified eutrophic lake system (McMahon & Read, 2013)

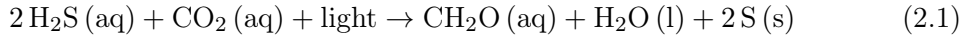
2.3.3. Behaviour of Iron

Fe, despite being one of the most abundant elements on Earth, typically exhibits low concentrations in aquatic environments due to its specific solubility characteristics. An exception to low abundance is anoxic groundwater, which often contains elevated levels of dissolved Fe (Schwoerbel & Brendelberger, 2022). In the environment, Fe predominantly occurs in two oxidation states: ferric Fe(III) and ferrous Fe(II). Ferric iron Fe(III) has low solubility at near-neutral pH levels, whereas ferrous Fe(II) is generally more soluble and typically exists as a bicarbonate complex, $\text{Fe}(\text{HCO}_3)_2$, making Fe(II) more readily available for biological processes (Kappler et al., 2021). The maintenance of Fe(II) in solution requires specific conditions, including O_2 saturation below 50 %, the presence of OM, high concentrations of free carbon dioxide (CO_2), and a pH below 7.5. Such conditions are most commonly found in groundwater and in the hypolimnion of lakes. When Fe(II) bicarbonate is exposed to O_2 or when the required reducing conditions are no longer maintained, Fe precipitates as ferric hydroxide, forming either $\text{Fe}(\text{OH})_3$ or $\text{Fe}(\text{OOH})$ minerals. The Fe precipitation process is commonly observed during the complete mixing (turnover) of lakes. The precipitation and subsequent deposition of Fe are significantly enhanced by Fe-oxidizing bacteria, such as *Thiobacillus ferrooxidans* and *Metallogenium* species, which oxidize Fe(II) to Fe(III) and act as chemolithoautotrophic organisms. Additionally, bacteria from genera like *Leptothrix*, *Crenothrix*, *Gallionella*, *Siderococcus*, and *Siderobacter* are found in iron hydroxide deposits, although their role as chemolithoautotrophs remains uncertain.

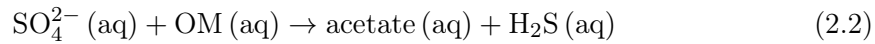
In the hypolimnion of eutrophic lakes, Fe compounds remain in solution during periods of stagnation, particularly in the SWI, where high concentrations of Fe can develop within distinct microstratifications. In contrast, within the epilimnetic layers, especially in the trophogenic zone, dissolved Fe is rapidly absorbed by primary producers and partially transported to deeper layers through processes such as calcite precipitation and adsorption onto Fe(OOH) particles. Organic complexing agents, including humic and fulvic acids derived from the decomposition of macrophytes, compete with iron-calcite precipitation and maintain Fe in solution even at higher redox potentials (Eh). Consequently, these organic Fe complexes serve as a critical source of Fe for primary producers (Schwoerbel & Brendelberger, 2022). The limited solubility of Fe(III) results in the precipitation of poorly crystalline iron (oxyhydr)oxides, such as ferrihydrite (Herndon et al., 2020). Ferrihydrite, however, is metastable and gradually transforms into more stable iron (oxyhydr)oxide minerals, including lepidocrocite, goethite, and hematite (Schwertmann & Cornell, 2008).

2.3.4. Behaviour of Sulfur

In lakes, the transformation processes of S play a crucial role in the biogeochemical cycle. In the absence of O₂ and other favorable electron acceptors, sulfate (SO₄²⁻) is reduced by microorganisms to hydrogen sulfide (H₂S), sulfide (S²⁻), and organically bound S, which accumulates in the sediment (Rudd et al., 1986). Additionally, H₂S is produced through the microbial degradation of proteins and is subsequently oxidized by sulfur bacteria, such as purple sulfur bacteria, through chemoautotrophic processes. In the presence of CO₂ and light, these bacteria produce elemental S and formaldehyde (CH₂O), as illustrated in Equation 2.1. This elemental S is further oxidized to SO₄²⁻ (Kusnezow, 1959).



Under anaerobic conditions, such as those found in the profundal zones of eutrophic lakes during stratification, H₂S is produced through dissimilatory SO₄²⁻ reduction (also known as desulfurization or SO₄²⁻ respiration) by anaerobic, S²⁻ producing and oxidizing bacteria, as shown in Equation 2.2.



These processes highlight the integral role of S transformations in the biogeochemical cycling of elements in lakes, particularly under anaerobic conditions, contributing to the accumulation of S compounds in sediments and influencing the overall ecosystem dynamics (Schwoerbel & Brendelberger, 2022).

2.3.5. Biogeochemical Dynamics in the Sediment-Water Interface

Precipitation, dissolution, and exchange processes at the SWI are crucial for the cycling of elements. Within the sediment, certain elements are preferentially adsorbed and can be released under specific conditions. The prevailing redox conditions play a critical

2. Theoretical Background

role in governing these processes and can be illustrated by the redox ladder in Figure 2.5 (Mortimer, 1941, 1942). The redox ladder shows the step-wise decline in Eh, which accompanies the successive reduction of redox-active elements to lower oxidation states (Kubeneck, 2024; McBride, 1994). In O_2 -rich environments, organic C acts as the primary electron donor in microbial respiration, with O_2 serving as the terminal electron acceptor (Kubeneck, 2024). The Gibbs free energy (ΔG) determines the sequence of reduction processes along the redox ladder. As one moves down the redox ladder, ΔG becomes increasingly positive, making the reactions less energetically favorable. Microorganisms preferentially use the most energetically favorable electron acceptors, leading to a vertical stratification of microbial communities. Sapkota et al. (2022) discuss identifying these redox conditions using an Indicator of Reduction in Soils device (IRIS), which detects anaerobic conditions in sediments through observable color changes.

Under anaerobic conditions, elements such as N, Mn, Fe, S, carbon (C), and hydrogen (H) can function as either electron acceptors or donors, depending on the specific microbial processes and geochemical conditions. A key example is the N cycle, where nitrate (NO_3^-) serves as an electron acceptor during denitrification. In this microbial process, NO_3^- is first reduced to NO_2^- , and may be further reduced to molecular nitrogen (N_2). Conversely, N can also act as an electron donor when NH_4^+ is released from OM via ammonification. Mn, predominantly present in sediments as

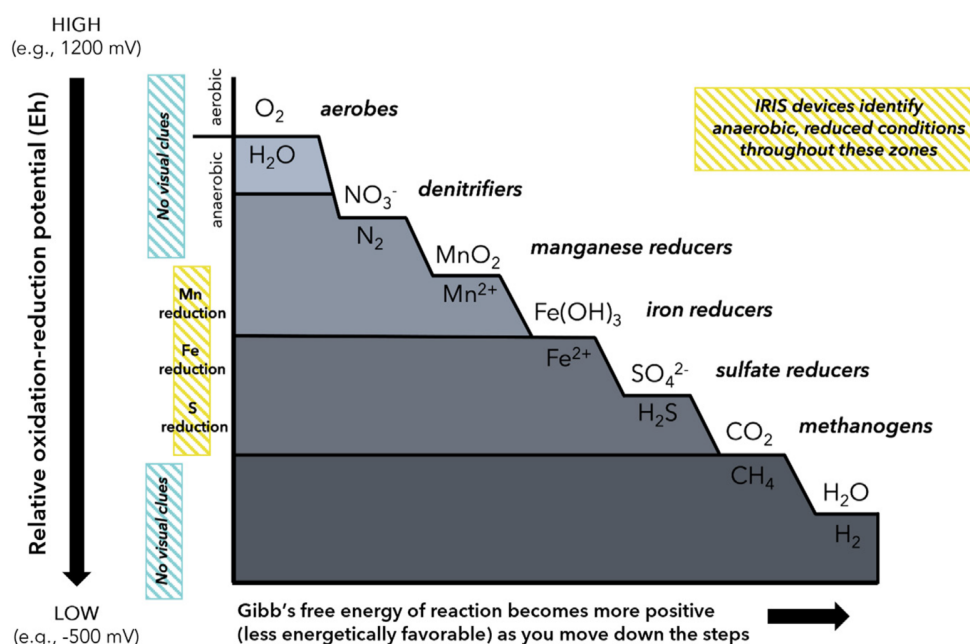


Figure 2.5.: Redox ladder in sediment with step-wise transformation of O, N, Mn, Fe, S, C, and H with decreasing Eh, displaying the redox pairs in both their oxidized and reduced forms. The relative scale is used since Eh depends on pH and other influencing factors. (Sapkota et al., 2022).

manganese(IV) oxide (MnO_2), undergoes reduction to Mn(II) ions under anaerobic conditions, functioning as a critical electron acceptor in microbial pathways facilitating the degradation of OM. Fe, another central element in the redox cycle of sediments, is predominantly present as Fe(III) under oxidizing conditions. In a reduced state, it is transformed into Fe(II) , where Fe(III) serves as an electron acceptor, especially in iron-reducing bacteria. However, Fe(II) can also be an electron donor in certain geochemical processes. S exists in various oxidation states, which can function as both electron acceptors and donors. SO_4^{2-} is also in the sediments reduced to H_2S in microbial reduction processes, where SO_4^{2-} serves as an electron acceptor. Conversely, elemental S can act as an electron donor in specific microbial processes. Organic substances in sediments often serve as an electron donor in microbial decomposition. Particularly during methanogenesis, OM is converted to methane (CH_4), where C acts as an electron donor.

Finally, H can act as an electron donor and acceptor, depending on the geochemical conditions and the microbes involved. In many anaerobic processes, such as SO_4^{2-} reduction to H_2S or methanogenesis, H is primarily used as an electron donor. These elements and their varying roles in the redox cycle are crucial for the microbial decomposition of OM and the transformation of elements in anaerobic sediment environments (Imboden & Lerman, 1978; Schwoerbel & Brendelberger, 2022; Stumm & Baccini, 1978).

Redox conditions in a lake fluctuate over time due to changes between circulation and stagnation phases, as well as the amount of OM decomposed in the profundal zone. These fluctuations cause the redox zone in the sediment to shift upward or downward, depending on O_2 availability and water stratification. The annual variation of the 0.2 V Eh line at the SWI of a eutrophic lake with a pH of 7 is shown in Figure 2.6. During the spring and autumn circulation, O_2 is transported to deeper water layers, typically resulting in $\text{Eh} = 0.6 \text{ V}$ at the SWI. However, despite the high O_2 concentrations, the oxidation zone penetrates only 0.2 to 3 mm into the sediment (Frenzel, 1990; Hayes & Phillips, 1958). This limited penetration depth restricts aerobic processes and maintains a reduced environment just below the sediment surface. In contrast, during the stagnation periods in summer and winter, particularly in eutrophic lakes, O_2 concentrations in the deeper water layers decrease, causing the reduction zone to shift significantly upwards until the reduction zone reaches the sediment surface and the overlying water. This upward movement of the reduction zone is accompanied by a continuous decline in Eh throughout the stagnation period, leading to increasingly reducing conditions. During this phase, a pronounced microstratification develops within the SWI, which is enhanced by the dissolution of substances from the sediment. When the Eh reaches 0.2 V, Fe will be reduced by microbes and P becomes mobilized. Further intensification of reducing conditions to $\text{Eh} = -0.1 \text{ V}$ leads to the reduction of SO_4^{2-} to H_2S and elemental S (Schwoerbel & Brendelberger, 2022). This microstratification is indicative of the steep chemical gradients that develop in this zone, reflecting dynamic changes in the redox environment (Elster, 1955). In holomictic lakes, microstratification is disrupted during each complete circulation, leading to the partial re-precipitation of dissolved substances or their transport to higher water layers, such as silicon (Si) (Mortimer, 1941).

2. Theoretical Background

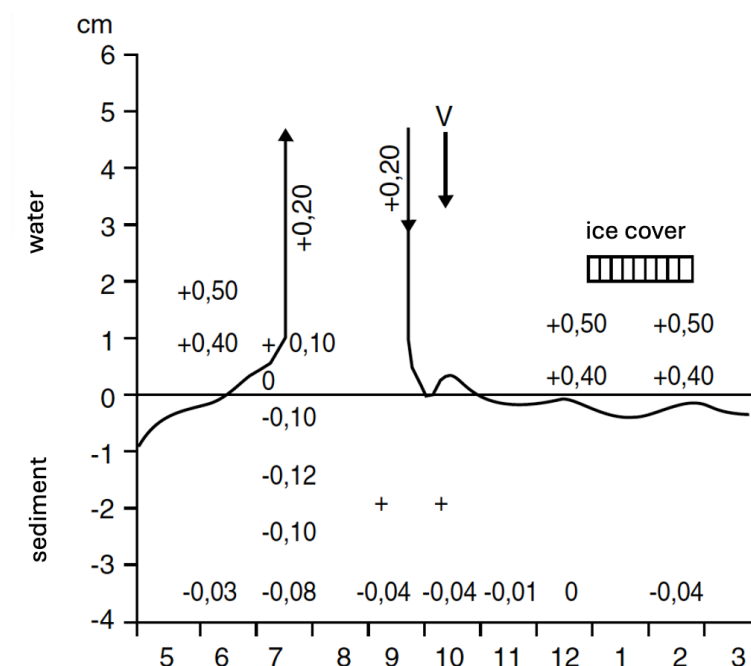


Figure 2.6.: Annual cycle of the 0.2 V Eh line in the SWI of an eutrophic lake. Numbers on the x-axis represent months (according to Mortimer (1941, 1942)).

Behaviour of Iron, Sulfur, and Phosphorus at the Sediment-Water Interface

The SWI is a crucial zone in the biogeochemical cycling of Fe, P, and S. The binding of these elements within sediments is a complex process influenced by various factors, including environmental conditions at the deposition site, the nature of the initial material, sedimentation rate, and prevailing redox conditions (Berner et al., 1993; Rothe et al., 2016; Ruttenberg & Berner, 1993).

In aqueous solutions, PO_4^{3-} often form complexes with H^+ and magnesium (Kubeneck, 2024). Additionally, PO_4^{3-} interacts with calcium (Ca) in calcium phosphate minerals such as hydroxylapatite, while PO_4^{3-} associates with Fe(II) and Fe(III) in iron phosphate minerals (Walton et al., 2023). PO_4^{3-} can also adsorb onto iron (oxyhydr)oxides and carbonate surfaces (Ruttenberg & Berner, 1993; Ruttenberg, 2003; Slomp et al., 1996). The release of PO_4^{3-} occurs through desorption reactions during the dissolution of minerals, making PO_4^{3-} available to microorganisms. The degradation of OM also releases bioavailable PO_4^{3-} , which can either be incorporated into microbial biomass or adsorbed by sediment components (Berner et al., 1993). The balance between biological PO_4^{3-} uptake, mineralization, weathering, co-precipitation, dissolution, and (de)sorption reactions regulates the PO_4^{3-} pool in sediments (Herndon et al., 2020).

Fe and P, mobilized under anaerobic conditions within sediments, tend to accumulate at the sediment surface under aerobic conditions through diffusion (Schwoerbel & Brendelberger, 2022). Studies by Tessenow (1972) have shown that P can be released up to a

depth of 6 cm, primarily affecting IP. The top sediment layer acts as a protective barrier, preventing the diffusion of Fe(II) and PO_4^{3-} into the overlying water as long as sufficient O_2 is present (Schönborn & Risse-Buhl, 2013). As long as the Eh in the sediment remains above 0.2 V, PO_4^{3-} remains bound to sediment particles and iron (oxyhydr)oxides with adsorbed PO_4^{3-} (Einsele, 1936; Golterman, 1995). However, if O_2 levels drop below 10 %, iron (oxyhydr)oxides will be reduced and dissolve into the pore water (Miller et al., 2001; Nriagu & Dell, 1974). Further decreases in O_2 concentration below 0.5 mg L^{-1} can cause a rapid release of PO_4^{3-} from the sediment (Frevert, 1980; Ostendorp & Frevert, 1979). In eutrophic lakes, the released amount can reach up to $12 \text{ mg m}^{-2} \text{ d}^{-1}$. Since Fe concentrations in the sediment are often too low to support significant iron (oxyhydr)oxides with adsorbed PO_4^{3-} formation, adsorption and desorption of PO_4^{3-} on sediment particles, influenced by Eh and pH, play a crucial role in P release (Thomas, 1973).

The adsorption and release of P are primarily governed by the equilibrium between the distribution of PO_4^{3-} between water and sediment (Twinch & Peters, 1984). Biological processes significantly influence this balance, as bacteria can release large amounts of PO_4^{3-} , and through decomposition, uptake, and synthesis of various substances, they can substantially alter conditions within the sediment (Gächter et al., 1988). Additionally, transport mechanisms at the sediment surface, such as wind-induced water movements and rising gas bubbles, promote the release of PO_4^{3-} (Boström et al., 1988; Enell & Löfgren, 1988). Macroorganisms living near the sediment surface, such as fish, tubificids, and *Chironomus* larvae, also contribute significantly to release processes and substance transformations through bioturbation (Frenzel, 1990; Van Rees et al., 1996; Weyhenmeyer, 1998). Eutrophic lakes are known to store large amounts of P in their sediments, with a significant portion of this P bound in OM (McMahon & Read, 2013). A substantial fraction of POP is stored as polyphosphate (poly P) within bacteria in the upper sediment layers (Hupfer et al., 1995). Under anaerobic conditions, heterotrophic microbes convert DOP and PolyP into DIP (Jassby et al., 1994).

These processes contribute to internal loading, where significant amounts of PO_4^{3-} are released during the summer, comparable to external inputs from inflows and wastewater. During complete lake mixing, however, PO_4^{3-} is not fully distributed throughout the water column; instead, under aerobic conditions, PO_4^{3-} is partially re-adsorbed as FeOOH P and settles to the lake bottom (Schönborn & Risse-Buhl, 2013). Consequently, sediment can act as a sink for PO_4^{3-} in aquatic systems by binding significant amounts and removing PO_4^{3-} from the water column (Lee, 1973; Riley & Prepas, 1984; Sondergaard et al., 2001). In the littoral zone of lakes, the release of PO_4^{3-} under aerobic conditions is more prevalent than in deeper zones. Submerged macrophytes influence sediment redox conditions by releasing O_2 through their roots. The formation of rising gas bubbles disrupts the sediment, enhancing the diffusion of PO_4^{3-} into the overlying water. Additionally, O_2 raises the sediment's redox potential, promoting the mobilization of PO_4^{3-} previously bound to iron (oxyhydr)oxides or other compounds. The sediments in the littoral zone are also characterized by higher porosity and OM content, further enhancing microbial decomposition and thus the release of PO_4^{3-} . In contrast, sediments in the deeper zones are denser and less permeable, leading to stronger binding of PO_4^{3-} under aerobic conditions. The reduced

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water movement in these deeper zones also contributes to the decreased mobilization of PO_4^{3-} (Bloesch, 1995; Pelegrí & Blackburn, 1996; Svensson, 1997; Weyhenmeyer, 1998). Dynamic redox conditions can also occur in eutrophic littoral sediments, which, depending on wind and wave conditions, can be exposed to both O_2 -rich epilimnetic water and anoxic hypolimnetic water (McMahon & Read, 2013). The release of P from sediments is just one part of the complex P cycle in lakes, where PP is continuously converted into dissolved P throughout the lake. In deep, stratified lakes, limited P availability due to sedimentation losses creates a cycle of release and uptake, with the hypolimnion acting as a temporary reservoir for deposited P. This release often occurs faster and on a larger scale than biotic uptake and frequently exceeds chemical precipitation processes, leading to seasonal accumulation of dissolved P in the deeper water layers. At the same time, the absence of light in these deeper layers prevents significant P uptake by phototrophic organisms, a process that is much more pronounced in the light-penetrated upper layers of the epilimnion.

In shallow lakes, P regeneration follows a similar process, but the lack of stable stratification, which contributes to P accumulation in deeper lakes, results in a different dynamic. In these systems, P release is not supported by seasonal accumulation, significantly affecting the dynamics of P availability and release, as illustrated in Figure 2.7. The temporary presence of a thin oxidized surface layer in sediments can influence short-term fluctuations in the P pool at the sediment surface but does not significantly impact long-term P binding. Over extended periods, P release is governed by an imbalance between P sedimentation and the binding capacity of anoxic sediment layers. P retention in lake sediments is highly dependent on sediment characteristics and land use in the watershed. The presence of redox-insensitive P binding systems, such as aluminum hydroxides and non-reducible Fe(III) minerals, can enhance P retention and prevent P release even under anoxic conditions (Hupfer & Lewandowski, 2008).

Iron (oxyhydr)oxide minerals are pivotal in the adsorption of PO_4^{3-} within sediments

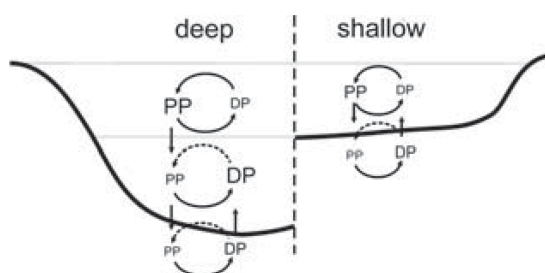
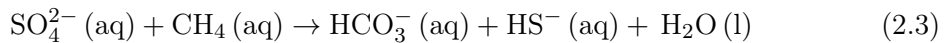


Figure 2.7.: The hypolimnion in deep lakes acts as a temporary sink for settled P, leading to seasonal accumulation, while in shallow lakes, the absence of a thermocline prevents P accumulation. In the epilimnion of shallow lakes, sedimentation-induced losses limit P availability, creating a direct pathway between release and uptake, DP = dissolved P, PP = PP (Hupfer & Lewandowski, 2008).

under oxic conditions (Cornell & Schwertmann, 2003; Kappler et al., 2021; Roden & Zachara, 1996). The effectiveness of these minerals in binding PO_4^{3-} is largely determined by their specific surface area and degree of crystallinity (Barron et al., 1988; Parfitt et al., 1975; Wang et al., 2013). Poorly crystalline iron (oxyhydr)oxides, such as ferrihydrite, exhibit a greater capacity for PO_4^{3-} sorption compared to more crystalline forms like goethite (Roden & Zachara, 1996; Williams et al., 1971). A solid-phase Fe/P molar ratio of approximately 2 has been identified as the critical threshold for the binding capacity of Fe(III) to PO_4^{3-} in Fe(III)-phosphate complexes (Gunnars et al., 2002). The crystallization of ferrihydrite into more stable iron (oxyhydr)oxides can reduce its PO_4^{3-} sorption capacity, thereby affecting the bioavailability of PO_4^{3-} (Kraal et al., 2020).

While iron (oxyhydr)oxides and the associated PO_4^{3-} are stable under oxic conditions, their stability is compromised under anoxic conditions. In the absence of O_2 , Fe(III) in iron (oxyhydr)oxides serve as an electron acceptor, leading to the reduction of Fe(III) to Fe(II) and the dissolution of these minerals (Mortimer, 1942). Released PO_4^{3-} can either diffuse into the overlying water, bind to more stable minerals like calcium carbonates and aluminum oxides, or contribute to the formation of authigenic PO_4^{3-} minerals such as vivianite, as illustrated in Figure 2.8. S has been identified as a key factor in the release of PO_4^{3-} . In the hypolimnion of eutrophic lakes, when H_2S is dissolved and S^{2-} is present in sediment, reducing conditions persist even with the introduction of O_2 during circulation (Hupfer & Lewandowski, 2008). S^{2-} , which competes with Fe(II) for P binding, originates from the decomposition of OM or the reduction of SO_4^{2-} at the SWI (Heinrich et al., 2022). Fe(II) reacts with S^{2-} to form insoluble FeS (pyrite), leading to the immobilization of Fe and S and the decoupling of the Fe and P cycles. As a result, less Fe is available for binding PO_4^{3-} , leading to the release of PO_4^{3-} from the sediment (Kubeneck, 2024; Ohle, 1964).

In underlying sediments, as the redox potential decreases further, the sulfate-methane transition zone (SMTZ) defines the boundary where SO_4^{2-} becomes increasingly depleted, and microbes utilize CH_4 as an electron donor and residual SO_4^{2-} as an electron acceptor in order to gain energy. This microbial process is known as anaerobic oxidation of methane (AOM) and displayed in Equation 2.3 (Schwoerbel & Brendelberger, 2022).



AOM is crucial for regulating CH_4 fluxes from sediments to the water column and has significant implications for the geochemistry of pore waters, particularly in the formation of minerals under sulfate-depleted conditions. Low SO_4^{2-} availability in the SMTZ limits sulfidic conditions, allowing Fe^{2+} to accumulate in the pore water instead of forming FeS_x species. Combined with PO_4^{3-} release, this creates conditions favorable for vivianite precipitation. Conversely, in sulfidic environments, Fe^{2+} is sequestered as S^{2-} , making vivianite formation less likely (Egger et al., 2015b; Heinrich et al., 2021; Kubeneck, 2024; Sivan et al., 2011). Various factors such as OM, S, Si, and C can influence the binding of P to Fe, as noted by Davison (1993), Hartikainen et al. (1996) and Kleeberg et al. (2013). These factors need further elaboration, as described in Heinrich et al. (2022).

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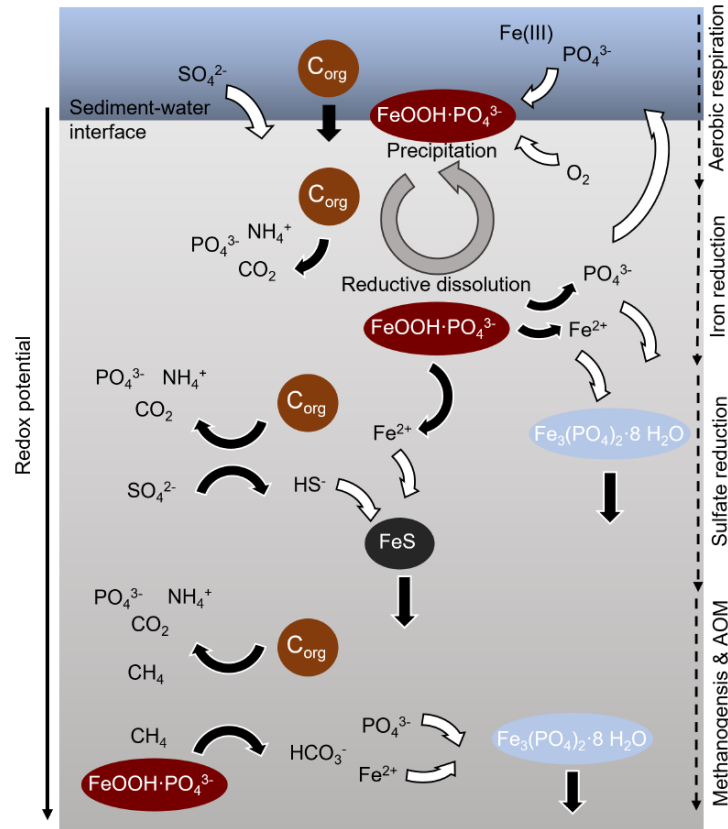


Figure 2.8.: Schematic representation of the interconnected Fe, S, and P cycles at the SWI. During microbial respiration of OM, O_2 is consumed first, followed by iron (oxyhydr)oxides, S, and finally, methanogenesis, as indicated by arrows on the right side. Ovals and circles denote solid phases, black arrows with white outlines indicate fluxes from solid phases and/or chemical reactions, and white arrows represent diffusion pathways. Abbreviation: Corg = OM (Kubeneck, 2024).

2.4. Vivianite in Lake Sediment

2.4.1. Significance and Characteristics of Vivianite

Lake sediments contain various minerals that play a crucial role in lakes' ecological and limnological processes. One of the most frequently occurring minerals in lake sediments is quartz, recognized for its high resistance to weathering and its ubiquity across various sedimentary environments. Another commonly present mineral is calcite, which can form as a result of biological processes or through chemical precipitation. Vivianite ($Fe_3(PO_4)_2 \cdot 8H_2O$), an iron phosphate mineral, and FeS both form under anoxic conditions when Fe and P or S are present.

2.4. Vivianite in Lake Sediment

These minerals are of significant importance to the biogeochemical processes in the lake, as they provide large surface areas that promote chemical reactions and microbial growth, thus influencing the adsorption and release of nutrients and pollutants (Heinrich et al., 2022). Vivianite plays a crucial role in biogeochemical processes, particularly in the context of the P cycle. Vivianite represents an effective mechanism for the long-term sequestration of P in sediments, thereby preventing the release of P into the water and contributing to the reduction of eutrophication in lakes (Heinrich et al., 2021). Thermodynamic models suggest that vivianite could reduce the concentration of dissolved PO_4^{3-} in soils and sediments to very low levels, within the range of a few mg L^{-1} , helping to maintain PO_4^{3-} levels below the thresholds that trigger eutrophication (Nriagu, 1972; Walpersdorf et al., 2013). Understanding the dynamics of vivianite can aid in the sustainable management of lakes through minimizing P release from sediments or improving P removal technologies in water treatment systems. Despite emerging evidence that vivianite can contribute to long-term P retention under reducing conditions, our understanding of its formation, composition, and stability in the environment remains incomplete (Heinrich et al., 2021, 2022; Rothe et al., 2016).

Vivianite, a member of the mineral group $(\text{M}_3(\text{XO}_4)_2 \cdot 8 \text{H}_2\text{O})$, where M represents a divalent cation such as Fe, Mn, magnesium, cobalt, nickel, or zinc, and X is either P or arsenic (Mori & Ito, 1950), is the most commonly occurring stable iron phosphate mineral in reducing sedimentary environments (Berner, 1981; Nriagu, 1972). Vivianite often occurs in the form of spheres, aggregates, or needles, ranging in size from a few micrometers to several centimeters (Henderson et al., 1984; Müller & Förstner, 1973; Taylor et al., 2008). Vivianite forms bluish-to-greenish crystals after contact with O_2 (as shown in Figure 2.9) within the monoclinic crystal system and belongs to the space group B2/m (Rouzies & Millet, 1993). In addition to Fe, vivianite often contains significant amounts of Mn and magnesium, which can substitute Fe within the mineral's crystal lattice. The presence of these trace elements provides insights into the surrounding geochemical conditions (Tessadri, 2000).

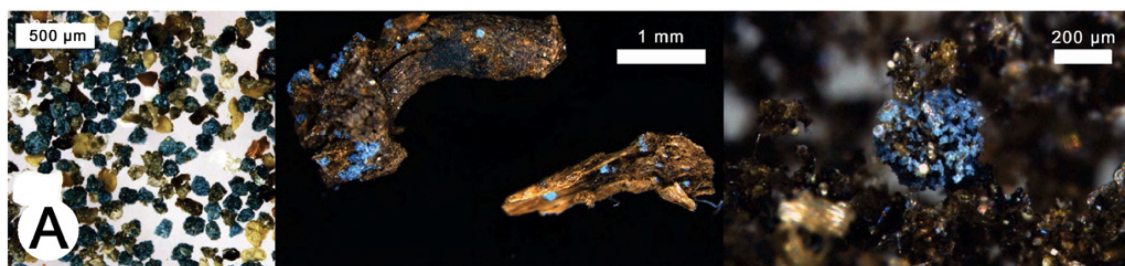


Figure 2.9.: Reflected light microscope images of vivianite nodules from surface sediments of three German lakes, from left to right: Lake Groß Glienicke, Polder Stangenhagen, and Lake Stechlin (Rothe et al., 2015, 2016).

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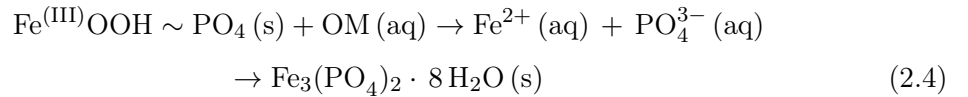
2.4.2. Occurrence and Formation of Vivianite

Vivianite is found globally in various aquatic freshwater and marine systems. In lake sediments, it is found in waters ranging from oligotrophic to eutrophic conditions. Additionally, it is prevalent in terrestrial habitats, including waterlogged soils, peatlands, wetlands, bogs, wastewater sludges, and hydrothermal deposits (Rothe et al., 2016). Vivianite has been found in Quaternary, post-glacial, modern, and near-surface deposits and is more frequently encountered in freshwater systems than in marine environments (Cosmidis et al., 2014).

Vivianite often coexists with a group of natural minerals that can serve as precursors to its formation. This group of minerals includes P minerals such as hydroxylapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) and anapaite ($\text{Ca}_2\text{Fe}(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$) (Stamatakis & Koukouzas, 2001), as well as Fe phases such as FeS_x , iron carbonates like siderite (FeCO_3) (Brauer et al., 1999; Suess, 1979), or iron silicates like limonite ($\text{FeO}(\text{OH}) \cdot n\text{H}_2\text{O}$) (Müller & Förstner, 1973). The formation of these minerals is strongly influenced by the properties of the porous and heterogeneous sediment structure (Rothe et al., 2016). Additionally, bacteria can act as crystallization nuclei, overcoming kinetic barriers to mineral formation (Sanchez-Roman et al., 2015). Thus, nucleation on a biological template can overcome the energy barriers more efficiently than mineral nucleation in a homogeneous solution.

The formation and stability of vivianite depend on several influencing factors (Burns, 1997; Egger et al., 2015a; Gächter & Müller, 2003). Environments, where vivianite occurs, are typically reducing, rich in Fe(II) and PO_4^{3-} , and low in HS^- . Vivianite crystals are often closely associated with OM, which promotes the development of reducing conditions while serving as a source of PO_4^{3-} (Nanzoy et al., 2010; Tessenow, 1974). Vivianite is also recognized as a biogenic mineral, formed through the metabolic activities of metal-reducing bacteria (Rothe et al., 2016). The reduction of iron(III) (oxyhydr)oxides, facilitated both abiotically and biotically, provides a source of Fe(II).

Iron(III) (oxyhydr)oxides play a crucial role in vivianite formation due to their ability to effectively capture PO_4^{3-} , although they are susceptible to microbial and chemical reduction (Melton et al., 2014). These compounds serve as a key source of Fe^{2+} and PO_4^{3-} , acting as essential precursors for the formation of vivianite, as shown in the schematic Equation 2.4. The reduction of sedimented iron(III) hydroxophosphate complexes and the rapid release of Fe under anoxic conditions are critical to the accumulation of Fe^{2+} and PO_4^{3-} , in the pore waters, which ultimately facilitates the precipitation of vivianite (Tessenow, 1974).



The mechanisms underlying vivianite crystal growth are not fully understood. Madsen and Hansen (2014) investigated synthetic vivianite formation in laboratory conditions, identifying spiral growth at low supersaturation levels and a combination of spiral and surface-nucleation growth at higher levels. Growth rates were reported between 0.2 $\mu\text{m/s}$

and 0.2 nm/s, indicating that vivianite nodules in sediments could develop within approximately six months, achieving sizes from 3 m to 30 mm, similar to those found in natural environments. However, understanding vivianite growth *in situ* remains complex due to interactions within sediment matrices, where microbial processes significantly influence nucleation and crystal development (Rothe et al., 2016).

While vivianite is thermodynamically unstable in the presence of HS^- (Nriagu, 1972), vivianite can still coexist with FeS minerals under certain conditions if the supply of Fe(II) exceeds the available HS^- (Dodd et al., 2003; Olsson et al., 1997; Rothe et al., 2015). A study by Heinrich et al. (2021) demonstrated that iron(III) (oxyhydr)oxide bound P, formed under oxic conditions at the SWI, can be converted to vivianite under anoxic conditions. This formation process occurred within 40 d in the experimental sediments, with approximately 70 % of the redox-sensitive P being transformed into redox-stable vivianite containing P (Heinrich et al., 2021).

Various environmental factors have been proposed to define the conditions favoring vivianite formation more precisely. The ratio of S to Fe is a critical determinant in vivianite formation, as it governs the availability of Fe^{2+} in pore water. Vivianite tends to develop in systems where S^{2-} production remains below the influx of Fe^{2+} , thereby preventing the depletion of Fe required for its precipitation (Berner, 1981; Gächter & Müller, 2003). A molar Fe/S ratio > 1 might indicate favorable conditions for vivianite formation in lake sediments (Canfield, 1989; Rothe et al., 2015). Such conditions are also typically found within and below the SMTZ, as described above and displayed in Figure 2.8 (Egger et al., 2015a; Slomp et al., 2013). Additionally, the molar $\text{Fe}/\text{PO}_4^{3-}$ ratio plays a role in vivianite formation. A theoretical ratio of 1.5 makes vivianite a very efficient phase for P sequestration (Kubeneck, 2024). A recent laboratory study showed that vivianite formed immediately at a molar $\text{Fe}/\text{PO}_4^{3-}$ ratio of 1.5, whereas no vivianite was formed under the studied conditions at ratios above 6 (Xiong et al., 2023).

Bacteria can influence mineral formation by altering their environment by adjusting ion concentrations and pH levels. This bacterial influence has both direct and indirect effects on the formation of vivianite in sediments. Directly, bacteria contribute to the supply of PO_4^{3-} , Fe(II), and S^{2-} by actively participating in the degradation of OM and utilizing electron acceptors such as Fe(III) and SO_4^{2-} . Indirectly, they influence redox conditions by consuming O_2 , NO_3^- , Fe(III), and other electron acceptors, leading to changes in conditions and CO_2 production, which lowers pH. These biological processes influence the saturation conditions in pore water, enabling the formation of secondary minerals (Suess, 1979; Vuillemin et al., 2013), and/or act as nucleation sites to overcome kinetic barriers (Sanchez-Roman et al., 2015). Nucleation on a biological template can thus occur before nucleation in a homogeneous solution (Rothe et al., 2016).

Vivianite formation has been linked to the activity of dissimilatory metal-reducing bacteria (DMRB), which couple the oxidation of OM with the reduction of Fe(III), as illustrated in Figure 2.10 (Glasauer et al., 2003; Zachara et al., 1998).

DMRB transformed hydrous ferric oxide into siderite and vivianite when Fe(II)-complexing ligands such as HCO_3^- and HPO_4^{2-} were present in the culture medium. Zachara et al. (1998) observed that biogenic vivianite and siderite formed through the

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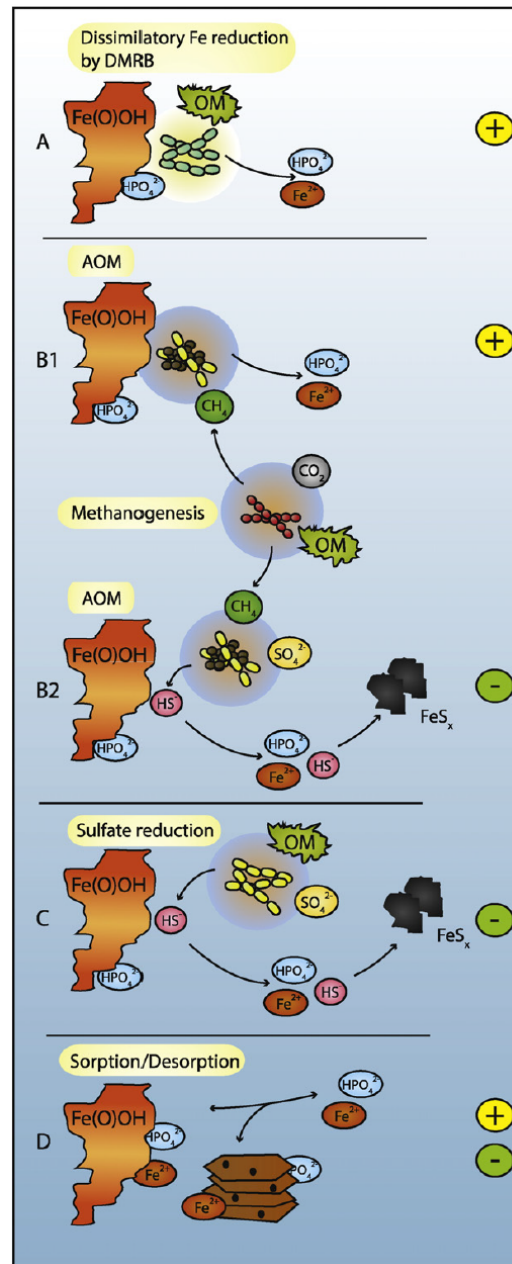


Figure 2.10.: Vivianite formation in cell-influenced microenvironments is influenced by (A) the reduction of Fe by DMRB and (B1) the anaerobic AOM with Fe facilitate the formation of authigenic vivianite. Conversely, processes that reduce Fe(II) concentrations in pore water, such as (B2) AOM with SO_4^{2-} and (C) SO_4^{2-} reduction, lead to the formation of FeS, thereby hindering vivianite formation. Additionally, (D) the sorption and desorption of Fe(II) and PO_4^{3-} on sediment particles can either lower or raise the concentrations of these ions in pore water, influencing vivianite formation (Rothe et al., 2016).

dissimilatory reduction of synthetic and natural Fe(II/III) oxides, with vivianite formation preceding that of siderite. A mechanism that may contribute to vivianite formation in sediments is AOM mediated by Fe, as described above and displayed in Figure 2.8. In reducing environments, CH₄ can be produced through methanogenesis and diffuse into upper sediment layers. There, microorganisms utilize CH₄ as an electron donor in a syntrophic partnership, using Fe(III) from iron(oxyhydr)oxides as electron acceptors to drive AOM (Egger et al., 2015b; Sivan et al., 2011). In sediments lacking HS⁻, this Fe-mediated AOM leads to an accumulation of Fe(II) and PO₄³⁻, supporting vivianite precipitation (compare Figure 2.10 B1 and B2). This plays a crucial role in the SMTZ, where formation of vivianite is likely to occur (Egger et al., 2015a; Jilbert & Slomp, 2013; Kubeneck, 2024).

In reduced sediment environments, vivianite remains stable if sufficient PO₄³⁻, Fe(II), and no excess S²⁻ are present in the pore water (Nriagu, 1972). When reactive Fe is bound by S²⁻ in the sediment, the Fe(II) concentrations are too low for vivianite formation. However, FeS_x and vivianite can coexist if sufficient Fe is available (Rothe et al., 2015). The formation of vivianite can be inhibited by free HS⁻ species, which are produced under prolonged anoxic conditions through microbial SO₄²⁻ reduction (compare Figure 2.10 C) (Nriagu, 1972). HS⁻ reacts with Fe(II) in the pore water, leading to the formation of insoluble FeS such as mackinawite, greigite, or pyrite (Berner, 1984; Rickard & Luther, 2007). Moreover, free HS⁻ facilitates the abiotic reduction of iron (oxyhydr)oxides, leading to further depletion of iron (oxyhydr)oxide supply. This corrosive process is influenced by factors such as pH and environmental conditions (Hansel et al., 2015). The reduced availability of iron (oxyhydr)oxides limits the binding of P through adsorption (Caraco et al., 1989; Roden & Edmonds, 1997). Furthermore, the formation of FeS minerals reduces the availability of Fe(II) for the precipitation of iron phosphate minerals such as vivianite (Egger et al., 2015a). Consequently, the ratio between free HS⁻ and the iron (oxyhydr)oxide supply plays a crucial role in P sequestration in reducing sediments (Kubeneck, 2024).

2.5. Profundal-Chironomid-Dynamics

2.5.1. Ecological Impact of Chironomids in Lake Ecosystems

The profundal fauna is influenced by nutrient conditions and O₂ concentrations in deeper waters, making the fauna a useful indicator of the metabolic state of a lake (Schwoerbel & Brendelberger, 2022). The family *Chironomidae* (commonly known as non-biting midges) is both highly diverse and widespread, with population densities up to 11,000 individuals per m² (Cranston et al., 1995; Mousavi, 2002).

In freshwater environments, *Chironomus* larvae often dominate the benthic invertebrate community and play a significant role in ecosystem productivity (Cranston et al., 1995; Mousavi, 2002; Wagner et al., 2012). They can contribute up to 50 % of the total secondary production in lakes, underscoring their importance in the benthic food web and the trophic structure of ecosystems (Armitage et al., 1995; Gratton & Zanden, 2009;

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Lindegaard, 1994).

When O₂ concentrations temporarily fall below a critical threshold or become completely depleted during summer stagnation, the profundal fauna becomes low in species diversity but high in individual abundance. *Chironomus* larvae, particularly of the genus *Chironomus*, can rapidly increase their populations under favorable conditions due to their short developmental cycles. In such scenarios, *Chironomus* larvae, along with oligochaetes from the genera *Tubifex* and *Limnodrilus*, dominate, leading to the characterization of these eutrophic systems as "Chironomus lakes" (Schwoerbel & Brendelberger, 2022).

Chironomids are particularly nutritious for fish, with a high caloric content (4.6-6.1 kcal g dw⁻¹), a high protein content (56 % of dw), and good digestibility (74 %) (Cummins & Wuycheck, 1971; Driver et al., 1974; Wagner et al., 2012).

Bioturbation refers to the mixing of sediments by organisms, such as insect larvae and worms, that move sediment particles through burrowing and feeding activities. These processes significantly influence sediment deposition and bacterial secondary production (van de Bund et al., 1994) and facilitate the transport of resting eggs to the SWI (Schwoerbel & Brendelberger, 2022). *Chironomus plumosus* larvae exhibit a particularly effective form of bioturbation. Their movements generate pumping rates of 57-70 mL h⁻¹, which can lead to the mixing of entire shallow lakes over several days (Roskosch et al., 2010). These larvae transport O₂, dissolved substances, and gases into their U-shaped sediment tubes (15-30 cm deep) (Hölker et al., 2015; van de Bund et al., 1994). The O₂ input creates complex redox gradients, reaching deeper layers than natural diffusion would allow (Lewandowski et al., 2007; Meile & Cappellen, 2003; Polerecky et al., 2006). The substantial pumping volume of *C. plumosus* is likely attributable to microbial oxygen consumption in the sediment, which, in turn, facilitates the intake of dissolved particles for feeding (Roskosch et al., 2011).

Therefore, the colonization of the profundal zone is closely tied to O₂ levels, benthic water movement, and the accumulation of OM. These factors interact with conditions in the trophogenic zone and lake depth, creating a strong connection between the profundal and pelagic zones (Jónasson, 1996).

2.5.2. Life Cycle of Chironomid Larvae

The life cycle of chironomids begins with the oviposition phase, where adult females lay their eggs in large, gelatinous masses either at the water's surface or attached to aquatic vegetation. These masses, which can contain hundreds to thousands of eggs, mark the initial stage of the larvae's development (Oliver, 1971). After a few days, the eggs hatch, and the larvae descend into the benthic sediments of lakes, rivers, or ponds.

As merolimnic organisms, chironomids experience a complex life cycle that bridges different habitats through various developmental stages (Wagner et al., 2012) as illustrated in Figure 2.11. The larvae go through four developmental stages, or instars, during which they molt multiple times. In these stages, they primarily consume OM, algae, and detritus present in the sediment. Adapted to low-oxygen environments, these larvae have evolved mechanisms to endure harsh conditions, such as reducing their metabolic rate or entering diapause — a state of suspended development until conditions improve (Wagner et al.,

2012).

The transformation to adulthood involves a dramatic metamorphosis from an aquatic larva to a terrestrial adult, mediated through the pupal stage. This stage, which can last from a few hours to several days depending on environmental factors such as temperature, water depth, and ascent speed (Oliver, 1971), typically begins shortly after ice melt and can persist until autumn. During this time, large swarms of nearly 100 species from the subfamilies *Tanypodinae* and *Chironominae* emerge, particularly in May and June (Armitage et al., 1995; Oliver, 1971). Species of the *Chironomus* genus,

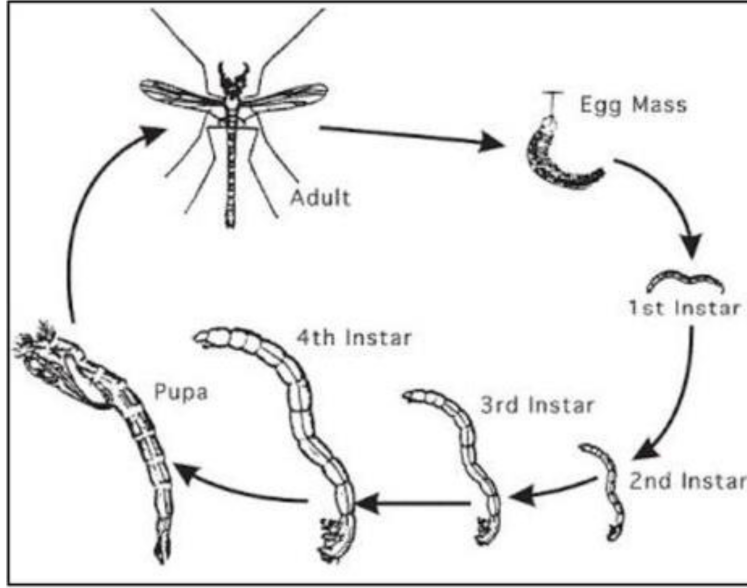


Figure 2.11.: Life cycle of *Chironomus* larvae from egg mass to adult (Karima, 2021).

particularly *C. anthracinus* and *C. plumosus*, can survive several weeks of complete O_2 deprivation by entering diapause until O_2 conditions improve. Alternatively, they reduce their metabolism to a minimum, deriving necessary energy from the fermentation of glycogen $((C_6H_{12}O_6)_n)$ to lactic acid $(C_3H_6O_3)$, alanine, succinate, and ethanol, as shown in Equation 2.5 (Frank, 1982; Wilps & Zebe, 1976).



Detailed experimental investigations on *C. anthracinus* in Lake Esrom, Denmark, have shown that under anoxic conditions at 10°C , after three days, only 50 % of the young larvae of the second and third instars survived; of the larger larvae of the fourth instar, 75 % survived after four weeks, but after seven weeks, only 10 % survived. Metabolism was reduced to 5 % during the first five days and to 1.5 % of oxidative energy gain between the 20th and 25th day, as evidenced by the depletion of glycogen reserves (Hamburger et al., 1995).

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This process of anoxibiosis requires a subsequent phase of intense O_2 uptake (recovery respiration) to oxidize the accumulated lactic acid and facilitate gluconeogenesis. Glycogen reserves in *Chironomus* larvae capable of anoxibiosis are significantly higher compared to those in species without gluconeogenesis ability, such as *Tanytarsus* larvae (Czeczuga & Bobiatynska-Ksök, 1968). At the end of the fourth larval stage, *Chironomus* larvae molt into pupae and typically remain at the lake bottom for several days (Wagner et al., 2012). Depending on the subfamily, they may stay in protective pupal cases (as in the *Chironomini*) or be partially free (as in the *Tanypodinae*) (Oliver, 1971). Just before emergence, the pupae fill with a gas bubble that separates the pupal skin from the developing adult, increasing buoyancy and facilitating ascent to the water surface (Armitage et al., 1995; Brackenbury, 2000).

Studies have shown that the ascent of chironomid pupae in standing waters often occurs synchronously, with peak emergence times mainly at dusk (Armitage et al., 1995). Once the pupae reach the surface, the adult insect emerges within 10-30 s (Brackenbury, 2000; Oliver, 1971). Once emerged, the adult *Chironomus* flies lead a short, terrestrial life primarily focused on reproduction. After mating, the females lay eggs again, thereby completing the life cycle (Mousavi, 2002).

2.5.3. Influence of Chironomid Larvae on Nutrient Transport

Chironomids actively pump oxygenated water through their burrows, significantly enhancing the O_2 concentration in the immediate vicinity. This localized O_2 concentration triggers a series of biogeochemical processes that can have widespread effects on sediment chemistry (Hupfer & Lewandowski, 2008).

Primarily, the increased O_2 levels stimulate nitrification, a microbial process where NH_4^+ is oxidized to NO_3^- . By enhancing nitrification, chironomids indirectly facilitate the transformation of N bound in the sediment into soluble forms, which can subsequently be released into the overlying water. Additionally, the bioturbation activity of chironomids can affect denitrification, a process in which NO_3^- is reduced under anoxic conditions to N_2 , which is then lost to the atmosphere. The constant alteration of redox conditions in the sediment caused by chironomid activities may lead to variability in denitrification, thereby impacting the overall N balance in aquatic systems (Brandes & Devol, 1995; Lewandowski & Hupfer, 2005). In eutrophic lakes, where elevated N levels contribute to algal blooms and O_2 depletion, the role of chironomids in regulating the N cycle becomes critical for maintaining water quality (Aller, 1994; Lewandowski & Hupfer, 2005). In sediments that lack macrozoobenthos, classical layered redox zonation is prevalent, where P is typically released through the dissolution of iron phosphates (Gächter & Müller, 2003). However, in sediments inhabited by chironomids, the classical layered redox zonation is significantly altered due to the biotic activities of *Chironomus* larvae. The introduction of O_2 by chironomids causes the oxidation of Fe(II) to iron (III) (oxyhydr)oxides, which leads to the co-precipitation of PO_4^{3-} . The co-precipitation reduces the concentration of soluble reactive phosphorus (SRP) in the pore water surrounding the burrows, thereby immobilizing PO_4^{3-} in the sediment and decreasing its availability in the overlying water column (Gunnars et al., 2002; Lewandowski et al., 2007; Lewandowski & Hupfer, 2005).

A study by Lewandowski et al. (2007) demonstrated that SRP concentrations near the burrows were significantly lower than in the surrounding sediment, with reductions of up to 56 %.

Furthermore, chironomids exert a significant influence on the S cycle by O_2 penetration into the sediment which consequently reduces SO_4^{2-} reduction rates. The decrease in SO_4^{2-} reduction leads to lower production of FeS, thus allowing more Fe(II) to remain available for oxidation to iron (oxyhydr)oxide. This iron (oxyhydr)oxide subsequently facilitates PO_4^{3-} binding. These interactions among S, Fe, and P cycles represent a key mechanism by which chironomids modulate biogeochemical processes within the sediment and are illustrated in 2.12 (Lewandowski & Hupfer, 2005). Under anoxic conditions, for example, when the aquatic larva undergoes metamorphosis, leaves its dwelling tube, and emerges as an adult, the chemical dynamics within the sediment change drastically. Fe(III) compounds that typically bind P are reduced to Fe(II) in anoxic conditions, resulting in the release of P that was previously immobilized and the possible formation of vivianite (Hupfer et al., 2019; Lewandowski & Hupfer, 2005; Roden & Edmonds, 1997). Furthermore, chironomids influence the composition and activity of microbial

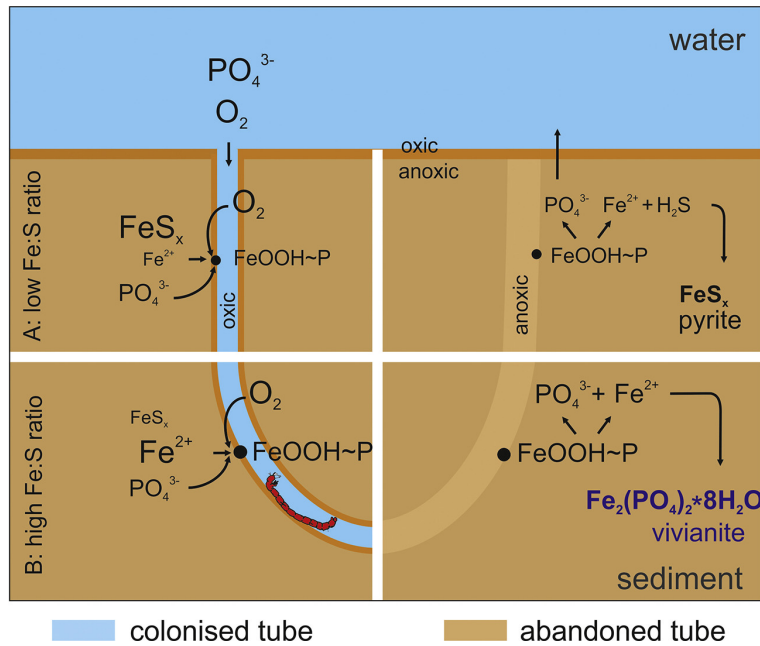


Figure 2.12.: The larvae's tube structures create oxic microzones where Fe(II) is oxidized to iron (oxyhydr)oxides (FeOOH), which effectively bind P. At a high Fe:S ratio, P is further stabilized under anoxic conditions as vivianite. In contrast, a low Fe:S ratio promotes the formation of FeS_x , reducing the availability of Fe for P binding and leading to potential P release. (Hupfer et al., 2019).

communities within the sediment, which in turn affects nutrient cycling. Their activities stimulate microbial activity, which mineralizes DOP, releasing PO_4^{3-} into the sediment

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pore water (Lewandowski & Hupfer, 2005; Tezuka, 1990). This released P can then diffuse into the overlying water where microbial decomposition of these nutrients further depletes O₂ levels. In eutrophic lakes, this can exacerbate O₂ depletion in the hypolimnion, enhancing conditions that favor anoxic processes such as SO₄²⁻ reduction and P release from sediments (Gächter & Müller, 2003; Lewandowski & Hupfer, 2005). The balance between these competing processes is crucial for maintaining the trophic equilibrium and ensuring the long-term water quality of a lake (Lewandowski & Hupfer, 2005).

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3.1. Overview of Experimental Setup

The experimental design, as depicted in Figure 3.1, investigated the effects of Chironomid larvae on P binding in lake sediments, with a particular focus on the formation of vivianite. Sediment samples with varying Fe content and Fe/S ratios were collected from Lake Müggelsee (MÜG) and Lake Arendsee (AR), while part of the MÜG sample was artificially enriched with Fe and P (MÜG Fe + P). These samples were introduced into acrylic glass aquaria and populated with *Chironomus plumosus* larvae and were regularly topped off with water from Lake Müggelsee to maintain a saturated system. The experiment included oxic and anoxic phases, after which the sediments were analyzed for their chemical composition and mineral formation. Following a 29 d oxic incubation period of

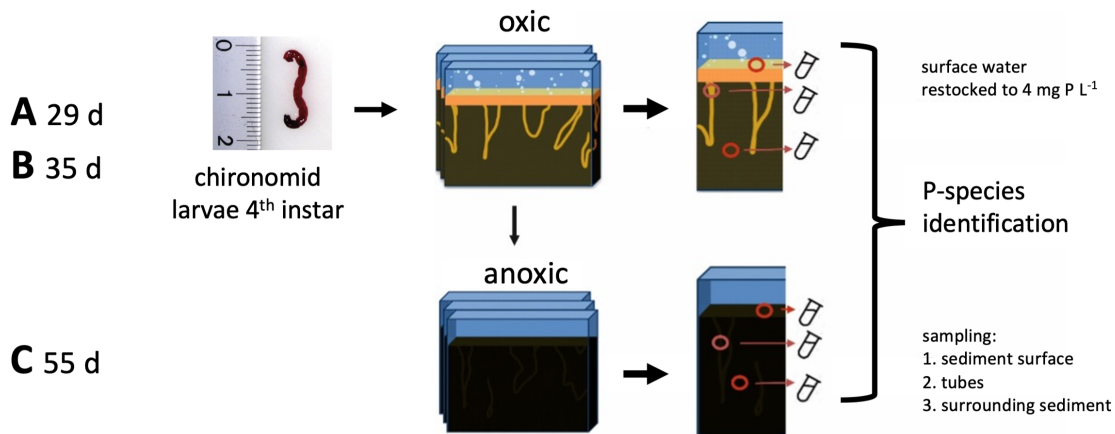


Figure 3.1.: Overview of the experimental design modified after Hupfer et al. (2019) with Chironomid-populated sediments and P-restocked water. Following incubation periods of 29 d for Part A, 35 d for Part B (oxic) and 119 d for Part C (anoxic), sediment surfaces, tubes, and surrounding sediments were collected and analyzed respectively.

experiment Part A, duplicate samples of each sediment type, MÜG, AR and MÜG Fe + P, were collected and analyzed, encompassing oxidized sediment surfaces, material along living tubes, and surrounding anaerobic sediments (sample numbers **6 - 14**). The sampling process was repeated after an additional 35 d under O₂ supply (Part B), collecting the samples **15 - 23** subsequently. In the following anoxic phase, after 101 d of Part C,

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each sediment type was sampled by collecting the material around the now abandoned tubes. Samples **24-26** were secured for microscopic vivianite identification and X-ray diffractometry (XRD) analysis. At day 119, duplicate samples from each sediment type were obtained and analyzed (sample numbers **27-35**), encompassing oxidized sediment surfaces, material along dead tubes, and surrounding anaerobic sediments. All findings are presented as individual values for specific sediment layers or as mean values for sediment types and their sampling procedure is illustrated in Appendix A.3.

3.2. Study Sites

The basic characteristics of the study sites, Lake Müggelsee and Lake Arendsee, are presented in Table 3.1 below.

Table 3.1.: Basic characteristics of Lake Müggelsee and Lake Arendsee, modified from Hupfer et al. (2019) and Shatwell and Köhler (2019).

Parameter	Lake Müggelsee	Lake Arendsee
Position (North, East)	52.4387°, 13.6517°	52.8906°, 11.4768°
Area [km ²]	7.3	5.14
Max depth [m]	8	49
Mean depth [m]	4.9	29.5
Mixis type	polymictic	dimictic
External P load [g m ⁻² yr ⁻¹]	2.8	0.30
TP [µg L ⁻¹]	150	186

3.2.1. Lake Müggelsee

Lake Müggelsee, situated in Berlin, Germany, is a shallow, polymictic lake. Covering an area of roughly 7.3 km², the lake has an average depth of 4.9 m and reaches a maximum depth of 8 m, as displayed in Figure 3.2. The River Spree, which drains a catchment area of about 7,000 km² comprising 36 % forest and 42 % agricultural land, primarily feeds the lake. Lake Müggelsee’s catchment area supports a population of approximately 720,000 people (Shatwell & Köhler, 2019).

The lake shows significant seasonal variations in nutrient levels, particularly in N and P. Historically, high nutrient loads resulted in severe eutrophication. However, long-term monitoring from the late 1970s to 2016 has documented a significant reduction in both N and P inputs, mainly due to enhanced wastewater treatment and improved agricultural practices (Shatwell & Köhler, 2019).

Despite these reductions, internal nutrient dynamics are crucial to the lake’s ecology. SRP levels are generally low in winter and spring due to reduced biological activity and limited sediment mobilization. In contrast, SRP levels rise considerably in summer, driven by the increased release of P from sediments, influenced by higher temperatures and enhanced biological activity (Gächter & Müller, 2003; Lewandowski & Hupfer, 2005).

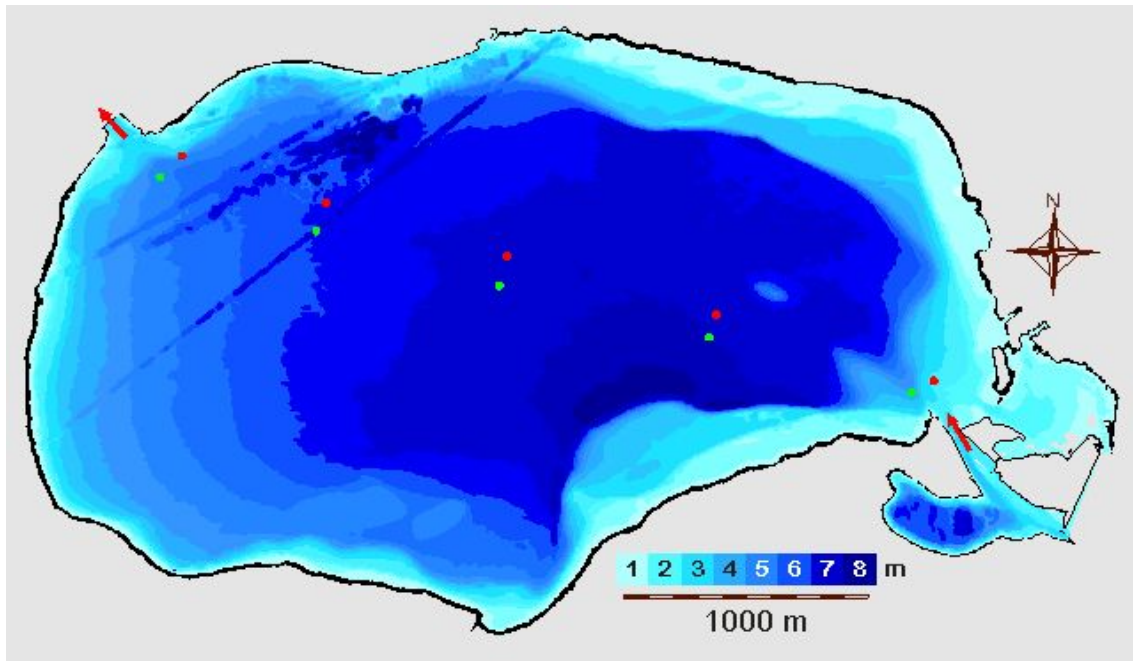


Figure 3.2.: The bathymetric map of Lake Müggelsee reveals a bowl-shaped depth profile, with maximum depths reaching 8 m in the central region and an average depth of 4.9 m. Shallower areas are predominantly located along the northern shores. Organic sediment deposits and the glacial origin of the lake contribute to this depth distribution (IGB, n.d.).

Lake Müggelsee hosts a diverse community of aquatic organisms, including phytoplankton species and benthic invertebrates such as Chironomid larvae. These larvae, with densities ranging from 500 to 2,000 individuals per square meter as indicated in studies from 2014 and 2015, play a vital role in bioturbation, facilitating nutrient cycling within the lake's sediment and water column, which significantly impacts the overall nutrient dynamics of the lake (Baranov et al., 2016; Roskosch et al., 2010).

3.2.2. Lake Arendsee

The presented map in Figure 3.3 illustrates both the surface and subsurface catchment areas of Lake Arendsee, as well as the land use in its vicinity. The surface watershed of Lake Arendsee covers 29.5 km², predominantly used for agriculture (52.1 %) and forestry (30.6 %). The town of Arendsee is situated on the lake's southwestern shore. The detailed bathymetry of Lake Arendsee shows depth contours at 10 m intervals, with the deepest point marked as the primary sampling station. The groundwater flow is depicted moving from the southeast to the northwest, passing through the town of Arendsee before discharging into Lake Arendsee. The total external P input is estimated at 1560 kg per

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year, with over half originating from P-enriched groundwater flowing beneath the town (Meinikmann, 2017).

Lake Arendsee is a dimictic hard-water lake located in northern Germany exhibiting significant hypolimnetic O₂ depletion towards the end of summer due to stratification (Rothe et al., 2016). Lake Arendsee spans an area of 5.14 km², with a maximum depth of 49 m and an average depth of 29 m (Lewandowski & Hupfer, 2005). Historically, the lake was solely groundwater-fed; however, Lake Arendsee is currently influenced by four ditches draining surrounding agricultural lands and an artificial outflow channel that transports water out of the lake.

Since at least the mid-20th century, Lake Arendsee has been classified as severely eutrophic (Scharf, 1998). Over the past forty years, the annual average TP content has seen a slight increase, currently reaching approximately 27.3 t, which corresponds to a TP concentration of 184 mg L⁻¹, with the epilimnetic TP concentration being 96 mg L⁻¹ during the growing

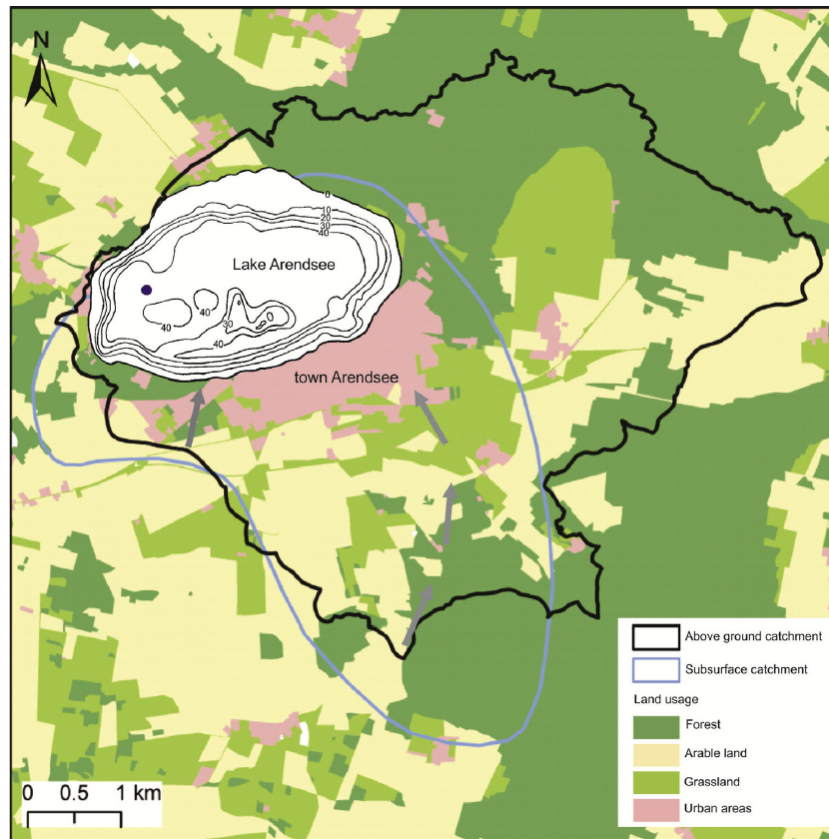


Figure 3.3.: The map illustrates the subsurface and surface catchment area of Lake Arendsee, along with its usage structure. Groundwater flows from southeast to northwest, passing through the town of Arendsee before reaching the lake with highlighted primary sampling station at the lake's deepest point (Hupfer et al., 2016; Meinikmann, 2017).

season. While seasonal variations in TP within the water column are relatively minor, there is notable vertical P redistribution during summer stratification, characterized by P release from the epilimnion and subsequent accumulation in the hypolimnion. The water quality is compromised by low transparency and frequent phytoplankton blooms, primarily dominated by cyanobacteria such as *Planktothrix rubescens* and nitrogen-fixing species like *Anabaena* (Meinikmann, 2017). Consequently, the lake's ecological status is considered poor, failing to meet the standards set by the EU Water Framework Directive (WFD) (Spears et al., 2013). Since the 1970s, a continuous decline in dissolved O₂ levels in the hypolimnion has been observed. Between 1976 and 1980, the volumetric O₂ concentration in depths of 20 to 48 m averaged 4.76 mg L⁻¹, dropping to 1.83 mg L⁻¹ between 2010 and 2014. The boundary of the layer with less than 2 mg L⁻¹ O₂ shifted from 42.4 m to 33.3 m during this time (Shatwell et al., 2013).

The sediment composition of Lake Arendsee has been thoroughly investigated. Sediment cores collected from the deepest point of the lake between 2000 and 2014 reveal a significant vertical gradient of TP, with higher concentrations in the upper layers. The mobile P pool in the sediment ranges between 0.84 g m⁻² and 1.47 g m⁻² (Lewandowski & Hupfer, 2005).

3.3. Preparations

3.3.1. Sampling Procedure

Sediment cores from Lake Müggelsee and Lake Arendsee were extracted using a USC 06000 corer (UWITEC, Mondsee, Austria), facilitating precise extraction of the desired horizontal level. Dark brown sediment samples, emitting a S²⁻ odor, were collected from Lake Müggelsee's upper layer (0-15 cm depth) at 7 m water depth, using 18 cores with a diameter of 6 cm each (52°440118' N, 13°659285' E). Additional 35 L sediment from Lake Müggelsee was collected using an Ekman Birge sediment grab sampler (HYDRO-BIOS Apparatebau GmbH, Kiel-Altenholz, Germany).

Light brown, more liquid sediment cores with a similar S²⁻ odor, as illustrated in Figure 3.4, were obtained from Lake Arendsee's 0-10 cm layer (11 cores, 6 cm diameter) at 48 m wdpt (52°889826' N, 11°460540' E). The artificial calcite layer deposited during a restoration attempt in 1995 by Hupfer et al. (2000), prevented the collection of deeper sediment layers.

3.3.2. Sediment Preparation

Subsequently, all sediment cores from each lake type were mixed and sieved through a 1 mm mesh to remove macrozoobenthos. After sieving, *Chironomus plumosus* larvae (4th instar, approximately 2 cm in length) were collected from the Lake Müggelsee sediments. To enhance the potential for vivianite formation during the experiment, the sediment from Lake Müggelsee was enriched with an iron-phosphate slurry (Fe-P slurry). The enrichment was accomplished using amorphous Fe(III) hydroxide powder (Fe(OH)₃), FerroSorp[®] Plus (HeGo Biotec, Fe content of 40 %,) and sodium hydrogen phosphate

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Figure 3.4.: Left: Sampling from a boat by operating a winch to retrieve sediment cores from the bottom of Lake Arendsee. Right: Sediment with annual varves.

($\text{NaHPO}_4 \cdot \text{H}_2\text{O}$). FerroSorp[®] Plus represents an adsorbent granulate engineered for the efficient removal of contaminants from water. FerroSorp[®] comprises chemically highly reactive $\text{Fe}(\text{OH})_3$ as its primary constituent, conducive to the sequestration of arsenate, PO_4^{3-} , or S^{2-} ions within aqueous environments.

Following the method described by Heinrich et al. (2021), 60 g FerroSorp[®] Plus was ground using an agate mortar, and suspended in a solution of ultra-pure water (300 mL) containing $\text{NaHPO}_4 \cdot \text{H}_2\text{O}$ (59.6 g). The suspension was mixed for 2 d to achieve adsorption equilibrium. After centrifugation, the supernatant was removed, and the FerroSorp[®] powder with adsorbed P was washed ten times with ultra-pure water to remove dissolved P from the solution.

To determine the loading of P onto the amorphous $\text{Fe}(\text{OH})_3$ powder, an initial test experiment (MÜG Fe + P Test) was conducted by mixing 1.92 g of Fe-P slurry with 41.3 g of wet sediment from Lake Müggelsee (3.72 g dw) resulting in a loading of 96 mg P g dw⁻¹ and a molar Fe/P ratio of 2.7 (vivianite has a Fe/P ratio of 1.5).

Subsequently, 159 g of wet prepared Fe-P slurry (77.9 g dw) was added to 3.5 L of wet sediment (346 g dw) collected from Lake Müggelsee to achieve a loading of 111 mg P g dw⁻¹ and a molar Fe/P ratio of 2.6 for MÜG Fe + P sample. The loading was determined using equation 3.1, based on their dw. The initial TP content of MÜG was 2.35 mg g dw⁻¹, and after loading, MÜG Fe + P exhibited a TP content of 22.1 mg g dw⁻¹.

$$\text{Loading} = \frac{m(\text{P})_{\text{MÜG Fe + P}} (m_{\text{MÜG}} + m_{\text{Fe-P slurry}}) - m(\text{P})_{\text{MÜG}} \cdot m_{\text{MÜG}}}{m_{\text{Fe-P slurry}}} \quad (3.1)$$

$$\text{Loading}_{\text{MÜG Fe + P}} = \frac{22.1 \frac{\text{mg}}{\text{g dw}} (346 \text{ g} + 77.9 \text{ g}) - 2.35 \frac{\text{mg}}{\text{g dw}} \cdot 346 \text{ g}}{77.9 \text{ g}} \approx 111 \frac{\text{mg}}{\text{g dw}}$$

The sediments were homogenized and analyzed thoroughly according to the described methods in Section 3.5 and stored in darkness at 16 °C until utilization.

3.4. Mesocosm Setup

Before commencement, three PVC containers, each with a capacity of approximately 28 L, were bespoke by the company RELI KUNSTSTOFFE Gerhard Reinhold e.K. (Erkner, Germany). These containers, characterized by internal dimensions of 49.3 x 22.3 x 25.5 cm, were outfitted with fixtures to each accommodate nine transparent acrylic glass aquaria (internal dimensions 20 x 17 x 1 cm, 340 mL) and are displayed in Appendix A.1. The dimensions of the aquarium glasses, with a width of 1 cm, allowed for easy visualization of the tubes constructed by chironomids. Additionally, they facilitated handling during the sampling of sediment aquaria and enabled clear identification of the different sampling areas, including the sediment surface, tube structures, and surrounding sediment.

The interstitial spaces between the acrylic glass aquaria were filled with 35 L of sediment from Lake Müggelsee across all three containers to prevent O₂ ingress through potential micro-cracks. Each container housed nine acrylic glass aquaria (shown in Appendix A.2) filled with the sediment samples MÜG, AR, and MÜG Fe + P respectively and the whole system was topped with water sourced from Lake Müggelsee to regulate O₂ intake solely through the surfaces.

3.4.1. Oxidic Incubation: Part A and B

Each acrylic aquarium was inhabited by two to three 3rd to 4th instar larvae of the species *Chironomus plumosus* which represents a larvae density of 1,000 to 1,500 individuals per m². Lake water was then carefully added to each aquarium, covering the sediment with a 3 cm layer, to avoid resuspension. The larvae began constructing tunnels immediately upon contact with the sediment surface. The experiment was conducted at T = 16 °C in complete darkness. Throughout the experiment, aeration of the overlying water in each aquarium was performed individually using plastic tubes, secured under the aquarium lids.

In natural lake environments, P is deposited into sediments through sinking OM (seston) and is released back into the water column during decomposition (Hupfer et al., 2019). To ensure sufficient P levels for the three simulated lake conditions using sediments from MÜG, AR, and MÜG Fe + P, the supernatant water was treated approximately every three days with an aqueous solution of NaHPO₄·H₂O to maintain $c(\text{SRP}) \approx 4 \text{ mg L}^{-1}$. Daily variations in P levels were monitored regularly in all containers using the ammonium molybdate method spectrophotometrically. Periodically, the depth of the tunnels constructed by the larvae was measured by carefully lifting individual aquaria from the surrounding sediment.

After 29 d of oxidic incubation (Part A), two acrylic glasses were removed from each

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sediment type in the containers. Samples of the two aquaria were collected from the oxidized sediment surface, the tunnel walls, and the surrounding anoxic sediment using a pipette syringe and combined to one homogeneous sample. The 1 cm thickness of the acrylic glasses made it easy to identify the chironomid tunnels by their light brown color, contrasting with the dark brown non-oxidized sediment, facilitating sampling from the tunnel walls. The glasses were then returned to their original positions.

After an additional 36 d, on day 64, another two acrylic glasses were sampled from each sediment type following the same procedure. For Part B of the experiment, samples were carefully taken again from the oxidized surface, tunnel walls, and surrounding sediments.

3.4.2. Anoxic Incubation: Part C

After 64 d, the anoxic phase, Part C of the experiment, began. Before altering the experimental parameters, the light-brown tubes of the chironomids of the remaining acrylic boxes of each sediment type were marked on the outer glass with a felt-tip pen. Subsequently, the aeration tubes and lids were removed from each acrylic box. P additions to the overlying water were also stopped, and the three containers with the different sediment types were incubated in darkness at 16 °C for an additional 119 d.

On day 101, one acrylic box from each container was removed, and the tube walls were sampled. These samples were immediately freeze-dried for vivianite formation analysis. Two acrylic boxes from each container were sampled as previously described on day 119. Using a pipette, samples were collected from the sediment surface, the now dark-brown abandoned tube walls, and the surrounding sediment, distinguishable by the previous felt-tip markings and a slightly brighter brown tone.

3.5. Analytical Methods

The collected sediments MÜG, AR and MÜG Fe + P underwent comprehensive chemical analyses to determine dry weight (dw), loss on ignition (LOI), P-fractions, their elemental composition, and present minerals.

The determination of dw and LOI was conducted using gravimetric methods (Sartorius research R 160 P, Sartorius). Initially, a defined quantity of the sample was weighed and then dried in an oven at a temperature of 105 °C until a constant mass was achieved. Subsequently, the sample was reweighed, and the dw content was calculated by subtracting the dried sample's mass from the original sample's mass.

For the determination of LOI, a specific amount of the dried sample was weighed and then heated in a muffle furnace at 450 °C to decompose organic and inorganic components or remove volatile compounds following Kleeberg et al. (2013). After cooling, the sample was reweighed, and the LOI was calculated by subtracting the initial heated sample's mass from the original sample's mass. LOI was expressed as a percentage of the original mass.

Following sequential P extraction, each fraction's $c(P)$ was determined using ammonium molybdate spectrometry (EN ISO 6878). The ammonium molybdate spectrometry method

required a photometer and a precision cuvette made of special optical glass (type 100-OS, 50 mm path length). The concentrations of the samples were then calculated using a calibration curve generated from P standards with known concentrations.

The sequential P extraction, outlined by Psenner et al. (1984) and modified by Hupfer et al. (1995), is suitable for examining sediments with high organic content and aims at the most distinct definition of individual organic and inorganic P fractions. Through the application of various reagents, extractions, and digestions of the components of the sediment separated by centrifugation, a separation procedure is conducted. This method leads to the classification of P into different categories, as displayed in Table 3.2.

Category	P Species
NH ₄ Cl TP	Loosely adsorbed P and P present in pore water
BD TP	Reductively soluble P, mainly bound to Fe hydroxides
SRP	Soluble reactive P, mainly Fe or aluminum oxides and vivianite
NRP	OM and poly P
HCl TP	P bound in carbonates and apatite
Rest TP	Difficultly degradable, unavailable P

Table 3.2.: Classification of different P species into different categories according to extraction method of Psenner et al. (1984) as adapted by Hupfer et al. (1995).

The fractions were identified based on the specific extracting agents used. Loosely adsorbed P and P in pore water were extracted using a N₂-saturated 1 M ammonium chloride solution (NH₄Cl TP). Reductively soluble P, mainly bound to Fe hydroxides, was extracted with a 0.11 M bicarbonate/dithionite solution (BD TP). Both of these fractions were analyzed after digesting TP with potassium persulfate. The fraction extracted with 1 M sodium hydroxide (NaOH) was divided into SRP and non-reactive P (NRP). NRP was calculated as the difference between TP (after digestion with potassium persulfate) and SRP. NaOH-SRP represented directly measurable soluble reactive P, which is associated with Fe or aluminum oxides (Psenner et al., 1984) and vivianite (Rothe et al., 2015). On the other hand, NaOH-NRP included non-reactive P released from OM and polyP. P bound in carbonates and apatite was extracted using 0.5 M hydrochloric acid (HCl TP) and determined after TP digestion. Finally, refractory P was measured following the digestion of the remaining sediment (Rest TP).

$c(\text{Fe})$ and $c(\text{Mn})$ in the BD and HCl extracts were determined using flame atomic absorption spectrometry (German standard methods DIN 38406 and EN ISO 12020). Before measurement, the samples were appropriately diluted and calibrated using standards of known concentration.

Additionally, aqua regia digestion serves to dissolve mineral and soil specimens, followed by inductively coupled plasma optical emission spectrometry (ICP-OES) analysis to measure the present metals.

The ARD (DIN EN 16174) leads to the extraction of most of Fe phases from the sediment, except for Fe bound in silicates, which remain non-reactive during early diagenesis (Rothe

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et al., 2015). Initial steps involved the weighing and transference of the samples 105 °C dried samples into Teflon vessels, subsequently subjecting them to 36 % hydrochloric acid and 65 % nitric acid (volume ratio 1:3). Following acid infusion, vessel sealing and preparation for microwave treatment (MLS GmbH; Leutkirch; Germany) ensured. Leveraging microwave technology facilitated swift and efficient execution of the digestion process, characterized by meticulously controlled temperature and microwave power parameters. The metals Al, Ca, Cu, Fe, K, Mg, Mn, Na, P, Ti, S, and Zn were determined in solid samples using ICP-OES (CAP 7000 series, Thermo Fisher Scientific Inc., Waltham, USA, DIN EN ISO 11885 (E 22) from September 2009).

The determination of C, N, and S in 105 °C dried sediments was carried out using a CNS elemental analyzer (Vario EL cube, Elementar Analysensysteme GmbH, Langenselbold, Germany) employing the high-temperature decomposition method (DIN ISO 13878:1998-11, DIN ISO 15178:2001-02). In the decomposition method, the sample is heated in a furnace, causing the thermal decomposition of organic compounds and the release of elements as gaseous compounds. These gases are then passed through an infra red detector to measure their concentrations.

XRD analysis of freeze-dried and pulverized (with XRD-Mill McCrone, Retsch GmbH, Haan, Germany) samples was employed to ascertain the presence of vivianite and other minerals such as calcite, quartz and pyrite. XRD examinations were conducted using a Bruker D2Phaser, equipped with a Cobalt X-ray source and an SSD160 detector with a 12 mm active length. The angular range was 10 to 90 ° 2 θ , utilizing a rotating sample platform at 10 rotations per minute. The configuration incorporated a step size of 0,0133 ° 2 θ , with a measurement duration of 0.6 s per step. The apparatus was outfitted with a 1-mm fixed divergence slit, primary and secondary Soller collimators at 2.5 °, a static knife edge 3 mm above the sample, and a 2.5 mm Fe k-beta filter. Phase identification was performed using the DIFFRAC. EVA V5.2 software by Bruker referencing the Crystallography Open Database, as reported by Gražulis et al. (2009).

4. Results and Discussion

4.1. Preliminary Results

The sediment composition of Lake Müggelsee and Lake Arendsee, as presented in Table 4.1, highlights the unique environmental conditions of these lakes, as described in Section 3.2. The samples MÜG and AR underwent comprehensive chemical analysis before use, as detailed in Section 3.5, and are compared here with literature data from Hupfer et al. (2019). The parameters include the contents of Ca, Fe, Mn, S, and TP in mg g dw^{-1} , as well as the molar Fe/P and Fe/S ratios and OM content.

Table 4.1.: Physiochemical differentiation of the utilized sediment types MÜG, AR and MÜG Fe + P at day 0 and available literature values from Hupfer et al. (2019): Contents of Ca, Fe, S, and TP in mg g dw^{-1} , molar Fe/P and Fe/S ratios, and OM content, determined as LOI at 450°C with errors. The literature values for Lake Müggelsee pertain to the sediment horizon of 0-10 cm, whereas the horizons used in the experiment encompass 0-15 cm, * refer to significant deviations of $> 5\%$.

Parameter	MÜG	MÜG _{Lit}	AR	AR _{Lit}	MÜG Fe + P
Ca	114±0	120	216±1	164	103±0
Fe	67.3±0.2	64.3	6.30±0.02	13.3	102±0
S	12.8±0	9.3	7.61±0.15	17.9	11.1±0.1
TP	2.35±0.01	3.30	1.23±0.03	2.52	22.1±0.1
Fe/P ratio	15.9±1.3*	10.8	2.8±0.6*	2.9	2.6±0.3*
Fe/S ratio	3.0 ±0.1	4.0	0.5±0.1*	0.4	5.3±0.5*
OM [%]	25.9±0	22.8	22.5±0	24.1	23.8±0

The notably higher Ca content of 216 mg g dw^{-1} in the AR sample in contrast to 114 mg g dw^{-1} in the MÜG sample is indicative of a hard-water lake. The Ca content in AR deviates by 24 % from the literature value, while the Ca content in MÜG exhibits only a 5 % deviation from its corresponding literature value. The variation might be attributed to changes in sediment composition at the time of sampling due to seasonal fluctuations. The Fe content is a key differentiator among the sediments, with MÜG displaying a tenfold higher value compared to AR. The artificially enriched MÜG Fe + P sediment exhibits an even higher Fe content of 102 mg g dw^{-1} , reflecting the experimental treatment designed to enhance vivianite formation potential. TP content is notably higher in the enriched MÜG Fe + P sediment ($22.1 \text{ mg g dw}^{-1}$), as expected from the Fe-P slurry treatment, compared to the natural MÜG and AR sediments. The TP content in the MÜG sediment shows a

4. Results and Discussion

deviation of 29 % from the literature value, which may be attributed to differences in the sampled sediment horizon (0-15 cm in the experiment versus 0-10 cm in the literature). The molar Fe/P ratio in the MÜG sediment is higher than the literature value and the AR sediment. While the high Fe/P ratio indicates a greater availability of Fe for potential binding with P, the higher ratio might not be optimal for vivianite formation, which is most favorable at a molar Fe/P ratio between 1.5 to 2.5. A high Fe/P ratio could lead to the formation of other Fe minerals or phases instead of vivianite such as Fe oxides or the favorable adsorption of PO_4^{3-} onto Fe(III) oxyhydroxides. The adsorption results in less P being available for forming vivianite, which can inhibit vivianite formation (Rothe et al., 2016). Conversely, if the Fe/P ratio is too low, there may not be sufficient Fe available to bind with P to form vivianite. The AR sediment and the artificially enriched MÜG Fe + P sample have a Fe/P ratio closely aligning with the theoretical Fe/P ratio of 1.5 in vivianite (Kubeneck, 2024). With a Fe/S ratio of 3.0, MÜG is more favorable for vivianite formation compared to AR with 0.5, which favors the formation of FeS and reduces the availability of Fe for vivianite formation. AR sediment was chosen to provide a comparative perspective on sediment conditions less conducive to vivianite formation. On the other hand, the artificially enriched MÜG Fe + P sediment exhibits an even higher Fe/S ratio of 5.3, indicating a lesser likelihood of Fe being sequestered as S^{2-} and enhancing its potential for vivianite formation. However, an excessively high Fe/S ratio could also lead to the formation of other Fe oxides or hydroxides as mentioned above, potentially limiting vivianite formation. OM content, determined by LOI, is relatively consistent across the sediment types, with slight variations that could influence the redox conditions and microbial activity in the sediments. OM content is highest in the MÜG sediment, slightly exceeding the literature value, which may reflect seasonal variations or differences in OM inputs and the utilization of different horizons. These differences in sediment composition allow a comprehensive analysis of how elemental composition, especially Fe/P and Fe/S ratios, influence the potential for vivianite formation under controlled experimental conditions.

The fractionated P distribution of the studied sediments led to yields between 81 % to 96 % and reveals differences in P binding and mobilizability, particularly in the BD, SRP, NRP, and HCl fractions (see Figure 4.1). The BD fraction, which primarily represents P bound to Fe hydroxides and mobilizable under anoxic conditions, shows substantial variability between the sediments. In the MÜG sediments, the BD fraction accounts for 46 % of TP, whereas in the AR sediment, the BD is considerably lower at 17 %. The MÜG Fe + P sediments also exhibit a high BD fraction of 37 %, highlighting the central role of Fe in P binding within these sediments, although the BD fraction is relatively lower than in the MÜG sediments. Under anoxic conditions in the sediment, the bound minerals could release Fe^{2+} and PO_4^{3-} , potentially favoring the formation of vivianite. In the MÜG sediments, the SRP fraction accounts for 11 %, indicating a moderate binding of P to aluminum or Fe oxides, while in the AR sediments, the SRP fraction is slightly lower at 8 %. Notably, the SRP fraction in the MÜG Fe + P sediments is remarkably high, comprising 50 % of the total P. The high SRP fraction can be attributed to the prior addition of amorphous Fe(III)-hydroxide powder ($\text{Fe}(\text{OH})_3$) and $\text{NaHPO}_4 \cdot \text{H}_2\text{O}$, which

4.2. Changes of Sediment Compositions during Oxic and after Anoxic Incubation

were adsorptively bound to the surface of $\text{Fe}(\text{OH})_3$. The NRP fraction also varies: in the MÜG sediments, NRP accounts for 18 %, indicating P binding from organic matter and poly P. In contrast, the AR sediments have a much higher NRP fraction of 36 %, while the MÜG Fe + P sediments show a relatively low NRP fraction of 4 %. The high NRP fraction in the AR sediments suggests stronger binding to organic P, which could imply a slower release of P under anoxic conditions, thereby contributing less to vivianite formation (Hupfer et al., 1995). The HCl fraction, representing P bound in carbonates and apatite, accounts for 19 % of the total P in the MÜG sediments. In the AR sediments, the HCl fraction is also at 17 %, whereas in the MÜG Fe + P sediments, the HCl fraction is much lower at 7 %.

The complete analysis of the sediments is provided in Appendix Section A.2.1.

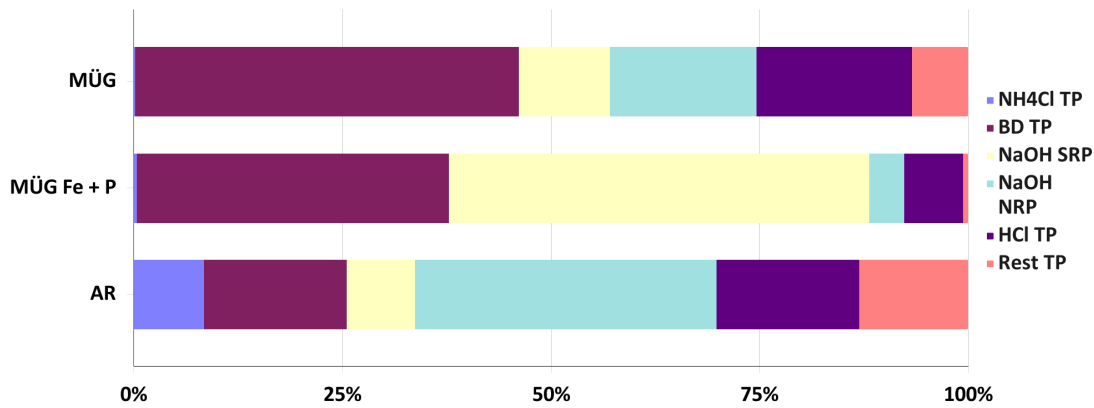


Figure 4.1.: P fractions in %, as determined after Psenner et al. (1984), of samples MÜG, AR, and MÜG Fe + P prior to the initiation of the experiment.

4.2. Changes of Sediment Compositions during Oxic and after Anoxic Incubation

The aeration of the aquaria resulted in the progressive development of an oxidized sediment surface with a light reddish-brown surface, eventually reaching a thickness of approximately 3 to 10 mm. Under comparable experimental conditions, as reported by Hupfer et al. (2019), O_2 saturation exceeded 90 %. Within a few days, *Chironomus* larvae created burrows with walls of a similar light reddish-brown color, as illustrated in Figure 4.2. The complete analysis of the sediments is provided in Appendix Section A.2.2 and A.2.3.

4. Results and Discussion

4.2.1. Iron and P Contents of Sediment Surface, Tubes, and Surroundings

The comparison of initial sediment properties with values obtained after 29 and 64 d under oxic conditions, as well as at day 119 after an anoxic incubation period, reveals that most elements remain relatively stable over time, with some showing slight variations. The mass (m) values of Fe and P contents in mg g dw^{-1} are particularly interesting, as depicted in Figure 4.3. In the MÜG sediment, surface $m(\text{Fe})$ initially rose by 4 % after 29 d, followed by a decrease of -4 % by day 64. However, by day 119, Fe levels increased again by 11 % to $74.8 \text{ mg g dw}^{-1}$, indicating fluctuating oxidation and re-accumulation processes. Within the tubes, Fe consistently increased, showing a 7 % rise over 64 d and an additional 5 % increase by day 119, reflecting continuous oxidation. The surrounding sediment followed a similar trend, with a 4 % increase by day 64 and an additional 5 % rise by day 119. Generally, the changes in the MÜG sediment are relatively moderate. In the AR sediment, $m(\text{Fe})$ at the surface increased more than tenfold from $6.30 \text{ mg g dw}^{-1}$ to $64.6 \text{ mg g dw}^{-1}$ after 64 d, followed by a slight increase of 2 % to $65.8 \text{ mg g dw}^{-1}$ after 119 d. Fe levels in the tubes also increased, rising by 133 % by day 64 and a further 16 % by day 119. The surrounding sediment exhibited a moderate increase of 7 % by day 64, with an additional 10 % rise by day 119. Here, the accumulation of Fe at the surface is

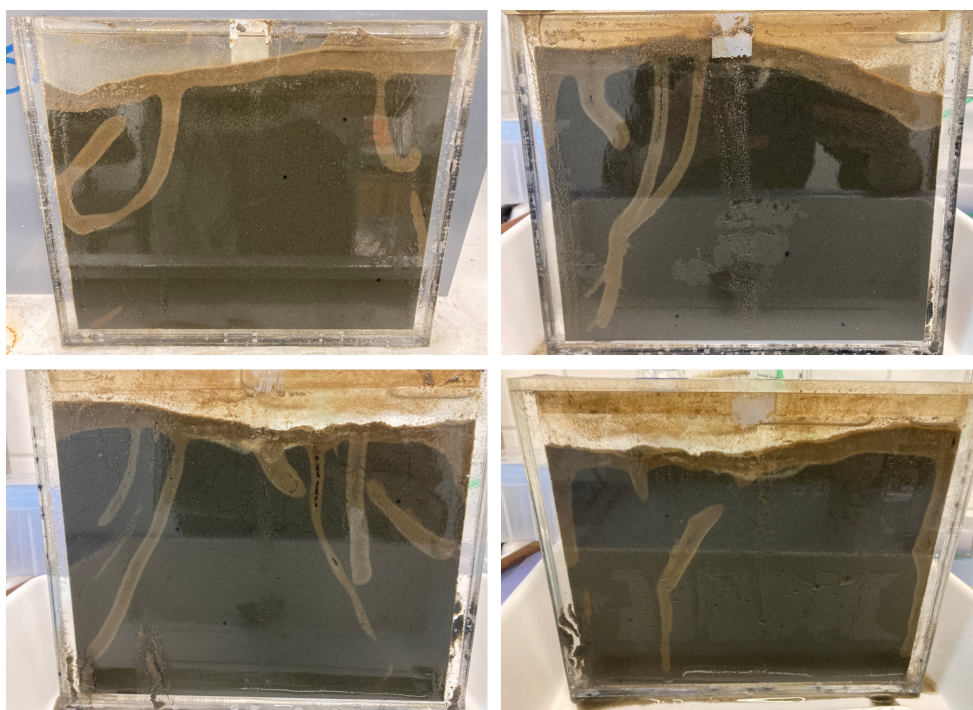


Figure 4.2.: Chironomid activity indicated by the construction of light brown tubes (oxidized sediment) in contrast to the surrounding anoxic dark brown sediment throughout the progression of the experiment.

4.2. Changes of Sediment Compositions during Oxic and after Anoxic Incubation

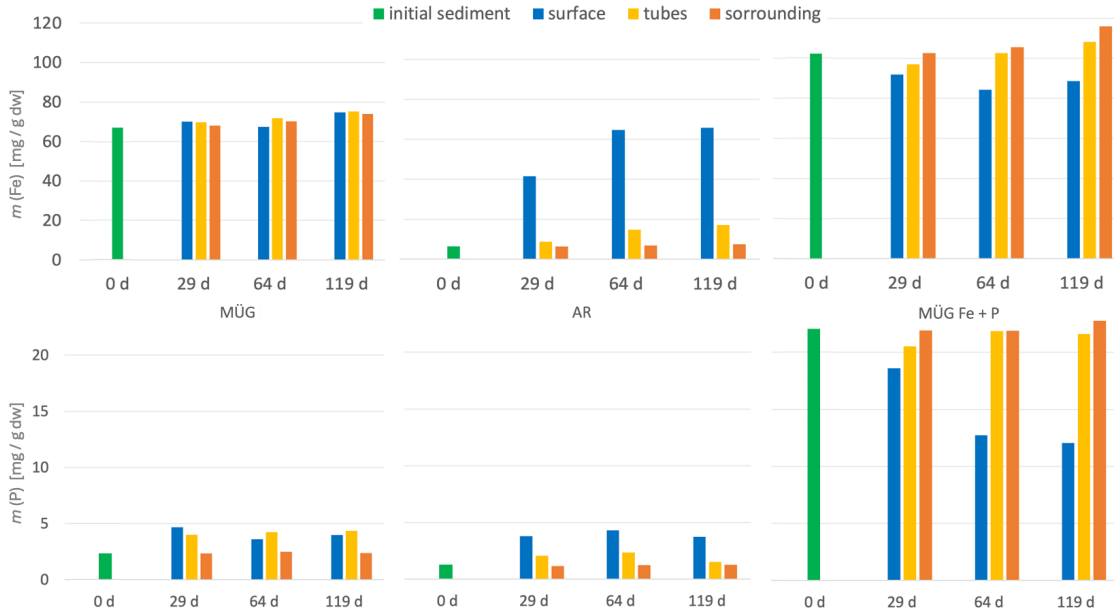


Figure 4.3.: $m(\text{Fe})$ and $m(\text{P})$ in mg g dw^{-1} of samples MÜG, AR, and MÜG Fe + P over time, showing the initial sediment, the oxidized sediments after 29 d and 64 d as well as the sedimentary composition after 119 d of anoxic incubation.

particularly pronounced compared to the other two sediment types. In the MÜG Fe + P sediment, surface $m(\text{Fe})$ decreased by -17 % after 64 d, but then partially recovered with a 5 % increase by day 119 reaching a lower value than initially measured. Fe in the tubes increased by 1 % by day 64, followed by an additional 5 % rise by day 119. The surrounding sediment showed a similar pattern, with a 3 % increase by day 64 and a more pronounced 10 % rise by day 119, indicating ongoing Fe accumulation. The MÜG Fe + P sediment type exhibits stronger fluctuations than the two previously described sediment types. The Fe at the sediment surface exhibits varying patterns. In the MÜG and MÜG Fe + P sediments, fluctuations suggest unstable oxidation processes, whereas in the AR sediment, a sharp increase indicates intensive mobilization and oxidation.

Hypothesis 1 proposes that *Chironomus* larvae increase the oxidized surface area within sediments, thereby enhancing the oxidation of Fe(II) to Fe(III). *Chironomus* larvae generate redox-active microzones that, upon reduction, could release Fe(II) and potentially lead to vivianite formation. The data observed in this study supports hypothesis 1. In all sediment types, Fe in the tubes exhibit a consistent increase, indicating that Fe(II) is undergoing oxidation and subsequent stabilization as Fe(III) complexes. The trend is consistent across samples, except a minor -5 % decrease observed in the MÜG Fe + P sediment after 29 d. Further validation is provided by the continuous increase in Fe in the surrounding sediment samples, particularly evident during the transition from oxic to anoxic conditions. The most pronounced increases in Fe during the transition suggest that

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Fe(III), previously stabilized in the oxidized tube walls, is reduced to Fe(II) under anoxic conditions. The reduction process supports the hypothesis that redox-active microzones, promoted by the larvae, facilitate the release of Fe(II) during anoxic conditions. The released Fe(II) then has the potential to react with PO_4^{3-} , potentially forming a stable compound such as vivianite.

For P in the MÜG sediment, surface concentrations initially almost doubled after 29 d, followed by a decrease of -22 % by 64 d, and then a slight increase of 10 % until 119 d, suggesting dynamic P binding from enriched surface water and alteration in release. In the tubes, P levels consistently rose by 86 % by 119 d, reflecting the influence of larvae activity. The surrounding sediment showed a minor fluctuation. In the AR sediment, surface P increased by 251 % by 64 d, followed by a slight decrease of -13 % by 119 d. Tube P levels initially rose by 91 % by 64 d but dropped by -34 % by 119 d. The surrounding sediment showed minimal changes. In the MÜG Fe + P sediment, surface P dropped by -42 % after 64 d, with a slight further decrease by -5 % by 119 d, indicating substantial P release. In contrast, tube P levels decreased by -1 % by 64 d and remained relatively stable thereafter. The surrounding sediment showed a slight increase of 4 % by 119 d, indicating ongoing P binding. In the MÜG and AR sediments, the initial rise in P suggests an accumulation of P at the sediment surface, reaching a threshold of 4 mg L^{-1} , corresponding to P in the enriched overlying water. In contrast, the marked decrease in P within the MÜG Fe + P sediment indicates a release of P into the overlying water driven by the diffusion gradient, since the overlying water also contains 4 mg L^{-1} of P.

The observed P dynamics within the tubes of the MÜG and AR sediments, particularly over the first 64 d, lend support to **Hypothesis 2**, which posits that bioturbation by *Chironomus* larvae enhances P diffusion within the sediment and may promote the formation of vivianite. During the first 64 d, the activity of *Chironomus* larvae likely facilitated the transport of P from the P-rich surface water into the sediment tubes. Under the prevailing oxic conditions within these tubes, P was presumably bound in minerals such as iron oxy(hydr)oxide phosphates. In the MÜG Fe + P sediment, the reduction in P could be attributed to the diffusion gradient driving P from the sediment to the surface and overlying water, which was also P-enriched. The process of oxic P binding might be competing with the diffusion gradient. The transition from oxic to anoxic conditions can lead to a decrease in P in the tubes of *Chironomus* larvae, as was observed in the AR sediment. The decrease indicates a diffusion of P from the tubes into the surrounding sediment or to the sediment surface. The P diffusion is supported by the increased P in the surrounding sediment in both the AR and MÜG Fe + P sediment, where P enrichment was observed. There was also an accumulation of P on the surface of the MÜG sediment. If P remains stable or even increases during the transition from oxic to anoxic conditions, as observed in the MÜG sediment, the P stabilization or increase could indicate the formation of vivianite. Such an increase would support **Hypothesis 2** that under anoxic conditions, P is sequestered in the sediment through the precipitation of vivianite.

The P enrichment from the overlying water into the sediment is also reflected in the continuous decline of $c(\text{SRP})$ during the initial weeks, as shown in Figure 4.4. The average daily decrease in $c(\text{SRP})$ in the overlying water over the first 29 d was approximately

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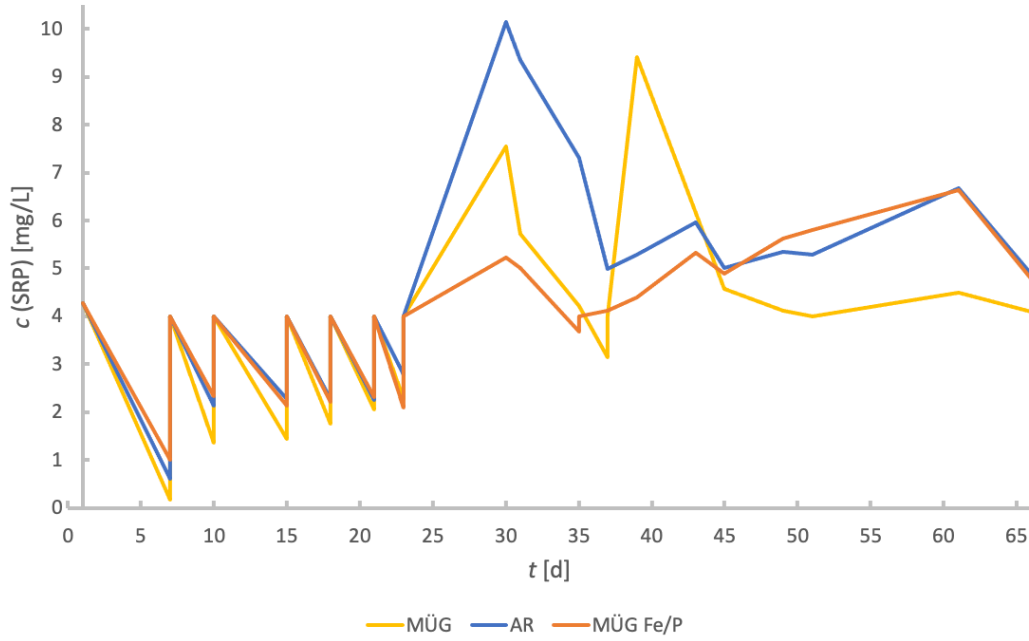


Figure 4.4.: Temporal changes in $c(\text{SRP})$ in surface water augmented with a NaHPO_4 solution over a 64 d period for the sediment types MÜG, AR, and MÜG Fe + P.

-2.2 mg L^{-1} .

Every few d, individual aquaria were removed from the surrounding sediment to check the activity of *Chironomus* larvae. Variability was observed, as depicted in Figure 4.2 with some aquaria exhibiting tunnels reaching the bottom. In contrast, others had tunnels of depths ranging from 4–6 cm, possibly attributable to differing larval developmental stages at the experiment's onset. The lifting of the aquaria disturbed the surface sediment and the adjacent sediment outside the acrylic boxes, which could explain the observed peaks in $c(\text{SRP})$ on day 29, ranging from 5.2 to 10.2 mg L^{-1} , as previously bound P in the sediment was released back into the water column. Similar P peaks were observed on day 39 in the MÜG sediment, likely also due to sediment resuspension. Following these events, $c(\text{SRP})$ stabilized between 4.0 and 6.6 mg L^{-1} . These findings illustrate both the variability and stabilization of $c(\text{SRP})$, reflecting the dynamic nature of nutrient cycling in the aquatic environment. In a comparable study by Hupfer et al. (2019) *Chironomus plumosus* larvae at the 4th larval stage were introduced into columns containing sediments from Lake Müggelsee and Lake Arendsee at varying larval densities. Due to differences in experimental conditions, direct comparisons of P uptake between the sediment types are limited. However, general trends can be observed: The presence of larvae led to a significantly higher P uptake ($p > 0.05$) in both sediment types compared to uninhabited control columns. This increase is attributed to the active transport of P from overlying water into the larval burrow walls, where P binds to oxidized Fe compounds through sorption processes. Furthermore, the Fe-rich sediments from Lake Müggelsee exhibited

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a higher P binding capacity than the relatively Fe-poor sediments from Lake Arendsee. These findings are consistent with the results presented here, highlighting the role of *Chironomus* larvae bioturbation and the influence of sediment composition on P binding and retention.

4.2.2. BD-TP and NaOH-SRP Fractions of *Chironomus* Larvae Tube Walls

In the tubes of MÜG, AR, and MÜG Fe + P sediments, $c(\text{BD TP})$ display distinct patterns of change across oxic and anoxic phases. According to Hypotheses 1 and 2, it is expected that the BD fraction would progressively increase during the oxic phase as Fe and P accumulate in the tube walls, forming iron (oxyhydr)oxide phosphates. The changing pattern is evident in both the AR and MÜG Fe + P tubes. In the AR tubes, a notable increase of 312 % over 29 d is observed, likely due to the high P in the overlying water. Subsequently, $c(\text{BD TP})$ stabilizes, with an additional increase of 39 % in the second oxic phase, reaching approximately 1 mg g dw^{-1} . In the MÜG Fe + P tubes, $c(\text{BD TP})$ initially increases by 29 %, followed by a marginal increase of 4 % during the second oxic phase. In the MÜG tubes without Fe and P enrichment, as shown in Figure 4.5, $c(\text{BD TP})$ fluctuate during the oxic phases, with an initial stabilization marked by a 117 % increase, followed by a 10 % decrease likely due to P release. During the transition to the anoxic phase, $c(\text{BD TP})$ increases again by 16 %, while the NaOH-SRP fraction decreases. The increase suggests an accumulation of reductively soluble PO_4^{3-} , such as iron (oxyhydr)oxide phosphates, along with a reduction in the Fe or aluminum oxides and vivianite fraction.

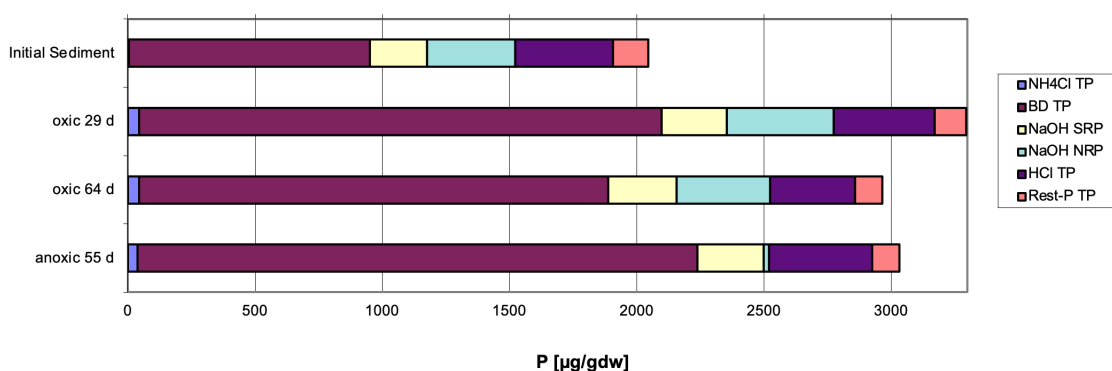


Figure 4.5.: P fractions of changes in MÜG tubes as determined after Psenner et al. (1984), from initial to oxic and further to anoxic phase in $\mu\text{g dw}^{-1}$.

During the shift from oxic to anoxic conditions, $c(\text{BD TP})$ in the AR and MÜG Fe + P tubes decreases sharply by 114 % and 146 %, respectively, as illustrated in Figure 4.6. The decrease indicates the dissolution of iron (oxyhydr)oxide phosphates in the tubes and the release of P from the AR sediment into the overlying water. In the MÜG Fe + P tubes, a slight redistribution occurs, with P moving from the tubes into the surrounding sediment's NaOH-SRP fraction.

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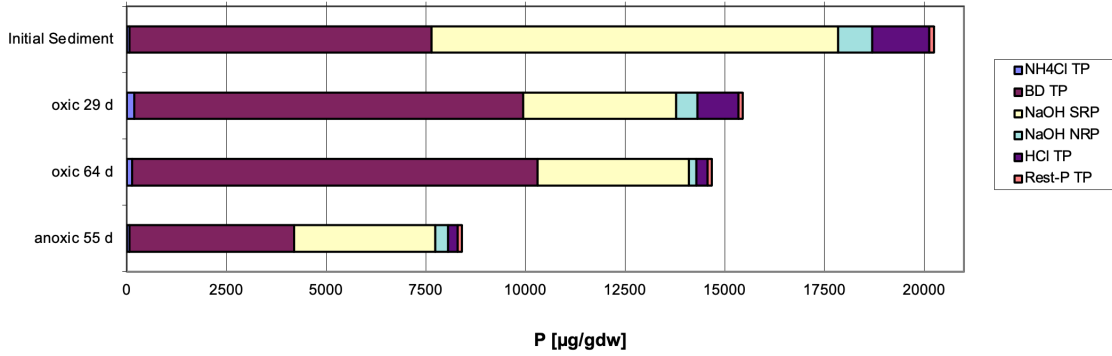


Figure 4.6.: P fractions of changes in MÜG Fe + P tubes as determined after Psenner et al. (1984), from initial to oxic and further to anoxic phase in $\mu\text{g dw}^{-1}$.

The changes in BD-TP and NaOH-SRP fractions within the tube walls of *Chironomus* larvae align with the findings of Hupfer et al. (2019) and Lewandowski et al. (2007). Both studies demonstrate that these tube walls serve as hot-spots for P binding, with BD-TP and NaOH-SRP fractions responding dynamically to redox conditions. During the oxic phase, O_2 diffusion through the tube walls promotes the formation of iron(III) oxyhydroxides, which act as adsorption sites for P. This process increases the BD-TP fraction, as P becomes associated with redox-sensitive, easily reducible Fe-bound forms. When conditions shift to anoxic, the redistribution of P fractions becomes apparent. Hupfer et al. (2019) and Lewandowski et al. (2007) both report that the reduction of Fe(III) to Fe(II) results in the dissolution of FeOOH, leading to the release of P. This change is reflected in a decrease in the BD-TP fraction, as P is released into porewater or adjacent sediment regions (here apparent in MÜG Fe + P sediment). Part of the released P is subsequently incorporated into the NaOH-SRP fraction of the surrounding sediment, suggesting the formation of more stable P compounds, such as vivianite. The results for the NaOH-SRP fraction are also consistent with the findings of Hupfer et al. (2019). This study identified the formation of vivianite as a key process in stabilizing P under anoxic conditions. Similarly, the present results indicate that P is mobilized from the NaOH-SRP fraction when redox conditions shift from oxic to anoxic.

4.2.3. Molar Fe/P and Fe/S Ratios

The changes in the molar BD Fe/P (as illustrated in Figure 4.7) and Fe/S (displayed in Table 4.2) ratios across different sediment types during the oxic phases (29 and 64 d) and the subsequent anoxic phase (119 d), reveal important insights into the processes of Fe and P interaction. In the tubes of the MÜG sediment, the Fe/P ratio increases from 3.3 after 29 d to 3.6 after 64 d, which is above the optimal range (1.5 to 2.5) for vivianite formation. However, the Fe/S ratio in the tubes is relatively high, starting at 3.5 after 29 d and increasing to 3.7 after 64 d. A high Fe/S ratio is beneficial for reducing the formation of FeS and ensuring more Fe is available for binding with PO_4^{3-} to form

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Table 4.2.: Molar Fe/S ratios in tubes of *Chironomus* larvae across the sediments MÜG, AR and MÜG Fe + P during oxic and anoxic incubation phases.

Sediment	29 d oxic	64 d oxic	119 d anoxic
MÜG	3.5±0	3.7	3.4
AR	0.5±0	0.8	0.7
MÜG Fe + P	5.9±0.1	6.0	5.5

vivianite. In the tubes of the AR sediment, the Fe/P ratio decreases from 1.7 after 29 d

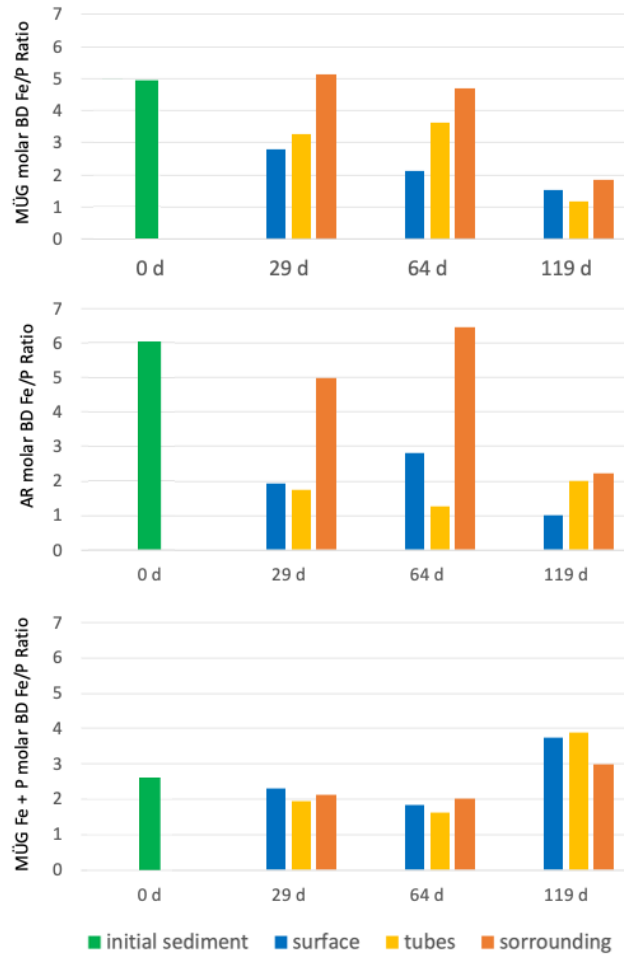


Figure 4.7.: Molar BD Fe/P ratios of surface, tubes, and surrounding sediments MÜG, AR, and MÜG Fe + P during oxic and anoxic incubation phases.

to 1.3 after 64 d, falling below the optimal range for vivianite formation. The lower Fe/P ratio suggests that P is more abundant relative to Fe, which could favor other PO_4^{3-}

interactions over vivianite crystallization. Additionally, the Fe/S ratio in the tubes is very low, starting at 0.55 after 29 d and slightly increasing to 0.85 after 64 d. The low Fe/S ratio indicates that Fe is more likely to react with sulfides, forming FeS rather than vivianite. The combination of a suboptimal Fe/P ratio and a low Fe/S ratio suggests that the conditions in the AR sediment tubes are not favorable for vivianite formation. In the MÜG Fe + P sediment tubes, the Fe/P ratio decreases from 1.9 after 29 d to 1.6 after 64 d, but the ratio remains within the optimal range for vivianite formation. The Fe/S ratio in these tubes is high, starting at 5.9 and increasing to 6.0 over the same period, which is well above the minimum threshold of 1.1 required to allow vivianite formation over FeS. However, no vivianite formation was observed despite the presence of optimal BD Fe/P and high Fe/S ratios. In contrast, the surrounding sediment exhibits molar BD Fe/P ratios between 2.0 and 3.0 and Fe/S ratios ranging from 5.4 to 5.7, which are above the ideal values for vivianite formation. Despite a slight reduction in the Fe/P ratio within the tube walls, the conditions in the MÜG Fe + P sediment tubes continue to be favorable for vivianite formation, as both the Fe/P and Fe/S ratios remain within the ranges that promote its crystallization. Thus, these observations align with **Hypothesis 3**, which proposes that *Chironomus* larvae facilitate the formation of vivianite in sediments with a Fe/P ratio of 1.5 to 2.5 and a Fe/S ratio exceeding 1, especially following the transition from oxic to anoxic conditions.

The findings of this study align with the results of Heinrich et al. (2021, 2022) and Rothe et al. (2016), all of which highlight the significance of Fe/P and Fe/S ratios in regulating vivianite precipitation in aquatic sediments. Heinrich et al. (2021) demonstrated that redox-sensitive Fe-P phases could be transformed into stable, redox-insensitive minerals like vivianite under anoxic conditions. Their laboratory experiments revealed that this transformation occurs within 40 d. Similarly, in the present study, vivianite formation was observed in the MÜG sediment after 55 d, under comparable anoxic conditions. Importantly, the Fe/P ratios in this sediment fell within the optimal range required for vivianite precipitation. Heinrich et al. (2022) emphasized the importance of Fe availability for P immobilization in sediments, demonstrating that high Fe/S ratios favor vivianite formation while minimizing FeS precipitation. This observation is consistent with the current study, where the MÜG Fe + P sediment exhibited $\text{Fe/S} > 5$, thereby creating an environment conducive to vivianite formation by ensuring sufficient Fe(II) availability. Rothe et al. (2016) highlighted the inhibitory effect of sulfides on vivianite formation, showing that FeS is formed rapidly when Fe(II) reacts with H_2S . This reaction sequesters Fe in FeS, reducing the amount of Fe available for vivianite precipitation. This pattern is reflected in the present study, as the AR sediment displayed low Fe/S ratios (0.5–0.8), suggesting that FeS formation is dominant under these conditions. As a result, vivianite formation is likely suppressed in this sediment due to the rapid sequestration of Fe in FeS.

4.3. Vivianite Detection by XRD

XRD is commonly employed for the identification and characterization of vivianite in sediments (Cosmidis et al., 2014; Taylor et al., 2008). However, its application is not

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without challenges. These arise from the low abundance of vivianite in samples, the size and crystallinity of the nodules, and interferences from other mineral phases (Emerson & Widmer, 1978). A minimum of 5 wt% of vivianite is required for the three most intense peaks to be distinctly visible in the XRD spectrum (Rothe et al., 2014). While vivianite is generally considered sensitive to oxidation, some studies indicate that its crystal structure remains stable at room temperature, enhancing the reliability of this analytical method (Rouzies & Millet, 1993).

Vivianite was not detected by XRD in any initial sediments or under oxic conditions, except in the surrounding sediment of the Fe- and P-enriched MÜG sediment, as displayed in Table 4.3. The observation is supported by the molar BD Fe/P ratios, which were too high in the anoxic surrounding sediments of the MÜG and AR sediments. In contrast, the ratio in the enriched sediment was approximately 2, which falls within the optimal range for vivianite formation. However, it remains unclear whether the vivianite formation in the surrounding sediment was directly caused by the activity of chironomids in the adjacent tubes and the associated increased release of Fe and P into the surrounding sediment. After 101 d of the anoxic phase, the tube walls from the three sediment samples were analyzed using XRD, and vivianite was detected in the tubes of the MÜG Fe + P sediment, but not in the tubes of MÜG and AR sediment. At the end of the anoxic phase, after 119 d, the sediments were reanalyzed, and vivianite was found in the tubes of the MÜG sediment as well as in the surrounding sediment of the MÜG Fe + P sediment, as shown in Figure 4.8. However, since sampling cannot ensure that only the tube walls

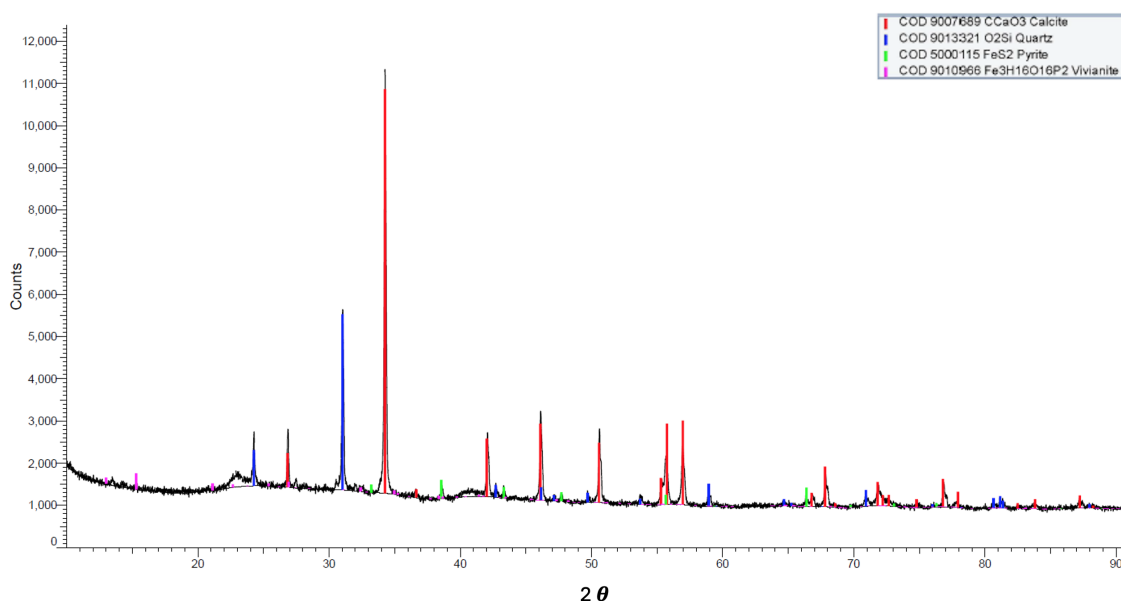


Figure 4.8.: XRD spectra of Lake Müggelsee tube sample **28** after 119 d anoxic with vivianite identification.

4.3. *Vivianite Detection by XRD*

were collected without contamination from the surrounding sediment, and considering that vivianite was detected in the tubes after 101 d but not after 119 d in the MÜG Fe + P sediment, the finding cannot be considered definitive. Nevertheless, the presence of vivianite in the tubes of the MÜG sediment supports the hypothesis that Chironomid larvae can trigger vivianite formation in lake sediments.

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Table 4.3.: Vivianite detection by XRD in sediment samples MÜG, AR, and MÜG Fe + P *Chironomus* larvae. Abbreviations: d = day, MÜG S = surface sediment, MÜG T = sediment from tubes, MÜG C = circumjacent or surrounding sediment etc..

Description	d	Sediment Type	Vivianite
Part 0 preliminary results	0	MÜG	-
		AR	-
		MÜG Fe + P	-
		FeP Slurry	-
Part A aerob	29	MÜG S	-
		MÜG T	-
		MÜG C	-
		AR S	-
		AR T	-
		AR C	-
		MÜG Fe + P S	-
		MÜG Fe + P T	-
		MÜG Fe + P C	-
Part B aerob	64	MÜG S	-
		MÜG T	-
		MÜG C	-
		AR S	-
		AR T	-
		AR C	-
		MÜG Fe + P S	-
		MÜG Fe + P T	-
		MÜG Fe + P C	detected
anaerob	101	MÜG T	-
		AR T	-
		MÜG Fe + P T	detected
Part C anaerob	119	MÜG S	-
		MÜG T	detected
		MÜG C	-
		AR S	-
		AR T	-
		AR C	-
		MÜG Fe + P S	-
		MÜG Fe + P T	-
		MÜG Fe + P C	detected

5. Conclusion

This master's thesis explored the role of *Chironomus* larvae in the formation of vivianite within lake sediments, focusing on their impact on P dynamics and sediment chemistry. The experiments conducted in the sediments of Lake Müggelsee and Lake Arendsee revealed intricate interactions between larval activity, redox conditions, and nutrient cycling. The findings confirmed that *Chironomus* larvae can promote vivianite formation under specific conditions. In the sediments of Lake Müggelsee, characterized by moderate concentrations of Fe and P with low S content, the activities of *Chironomus* larvae led to an increased oxidized surface area. The oxidation process allowed the accumulation of Fe (oxyhydr)oxides, which could subsequently convert into vivianite under oxic conditions. In contrast, the sediments from Lake Arendsee, which exhibited low Fe and P concentrations but high sulfur levels, did not support vivianite formation despite the presence of *Chironomus* larvae. The observation suggests that while the larvae facilitate P and Fe diffusion, the specific nutrient conditions in Lake Arendsee were not favorable to vivianite precipitation. Additionally, although sediment from Lake Müggelsee was enriched in Fe and P, and displayed a high Fe/S ratio, vivianite formation was not observed. The lack of vivianite formation indicates that Fe/P and Fe/S ratios alone are insufficient predictors of vivianite formation. Interestingly, vivianite formation was detected in the surrounding sediment of the MÜG Fe + P sediment type, where increases in Fe and P concentrations and optimal Fe/P ratios for vivianite formation were confirmed by XRD analysis.

The results of this study underscore the need for a deeper understanding of the factors influencing vivianite formation and contribute significantly to an expanded knowledge of P dynamics in freshwater systems. Specifically, the potential role of *Chironomus* larvae in the P cycle is highlighted, suggesting that integrating biological factors into sediment and nutrient management strategies could offer innovative approaches to combat eutrophication and improve water quality.

Future research should focus on establishing monitoring programs to continuously assess the population density and activity of Chironomid larvae in aquatic systems. Such data would enhance the scientific basis for understanding larval behavior and the conditions influencing their colonization by macrozoobenthos and macrophytes. On this basis, targeted biologically supported sediment management strategies could be developed, which would optimize environmental parameters such as oxygen levels and substrate structure to enhance larval activity. Integrating these biological approaches into existing nutrient management practices could improve their effectiveness by combining the P mobilization capabilities of *Chironomus* larvae with other P removal techniques, such as chemical precipitation. Additionally, addressing Fe deficiency through targeted Fe addition could facilitate the long-term binding of P as vivianite in sediments.

To comprehensively investigate the long-term impacts of vivianite on water quality and

5. Conclusion

the complex interactions between nutrient inputs, sediment geochemistry, and feedback mechanisms, specific research approaches are necessary. This includes implementing long-term monitoring systems in water bodies to continuously collect data on P and Fe concentrations, pH, and oxygen levels. Such data would allow for the identification of long-term trends and assessment of vivianite's effects on water quality over extended periods. Furthermore, controlled laboratory and extensive field studies should be conducted to explore the interactions between vivianite, nutrients, and sediment geochemistry. These studies should involve targeted manipulation of sediment samples and observation of vivianite formation under varying environmental conditions. The results from these studies should be integrated into numerical models that simulate P dynamics and vivianite impacts, enabling precise predictions of the long-term effects on water quality.

Future research should also investigate the potential impacts of climate change on eutrophication dynamics, specifically examining how shifts in environmental conditions could influence vivianite formation and P cycling. Understanding these interactions will be crucial for assessing the effectiveness of both natural and engineered remediation strategies in mitigating eutrophication.

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Acronyms

ΔG Gibbs free energy. 14

m mass. 44

AOM anaerobic oxidation of methane. 19

C carbon. 14

Ca calcium. 16

CH₄ methane. 15

CO₂ carbon dioxide. 12

DIP dissolved inorganic phosphorus. 11

DMRB dissimilatory metal-reducing bacteria. 23

DOP dissolved organic phosphorus. 11

dw dry weight. 26, 38

Eh redox potentials. 13

Fe iron. 3

g gram. 3

H hydrogen. 14

L Liter. 3

LOI loss on ignition. 38

Mn manganese. 10

MnO₂ manganese(IV) oxide. 15

N nitrogen. 1

N₂	molecular nitrogen.	14
NH₄⁺	ammonium.	10
NO₂⁻	nitrite.	10
NO₃⁻	nitrate.	14
O₂	oxygen.	1
OM	organic matter.	1
P	phosphorus.	1
PIP	particulate inorganic phosphorus.	11
PO₄³⁻	orthophosphate.	3
poly P	polyphosphate.	17
POP	particulate organic phosphorus.	11
PP	particulate phosphorus.	11
S	sulfur.	3
Si	silicon.	15
SMTZ	sulfate-methane transition zone.	19
SRP	soluble reactive phosphorus.	28
SWI	sediment-water interface.	3
TN	total nitrogen.	2
TP	total phosphorus.	1
XRD	X-ray diffractometry.	32

A. Appendix

A.1. Experimental Setup and Sequence of Sampling

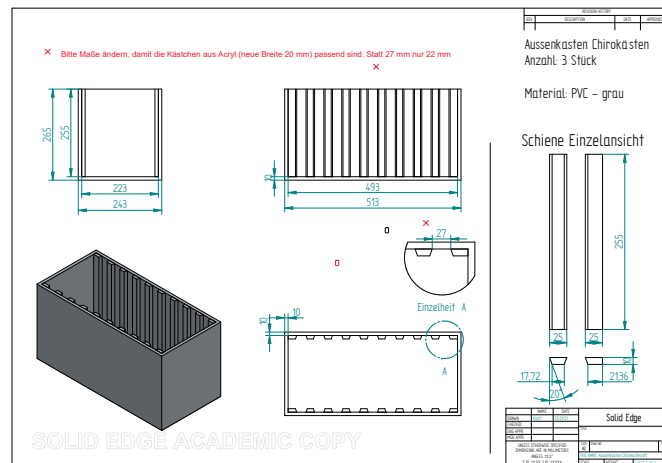


Figure A.1.: PVC mantle box for the experimental setup.

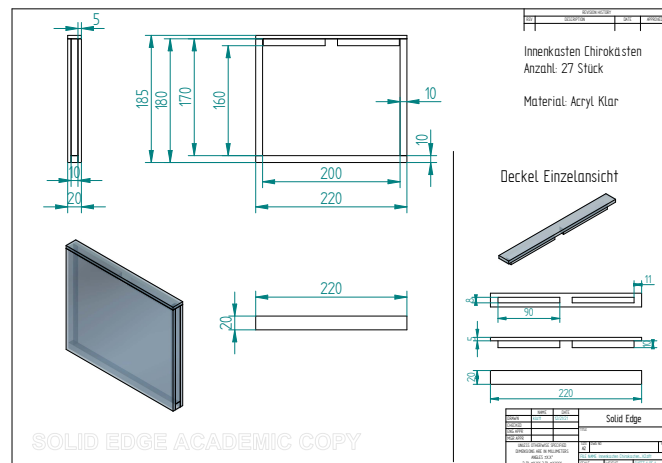


Figure A.2.: PVC inner box for the experimental setup.

A.1. Experimental Setup and Sequence of Sampling

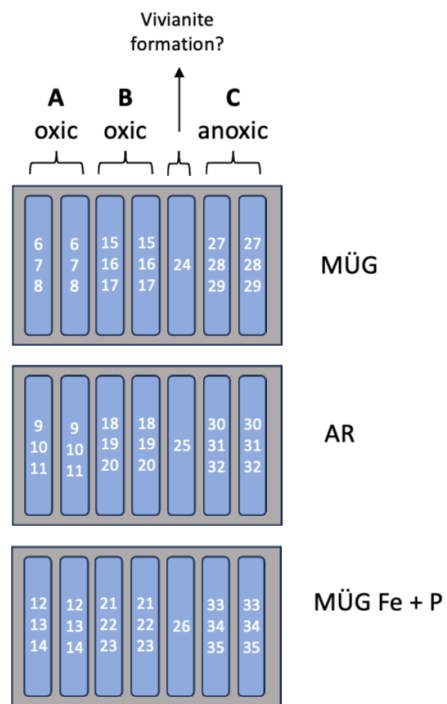


Figure A.3.: Sampling of duplicates from all sediment types of oxic (Part A and B) and anoxic (Part C) incubation. Between the oxic and anoxic phases, the sediment types were examined to determine the occurrence of vivianite.

A.2. Data of Experimental Results

A.2.1. Data of Preliminary Results

Table A.1.: Initial elemental composition of sediment samples from L. Müggelsee (MÜG, 0-15 cm dpt, 7 m wdpt), sediment from L. Arendsee (AR, 0-10 cm dpt, 48 m wdpt), iron-stocked sediment from L. Müggelsee (MÜG Fe + P, 0-15 cm dpt, 7 m wdpt) and the prepared Fe/P slurry. Values in mg gdw⁻¹ if not indicated otherwise.

Parameter	MÜG	AR	MÜG Fe/P	Fe-P slurry
Al	12.1	3.84	9.9	1.73
C [%]	16.47	17.88	13.06	0.33
Ca	114	216	103	42.5
Cu	0.08	0.02	0.06	0.01
dw [%]	9	6	11	49
Fe	67.3	6.30	102	251
Fe/P [molar]	15.9	2.8	2.6	1.4
Fe/S [molar]	3.0	0.5	5.3	-
K	1.98	1.10	1.74	0.46
LOI [%]	25.9	22.5	23.8	-
Mg	2.68	2.10	2.87	3.56
Mn	1.39	0.68	3.22	10.7
N [%]	1.50	1.32	1.19	0.08
Na	0.54	0.69	7.95	38.5
P	2.35	1.23	22.1	101
S	12.8	7.61	11.1	0.07
Ti	0.46	0.20	0.38	0.03
Vivianite	-	-	-	-
Zn	0.40	0.08	0.33	0.06

Table A.2.: P fractions according to the method of Psenner et al. (1984) of the preliminary sediment samples MÜG, AR, and MÜG Fe + P. Fractions include NH₄Cl TP, BD TP, SRP, NRP, HCl TP, and Rest TP with their values in mg gdw⁻¹ if not indicated otherwise.

Parameter	NH ₄ Cl	BD	SRP	NRP	HCl	Rest	TP	Yield [%]
MÜG	0.004	0.95	0.23	0.35	0.38	0.14	2.05	87
AR	0.08	0.17	0.08	0.36	0.17	0.13	1.00	81
MÜG Fe + P	0.07	7.57	10.2	0.85	1.43	0.13	20.3	96

A.2. Data of Experimental Results

Table A.3.: Fe and Mn values of P fractions of preliminary sediment samples MÜG, AR, and MÜG Fe + P. BLD: below limit of detection, values in mg gdw^{-1} .

Parameter	BD Fe	BD Fe/P Ratio	BD Mn	HCl Fe	HCl Mn
MÜG	8.46	4.95	0.343	42.03	0.73
AR	1.87	6.03	0.46	BLD	BLD
MÜG Fe + P	35.8	2.62	1.59	50.7	1.41

A.2.2. Data of Oxidic Incubation

Table A.4.: Elemental composition of sediment samples MÜG, and AR after **29 d** of oxidic incubation. Abbreviations MÜG S = surface sediment, MÜG T = sediment from tubes, MÜG C = circumjacent or surrounding sediment etc.. Values in mg gdw^{-1} if not indicated otherwise.

Parameter	MÜG S	MÜG T	MÜG C	AR S	AR T	AR C
Al	12.0	11.9	12.1	8.41	4.17	3.84
C [%]	15.9	16.1	16.3	15.8	17.1	17.5
Ca	116	117	117	158	216	212
Cu	0.10	0.09	0.09	0.06	0.03	0.02
dw [%]	8	8	8	7	7	7
Fe	70.1	69.8	68.0	41.5	8.65	6.28
Fe/P [molar]	8.3	9.6	16.0	6.1	2.3	3.0
Fe/S [molar]	3.4	3.5	3.0	1.9	0.5	0.4
K	2.18	2.10	2.06	1.79	1.21	1.07
LOI [%]	26	26	27	24	21	39
Mg	2.92	2.86	2.65	2.73	2.40	2.12
Mn	1.88	1.91	1.45	1.94	1.04	0.65
N [%]	1.47	1.49	1.50	1.30	1.30	1.32
Na	1.03	0.93	0.74	1.22	1.12	0.80
P	4.67	4.03	2.36	3.80	2.06	1.16
S	11.9	11.3	13.1	12.3	9.08	8.53
Ti	0.47	0.45	0.47	0.35	0.20	0.20
Vivianite	-	-	-	-	-	-
Zn	0.40	0.40	0.40	0.26	0.10	0.08

A. Appendix

Table A.5.: Elemental composition of sediment samples MÜG Fe + P after **29 d** of oxic incubation. Abbreviations MÜG Fe + P S = surface sediment, MÜG Fe + P T = sediment from tubes, MÜG Fe + P C = circumjacent or surrounding sediment etc.. Values in mg gdw⁻¹ if not indicated otherwise.

Parameter	MÜG Fe + P S	MÜG Fe + P T	MÜG Fe + P C
Al	10.0	10.2	10.2
Ca	108	106	105
C [%]	13.1	13.3	13.3
Cu	0.07	0.07	0.07
dw	10	9	10
Fe	92.0	97.0	103
Fe/P [molar]	2.7	2.6	2.6
Fe/S [molar]	5.5	5.9	5.6
K	1.98	1.97	1.82
LOI	22	27	24
Mg	3.11	3.17	3.01
Mn	2.96	3.21	3.20
Na	3.42	3.16	5.56
N [%]	1.18	1.22	1.23
P	18.6	20.5	21.9
S	9.53	9.38	10.6
Ti	0.39	0.39	0.39
Vivianite	-	-	-
Zn	0.33	0.33	0.33

Table A.6.: P fractions according to the method of Psenner et al. (1984) of the sediment samples MÜG, AR, and MÜG Fe + P after **29 d** of oxic incubation. Fractions include NH_4Cl TP, BD TP, SRP, NRP, HCl TP, and Rest TP with their values in mg gdw^{-1} if not indicated otherwise. Abbreviations MÜG S = surface sediment, MÜG T = sediment from tubes, MÜG C = circumjacent or surrounding sediment etc..

Parameter	NH_4Cl	BD	SRP	NRP	HCl	Rest	TP	Yield [%]
MÜG S	0.15	2.21	0.26	0.43	0.41	0.12	3.57	77
MÜG T	0.04	2.05	0.26	0.42	0.40	0.12	3.29	82
MÜG C	0.004	0.75	0.35	0.35	0.38	0.12	1.95	83
AR S	0.31	1.86	0.18	0.37	0.26	0.10	3.08	81
AR T	0.16	0.71	0.11	0.33	0.21	0.08	1.60	78
AR C	0.05	0.17	0.09	0.30	0.19	0.08	0.87	75
MÜG Fe + P S	0.22	7.17	3.28	0.38	1.06	0.11	12.2	66
MÜG Fe + P T	0.19	9.76	3.83	0.53	1.03	0.12	15.5	75
MÜG Fe + P C	0.03	9.09	5.04	0.28	1.46	0.12	16.0	73

Table A.7.: Fe and Mn values of P fractions of sediment samples MÜG, AR, and MÜG Fe + P after **29 d** of oxic incubation with their values in mg gdw^{-1} . Abbreviations MÜG S = surface sediment, MÜG T = sediment from tubes, MÜG C = circumjacent or surrounding sediment etc..

Parameter	BD Fe	BD Fe/P [molar]	BD Mn	HCl Fe	HCl Mn
MÜG S	11.13	2.79	0.96	40.5	0.75
MÜG T	12.10	3.27	0.96	43.6	0.80
MÜG C	6.90	5.12	0.35	45.1	0.87
AR S	6.41	1.91	1.20	21.7	0.49
AR T	2.22	1.74	0.73	1.79	0.17
AR C	1.52	4.98	0.32	0.75	0.11
MÜG Fe + P S	29.7	2.30	1.64	42.2	1.03
MÜG Fe + P T	34.2	1.94	1.80	46.8	1.08
MÜG Fe + P C	34.9	2.13	1.38	52.3	1.41

A. Appendix

Table A.8.: Elemental composition of sediment samples MÜG, and AR after **64 d** of oxic incubation. Abbreviations MÜG S = surface sediment, MÜG T = sediment from tubes, MÜG C = circumjacent or surrounding sediment etc.. Values in mg gdw⁻¹ if not indicated otherwise.

Parameter	MÜG S	MÜG T	MÜG C	AR S	AR T	AR C
Al	11.4	11.9	12.0	11.4	4.94	3.88
Ca	117	119	120	130	210	216
Cu	0.12	0.09	0.08	0.13	0.05	0.03
Fe	67.4	71.7	70.2	64.6	14.7	6.8
Fe/P [molar]	10.3	9.33	15.6	8.32	3.48	3.03
Fe/S [molar]	3.3	3.68	2.9	2.72	0.85	0.43
K	2.20	2.23	2.11	2.15	1.40	1.08
Mg	2.83	2.82	2.70	3.00	2.58	2.17
Mn	2.13	1.82	1.42	2.50	1.13	0.69
Na	0.99	0.94	0.82	1.15	1.43	1.08
P	3.63	4.26	2.50	4.31	2.34	1.24
S	11.9	11.2	13.9	13.7	9.94	9.05
Ti	0.45	0.46	0.48	0.44	0.26	0.21
Zn	0.41	0.40	0.42	0.39	0.13	0.09

Table A.9.: Elemental composition of sediment samples MÜG Fe + P after **64 d** of oxic incubation. Abbreviations: MÜG Fe + P S = surface sediment, MÜG Fe + P T = sediment from tubes, MÜG Fe + P C = circumjacent or surrounding sediment etc., and values in mg gdw⁻¹ if not indicated otherwise.

Parameter	MÜG Fe + P S	MÜG Fe + P T	MÜG Fe + P C
Al	10.8	10.3	10.4
Ca	106	109	106
C [%]	14.0	13.2	13.4
Cu	0.13	0.09	0.08
dw	0.08	0.11	0.12
Fe	84.3	103	106
Fe/P [molar]	3.67	2.60	2.67
Fe/S [molar]	4.17	5.97	5.41
K	2.01	2.01	1.90
LOI	0.24	0.25	0.25
Mg	3.16	3.23	3.09
Mn	2.72	3.70	3.22
Na	3.74	3.88	4.38
N [%]	1.24	1.19	1.24
P	12.7	21.9	21.9
S	11.6	9.87	11.2
Ti	0.42	0.40	0.40
Vivianite	-	-	detected
Zn	0.37	0.35	0.35

A.2. Data of Experimental Results

Table A.10.: P fractions according to the method of Psenner et al. (1984) of the sediment samples MÜG, AR, and MÜG Fe + P after **64 d** of oxic incubation. Fractions include NH₄Cl TP, BD TP, SRP, NRP, HCl TP, and Rest TP with their values in mg gdw⁻¹ if not indicated otherwise. Abbreviations MÜG S = surface sediment, MÜG T = sediment from tubes, MÜG C = circumjacent or surrounding sediment etc..

Parameter	NH ₄ Cl	BD	SRP	NRP	HCl	Rest	TP	Yield [%]
MÜG S	0.10	1.85	0.30	0.35	0.37	0.11	3.08	85
MÜG T	0.04	1.85	0.27	0.37	0.33	0.11	2.97	70
MÜG C	0.006	0.74	0.31	0.26	0.29	0.11	1.72	69
AR S	0.16	1.73	0.21	0.39	0.16	0.10	2.75	64
AR T	0.14	0.98	0.11	0.37	0.06	0.09	1.74	75
AR C	0.06	0.13	0.09	0.34	0.04	0.09	0.75	61
MÜG Fe + P S	0.18	7.39	1.25	0.28	0.12	0.10	9.32	73
MÜG Fe + P T	0.14	10.2	3.79	0.19	0.28	0.11	14.7	67
MÜG Fe + P C	0.03	8.04	6.41	0.30	0.39	0.11	15.3	70

Table A.11.: Fe and Mn values of P fractions of sediment samples MÜG, AR, and MÜG Fe + P after **64 d** of oxic incubation with their values in mg gdw⁻¹. Abbreviations MÜG S = surface sediment, MÜG T = sediment from tubes, MÜG C = circumjacent or surrounding sediment etc..

Parameter	BD Fe	BD Fe/P [molar]	BD Mn	HCl Fe	HCl Mn
MÜG S	7.09	2.12	1.35	39.1	0.84
MÜG T	12.1	3.64	0.83	38.3	0.74
MÜG C	6.30	4.70	0.31	43.9	0.83
AR S	8.70	2.79	1.51	33.1	0.77
AR T	2.23	1.26	0.86	4.28	0.17
AR C	1.47	6.46	0.00	0.80	0.07
MÜG Fe + P S	24.3	1.83	1.65	38.0	0.84
MÜG Fe + P T	29.8	1.62	1.86	40.6	1.05
MÜG Fe + P C	29.3	2.02	1.29	53.2	1.68

A.2.3. Data of Anoxic Incubation

Table A.12.: Elemental composition of sediment samples MÜG, and AR after **119 d** of anoxic incubation. Abbreviations MÜG S = surface sediment, MÜG T = sediment from tubes, MÜG C = circumjacent or surrounding sediment etc.. Values in mggdw^{-1} if not indicated otherwise.

Parameter	MÜG S	MÜG T	MÜG C	AR S	AR T	AR C
Al	12.6	12.7	13.0	12.0	5.58	4.16
C [%]	15.8	15.9	16.2	16.2	17.2	17.5
Ca	121	122	123	135	214	220
Cu	0.12	0.09	0.09	0.15	0.05	0.02
dw	0.07	0.08	0.10	0.06	0.06	0.07
Fe	74.8	75.2	74.0	65.8	17.0	7.41
Fe/P [molar]	10.4	9.5	17.2	9.77	6.13	3.20
Fe/S [molar]	3.15	3.40	2.78	1.99	0.73	0.47
K	2.35	2.37	2.28	2.47	1.47	1.18
LOI	0.26	0.25	0.25	0.23	0.22	0.21
Mg	3.28	3.09	2.97	3.20	2.86	2.35
Mn	1.49	1.48	1.44	1.67	0.75	0.66
N [%]	1.40	1.44	1.48	1.43	1.30	1.24
Na	1.56	1.30	1.08	1.42	1.73	1.08
P	4.0	4.4	2.4	3.7	1.54	1.28
S	13.6	12.7	15.3	19.0	13.3	9.02
Ti	0.46	0.46	0.46	0.39	0.27	0.23
Vivianite	-	detected	-	-	-	-
Zn	0.42	0.40	0.57	0.44	0.15	0.10

Table A.13.: Elemental composition of sediment samples MÜG Fe + P after **119 d** of anoxic incubation. Abbreviations: MÜG Fe + P S = surface sediment, MÜG Fe + P T = sediment from tubes, MÜG Fe + P C = circumjacent or surrounding sediment etc., and values in mg gdw⁻¹ if not indicated otherwise.

Parameter	MÜG Fe + P S	MÜG Fe + P T	MÜG Fe + P C
Al	11.5	10.6	10.6
C [%]	14.3	12.8	13.0
Ca	118	110	108
Cu	0.10	0.08	0.07
dw	0.07	0.10	0.12
Fe	88.6	108	116
Fe/P [molar]	4.1	2.8	2.8
Fe/S [molar]	3.74	5.51	5.68
K	2.15	2.10	1.98
LOI	0.24	0.23	0.23
Mg	3.33	3.25	3.31
Mn	2.55	3.37	3.49
N [%]	1.26	1.15	1.18
Na	4.26	4.81	4.25
P	12.1	21.6	22.8
S	13.6	11.3	11.7
Ti	0.45	0.40	0.41
Vivianite	-	-	detected
Zn	0.39	0.36	0.35

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Table A.14.: P fractions according to the method of Psenner et al. (1984) of the sediment samples MÜG, AR, and MÜG Fe + P after **119 d** of anoxic incubation. Fractions include NH_4Cl TP, BD TP, SRP, NRP, HCl TP, and Rest TP with their values in mg gdw^{-1} if not indicated otherwise. Abbreviations MÜG S = surface sediment, MÜG T = sediment from tubes, MÜG C = circumjacent or surrounding sediment etc..

Parameter	NH_4Cl	BD	SRP	NRP	HCl	Rest	TP	Yield [%]
MÜG S	0.05	2.21	0.27	0.01	0.28	0.07	2.92	73
MÜG T	0.04	2.20	0.26	0.02	0.41	0.07	3.03	69
MÜG C	0.004	0.77	0.29	-0.03	0.38	0.08	1.51	63
AR S	0.01	1.96	0.20	0.25	0.32	0.07	2.83	76
AR T	0.01	0.46	0.09	0.27	0.21	0.02	1.14	74
AR C	0.04	0.25	0.09	0.23	0.06	0.01	0.76	59
MÜG Fe + P S	0.10	3.57	1.07	0.47	0.12	0.08	5.41	45
MÜG Fe + P T	0.07	4.14	3.54	0.31	0.25	0.10	8.41	39
MÜG Fe + P C	0.02	4.29	7.80	0.21	0.37	0.04	12.8	56

Table A.15.: Fe and Mn values of P fractions of sediment samples MÜG, AR, and MÜG Fe + P after **119 d** of anoxic incubation with their values in mg gdw^{-1} . Abbreviations MÜG S = surface sediment, MÜG T = sediment from tubes, MÜG C = circumjacent or surrounding sediment etc..

Parameter	BD Fe	BD Fe/P [molar]	BD Mn	HCl Fe	HCl Mn
MÜG S	1.54	0.46	0.27	47.0	0.07
MÜG T	1.19	0.39	0.26	44.5	0.07
MÜG C	1.87	0.26	0.29	48.4	0.08
AR S	1.02	0.34	0.20	39.6	0.07
AR T	2.01	0.15	0.09	6.34	0.02
AR C	2.23	0.17	0.09	1.27	0.01
MÜG Fe + P S	3.73	1.11	1.07	43.4	0.08
MÜG Fe + P T	3.88	1.17	3.54	42.5	0.10
MÜG Fe + P C	2.98	0.84	7.80	59.4	0.04

A.3. XRD Spectra

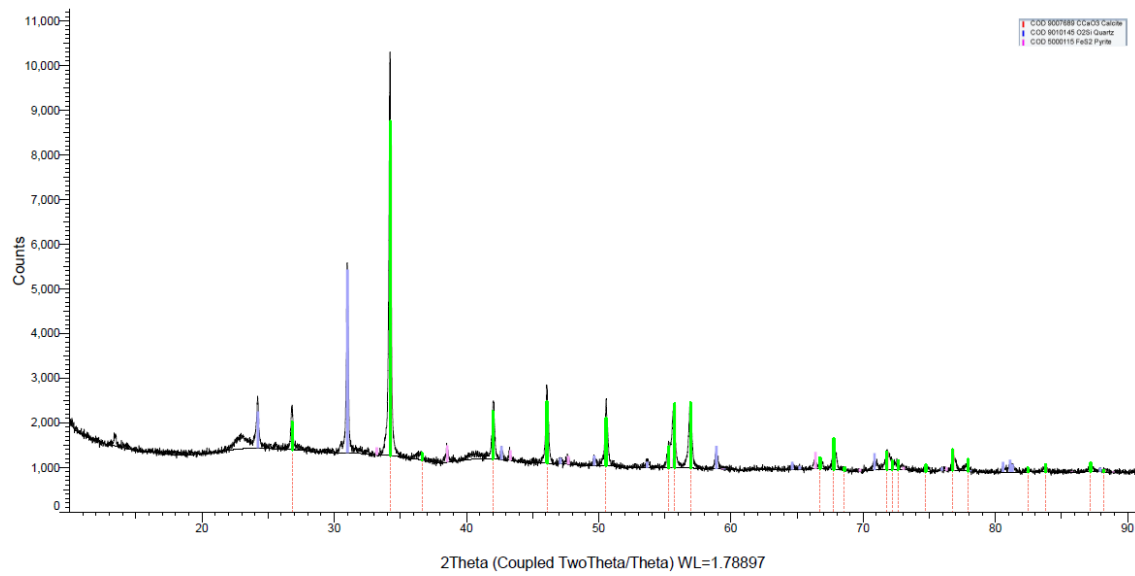


Figure A.4.: XRD spectra of L. Müggelsee sample 1 (0-15 cm dpt, 7 m wdpt).

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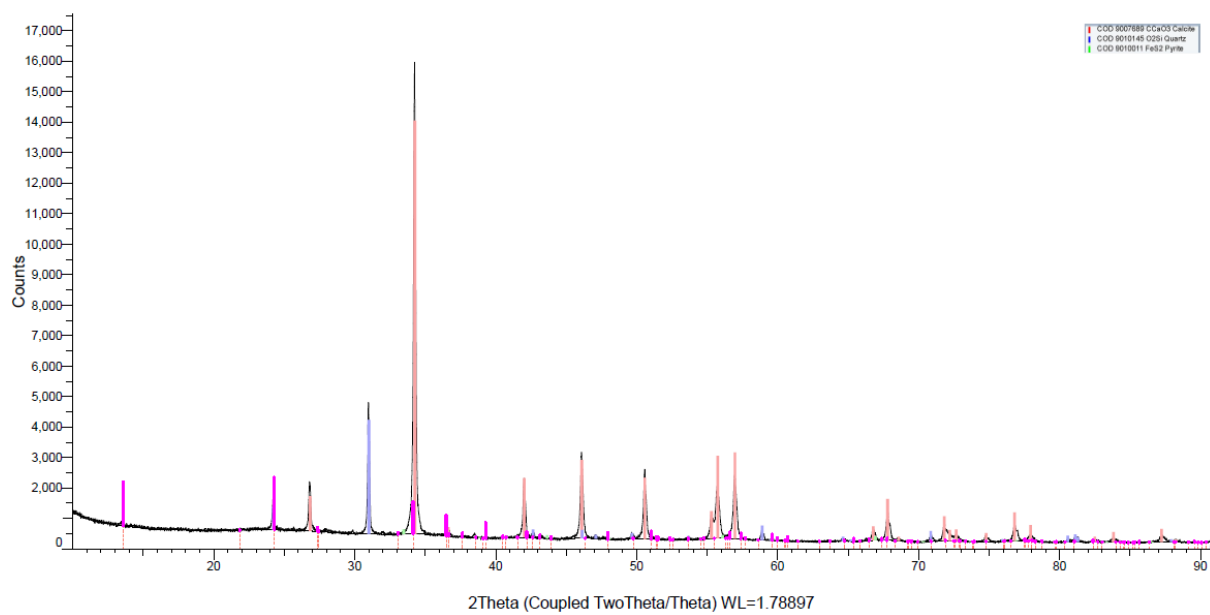


Figure A.5.: XRD spectra of L. Arendsee sample **2** (0-10 cm dpt, 48 m wdpt).

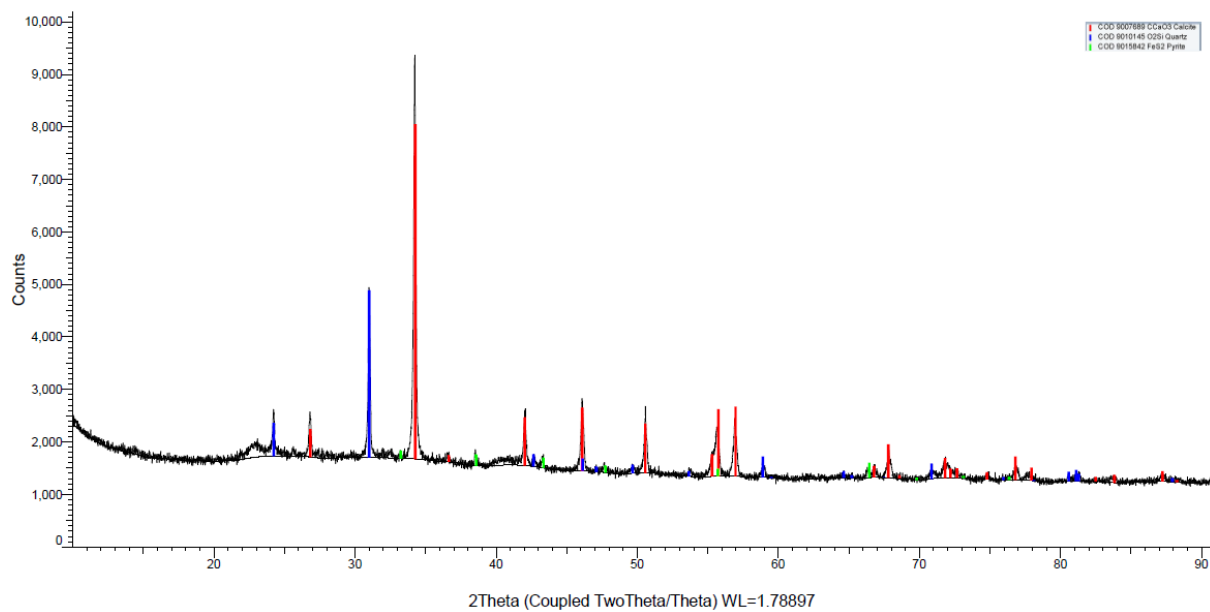


Figure A.6.: XRD spectra of L. Müggelsee Test sample enriched with Fe + P ((**3**), 0-15 cm dpt, 7 m wdpt).

A.3. XRD Spectra

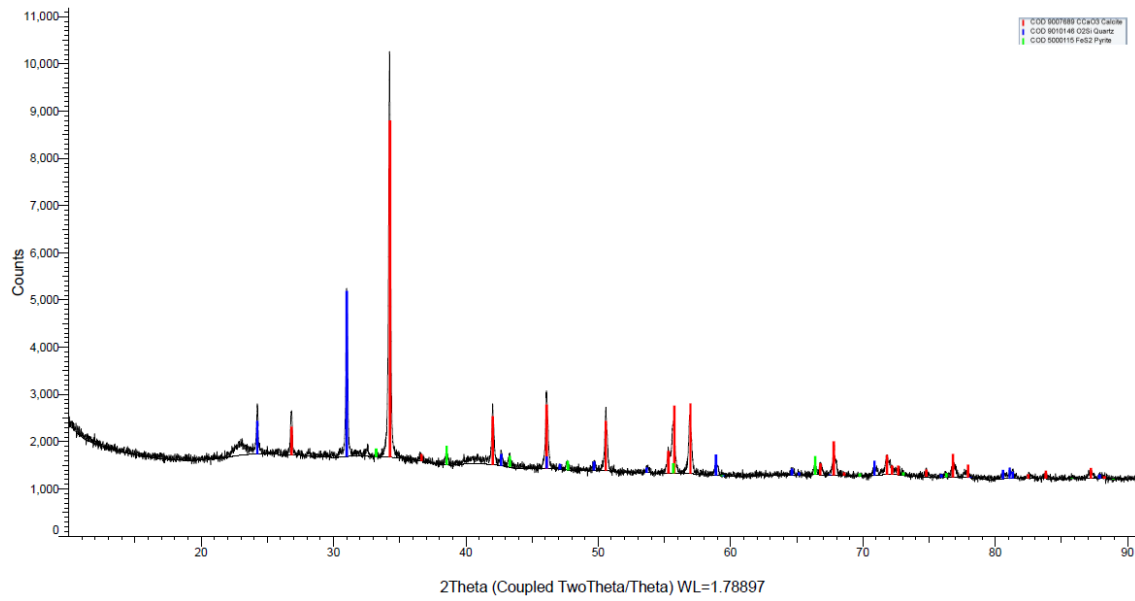


Figure A.7.: XRD spectra of L. Müggelsee sample enriched with Fe + P ((4), 0-15 cm dpt, 7 m wdpt).

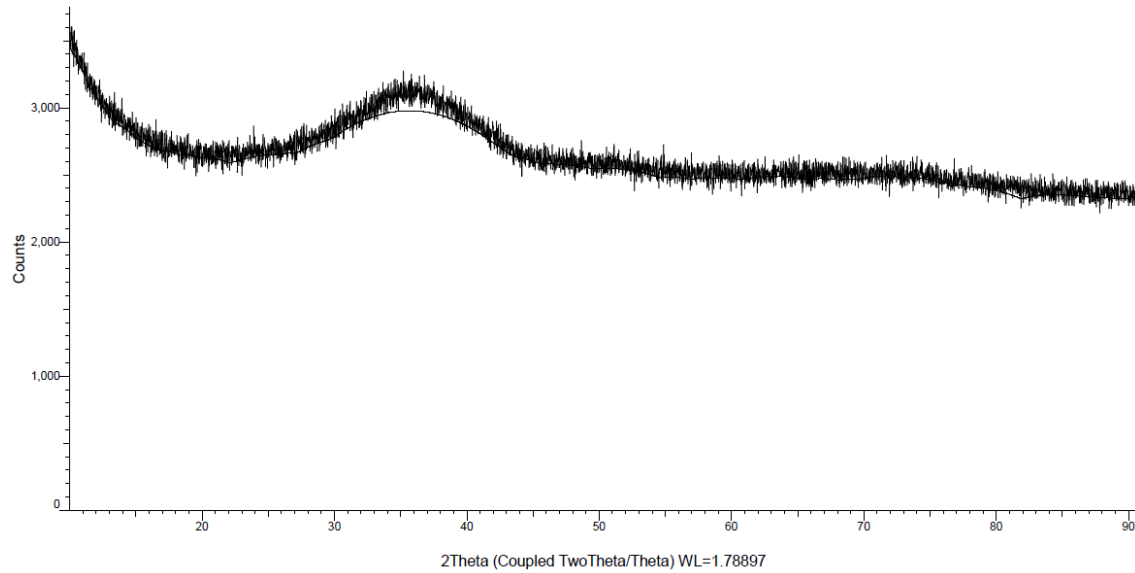


Figure A.8.: XRD spectra of Fe + P slurry (5).

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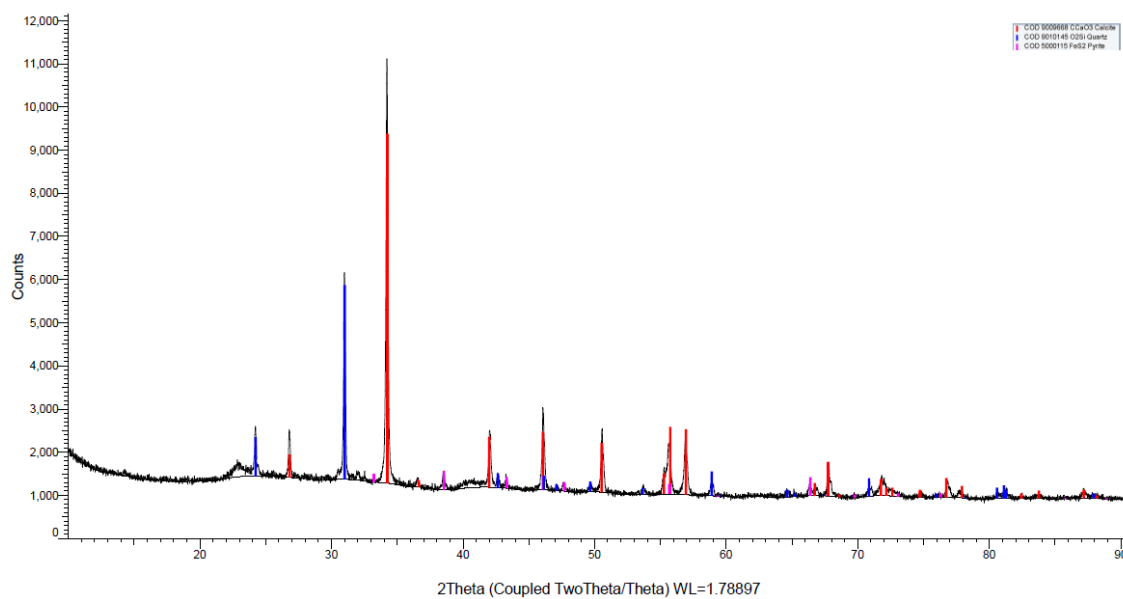


Figure A.9.: XRD spectra of L. Müggelsee surface sample **6** after **29 d** aerob aerob.

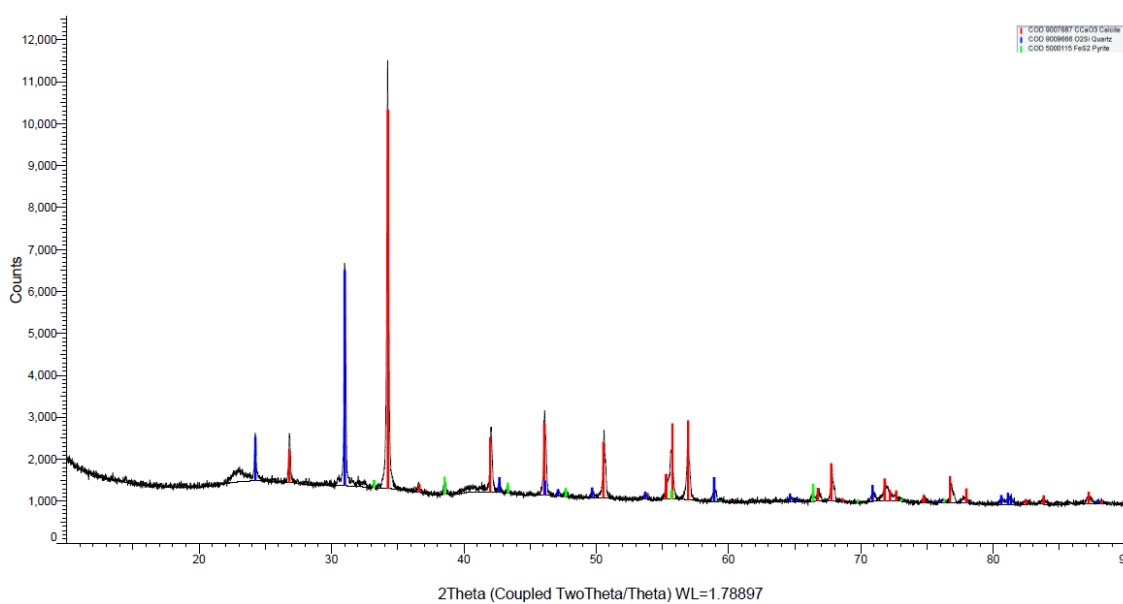


Figure A.10.: XRD spectra of L. Müggelsee tube sample **7** after **29 d** aerob aerob.

A.3. XRD Spectra

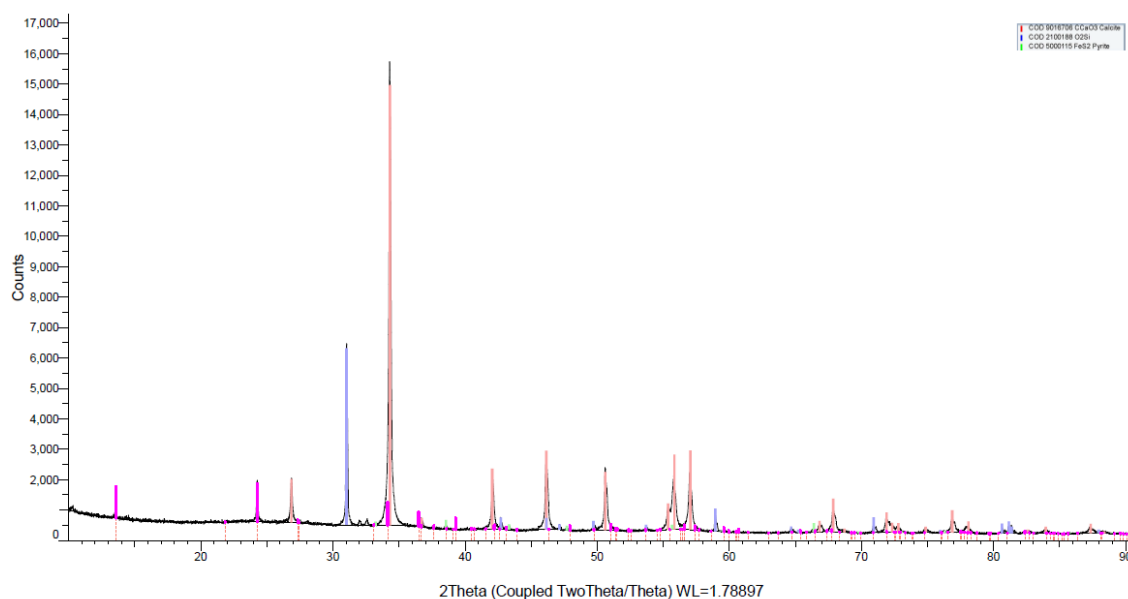


Figure A.11.: XRD spectra of L. Müggelsee surrounding sediment sample **8** after **29 d** aerob aerob.

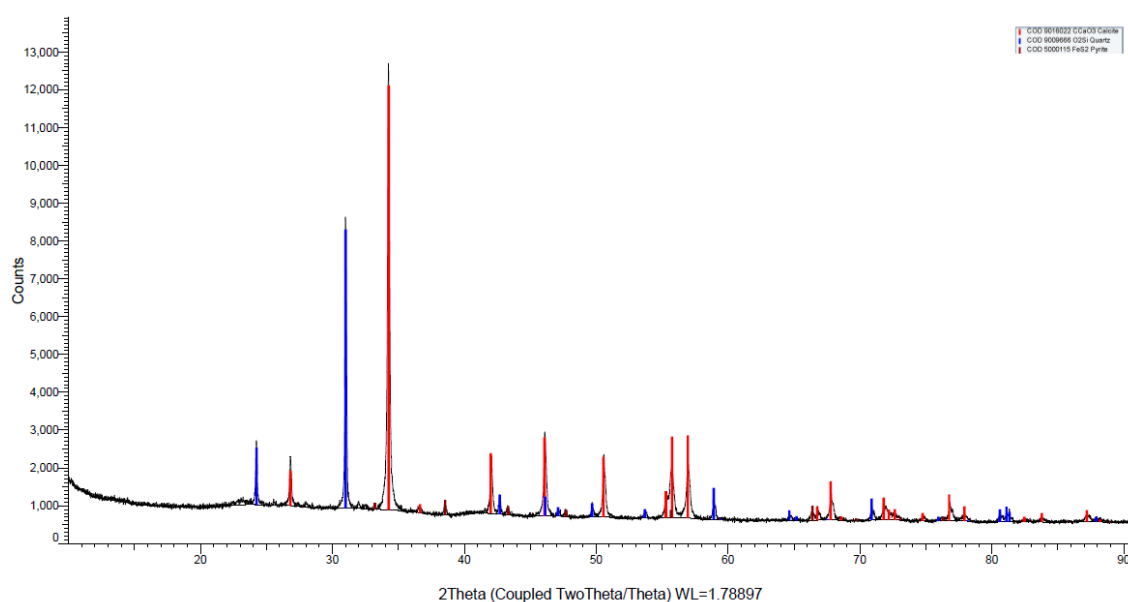


Figure A.12.: XRD spectra of L. Arendsee surface sediment sample **9** after **29 d** aerob aerob.

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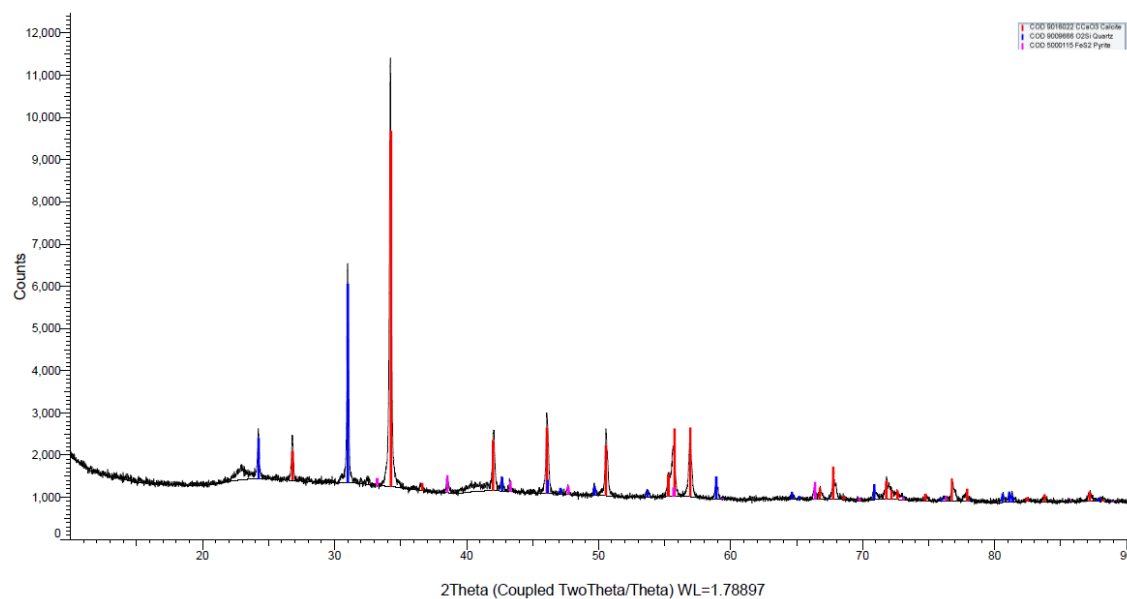


Figure A.13.: XRD spectra of L. Arendsee tube sample **10** after **29 d** aerob aerob.

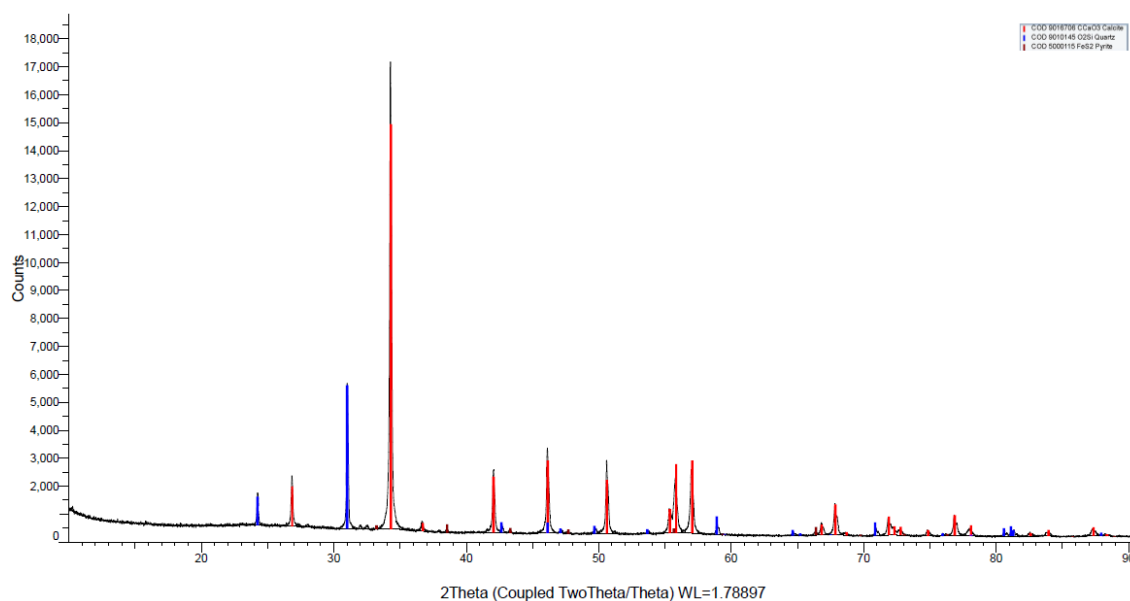


Figure A.14.: XRD spectra of L. Arendsee surrounding sediment sample **11** after **29 d** aerob aerob.

A.3. XRD Spectra

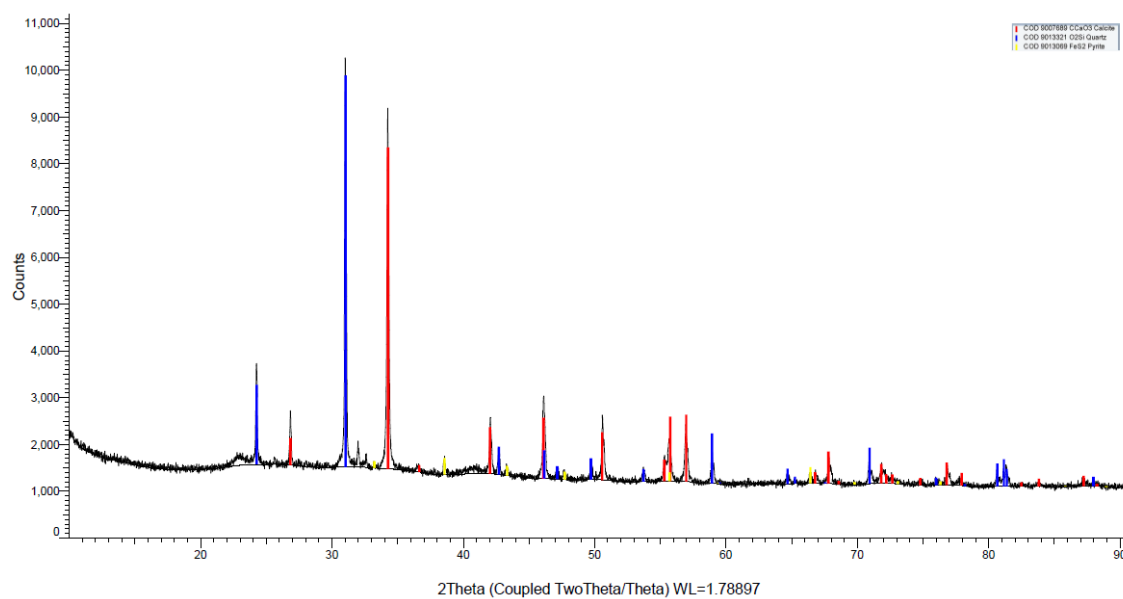


Figure A.15.: XRD spectra of MÜG Fe + P surface sample **12** after **29 d** aerob aerob.

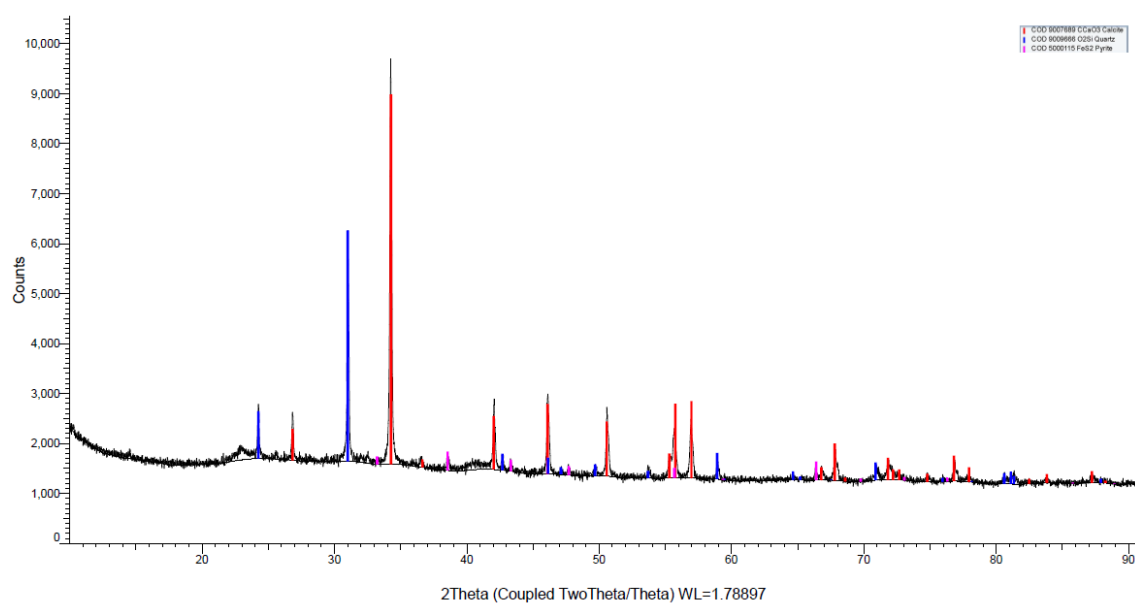


Figure A.16.: XRD spectra of MÜG Fe + P tube sample **13** after **29 d** aerob aerob.

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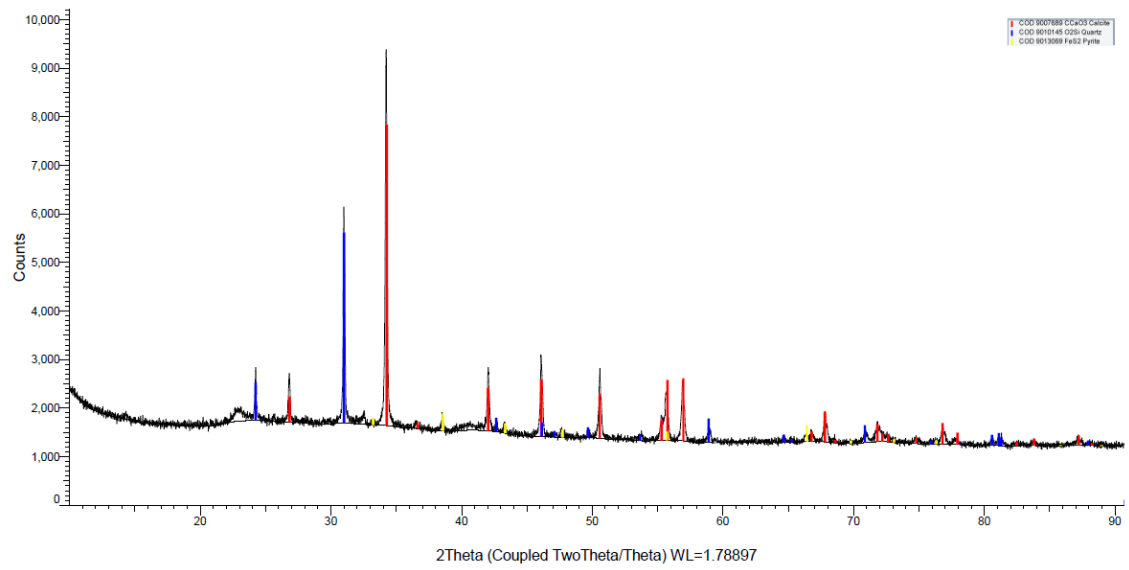


Figure A.17.: XRD spectra of MÜG Fe + P surrounding sediment sample **14** after **29 d** aerob. aerob.

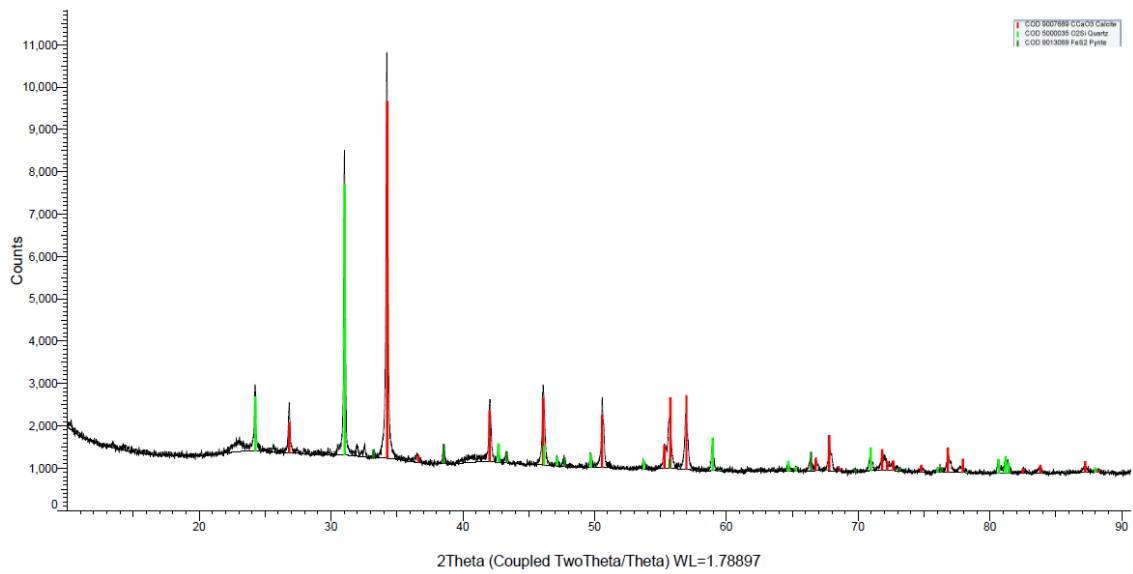


Figure A.18.: XRD spectra of L. Müggelsee surface sample **15** after **64 d** aerob.

A.3. XRD Spectra

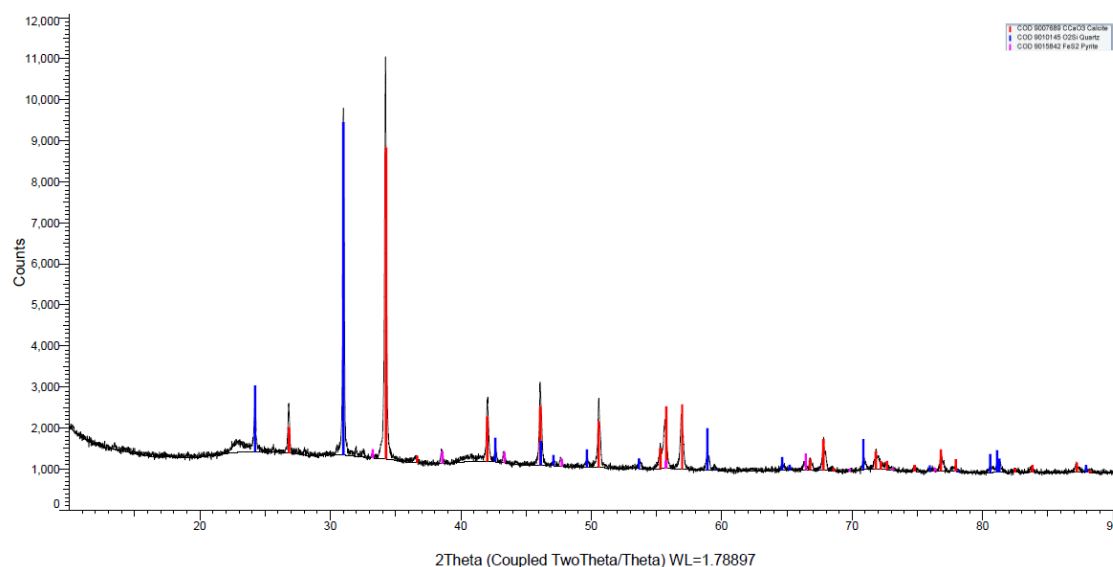


Figure A.19.: XRD spectra of L. Müggelsee tube sample **16** after **64 d** aerob.

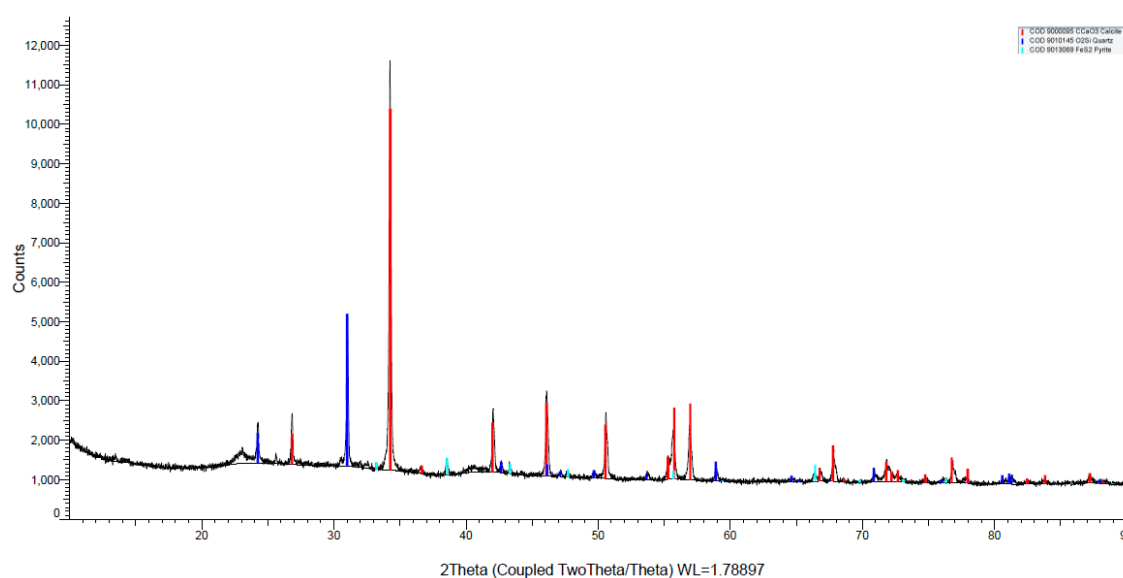


Figure A.20.: XRD spectra of L. Müggelsee surrounding sediment sample **17** after **64 d** aerob.

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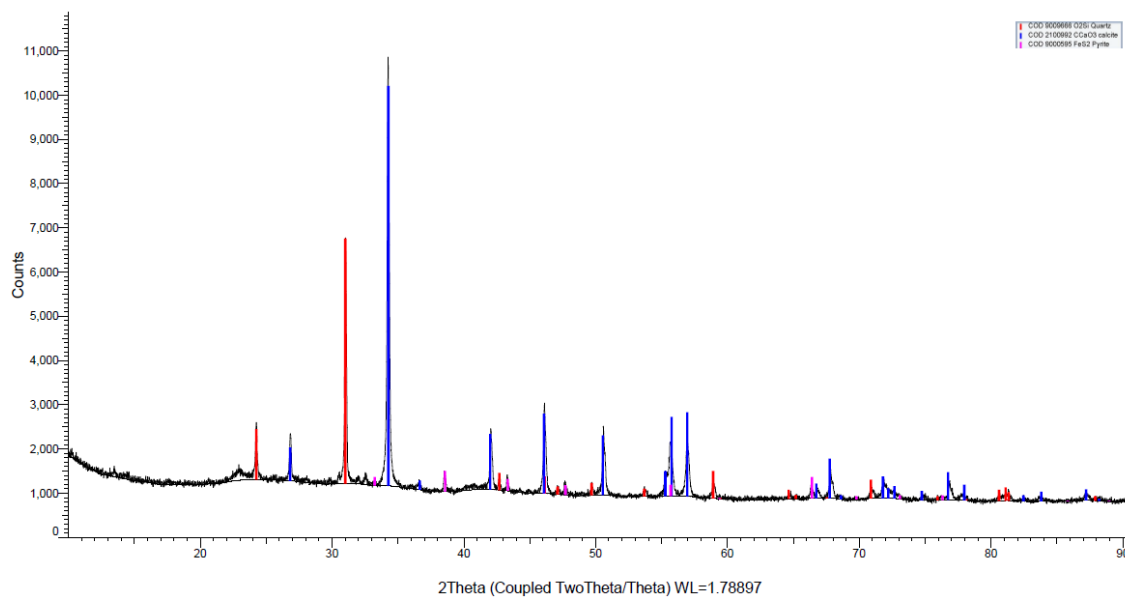


Figure A.21.: XRD spectra of L. Arendsee surface sediment sample **18** after **64 d** aerob.

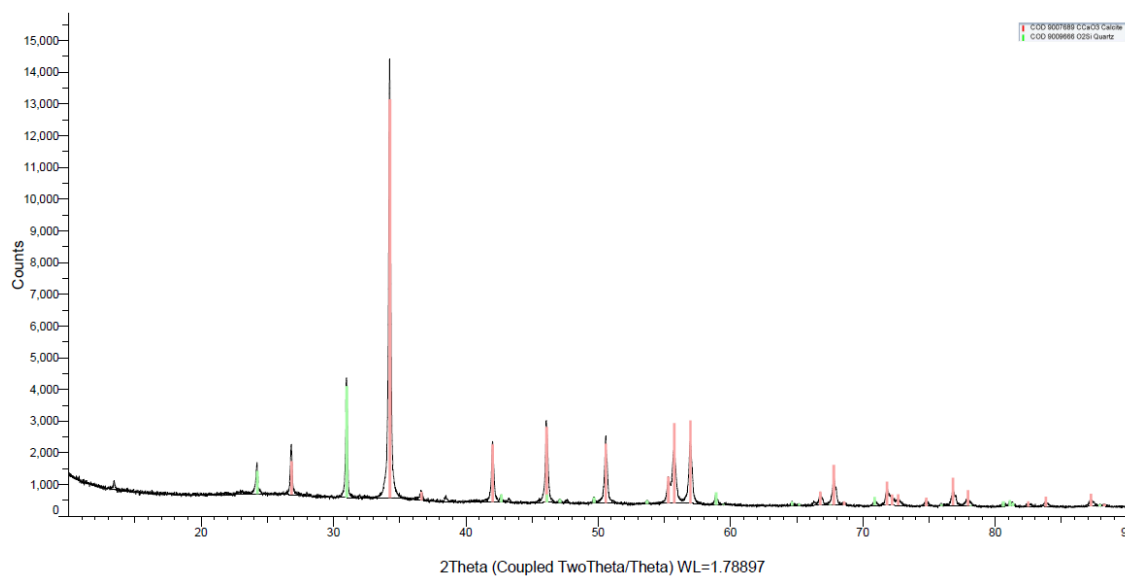


Figure A.22.: XRD spectra of L. Arendsee tube sample **19** after **64 d** aerob.

A.3. XRD Spectra

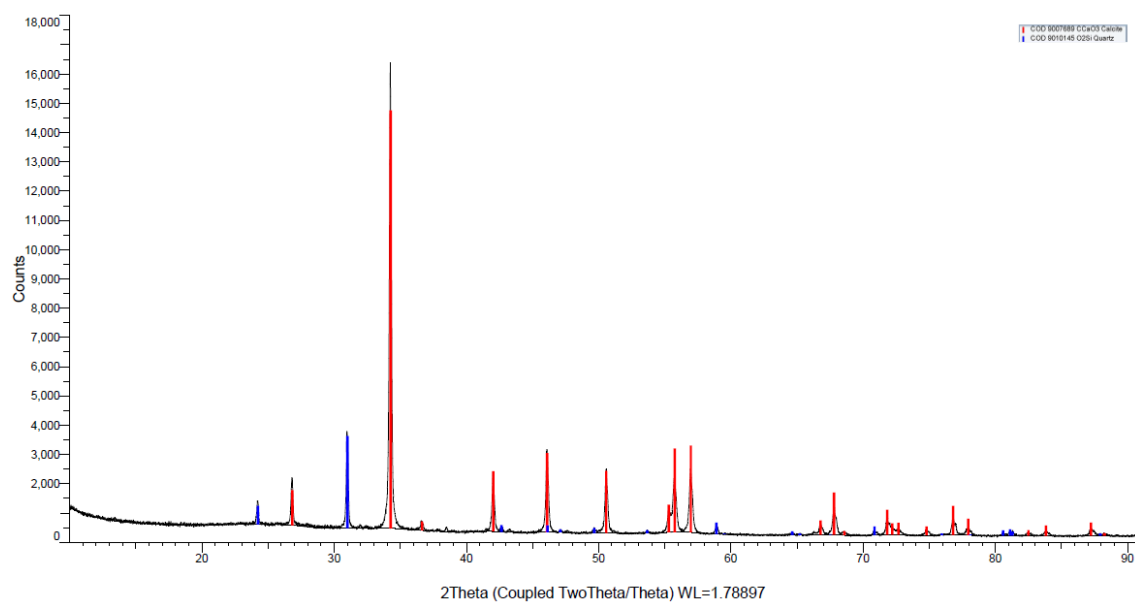


Figure A.23.: XRD spectra of L. Arendsee surrounding sediment sample **20** after **64 d** aerob.

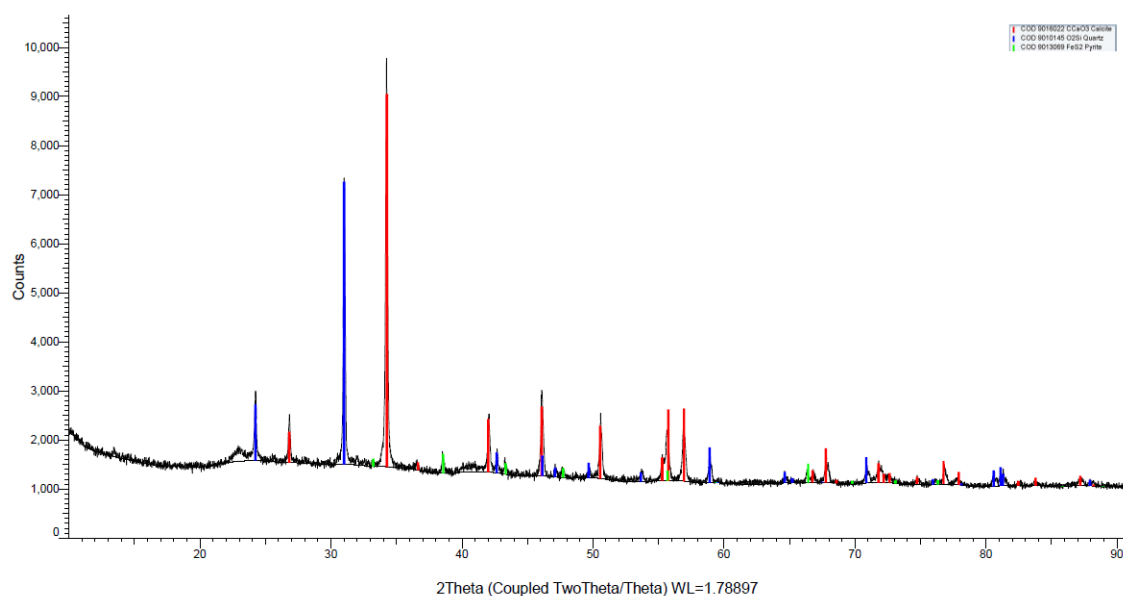


Figure A.24.: XRD spectra of MÜG Fe + P surface sample **21** after **64 d** aerob.

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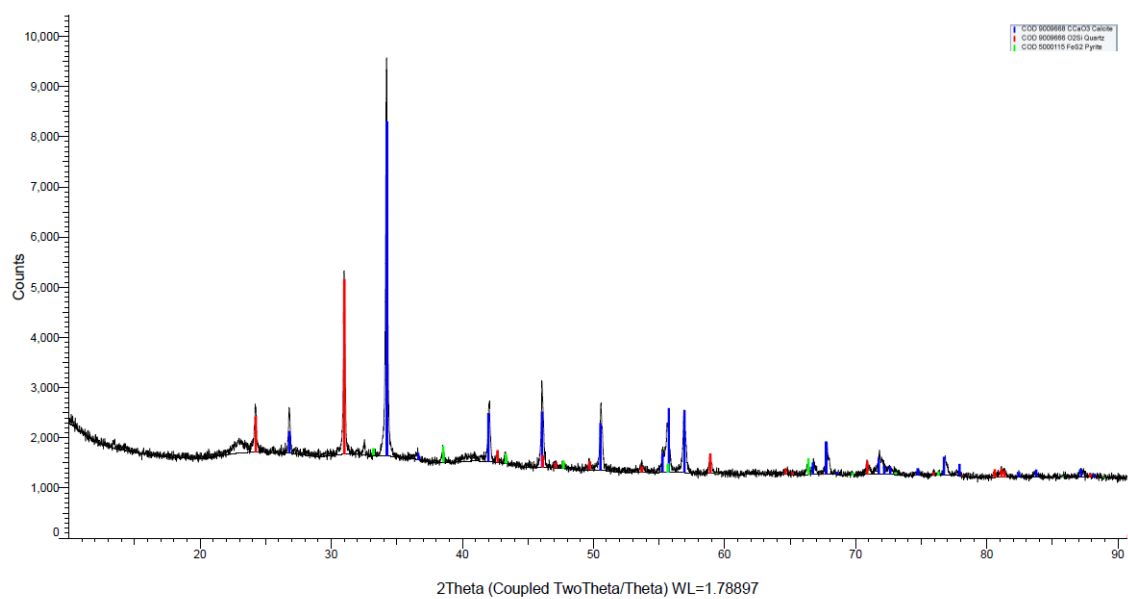


Figure A.25.: XRD spectra of MÜG Fe + P tube sample **22** after **64 d** aerob.

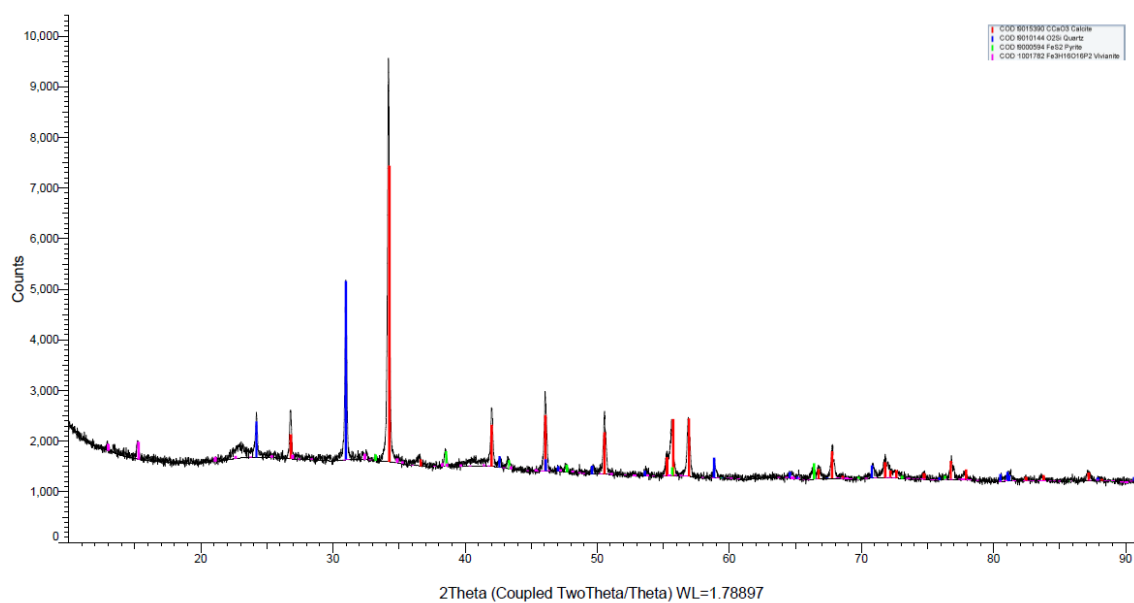


Figure A.26.: XRD spectra of MÜG Fe + P surrounding sediment sample **23** after **64 d** aerob.

A.3. XRD Spectra

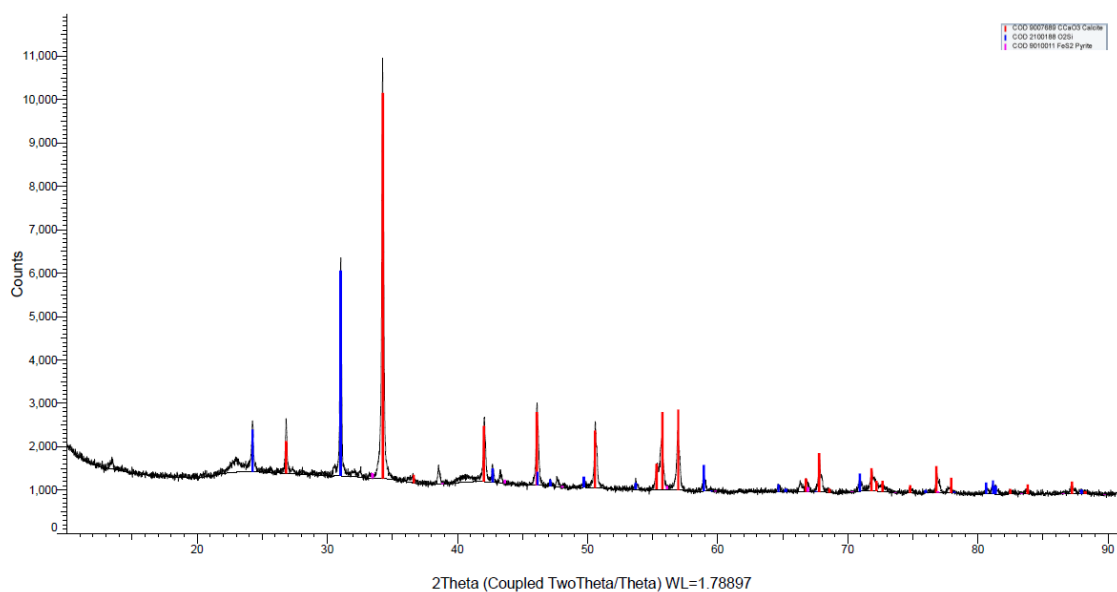


Figure A.27.: XRD spectra of L. Müggelsee tube sample **24** after 101 d anaerob.

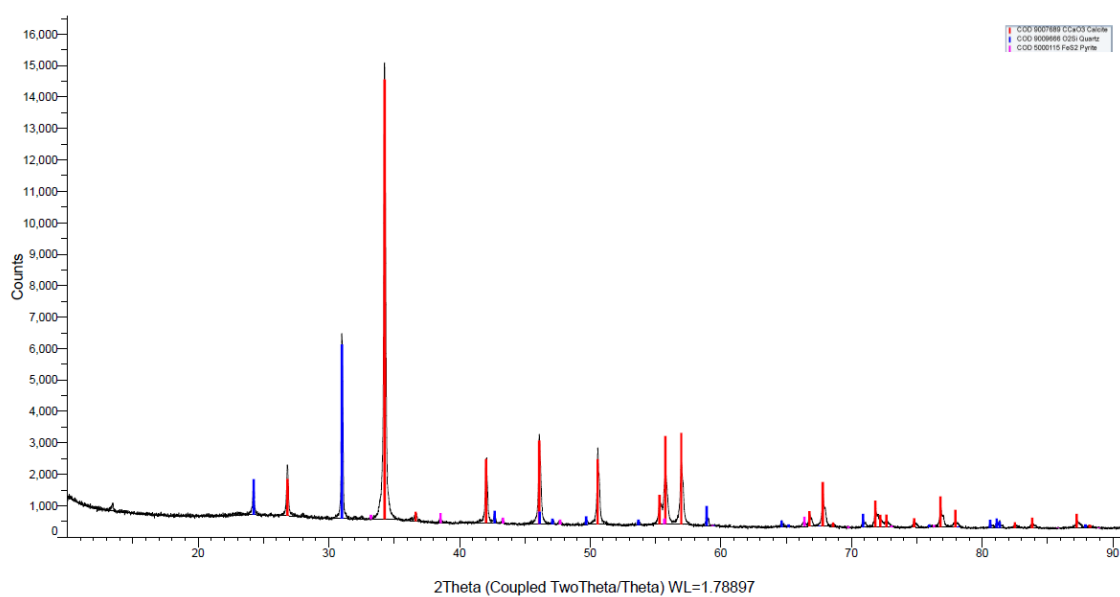


Figure A.28.: XRD spectra of L. Arendsee tube sample **25** after 101 d anaerob.

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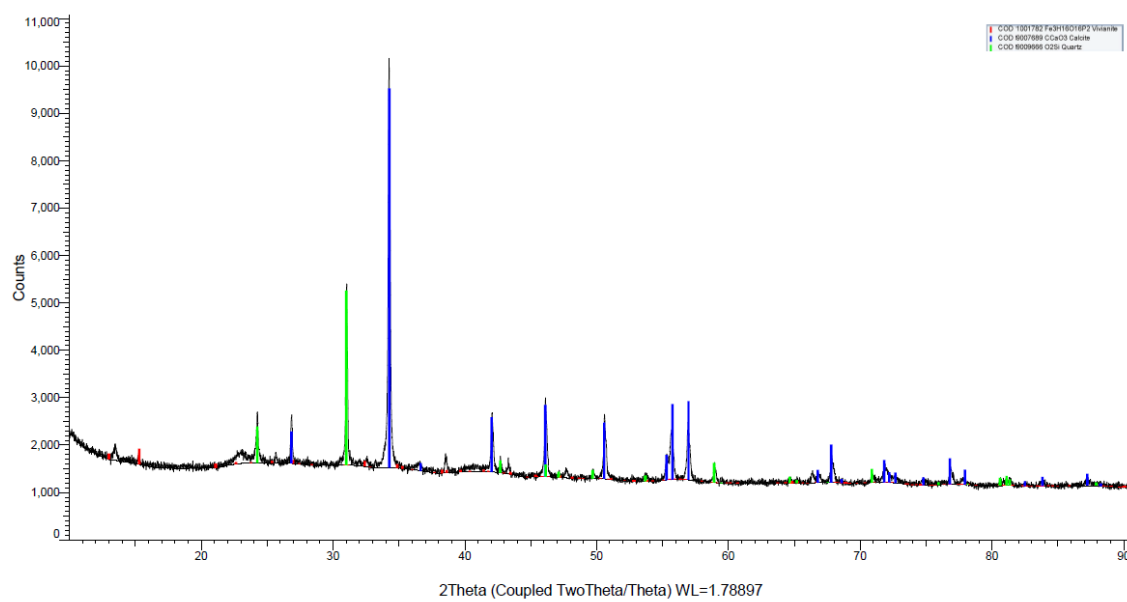


Figure A.29.: XRD spectra of MÜG Fe + P tube sample **26** after 101 d anaerob.

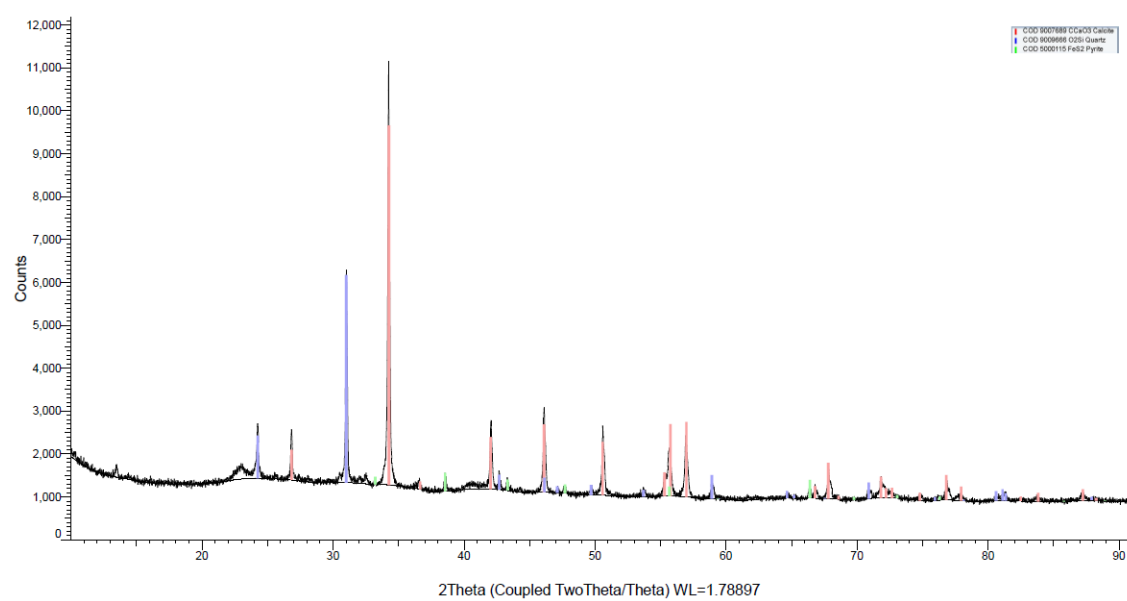


Figure A.30.: XRD spectra of L. Müggelsee surface sample **27** after 119 d anaerob.

A.3. XRD Spectra

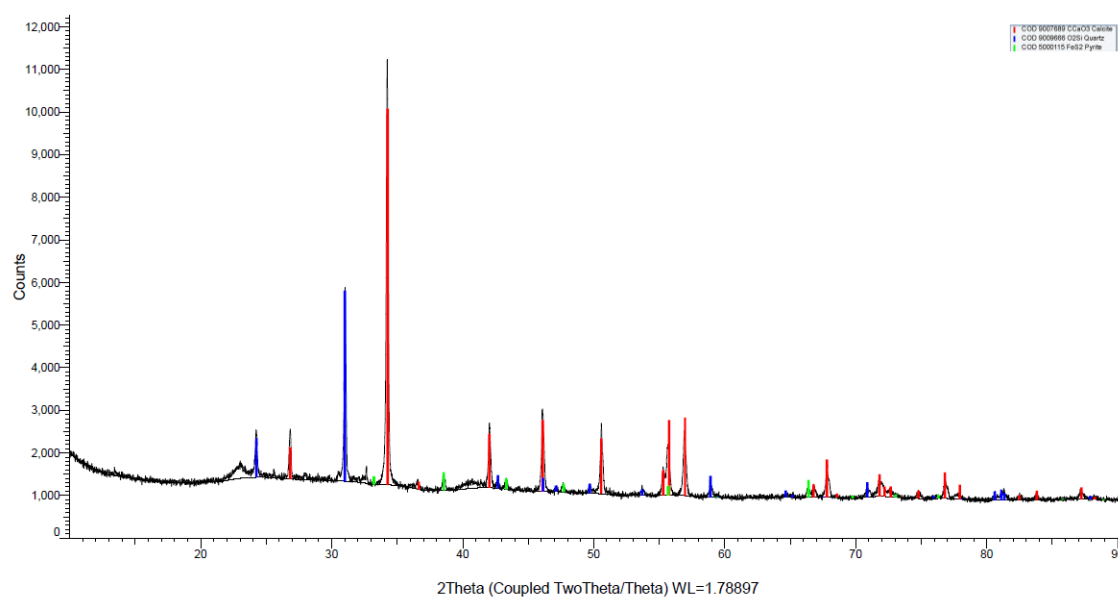


Figure A.31.: XRD spectra of L. Müggelsee surrounding sediment sample **29** after 119 d anaerob.

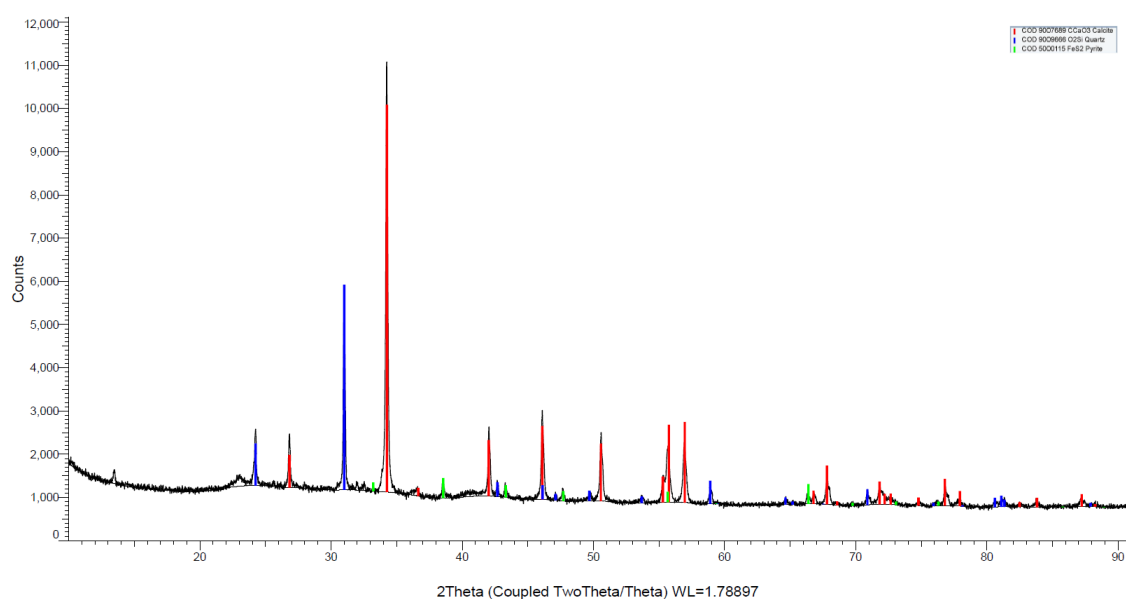


Figure A.32.: XRD spectra of L. Arendsee surface sediment sample **30** after 119 d anaerob.

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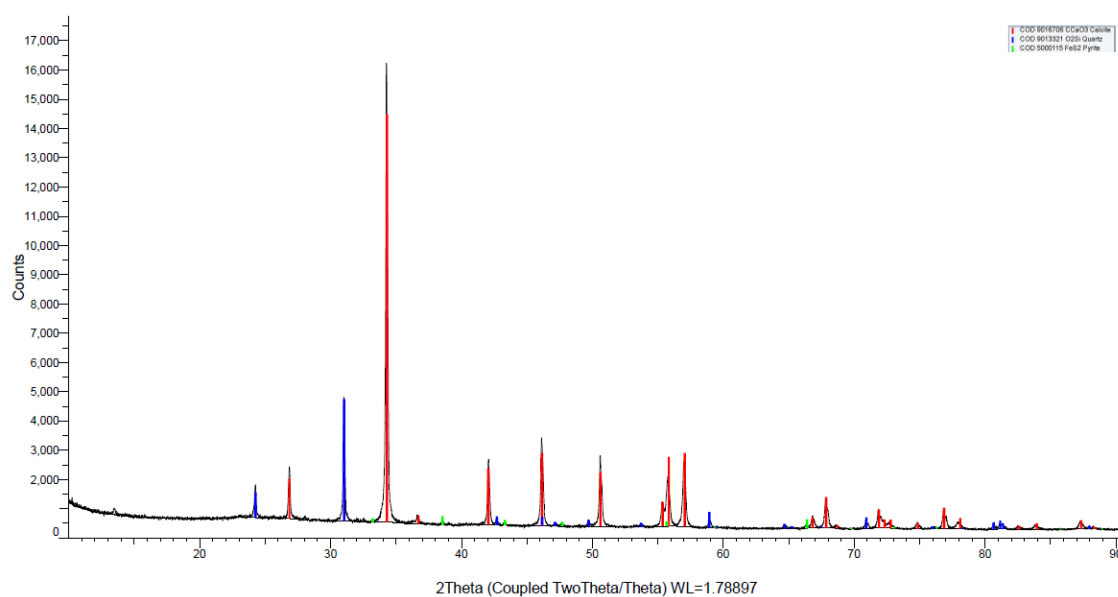


Figure A.33.: XRD spectra of L. Arendsee tube sample **31** after 119 d anaerob.

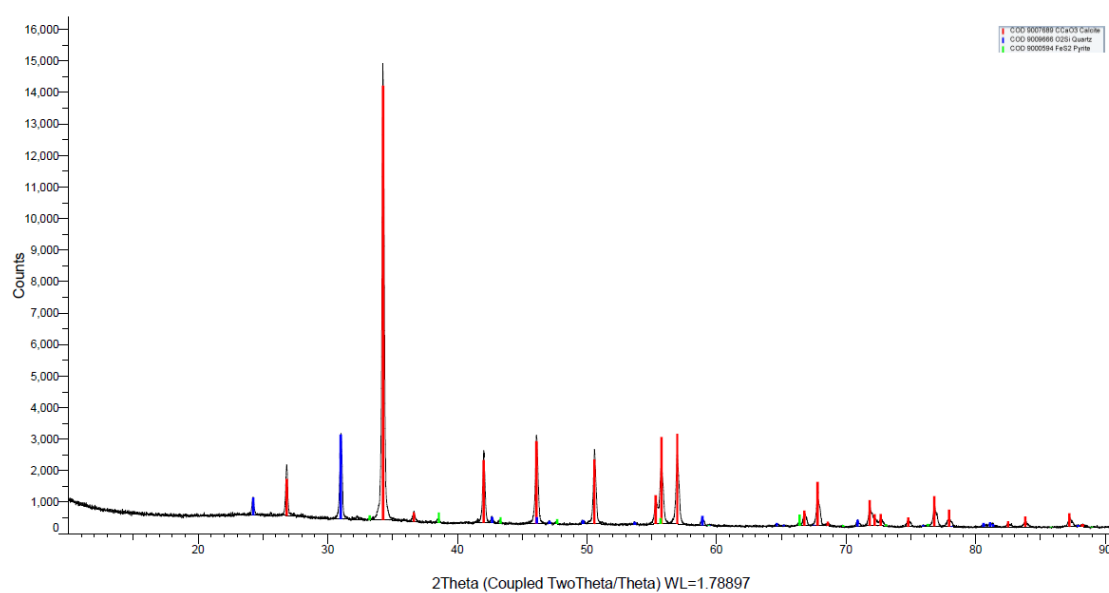


Figure A.34.: XRD spectra of L. Arendsee surrounding sediment sample **32** after 119 d anaerob.

A.3. XRD Spectra

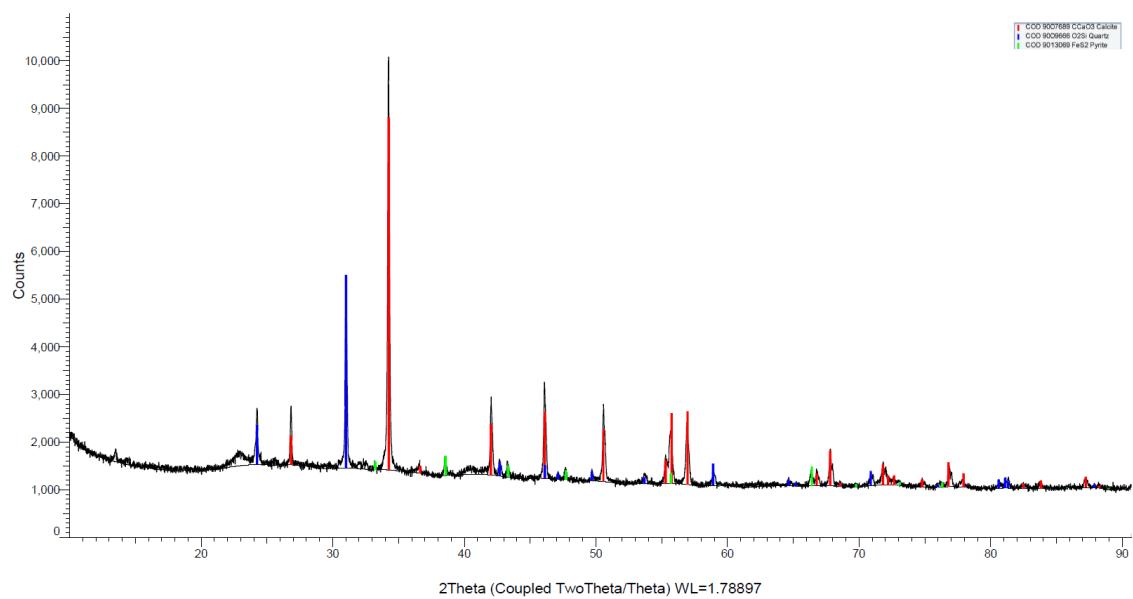


Figure A.35.: XRD spectra of MÜG Fe + P surface sample **33** after 119 d anaerob.

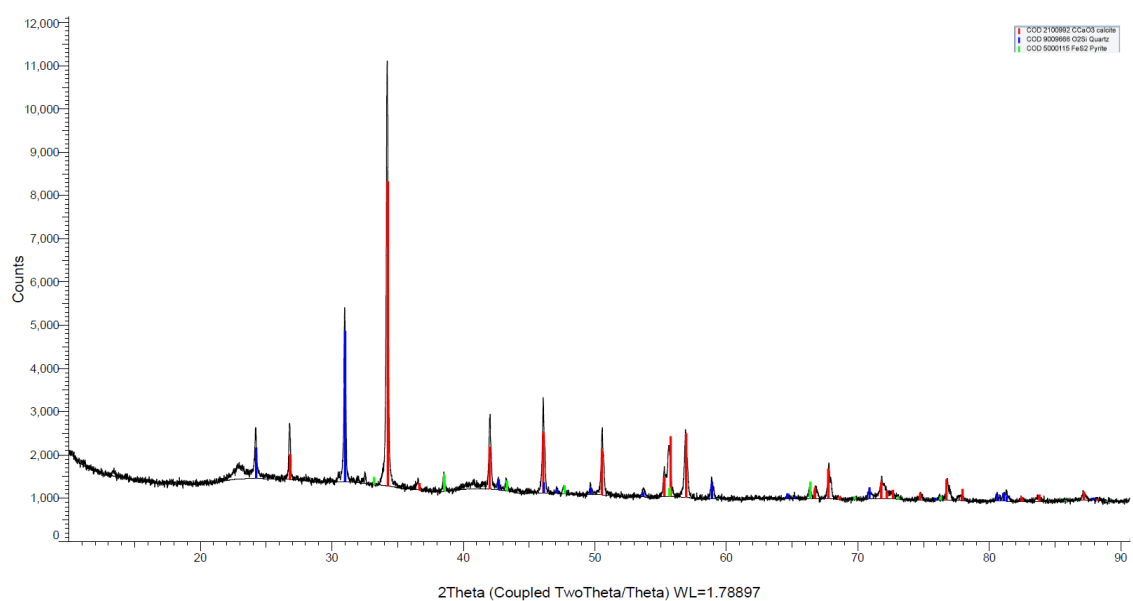


Figure A.36.: XRD spectra of MÜG Fe + P tube sample **34** after 119 d anaerob.

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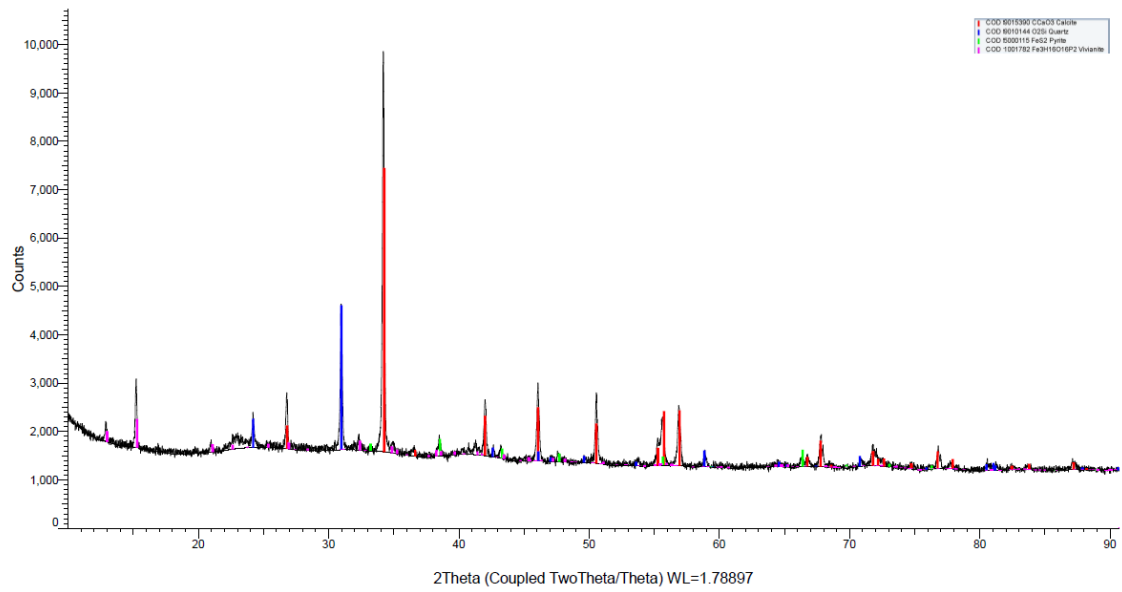


Figure A.37.: XRD spectra of MÜG Fe + P surrounding sediment sample **35** after 119 d anaerob.